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DETERMINATION OF SULFURIC ACID, TOTAL PARTICLE-PHASE ACIDITY AND NITRIC ACID IN AMBIENT AIR

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ABSTRACT

A study was conducted to evaluate measurement methods for sulfuric acid, strong acids in particulate matter, and nitric acid in ambient air. Selective extraction of H_2SO_4 with benzaldehyde and titrimetry for strong acids were evaluated and compared using laboratory-generated mixtures of ≤ 0.3 µm diameter H_2SO_4, $(NH_4)_2SO_4$, and NH_4HSO_4 aerosols on clean and atmospheric particulate-loaded filters. Filter media were selected based on filtration efficiency and acid recovery with ≤ 0.3 µm H_2SO_4 aerosols. Nitric acid collection by filter methods (NaCl-impregnated cellulose and nylon filters) were compared at varying HNO_3 concentrations, relative humidity levels and flow rates. Quantitation of nitric acid, as nitrate, employed an automated copper-cadmium reduction plus diazotization procedure. An ammonia denuder was employed in field sampling together with removal of non-respirable particles to increase the stability of H_2SO_4 following collection.

The presence of atmospheric particulate matter was shown to sharply reduce recoveries of laboratory-generated H_2SO_4 but recoveries of total strong acid usually remained $\geq 60\%$. Anhydrous benzaldehyde was found to extract NH_4HSO_4 to a substantial degree. Laboratory-generated nitric acid was collected with high efficiency by both nylon and 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.

Samples collected in Pittsburg, CA showed good correlation between sulfuric acid and particulate strong acid measurements. As much as 0.6 $\mu g/m^3$ H_2SO_4 and 1.6 $\mu g/m^3$ acidity, expressed as H_2SO_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 $\mu g/m^3$. Simultaneous gas phase ammonia measurements were made to assist in interpreting the particulate sample results. Glass fiber filters were shown to collect, quantitatively, both particulate nitrate and gas phase nitric acid. This is consistent with earlier studies of artifact particulate nitrate formation.

EXECUTIVE SUMMARY

A combined laboratory and field study has investigated methods for the determination of sulfuric acid and strong acids in atmospheric particulates as well as nitric acid, a gas at ambient concentrations. The procedures for particulate acids employed sampling with inert filters, processing of samples under conditions designed to preserve strong acids followed by analytical techniques appropriate for sulfuric acid (H_2SO_4) and strong acids. To stabilize strong acids on filters, > 3 μm 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. H_2SO_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 pre-filter. The efficiency for collection of nitric acid was > 96% for NaCl-impregnated Whatman 41 filters. For nylon (Duralon) the efficiency appeared to depend on the total amount of nitric acid sampled. However, at atmospheric levels its efficiency was equivalent to that for NaCl-impregnated filters. Following its extraction, nitric acid was determined as nitrate by the automated copper-cadmiun reduction, diazotization procedure.

Based on filtration efficiencies and recovery studies with submicron sulfuric acid aerosol, acid-washed quartz fiber and one micron pore size Teflon filters were selected for use in sampling H_2SO_4 and H^+. Recoveries of laboratory-generated H_2SO_4 aerosol from clean filters ranged from 60 to 75%, and by titration, 80 to 100%. However, the presence of respirable atmospheric particulate (< 3.5 μm) matter reduced the recoveries of sulfuric acid to ≤ 30%. Recoveries of strong acid remained about 60% which is consistent with the formation of ammonium acid sulfate (NH_4HSO_4). In the absence of atmospheric particulate matter the efficiency for extraction of this acid sulfate by benzaldehyde was 45 ± 3%, which is higher than that reported by other investigators. In the presence of atmospheric particulate matter, NH_4HSO_4 was not extracted by benzaldehyde, however.

In three days of continuous sampling conducted at Pittsburg, CA, total strong acid and sulfuric acid maxima correlated well. Agreement between nitric acid methods was excellent. Ammonia and particle phase ammonium showed strong correlation consistent with the important role of ammonia as an aerosol precursor or reactant with acidic aerosols. Samples showed up to 0.6 $\mu g/m^3$ H_2SO_4 and 1.6 $\mu g/m^3$ strong acid expressed as H_2SO_4. Based on laboratory studies, these represent lower limit values. These results may be compared to the current sulfate standard of 25 $\mu g/m^3$ total water soluble sulfate (24 hour average).

A glass fiber filter, Gelman A, was shown to provide a measure of total nitrate (i.e. gaseous nitric acid plus particulate nitrate) rather than of particulate nitrate alone. This work confirms our prior studies demonstrating that gaseous nitric acid and not nitrogen dioxide (present at about 40 $\mu g/m^3$ during most of the field sampling) is the dominant contributor to artifact particulate nitrate.

Principal conclusions from the current study are as follows:

1. Measurement of sulfuric acid and total acidity can be made by benzaldehyde extraction and titration with laboratory-generated H_2SO_4 aerosol on clean filters with a recovery of $> 60\%$ of the true value. However, the presence of respirable atmospheric particulate matter decreased recoveries of H_2SO_4 to below 30%. Strong acid recoveries usually remained above 60%. Furthermore, the elimination of large, soil-related particles by use of a cyclone, alone, or in combination with ammonia removal is probably insufficient to permit measurement of H_2SO_4 at least for samples collected from $\geq 10\ m^3$ of air. Emphasis must be given to shorter term or lower flow rate sampling to decrease acid interaction with other aerosol constituents.

2. Additional work is needed to clarify the interference effects of ammonium acid sulfate in H_2SO_4 and strong acid measurements.

3. Gaseous nitric acid can be measured by collection with either nylon or sodium chloride impregnated cellulose filters at ambient concentrations, with excellent agreement between methods. A 15% uncertainty in HNO_3 value remains, resulting from variability in the extent of nitric acid retained by adsorption on particulate-loaded pre-filters. This uncertainty should be eliminated by AIHL studies extending the present work.

4. Artifact nitrate formation on glass fiber filters in field sampling corresponded to the collection of 100% of the ambient nitric acid. Thus it is likely that nitrate values obtained by the present ARB Hi-vol network represent the sum of particulate nitrate and nitric acid rather than particulate nitrate, alone.

5. Further studies are needed employing continuous methods for H_2SO_4 in an effort to overcome the large negative interference by other aerosol constituents. Since positive errors are more probable with continuous methods (e.g. volatilization of sulfate salts as well as H_2SO_4), simultaneous application of continuous and the integrated techniques described herein should provide both lower and upper limits to the true H_2SO_4 level.

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I. INTRODUCTION

A. Sulfuric Acid and Particle Phase Acidity

California's significant harm level for airborne sulfate of 25 μg/m^3 is based upon water-soluble sulfate in 24-hour high volume filter samples. Such sulfate may include ammonium sulfate, ammonium acid sulfate, sulfuric acid as well as various metal and mixed metal ammonium salts. Some of these are relatively harmless (e.g., calcium sulfate), while others appear relatively hazardous (e.g., sulfuric acid). In part, the rationale for setting the California standard is based on the presumption that a significant route for formation of the currently measured water-soluble sulfate involves sulfuric acid; but the actual levels in the atmosphere are unknown. In part, because of the lack of specific data on ambient particulate sulfuric acid levels, the standard has met significant opposition. As yet, no technique has received general acceptance for determining sulfuric acid or any other individual sulfate compound in ambient air.

Existing techniques for determining sulfuric acid in ambient air may be divided into continuous and integrated methods. The continuous methods rely on such physical properties as changes in light scattering induced by the addition of ammonia (the humidified nephelometer technique)[1,3] to provide both qualitative and quantitative data on acid sulfates (i.e. sulfuric acid and/or ammonium acid sulfate). While acid sulfates were measured in St. Louis, none were detectable in Los Angeles by this technique.[3]

The greater volatility of sulfuric acid, relative to its ammonium salts, has been utilized in both continuous[2-4] and integrated methods.[6] One approximately continuous method employs an acid gas diffusion denuder to remove SO_2 and H_2SO_4 when in gas phase.[2] By cycling the temperature of the ambient air pumped through the instrument up to about 150°C, H_2SO_4 aerosol is vaporized allowing it to be trapped by the denuder. The decrease in sulfur reaching the flame photometric detector, relative to the level at room temperature, provides a measure of sulfuric acid. However, since H_2SO_4 is measured by difference and since the level of SO_2 plus sulfate salts will generally by much greater than that of H_2SO_4, precision can be expected to be poor.

Integrated sampling techniques usually involve collection of H_2SO_4 on a filter or in a liquid medium. EPA's Method 8 relies on an isopropanol-water solution as a trapping medium.[5] However, it is subject to substantial positive error from SO_2. Collection and analysis of sulfuric acid in filter samples has been studied extensively. The reader is referred to a recent review by Newman.[7] The problems inherent in determining ambient air concentrations of sulfuric acid from such samples result from both sampling and analytical errors, including:

1. Penetration through the filter.

2. Fixation and oxidation of SO_2 to sulfate by interaction with the filter and adsorbed water.

3. Irreversible reaction of sulfuric acid and acid sulfates with the filter.

4. Oxidation of SO_2 to H_2SO_4 promoted by constituents of the collected atmospheric particulate matter which may be catalytically active (e.g., manganese, iron and vanadium compounds).

5. Neutralization of sulfuric acid and acid sulfates by basic particles (e.g., $CaCO_3$) or gaseous pollutants (e.g., NH_3), reaction with NaCl (and loss of HCl) or reaction with nitrate salts (and loss of HNO_3).

6. Interference due to other sulfates [e.g., $(NH_4)_2SO_4$, NH_4HSO_4].

7. Interferences in the quantitation method used due to other ionic species extracted from the filter medium or particulate matter (e.g., Ca^{+2} and $PO_4^{=}$ can be interferents in wet chemical methods).

Attempts to overcome some of these problems include reaction of sulfuric acid on the filter or within the sampler inlet to form a derivative which can still be distinguished from $(NH_4)_2SO_4$ and NH_4HSO_4.[42,43] The Atlantic Research Institute's approach employed acetaldehyde oxime to form a salt with H_2SO_4.[42] Initial studies suggested this derivative was decomposed to a volatile, sulfur-containing species at a temperature well below the decomposition temperature for the ammonium salts. If true, the volatile sulfur species could be measured with a flame photometric detector to provide an indirect measure of H_2SO_4. However, recent work has demonstrated that the temperature for volatilization of these materials is particle size-dependent, limiting the potential for specificity.[44] This approach appears to have been abandoned.

Because of the rationale stated above for imposing the California sulfate standard, a need exists for a validated technique to monitor sulfuric acid. The present study was conducted in an effort to satisfy this need.

In addition to techniques specific for H_2SO_4, evaluation of techniques for total particulate strong acidity was included since this is conceptually simpler and possibly of equivalent medical significance.

B. Nitric Acid

Under ambient conditions nitric acid is believed to exist principally in gas phase. The measurement of nitric acid in ambient air has been reported by Spicer, sampling at West Covina, California[8] and elsewhere, and by Okita, sampling in Tokyo[9]. For the California site, a mean maximum for the acid of about 25 $\mu g/m^3$ was observed. Both the California and Japanese studies measured nitric acid in the gas phase. However, nitric acid may also exist in particle phase adsorbed on other aerosol constituents where it may contribute to the observed acidity of the aerosol (as well as to the observed nitrate). Such adsorption may occur both before and after collection of the aerosol on a filter.

In addition to possible adsorption on particles, nitric acid has been demonstrated to adsorb readily on various filter media. If ambient nitric acid adsorbs on filter media, it should contribute to the observed particulate nitrate as well as to particulate acidity. Appel et al[10,11] demonstrated that the pattern of artifact particulate nitrate formation in ambient air was consistent with nitric acid adsorption as the dominant precursor.

In addition to providing data on a potentially hazardous pollutant, a reliable technique for monitoring gaseous nitric acid in ambient air can be used (1) to assist in evaluating the extent of artifact particulate nitrate formation under conditions used for routine monitoring, and (2) to evaluate the contribution to the total particulate acidity of nitric acid adsorbed on filter media and aerosol constituents.

The nitric acid methods in current use and their corresponding investigators are listed in <u>Table 1</u>. The methods can be divided into continuous and integrated techniques. An exception is the Fourier Transform IR technique which was operated to provide analysis of grab samples at 20 minute intervals. The immobility, high cost, and sophistication of this procedure limit its general use.

The two continuous methods utilize an inert pre-filter to remove particle-phase nitrates and either a modified Mast coulometric ozone analyzer or a modified chemiluminescence $NO-NO_2$ monitor. The Mast analyzer is converted to measure total gas phase acids by changing the chemicals employed and the instrument plumbing. By periodically diverting the sample air flow through a nylon filter to selectively remove HNO_3, the nitric acid concentration is obtained by difference. This approach suffers from relatively high instrument noise levels. Only Spicer and co-workers have been able to achieve the limit of detection quoted, 2-5 ppb. Spicer's evaluation of potential interference effects with this method is given in <u>Table 2</u>.

Only formic acid provides interference ($\leq$ 10%) at realistic concentrations. However, the maximum formic acid level found in Los Angeles was 6 ppb implying $\leq$ 0.6 ppb interference. Spicer considers the electro-chemical method to be decidedly inferior to the chemiluminescent analyzer approach in both limit of detection and response time.

The modified chemiluminescent NO_x monitor also uses a nylon filter to selectively remove HNO_3 from one instrument channel. At 300-325°C NO_2, HNO_3 and PAN are completely converted to NO on a molybdenum catalyst. No conversion of ammonia was found at these temperatures. Since PAN is not retained on the nylon filter to a significant degree, both channels register the effect of PAN equally and no interference results. By means of a chopper, two channels provide continuous measurement of $NO_x + HNO_3$ and NO_x alone.

Considering the integrated sampling methods, after pre-filtration of particle phase nitrates on inert filters, quantitative collection of nitric acid on nylon filters at levels down to 0.5 ppb has been reported. Although Millipore no longer supplies Duralon (nylon) filters, Ghia Corp. produces nylon filters which have been found equally suitable.[15]

Table 1

Summary of Nitric Acid Method in Current Use

Method	Method Description	Reported Limit of Detection, ppb	Principal Investigator	Ref.
Fourier Transform IR	Kilometer pathlength infrared cell. Units at Claremont and Riverside, CA.	7	J. N. Pitts, Jr	12, 13, 20
Okita	HNO_3 collected on NaCl impregnated filters following an inert pre-filter yielding integrated sample. Nitrate measured by wet chemistry.	≤ 0.4	T. Okita	9
		ca. 0.1	L. Newman	13, 14
Chemiluminescence	A dual channel NO_x monitor (e.g. Teco 14D) with a nylon filter in one channel yields (HNO_3) by difference. Provides continuous measurement.	< 1	C. Spicer	13, 15, 25
		ca. 0.3	D. Stedman	13, 16
← Nylon Filter (Spicer)	HNO_3 collected on nylon filter following an inert pre-filter yielding integrated sample. Nitrate measured by wet chemistry.	≤ 0.5	A. Lazrus	13, 17
		---	C. Spicer	15
Nylon Filter-GLC	HNO_3 collected on nylon fiber following inert pre-filter yielding integrated sample. Nitrate converted to nitrobenzene which is measured by GLC-EC.	≤ 0.5	R. E. Sievers	13, 18
Modified Mast Electrochemical (Spicer)	From total gas phase acid less HNO_3 removed by nylon, HNO_3 measured by difference. Use inert pre-filter. Continuous measurement.	2-5	C. Spicer	13, 15, 19

Table 2

Evaluation of Interferences to Coulometric Nitric Acid Monitoring

Specie	Comment
Ozone	No interference up to 0.8 ppm
Nitrogen Dioxide	No interference up to 1 ppm
Sulfur Dioxide	No interference up to 1.1 ppm
Sulfuric Acid	No interference up to 100 $\mu g/m^3$
Hydrochloric Acid	No interference up to 0.4 ppm
Formaldehyde	No interference up to 0.5 ppm
Peroxyacetyl Nitrate	No interference up to 0.2 ppm
Formic Acid	Variable interference between 0-10% of formic acid concentration.
Nitrous Acid	No inference up to 0.4 ppm

Nylon filters, nylon or cotton fiber packed in Teflon tubes have all been used for HNO_3 removal. In each case quantitative HNO_3 retention is claimed without interference from NO and NO_2. Using 100 mg nylon fiber packing, sampling rates up to 10 lpm could be used. However, the efficiency of nitric acid extraction from nylon was reported to depend on the extraction medium.[16,17] Extraction in distilled water caused low recoveries at low HNO_3 concentrations. Using 0.1N NaOH, 1% aqueous NaOH or "acid solutions" for extraction, quantitative recoveries were claimed.

Nitric acid has also been collected on filters loaded with NaCl employing pre-filtration with inert filters.[9,14] Fixation of HNO_3 is believed to proceed via the reaction:

$$HNO_3\ (gas) + NaCl \rightarrow HCl\ (gas) + NaNO_3$$

Following collection, nitrate can be determined wet chemically. Okita[9] employed a lo-vol system with a 1 µm pore size Fluoropore pre-filter followed by a single 50 mm diameter inpregnated cellulose filter. A mean collection efficiency of 96.6% for a single filter was determined at 20 lpm. NO_2 showed increasing interference with increasing R.H. For example, 1.5 ppm NO_2 at 93% R.H. yielded about 5% positive interference.

Newman used a hi-vol configuration with 5" diameter (127 mm) filters in which acid-washed Pallflex 2500 QAO quartz fiber was used for the pre-filter. Two S and S 2W cellulose filters impregnated with NaCl were routinely run in series to collect HNO_3. At high R.H. (e.g. $\geq$ 90%) collection of HNO_3 on the pre-filter became significant. Under these conditions, the HNO_3 was desorbed and collected on the impregnated filters by sampling warm air provided by a heat gun for 10 minutes after the collection period.

C. Chemistry of HNO_3 as Related to HNO_3 and Nitrate Sampling

Rapid advances in understanding the chemistry of atmospheric nitric acid and nitrates are currently being made. We summarize here those elements relevant to our current program as well as to ARB's nitrate sampling efforts.

It has been proposed that the observed concentration of nitric acid and particulate nitrate in the atmosphere are interrelated by the equilibrium:

$$NH_4NO_3(s) \rightleftarrows HNO_3(g) + NH_3(g)$$

$$K = (HNO_3)(NH_3)$$

Two estimates of this equilibrium constant have been made:

Using Fourier Transform infra-red spectroscopy to measure 62 pairs of HNO_3 and NH_3 values under varying atmospheric conditions, a mean value for K of 162 $(ppb)^2$ was reported.[12] Seinfeld[21] has made similar calculations of apparent equilibrium constants from simultaneous HNO_3 and NH_3 data obtained from Spicer. His observed values range from ca. 7 to ca. 200 $(ppb)^2$ with most values around 30 $(ppb)^2$.

The observed K appears to vary with temperature and relative humidity. The temperature dependence paralleled that for the equilibrium constant obtained from laboratory measurements of the vapor pressure of NH_4NO_3 at temperatures > 76°C. For dry NH_4NO_3 at 25°C, a K = 51 $(ppb)^2$ can be calculated by extrapolation from these lab data. At high relative humidity values, the apparent atmospheric equilibrium constant, as defined above, was increased by up to a factor of ca. 6 relative to values at < 60% R.H.

If such an atmospheric equilibrium exists then a fraction of total nitrate (i.e. nitric acid plus NH_4NO_3 + MNO_3 where M is a metal) collected on a filter could be lost by volatilization into air with lower ammonia concentration passing through the filter. Indeed, R. K. Stevens has confirmed loss of NH_4NO_3 from filters into a stream of ammonia-free air.[22] Evaporative loss of nitrate from a pre-filter used in connection with nitric acid sampling should lead to an equivalent enhancement in levels of HNO_3.

A second source of error involving particulate nitrate and HNO_3 is by reaction of particulate nitrate with acids. For example:

$$NH_4NO_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + HNO_3(gas)$$

Again, particulate nitrate is lost from a pre-filter and a positive error in HNO_3 measurement would result. This mechanism was first demonstrated in smog chamber studies[23] but has since been inferred from atmospheric data under situations in which atmospheric sulfuric acid levels exceeded ammonium nitrate concentrations.[24] Loss of nitrate was demonstrated by addition of a tenfold excess of ca. 0.2 µm particle size H_2SO_4 aerosol to a filter containing 0.2 µm particle size ammonium nitrate.[22]

It should be noted that neither evaporative loss nor loss by acid reaction would be expected on alkaline filters (e.g. glass fiber hi-vol filters) since any HNO_3 formed should be immediately trapped by the filter. However, such negative errors could be noticeable with inert filters such as Fluoropore. Thus the ratio of atmospheric particulate nitrate observed on reactive vs. inert (e.g. Teflon) filters may reflect, in part, nitrate values on the inert filters which are too low.

The AIHL study of artifact nitrate formation[10] observed a mean ratio of 2.2 for NO_3^- on MSA 1106BH relative to that of Fluoropore for 24-hour samples. It is unlikely that this ratio was grossly influenced by reaction with acids since similar results were observed at San Jose and Los Alamitos, sites which should differ markedly in H_2SO_4 levels, if present. However, this ratio may contain some error because of evaporative loss from Fluoropore filters. The influence of evaporative loss may be visible in comparing observed 24-hour nitrate values from those calculated from four successive six hour samples. The ratio calculated/observed was about 1.3 for Fluoropore and close to 1.0 for filters considered more likely to form artifact nitrate. Loss of nitrate during 24-hour sampling with Fluoropore due to either evaporation or (less likely) acid reaction could have caused this result.

II. TECHNICAL SUMMARY AND CONCLUSIONS

A combined laboratory and field study has investigated methods for the determination of sulfuric acid and nitric acids as well as strong acids in atmospheric particulates. The sulfuric acid method, developed at the Brookhaven National Laboratory (BNL) employs benzaldehyde for selective extraction of sulfuric acid. This procedure was adapted for use with low volume samples by using the AIHL microchemical sulfate procedure for quantitation of sulfate following its separation from the benzaldehyde. Residual benzaldehyde and its oxidation products were shown not to interfere with the sulfate analyses. Nitric acid sampling was done with nylon filters and sodium chloride-impregnated cellulose filters following removal of particulate nitrate with a Teflon filter (1 µm pore size Zefluor, Ghia Corp.). Following extraction, nitric acid was measured as nitrate by the automated, copper-cadmium reduction, diazotization method.

A micro-titrimetric procedure developed by C. Brosset was used to assess strong acids. The output signal was processed with an anti-log amplifier to permit automatic generation of Gran's titration plots. Subsequent work established that by adding to each sample an amount of strong acid sufficient to produce pH = 4.0 in distilled water and then titrating each sample back to this pH, interference from weak acids was largely eliminated without reliance on extrapolations from Gran's plots. In the mixtures H_2SO_4-hexanedioic acid (pKa = 4.4) and H_2SO_4-benzoic acid (pKa = 4.0) the organic acid interference was 0 and 18%, respectively, while permitting 96% determination of the H_2SO_4. Under the same conditions, aluminum and ammonium sulfates showed no interference while ferric sulfate behaved as a dibasic strong acid in aqueous solution. Accordingly, determination of water-soluble iron in atmospheric samples was considered necessary to exclude this source of potential interference.

An analytical procedure for strong acid developed by P. West utilizing indicators was briefly evaluated and rejected because of insufficient selectivity and sensitivity.

Eight quartz and Teflon filter types were evaluated for use in sulfuric acid sampling by determining efficiencies for collecting $\leq$ 0.3 µm H_2SO_4 aerosol and by recovery studies. One µm Fluoropore, 1 µm Teflo (Ghia Corp. Teflon), Gelman microquartz and acid-washed Pallflex 2500 QAO quartz exhibited > 98% collection efficiencies; 3 µm Fluoropore, 3 µm Teflo and Zefluor (Ghia Corp. Teflon), 5 µm Mitex and 0.5 µm unbacked Fluoropore exhibited lower values. Based on their freedom from artifact sulfate formation, high filtration efficiency, and ease in handling, 1 µm pore size Zefluor Teflon filters (Ghia Corp.) and acid-washed Pallflex 2500 QAO quartz filters were chosen for low and high volume particulate acid sampling, respectively.

The recovery of ca. 10 µg sulfuric acid aerosol by benzaldehyde extraction from clean quartz filters averaged 60% compared to 75% recovery reported by BNL for similar conditions. With Teflon filters, recoveries were about 70%. Storage of sulfuric acid aerosol on these clean filters in air-tight containers was sufficient to prevent its neutralization. However, the presence of atmospheric particulate matter caused relatively rapid (if not immediate) loss of H_2SO_4, with recoveries by benzaldehyde extraction of $\leq$ 30%. Recoveries of total particulate acidity remained relatively high, 60-70%, suggesting that reaction of H_2SO_4 with $(NH_4)_2SO_4$ was occurring forming the strong acid, NH_4HSO_4 (ammonium acid sulfate).

Direct evaluation of interference effects from $(NH_4)_2SO_4$ in the absence of atmospheric particulates was also consistent with formation of NH_4HSO_4. However, it appeared that substantial amounts of the acid sulfate were extracted into anhydrous benzaldehyde. Using clean filters loaded with NH_4HSO_4 aerosol, alone, and in the presence of H_2SO_4, benzaldehyde was determined to extract, on average, 53% of this salt. It has been suggested that the water content of the sample and benzaldehyde determine the extent of NH_4HSO_4 extraction. We believe the extraction of the undried acid salt into anhydrous benzaldehyde in the present work reflects the influence of its small particle size increasing the rate of solution. Prior studies were conducted with filter samples prepared by spotting with aqueous solutions. In the presence of atmospheric particulate matter, a positive interference by NH_4HSO_4 in the benzaldehyde extraction method was not observed; evidently both H_2SO_4 and the HSO_4^- react with aerosol constituents. The median recovery of total strong acid was 36% by titration. It remains unclear why recovery of strong acid, following atmospheric particulate-H_2SO_4 interaction, was substantially higher if the acid sulfate was the dominant strong acid being measured.

For low volume filter sampling , an ammonia denuder was fabricated and shown to remove > 99% NH_3 at the 100 ppb level. It was intended to minimize neutralization of acid sulfates after their collection by removing NH_3 ahead of the filter. However, use of an ammonia denuder with a nearly neutral pH glass fiber pre-filter was found ineffective in preserving H_2SO_4 aerosol on a Teflon filter when exposed to ambient air. We speculate that dissociation of NH_4NO_3 on the pre-filter may provide the NH_3 needed to neutralize the acid on the downstream filter. Since a pre-filter is not used in atmospheric sampling for H_2SO_4, this experiment may not be totally relevant.

