

Volume I

EFFECT OF ENVIRONMENTAL VARIABLES AND SAMPLING MEDIA ON  
THE COLLECTION OF ATMOSPHERIC SULFATE AND NITRATE

(Contract No. ARB 5-1032)

Final Report

January 1978

Prepared by

B. R. Appel, Y. Tokiwa, S. M. Wall, E. M. Hoffer  
M. Haik and J. J. Wesolowski

Air and Industrial Hygiene Laboratory  
Laboratory Services Branch  
California Department of Health  
2151 Berkeley Way  
Berkeley, CA 94704

for: California Air Resources Board  
Research Section  
P. O. Box 2815  
Sacramento, CA 95812

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890  
A6  
v.1  
c.2

LIBRARY  
AIR RESOURCES BOARD  
P. O. BOX 2815  
SACRAMENTO, CA 95812

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## ABSTRACT

A study was conducted to evaluate errors in the determination of atmospheric sulfate and nitrate employing filter sampling. Seven filter media were evaluated including Fluoropore, Whatman 41, Gelman GA-1, Gelman A, Gelman Spectrograde, Gelman EPA Grade and MSA 1106BH. The evaluation employed both field sampling and laboratory studies of the interaction of filter media, particulate matter and potential oxidation catalysts with pollutant gases ( $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{O}_3$ ).

Field studies demonstrated that fluoropore filter samples exhibited the lowest levels of artifact sulfate and nitrate, consistent with the behavior of clean Fluoropore filters in laboratory exposure studies. Glass and cellulose fiber high volume filter samples provided significant levels of both artifact sulfate and nitrate in field and laboratory studies. Particulate matter exhibited only a negligible role in influencing artifact sulfate. Manganese and copper oxide on filters was shown to produce sulfate from  $\text{SO}_2$  exposures. Soot, iron and vanadium oxides had no effect. Further work is necessary to establish the relevance of the results with metals to atmospheric conditions. Fluoropore filters are recommended for future atmospheric sulfate and nitrate monitoring.

## Executive Summary

A combined field sampling and laboratory study has elucidated factors contributing to errors in measuring ambient concentrations of sulfate and nitrate by filter sampling. Past studies have demonstrated substantial differences in observed levels of these materials depending on the type of filter used. Errors using glass fiber filters were shown to be larger than with other filter types. The cause of the sulfate error appeared to be the collection of sulfur dioxide ( $\text{SO}_2$ ), an acidic gas, on filter media with appreciable alkalinity leading to positive error in the measured value of particulate sulfate. The error due to  $\text{SO}_2$  collection is referred to as "artifact sulfate". There also is some data which indicate that gas phase nitric acid ( $\text{HNO}_3$ ) and nitrogen dioxide ( $\text{NO}_2$ ) can be collected by filters, giving rise to "artifact nitrate" formation.

The goal of the current program was to evaluate a series of filter media of relevance to the California Air Resources Board with respect to errors in measuring sulfate and nitrate. The filters chosen included Gelman "EPA Grade" glass fiber, the currently used filter medium for high volume samplers, three other glass fiber filters, a cellulose filter, and both a Teflon and a cellulose acetate membrane filter.

The filters studied were evaluated in side-by-side field sampling at two locations in California. Both low and high volume sampling were done, the former with and without particle size segregation. Laboratory studies of artifact sulfate employed varying simulated atmospheric conditions and examined the role sulfite, ammonia, ozone, nitrogen dioxide, atmospheric particulate matter, and five potential catalysts for  $\text{SO}_2$  to sulfate conversion in influencing observed sulfate levels. Artifact nitrate studies evaluated the role of both nitrogen dioxide and nitric acid under varying simulated atmospheric conditions and the influence of nitrite, ammonia, ozone and  $\text{SO}_2$  on observed nitrate.

Field sampling revealed up to a factor of three in the mean 24-hour average observed sulfate among filters, with Teflon filters (Fluoropore) and glass fiber filters (MSA 1106BH) showing the largest difference.\* With one exception the results indicate increasing sulfate with increasing filter pH.

Nitrate results from field sampling revealed up to a factor of 2.4 in mean 24-hour nitrate results, with Fluoropore and MSA 1106BH again showing the largest differences.

Laboratory studies of the interaction of  $\text{SO}_2$  with clean filters demonstrated up to 5.3 and 3.5  $\mu\text{g}/\text{m}^3$  artifact sulfate for 24-hour  $\text{SO}_2$  exposures (0.1 ppm) on MSA 1106BH and EPA Grade filters. These are considered upper limit values for artifact sulfate levels to be encountered in ambient air sampling. Fluoropore filters caused negligible amounts of artifact sulfate formation. Artifact sulfate increased with increasing humidity. Ammonia near ambient levels had no effect, but ozone at 0.5 ppm led to substantial increases with

\*The "EPA Grade" filters were not available in time for field sampling. Results of laboratory evaluations suggest that field sampling results with this filter should be similar to those for MSA 1106BH.

both EPA Grade and MSA 1106BH filters. Atmospheric particulate matter caused a slight decrease in artifact sulfate over that found with clean filters. Of the potential metal catalysts, only manganese oxide caused a substantial increase in the observed level of artifact sulfate. The significance of this finding to atmospheric conditions cannot be assessed without further study. A qualitative summary of the effects of the variables studied in artifact sulfate formation is given in Table 1.

Laboratory studies of artifact nitrate indicated that filter collection of nitric acid is substantially greater than with nitrogen dioxide. Gelman Spectrograde (a silicone-coated glass fiber filter) caused the highest level of artifact nitrate, removing 53% of the  $\text{HNO}_3$  in the air stream at 50% relative humidity. Fluoropore filters caused the minimum levels of artifact nitrate.

Based upon the present study. Fluoropore filters are the optimal choice for sampling sulfate and nitrate with almost negligible artifact formation. However the filters can only be used for low volume sampling. Among the hi-volume filter media evaluated, Gelman A (at least from the batch studied) is probably the best choice. However, artifact sulfate and nitrate levels remain substantial on this filter type. Furthermore, the likelihood of batch-to-batch variations with this filter makes evaluation of the extent of artifact nitrate and sulfate with each batch a necessary quality assurance procedure.

Although unavailable for field studies in the current program, laboratory work with Gelman EPA Grade suggests this filter type would provide significant levels of both artifact sulfate and nitrate. Since this filter type has been used by the National Air Surveillance Network, the resulting sulfate and nitrate data should be viewed with caution.

We recommend that, commencing as soon as practicable, a network of low volume samplers, employing Fluoropore be installed to run in parallel for a period of time (perhaps one year) with the current hi-vol network, at selected locations. The stations chosen might be the same as those to be used in the pilot ARB size segregated particle monitoring program. Sulfate, nitrate and TSP determinations should be carried out on both filter types to establish a long term comparison. Subsequently, sulfate and nitrate monitoring should employ only Fluoropore filters.

Because of the decreased sample size obtained with the low volume samplers we recommend sulfate analyses be carried out by the AIHL microchemical method in place of AIHL Method 61 and nitrate, by the copper-cadmium reduction-diazotization procedure automated for the Technicon autoanalyzer. Complete elimination of hi-vol sampling, as currently done, should be considered a goal to be implemented at the earliest practicable date. Until then the hi-vol sample could continue to be used for characterization of organics, determination of Pb and other metals of possible interest.

Table 1

Summary of the Effect of Variables on Artifact Sulfate Formation  
from SO<sub>2</sub>-Filter Interaction (0.1-0.5 ppm SO<sub>2</sub>)

<u>Variable</u>	<u>Effect</u>
Filter pH	Large increase at high pH
Relative humidity at constant temperature	Large increase at high RH with high pH filters
Relative humidity at constant absolute humidity	Large increase at high RH with high pH filters
O <sub>3</sub>	Generally large increase especially at lower RH
MnO <sub>2</sub> (and/or Mn <sub>2</sub> O <sub>3</sub> )	Large increase
CuO	Small increase
Temperature	Small, for range 7-35°C
SO <sub>2</sub> exposure time	Negligible 6-24 hours except Spectrograde and Whatman 41
Flow rate	Slight in 6-24 hour exposures for range 0.6-1.3 cfm <sup>a</sup>
NH <sub>3</sub>	Slight at 40 and 90 ppb NH <sub>3</sub>
Carbon (soot)	None
Atmospheric particulate matter <sup>b</sup>	Slight decrease
Fe(OH) <sub>3</sub> (and Fe <sub>2</sub> O <sub>3</sub> )	Slight decrease
V <sub>2</sub> O <sub>5</sub>	Slight decrease
NO <sub>2</sub>	Results equivocal but some indication of decrease

a. Face velocity 20-47 cm/sec using 47 mm filters with exposed diameter 41 mm.

b. Total and respirable particulate samples collected on Gelman GA-1 filters for 6 and 24 hours.

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## Acknowledgments

The authors wish to gratefully acknowledge Drs. Walter John, Georg Reischl, Susanne Hering and Mr. Glen Sasaki for determination of filtration efficiencies and preparation of filters loaded with monodisperse metal particulates for the catalyst studies described herein. Dr. John also designed and calibrated the cyclone used for sampling respirable particulates. Dr. Evaldo Kothny carried out a number of the analyses reported here and, in addition, provided valuable comments.

Messrs. Dario Levaggi, Wayman Siu and Clayton Ong of the Bay Area Air Pollution Control District generously provided use of their San Jose station facilities and air monitoring data for field sampling. Similarly, Captain William K. Carr, Commanding Officer, Naval Air Station, Los Alamitos, provided use of his facilities in Los Alamitos. Their cooperation is gratefully acknowledged. Mr. William Bope, Southern California Air Quality Management District (Southern Section) provided air monitoring data.

Finally, we wish to acknowledge Drs. Jack Suder and John Holmes of the California Air Resources Board for their continued interest and support.