The efficiency for collection of nitric acid was > 96% for NaCl-impregnated Whatman 41 filters. For nylon (Duralon) the efficiency appeared to depend on the total amount of nitric acid sampled. However, at atmospheric levels its efficiency was equivalent to that for NaCl-impregnated filters. Duralon (Millipore Corp.) and Ghia Corp. nylon filters were equivalent at up to 300 $\mu g/m^3$ HNO_3. Teflon and acid-washed quartz filters showed negligible artifact nitrate formation with NO_2 at 90% relative humidity. Results for artifact particulate nitrate due to nitric acid collected on clean and particulate-loaded filters were variable, with up to 16% HNO_3 retention, probably reflecting the effect of variability in losses of adsorbed nitric acid in storage and handling. In all cases Teflon filters showed the least artifact particulate nitrate from nitric acid. Heating of the pre-filter and holder during or just following sampling to transfer adsorbed nitric acid to the collection filter appeared to be desirable to maximize nitric acid recovery. Such a procedure was used in field sampling.

Sampling was done in Pittsburg, CA for strong particulate acid, H_2SO_4, HNO_3, NH_3, NO_3^-, $SO_4^=$, NH_4^+, SO_2, NO and NO_2 for a 72-hour period in early February, 1979. Side-by-side sampling was done with a respirable particulate hi-vol (acid washed quartz fiber filter), and a respirable particulate lo-vol sampler (Teflon filter) the latter employing an ammonia denuder. Ammonia was sampled with oxalic acid-impregnated filters using glass fiber (pH = 7.6) pre-filters. Filter changes were made at 2 to 8 hour intervals. The nitric acid and ammonia samplers' pre-filters were briefly heated at ca. 50°C following sampling to maximize recoveries on the collection filters.

The highest H_2SO_4 level observed was 0.6 $\mu g/m^3$ which coincided with a maximum in total particulate acidity (1.6 $\mu g/m^3$ expressed as H_2SO_4). While acidity was measurable, no H_2SO_4 was detectable with the hi-vol sampler. Ferric ion was shown to be a minor (< 10%) contributor to the total strong acid. There was no obvious benefit in using the denuder. Based on the preceding laboratory studies, these results represent lower limits to the true levels of H_2SO_4 and strong acid, which may be a factor of three higher. These initial results may be compared to the current California significant harm level standard for 24-hour average water-soluble sulfate, 25 $\mu g/m^3$.

The two sampling procedures for nitric acid showed average agreement within 4%, with levels of nitric acid in the range 0.7 to 4 $\mu g/m^3$ (0.3 to 1.5 ppb). Ammonia levels ranged from zero to 13 $\mu g/m^3$ (19 ppb). The diurnal variations for NH_3 and particulate NH_4^+ were strongly correlated even though NH_3 and HNO_3 levels were well below values causing saturation with respect to NH_4NO_3 formation. The cation-anion balance in the aerosol phase indicated a substantial excess of NH_4^+ consistent with the presence of other important anions (not determined) such as Cl^-, or with the collection of NH_3 by adsorption on the filter and/or particulate. The latter would be consistent with prior observations of the volatility behavior of particulate bound NH_3 in atmospheric samples.

Comparison of the total nitrate (i.e particulate nitrate collected on a Teflon pre-filter plus nitric acid retained on an active filter downstream) with the nitrate observed on a glass fiber filter (Gelman A) showed agreement, on average, within 3%. Thus, at least at the low HNO_3 levels encountered, these glass fiber filters collected all the true particulate nitrate as well as the nitric acid. Ambient NO_2 appeared to play no role in influencing artifact particulate nitrate, consistent with prior studies.

A sampling study for H_2SO_4, HNO_3, particulate acidity and true particulate nitrate in the South Coast Air Basin is planned for the summer, 1979.

Principal conclusions from the current study are as follows:

1. Measurement of sulfuric acid and total acidity can be made by benzaldehyde extraction and titration with laboratory-generated H_2SO_4 aerosol on clean filters with a recovery of > 60% of the true value. However, the presence of respirable atmospheric particulate matter decreased recoveries of H_2SO_4 to below 30%. Strong acid recoveries usually remained above 60%. Furthermore, the elimination of large, soil-related particles by use of a cyclone, alone, or in combination with ammonia removal is probably insufficient to permit measurement of H_2SO_4 at least for samples collected from $\geq$ 10 m^3 of air. Emphasis must be given to shorter term or lower flow rate sampling to decrease acid interaction with other aerosol constituents.

2. Additional work is needed to clarify the interference effects of ammonium acid sulfate in H_2SO_4 and strong acid measurements.

3. Gaseous nitric acid can be measured by collection with either nylon or sodium chloride impregnated cellulose filters at ambient concentrations, with excellent agreement between methods. A 15% uncertainty in HNO_3 value remains, resulting from variability in the extent of nitric acid retained by adsorption on particulate-loaded pre-filters. This uncertainty should be eliminated by AIHL studies extending the present work.

4. Artifact nitrate formation on glass fiber filters in field sampling corresponded to the collection of 100% of the ambient nitric acid. Thus it is likely that nitrate values obtained by the present ARB Hi-vol network represent the sum of particulate nitrate and nitric acid rather than particulate nitrate, alone.

5. Further studies are needed employing continuous methods for H_2SO_4 in an effort to overcome the large negative interference by other aerosol constituents. Since positive errors are more probable with continuous methods (e.g. volatilization of sulfate salts as well as H_2SO_4), simultaneous application of continuous and the integrated techniques described herein should provide both lower and upper limits to the true H_2SO_4 level.

III. SULFURIC ACID MEASUREMENT BY SELECTIVE EXTRACTION

A. Introduction

Leahy et al at Brookhaven National Laboratory (BNL) have demonstrated the selectivity of benzaldehyde for extraction of sulfuric acid (Table 3); ammonium sulfate and acid sulfate are relatively insoluble.[27] The H_2SO_4 removed is extracted from the benzaldehyde into water by liquid-liquid extraction. Once in the water phase, the sulfate from the H_2SO_4 can be analyzed by any procedure with adequate sensitivity. For our work these analyses were done by the AIHL microchemical method.[28] This is a colorimetric procedure operating in the range 1 to 14 μg/ml.

From the data given in Table 3, the recovery of the acid appeared to depend somewhat on filter type and amount of acid. For samples $\geq$ 10 μg collected on acid treated quartz, a recovery of $\geq$ 75% was found in the absence of atmospheric particulates. Employing atmospheric samples collected on acid treated quartz filters without protection from ammonia, BNL found sulfuric acid levels of up to 0.16 μmoles/m^3 (15 μg/m^3) from aerial sampling in the St. Louis urban plume. Sulfuric acid in general was only measurable when the H^+/NH_4^+ molar ratio was > 1. Otherwise, any sulfuric acid initially present was presumably be converted to the acid sulfate, NH_4HSO_4. While still titratable as a strong acid (see Section IV) the acid sulfate seemed to be relatively insoluble in benzaldehyde. The conversion of the sulfuric acid to the acid sulfate could involve reaction with gaseous ammonia and/or reaction with sulfate salts such as ammonium sulfate.

An independent evaluation of the BNL selective extraction procedure was performed by the Southern Research Institute (SRI)[30]. Their work demonstrated H_2SO_4 recoveries of approximately 90% (C.V. $\leq$ 5%) from Teflon (Mitex) filters using a microtitration of sulfate with barium perchlorate to a thorin end point. The minimum quantity of H_2SO_4 that could be determined was 5 μg. Calcium sulfate, NH_4HSO_4 and $(NH_4)_2SO_4$ in the absence of H_2SO_4, were shown to be > 95% insoluble in anhydrous distilled benzaldehyde, stored under N_2, when spiked onto filters. However, in another study of the BNL method using reagent grade benzaldehyde, about 25% of NH_4HSO_4 was solubilized.[41]

Following partial neutralization by NH_3 of an H_2SO_4 aerosol on a clean Mitex filter, SRI workers found that what was thought to be H_2SO_4 was still extractable by benzaldehyde. For example, after adding 0.41 μequiv NH_3 to 0.80 μequiv H_2SO_4, 0.29 μequiv of NH_4^+ were found in the aerosol and 0.57 μequiv residual H_2SO_4 were determined by extraction. If it is assumed that a given aerosol particle is either completely neutralized to $(NH_4)_2SO_4$ or remains as H_2SO_4 then the theoretical amount of H_2SO_4 which should remain is $0.80 - \frac{0.29}{2} = 0.66$ μequiv, only 16% greater than observed. If all acid particles were neutralized to the same degree, then in the above example, 50% of all H_2SO_4 particles would have been converted to NH_4HSO_4 and 0.40 μequiv of H_2SO_4 would remain (about 30% below the observed). Assuming that NH_4HSO_4 remained insoluble in benzaldehyde, preferential neutralization to $(NH_4)_2SO_4$ of an upper layer of acid particles is inferred.

Table 3

Benzaldehyde Extraction of H_2SO_4 and NH_4HSO_4 from Filters[a]

Amount	Sample	No. of Determinations	Filter Material	% Recovery
10 µg	H_2SO_4	2	Quartz	75
20-40 µg	H_2SO_4	2	Mitex 5 µm	71
30 µg	H_2SO_4	1	Fluoropore 0.2 µm	90
20-40 µg	H_2SO_4	4	Quartz	78
70-80 µg	H_2SO_4	4	Quartz	86
100 µg	H_2SO_4	5	Any of the above	94 ± 8
10-70 µg	NH_4HSO_4	3	Fluoropore 0.2 µm	1.2

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a. Data from Reference 29.

D. J. Eatough and co-workers evaluated the technique for analysis of H_2SO_4 in smelter flue dust samples.[31] The level of contaminant benzoic acid in benzaldehyde was found to be critical in influencing the selectivity of H_2SO_4 extraction. In the presence of benzoic acid, bevalent metal sulfates (e.g. Cu, Zn, Pb sulfates) were also extracted.

In the current program both clean and soiled filters were loaded with sulfuric acid alone, and in the presence of $(NH_4)_2SO_4$ and NH_4HSO_4. The filters were analyzed by both benzaldehyde extraction and the titrimetric method for strong acid as reported in Section VII.

B. Method Development

1. Effect of Benzaldehyde on the AIHL Microsulfate Method

Benzaldehyde is soluble in water to the extent of 0.3%. The aqueous extract analyzed for sulfate is saturated with benzaldehyde and also contains the oxidation product, benzoic acid. To assess the response of the microsulfate method to these contaminants, working curves were constructed using aqueous H_2SO_4 standards with and without contacting with benzaldehyde. H_2SO_4 solutions were shaken with varying amounts of benzaldehyde and then centrifuged. Both redistilled and unpurified benzaldehyde were used.

Results were compared to simultaneous sulfate analyses of H_2SO_4 solutions without benzaldehyde extraction (Table 4). While the linearity of response remained unaffected, both the slope and intercept can be altered. No consistent trend is evident in the changes observed. Since in all cases a new working curve is prepared for each set of samples using benzaldehyde-extracted standards, such changes are likely to be insignificant. No effect of the ratio of benzaldehyde/water was observable. Accordingly, the AIHL microsulfate was considered compatible with the benzaldehyde extraction technique.

2. Procedure for Sample Analysis

Filter samples with laboratory-generated or atmospheric aerosols were sectioned as necessary and transferred to Teflon-lined screw capped test tubes in an NH_3-free chamber. No drying of samples was done. The tubes were flushed with argon, capped and stored in a dessicator under argon pending analysis. Ten ml anhydrous benzaldehyde were added under argon and the samples shaken 30 minutes (60 minutes for atmospheric samples) on an Eberbach Model 6000 platform shaker at 90 oscillations per minute.* Samples were then centrifuged 2 to 3 minutes at an estimated 2500 rpm. Eight ml aliquots were transferred to a new set of test tubes containing 3 ml H_2O under argon (benzaldehyde/water ratio 2.7). The mixtures were shaken 30 minutes as above, centrifuged briefly, and an aliquot of the aqueous phase ($\leq$ 1.0 ml) removed for sulfate analysis by the AIHL microchemical method.[28]

Sulfate standards were prepared in 3 ml H_2O. Eight ml benzaldehyde were added to each of these and the standards shaken and analyzed together with each batch of samples.

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*For field samples in which H_2SO_4 aerosol might be physically shielded by other aerosol constituents the longer extraction period was considered desirable.

Table 4

The Effect of Benzaldehyde on Working Curves for the AIHL Microsulfate Method[a]

ØCHO/H_2O, v/v[b]	With Benzaldehyde			Without Benzaldehyde		
	Slope	Intercept	r	Slope	Intercept	r
1.0	0.0585	-0.0153	0.999	0.0540	-0.003	0.999
1.0	0.0581	-0.0570	0.999	0.0558	-0.016	0.999
1.7[c]	0.0523	-0.008	0.999	---	---	---
3.3[c]	0.0470	-0.0720	0.994	---	---	---
3.3[c]	0.0538	+0.0264	0.999	0.0546	-0.003	0.999
Mean	0.0539	-0.025		0.0548	-0.0073	
Std. Dev.	0.0047	0.0396		0.0009	0.0075	

---

a. In all cases 3.0 ml of H_2SO_4 standards were extracted.

b. Benzaldehyde/water volume ratio.

c. Benzaldehyde distilled in inert atmosphere.

C. Benzaldehyde Purification and Storage

Pre-dried benzaldehyde was redistilled from Linde type 4A molecular sieve at 40 mm Hg under nitrogen through a 12" Vigreaux column, stored with protection from light, and dispensed under argon. Freshly distilled benzaldehyde was found to contain 0.06 ± .006%w benzoic acid. After five months storage and immediately following interference studies with NH_4HSO_4 (Section VII), reanalysis indicated 0.6 ± 0.06%w benzoic acid. Thus the acid content had increased by a factor of 10.

An estimate of the water content of the benzaldehyde following 5 months storage was made by comparing the color change of anhydrous copper sulfate in benzaldehyde to that in chloroform with known water content. The results indicated $\leq$ 0.004%w water.

IV. THE MICROTITRATION METHOD FOR STRONG ACID

A. Introduction

C. Brosset and co-workers have employed microtitrations of aqueous extracts of particulate matter to measure the acidity of such samples.[32-34] To measure strong acids in mixtures with weak acids, Gran's plots were used. In a conventional potentiometric titration an "S" shaped titration plot such as Figure 1A is obtained. In a Gran's plot, the ml of titrant (NaOH) added is plotted against the concentration of H^+ remaining. If the volume change due to the added titrant is negligible, the result is a linear titration plot (Figure 1B). The right hand portion of the plot is shown as the mirror image of the actual plot of (H^+) vs. ml titrant or as the increasing concentration of unneutralized hydroxide. Real titration curves typically show curvature near the equivalence point (i.e. the ml of titrant corresponding to zero sample in the Gran's plot). The advantage of the Gran's plot is that the endpoint can be accurately determined by extrapolating from the initial linear portion of the curves.

Brosset reported that in atmospheric samples, titrated in the absence of CO_2, strong acids ($pKa < ca. 3$) can be distinguished from weak acids ($pKa > ca. 7$). A tabulation of acidity constants for some acids of possible significance is given in Table 5. In the presence of a mixture of one or more strong and weak acids, the Gran's plot exhibits a linear section followed by a curved section. Extrapolation of the linear section to the horizontal axis gives the total strong acids present. Figure 2 illustrates Brosset's data as a Gran's plot for a mixture of sulfuric acid and hydrated Al^{+3}, $Al(H_2O)_6{}^{3+}$ which titrates as a strong monoprotic acid.* Extrapolation of the linear portion yields a total H^+ of 0.8×10^{-6} moles H^+ compared to a theoretical value of 0.85×10^{-6} moles H^+ (from H_2SO_4 and the hydrated aluminum ion). Quantitation of weak acids (as defined above) in the presence of strong acids does not appear feasible.

The instrument evaluated for the analysis at AIHL was the "Autoburette AB 12" manufactured by Radiometer of Denmark with 250 µl capacity. Using 0.01 N NaOH, each microliter neutralizes about 0.5 µg H_2SO_4. The readout of the volumetric counter allows a precision of 0.1 µl, and the pH meter digital display, a precision of 0.001 units of pH. The instrument titrates automatically to a preset value of pH. The speed of titrant addition can be regulated by adjusting the speed of the piston of the burette or by a proportional time chopper, which reduces the increments of addition of titrant as the value of the measured pH approaches the preset value. The endpoint is sensed by a delay mechanism, which at a preset value of waiting time shuts off the instrument.

The relationship between H^+ concentration and electrode response as well as an antilog amplifier circuit for processing the electrode output to generate Gran's plots automatically are shown in Appendix A.

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*The axes have been multiplied by volumes to obtain sample and titrant in moles.

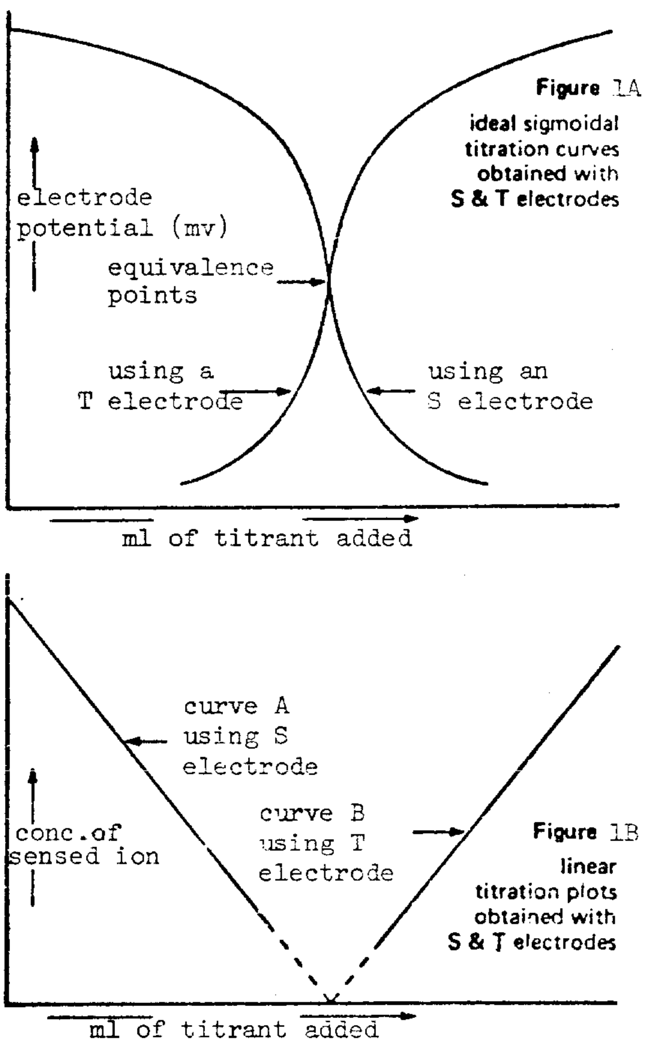

Figure 1 Comparison of Conventional Titrimetric Data (1A) and Linear Titration Plots Following Sample (S) and Titrant (T) Concentrations (1B)

Table 5[a]

Anthropogenic Acids and Their Approximate Strength

Acid	Strength (pKa)	Acid	Strength (pKa)	Acid	Strength (pKa)
HCl	strong	HF	3.2	$B(OH)_3$	9.0
HNO_3	strong	$Fe(H_2O)_6{}^{3+}$	∿ 3	$NH_4{}^+$	9.3
H_2SO_4	strong	$Fe(H_2O)_5OH^{2+}$	∿ 3	HCN	9.4
H_2SO_3	1.9	benzoic	4.2[b]		
$HSO_4{}^-$	2.0	adipic (pKa_1)	4.4[b]		
H_3PO_4	2.1	acetic	4.8[b]		
		$Al(H_2O)_6{}^{3+}$	∿ 5		
		H_2S	6.9		
		$HSO_3{}^-$	7.2		
		$H_2PO_4{}^-$	7.2		

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[a] Data from reference 33 except as noted.

[b] Data from reference 45.

Gran's Plot Titration of Mixed Acids

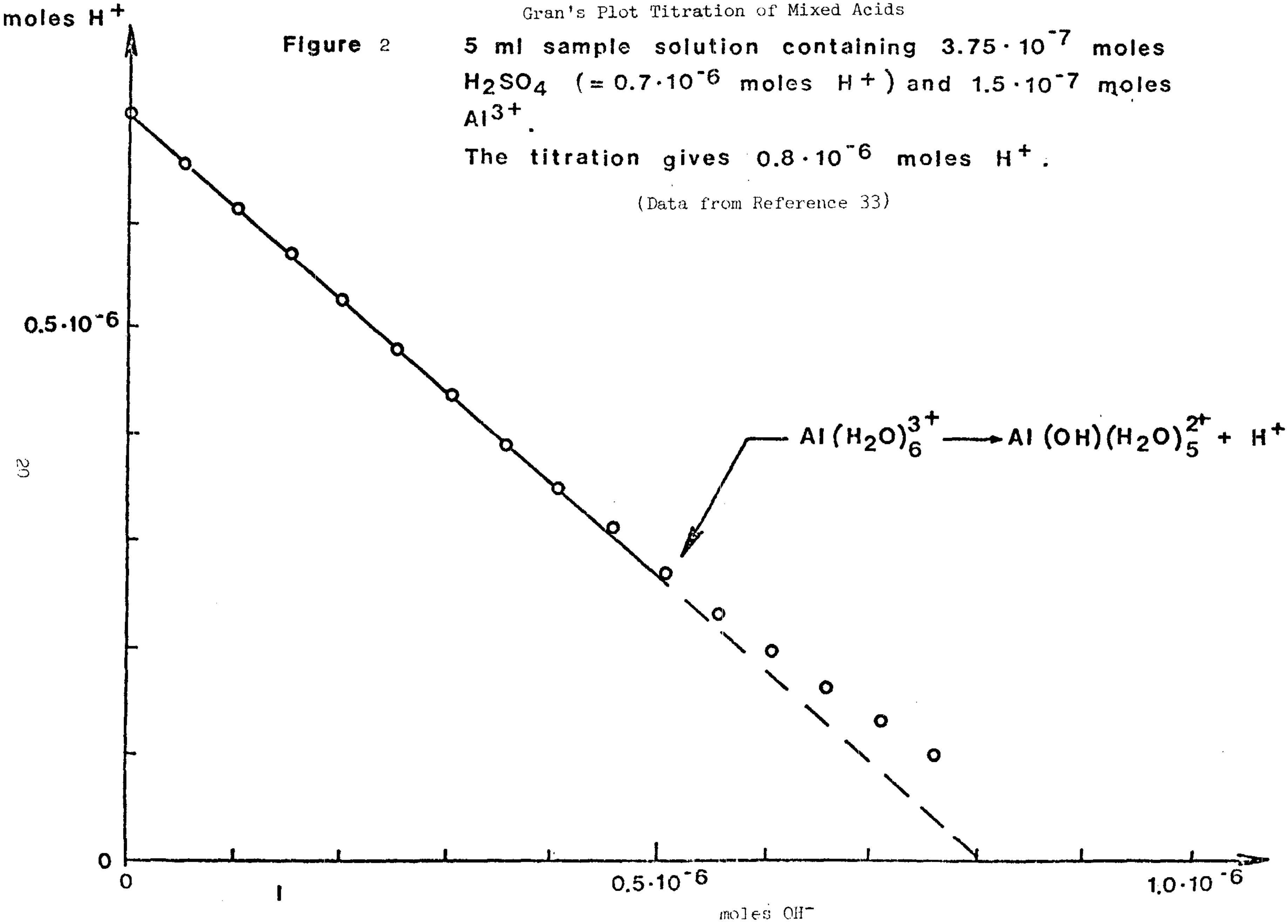


Figure 2 5 ml sample solution containing $3.75 \cdot 10^{-7}$ moles H_2SO_4 ($= 0.7 \cdot 10^{-6}$ moles H^+) and $1.5 \cdot 10^{-7}$ moles Al^{3+}.

The titration gives $0.8 \cdot 10^{-6}$ moles H^+.

(Data from Reference 33)

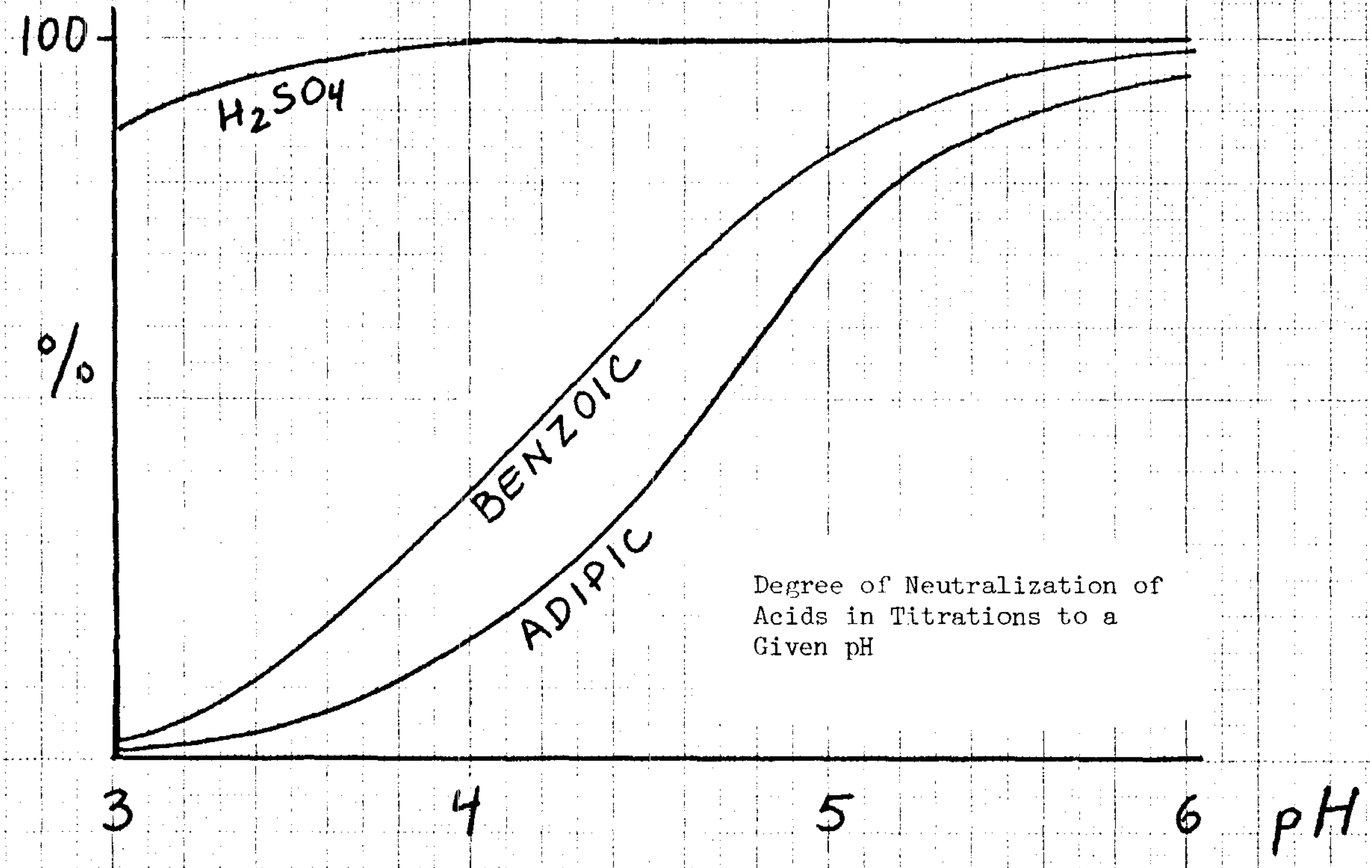
B. Interference Studies and Alternatives to Use of a Gran's Plots

Figure 3 shows the fraction of individual acids, in distilled H_2O, titratable by NaOH at a given pH using the Radiometer automatic titrator. It reflects directly the degree of ionization of each acid at a given pH when in the presence of ions formed by neutralization (e.g. Na^+, adipate ion) but without other added electrolyte. The degree of ionization is a function of the acid considered and varies with the ionic strength of the medium. While H_2SO_4 is nearly totally ionized at pH $\geq$ 4 (and, therefore, the equivalents of base added to neutralize the H_3O^+ in solution is equal to the equivalent of H_2SO_4 in the sample) organic acids show reduced ionization at pH values below 7 and approach zero at pH 3 and below. The degree of ionization of organic acids in a mixture with strong acids (e.g. H_2SO_4, HNO_3) and salts may differ substantially from that for pure, individual acids in distilled water. For example, the ionization of acid, HA, in solution reflects the equilibium $HA + H_2O \rightleftarrows H_3O^+ + A^-$. Addition of strong acid should shift the equilibrium to the left while addition of neutral electrolyte favors increased ionization by lowering activity coefficients for the ionic species. As the result of repressed ionization, weak acids should exhibit lesser interference in the titration of strong acids than is implied by Figure 3. Furthermore, by titrating such mixtures to pH = 4 (rather than 7), $\geq$ 96% of the H_2SO_4 should be determined while benzoic acid should exhibit $\leq$ 37% positive interference and adipic acid (hexanedioic acid), $\leq$ 17% positive interference.

As a trial of interference effects and of analytical techniques, a set of ten solutions were prepared containing H_2SO_4 plus hexanedioic acid, H_2SO_4 plus benzoic acid, and H_2SO_4 plus both organic acids. Assuming a 24-hour collection of H_2SO_4 at 1 $\mu g/m^3$ with a low volume (20 m^3) sampler and extraction into 5 ml of water, an acid concentration of 0.4 μequiv/5 ml would be expected. The ten solutions were adjusted to provide concentrations in this range. To 5 ml of each sample was added sufficient HNO_3 to reach pH = 4.0 in a pure water solution. The observed pH was between 3.4 and 3.8. The solution was then titrated back to pH = 4.0. In only three cases (VII, VIII, IX of Table 6) was the Gran's plot non-linear. The difference in results between the extrapolated intercept (from initial slope) at pH = 4 and the observed intercept was $\leq$ 10% in these cases.

The observed intercept corresponds to the volume of titrant required to reach pH = 4.0. Under these circumstances an extrapolated intercept was generally unnecessary and the volume of titrant could be obtained with better precision from the digital readout of titrant volume. These studies suggested that by titrating to pH = 4.0, Gran's plots were usually unnecessary.

Results for analysis of the ten known mixtures, with direct reading of titrant volume required to reach pH = 4.0 (i.e. without extrapolation from a Gran's plot) are given in Table 6 and plotted as μg/ml in Figure 4. They generally show excellent agreement with true values. The presence of benzoic acid (pKa = 4.2), which is distinctly more



Degree of Neutralization of Acids in Titrations to a Given pH

Figure 3

Table 6

Analysis of H_2SO_4 by Gran's Titration in Mixtures with Weak Acids[a] (μequiv/5 ml)

Sample	H_2SO_4	Hexanedoic Acid	Benzoic Acid	Observed Strong Acid
I	0.40	0.40	0	0.41
II	0.20	0.40	0	0.21
III	0.40	0.20	0	0.39
IV	0.50	0	0.20	0.51
V	0.20	0	0.50	0.29
VI	0.40	0.20	0.20	0.43
VII	0.20	0.20	0.20	0.22
VIII	0.79	0.80	0	0.78
IX	0.79	0.40	0	0.77
X	0.79	0.20	0	0.74

---

a. Titrations to pH = 4.0. Results corrected by division by 0.96 for the 4% H_2SO_4 remaining unneutralized at pH = 4.0 in a single system containing KNO_3 at the concentration used with samples. The percentage unneutralized varies slightly from day-to-day leading to correction of 3-6%.

COMPARISON OF OBSERVED AND TRUE SULFURIC ACID
IN MIXTURES WITH WEAK ACID

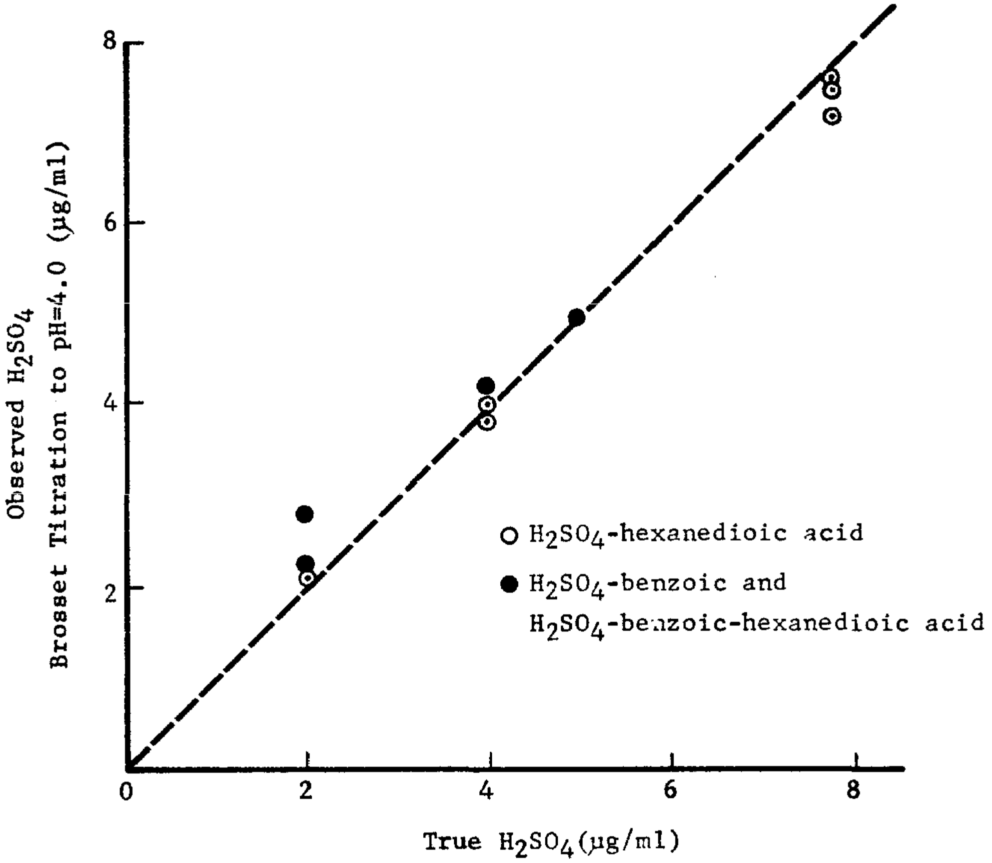


Figure 4

acidic than adipic acid ($pKa_1 = 4.4$), caused a consistently positive error. The largest error was observed for sample V which was about 30% H_2SO_4 and 70% benzoic acid (on an equivalents basis). The results suggest an 18% positive interference by benzoic acid at this concentration compared to the value $\leq$ 37% predicted from Figure 3.

For the remainder of this study all microtitration data were based on titrations to pH = 4.0 with direct reading of titrant volume. With ambient air samples, Gran's plots were made to verify that the slope was equivalent to that for sulfuric acid.* In all cases where there was sufficient strong acid to permit determination, this was the case.

In a similar manner interference effects of aluminum and ferric salts and ammonium sulfate was evaluated by analyzing 0.2 μequivalents of H_2SO_4 alone and in mixtures with one of the interferents. Results were calculated both from the recorded volume of titrant (0.010N NaOH) required to reach the starting pH (4.0) and, graphically, from the simultaneously constructed Gran's plot. The results (Table 7) indicate no interference from $(NH_4)_2SO_4$. This is consistent with expectations since the resulting HSO_4^- (pKa = 2.0) should still be titrated as a strong acid. Similarly the Al^{+3} salt showed $\leq$ 10% interference. However, interference from the Fe^{+3} salt was strong. In aqueous solution this hydrolyzes to $Fe(H_2O)^{+3}$ which, in turn, dissociates as a dibasic acid ($pK_1 \approx pK_2 \approx 3$). Thus 0.134 μmoles Fe^{+3} (from 0.067 μmoles $Fe_2(SO_4)_3$) should yield 0.27 μmoles H^+. This compares to 0.26 ± 0.04 μequiv (or μmoles) H^+ observed, averaging results by both techniques with and without added H_2SO_4.

The degree of interference from Fe^{+3} in atmospheric samples depends on the extent of water solubility of the iron in particulate matter. Selected aqueous extracts were analyzed for iron concentrations by atomic absorption as discussed in Section X.

---

*The slope for H_2SO_4 is not distinguishable from that for HSO_4^- and other strong acids.

Table 7

Interference Effects in H^+ Determination by Titrimetry

Sample[a]	Observed H^+ (μequiv) Titrimetry[b]	Gran's Plot to pH = 4.0[c]
0.20 μequiv H_2SO_4	0.22 ± .01	0.21 ± .02
0.20 μequiv H_2SO_4 + 4 μmole$(NH_4)_2SO_4$	0.20	0.20
0.20 μequiv H_2SO_4 + 0.067 μmoles $Al_2(SO_4)_3$[d]	0.22	0.20
0.20 μequiv H_2SO_4 + 0.067 μmoles $Fe_2(SO_4)_3$[d]	0.46	0.42[e]
0.067 μmoles $Al_2(SO_4)_3$[d]	0.02	0.00
0.067 μmoles $Fe_2(SO_4)_3$[d]	0.31	0.26[e]

---

a. All samples have 0.88 μeq HNO_3 in 5 ml H_2O yielding pH = 4.0 in pure water.

b. Based on volume of base to reach pH = 4.0.

c. Volume of base to reach pH = 4 from automatic generation of Gran's plot. Except as noted, Gran's plot was linear to pH = 4 requiring no extrapolation.

d. 0.067 μmoles yields 0.2 μmoles sulfate.

e. Extrapolated from initial slope.

V. THE WEST METHOD FOR TOTAL ACIDITY

A. Introduction

The West procedure[26] is based on the displacement of the equilibrium between an indicator in its basic (In^-) and acidic form (HIn) in the presence of acids:

$$K = \frac{[H^+]\,[In^-]}{HIn}$$

$$\text{or } \frac{[In^-]}{[HIn]} = \frac{[\text{form with alkaline color}]}{[\text{form with acid color}]} = \frac{K}{[H^+]}$$

In this technique bromphenol blue (BPB), which is protonated at about pH = 4, was selected because it is not affected by carbon dioxide and because it provides an appropriate working range with strong acids. The measured absorbance at approximately 590 nm is used as a direct measure of the H^+.

B. Evaluation

Initial studies at AIHL sought 1) to reproduce the reported working curve, 2) to estimate the working range of the method, 3) to adapt the method for use with 10 ml rather than 100 ml samples and 4) to evaluate the effects of possible interferents.

A comparison of the lower portion of West's working curve relating total acid (as µg/ml H_2SO_4) and absorbance is shown in Figure 5. The solid lines represent several AIHL trials differing in the freshness of the reagent or length of standing of solutions. The AIHL results show generally better agreement with West's data at higher concentrations. Below 1 µg/ml the method loses sensitivity.

For this method to be useful with low volume filter samples it is essential to demonstrate its usefulness with smaller aqueous extracts. Figure 6 shows three trials differing in order of addition of acid and indicator and time for standing before reading absorbance (30 or 60 minutes). The results for the three trials showed excellent reproducibility and a useful working curve in the range 1 to at least 15 µg/ml, using H_2SO_4. For these trials, absorbance readings were made at 592 nm rather than 587 nm as specified by West. Using a B&L Model UV 200 spectrophotometer, 592 nm corresponded to the mid-point of the absorbance maximum.

The effect of the following potential interferents was briefly evaluated:

CO_2	$Al_2(SO_4)_3$
$Fe_2(SO_4)_3$	$(NH_4)_2SO_4$
$FeSO_4$	NH_4HSO_4

In separate experiments, each of the sulfate salts was added at a concentration sufficient to produce 10 µg/ml $SO_4^=$ (assuming complete ionization and dissociation). Carbon dioxide was added

Figure 5

COMPARISON OF AIHL AND WEST RESULTS FOR CALIBRATION CURVE (100 ml solutions)

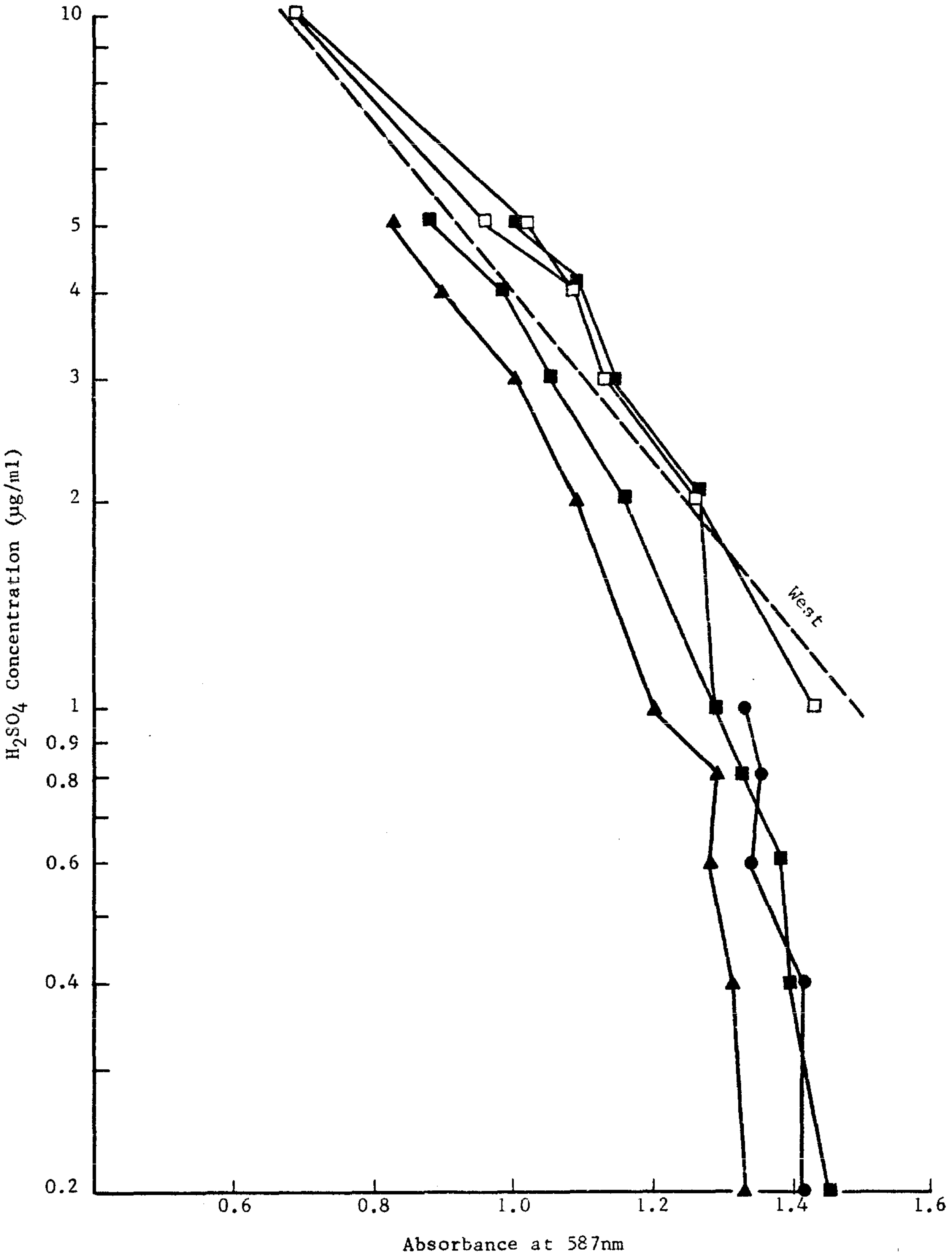
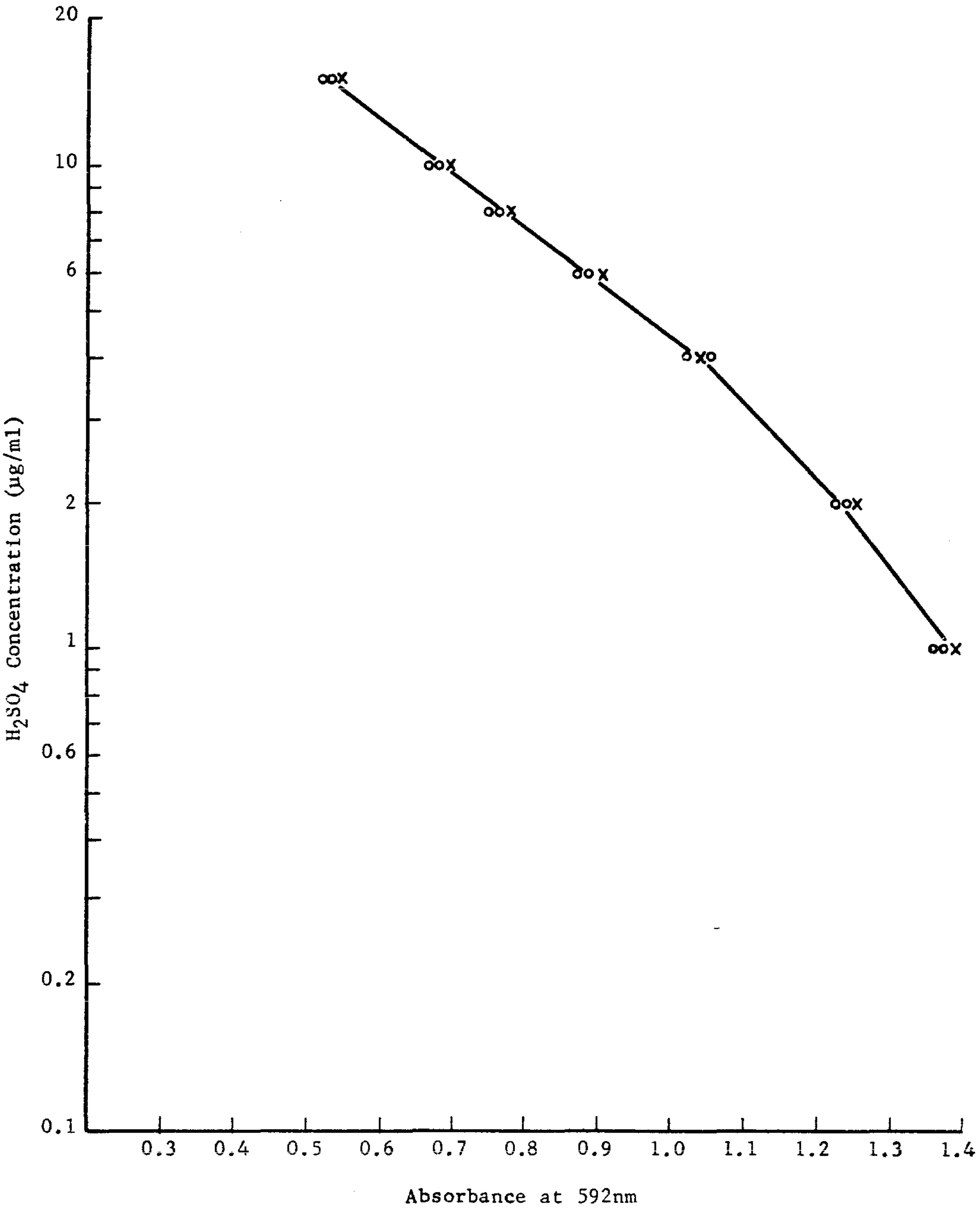


Figure 6

CALIBRATION CURVE FOR WEST METHOD
(10ml solutions)



by saturating an aqueous solution with gaseous CO_2. The response for CO_2 in this solution was equivalent to 3.3 μg/ml H_2SO_4. Since a dissolved CO_2 level of < 1% of saturation is more typical, a negligible effect of atmospheric CO_2 is expected, which is consistent with West's claims. The results for $Fe_2(SO_4)_3$ (ferric sulfate) and NH_4HSO_4 (ammonium acid sulfate) indicate complete hydrolysis to a strong acid (i.e. one equivalent of sulfate yielded one equivalent of H^+). With NH_4HSO_4 the equivalence of sulfate and H^+ was also demonstrated at the 5 μg/ml sulfate level. Thus, if present, these materials would be indistinguishable from sulfuric acid. However, $FeSO_4$, $Al_2(SO_4)_3$ and $(NH_4)_2SO_4$ showed no measurable interference.

To complete these studies of interference effects known amounts of sulfuric acid were analyzed in mixtures with two weak acids, hexanedioic acid ($pKa_1 = 4.4$) and benzoic acid ($pKa = 4.2$). The results shown in Table 8 indicate positive interference by both acids of, on average, 18%. Since aliphatic dicarboxylic acids are likely components in atmospheric samples[46], this method was considered of limited value and it was dropped from further studies.

Table 8

Analysis of H_2SO_4 by the West Method in Mixtures with Weak Acids (μequiv/5 ml)

Sample	H_2SO_4	Hexanedoic Acid	Benzoic Acid	Observed Strong Acid
I	0.40	0.40	0	0.47
II	0.20	0.40	0	0.44
III	0.40	0.20	0	0.45
IV	0.50	0	0.20	0.55
V	0.20	0	0.50	0.36
VI	0.40	0.20	0.20	0.48
VII	0.20	0.20	0.20	0.48
VIII	0.79	0.80	0	0.81
IX	0.79	0.40	0	0.73
X	0.79	0.20	0	0.75

Ratio of Means Obs./True = 1.18

VI. EVALUATION OF FILTER MEDIA FOR SULFURIC ACID AND PARTICLE PHASE STRONG ACID MEASUREMENTS

A. Artifact Sulfate Formation on Filters with Sulfur Dioxide

Filters to be used for H_2SO_4 sampling must minimize artifact sulfate formation due to filter-SO_2 interaction. Accordingly, the following filters were evaluated for artifact sulfate:

Acid-Treated Quartz (Pallflex 2500 QAO)*
Gelman Microquartz
Mitex, 5 μm
Fluoropore, 1 μm
Fluoropore, 3 μm
Teflo, 1 μm
Teflo, 3 μm
Zefluor, 3 μm

The filters were exposed to 0.2 ppm SO_2 at 50 and 90% R.H. in 2-hour periods. Two trials were made with each condition. Flow rates were 22 lpm except with the quartz filter. This was run at a flow rate of 1.3 cfm to provide a face velocity equivalent to that of an 8 x 10" filter at 40 cfm. None of the filters formed measurable (i.e. $\geq$ 5 μg/$SO_4^=$/filter) levels of artifact sulfate.

Retention of SO_2 as sulfuric acid, if significant, would have caused increased values of both sulfuric acid by benzaldehyde extraction and increase in particulate acidity. Retention of NO_x species such as HNO_3 would also have caused increase in particulate acidity. Studies of retention of NO_2 and HNO_3 on filter media, including those used for sulfuric acid and particulate acid measurement, are included in Section VIII.

B. Efficiencies of Filter Media for H_2SO_4 Collection

Filter efficiencies for $\leq$ 0.3 μm H_2SO_4 particles were determined by sampling laboratory-generated H_2SO_4 aerosol at 1 cfm (face velocity 34 cm/sec) with a 47 mm multiple filter holder (Nuclepore #470400) containing the filter type under evaluation followed by a 1 μm Fluoropore filter (after-filter) to collect any aerosol which penetrated through the initial filter. Fluoropore (1 μm) was employed as the after-filter in all evaluations based on its high collection efficiency** and high sulfuric acid recovery with water extraction. Immediately following exposure, the filter being evaluated, the underlying filter support grid and Fluoropore after-filter were extracted in 5 ml of distilled water with periodic, vigorous manual agitation for 48 hours at room temperature (22°C). Sulfate analyses

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*The acid treatment procedure is described in Appendix H.

**Liu and Lee[47] reported > 99.99% efficiency for this filter with 0.03 to 1 μm diameter dioctyl phthalate particles while John and Reischl[37] found > 99.9% efficiency with room air dust.

were performed by the AIHL microsulfate method.[28] Analysis of the filter support screen was included as it was the only filter holder surface upstream of the after-filter capable of collecting detectable amounts of sulfate. Design of the sulfuric acid aerosol generator and characterization of the aerosols produced are discussed in Appendix B.

Filtration efficiencies for a filter were determined as the fraction of H_2SO_4 on the filter compared to the total H_2SO_4 on it, the after-filter, and the filter screen. H_2SO_4 penetrating the after-filter (1 µm Fluoropore) was ignored, based on studies in which an impinger was used following the after-filter (see Appendix B).

Nine filter types were evaluated for filtration efficiency including two quartz and seven Teflon filters. The latter included Fluoropore in three pore sizes and two types of Teflon filter from the Ghia Corporation, "Teflo" (Teflon filters bonded to a polyester ring about the perimeter) and "Zefluor" (Teflon filters stiffened with a backing of a coarse Teflon). In addition to filtration efficiency, ease in mounting, cutting and H_2SO_4 recovery were evaluated.

Results of the filter efficiency evaluation are given in Table 9. In general the efficiency decreased with increasing nominal pore size; both 1 µm Teflon filters, Fluoropore and Teflo, showed about 98% efficiency. The 0.5 µm unbacked Fluoropore results appear anomalous. Both quartz fiber filters showed > 98% efficiency.

The current program for H_2SO_4 collection required one filter medium suitable for hi-vol sampling and at least one for lo-vol sampling. Based on its ease of handling and cutting, the Zefluor type Teflon filter was selected for further study. Because of the decreased efficiency of the Ghia 3 µm compared to their 1 µm filter the 1 µm pore size Zefluor filter was chosen.

Based on ease of handling, collection efficiency, and lack of artifact sulfate formation both acid washed quartz and Gelman microquartz appeared suitable for further evaluation.