## I. Introduction

The collection of atmospheric sulfates and nitrates on filter media is hampered by several potential sources of error. These may be stated in generalized terms for particulate constituent A as follows:

$$(A)_{\text{obs}} = (A)_{\text{correct}} - (A \text{ lost by penetration through the filter})$$

- (A lost by incomplete extraction)
- (A lost by reaction with filter)
- + (A formed on filter from gaseous materials)
- + (A formed by interaction with particulate constituents)

Available data indicate that results for atmospheric particulate sulfate collected on glass fiber high-volume filters will, in general, be too high by 1-4  $\mu\text{g}/\text{m}^3$ .<sup>1,2</sup> The principal cause of this error appears to be the collection of significant quantities of sulfur dioxide on such filters because they are distinctly alkaline. The collected sulfur dioxide, when hydrated, exists as some combination of sulfite ( $\text{SO}_3^-$ ) and sulfate ( $\text{SO}_4^-$ ). However, under usual extraction and analytical conditions sulfite, if present, is oxidized to sulfate and represents a 100% positive interference in sulfate measurement.<sup>3\*</sup> The observed sulfate attributable to collection of  $\text{SO}_2$  is usually referred to as "artifact sulfate". It has also been shown that ions extractable from such filters can lead to positive errors in sulfate determinations by commonly used procedures.<sup>4</sup>

The role of particulate matter constituents in artifact sulfate formation remains unclear. While laboratory studies demonstrate that under some conditions ions from the metals iron, vanadium and copper can enhance oxidation of sulfite in aqueous solutions<sup>5,6,7</sup>, these metals failed to similarly enhance such oxidation when supported on filters.<sup>1</sup> Recent attempts to demonstrate the catalytic role of atmospheric particulate matter in  $\text{SO}_2$  conversion have similarly failed to find evidence of significant activity.<sup>2</sup>

Sampling errors in the collection of atmospheric nitrates have been noted only recently. Appel, et al., observed that nitrate serially collected on Gelman GA-1 cellulose acetate filters exhibited, on average, nearly twice the values obtained with a single 24-hour high-volume sample collected simultaneously on Whatman 41 (cellulose) filters.<sup>8</sup> In side-by-side sampling by the Southern California Air Quality Management District (Metropolitan Zone), Gelman "Spectrograde" glass fiber filters were observed to collect, on average, about three times the nitrate observed

\*Throughout this report, unless analyses for sulfite are given, the term "sulfate" will be understood to include the sum of sulfate and sulfite removed by aqueous extraction from filter media.

on Gelman type A glass fiber filters.<sup>9</sup> Spicer reported that Gelman AA glass fiber filters, (batch 8188, used by the EPA's NASN network until recently) collected nearly 20 times the level of nitrate observed on a quartz fiber filter.<sup>10</sup> In limited laboratory studies<sup>11</sup> carried out at Battelle, glass fiber filters were shown to collect both nitrogen dioxide (NO<sub>2</sub>) and vapor phase nitric acid (HNO<sub>3</sub>) with substantially higher collection of the acid. Spectrograde filter, which exhibited a nearly neutral pH, collected substantially more HNO<sub>3</sub> than did typical high pH glass fiber filters. Thus, positive errors in collection of atmospheric particulate nitrate appears to be related to the collection of gaseous HNO<sub>3</sub> and NO<sub>2</sub>.

The present study of artifact sulfate and nitrate formation was undertaken to evaluate a series of filter media considered relevant to the California Air Resources Board programs. In addition, the role of catalysts present in atmospheric samples on the collection of SO<sub>2</sub> was explored.

The filter media studied include:

1. Gelman type A (glass fiber)
2. Gelman "Spectrograde" (glass fiber)
3. Gelman "EPA Grade" (glass fiber)
4. MSA 1106BH (glass fiber)
5. Whatman 41 (cellulose)
6. Gelman GA-1, 5 μm pore size (cellulose acetate)
7. Fluoropore FALP, 1 μm pore size (Teflon)

The "EPA Grade" glass fiber filter is being distributed nationwide by the EPA and has been used by all sampling networks in California since July 1, 1977. "EPA Grade" filters were not evaluated for artifact sulfate and nitrate formation prior to their distribution and use. They replace MSA 1106BH at ARB monitoring sites. Gelman "Spectrograde" and Whatman 41 are among the various media which were used by local monitoring districts in California prior to the above date. Among the glass fiber filters, Gelman "Spectrograde" is unique in having a silicone resin surface coating, which is intended to minimize artifact sulfate formation by masking the alkaline glass surface. Gelman GA-1 and Fluoropore FALP are for use in low-volume samplers. These filters have been used in various research programs and, to a limited extent, in monitoring. Based on prior work, both filters offered promise of providing efficient collection of particulate matter while minimizing artifact sulfate due to interactions with the filter.

This study was designed to measure the error in monitoring atmospheric sulfate and nitrate using the above-mentioned filter media as well as to recommend media for future monitoring programs.

The program includes both laboratory evaluation of filter media exposed to pollutants and side-by-side field sampling. The latter served two purposes: To provide samples for laboratory evaluation of the catalytic effect of actual particulate constituents on artifact sulfate formation, and secondly, to provide a side-by-side comparison of filter media varying such parameters as flow rates, particle size segregation, and sampling periods.

The specific goals are:

1. To determine, in chamber exposure experiments, the formation of artifact sulfate and nitrate resulting from  $\text{SO}_2$ ,  $\text{NO}_2$  or  $\text{HNO}_3$  under varying simulated climatic conditions.
2. To evaluate the influence of ammonia and ozone on the collection of sulfur dioxide and nitrogen dioxide on filter media.
3. To determine the effectiveness of carbon, iron, manganese, vanadium and copper in influencing the collection of sulfur dioxide on filter media.
4. To determine the combined influence of filter media and particulate matter constituents on collection of atmospheric sulfate and nitrate.

## II. Technical Summary and Conclusions

A combined field sampling and laboratory study has elucidated sources of errors in determining ambient concentrations of sulfate and nitrate by filter sampling. Seven filter types were evaluated:

	<u>pH</u>
Fluoropore FALP, 1 $\mu$ m pore size (Teflon)	5.8
Gelman GA-1, 5 $\mu$ m pore size (cellulose acetate)	5.5
Whatman 41 (cellulose)	4.6
Gelman A (binder free glass fiber)	7.6
Gelman Spectrograde (silicone treated glass fiber)	6.2
MSA 1106BH (binder free glass fiber)	9.4
Gelman "EPA Grade"* (binder free glass fiber)	9.3

Field sampling was done at San Jose and Los Alamitos for a total of 14, 24-hour periods. In addition to filter media comparisons, the field sampling permitted comparison of hi-volume and lo-vol sampling, the latter with and without particle size segregation using a cyclone separator. Short term and 24-hour samples were also compared. Filter samples were also analyzed for total suspended particulate, total carbon, total organic carbon, elemental carbon and metals by  $\alpha$ -particle induced x-ray fluorescence analysis ( $\alpha$ -XRFA), all of which were necessary for the total evaluation of the filters.

The laboratory phase included an evaluation of artifact sulfate and sulfite formation resulting from interaction between  $\text{SO}_2$  and clean filter media as a function of filter type, time, flow rate, temperature, relative humidity and concentrations of  $\text{SO}_2$ , ammonia, ozone and  $\text{NO}_2$ . Sulfate formation due to interactions between  $\text{SO}_2$  and potential oxidation catalysts as well as atmospheric particulate matter was also evaluated. Similarly, artifact nitrate formation with nitric acid and  $\text{NO}_2$  was evaluated as a function of filter type, time, flow rate,  $\text{NO}_x$  concentration, temperature, relative humidity, ozone and  $\text{SO}_2$  concentrations using clean filter only.

Results from the field sampling revealed a range of a factor of three in the observed sulfate levels on different filters, with Fluoropore (lo-vol) and MSA 1106BH (lo-vol) results representing the low and high extremes, respectively. Among the 24-hour high volume filter samples, Spectrograde and MSA 1106BH yielded the highest mean level of artifact sulfate ( $3.1 \mu\text{g}/\text{m}^3$ )\*\* and Whatman 41, the lowest. Excepting Spectrograde, the results generally indicate increasing observed sulfate with increasing filter pH. Comparing sulfate collected on low volume total and respirable particulate samplers, Fluoropore filters yielded a generally lower fraction of respirable sulfate compared to the other filters.

\*Manufacturer's designation. This filter became available too late for field evaluation.

\*\*By comparison to Fluoropore results.

Despite significant differences between sulfate levels, the diurnal patterns obtained on different filters, in side-by-side sampling, were generally similar. Diurnal patterns for sulfate at Los Alamitos were usually similar to those for SO<sub>2</sub>, both peaking in the afternoon. At San Jose, SO<sub>2</sub> levels were below detectable limits preventing such comparisons.

Nitrate results from field sampling revealed a range of a factor of 2.4 in mean 24-hour nitrate results, with Fluoropore (lo-vol) and MSA 1106BH (lo-vol) the low and high extremes, respectively (as with sulfate). Fluoropore also exhibited the smallest mean fraction of respirable nitrate (0.68). As with sulfate, the diurnal patterns for nitrate were similar on the different filters and at San Jose often resembled that for NO<sub>2</sub>.<sup>\*</sup> However, there were indications of enhanced artifact nitrate on MSA 1106BH during an NO<sub>2</sub> maximum with somewhat elevated ozone levels. Among the 24-hour hi-volume samples, MSA 1106BH yielded the highest mean level of artifact nitrate (9 µg/m<sup>3</sup>) calculated by subtracting mean nitrate results obtained on Fluoropore.

The Los Alamitos site was chosen because its proximity to a power plant led to elevated SO<sub>2</sub> levels and presumably enhanced levels of fuel oil combustion-related metals (vanadium, nickel, iron) which might catalyze conversion of SO<sub>2</sub> to sulfate. However, vanadium concentrations at the site were generally below detectable limits by α-XRFA. Nickel levels were sufficiently elevated to permit trials for correlations with the observed sulfate. The low correlation coefficient (0.5) suggests important sources of nickel and/or sulfate in addition to the power plant.

Laboratory studies of artifact sulfate formation revealed trends similar to those in field sampling; the degree of SO<sub>2</sub> collection leading to artifact sulfate increased with filter pH with negligible levels on Fluoropore filters. Spectrograde filters (pH = 6.2) were notable exceptions exhibiting only moderate levels of artifact sulfate. Artifact sulfate increased sharply with increasing relative humidity (e.g. from ca. 160 to 340 µg/filter for EPA Grade with 0.1 ppm SO<sub>2</sub> at 20°C), and showed lesser increases with SO<sub>2</sub> concentration and increasing temperature. Addition of ammonia near ambient levels had no effect, but ozone addition led to substantial increases in artifact sulfate with the high pH filters (e.g. from 165 to 312 µg/filter for EPA Grade filters on adding 0.5 ppm O<sub>3</sub> to 0.1 ppm SO<sub>2</sub> at 20°C). Twenty-four-hour exposure of the high pH filters, MSA 1106BH and EPA Grade, to 0.1 ppm SO<sub>2</sub> at hi-vol flow rates, led to artifact sulfate levels of 5.3 and 3.5 µg/m<sup>3</sup>, respectively. These are considered upper limit values to the artifact sulfate to be encountered in ambient air sampling. The presence of NO<sub>x</sub> was shown to substantially depress artifact sulfate formation from 0.1 ppm SO<sub>2</sub>. This is consistent with the competition of all acidic gases for a limited number of sites. The relatively high level of artifact sulfate on Spectrograde in atmospheric sampling may reflect the effect of such competition. For example, the high pH filters may be substantially neutralized by acidic gases other than SO<sub>2</sub> to a much greater degree than Spectrograde. This rational

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<sup>\*</sup>NO<sub>2</sub> data were not available at the Los Alamitos site.

must relate to pollutants other than  $\text{NO}_x$  since artifact sulfate results on Spectrograde were sharply reduced in the presence of  $\text{NO}_x$ .