Table 9

Collection Efficiencies of Selected Filters for $\leq$ 0.3 µm Sulfuric Acid Aerosol (µg $SO_4^=$)

Filter Type	1st Filter	Screen	2nd Filter	Filter[a] Collection Eff. (%)
Fluoropore, 1 µm[c]	549	5.0	6.0	98.0
	503	4.0	6.5	97.9
Teflo[d], 1 µm	1069	5.9	6.2	98.9
	746	5.2	9.6	98.1
Fluoropore, 3 µm[c]	534	N/A[b]	8.5	N/A
	560	8.3 ± 1.1	5.0	97.7 ± .2
Teflo[d], 3 µm	709	10.4	26.4	95.1
	657	10.5	18.0	95.8
Zefluor[d], 3 µm (thin backing)	673	14.8	15.7	95.7
	624	12.6	15.9	95.6
Mitex, 5 µm[c]	317	8.0	11.5	94.2
	384	8.5	14	94.5
Microquartz[e]	453	3.0	1.5	99.0
	470	0.5	1.5	99.6
Acid Washed Quartz (Pallflex 2500 QAO)[f]	537	1.5	6.5	98.5
	516	1.5	7.0	98.4
Unbacked Fluoropore, 0.5 µm[c]	440	4.0	14.8 ± 3.2	95.9 ± 0.7
	429	5.5	12	96.1

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a. Filter collection Efficiency % $= 1 - \left[\frac{(\text{Screen}) + (\text{2nd filter})}{(\text{1st filter}) + (\text{Screen}) + (\text{2nd filter})}\right] \times 100$

b. N/A = data not available.

c. Millipore Corp.

d. Ghia Corp., Pleasanton, CA.

e. Gelman Instruments Co.

f. Pallflex Products Corp., Putnam, CT.

VII. EVALUATION OF H_2SO_4 AND ACIDITY METHODS USING LABORATORY AEROSOLS

A. Preliminary Study for Filter Selection

The objective of this preliminary study was to select filters showing high recoveries of H_2SO_4 for detailed evaluation. Loss of H_2SO_4 in these studies could be ascribed to acid-filter interaction since great care was taken to minimize the possibility of neutralization by ambient ammonia.*

Three filters of each of six types were loaded with a nominal 60-80 μg H_2SO_4. Filters were cut in half in an NH_3 free chamber, and twice distilled water added to one set of filter halves, contained in sealed polystyrene tubes, for strong acid and sulfate measurement. The second set of filter halves was placed in sealed glass tubes for benzaldehyde extraction and H_2SO_4 determination. Sample transport and storage was done under argon to minimize neutralization by atmospheric ammonia.

Results of H_2SO_4, H^+ and $SO_4^=$ analyses are given in Table 10. Acid-washed quartz showed 95 ± 7% and 96 ± 26% recoveries by titration and benzaldehyde extraction, respectively. One and 3 μm Fluoropore yielded about 90% acid by both techniques. Recoveries with unbacked Fluoropore (0.5 μm) were close to quantitative, prompting further evaluation of similar Teflon filters lacking a polyethylene backing but with somewhat greater pore size.

B. Recovery Studies with Inert Filters

H_2SO_4 recoveries were determined with acid-treated quartz and Teflon membrane filters using about 50 μg per filter H_2SO_4 loadings. Filters were quartered as described in Appendix B. One quarter was used for benzaldehyde extraction and the remaining quarters were used for H^+ measurement and sulfate determinations. The expected level of H_2SO_4 was about 13 μg extracted by benzaldehyde and 39 μg for the other analyses. The results are given in Table 11. The acid levels determined titrimetrically were similar to those in Table 10. Recoveries of the acid by titration were relatively high and similar for the two experiments using acid-washed quartz and 1 μm Fluoropore. Recovery of the acid by benzaldehyde extraction is somewhat lower in Table 11 compared to Table 10. This is to be expected since the H_2SO_4 levels are lower. Recovery of ca. 10 μg H_2SO_4 from acid-washed Pallflex 2500 QAO averaged 60% (Table 11) which compares to 75% recovery reported by BNL for similar conditions. Zefluor, a Teflon filter backed with coarse Teflon, showed a somewhat lower recovery of acid by titration compared to Fluoropore or acid-washed quartz. However, average recovery of H_2SO_4 by benzaldehyde extraction was slightly higher.

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*Loss of H_2SO_4 by neutralization with NH_3 during and after sampling and by interaction with particulate matter is considered following choice of filter media.

Table 10

Preliminary Screening of H_2SO_4 Recovery from Candidate Filters (µg $SO_4^{=}/\frac{1}{2}$ filter)

Filter Type	No.	H^+(titrimetric)[a]	H_2SO_4(benzaldehyde extraction)	$SO_4^{=}$[d]	$\frac{H^+\text{(titrimetric)}}{SO_4^{=}} \times 100$[e]	$\frac{H_2SO_4}{SO_4^{=}} \times 100$[f]
Acid Washed Quartz	76	39.5[b]	55.2	44.2	89	125
	77	44.0[b]	35.2	47.1	93	75
	78	42.6[b]	37.1	41.6	102	89
Gelman Microquartz	79	0[c]	34.1	7.3	0	470
	80	0[c]	47.4	26.1	0	180
	81	0[c]	0	6.6	0	0
Mitex, 5 µm pore size	85	5.0	32.0	8.8	57	340
	86	25.4	27.4	22.4	113	122
	87	12.5	24.1	28.2	44	85
Fluoropore, 1 µm pore size	82	32.3[b]	27.4	36.5	88	75
	83	32.8[b]	30.6	35.8	92	85
	84	32.1[b]	32.7	33.7	95	97
Fluoropore, 3 µm pore size	88	34.5	33.5	38.9	89	86
	89	30.4	30.7	33.6	99	91
	90	29.1	27.2	31.9	91	85
Fluoropore, 0.5 µm (unbacked)	91	25.0	23.8	23.8	105	100
	92	29.5	35.0	32.2	92	109
	93	34.2	26.0	31.6	108	82

a. Except as noted results are not corrected for filter blank.
b. Results corrected using filter blank values given in Table 3.
c. Subsequent studies indicated a filter blank of ca. -40 (i.e. the filter is alkaline).
d. Using the AIHL microchemical method.
e. Percent recovery of acid by titration.
f. Percent recovery of acid by benzaldehyde extraction.

Table 11

H_2SO_4 Recovery from Inert Filter Media (μg $SO_4^=$/½ filter)

Filter Type	No.	H^+(titrimetric)[a]	H_2SO_4(benzaldehyde extraction)[b]	$SO_4^=$[b,c]	$\frac{H^+(\text{titrimetric})}{SO_4^=} \times 100$[d]	$\frac{H_2SO_4}{SO_4^=} \times 100$[d]
Acid Washed Quartz	147AQ	34.5	18.0	34.5	100	52
	148AQ	28.7	20.6	29.8	96	69
	149AQ	35.8	25.4	37.1	96	68
	150AQ	30.0	17.8	35.5	85	50
Fluoropore, 1 μm pore size	139F1	33.2	28.0	33.8	98	83
	140F1	29.3	16.4	31.1	94	53
	141F1	31.9	20.0	32.9	97	61
	142F1	25.4	23.1	29.6	86	78
Zefluor, 1 μm pore size	143ZT1	24.9	21.1	30.1	83	70
	144ZT1	27.6	23.3	33.5	82	70
	145ZT1	20.4	18.9	23.3	88	81
	146ZT1	31.5	23.6	31.9	99	74

Ratio of Means:	$\frac{H^+(\text{titrimetric})}{SO_4^=} \times 100$	$\frac{H_2SO_4}{SO_4^=} \times 100$
Acid Washed Quartz:	94	60
Fluoropore, 1 μm:	94	69
Zefluor, 1 μm:	88	73

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a. Filter blanks (from recovery of H^+ added to aqueous filter extract as μg $SO_4^=$/½ filter):

Acid washed quartz = -1.9 ± 1.0
Fluoropore, 1 μm = -1.2 ± 1.1
Zefluor, 1 μm = -2.1 ± 0.7

b. Filter blanks below detectable limits in all cases.

c. Analyses by AIHL microchemical method.

d. See footnotes e and f, Table 8.

C. Storage Stability of H_2SO_4 on Clean, Inert Filters

Preceding studies demonstrated that clean, acid-washed Pallflex 2500 QAO quartz and Teflon filters (e.g. Fluoropore or Zefluor) gave relatively high recoveries of sulfuric acid within 48 hours of filter loading with laboratory-generated H_2SO_4 aerosol. To evaluate the effect of storage of H_2SO_4 recovery, sets of four quartz and 1 µm pore size Zefluor filters were loaded with about 50 µg H_2SO_4 each. Since the filter loading was not sufficiently reproducible, equal loadings on each filter could not be obtained. To permit monitoring of changes with time, each loaded filter was cut into quarters, and one quarter from each was combined and packaged in closed, Millipore disposable plastic Petri dishes. With this strategy the total H_2SO_4 on the four quarters in each of four boxes was equal within the precision of sectioning one filter into equal quarters (C.V. = 2.5%). Zefluor filters were treated similarly. To evaluate storage stability four plastic bags were sealed each containing one loaded quartz, one loaded Zefluor and one each blank filter of each type, all in quarters inside closed Millipore Petri dishes. Two bags were opened after one week of storage in laboratory air and analyzed for H^+ and H_2SO_4. The results were compared to those for two bags of samples analyzed within 48 hours of loading (Table 12).

Using the benzaldehyde extraction technique, the results indicate, on average 71 ± 6% and 91 ± 10% recovery of the acid from AW quartz and Zefluor filters, respectively. Using the titrimetric method, recovery of the acid was 85 ± 18% and 93 ± 11% for quartz and Zefluor filters, respectively. In all cases, an apparent increase in acidity with storage time was observed. Further trials would be needed to establish this as a consistent trend and establish its cause. However, the present results serve to confirm that, in the absence of ammonia and particulate matter, storage of the acid does not cause measurable loss.

D. Interference of Atmospheric Particulates in H_2SO_4 Determination

1. Introduction

To evaluate the effect of atmospheric particulate matter on recovery of H_2SO_4, sulfuric acid aerosol was added to particulate samples collected on both acid-washed quartz and Teflon (1 µm pore size Fluoropore filters. An 8"x 10" quartz filter was loaded with atmospheric particulate by sampling in Berkeley for 24 hours at ca. 40 cfm during a period of relatively heavy pollution (compared to typical Berkeley pollution levels) using a high volume respirable particulate sampler (particles $\geq$ 3.5 µm are removed with a cyclone). The purpose of the cyclone was to exclude much of the soil particulates which might neutralize sulfuric acid. From this filter 12, 47 mm discs were punched. Five of these were loaded with approximately 100 µg H_2SO_4, five with 50 µg H_2SO_4 and two with none to permit measurement of the initial sulfate and acid levels.

Table 12

Storage Stability of H_2SO_4 on Clean Filters (as μg $SO_4^=$ per filter)

Filter	H_2SO_4 added	H_2SO_4 (benzaldehyde extraction)[a]		H^+ (titrimetric)[b]	
		initial[c]	one week	initial	one week
Acid-washed Quartz	61 ± 3[d]	41	46	44	60
Zefluor, 1 μm	50.8 ± 0.7	43	50	43	51

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a. Filter blanks ca. 1 μg/filter which is below the limit of reliable quantitation.

b. Corrected for the mean blank for quartz = -3.9 ± 2.0 and Zefluor = -4.2 ± 1.4 μg $SO_4^=$/filter. Note that μg H_2SO_4/filter is not significantly different than μg $SO_4^=$/filter.

c. Analysis completed within 48 hours of filter loading.

d. Based on analysis for total H_2O-soluble sulfate following analysis for H^+.

Since it was not feasible to obtain simultaneous atmospheric samples on 47 mm Fluoropore filters, 14, 24-hour samples were obtained in Berkeley over a period of about 3 weeks in October 1978. Of these, four were analyzed without added H_2SO_4 and the mean and standard deviation for atmospheric sulfate assumed to relate to all samples. Initial sulfuric acid loadings were calculated by subtracting this mean from the total sulfate measured after adding acid. Five samples were loaded with approximately 50 µg, and five with approximately 100 µg H_2SO_4. Filters were then analyzed for sulfuric acid, total acidity and sulfate after varying storage periods following filter loading.

2. Results

The results given in Table 13 are expressed as percent H_2SO_4 recoveries. Acid recovery values for quartz filters should be considered more reliable since the atmospheric sulfate level of the samples was accurately established. Results have been corrected for the acidity observed in the atmospheric samples.

The results by benzaldehyde extraction indicate, in most cases, < 20% recovery of H_2SO_4. These findings contrast with those by the titrimetric method which gave an overall mean recovery of 64 ± 15%. These findings are consistent with the reaction of > 80% of the H_2SO_4 with $(NH_4)_2SO_4$ to yield NH_4HSO_4. This salt would be still be titrated as an equivalent amount of strong acid but would not be recovered by the benzaldehyde extraction method. The initial level of sulfate on the quartz filter, 206 µg/filter as sulfate, probably existed primarily as $(NH_4)_2SO_4$. As such, it represented more than twice the level of sulfuric acid added. The initial sulfate level on Fluoropore, 60 ± 13 µg, indicates that the added H_2SO_4 could be about twice the molar level of ammonium sulfate. Recoveries of acid up to about 50% by benzaldehyde extraction were observed with the high H_2SO_4/initial sulfate ratio.

3. Conclusions

a. The reaction of ≤ 0.3 µm sulfuric acid aerosol with previously collected particulate matter appears to occur relatively soon after contact. No loss with storage time between 42 and 216 hours was observed.

b. The removal of large particles from the air stream may be useful but it does not prevent transformation of H_2SO_4 to a form not extracted by benzaldehyde.

c. Results are consistent with the reaction of a large fraction of H_2SO_4 with $SO_4^=$ forming 2 moles of HSO_4^- per mole of H_2SO_4. The HSO_4^- is indistinguishable from H_2SO_4 by titration.

d. Under conditions in which moles of $H_2SO_4 \leq$ moles$(NH_4)_2SO_4$ it appears doubtful that H_2SO_4 can escape conversion to HSO_4^-. However, further work is necessary to confirm this with lightly loaded atmospheric samples.

Table 13

Sulfuric Acid Recovery from Particulate-Loaded Filters (%)

Filter	Mean µg Added H_2SO_4	% H_2SO_4 Recovered 42 Hours H^+[d]	42 Hours ϕCHO[e]	96 Hours H^+[d]	96 Hours ϕCHO[e]	216 Hours H^+[d]	216 Hours ϕCHO[e]
Acid-Washed Quartz[a]	46	67	< 19	49	21	65	< 33
	46	80	< 18	--	--	98	< 11
	82	58	< 9	73	10	67	< 11
	82	61	< 11	--	--	66	< 11
	Mean:	67 ± 11	< 14	61 ± 17	16 ± 8	74 ± 16	< 17
Fluoropore, 1 µm[b]	54	51	7	37	ca.0	(176)[c]	ca.0
	54	51	ca.0	--	--	59	ca.0
	96	74	48	35	31	80	54
	96	69	24	--	--	67	10
	Mean:	61 ± 12	20 ± 21	36 ± 1.4	15 ± 22	69 ± 11	32 ± 31

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a. Mean $SO_4^=$ loading without added H_2SO_4: 205.5 ± 3.8 µg/filter. All discs cut from the same 8 x 10" filter for loading with H_2SO_4. Results corrected for the acidity observed for the atmospheric samples by titration, 24.5 ± 8. By benzaldehyde extraction, H_2SO_4 below detection (<8).

b. Mean $SO_4^=$ loading without added H_2SO_4: 60.2 ± 13 µg/filter for four filters collected on different days. Results corrected for acidity observed for the atmospheric samples by titration, -3.6 ± 2.9 by titration and 12.5 ± 3 by benzaldehyde extraction.

c. Excluded from mean.

d. By titration

e. By benzaldehyde extraction.

E. Interference of $(NH_4)_2SO_4$ in H_2SO_4 Determination

1. Introduction

Studies, described above, of atmospheric particulate matter interference were consistent with the formation of HSO_4^- from H_2SO_4 and $(NH_4)_2SO_4$, since strong acid was still titratable but no H_2SO_4 was extractable by benzaldehyde. To evaluate this more directly, clean 1 µm pore size Zefluor filters were first loaded with $(NH_4)_2SO_4$ aerosol (< 0.3 µm particle diameter) in sets of three. Two of the three filters from each of two sets were then loaded with ≤ 0.3 µm H_2SO_4 aerosol at two levels. Sulfate analysis (following H^+ determination) gave the sum of sulfuric acid and ammonium sulfate. Sulfate analysis of the third filter in each set gave the level of $(NH_4)_2SO_4$. Since the filters within a set were equivalent in $(NH_4)_2SO_4$ loading within 2% (Appendix D), H_2SO_4 loadings were obtainable by difference.

2. Results and Conclusions

From the results given in Table 14 it is concluded that:

a. At the lower H_2SO_4 level, results are subject to large uncertainty because of the reliance on a difference technique to determine H_2SO_4.

b. Recovery by titration of strong acid, expressed as H_2SO_4, averages 128%.

c. Recovery of H_2SO_4 by benzaldehyde extraction is anomalously high when compared to the level of H_2SO_4 and to results of previous experiments without $(NH_4)_2SO_4$. The results are consistent with the extraction of substantial quantities of ammonium acid sulfate (NH_4HSO_4) by benzaldehyde, the latter being formed from interaction of H_2SO_4 and $(NH_4)_2SO_4$.

d. Direct evaluation of interference effects with NH_4HSO_4 is needed.

F. Interference of NH_4HSO_4 in H_2SO_4 Determinations

1. Introduction

Ammonium acid sulfate (NH_4HSO_4) titrates as a strong acid, indistinguishable from H_2SO_4. However, studies at BNL indicated only slight solubility for dry NH_4HSO_4 in benzaldehyde. To evaluate the potential interference of NH_4HSO_4 on sulfuric acid determination by benzaldehyde extraction under the conditions used in this study, two experiments were performed. In the first, sets of three clean Zefluor filters were simultaneously loaded with equal amounts of NH_4HSO_4 aerosol (≤ 0.3 µm)* followed by sulfuric acid aerosol on two filters from each set. The level of H_2SO_4 added could then be obtained by difference and compared to the observed H_2SO_4.

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*A malfunction in the optical particle counter prevented monitoring particle size. The conditions used were those previously found to yield ≤ 0.3 µm for 99% of all particles using $(NH_4)_2SO_4$.

Table 14

Interference of Ammonium Sulfate [$(NH_4)_2SO_4$] on Sulfuric Acid Measurement (as μg sulfate per filter)

Set	$(NH_4)_2SO_4$[a]	$(NH_4)_2SO_4$ + H_2SO_4		H_2SO_4 (by difference)		H_2SO_4 by Benzaldehyde Ext.		H_2SO_4 by Titration	
		Filter A	Filter B	Filter A	Filter B	Filter A	Filter B	Filter A	Filter B
1	81.6 ± 4.5	113	122	32 ± 6.7	41 ± 6.7	41	42	46	44
2	89.6 ± 2.8	97	100	7 ± 5	10 ± 5.5	21	21	15	12

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a. Mean ± σ for two determinations made by analyzing separate halves of the same filter.

In the second experiment, NH_4HSO_4 was added in equal amounts to sets of three quartz filters loaded with equal levels of atmospheric particulate matter.** This was followed by deposition of H_2SO_4 aerosol on two of the three discs. Both NH_4HSO_4 and H_2SO_4 were calculated by difference.

2. Interference of NH_2HSO_4 on Clean Teflon Filters

Table 15 shows the extent of interference of ca. 100 μg NH_4HSO_4 (as $SO_4^{=}$) on the analysis of 0 to 60 μg H_2SO_4. Between 39 and 71% of the NH_4HSO_4 was extracted by benzaldehyde. The presence of H_2SO_4 did not have a consistent effect on the extent of NH_4HSO_4interference. In the absence of H_2SO_4, 45 ± 3% of the NH_4HSO_4 was extracted. This compares to about 25% extraction reported by Richards et al[41] and < 5% reported by Barrett el al.[30]

The latter group as well as BNL employed filters spiked with aqueous solutions of the salt and then dried rather than adding the salt as a submicron aerosol. An additional source of variability arises from the water content of the benzaldehyde-salt system. BNL and Richards et al employed benzaldehyde without purification. As noted by Barrett, et al, such benzaldehyde contains appreciable water causing increased extraction of salts such as NH_4HSO_4. However, both BNL and Richards et al dried each sample (rather than the benzaldehyde) prior to extraction.

In the present work the benzaldehyde had been initially stored over Linde molecular sieve Type 3A, vacuum distilled from fresh molecular sieve under argon, stored with protection from light and air and dispensed through Teflon stopcocks by pressuring with argon. After five months storage its water content was determined to be ≤ 0.004%w and its benzoic acid content, 0.6%w. However, the samples were not dried. Assuming that after air contact the NH_4HSO_4-loaded filter absorbed an amount of water equal to the weight of salt (ca. 100 μg) the water content of the 10 ml benzaldehyde due to this source would reach 0.02%w. (The water saturation level is 0.3%.) It appears doubtful that water from either laboratory or atmospheric samples could influence the extent of extraction into dried benzaldehyde. Variation in rate of extraction of the acid sulfate with particle size may be a more significant factor causing variability in results between investigators. Further work is needed to evaluate this possibility.

3. NH_4HSO_4 Interference on Atmospheric Particulate-Loaded Filters

Table 16 summarizes the level of atmospheric sulfate, NH_4HSO_4 and H_2SO_4 added, and recovered levels of acid. In both sets, approximately 120 μg NH_4HSO_4 (as sulfate) was combined with about 50 μg H_2SO_4 in the presence of about 150 μg atmospheric sulfate and other aerosol constituents on quartz filters. In all cases the level of H_2SO_4 observed by benzaldehyde extraction was below the level added. Apparently, both the acid sulfate and sulfuric acid reacted to a major extent with aerosol constituents preventing assessment of interference effects by NH_4HSO_4. The average recovery of strong acid (by titration) was only 36%.

**A series of 47 mm discs were cut from an 8 x 10" sheet following sampling respirable particulate for 5 hours at ca. 40 cfm (15.2 m^3 per 47 mm disc).

Table 15

Interference of NH_4HSO_4 on H_2SO_4 Determination on Clean Zefluor Filters (as μg sulfate per filter)

Set	Filter	NH_4HSO_4	NH_4HSO_4 + H_2SO_4	H_2SO_4 (by difference)	H_2SO_4 Benzaldehyde Ext.	H_2SO_4 by Titration	% Interference by NH_4HSO_4 in Benzaldehyde Ext.[d]	% Recovery of H^+ by Titration
1	A	97.6	–[a]	0	42	42	43	86
	B	N.D.[b]	82.2[c]	- 15[c]	87	50	–	–
	C	N.D.[b]	150	52	86	80	65	84
2	A	99.6	–[c]	0	47	60	47	120
	B	N.D.[b]	136	36	107	72	71	84
	C	N.D.[b]	162	62	101	94	39	85
							Median: 47%	Median: 85%

---

a. No H_2SO_4 added to this filter.

b. Assumed equal to value for filter A of the same set (see Appendix D).

c. Probably analytical error.

d. The percent NH_4HSO_4 extracted into benzaldehyde.

Table 16

Interference of NH_4HSO_4 on H_2SO_4 Determination in the Presence of Atmospheric Particulate Matter[a] (as µg sulfate per filter)

Set	Filter	Atm $SO_4^=$ + NH_4HSO_4	Atm $SO_4^=$ + NH_4HSO_4 + H_2SO_4	NH_4HSO_4 (by difference)	H_2SO_4 (by difference)	H_2SO_4 by Benzaldehyde Ext.[b]	H_2SO_4 by Titration[c]	% Interference by NH_4HSO_4 Benzaldehyde Ext.	% Recovery of H^+ by Titration
	A	269 ± 2.3	-	118 ± 12	0	ca. 0	18	Not measurable	31
1	B	N.D.[d]	317 ± 1.4	118 ± 12	48 ± 3	ca. 0	46	Not measurable	43
	C	N.D.[d]	325 ± 2	118 ± 12	56 ± 3	12.5	44	Not measurable	38
	A	281 ± 1.4	-	130 ± 12	0	ca. 0	16	Not measurable	24
2	B	N.D.[d]	330 ± 2	130 ± 12	49 ± 2	7.8	32	Not measurable	33
	C	N.D.[d]	339 ± 1	130 ± 12	58 ± 2	13.7	46	Not measurable	38
								Median:	36%

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a. Mean atmospheric sulfate level 151 ± 12 µg/47 mm disc cut from single 8 x 10" filter.

b. No H_2SO_4 detectable in atmospheric particulate.

c. Results corrected for 24 µg H_2SO_4 (as $SO_4^=$) per filter for the atmospheric particulate matter.

d. Assumed equal to value for filter A of same set (see Appendix D).

VIII. NITRIC ACID MEASUREMENT

A. Introduction

Previous studies evaluated the use of a coulometric method for continuous nitric acid measurement. While the method proved adequate for laboratory use at concentrations > 0.1 ppm, it lacked sensitivity for ambient concentrations. A Teco, single channel chemiluminescent NO-NO_2 analyzer was used for laboratory analysis of nitric acid at < 0.1 ppm, but could not be used for field sampling because of NO-NO_2 interference.

The present study has evaluated two integrated sampling techniques, one employing NaCl-impregnated filters[9], and the second, nylon filters for HNO_3 collection.[15] This approach requires initial removal of particulate nitrate with a pre-filter and penetration of HNO_3 to the collector mounted as an after-filter.

Our studies included assessment of artifact nitrate formation on NaCl-impregnated and nylon filters with NO_2, the degree of retention of nitric acid on the inert filters used for pre-filters, with and without atmospheric particulate matter, and comparison of the two techniques.

B. Artifact Particulate Nitrate Formation

1. Clean Filter-NO_2 Interaction

Previous AIHL studies of artifact particulate nitrate formation demonstrated only slight retention of NO_2 at $\leq$ 90% R.H. using a wide variety of filter types. For the present study it was necessary to establish that the filters intended to collect nitric acid, viz., nylon (Duralon and Ghia nylon) and NaCl-impregnated cellulose (Whatman 41) did not cause errors due to NO_2 collection. Prior studies with Duralon filters demonstrated little NO_2 retention at or close to ambient concentrations. However, NaCl impregnated cellulose filters have been reported to retain NO_2 somewhat at high relative humidity.[9]

The present study employed 0.5 ppm NO_2 at 90% R.H., with and without added 0.1 ppm NH_3, in 6-hour exposures. Following exposures samples were refrigerated to minimize desorption as well as oxidation of nitrogen-containing species. Extractions were done by mechanical shaking for 30 min. in 5-10 ml H_2O at room temperature except with nylon filters. The latter were extracted in 0.1N NaOH as discussed in Appendix E. The results are given in Table 17 together with those for a blank run made immediately before the trials with added NO_2. In spite of a careful detergent-water wash and clean air purge, the interior walls of the exposure system remained contaminated with a material which desorbed and was collected and analyzed as nitrate. The 6-hour chamber blank run conducted with two Duralon and two NaCl/Whatman 41 filters in parallel observed about 3-9 $\mu g/m^3$ artifact nitrate, with the higher level on the latter filters.