Wet chemical analytical methods for sulfate do not distinguish between sulfite ( $\text{SO}_3^-$ ) and sulfate ( $\text{SO}_4^-$ ) since  $\text{SO}_3^-$  is oxidized to sulfate under extraction and/or analysis conditions. In evaluating artifact sulfate formation from  $\text{SO}_2$ -clean filter interaction, the  $\text{SO}_3^-/\text{SO}_4^-$  ratio was determined immediately after the  $\text{SO}_2$  exposures and found to be highest for the high pH filters ( $\text{SO}_3^-/\text{SO}_4^-$  mole ratio 0.9 for MSA 1106BH and 1.7 for EPA Grade). Thus sulfite may play an important role in contributing to artifact sulfate.

The interaction of  $\text{SO}_2$  with five potential catalysts including combustion derived carbon ("soot"),  $\text{CuO}$  (or  $\text{Cu}(\text{OH})_2$ ),  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$  (or  $\text{Mn}_2\text{O}_3$ ) and  $\text{Fe}(\text{OH})_3$  (or  $\text{Fe}_2\text{O}_3$ ) supported on filter media was evaluated with these materials loaded on MSA 1106BH, Fluoropore and, for carbon only, Gelman A filters. With carbon,  $\text{V}_2\text{O}_5$  and the ferric oxide, no increase in artifact sulfate was seen. Indeed, for  $\text{V}_2\text{O}_5$  and ferric oxide artifact sulfate was less than observed for clean filter- $\text{SO}_2$  interactions. With cupric oxide, however, a small increase in artifact sulfate was seen while with the manganese oxide, the increase was large (up to 260  $\mu\text{g}/\text{filter}$ ). The latter increase was consistent with formation of manganese sulfate as the principal sulfate product. Thus the manganese oxide may not be functioning as a catalyst but merely as a reactant with sulfur dioxide. The relevance of the observed enhancements to atmospheric sulfate formation cannot be deduced without further studies.

$\text{SO}_2$  exposure of particulate loaded filters gave no indication that particulate- $\text{SO}_2$  interactions contribute to artifact sulfate formation in ambient air sampling. Indeed, the observed artifact sulfate was reduced relative to that expected due to clean filter- $\text{SO}_2$  interaction. The concentration of manganese in the samples used was generally below detection limits.

In laboratory studies of artifact nitrate formation, passing  $\text{NO}_2$  through clean filter media, revealed up to 2.3  $\mu\text{g}/\text{m}^3$  artifact nitrate in 6-hour exposures. The artifact nitrate formed increased with filter pH. In the presence of 0.5 ppm ozone, artifact nitrate increased by up to 7  $\mu\text{g}/\text{m}^3$  with the high pH filters, compared to levels without ozone. Ammonia had no effect on  $\text{NO}_2$ -related artifact nitrate. In the absence of ozone, artifact nitrate due to  $\text{NO}_2$ -clean filter interactions is insufficient to explain the differences noted above in atmospheric nitrate results among the filters used.

In contrast to  $\text{NO}_2$ , gaseous nitric acid (at 0.2-0.5 ppm) led to large artifact nitrate levels except on Fluoropore filters (e.g. 200  $\mu\text{g}/\text{m}^3$  in 6-hour exposures on EPA Grade). The collection of nitric acid increased sharply with increasing relative humidity. In contrast to results with  $\text{NO}_2$ , Spectrograde filters (pH = 6.2) collected the greatest amount of nitric acid under all conditions. With 0.2 ppm  $\text{HNO}_3$  the efficiency of the filters for collecting  $\text{HNO}_3$  ranged from  $\leq 1\%$  for Fluoropore to 53% for Spectrograde. Spectrograde filters also differed from the other filter types in yielding increased, rather than decreased, artifact nitrate with increasing temperature in the range 7 to 35°C, implying chemical reaction with the silicone coating. The analytical method used

for nitrate does not distinguish between nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) but can be easily modified to do so. It was demonstrated that, with all filters, the  $\text{NO}_2^-/\text{NO}_3^-$  ratios resulting from  $\text{NO}_2$  and  $\text{HNO}_3$ -clean filter interaction was close to zero. Thus, while chemical reaction with the silicone resin is a plausible mechanism to rationalize the high artifact nitrate with Spectrograde filters, such reactions do not appear to involve reduction of nitrate to nitrite.

The extent of artifact nitrate attributable to nitric acid in ambient air sampling cannot be directly assessed without nitric acid concentration data. The present laboratory study, together with reports of up to 25  $\mu\text{g}/\text{m}^3$   $\text{HNO}_3$  in the South Coast Air Basin,<sup>17</sup> do, however, support  $\text{HNO}_3$  as a likely important contributor to the nitrate differences between filters observed in field sampling for this program.

### Conclusions and Recommendations

Based upon the present study, Fluoropore filters, with almost negligible artifactual errors are the best choice for sampling sulfate and nitrate. However, the filters can only be used for low volume sampling. Among the hi-volume filter media evaluated, Gelman A (at least from the batch studied) is the best choice. However, artifact sulfate and nitrate levels remain substantial on this filter type. Furthermore, the likelihood of batch-to-batch variations makes evaluation of the extent of artifact nitrate and sulfate with each batch a necessary quality assurance procedure.

Although unavailable for field studies in the current program, laboratory work with Gelman EPA Grade suggests this filter type would provide significant levels of both artifact sulfate and nitrate. Since this filter type has been used by the National Air Surveillance Network the resulting sulfate and nitrate data should be viewed with caution.

We recommend that, commencing as soon as practicable, a network of low volume samplers employing Fluoropore be installed to run in parallel for a period of time (perhaps one year) with the current hi-vol network, at selected locations. The stations chosen might be the same as those to be used in the pilot ARB size segregation program. Sulfate, nitrate and TSP determinations should be carried out on both filter types to establish a long term comparison. Subsequently, sulfate and nitrate monitoring should employ only Fluoropore filters.

Because of the decreased sample size obtained with the low volume samplers we recommend sulfate analyses be carried out by the AIHL microchemical method in place of AIHL Method 61 and nitrate, by the copper-cadmium reduction-diazotization procedure automated for the Technicon autoanalyzer. Complete elimination of hi-vol sampling, as currently done, should be considered a goal to be implemented at the earliest practicable date. Until then the hi-vol sample could continue to be used for characterization of organics, determination of Pb and other metals of possible interest.

### III. Experimental

#### A. Field Sampling

##### 1. Sampling Sites

Field sampling was conducted at two locations; one in an area of moderate particulate matter concentrations but minimal SO<sub>2</sub> concentrations (San Jose) and the other in an area of high particulate matter (potentially including catalysts for SO<sub>2</sub> oxidation) and SO<sub>2</sub> emissions (Los Alamitos). The sampling sites were the San Jose air monitoring station of the Bay Area Air Pollution Control District (BAAPCD) and the roof of Hangar One at the Los Alamitos Naval Air Station (NAS) near Long Beach.

The BAAPCD site is located in the Santa Clara Valley at the southern end of the San Francisco Bay and has no major local sources of SO<sub>2</sub>. The station is about three blocks north of San Jose's downtown area and is enclosed by three freeways, U.S. 101, Highway 17 and Interstate 280, the latter being the closest (0.5 miles to the south).

The NAS site is about three miles northeast of Southern California Edison's Los Alamitos Steam Power Plant, and significant ground level concentrations of SO<sub>2</sub> and fuel oil fly ash are expected. The Southern California Air Pollution Control District's Los Alamitos air monitoring station, about one mile east of the NAS site, provided concurrent gaseous pollutant and meteorological data. The NAS site provided some wind data.

##### 2. Equipment

Samples were collected as a function of particle size, sampling media and collection time with 47 mm filters, and as a function of sampling media and time with 8 x 10" high-volume filters.

The low-volume sampling system consisted of three 47 mm filters, two for total and one for the refined particles (Figures 1 and 2). The refined filter collected particles smaller than 3.5  $\mu$ m in aerodynamic diameter. A cyclone\* (Figure 3) ahead of the refined filter was used to remove larger particles. One of the total filters operated for 24 hours. The other total filter and the refined filters were changed every six hours. The minimum time between filter

\*The cyclone was designed to have a 50% cutoff at 3.5  $\mu$ m at a flow rate of approximately 0.6 cfm.