Table 17

ARTIFACT PARTICULATE NITRATE FROM SIX-HOUR EXPOSURES TO NO_2 AT 90% R.H. WITH AND WITHOUT ADDED NH_3[a]

($\mu g/m^3$)

Filter/Conditions	Chamber Blank Run[b]	0.5 ppm NO_2 (940 $\mu g/m^3$) 0 NH_3	0.5 ppm NO_2 (940 $\mu g/m^3$) 0.1 ppm NH_3 (70 $\mu g/m^3$)
Duralon	2.6 ± 0.2	6.1 ± 0	2.6 ± 0.1
NaCl/W41	8.5 ± 0.3	5.6 ± 1 8.3 (9 lpm)	2.9 ± 0.4 2.4 (10 lpm)
Ghia Nylon	---	5.3 ± 0.6	1.9 ± 0.2
Zefluor Pre-filter Duralon After-filter	---	2.5[c]	1.0[c]
Zefluor Pre-filter NaCl/W41 After-filter	---	1.6[c]	0.5[c]

[a] Except as noted all results obtained at ca. 20 lpm and 21 ± 1°C.

[b] Exposure system was cleaned with aqueous detergent, rinsed with distilled water and air dried. Blank run made after purging system overnight with purified air.

[c] Results for pre-filter plus after-filter.

Runs with NO_2, with and without ammonia, were done with filter pairs as above at 20 lpm plus an NaCl/W41 filter at 10 lpm. In addition, filters with Teflon pre-filters such as would be used in field sampling for nitric acid, were also evaluated. Comparing results with added NO_2 to those in the blank run, Duralon exhibited a small increase (corresponding to 0.3% NO_2 retention) while results with NaCl/W41 decreased slightly. The filters with pre-filters showed total nitrate levels $\leq$ the controls. The addition of ammonia caused a decrease in observed artifact particulate nitrate. This parallels observations previously reported using glass fiber, cellulose acetate and Teflon filters.[10,11]

In summary the level of artifact particulate nitrate from NO_2 appears negligibly small. Published reports of significant NO_2 collection on NaCl impregnated filters may have been influenced to some degree by system contamination.

2. Filter-HNO_3 Interactions

Previous work at AIHL demonstrated, in many cases, retention of gas phase nitric acid on clean filter media leading to what is referred to as artifact particulate nitrate. Those studies were restricted to acid levels of $\geq$ ca. 500 $\mu g/m^3$ which is about an order of magnitude higher than the highest ambient air nitric acid levels expected. The present study extended this work down to 165 $\mu g/m^3$ as measured with Duralon filters, and included clean filters intended for sampling total particle-phase acids, as well as pre-filters for HNO_3 measurement with and without atmospheric particulate matter. Fluoropore filters were included to permit comparison with prior work. Filters were refrigerated at 5°C following exposures until immediately prior to extraction to minimize desorption.

The results given in Table 18 show about 2% retention of HNO_3 on clean Teflon filters except for Zefluor at > 500 $\mu g/m^3$ HNO_3. Acid-treated quartz exhibited higher but variable retention relative to Teflon filters. The effect of particulate addition was to sharply increase the nitric acid retained.

We conclude that Teflon filters are preferable for use as pre-filters in sampling nitric acid on nylon or NaCl/W41. The enhancement of HNO_3 retention on Fluoropore filters by particulate matter suggests that filter changes be made as frequently as possible.

C. Comparison of Nitric Acid Sampling Methods

To compare filter methods for nitric acid, 47 mm Duralon and Ghia nylon filters and NaCl-impregnated Whatman 41 filters were exposed side-by-side with ca. 200 to 500 $\mu g/m^3$ HNO_3 at 50 or 80% relative humidity and at 10 and 20 lpm (Table 19). To evaluate the methods under simulated field sampling conditions, the Duralon and NaCl/W41 filters were mounted in Nuclepore double filter holders with Zefluor pre-filters. In an effort to assess wall loss in the double filter holders, these were washed with distilled water and analyzed for nitrate following each exposure. The two runs at 50% R.H. employed

Table 18

NITRIC ACID COLLECTION ON "INERT" FILTERS AT 50% R.H. ($\mu g/m^3$)[a]

Filter	HNO_3 Concentration ($\mu g/m^3$)	
	165 ± 5	557 ± 117
Fluoropore (Teflon)	2.9 ± 0.6	8.9 ± 0.6
Zefluor (Teflon)	3.6 ± 4	33 ± 12
Acid-treated Quartz[b]	16 ± 14	147[c]
Fluoropore + 23 m^3 air sample	47 ± 31	56 ± 30
Gelman GA-1 (cellulose acetate)	35 ± 7	57 ± 30

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a. Except as noted, samples exposed for 6 hours at 21 ± 1°C and 22 lpm.

b. Flow rate 37 lpm to match face velocity in a high volume sampler.

c. Single value.

Table 19

COMPARISON OF METHODS FOR NITRIC ACID DETERMINATION (as $\mu g/m^3$ NO_3^-)

Sampler	Exposure Conditions:	50% R.H. at $2x10^2$ $\mu g/m^3$ HNO_3		80% R.H. at $3x10^2$ $\mu g/m^3$ HNO_3		80% R.H. at $5x10^2$ $\mu g/m^3$ HNO_3	
		10 lpm	20 lpm	10 lpm	20 lpm	10 lpm	20 lpm
Duralon filter		157 ± 15	154 ± 28	284	279	569	522
NaCl/W41 filter		190 ± 4	182 ± 11	472	331 ± 2	577	548 ± 51
Ghia nylon filter		178 ± 23	148 ± 28	285	276	402	476
Zefluor pre-filter			0.7 ± 0.7		44[b]		34[b]
Duralon after-filter		---	130 ± 31	---	236	---	153
Holder			3.5 ± 0.4		4.5		5.6
			Σ = 134 ± 31		Σ 285		Σ 193
Zefluor pre-filter			0.5 ± 0.3		25[b]		40[b]
NaCl/W41 after-filter		---	128 ± 56	---	233	---	329
Holder			6.7 ± 2.7		5		5
			Σ = 135 ± 56		Σ 262		Σ 374

a. All samples stored at room temperature following HNO_3 exposure.

b. Pre-filter pre-loaded with atmospheric particulate sampling 4 hours at 16 lpm. Value corrected by about 10% to allow for estimated level of atmospheric nitrate.

clean Zefluor filters while those at 80% R.H. were done with filters pre-loaded with atmospheric particulate matter. In all cases, samples were maintained at room temperature following exposures to simulate field sampling conditions.

From the results in Table 19 it is concluded that:

1. There was no significant effect of a change in flow rate, in the range 10 to 20 lpm.

2. Duralon (Millipore Corp.) and Ghia Corp., nylon filters are equivalent except at HNO_3 concentrations > 500 μg/m^3.

3. Although Duralon and Ghia nylon filters showed no flow rate dependence, both gave lower nitric acid recoveries as compared to NaCl/Whatman 41 (average 21% lower at < 500 μg/m^3 HNO_3).

4. Nitric acid recovered from the filter pairs plus holder at > 500 μg/m^3 was less than that recovered by the corresponding single filter. Below 200 μg/m^3 HNO_3 the agreement was within experimental error, however. The results suggest that adsorbed HNO_3 on the pre-filter, particulate matter or filter holder may be lost before extraction of nitrate can be accomplished. Heating the 2-filter sampler to desorb HNO_3 from the pre-filter and walls to permit its transfer to the collecting filter (as employed by Okita9) may overcome this problem.

5. The level of nitric acid retained on the Zefluor pre-filters bearing particulate matter was greatly in excess of that without particulate matter, making adsorption on, or reaction with the particulate matter likely. However, adsorption on clean Zefluor was determined at 50% relative humidity. Since adsorption of HNO_3 on clean Zefluor is expected to be somewhat greater at 80% R.H., no quantitative assessment of HNO_3- particulate interaction can be made from these data.

The lower nitric acid recoveries from nylon compared to NaCl-impregnated filters suggested lower collection efficiencies with the nylon filters. To evaluate collection efficiency more directly, a clean nylon and a NaCl-impregnated filter were each paired with a clean NaCl-impregnated after-filter. The percentage of the total recovered nitric acid which was on the first filter in series provided a measure of its efficiency. The results for NaCl on Whatman 41 were 97.4 ± 1.4% at 50 and 80% R.H. sampling 220-350 μg/m^3 HNO_3 for 6 hours at 20 lpm. For the same conditions Duralon nylon filters showed 58.7 ± 9.1% efficiency.

The efficiency of a Duralon filter for collection of 220-350 μg/m^3 HNO_3 for ca. 60 minutes at 1 lpm was evaluated by adding the filter to the sampling line of a Teco chemiluminescent NO_x analyzer. The total signal, representing the sum of HNO_3, NO_2, and NO, was reduced to < 2.9% of its original value. Thus the efficiency of the filter for HNO_3 removal was > 97.1% under these conditions. Accordingly, the efficiency of nylon filters appears to increase with decreasing total nitric acid sampled. The very low flow rate of the Teco might also increase efficiency to some degree.

IX. EVALUATION OF A DENUDER FOR AMMONIA REMOVAL AND OF OXALIC ACID IMPREGNATED FILTERS FOR AMMONIA SAMPLING

A. Experimental Techniques

The field studies employed an ammonia denuder on the inlet to a lo-volume filter sampling unit. This was included in an effort to eliminate the neutralization of collected sulfuric acid particles by atmospheric ammonia. The denuder was patterned after that developed by Stevens and Dzubay.[35] It consists of an array of parallel glass tubes forming a laminar flow element which is coated on the inner surfaces with fused phosphorous acid. Gases diffuse to the walls of the denuder much more rapidly than aerosols which permits removal of ammonia with minimal losses of particulate matter.

The theoretical basis for denuder design was obtained from the solution of the steady state mass diffusion equation governing the concentration of particles within a fluid moving in a circular tube.[49] For laminar viscous flow:

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

where $\Delta = DL\Pi/4Q$ and

D = diffusion coefficient (cm^2/sec) For NH_3, $D = 0.4$

L = total length of tube (cm)

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

C_o = concentration entering tube

$\overline{C}$ = average concentration exiting tube

$(1 - \overline{C}/C_o) \times 100$ = percent removal

This expression is valid if the Reynolds number is kept below 2000 to prevent turbulent flow.

Based on this design, at 99% ammonia removal, $\leq$ 6% of an 0.01 µm aerosol of density 1.0 should be lost to the tube walls for these flow rates. It should be noted that tube diameter is not critical as long as the Reynolds number is maintained below 2000. The total tube length is independent of tube geometry. Accordingly, the most compact denuder configuration consists of an array of shorter parallel tubes, the sum of whose lengths yield the desired total tube length. This configuration has the additional advantage of minimizing the flow turbulence in the denuder system. Table 20 lists the optimum denuder tube configurations for three flow rates and the corresponding Reynolds number.

Table 20

Denuder Tube Configuration

Flow rate[a] (ℓ/min)	Total Tube[c] Length Required (cm)	Tube Configuration[b] No. Tubes @ 30 cm Length	Reynolds Number
15.9	250	9	480
22.0	350	12	460
37.4	600	20	480

---

a. Flow rates 15.9 and 37.4 ℓ/min correspond to face velocity of a hi-vol sampler at 40 CFM scaled to 25 mm and 47 mm filters, respectively. 22 ℓ/min is the maximum flow rate to be used with the AIHL cyclone.

b. Tubes are 0.6 cm inner diameter.

c. Total tube length for 99% NH_3 removal.

For evaluation of the ammonia denuder as well as atmospheric sampling, a technique for gas phase ammonia was required. The procedure used was a modification of a technique described by Richards et al.[41] Gelman AE glass fiber filters were washed with 0.1N HCl, air dried and then heated for 4 hours at 400°C. To 47 mm filter discs was added 0.7 ml of a freshly prepared 5%w oxalic acid in ethanol solution. The solvent was evaporated under N_2.

B. Results

The ammonia denuder was evaluated for use at a flow rate of 22 lpm by sampling air containing approximately 100 ppb ammonia for two six-hour periods at 50% R.H. and at 80-90% R.H., respectively. Downstream of the sampler the ammonia penetrating the denuder was collected on an oxalic acid impregnated Gelman AE glass fiber filter (OAE). The ammonia level upstream of the denuder was measured by two sets of two OAE filters in series. This design permitted measurement of the efficiency of the ammonia denuder as well as the efficiency of the OAE filters for NH_3 collection, and the precision of the NH_3 determination. The filter samplers provided an integrated sample for the six-hour period. In addition, three midget impingers in series containing 0.1N H_2SO_4 were used to collect 3 or 4, one hour NH_3 samples upstream of the denuder throughout the six-hour runs for comparison with the OAE filter results.

Following collection, the ammonia was determined as NH_3^+ using the indophenol blue procedure.[38]* Filter storage was < 48 hours prior to extraction and analysis.

The OAE filter blank for NH_4^+ was 1.0 ± 0.7 µg/filter (n = 4). Accordingly, the limit of detection for NH_3, as NH_4^+, is considered 2.4 µg/filter (i.e. the mean blank + 2σ of the blank). The efficiency of single OAE filters for ammonia collection, shown in Table 21, is based on the total NH_4^+ retained by two filters in series. With the ammonia level used, ca. 75 µg/m^3 (107 ppb), the efficiency for a single filter was $\geq$ 98%.

Results for the denuder evaluation are given in Table 22 indicating > 99% ammonia removal. Assuming this efficiency to be relevant at a more typical ambient concentrations, 5 µg/m^3, then 0.03 µg/m^3 NH_3 would penetrate to the filter collecting sulfuric acid. This concentration is sufficient to convert up to 0.09 µg/m^3 H_2SO_4 to NH_4HSO_4.

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*A comparison of the indophenol blue procedure to the automated methylthymol blue sulfate method[39] in analysis of $(NH_4)_2SO_4$ is given in Appendix D. The coefficient of variation of the indophenol blue procedure was previously determined to be 5%.[40]

Table 21

Efficiency of Oxalic Acid Impregnated Gelman AE Glass Fiber Filters for Ammonia Collection with Approximately 75 $\mu g/m^3$ NH_3[a]

Relative Humidity (%)	Efficiency for Single Filter (%)[b] Set 1	Set 2
50	98.1	99.3
80-90	99.1	97.7

---

a. Sampling rate 25 lpm.

b. The fraction of the total ammonia obtained on the first filter compared to the total ammonia retained by the two filters in series.

Table 22

Efficiency of the Ammonia Denuder at 22 lpm[a]

Relative Humidity (%)	Ammonia Concentration[b] ($\mu g/m^3$) Filter Set 1	Filter Set 2	Impinger	Ammonia Penetrating Denuder ($\mu g/m^3$)	Efficiency of NH_3 Removal (%)[e]
50	96	57	62 ± 9[d]	0.47	99.3
80-90	70	73	94 ± 57[d]	0.51	99.3

---

a. Sampling time: 6 hours, 20°C.

b. Filter samplers operated at 25 lpm and the impingers, at 1.0 lpm. Results are for total ammonia retained in each set of two filters in series.

c. Based on mean of three determinations of upstream concentration.

d. Six hour mean values estimated from 3-4 one hour bubbler samples collected with three midget impingers in series.

C. Stability of H_2SO_4 on Filters in Particle and Ammonia Free Air*

While it was shown that the NH_3 denuder could remove > 99% of the ammonia in an air stream containing about 100 ppb (70 $\mu g/m^3$) NH_3, it was desirable to evaluate the stability of sulfuric acid on an inert filter protected with such a denuder, as well as a pre-filter to remove particulate matter. For this purpose, Berkeley ambient air was passed through two H_2SO_4 loaded-Zefluor filters at one time at 22 lpm. Each filter contained 60 to 80 μg H_2SO_4 ($\leq$ 3 μm particle size). Both Zefluor filters were preceded by Gelman A (pH = 7.6) glass fiber filters to remove particulate matter. In front of one stacked filter pair was a cyclone to remove particles > 2.5 μm and a NH_3 denuder in series. The second stacked filter pair sampled ambient air directly.

Results for recovery of H_2SO_4 after two six-hour sampling trials are given in Table 23. Recovery of H_2SO_4 by benzaldehyde extraction averaged 16% and 38% for two trials. By titration, recovery of the acid was zero in one case and averaged 45% in the second. Ambient NH_3 levels were not measured during these trials but probably were 2-5 $\mu g/m^3$ based on Pittsburg, CA, results.

The remarkable feature of these results is that the denuder had no significant effect on the recovery of H_2SO_4 or H^+. Assuming the observed denuder efficiency for NH_3 removal extends to ambient concentration, ambient NH_3 cannot account for the acid loss. However, a decrease in denuder efficiency to 50%, with an average NH_3 level of 5 $\mu g/m^3$, would provide sufficient NH_3 to neutralize all of the acid present, assuming 100% efficiency for the reaction. Alternatively, NH_4NO_3 may decompose to NH_3 + HNO_3 on the Gelman A pre-filter, with neutralization of the H_2SO_4 by NH_3. Since atmospheric sampling for H_2SO_4 with the denuder is done without a pre-filter, the above mechanism would have to take place on the same filter bearing the H_2SO_4. Thus this experiment might not be relevant to field sampling conditions.

Further studies are needed to determine the cause of H_2SO_4 loss in this experiment and to evaluate its relevance to atmospheric sampling.

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*This experiment was suggested by Willard Richards, Rockwell International.

Table 23

Stability of ≤ 0.3 µm H_2SO_4 Aerosol on Zefluor Filters in Particle Free Ambient Air Using an Ammonia Denuder and Gelman A Pre-filter

Trial	Filter	µg H_2SO_4 Loaded (as $SO_4^=$)	µg H_2SO_4 Recovered by Benzaldehyde (as $SO_4^=$)	µg H_2SO_4 Recovered by H^+ Titration[a] (as $SO_4^=$)	Percent Recovery	
					ØCHO	Titration
1	A (with denuder)	84.0	11.0	0	13	0
	B	59.2	10.8	0	18	0
2	C (with denuder)	64.2	20	32	31	50
	D	72.4	33.5	28	46	39

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a. Results corrected for filter blank = -4.2 ± 1.4 µg/47 mm filter.

X. FIELD SAMPLING STUDIES

A. Preliminary Trials - Berkeley

1. Introduction

As a preliminary trial, a 24-hour, a 90-minute and a 5-hour respirable particulate hi-vol sample were collected in Berkeley, the 90 min. sample during an early morning foggy period. In all cases acid-wash quartz filters were used without an NH_3 denuder. The results are discussed in relation to possible interference effects.

2. Results for 24-hour Samples

Two 47 mm acid-washed quartz discs from the 24-hour hi-vol respirable particulate matter sampler were analyzed for H_2SO_4 and strong acid. Results by the benzaldehyde extraction technique were below detectable levels. The results by titration, $0.51 \pm .16$ μequivalents H^+/filter correspond to an H_2SO_4 level of 25 ± 8 μg/filter or to a concentration of NH_4HSO_4 of 59 ± 18 μg/filter. The absence of H_2SO_4 by benzaldehyde extraction and the demonstration of relatively rapid reaction of H_2SO_4 with atmospheric particles forming a species which still titrates as a strong acid, suggests that NH_4HSO_4 accounts for the observed results. The 24-hour average atmospheric concentration of strong acid from this sample was 0.007 ± 0.002 μequiv/m^3 ($0.4 \pm .1$ μg/m^3 as H_2SO_4).

Water-soluble iron would be another source of strong acid by the titrimetric method. Accordingly, 35 cm^2 of the 24-hour loaded filter sample was extracted with water and the extract analyzed for Fe by atomic absorption. The results indicated 10 ± 1 μg Fe/35 cm^2. Assuming the Fe to be exclusively Fe^{+3}, this amount of iron would titrate as 0.0025 μequiv acid/m^3. Thus iron could represent as much as 36% of the $0.007 \pm .002$ μequiv/m^3 total strong acid observed.

3. Results with Short Term Samples

A 90-minute hi-vol respirable particulate sample collected on quartz fiber during an early morning foggy period gave negligible H_2SO_4 but measurable strong acidity by titration, 0.03 μequiv/m^3. This corresponds to 1.5 μg/m^3 expressed as H_2SO_4.

A 5-hour hi-vol respirable particulate sample collected between 1000 and 1500 hours on quartz fiber also yielded negligible H_2SO_4 and 0.03 μequiv/m^3 strong acid corresponding to 1.6 μg/m^3, expressed as H_2SO_4.

B. Trials in Pittsburg, CA

1. Introduction

Samples were collected for three consecutive days in February 1979 at the Pittsburg station of the Bay Area Air Quality Management District. The strategy for sample collection and analysis is shown in Table 24. In addition, the BAAQMD supplied ozone, SO_2 (by coulometry), wind speed and direction data. Diurnal variations for gaseous pollutants and meteorological variables are included in Appendix I.

Ammonia was sampled on oxalic acid-impregnated Gelman AE glass fiber filters following a Gelman A glass fiber pre-filter using a technique similar to that of Richards et al.[41] Filter changes were made at the same times as for the respirable particulate hi-vol sampler. Ammonia was monitored since, together with the concentration of nitric acid, it may determine the level of particulate nitrate observed.

To minimize loss of nitric acid and ammonia by adsorption on pre-filters and filter holder surfaces, heated air was passed through the nitric acid and ammonia samplers following each sampling period. The procedure followed is described in Appendix F. Following collection the hi-vol samples were stored in Saran wrap-lined manila folders inside sealed plastic bags at room temperature. The remaining filter samples were stored in plastic Millipore boxes in sealed plastic bags at room temperature.

The results, expressed as both $\mu g/m^3$ and μequivalents/m^3, are included in Tables 25 to 30.

2. H_2SO_4 and Total Particulate Acidity

All H_2SO_4 results on the quartz fiber samples and most of those on Zefluor were below limits of detection (typically 0.4 $\mu g/m^3$ for the short term samples). Higher levels of sulfuric acids coincided with maxima in H^+ concentration by titration. The highest sulfuric acid value found, 0.6 $\mu g/m^3$ (0.012 μequiv/m^3) included a time period on February 8 in which a white plume, more persistant than steam, was visible from the PG&E power plant 1/4 mile to the north. During most of this period the wind came from the north.

Diurnal variations in SO_2 concentration also correlate with wind direction; most elevated SO_2 values occurred with wind coming from the NW to NE quadrant, consistent with the nearby power plant as the predominant source.

As with the Berkeley samples, an evaluation was made of the extent of possible interference by Fe^{+3} in total acidity measurements. For this purpose, two quartz filter samples from each sampling day representing the maximum and typical acidity levels for that period, were analyzed for total water soluble iron by flame atomic absorption. All results were at or below the limit of detection. Accordingly, the Fe^{+3} concentration upper limit was 0.04 to 0.09 $\mu g/m^3$. This corresponds, in turn to 0.001 to 0.003 μequiv/m^3 H^+ or about 10% of the observed acidity, which is not significant.

Table 24

Sampling Strategy for Pittsburg Samples

Sampler	Collection Medium	Samples per 24 hr	Species Determined
Respirable (< 3.5 µm) Hi-vol sampler (40 cfm)	Acid-washed Pallflex 2500QAO quartz fiber filter	6	H_2SO_4, H^+, NO_3^-, $SO_4^=$, NH_4^+
Respirable (< 2.5 µm) Lo-vol sampler (22 lpm) with NH_3 denuder	1 µm pore size Zefluor filter (Ghia Corp.)	3	H_2SO_4, H^+, $SO_4^=$
Ammonia	Oxalic acid on Gelman AE glass fiber with Gelman A pre-filter	6	NH_3 NO_3^- (pre-filter)
Nitric acid	NaCl-impregnated Whatman 41 with Zefluor pre-filter	3	HNO_3 as NO_3^- NO_3^-, $SO_4^=$ (pre-filter)
Nitric acid	Nylon (Duralon) 1.2 µm filters with Zefluor pre-filter	3	HNO_3 as NO_3^- NO_3^-, $SO_4^=$ (pre-filter)
Meloy SA-160	---	Continuous	SO_2
TECO 14B	---	Continuous	NO, NO_2
Environment 1	---	Continuous	Condensation nuclei

Table 25

Analysis of Zefluor Respirable Particulate Samples (with NH_3 denuder) from Pittsburg, CA ($\mu g/m^3$)

	February 5, 1979			February 6, 1979			February 7, 1979		
Time	H^{+}[a]	H_2SO_4	$SO_4^{=}$	H^{+}[a]	H_2SO_4	$SO_4^{=}$	H^{+}[a]	H_2SO_4	$SO_4^{=}$
06-14	≤ 0.8	< 0.7	-[b]	$0.6 \pm .1$	N.D.	1.3	≤ 0.4	< 0.4	4.2
14-22	≤ 0.4	$0.5 \pm .1$	4.9	≤ 0.4	< 0.3	2.4	$1.1 \pm .1$	$0.6 \pm .1$	4.6
22-06	≤ 0.4	< 0.4	4.0	≤ 0.4	< 0.4	4.1	$0.7 \pm .2$	$0.5 \pm .3$	7.7

---

a. As $\mu g/m^3$ H_2SO_4

b. Filter plugged during run

Table 26

Analysis of Zefluor Respirable Particulate Samples (with NH_3 denuder) from Pittsburg, CA (μequiv/m^3) x 10^2

	February 5, 1979			February 6, 1979			February 7, 1979		
Time	H^+	H_2SO_4	$SO_4^=$	H^+	H_2SO_4	$SO_4^=$	H^+	H_2SO_4	$SO_4^=$
06-14	$\leq$ 1.6	< 1.4	a	1.2±0.2	N.D.	2.8	$\leq$ 0.8	< 0.8	8.8
14-22	$\leq$ 0.8	1.0±0.2	10	$\leq$ 0.8	< 0.6	5.0	2.2±0.2	1.2±0.2	9.6
22-06	$\leq$ 0.8	< 0.8	8.4	$\leq$ 0.8	< 0.8	8.6	1.4±0.4	1.0±0.6	16

---

a. Filter plugged during run.