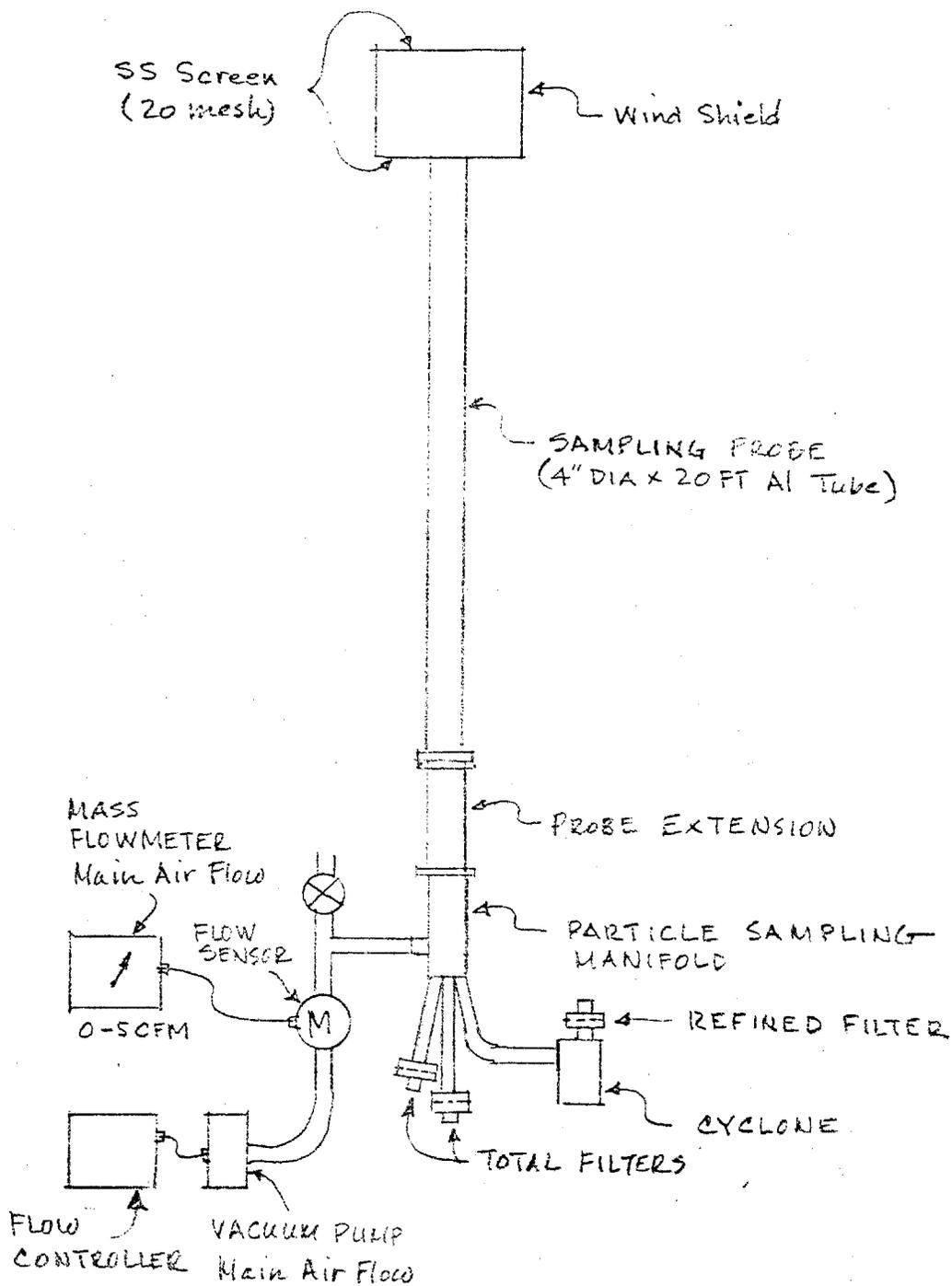
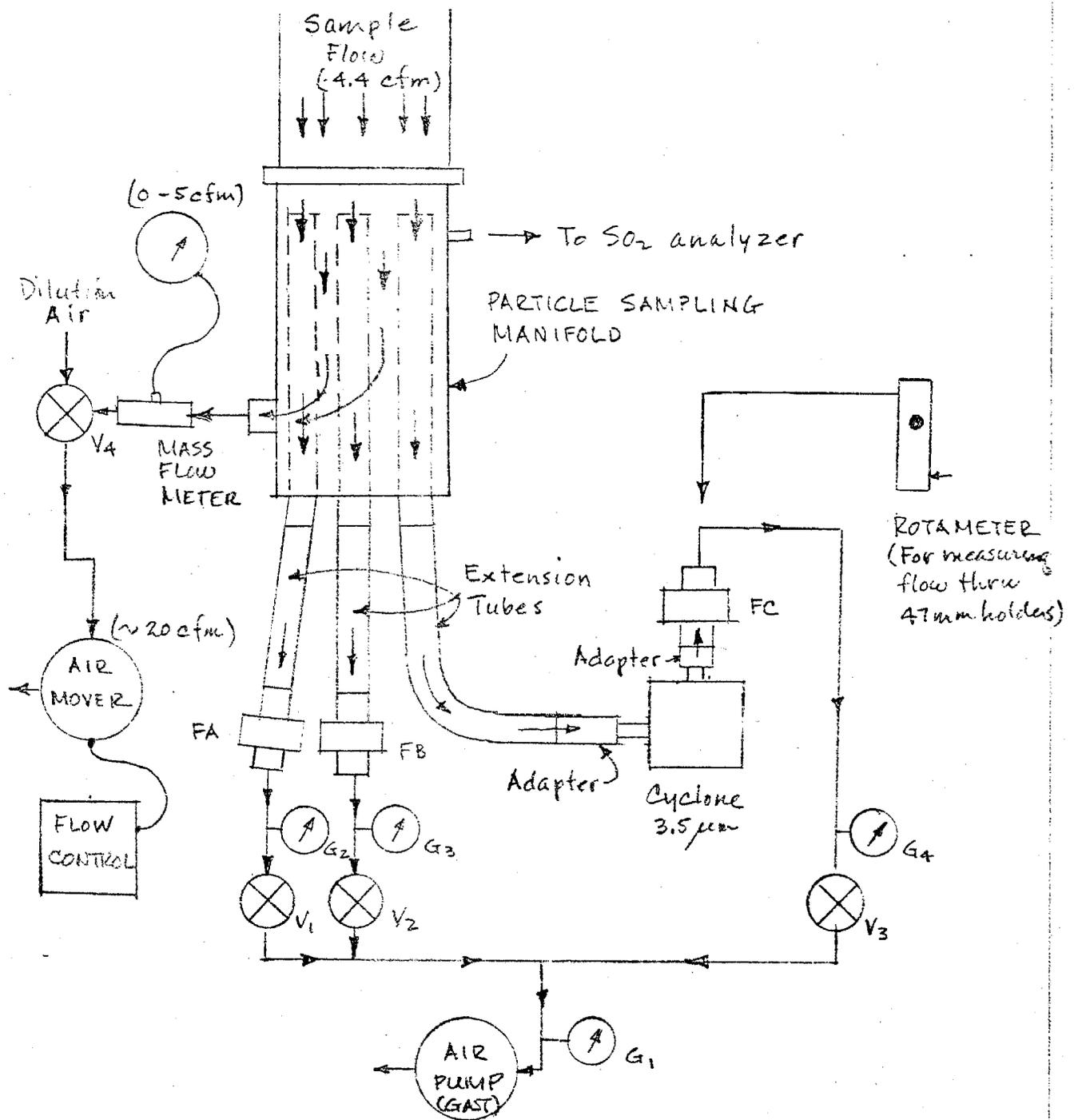


Figure 1

General View-Low Volume Sampling System



**LEGEND**

- FA - 47mm Holder - Total
- FB - 47mm Holder - Total
- FC - 47mm Holder - Refined
- G<sub>1</sub>-G<sub>4</sub> - Gauge, Vacuum, o-ring
- V<sub>1</sub>-V<sub>4</sub> - Valve, metering

Figure 2

Diagram - Detail of Low Volume Sampling System

# CYCLONE

Mat'l: Body - 6061 Al  
 Nozzle - 316 SS  
 Scale:  $1/2" = 1"$

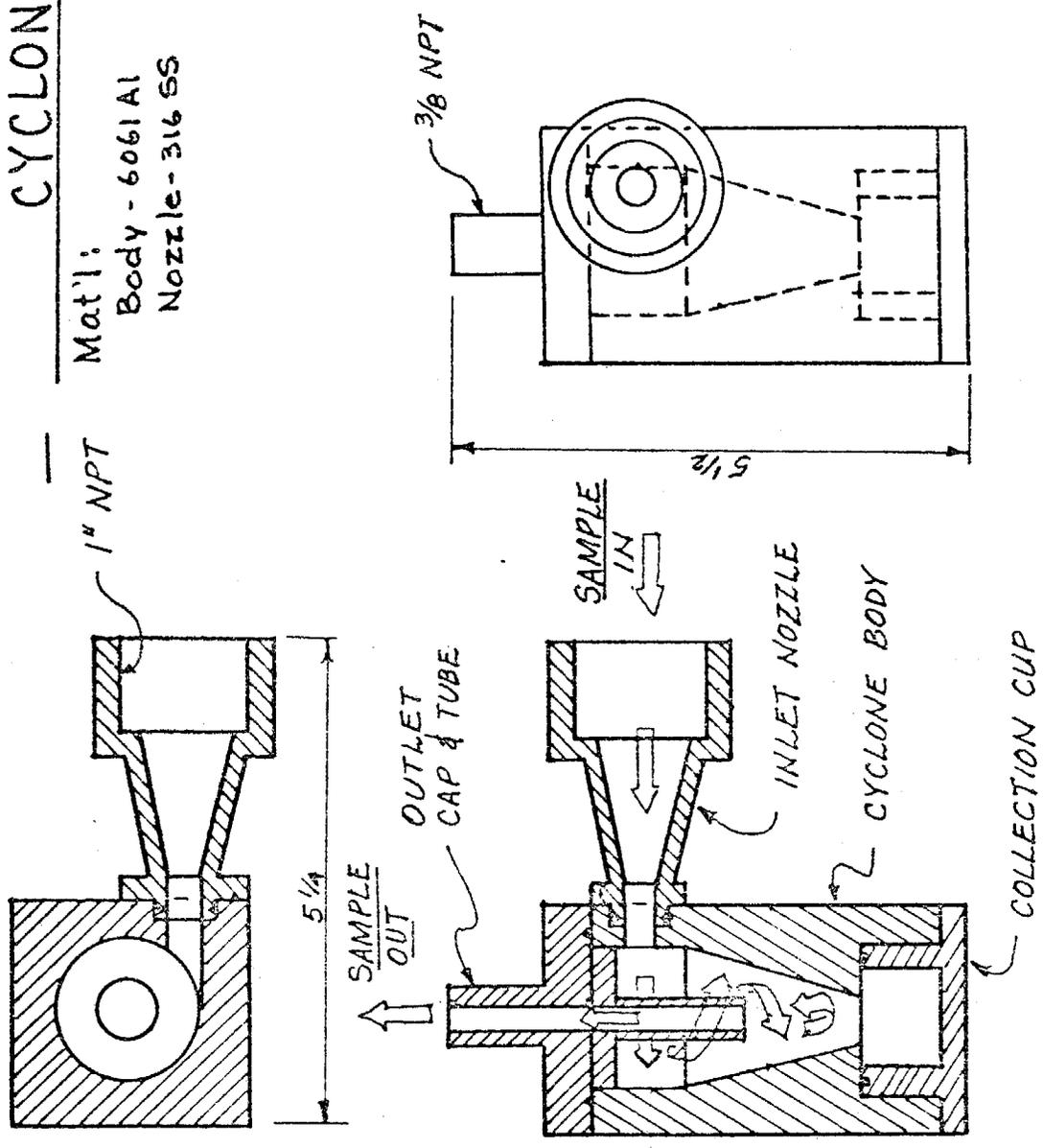


Figure 3  
 Cyclone

changes was dictated by the flow rate needed for the cyclone, which limited the sampling rate to 0.56 cfm, and the need to collect sufficient particulate matter for the analysis of sulfate. Although higher flow rates could have been used with the two total filters, probable complications in data interpretation made this unwise.

The six high-volume samplers were calibrated and tested for equivalence as discussed in Appendix A. The calibration was checked at each site to reveal any changes during transport.

The particle sample probe and manifold was designed to provide isokinetic sampling of particles. With a sampling rate of 0.56 cfm for all low-volume samplers, a total flow rate through the probe of 4.4 cfm was calculated to achieve isokinetic sampling.

At San Jose, the low-volume sampling system was installed at the station permitting filter changes inside the station. At Los Alamitos, a portable stand was used to support the sampling probe and manifold. A portable enclosure was fabricated for sheltering the filter changing operations, the SO<sub>2</sub> analyzer/recorder unit and the line voltage recorder. The shelter had provisions for securing the support gases (H<sub>2</sub>, SO<sub>2</sub>, standard, air) and the main flow monitor to the shelter sides and was equipped with a fluorescent light for operation at night.

A Meloy SA-160 flamephotometric sulfur analyzer was used to continuously monitor ambient SO<sub>2</sub> levels in the particle sampling manifold and thereby verify transport of SO<sub>2</sub> from important sources to the sampling site. This instrument had been checked and calibrated by the AIHL staff.

The low-volume sampling probe was fabricated from aluminum pipe and provided a calculated residence time of about 25 seconds. This may have caused some loss of SO<sub>2</sub>. Since accuracy in SO<sub>2</sub> monitoring was not considered crucial for the present application, the degree of loss was not determined.

### 3. Sampling in San Jose

The sampling scheme used in San Jose is given in Table 2. The high-volume samplers on the roof were arranged in a rectangular array shown in Figure 4. Sampling was done in the period October 4-10, 1975.

In addition to particulate samples, the hourly average air monitoring and meteorological data were obtained as reported by the San Jose BAAPCD station during the sampling period.

Table 2

Field Sampling Scheme for Sulfate-Nitrate Sampling Study at San Jose

Sample <sup>a</sup>	No. Filters/ 24-hr. Exp.	Medium for Experiment					
		A	B	C	D	E	F
Respirable fraction, low vol.	4	Fluoropore	GA-1	MSA	Gelman A	Gelman Spec.	GA-1
Total filter, low vol.	4	Fluoropore	GA-1	MSA	Gelman A	Gelman Spec.	GA-1
Total filter, low vol.	1	Fluoropore	GA-1	MSA	Gelman	Gelman Spec.	GA-1
HI volume	1	Gelman A	Gelman A	Gelman A	Gelman A	Gelman A	Gelman A
HI volume	4	Gelman A	Gelman Spec.	W41	MSA	Gelman A	Gelman A
HI volume	1	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman Spec.
HI volume	1	Gelman A	Gelman Spec.	W41	MSA	Gelman Spec.	Gelman A
HI volume	1	Whatman 41	MSA	W41	MSA	W41	Whatman 41

filters/exp. = 17

filters for San Jose = 102

a. The low-vol filters are 47 mm operated at ca. 0.6 cfm and the hi-vols, 8 x 10" operated at ca. 40 cfm.

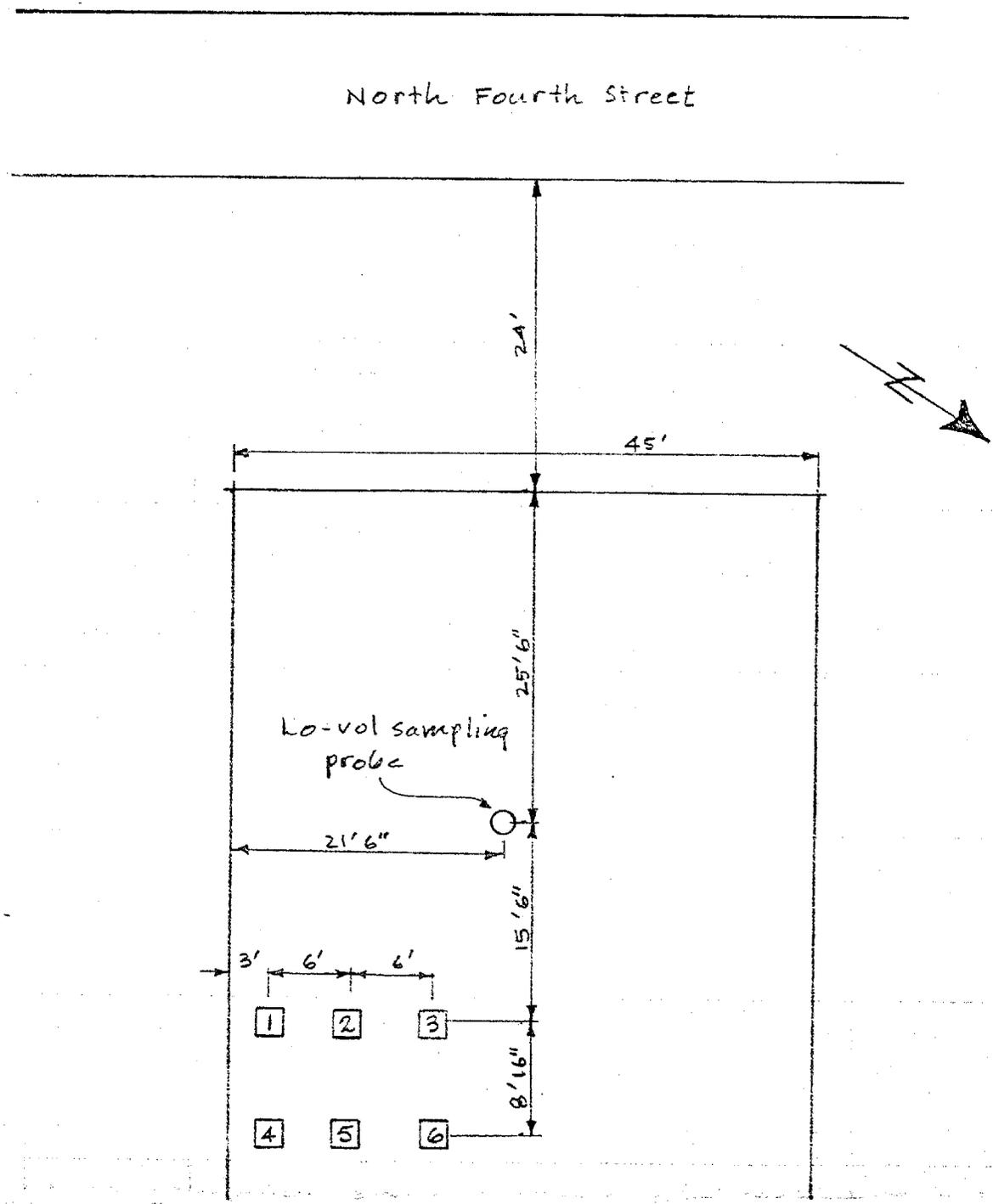


Figure 4

Plan showing location of high volume samplers and low volume sampling probe on roof at San Jose monitoring station.

#### 4. Sampling in Los Alamitos

The sampling equipment was arranged on the roof as shown in Figure 5. Sampling was done in the period October 28-November 5, 1975, according to the scheme in Table 3. Also obtained were the available pollutant gas and aerosol data as well as meteorological data collected during the period by the Southern California Air Pollution Control District at the Southern Zone's air monitoring station, one-half mile east of the hangar.

#### B. Pollutant Gas Generation and Laboratory Exposure System

Figure 6 shows the system fabricated for generating and exposing the clean and loaded filters to  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$  and  $\text{O}_3$  under a variety of temperature and humidity conditions. It consists of three subsections providing clean air, the test gas generation (both pollutant and humidity) and the filter exposure manifold. Except for the air mover, the entire system was housed in a temperature controlled environment. Temperature was controllable to  $\pm 1^\circ\text{C}$  in the range 5-35°C.

Concentrations of all gases as well as relative humidity and temperature were monitored continuously. In general, temperature and concentrations remained within  $\pm 10\%$ , and relative humidity, within  $\pm 3\%$  relative humidity of the intended values. However, for  $\text{SO}_2$  at 0.10 ppm, and  $\text{HNO}_3$  at 0.2 ppm, the concentration fluctuated within a range of  $\pm 20\%$ . When citing results, it will be noted when these variables differed by more than the corresponding variations from the intended levels.

##### 1. Clean Air Production

The clean air section employed ambient air partially dried ( $\text{RH} < 30\%$ ) by the environmental chamber dehumidifier. Ozone (produced by passing oxygen over a pencil type mercury lamp) was added to oxidize any  $\text{NO}$  to  $\text{NO}_2$  and the  $\text{O}_3$  level was monitored continuously. The air was then passed through a series of beds containing triethanolamine for removing  $\text{NO}_2$ , soda lime for removing acid gases and mists, activated charcoal for removing ozone and organic vapors and a molecular sieve bed to remove residual water. A HEPA filter removed particles released from the chemical bed. The flow was monitored by measuring the pressure drop across a sharp-edged orifice plate (made from 4" diameter PVC pipe union and a melamine sheet) with a 0 to 8"  $\text{H}_2\text{O}$  inclined manometer (Meriam Instrument Company). The orifice and manometer were calibrated against a vane anemometer (Taylor Instrument Company, Serial No. 9378) operating in a 4" duct.

The housing for the chemical purification stages consists of an airtight box containing four removable trays (A-D) filled with the absorbents indicated in Figure 6. Trays A, B and D are 14 cm

Table 3

Field Sampling Scheme for Sulfate-Nitrate Sampling Study at Los Alamitos

Sample <sup>a</sup>	No. Filters/ 24-hr. Exp.	Medium for Experiment						
		A	B	C	D	E	F and G	H
Respirable fraction, low vol.	4	Fluoropore	GA-1	MSA	Gelman A	Gelman Spec.	Fluoropore	GA-1
Total filter, low vol.	4	Fluoropore	GA-1	MSA	Gelman A	Gelman Spec.	Fluoropore	GA-1
Total filter, low vol.	1	Fluoropore	GA-1	MSA	Gelman	Gelman Spec.	Fluoropore	GA-1
Hi volume	1	Gelman A	Gelman A	Gelman A	Gelman A	Gelman A	MSA <sup>b</sup>	Gelman A
Hi volume	4	Gelman A	Gelman Spec.	W41	MSA	Gelman A	Gelman A <sup>c</sup>	Gelman A
Hi volume	1	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman Spec.	Gelman A <sup>d</sup>	Gelman Spec.
Hi volume	1	Gelman A	Gelman Spec.	W41	MSA	Gelman Spec.	Gelman Spec.	Gelman A
Hi volume	1	Whatman 41	MSA	W41	MSA	W41	MSA	Whatman 41

filters/exp. = 17

filters for Los Alamitos = 136

- a. The low-vol filters are 47 mm operated at ca. 0.6 cfm and the hi-vols, 8 x 10" operated at ca. 40 cfm.
- b. Run on hi-vol previously used for Gelman A only.
- c. Run on hi-vol previously used for 24-hour filters.
- d. Run on hi-vol previously used for 4-6 hour filters.