Table 27

Analysis of Acid-Washed Quartz Respirable Particulate Samples from Pittsburg, CA (μg/m^3)

Time	H^+[a]	H_2SO_4	$SO_4^=$[b]	NO_3^-[c]	NH_4^+[d]
		February 5, 1979			
06-08	0.8±.3	< 0.3	2.87	10.7	6.5
08-10	1.6±.3	< 0.4	5.78	13.0	10.5
10-14	0.7±.2	< 0.2	3.36	10.9	5.6
1430-1830	0.6±.2	< 0.2	1.34	1.01	1.5
1830-2230	0.7±.2	< 0.2	2.73	3.94	2.7
2230-0630	0.45±.1	< 0.1	1.35	1.34	1.2
		February 6, 1979			
0630-0830	≤ 0.6	< 0.3	1.48	0.74	1.0
09-11	1.1±.4	< 0.3	1.67	0.75	2.1
11-15	0.5±.2	< 0.2	1.55	0.49	1.1
15-19	0.5±.2	< 0.2	1.23	1.19	1.0
19-23	0.5±.2	< 0.2	1.33	1.47	1.4
23-07	0.5±.1	< 0.1	1.40	0.88	0.8
		February 7, 1979			
07-09	1.0±.3	< 0.3	---	1.74	2.0
09-11	1.6±.4	< 0.3	1.39	2.25	2.8
11-15	1.0±.2	< 0.2	2.13	3.67	2.4
1530-1930	1.5±.2	< 0.2	2.58	4.50	2.8
1930-23	1.2±.2	< 0.3	2.54	7.49	6.0
2330-0730	0.5±.1	< 0.1	6.53	14.6	6.4

---

a. Expressed as H_2SO_4.

b. Precision using the AIHL microsulfate method was ± 10-15% in the range of these samples.

c. Precision using the automated Cu-Cd reduction, diazotization procedure was estimated as ± 25% in the range 0.5 to 0.75 μg/m^3 and < 10% at > 1 μg/m^3.

d. Precision by the indophenol blue method.

Table 28

Analysis of Acid-Washed Quartz Respirable Particulate Samples from Pittsburg, CA (μequiv/m^3) x 10^2

Time	H^+	H_2SO_4	$SO_4^=$	NO_3^-	NH_4^+
February 5, 1979					
06-08	1.6±0.6	< 0.6	5.97	17.3	36
08-10	3.3±0.6	< 0.8	12.0	21.0	58.3
10-14	1.4±0.4	< 0.4	7.00	17.6	31
1430-1830	1.2±0.4	< 0.4	2.79	1.6	8.3
1830-2230	1.4±0.4	< 0.4	5.69	6.4	15
2230-0630	0.9±0.2	< 0.2	2.81	2.2	6.7
February 6, 1979					
0630-0830	< 1.2	< 0.6	3.08	1.2	5.6
09-11	2.2±0.8	< 0.6	3.48	1.2	12
11-15	1.0±0.4	< 0.4	3.23	0.8	6.1
15-19	1.0±0.4	< 0.4	2.56	1.9	5.6
19-23	1.0±0.4	< 0.4	2.77	2.4	7.8
23-07	1.0±0.2	< 0.2	2.92	1.4	4.4
February 7, 1979					
07-09	2.0±0.6	< 0.6	---	2.8	11
09-11	3.3±0.8	< 0.6	2.90	3.6	16
11-15	2.0±0.4	< 0.4	4.44	5.9	13
1530-1930	3.1±0.4	< 0.4	5.38	7.2	16
1930-23	2.4±0.4	< 0.6	5.29	12.1	33
2330-0730	1.1±0.2	< 0.2	13.6	23.5	36

Table 29

Analysis of Nitric Acid and Ammonia Samples from Pittsburg,CA ($\mu g/m^3$)

Ammonia Sampler

Time	February 5, 1979		February 6, 1979		February 7, 1979	
	Prefilter NO_3^-	NH_3 as NH_4^+	Prefilter NO_3^-	NH_3 as NH_4^+	Prefilter NO_3^-	NH_3 as NH_4^+
07-09	16.3	9.96	1.2	4.00	4.57	3.34
09-11	23.5	13.3	1.8	2.94	---	---
11-15	16.4	6.35	3.14	0	9.19	2.98
15-19	6.16	3.19	4.67	3.32	11.5	3.80
20-24	7.58	9.49	4.15	4.25	16.0	6.08
24-08	2.03	3.75	2.22	1.59	19.2	14.4

Nitric Acid Samplers

Time	Prefilter NO_3^-	Prefilter $SO_4^=$	NaCl/W41 HNO_3(as NO_3^-)	Prefilter NO_3^-	Prefilter $SO_4^=$	Duralon Nylon HNO_3(as NO_3^-)
			February 5, 1979			
06-14	13.0	3.54	2.22	14.1	3.65	3.27
1430-2230	5.86	1.95	3.75	2.83	1.82	3.28
23-07	1.71	1.54	0.90	1.67	1.56	0.91
			February 6, 1979			
07-15	0.39	1.08	1.71	0.46	1.07	1.47
1530-2330	---	---	1.02	2.53	1.62	1.03
24-08	1.83	1.57	0.72	1.38	1.36	0.79
			February 7, 1979			
08-16	5.08	3.03	2.61	4.74	3.10	2.63
16-24	10.7	3.12	3.85	10.1	2.99	3.99
24-08	18.9	3.88	3.49	10.7	(7.65)[a]	(9.05)[a]

---

[a] Results suggests leakage around poorly fitting prefilter.

Table 30

Analysis of Nitric Acid and Ammonia Samples from Pittsburg,CA (μequiv/m^3) x 10^2

Ammonia Sampler

Time	February 5, 1979 Prefilter NO_3^-[b]	 NH_3 as NH_4^+	February 6, 1979 Prefilter NO_3^-	 NH_3 as NH_4^+	February 7, 1979 Prefilter NO_3^-	 NH_3 as NH_4^+
07-09	26.3	55	1.9	22	7.4	19
09-11	37.9	74	2.9	16	---	---
11-15	26.5	35	5.1	0	14.8	17
15-19	9.9	18	7.5	18	18.5	21
20-24	12	53	6.7	24	25.8	34
24-08	3.3	21	3.6	9	31.0	80

Nitric Acid Samplers

Time	Prefilter[c] NO_3^-	 $SO_4^=$	NaCl/W41 HNO_3(as NO_3^-)	Prefilter NO_3^-	 $SO_4^=$	Duralon Nylon HNO_3(as NO_3^-)
			February 5, 1979			
06-14	21.0	7.78	3.6	22.7	7.60	5.3
1430-2230	9.5	4.06	6.0	4.6	3.80	5.3
23-07	2.8	3.20	1.5	2.7	3.24	1.5
			February 6, 1979			
07-15	0.6	2.24	2.8	0.7	4.46	2.4
1530-2330	---	---	1.6	4.1	3.38	1.7
24-08	3.0	3.28	1.2	2.2	2.84	1.3
			February 7, 1979			
08-16	8.2	6.32	4.2	7.7	6.46	4.2
16-24	17.3	6.50	6.2	16.3	6.72	6.4
24-08	30.5	8.08	5.6	17.3	16.0[a]	14.6[a]

---

a. Results suggest leakage around poorly fitting prefilter.

b. Gelman A glass fiber.

c. Teflon (Zefluor) membrane.

3. Effectiveness of NH_3 Denuder

Since the lo-vol respirable particulate samplers were preceded by an ammonia denuder, the higher H_2SO_4 levels observed on Zefluor filters compared to results on the quartz hi-vol respirable particulate samples might be ascribed to the denuder. However, the Berkeley atmospheric samples previously described, which were collected without a denuder, as well as the spiked quartz and Zefluor filters bearing atmospheric particulate matter showed similar trends. Thus, there is no clear indication from the Pittsburg findings that the denuder was useful.

4. Nitric Acid, Ammonia and Comparison of Diurnal Patterns

Nitric acid values ranged from 0.7 to 4.0 $\mu g/m^3$ with excellent agreement between results with NaCl/W41 and Duralon filters (ratio of means nylon/NaCl filter = 1.04, n = 8). Ammonia levels ranged from 0 to 13 $\mu g/m^3$.

To evaluate the internal consistency of the results and to identify sources of strong acid, diurnal variations of particulate H^+, NO_3^-, $SO_4^=$, NH_4^+ and gaseous NH_3 and HNO_3 are shown in Figure 7, in units of $\mu equiv/m^3$. NH_3 and NH_4^+ show very similar diurnal patterns with maxima at approximately 12 hour intervals. These results raised suspicions that the acid-washed quartz filters were trapping NH_3. However, as described in Appendix G, a control experiment placed the limit of collection of NH_3 on these filters at $\leq$ 10%.

The collection of nitric acid by adsorption on the filter samples could contribute to the total particulate acidity. Comparison of diurnal variations of HNO_3 and particulate H^+ shows only moderate correlation, however.

Ammonium is present in substantial excess relative to the sum of NO_3^- and $SO_4^=$ and is about a factor of ten more abundant than H^+ in these particulate samples at the time of analysis. We conclude that the source of strong acid in these samples is probably NH_4HSO_4, primarily, with adsorbed HNO_3 a possible minor contributor.

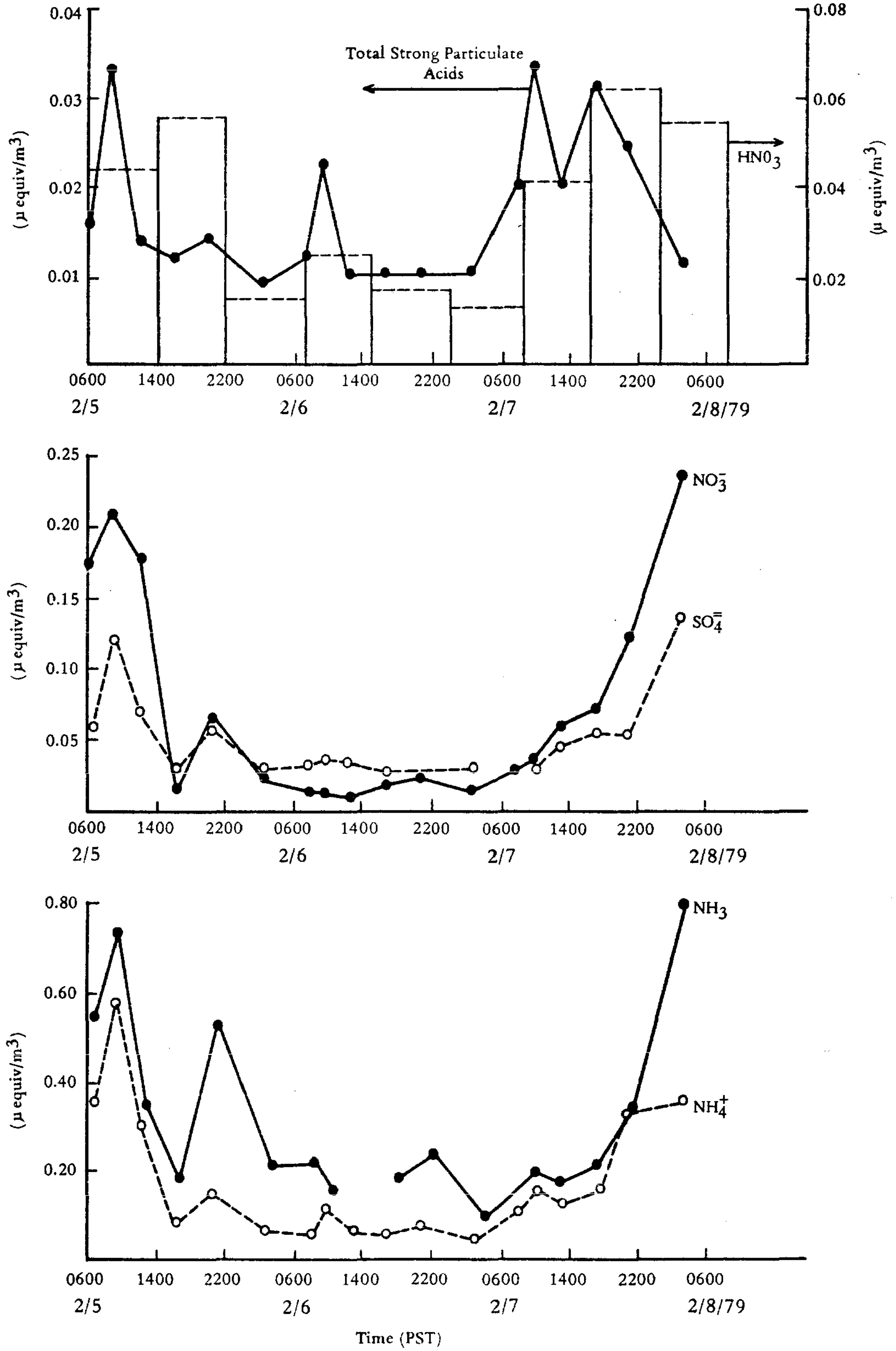
Concerning the relationship between particulate nitrate, NH_3 and HNO_3, diurnal variations do not suggest a strong negative correlation between NH_3 and HNO_3 as required by the equilibrium discussed in Section IC. However, the level of NH_3 and HNO_3 were sufficiently low such that saturation with respect to NH_4HNO_3 would generally not have occurred based on an assumed equilibrium constant of 30 $(ppb)^2$.

5. Evaluation of a Glass Fiber Filter as a Total Nitrate Sampler

Earlier studies suggested that nitric acid rather than NO_2 was the dominant source of artifact particulate nitrate in atmospheric sampling.[11] Accordingly, it was considered likely that the observed particulate nitrate on a glass fiber filter would be equivalent to particulate nitrate plus nitric acid nitrate (i.e. total nitrate) as measured by the Teflon (Zefluor) pre-filter—nylon (or NaCl/W41)

Figure 7

DIURNAL VARIATIONS FOR AEROSOL CONSTITUENTS, NITRIC ACID AND AMMONIA
PITTSBURG, CALIFORNIA



sampler. For this reason Gelman A glass fiber pre-filters to the NH_3 sampler were analyzed for nitrate. To permit comparison of these nitrate results to those on the Zefluor-nylon (or NaCl/W41) sampler, 8-hour average nitrate values were calculated from the 2 or 4-hour Gelman A samples. Table 31 includes these values together with those for Zefluor filter nitrate, nitric acid, and their total (as NO_3^-). Zefluor filter results are mean values for two filters sampling simultaneously for 8 hours, and the nitric acid results, means for samples collected on nylon and NaCl/W41. The ratio of means, Gelman A nitrate/total nitrate is 0.97. Thus, at least under conditions of relatively low nitric acid levels, the Gelman A glass fiber filters approximated a total nitrate sampler. Nitrogen dioxide, which was present at about 0.02 ppm (40 $\mu g/m^3$) throughout most of the sampling (Appendix I), did not appear to influence the level of artifact nitrate.

Table 31

COMPARISON OF NITRATE ON GELMAN A GLASS FIBER FILTERS WITH TOTAL NITRATE ($\mu g\ NO_3^-/m^3$)

	Approx. Time Period	Prefilter NO_3^-	Nylon and NaCl/W41 HNO_3 as NO_3^-	Total NO_3^-	Gelman A NO_3^-
	06-14	13.55	2.75	16.3	18.2
Feb. 5	1430-2330	4.35	3.52	7.86	6.87
	23-07	1.42	0.91	2.33	2.03
	07-15	0.43	1.59	2.02	2.32
Feb. 6	1530-2330	2.53*	1.03	3.56	4.41
	24-08	1.61	0.76	2.36	2.22
	08-15	4.91	2.62	7.53	7.65
Feb. 7	1530-2330	10.4	3.92	14.3	13.8
	2330-0730	18.9*	3.49*	22.4	19.2

Ratio of Means: Gelman A/Total NO_3^- = 0.97

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*Value from only one filter.

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Antilog Signal Processing for Gran's Titration

The concentration of H^+ can be expressed as follows:

$$[H^+] = \text{antilog} \left[\frac{E}{S} \right] - E_1$$

where $E_1 = \text{antilog} \left(\frac{E_0}{S} \right)$ = a constant

S = slope of electrode (millivolt per pH unit)

E = electrode potential

Plotting antilog $(\frac{E}{S})$ against titrant added yields an initially linear curve which can be extrapolated to the equivalence point based on a minimum number of data points. However, a disadvantage of the technique is the time required to convert observed pH values to the corresponding (H^+).

R. K. Stevens and co-workers reported the use of an antilog amplifier to directly convert the pH to H^+ thereby permitting automatic generation of Gran's plots.[35] For the present study an improved version of their system was designed and constructed.

For the AIHL system, Gran's plots are made directly from the analog output signal from the Radiometer pH meter (#PHM64Sa) using the circuit shown in Figure A-1. The output voltage (E_{in}) from the pH meter is introduced to the non-inverting input of a 741K operational amplifier* (op-amp) in a voltage follower configuration to provide a high impedance interface with the pH meter. The signal is then offset to the correct input range for the 755N antilog amplifier* with a 100K potentiometer before entering the inverting input of a second 741K op-amp. This op-amp divides the electrode potential by the slope of the electrode yielding (E/S). The antilog calculation performed by the 755N device yields the required Gran's function (antilog E/S). A table of the input and output voltages of the Gran's function generator are included in the figure. During titrations the Gran's plot is produced on a 100 mv strip chart recorder at a fixed chart speed synchronized with the titrant addition. Precise values for volume of titrant added are recorded manually from a digital readout on the titrator.

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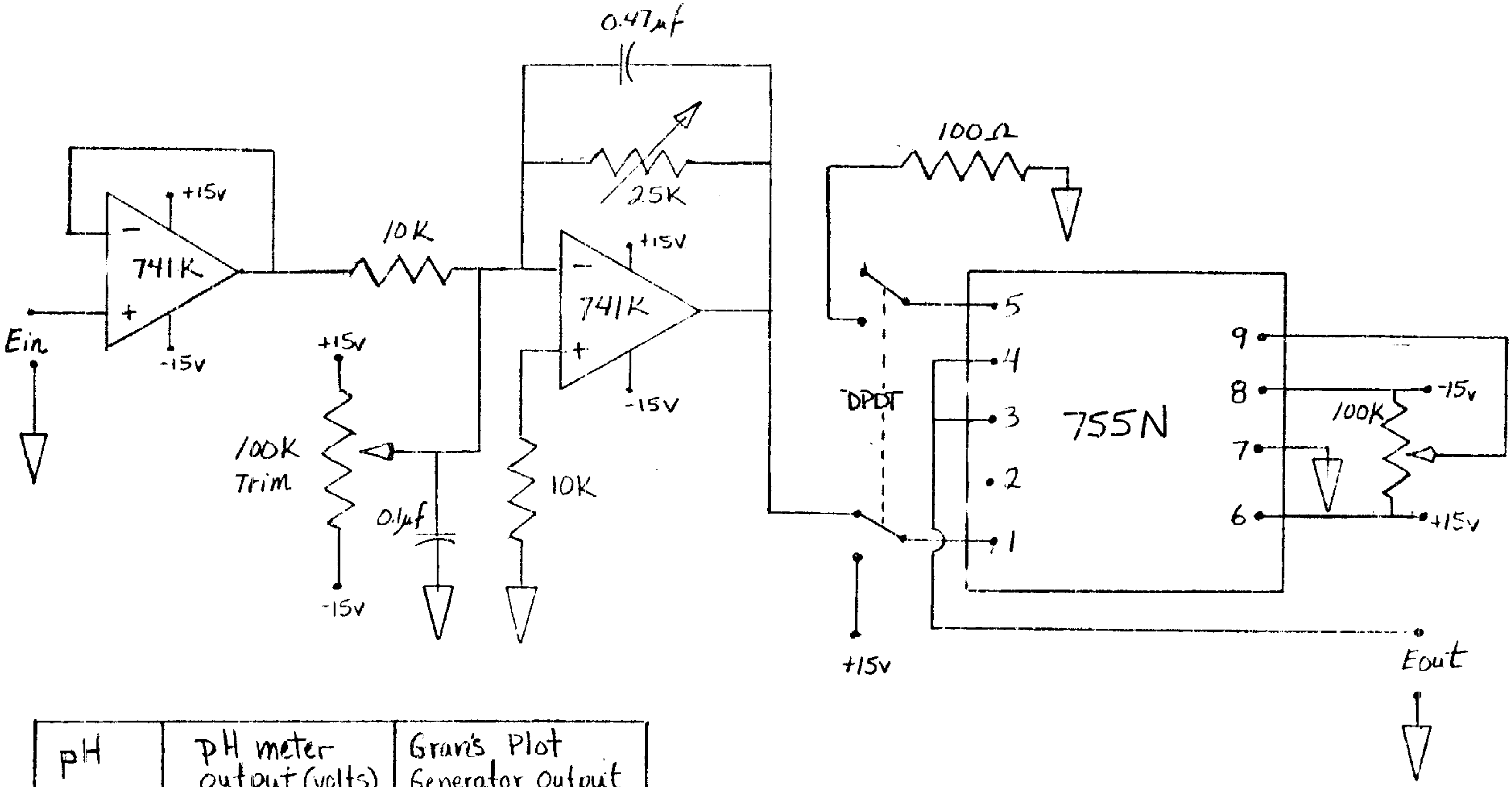
*Analog Devices, Norwood, Mass.



pH	pH meter output (volts)	Gran's Plot Generator Output
3.0	-1.5	10.0v
4.0	-2.0	1.0 v
5.0	-2.5	100 mv
6.0	-3.0	10.0mv
7.0	-3.5	1.0 mv

Figure A-1 Gran's Plot Function Generator

Appendix B

Sulfuric Acid Aerosol Generation

To develop and validate reliable methods for collection and analysis of airborne sulfuric acid particles, a convenient method for producing a well characterized submicron aerosol was necessary. Such an aerosol generator was developed in our laboratory[50] and is shown schematically in Figure B-1.

Aerosol is generated by passing very dry nitrogen through fuming sulfuric acid, diluting and heating the effluent vapor and injecting it into a stream of humidified air through a small diameter nozzle. This technique has been shown to produce a monodisperse aerosol over the range 0.3 to 1.0 μm particle diameter as measured by a Royco PC 200B optical counter (coefficient of variation < 0.2). The diameter of the particles produced can be selected by setting the generator operating parameters to the corresponding experimentally determined values. For the current program the generator has been operated so as to produce particles ≤ 0.3 μm optical diameters.

To assess the mass output rate of the generator, the aerosol was sampled at 1 CFM for one hour through a 1 μm pore size polyethylene backed Fluoropore filter followed by a Greenburg-Smith impinger containing 70 ml of distilled water. The impinger was included to collect H_2SO_4 vapor which penetrated the filter plus any SO_3 present in the generator output. The efficiency of this impinger for such collection was not established, however. The filter was subsequently extracted in 5 ml distilled water, and both the filter extract and impinger solution analyzed by the flash vaporization-flame photometric detection method for sulfur.[51,52] The results of several runs performed over the course of one day of continuous generator operation are included as Table B-1. Based on these data, the generator's aerosol output was 557 ± 65 μg/m^3 which allows a 47 mm filter loading rate of 16 ± 1.7 μg H_2SO_4/min at 1 CFM. Results indicate 42 μg/m^3 $SO_4^{=}$ collected by the impinger which corresponds to 7% of the generator output. Since the efficiency of the impinger was not established this value provides an lower limit estimate to the sulfur species reaching the filter.

Although the number of particles < 0.3 μm could not be measured a comparison of Royco data for particles in the 0.3 to 1 μm range with the sulfate results from filter plus impinger samples permits estimation of the proportion of H_2SO_4 particles < 0.3 μm in the generator output. Assuming an average density of 1.7 g/cm^3 for the generated aerosol*, this comparison indicates that particles less than 0.3 μm account for 97% of the H_2SO_4 mass. All particles generated were less than 0.4 μm in diameter.

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*The density of H_2SO_4 is 1.83 for 100% H_2SO_4 and 1.67 for 75%w H_2SO_4 (25%w H_2O).

Figure B-1

Sulfuric Acid Aerosol Generator and Sampling System

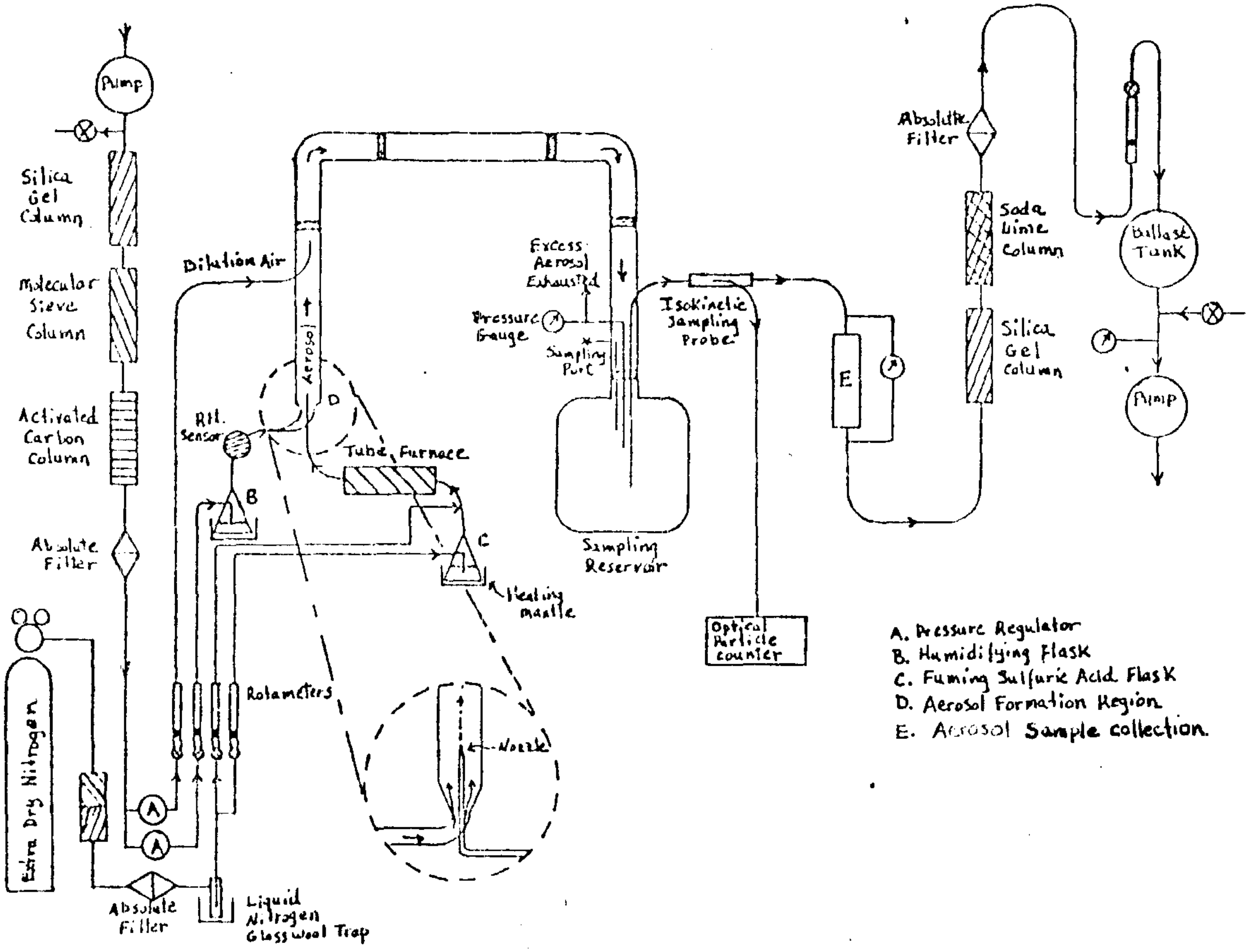

Table B-1

Results with the H_2SO_4 Generator[a]

	Run			Mean ± 1 σ
	#1	#2	#3	
Total H_2SO_4 collected,[b] μg	900	1105	1070	1022 ± 107
Loading on first 1 μm Fluoropore filter (%)	91	92	94.5	93
Loading on 2nd 1 μm Fluoropore filter (%)[c]	--	--	0.5	--
Loading in impinger (%)	9	8	5	7
Aerosol concentration at 1 cfm, (μg/m^3)[d]	482	598	590	557 ± 65
Filter loading rate at 1 cfm, μg/min	14	17	17	16

---

a. All particles ≤ 0.4 μm.

b. Sum of the H_2SO_4 on filters plus impinger.

c. Second filter in series between first filter and impinger.

d. Based on mass collected by filter.

Appendix C

Uniformity of H_2SO_4 Deposition and Sectioning of Filter Discs

The H_2SO_4 aerosol generator as well as the intended lo-volume field sampling system for H_2SO_4 employed 47 mm filters which required sectioning for analysis by different methods. Before beginning the intermethod comparison it was necessary to establish that 1) 47 mm filters could be reproducibly sectioned by a technique which would minimize losses of H_2SO_4 and 2) that the filter was uniformly loaded by the generator.

Filter cutting was done in a chamber under a stream of N_2 which minimized NH_3 exposure. A cookie-cutter type device was fabricated to provide reproducible sectioning of filters into four quarters. For this operation the filter was immobilized and flattened in a holder using slight suction. The precision and equivalence of the resulting sections as well as loss of filter in cutting was established by weighing the pieces cut from Fluoropore filters. Based on weighing sections from five filters, the average weight loss during cutting was 1.1 $\pm$ .6%. The 20 filter sections were equivalent within a mean coefficient of variation of 2.5%.

To establish the uniformity of H_2SO_4 loading, five 47 mm filters were loaded with about 200 μg of $\leq$ 0.3 μm H_2SO_4 aerosol, sectioned into quarters and the quarters analyzed for sulfate employing the automated methylthymol blue (MTB) procedure. The results are shown in Table C-1 and indicate variations of 4% or less. Since the variability in results due only to the analytical method is at least 2%, the variability in deposition between quarters is $\leq$ 2%.

Table C-1

Uniformity of H_2SO_4 Deposition on 47 mm Filters

Sample ID	Mean $SO_4^{=}$ Per Quarter Filter (μg)	Coefficient of Variation (%)
133F1	58.5 ± 2.5	4.3
134F1	46.0 ± 0.8	1.7
135F1	46.3 ± 1.9	4.2
136F1	45.0 ± 1.1	2.4
137F1	37.9 ± 1.0	2.6
138F1 (Blank)*	< 2.5	---

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*Sample to assess contamination of clean filter by cutter following sectioning of loaded filters.

Appendix D

Aerosol Generation with a Nebulizer

A nebulizer-type aerosol generator was constructed and used to provide $(NH_4)_2SO_4$ and NH_4HSO_4 aerosols (Figure D-1). Aerosol was generated from a dilute aqueous solution of the ammonium salt by a glass nebulizer operated at 20 psi with dry air. The nebulizer design incorporates an atomization jet impaction surface to provide a rather sharp cut point for removing any relatively large particles. Coagulation of the particles is inhibited by constantly purging the nebulizer chamber with dry dispersion air, which also serves to transport the aerosol to the dilution air inlet. The dry dilution and dispersion air (< 1% RH) evaporates water from the particles until the aerosol is reduced to equilibrium size as calculated from the equation:*

$$D_p = D_d \left[\frac{C\rho_d}{\rho_p} \right]^{\frac{1}{3}}$$

where D_p = final particle diameter (μm)

D_d = initial droplet diameter (from nebulizer)

ρ_d = density of dry particle (g/cm)

ρ_p = density of droplet

C = weight fraction of ammonium sulfate salt in solution

The initial droplet diameter produced by the nebulizer is < 2 μm, which would yield an aerosol of < 0.35 μm diameter after water evaporation from a 1% (w/w) solution of the ammonium sulfate salt. To prevent an increase in the particle size with time due to evaporation of water from the aerosol solution in the nebulizer chamber, the nebulizer solution drainage is not recycled into the fresh solution reservoir. Based on particle sizing with a Royco 200B optical particle counter, an average particle size of < 0.3 μm was achieved with $(NH_4)_2SO_4$. The generator was operated such that 99% of all particles were ≤ 0.3 μm as determined by comparing the aerosol mass and Royco 200B optical particle counter data.

The aerosol reaches equilibrium size during transport through the 1-1/2" ID tubular flow reactor and is collected from a plexiglass manifold using three 47 mm polycarbonate filter holders. Loading rate per filter was about 80 μg sulfate/hour. Using ammonium sulfate, comparison of the filter weight increase (ΔW) for filters conditioned at 44% R.H. to the sulfate observed by the automated MTB method yielded the relationship:

$$(SO_4^{=})_{MTB} = -26.9 + 0.938\ (\Delta W)$$

$$r = 0.982$$

$$S_{y.x} = 12.3$$

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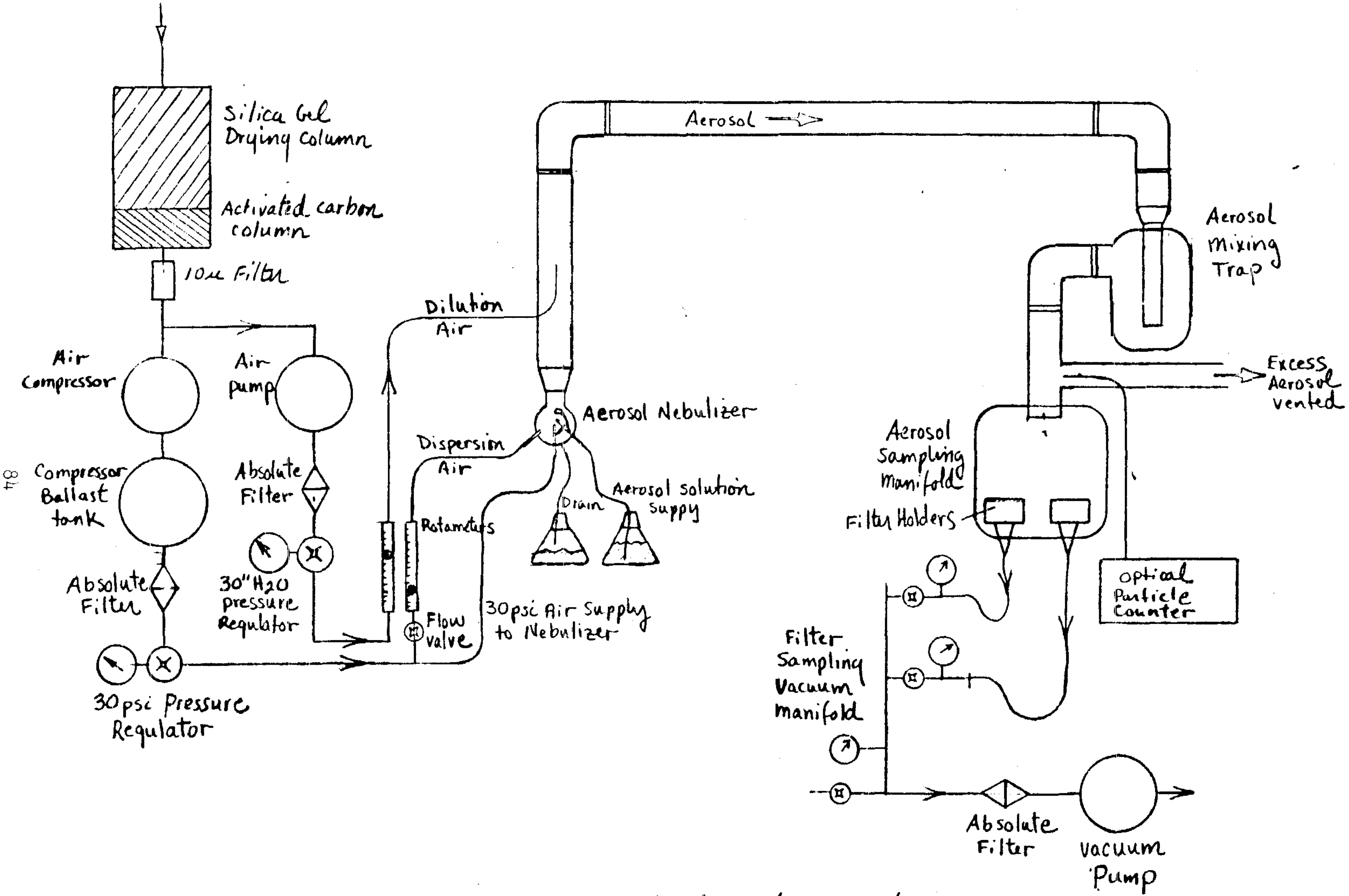
*R. Dennis, Handbook on Aerosols, ERDA Report #TID-26608 (1976).



Ammonium Sulfate Salts Aerosol Generator

Figure D-1

To evaluate the equivalence of sulfate loadings between filters, uniformity of deposition within one filter, and loss of ammonia from filters causing strong acid formation, two sets of three filters were each loaded with about 200 μg $(NH_4)_2SO_4$ per filter using Ghia Zefluor filters. The filters were quartered as described in Appendix C and the quarters analyzed for $SO_4^=$, (automated MTB), NH_4^+ (indophenol blue procedure) and H^+ by the titrimetric method.

Based on the mean sulfate result for four quarters (Table D-1) the three filters had equivalent loadings within 2% (C.V.). The uniformity of deposition on the four quarters within one filter was 5.7% (median C.V. for 6 filters).

Based on the mean observed sulfate per filter quarter and the composition $(NH_4)_2SO_4$, the expected concentration of NH_4^+ was calculated. The results given in Table D-1 show about 2% excess of NH_4^+, which is within the combined experimental error of the analytical methods. This suggests that the analytical methods for sulfate and ammonium are consistent with one another and that there is no loss of NH_3 during aerosol formation. The latter was confirmed by direct titration for strong acid. No acidity was detectable.

Table D-1 Comparison of Calculated and Observed Ammonium Concentrations for Ammonium Sulfate Aerosols

Set	Filter	μmoles $SO_4^=$ per quarter [a]	$\frac{\text{observed μmoles } NH_4^+}{\text{calculated μmoles } NH_4^+}$ [b]
A	18ZT1	0.66 ± .05	1.06
A	19ZT1	0.69 ± .03	1.02
A	20ZT1	0.68 ± .04	1.01
B	21ZT1	0.74 ± .07	1.03
B	22ZT1	0.71 ± .04	0.99
B	23ZT1	0.73 ± .04	0.99
		Median:	1.02

a. Mean ± σ for 4 quarters.

b. Calculation based on stoichiometry for $(NH_4)_2SO_4$.

Nitrate Extraction and Analysis with Nylon and NaCl Impregnated Filters

Nitric acid collected on nylon and sodium chloride-impregnated Whatman 41 (NaCl/W41) (cellulose) filters was analyzed as nitrate by the automated Cu-Cd reduction, diazotization procedure following extraction. Extractions of laboratory-generated HNO_3 from clean NaCl-impregnated or nylon filters used 30-minute mechanical shaking (Eberbach Model 6000). With atmospheric samples, 60 minutes shaking time was used. The NaCl-impregnated filters were extracted with distilled water and the nylon filters, with 0.1N NaOH.[17]

To establish that the sampling media did not interfere in the subsequent analysis, an NaCl/W41 filter was added to 10 ml standard solutions containing 5 μg/ml nitrate. The level of nitrate in the extract remained unchanged The filter blank was below detection (approx. 0.2 μg/ml or 2 μg/47 mm filter).

For the nylon filters, following extraction in 5 or 10 ml base, an equal volume of 0.1N HCl was added to neutralize the solution. Some care was required because of the observed dependence of the nitrate result on pH (<u>Figure E-1</u>). Over a pH range of 2-10 the error was $\leq$ 10%.

The filter blank observed for Duralon nylon filters was 6.9 ± 0.1 μg/47 mm filter. The NaOH and HCl solutions had no detectable nitrate.

Nitrate Recovery as a Function of pH Using
The Automated Cu-Cd Reduction-Diazotization Method

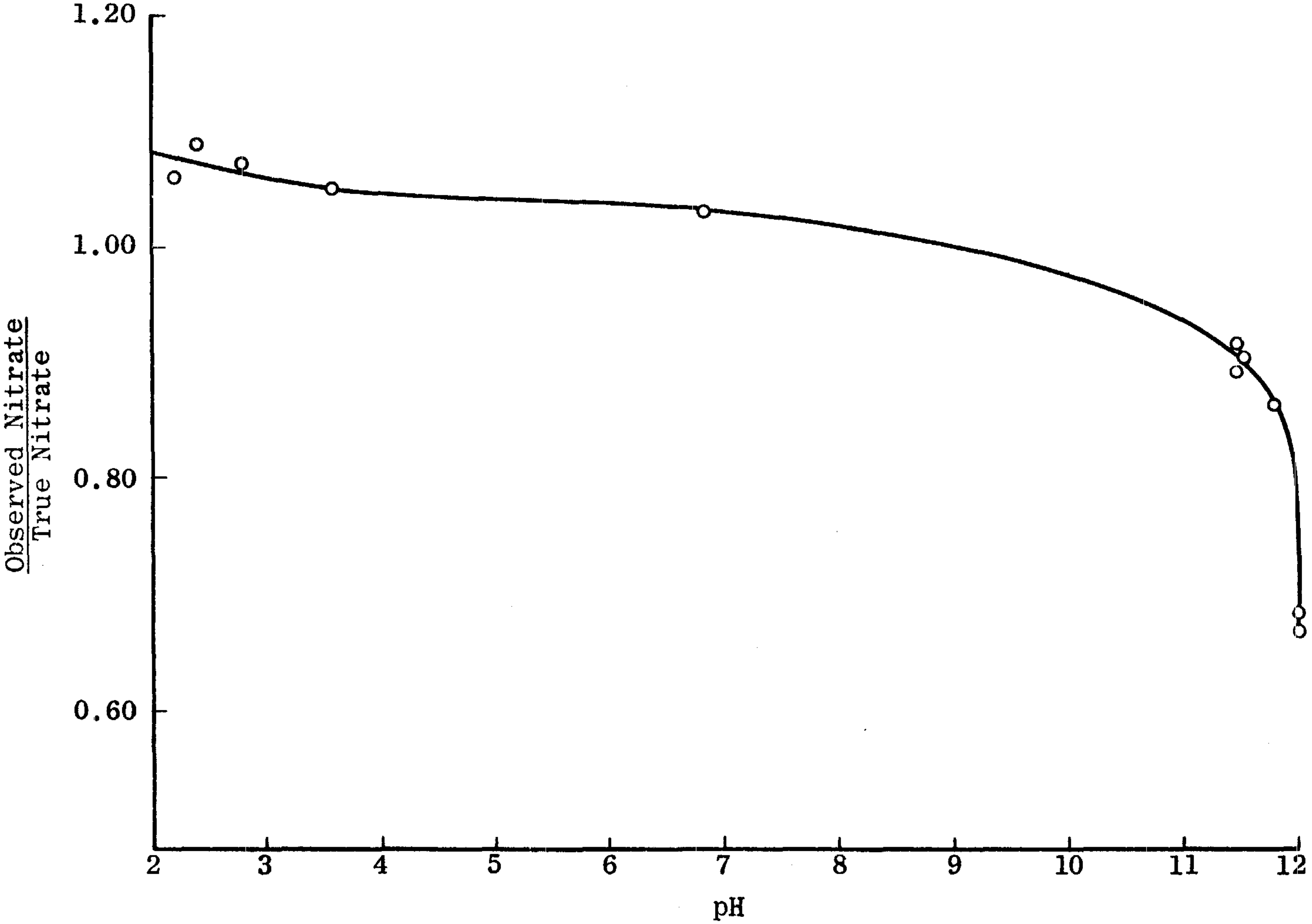


Figure E-1

Filter Heating Technique for Serial Filter Holder Samples

The apparatus used for this procedure is shown in Figure F-1. A heat gun is used to force hot air through a 2" copper Tee used as a flow distribution manifold. The filter holder to be heated is attached to the manifold vertical side arm and the heated air drawn through the filters by applying a vacuum source. The temperature of the volatilization air is controlled by admitting a desired amount of unheated ambient air through variable bleed holes in a collar fitted to the manifold side arm. Rotation of the bleed collar allows adjustment of the size of the bleed holes to set the required volatization air temperature. To ensure reproducible heating of the filter stack samplers, a filter holder specially fitted with thermistors upstream and downstream of the particle pre-filter (see figure) was peridically used as a temperature reference.

The following protocol was used for the loaded filter heating technique when sampling HNO_3 or NH_3:

1. Turn on heat gun and allow 10 min. to establish thermal equilibrium.

2. Measure flow rate of loaded filter stack and disconnect from vacuum source.

3. Connect temperature reference filter holder to vacuum and set flow rate equal to that of loaded sampler to be heated.

4. Estimate from Figure F-2 the temperature required to reduce volatization air relative humidity to less than 15% (typically 45-50°C).

5. Install temperature reference filter holder on heated air manifold and set corresponding temperature using air bleed collar.

6. Attach filter holder containing collected samples on heated air manifold, connect holder to vacuum source and draw heated air through filters for three minutes.

7. Dismount loaded filters from filter holder and store in air-tight plastic Millipore boxes.

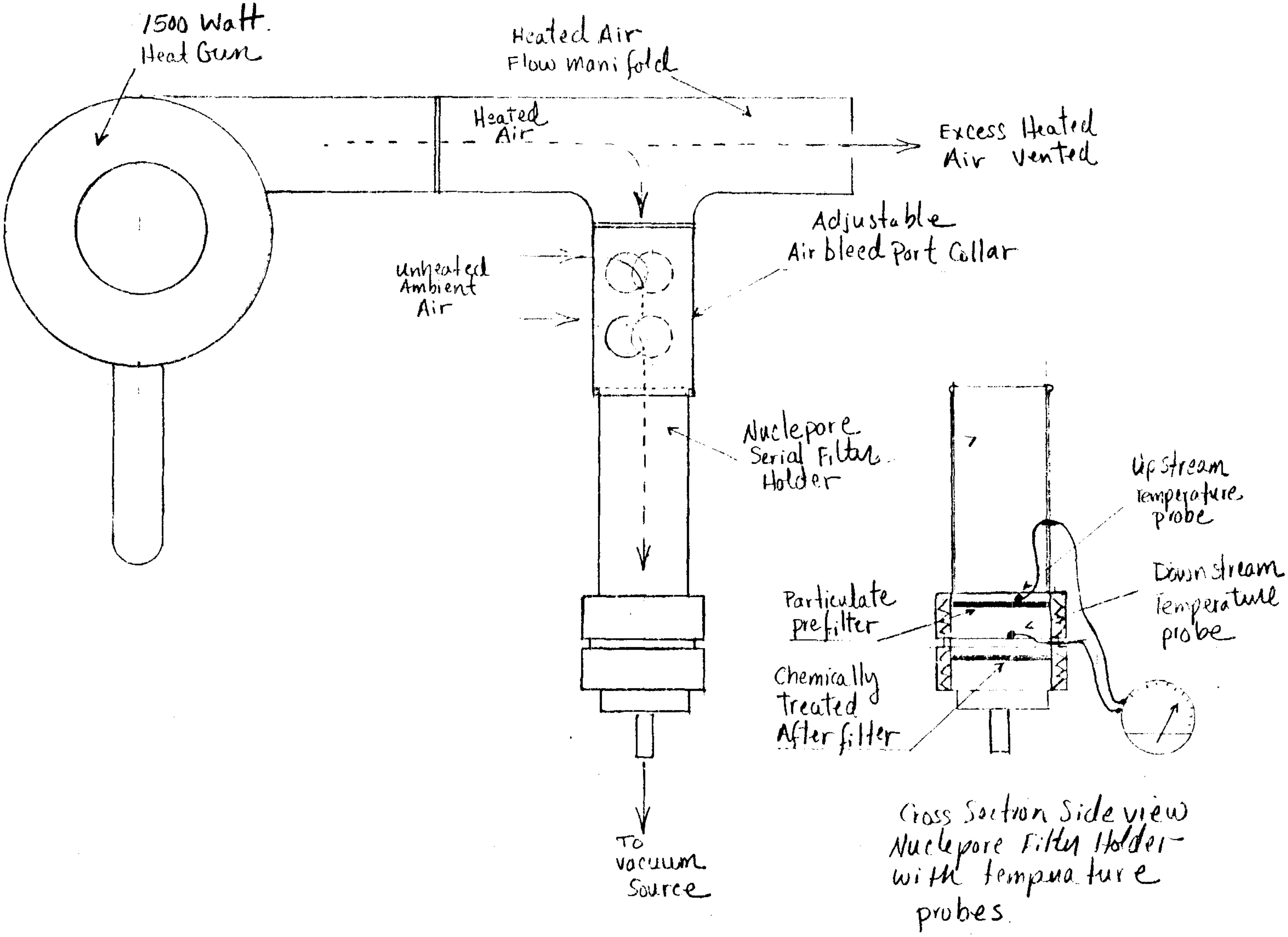
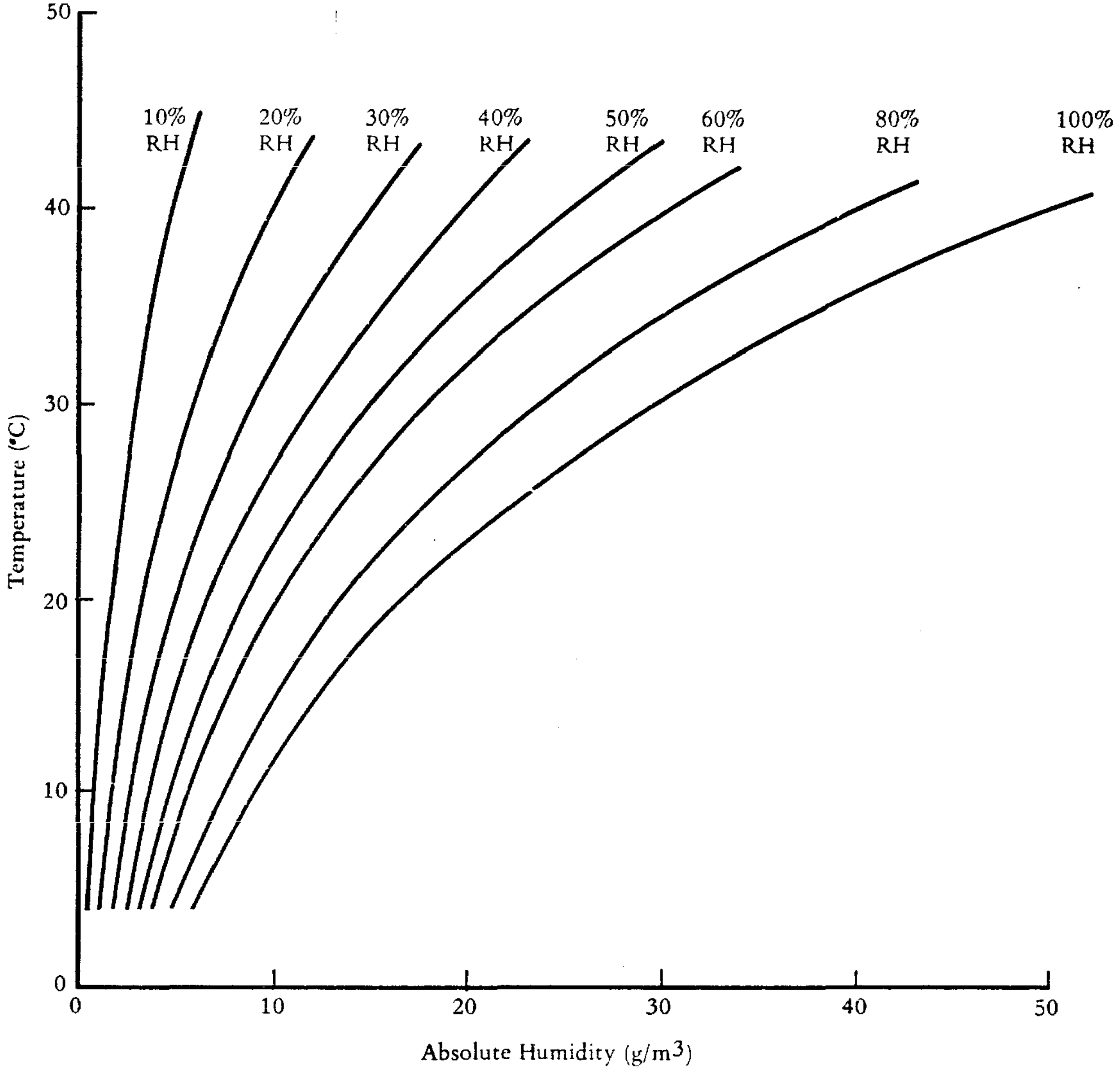


Figure F-1 System for Heating Filter Sampler to Desorb NH_3 and HNO_3

ISOPLETHS FOR RELATIVE HUMIDITY AT VARYING TEMPERATURE



Note: Data from Chemical Rubber Co., Handbook of Chemistry and Physics, 34th ed. P 2134.

Figure F-2

Collection of Ammonia on Acid Washed Pallflex 2500 QAO Quartz Fiber Filters

The striking similarity in diurnal variations for ammonia and NH_4^+ in particulate matter noted in Pittsburg sampling raised the suspicion that acid washed quartz filters were collecting ammonia. To evaluate this possibility ambient Berkeley air was sampled for 6 hours through 47 mm quartz filters following particulate removal with slightly alkaline Gelman A (pH = 7.6) pre-filters. The flow rate was adjusted to 1.32 cfm to provide a face velocity equal to that of the 8 x 10" filter at 40 cfm.

The results for two trials run simultaneously are given in Table G-1. Particulate NH_4^+ levels were about 2 $\mu g/m^3$ on the pre-filter. While ambient NH_3 values were not obtained because of experimental difficulties, we estimate NH_3 concentrations to be $\geq 3\ \mu g/m^3$ based on results in Pittsburg as well as previously published results for urban areas.[40] Accordingly the quartz filters are concluded to be $\leq 10\%$ efficient for NH_3 collection.