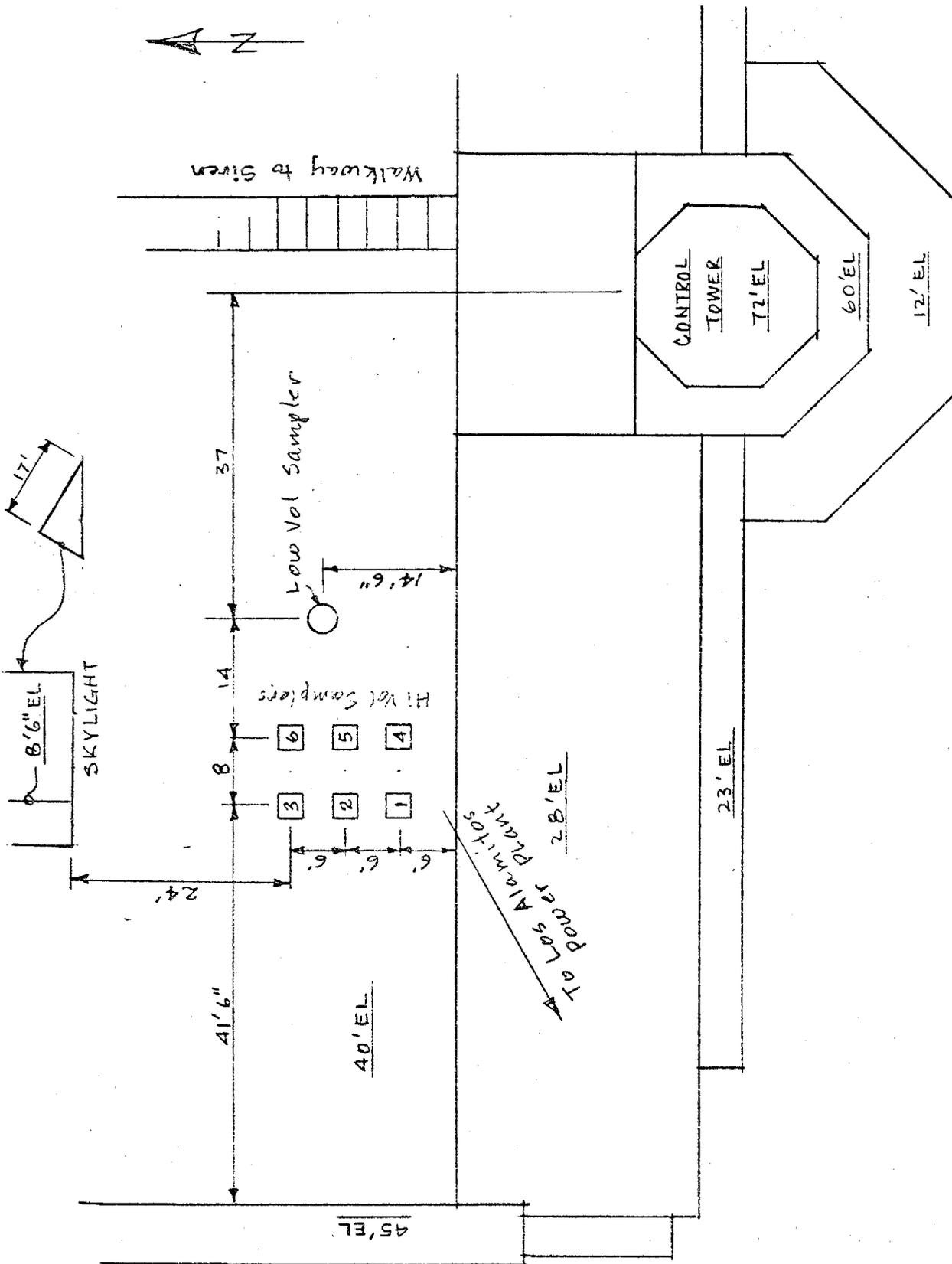


Figure 5

Roof plan of Hangar 1 showing arrangement of hi-vol and lo-vol samplers with respect to location of major roof top structures.

Note: Exposure system housed in chamber.

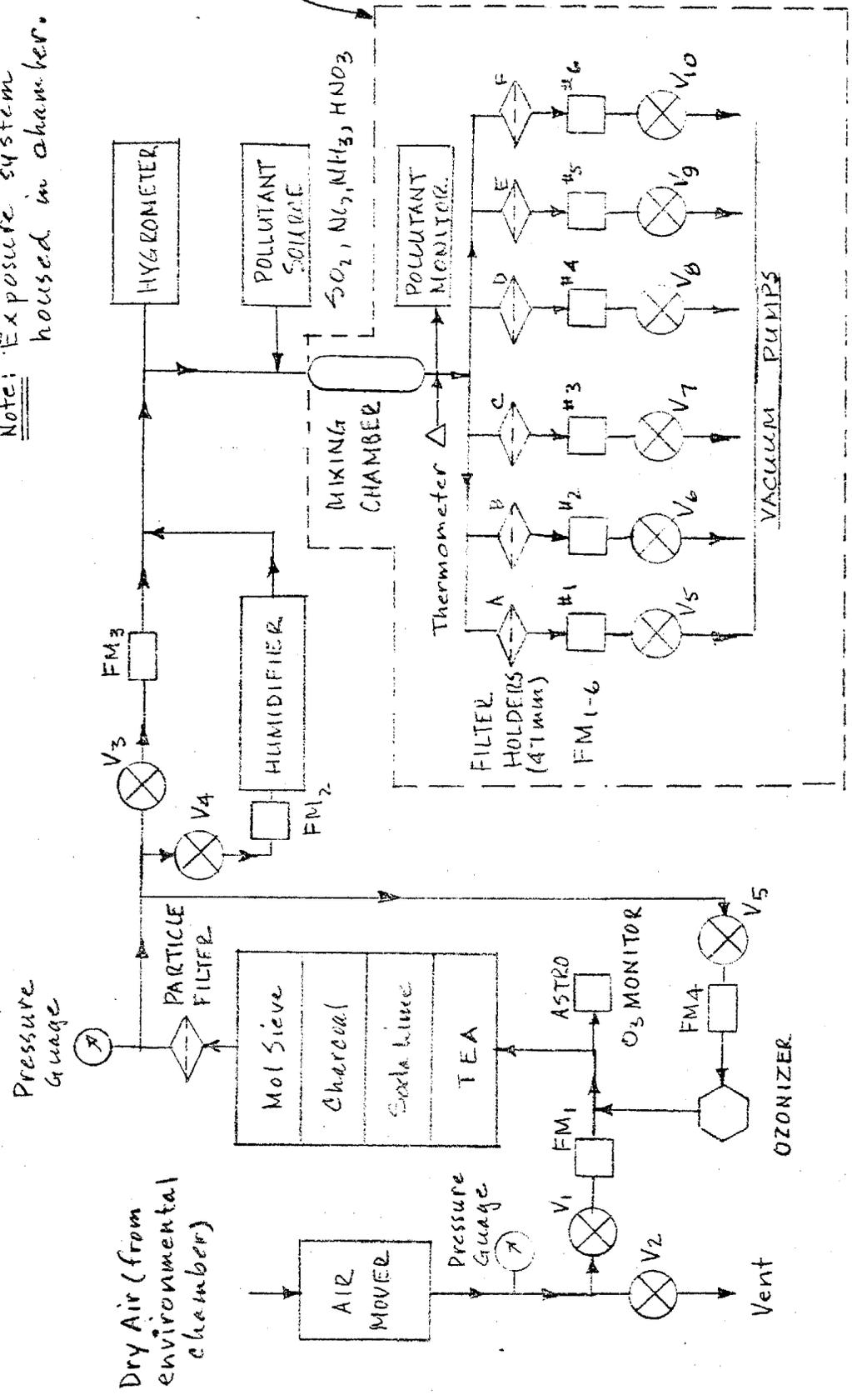


Figure 6

System for Generating Test Gases and Exposing Filters

high square wooden boxes (volume: 38.2 liters) with stainless steel screens (500 micrometer) enclosing the top and bottom surfaces to retain the absorbent. Tray C is a commercial activated charcoal bed containing 20 kg of charcoal. Tray D, which was not used in the current program, provides space for a desiccant fill or other additional absorbent.

The tray dimensions and fill granule sizes were selected to provide ample absorption capacity and yet offer minimal restriction to flow. With Trays A, B and C filled, the resistance under the conditions of maximum flow (16 cfm) was about 3.4 inches H<sub>2</sub>O. Thus, the flow can easily accommodate the requirements of seven 47 mm filters at 1.32 cfm each and six 25 mm filters at 0.1 cfm each, simultaneously. Under these flow conditions and with 0.3 to 0.5 ppm O<sub>3</sub> added to the stream, the O<sub>3</sub> and SO<sub>2</sub> values in the clean air were less than 0.005 ppm while the NO<sub>2</sub> ranged from 0.02 to 0.06 ppm depending on the ambient NO<sub>x</sub> levels.

## 2. Humidity and Gaseous Pollutant Production

Humidified air was produced by passing a portion of the clean, dry air flow over water heated slightly above ambient and recombining the wet stream with dry air. The moisture was monitored continuously with a salt-bridge type hygrometer and recorded on a strip chart recorder.

The humidifier consisted of a horizontal glass cylinder closed on both ends by  $\frac{1}{4}$  inch thick aluminum plates. A float valve maintained a fixed water level and an electric heater element was used to raise the water temperature above ambient. The water temperature was maintained to  $\pm 1^\circ\text{C}$  by a thermal sensor and controller. The heated water was circulated by an external pump to insure temperature uniformity. The system can produce humidities in the exposure system between 15 and 100%  $\pm 3\%$  RH at temperatures between 5 to 35°C.

## 3. Multiple Port Filter Exposure Manifold

The filter media were evaluated by passing, at specified temperature and humidity conditions, the various pollutant test gases simultaneously through 47 and 25 mm diameter sections of the different filter types. Test gas volumes were determined by measuring the pollutant gas flow rate through the filters both at the start and end of each run with calibrated rotameters. The rotameter calibrations were referenced against a wet test meter which, in turn, had been referenced against a spirometer.

The temperature conditions were established by adjusting the exposure manifold environment (chamber) to the temperatures specified for each test. The temperature of the test gas was monitored with a thermometer in the gas line.

To study the role of environmental and sampling media variables in the collection of sulfate and nitrate requires that each media type be exposed to the same conditions. The pyrex and stainless steel exposure manifold, shown in Figure 7, was designed to assure equal treatment of all filters. It is similar in design to the isokinetic low-volume particle sampling manifold used for field sampling and can accommodate up to seven 47 mm and six 25 mm filters, simultaneously. The design also provides for isokinetic sampling capability for both size filters. For continuous monitoring of pollutant gas absorption, a sampling port was installed in one sampling tube downstream of the filter holder. This permitted monitoring of the pollutant gas concentrations before and after the filter.