Table G-1

Collection of Ambient NH_3 on Acid Washed Pallflex 2500 QAO Quartz Filters

Trial	Filter	NH_4^+ in Particulate ($\mu g/m^3$)	NH_3 on Quartz ($\mu g/m^3$)[a]
1	Gelman A (pre-filter)	1.9	---
	Pallflex Quartz	---	0.34
2	Gelman A (pre-filter)	1.9	---
	Pallflex Quartz	---	0.26

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a. Results corrected for filter blank run in same batch. Filter blank 3.5 ± 0.7 μg/47 mm filter. Blank represented about 50% of the gross NH_3 (as NH_4^+) observed on the quartz filters.

AIHL Version of the Brookhaven Method for the Preparation of Quartz Filters for H_2SO_4 Sampling.

Apparatus and Equipment

Stainless steel pan, 10½" x 18¼", lined with Tedlar film
Glass rod tray, 9" x 11" (Fig. 1)
Glass rod tray, 8" x 10" (Fig. 2)
Steambath
Muffle furnace
Drying oven
Plastic buchner funnel, 8-3/4" x 10-3/4"
Suction flask
Ultrasonic bath with detachable 10" x 14" tub, Blackstone Model SG2A
Drying rack with removable screens
Laminar flow hood
Pancake spatulas (2)
Micro spatula, thin blade

Reagents and Supplies

Reagent grade H_3PO_4, 85%
Quartz filter material, 8" x 10" (QAO 2500 Pallflex Corp., Putnam, Conn.)
Glass fiber filters, 8" x 10"

Procedure

1. Six 8" x 10" Pallflex QAO 2500 quartz filters are used with the backing removed. Three filters are stacked and then an 8½" x 10½" liner is placed on top. This liner consists of two 5¼" x 8½" pieces of quartz filters which have been previously treated by this method and may be reused. Three more 8" x 10" quartz filters are stacked on top of the liner.

2.* The filter stack is washed with distilled H_2O using a prewashed glass fiber filter-lined plastic buchner funnel and suction. A liter of H_2O, poured in small portions from a 250 ml Erlenmeyer, is used for each group of filters. The filters are removed from the funnel by pressing a sheet of aluminum foil into the funnel so that it fits flush against the filters. The ends of the foil should extend up and over the walls of the funnel. The funnel is then placed upside down on the bench top and clean air is blown into the funnel to disengage the filters. The funnel is then lifted off the aluminum foil. The glass fiber filter is removed from the filter stack and replaced into the funnel.

3. The aluminum foil is removed and the stack is lined top and bottom by quartz filters. The quartz material is then placed in a cold muffle furnace and ignited at 750°C for 4 hours (including warmup time). Note that the quartz liners may be reused.

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*For some batches of filters as supplied by Pallflex, it was necessary to ignite the filters initially as described in par. 3. Otherwise the filters stuck together following step 2 causing damage. In these cases, filters were fired a second time at 750°C under par. 3.

4. The outer quartz liners are removed and the cooled quartz material (6 sheets and the middle liner) is placed on the larger glass rod tray. The smaller glass rod tray is placed on top and the unit is carefully placed in a Tedlar-lined stainless steel tray containing hot (steambath temperature) concentrated H_3PO_4. The top glass rod tray prevents the filters from floating. The H_3PO_4 level must be high enough to cover the quartz material and is reused. The filter stack is allowed to soak 30 min.

5. The glass tray assembly is removed from the acid bath and placed in the tub from the sonic bath, which has been removed from the sonic bath apparatus and placed next to the acid bath. After the transfer, the tub is replaced in the ultrasonic unit and distilled H_2O is added slowly and carefully to cover the assembly. The filter material is very weak at this time and may be damaged by the force of pouring water. The bath is then agitated for 15 min. at the lowest setting. This procedure is repeated twice more, removing the glass rod tray assembly fron the bath for each change of H_2O.

6. The group of filter sheets is transferred to the buchner funnel. Transfer is most easily accomplished by removing the assembly from the sonic bath, inverting it, and placing it upon two beakers for support. The larger glass rod tray, now on top, is removed, and the plastic buchner funnel is gently placed over the filters on the remaining tray. The funnel, filters, and tray are then inverted and placed on a filter flask. The filters should be flat with no wrinkles.

7. The filter material is rinsed thoroughly with distilled H_2O using suction. Rinsing is continued until 4 liters have been collected. The filter material is still weak.

8. The wet stack of filters is removed from the funnel as in (2) and lined top and bottom with overlapping quartz sheets. This stack is then placed in the cold muffle furnace and again ignited to 750°C. At the conclusion of this step there is a noticeable improvement in the tensile strength of the quartz.

9. The filters should separate easily into two stacks of three; the liner may be removed at this time. Individual filters are then separated by gently working around the edges and in towards the center with a small spatula.

10. The filters are placed in the large glass rod tray, which is then placed in the ultrasonic bath. Two liters of a pH 5 H_3PO_4 solution are added and the bath is excited for 15 min. at the maximum setting.

11. The glass rod tray containing the six filters is removed from the bath. The filters are then individually removed from the stack with large pancake spatulas and placed on the screens in the drying rack.

12. Preliminary drying is carried out in the laminar flow hood overnight. Final drying is accomplished in the drying oven at 65-75°C.

13. The cooled filters are each placed in a plastic film-lined manila folder. These folders are placed in a plastic bag which is then taped shut and stored in the clean air bench.

Notes on the Procedure

1. The purpose of the initial ignition step (3) is to remove organic binding substance from the quartz material. If the quartz is placed in the hot concentrated H_3PO_4 without ignition, discoloration of the acid may occur. A stack of 30 filter sheets have been ignited at one time (by Brookhaven) with no difficulties. If more than one filter batch is to be ignited, however, liners should be placed between each set of 6 filters to allow easy separation.

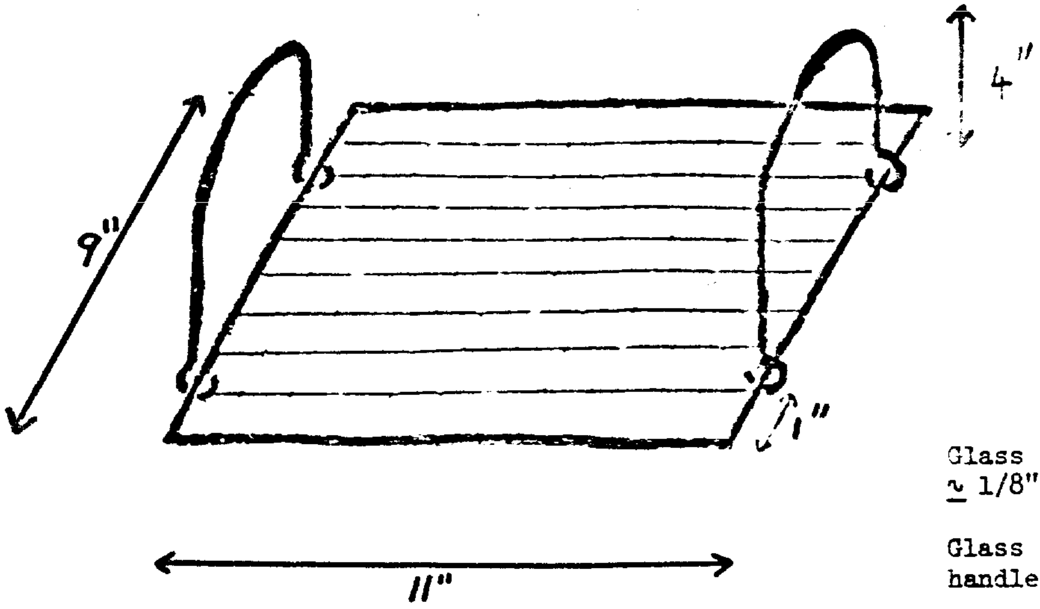
2. The quartz becomes translucent when saturated with concentrated H_3PO_4 and easily damaged. After prolonged soaking in H_2O, a return of the characteristic white color of the quartz will be noticed, although the filters remain fragile.

3. In step 8, the rate of filtration will decline as the glass fiber lining on the buchner funnel is used over and over. After 3 groups of quartz material (6 sheets plus the middle liner) have been rinsed, new glass fiber material should be used.

4. The increase in quartz tensile strength indicated after completion of step 9 is probably caused by the formation of a type of phosphate glass (residual phosphate remaining despite the rinsing step 8). If the filters are not thoroughly rinsed they become very stiff or brittle, (easily cracked), after ignition step 9 and cannot be separated.

5. Dilute H_3PO_4, pH 5 used in step 11 is conveniently prepared by diluting one drop of concentrated H_3PO_4 to a liter. A further dilution of this stock solution by 1 to 50 will yield a pH of approximately 5. The soak procedure in the ultrasonic cleaner allows a uniform distribution of very slight acidity resulting in repeatable blank values for the microtitration of H^+. The pH 5 solution should be prepared for use from the stock solution daily and may be used for several groups of filters.

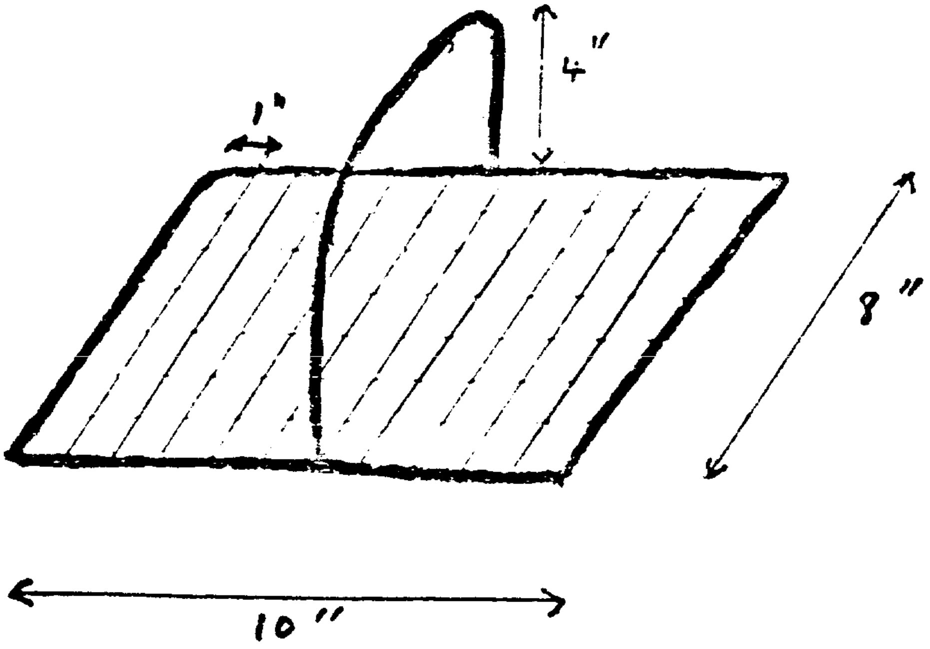
Figure H-1
GLASS ROD TRAY



Glass rods for screen ≃ 1/8" diameter.

Glass rods for frame and handles ≃ 1/4" diameter.

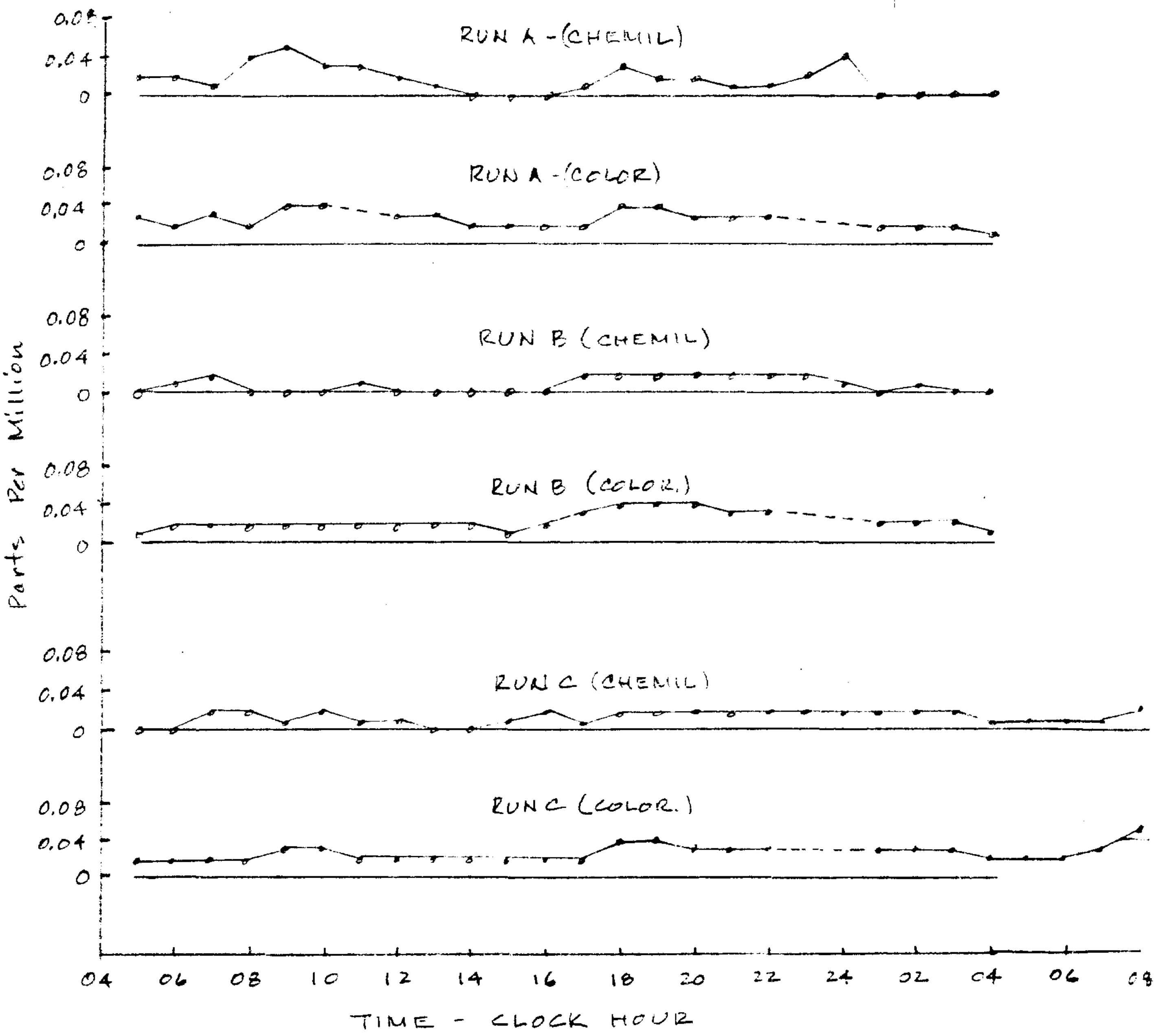
Figure H-2
GLASS ROD FRAME



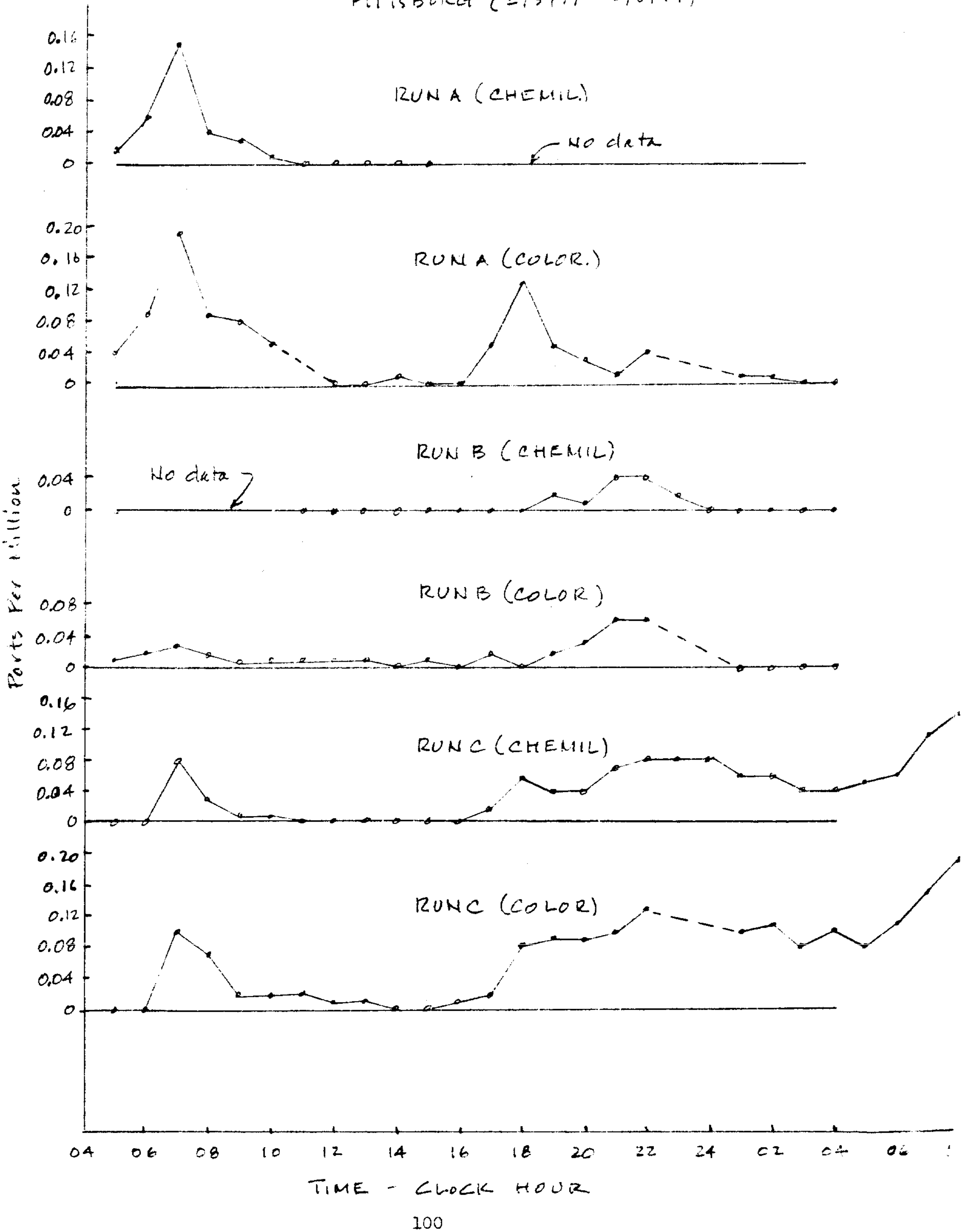
Appendix I

Diurnal Variations for NO, NO_2, O_3, SO_2, Soiling Index,Windspeed and Direction During Pittsburg Sampling.

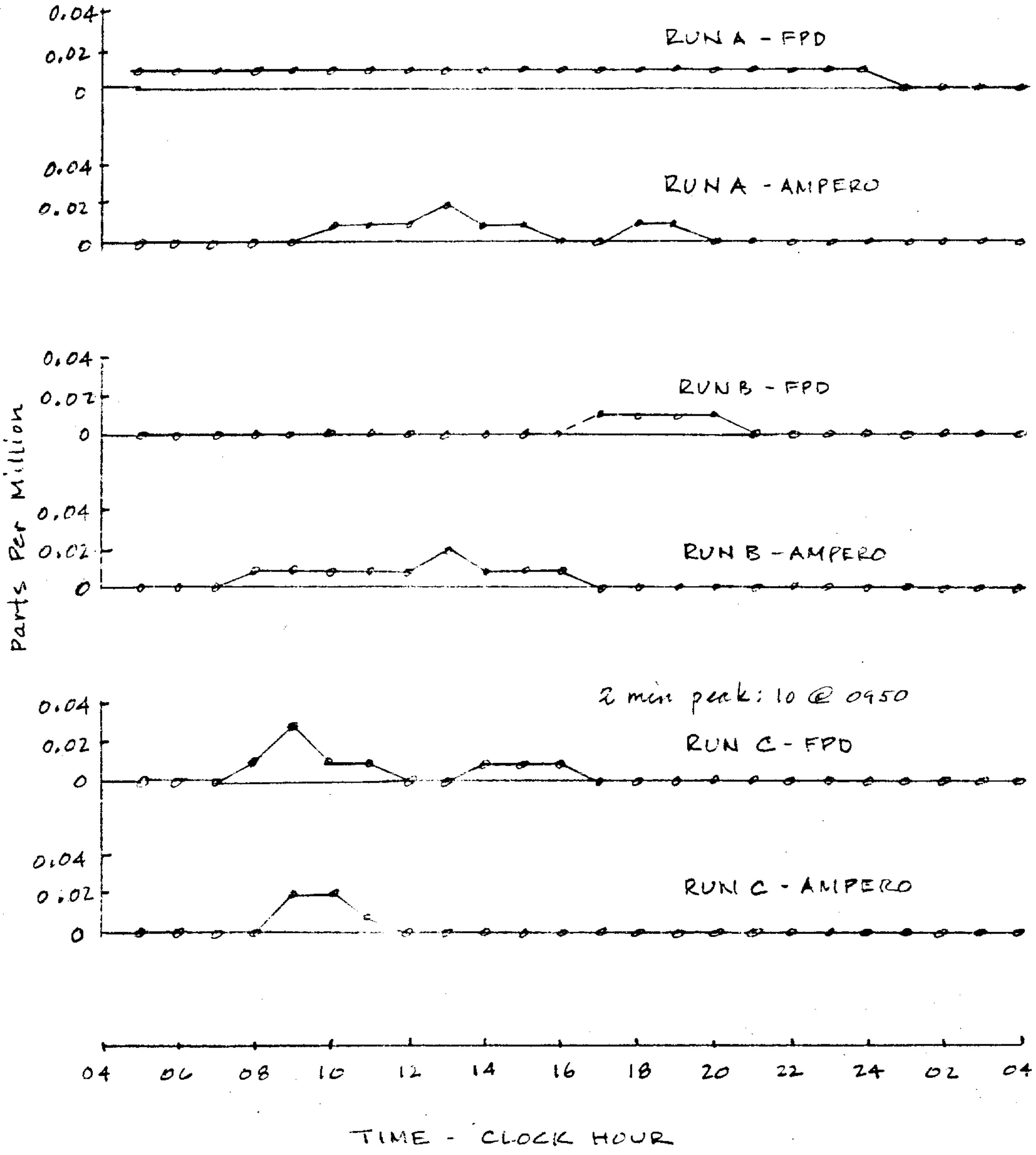
HOURLY AVERAGE NITROGEN DIOXIDE LEVELS DURING SAMPLING AT PITTSBURGH (2/5/79 - 2/8/79)



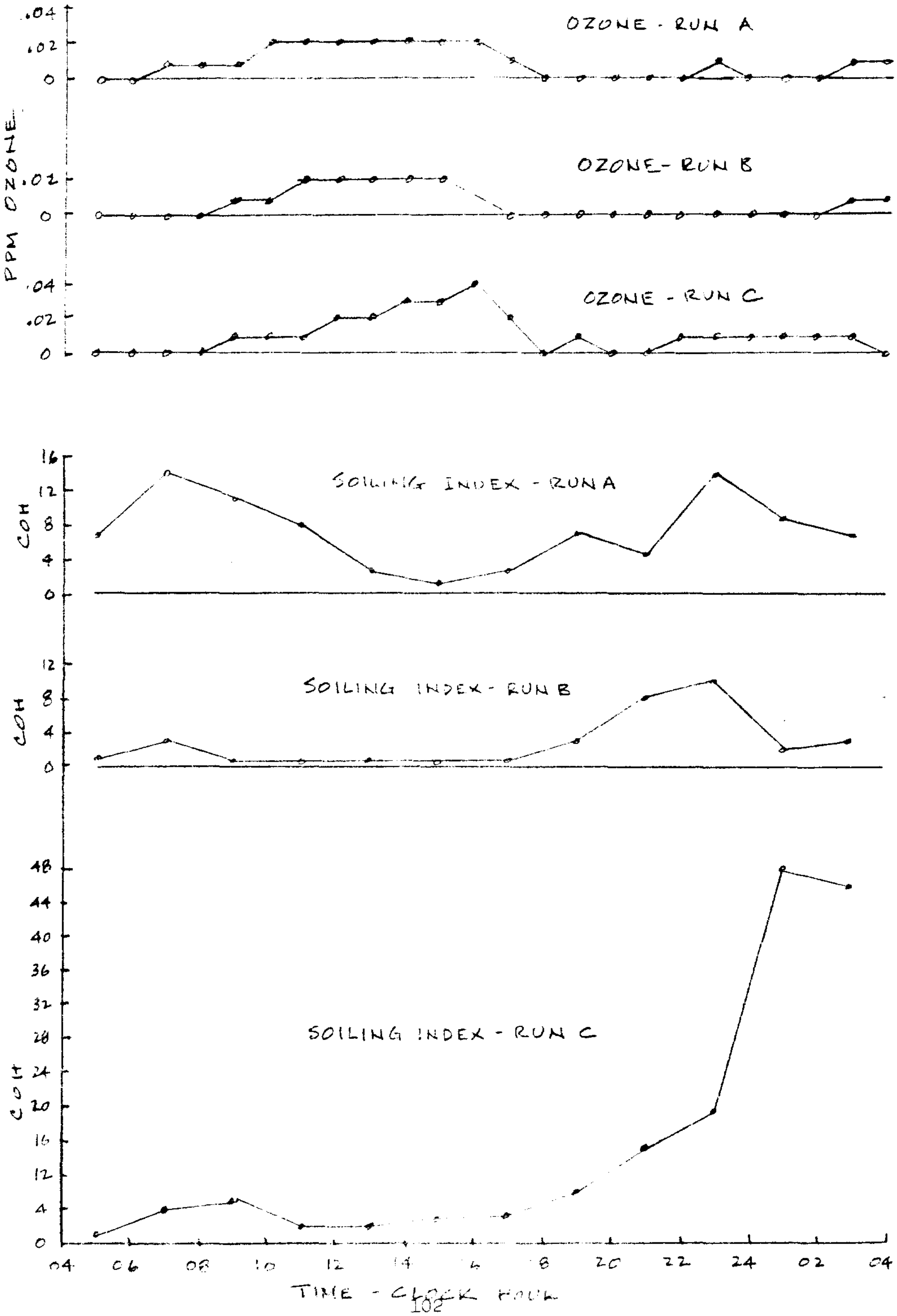
HOURLY AVERAGE
NITRIC OXIDE LEVELS DURING SAMPLING AT
PITTSBURG (2/5/79 - 2/8/79)



HOURLY AVERAGE SO_2 LEVELS DURING SAMPLING
AT PITTSBURG (2/5/79 - 2/8/79)



OZONE & SOILING INDEX LEVELS DURING SAMPLING AT PITTSBURG (2/5/79-2/8/79)



HOURLY AVERAGE WIND DIRECTION & WIND SPEED AND MAXIMUM TEMPERATURE DURING SAMPLING AT PITTSBURG (2/5/79 - 2/6/79)