#### 4. SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> Production and Monitoring

The SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> pollutant gas concentrations for the filter exposures were produced by metering (through flow meters) a 10,000 ppm (1% v/v) in nitrogen stock pollutant into the clean dilution air of the exposure system. The 1% stock gas was prepared by introducing appropriate volumes of the respective pure pollutant gases into evacuated high pressure steel cylinders and pressurizing (usually to 1000 psig) each cylinder with nitrogen.

The gas concentrations produced were monitored with continuous analyzers connected to strip chart recorders. The monitors are identified in Table 4. Calibration, measurement principles and operational aspects are described in Appendix B.

#### 5. Nitric Acid Production

Anhydrous gaseous nitric acid in nitrogen was prepared from the anhydrous liquid acid. Preparation of both the liquid and dilute gaseous acid are described in Appendix C.

#### 6. Nitric Acid Monitoring and Analysis

The nitric acid level in the filter exposure system was monitored with a Mast Microcoulomb Meter (Model 724-21) modified as described by Miller and Spicer<sup>17</sup> to sense acid gases instead of oxidants. The required modifications, as shown in Figure 8, include: 1) use of an iodate-iodide sensing reagent, 2) replacement of Tygon tubing with Teflon tubing, 3) protection of the reagent from the atmosphere by means of an activated carbon column to scrub the reagent reservoir replacement air and 4) provisions for alternately passing the sample air either through a nylon (Duralon) filter which removes nitric acid quantitatively or directly to the detector where total acid is measured. A two-cycle timer connected to a three-way solenoid valve allows switching the sample streams. The nitric acid concentration was

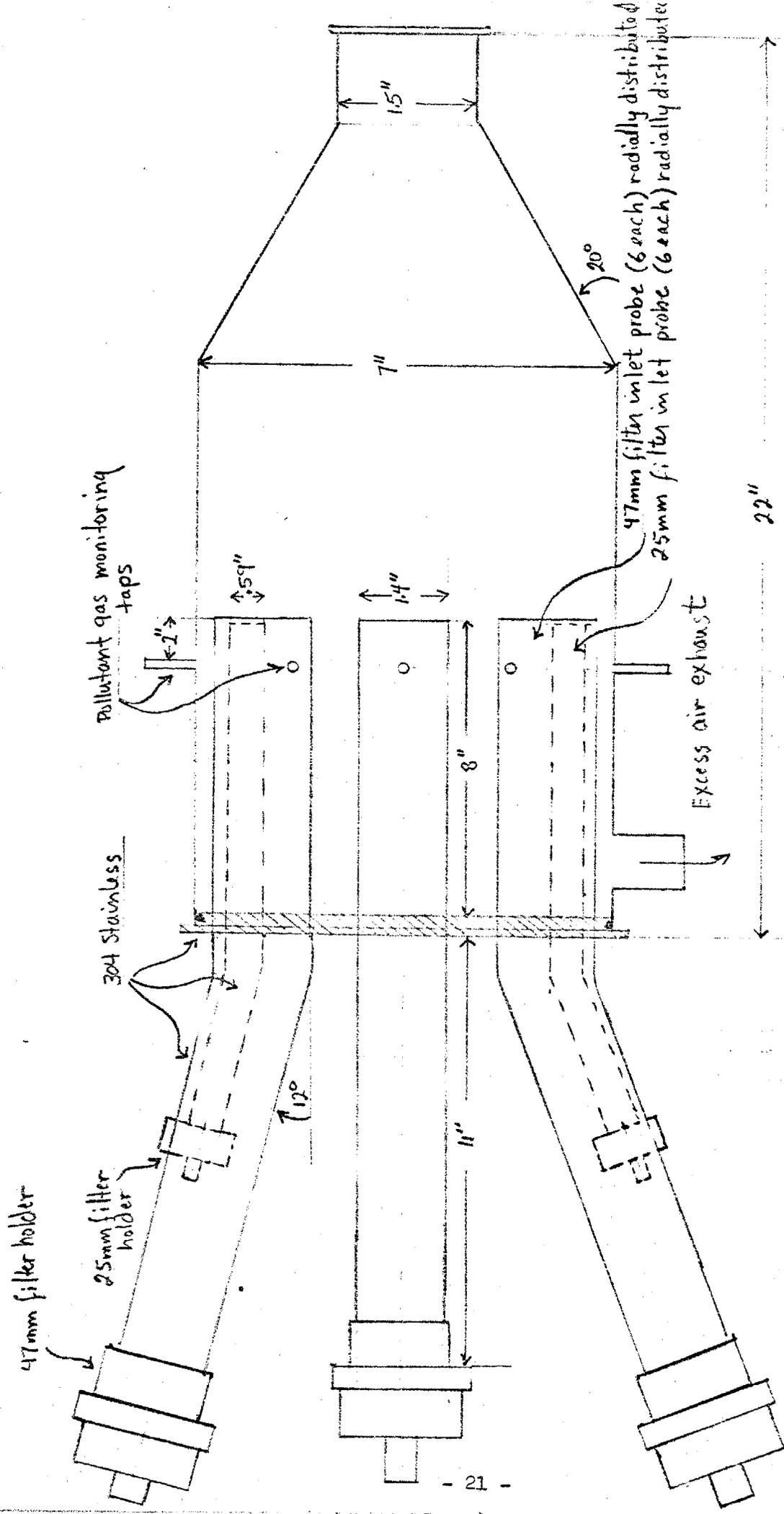


Figure 7

Exposure Manifold

Table 4

POLLUTANT ANALYZERS USED IN LABORATORY  
EXPOSURE STUDIES

<u>Pollutant</u>	<u>Analyzer - Model/Manufacturer</u>	<u>Measurement Principle</u>
NO <sub>2</sub>	TECO Model 14 B NO-NO <sub>2</sub> -NO <sub>x</sub> Analyzer Thermo-Electron Corporation Waltham, MA	Chemiluminescent
NH <sub>3</sub>	Lear Siegler SM 100 Air Monitoring System Lear Siegler, Inc. Environmental Technology Division Englewood, CO	Second Derivative UV
SO <sub>2</sub>	Meloy SA 160-2 Sulfur Analyzer Meloy Laboratories, Inc. Springfield, VA	Flame Photometric
O <sub>3</sub>	Bendix Model 8002 Ozone Analyzer The Bendix Corporation Process Instruments Division Lewisburg, WV	Chemiluminescent
HNO <sub>3</sub>	Mast Microcoulomb Meter Model 724-24 (Modified for Sensing Acids) Mast Development Co. Davenport, IA	Amperometric

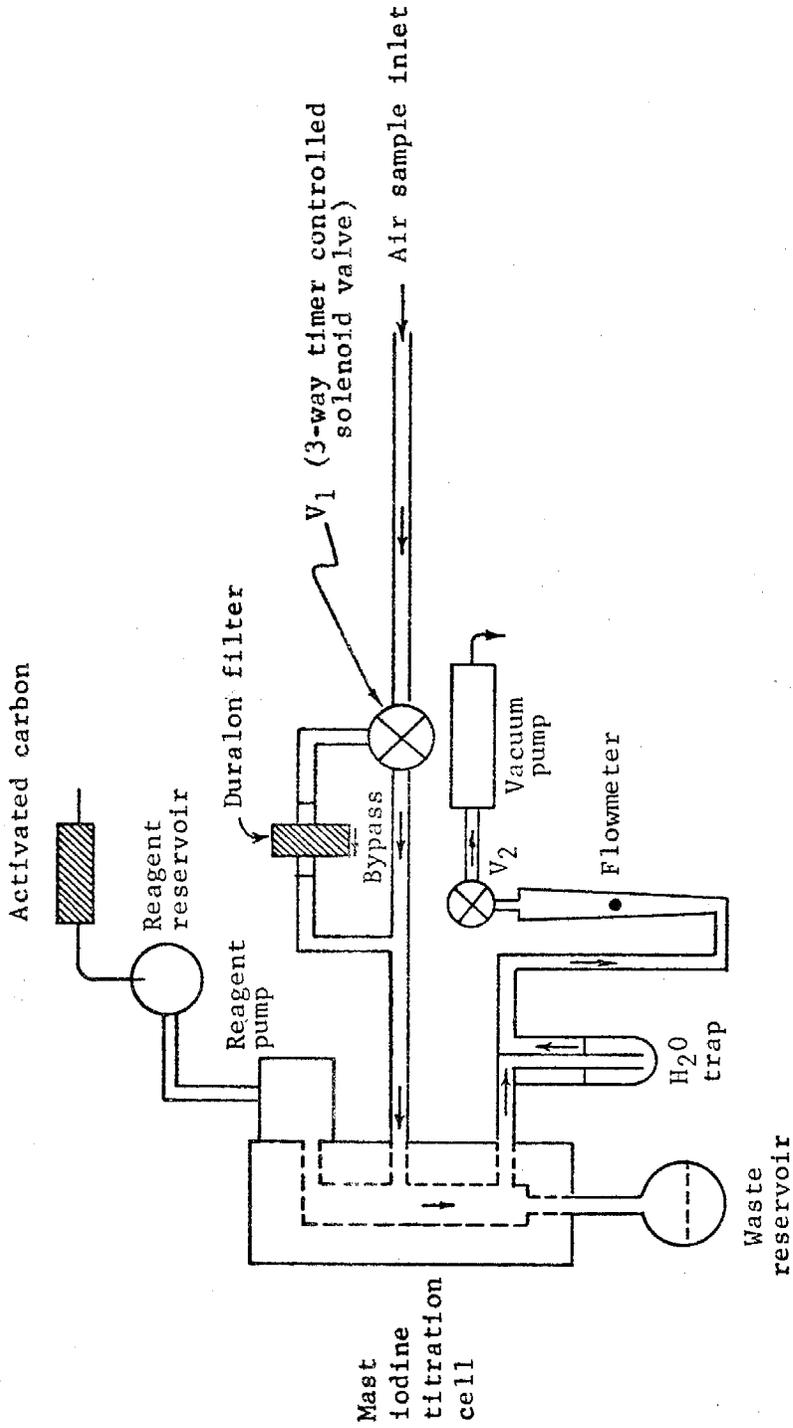


Figure 8. NITRIC ACID ANALYZER

determined by difference. As nitric acid was the only acidic gas expected to be present in the exposure system, the instrument was operated in the total acid mode with periodic switching to the Duralon channel to determine the instrument baseline. The instrument appeared to be unresponsive to trace quantities of  $\text{NO}_2$  ( $< 0.1$  ppm) present during filter exposures.

Nitric acid concentrations were also monitored by a Teco (Model 14B) chemiluminescence  $\text{NO-NO}_2\text{-NO}_x$  analyzer operated in  $\text{NO}_x$  mode (see Appendix B for description). The instrument was determined to be quantitative for low levels of nitric acid ( $< 1$  ppm) and was calibrated simultaneously with the modified Mast meter in the range 0.1 to 1.0 ppm  $\text{HNO}_3$  (see Appendix D). As the Teco responded to both  $\text{NO}_x$  and  $\text{HNO}_3$  in this mode, the analyzer inlet air stream was periodically drawn through a Duralon filter. This permitted establishing the exposure system  $\text{NO}_x$  level to allow determination of  $\text{HNO}_3$  by difference.

Nitric acid monitors were calibrated against a reference method shortly before use. As a reference procedure, 500-1200 ppm nitric acid in nitrogen were sampled with 0.1N NaOH in a Smith-Greenburg impinger and the resulting nitrate determined with a nitrate specific electrode (Orion Model #93-07-01). The calibration gas was then fed into a dynamic dilution system where varying quantities of dry nitrogen were added to achieve accurately known concentrations in the range 0.1 to 1.0 ppm. A more detailed description of the instrument calibration is included in Appendix D.

Accuracy and precision of the nitrate specific electrode technique were assessed by means of standard solutions run as unknowns by the analyst. These solutions were prepared in 0.1N NaOH as used in sampling  $\text{HNO}_3$ . As long as the sodium and phosphate electrolyte concentrations of the sample and the outer chamber filling solution of the electrode were identical nitrate recovery by this method was found to be  $97.5 \pm 1.0\%$ . The protocol adopted (as presented in Appendix E) was designed to achieve this accuracy with standards.

### C. Wet Chemical Analytical Methods

#### 1. Filter pH

The protocol is that specified by the EPA which states: <sup>24</sup>

"Prepare a 0.05 M KCl solution using  $\text{CO}_2$ -free water. The pH of this solution should be  $7.0 \pm .3$ . Cut a nine square inch ( $58 \text{ cm}^2$ ) section of a glass fiber filter with a pizza cutter. Place the filter in a 125 ml Erlenmeyer flask. Add 15 ml of

0.05 M KCl and stopper the flask. Stir with a magnetic stirrer for 10 minutes at 60 RPM Determine the pH of the extract." With 47 mm filters, this protocol was modified slightly by extracting four filters simultaneously with total area of 10.8 in<sup>2</sup>.

## 2. Water Extraction of Atmospheric Samples

Samples collected on 8 x 10" filters were extracted by refluxing in water for 90 minutes followed by filtration through pre-washed Whatman 41 filters. Particulate samples on 47 mm filters were extracted by static immersion in 5 ml H<sub>2</sub>O at 80°C.<sup>15,16</sup> In both cases, aliquots were removed and stored at -20°C for nitrate analyses.

## 3. Sulfate

Sulfate from atmospheric samples was analyzed by two techniques, the semi-automated Brosset procedure<sup>4</sup> and the AIHL microsulfate method.<sup>15</sup> The Brosset technique includes removal of cationic interferences while the AIHL method, as used here, does not. It was intended that all field samples be analyzed for sulfate by the Brosset procedure. Following sulfate analysis of the hi-vol filter samples, it became evident that the low-volume filters could contain insufficient sulfate for reliable analysis by the Brosset procedure. Accordingly, the low-volume samples were analyzed by the AIHL microchemical method following a protocol which had been extensively evaluated under an EPA sponsored study.<sup>3</sup>

A comparison of results from these two techniques and the Dionex ion chromatograph is given in Table 5. On average, results by the Brosset method are 9% higher than by Dionex procedure while the AIHL method results are, on average, 10% lower than by Dionex. Using EPA sulfate audit strips, (i.e., glass fiber filter strips spiked with K<sub>2</sub>SO<sub>4</sub>) the mean sulfate recovery by the Brosset technique was 104% compared to 96% for the AIHL technique. However, with the present atmospheric samples a clear indication of negative interference from cations in the sample (probably calcium) was obtained: re-analysis of each of the 16 extracts by the AIHL technique after ion-exchange treatment showed an increased result in every case. Overall results by the AIHL technique with ion exchange were not significantly different from those by the Dionex procedure. Regrettably, this modification of the AIHL method to permit ion exchange with small extract volumes was not available when the low-volume samples from the present study were being analyzed.

Since comparison of low-volume and high-volume atmospheric results is an important part of this work, the low-volume atmospheric sulfate data (by the AIHL method without ion exchange) was adjusted to correspond to those by the Brosset procedure based upon a regression line given in Figure 9.

Table 5

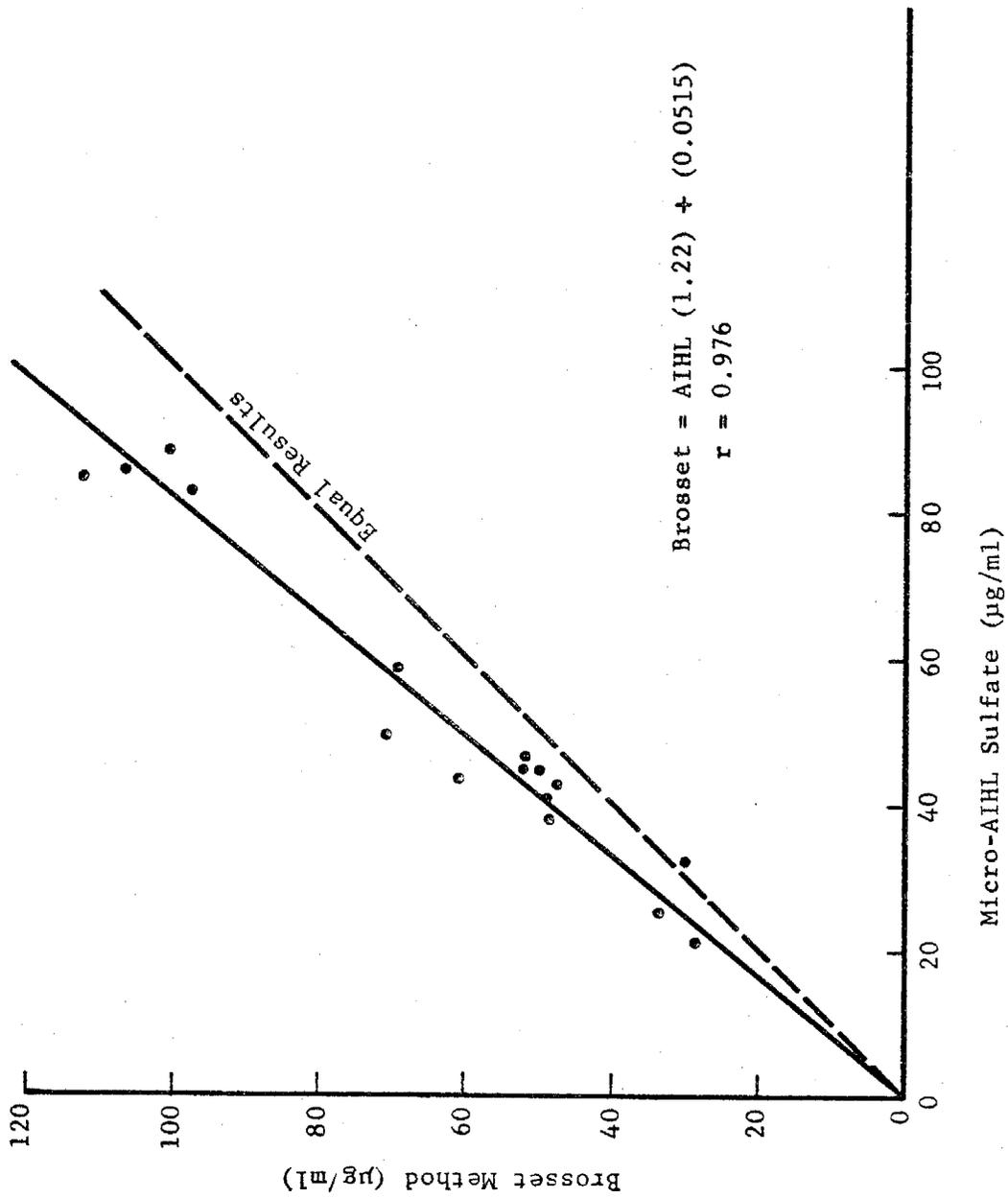
INTERMETHOD COMPARISON OF SULFATE METHODS<sup>a</sup>  
(mg/ml sulfate)

<u>Sample</u>	<u>Dionex Ion Chromatograph</u> <sup>b</sup>	<u>Brosset</u>	<u>AIHL</u>	
			<u>With Ion Exchange</u> <sup>c</sup>	<u>No Ion Exchange</u>
1	27.7	28.4	29.7	21.0
2	30.4	33.4	31.2	25.6
3	51.3	51.7	49.6	46.4
4	47.3	61.3	48.0	42.8
5	52.9	52.4	51.6	45.1
6	47.9	50.5	48.6	44.4
7	46.0	48.4	49.1	43.0
8	86.6	97.7	88.5	82.6
9	103.4	100.5	99.1	88.5
10	70.0	69.1	68.2	58.7
11	49.6	49.3	50.5	41.5
12	41.8	48.8	43.3	38.0
13	35.9	29.8	38.1	31.7
14	90.7	112.8	89.6	84.5
15	54.0	71.1	54.6	49.4
16	88.5	106.5	90.6	86.5

Ratio of

Means:                      1.00                      1.09                      1.01                      0.90

- a. Samples used are 24-hour hi-volume samples collected on Gelman A glass fiber filters on different days in San Jose and Los Alamitos, California.
- b. Model 10.
- c. Both samples and standards treated with ion exchange resin.



INTER-METHOD COMPARISON OF SULFATE METHODS

Figure 9

For characterization of blank filters, all analyses employed the Brosset procedure.

#### 4. Nitrate

Analyses were done within one week of the extraction using the Cu-Cd reduction (to nitrite) diazotization method automated for the Technicon Autoanalyzer II (Technicon Industrial Method 100-70W). The precision of the method, expressed as a mean coefficient of variation for 25 samples analyzed with two determinations was 1.7%. No difference in precision between hi-vol and low-vol samples was seen.

Results for Technicon nitrate analysis of 16 hi-vol extracts, including samples from nearly all episodes at San Jose and Los Alamitos are compared to those for the Dionex ion chromatograph in Table 6. The ratio of means for the two techniques was 1.00 indicating, on average, excellent agreement. Inspection of individual pairs indicate differences up to 12%, however.

#### 5. Nitrite

Nitrite was determined by the nitrate procedure omitting the Cu-Cd reduction step. To establish the accuracy of this procedure relative to that for nitrate, a solution containing 4  $\mu\text{g/ml NO}_3^-$  and 4  $\mu\text{g/ml NO}_2^-$  (calculated as  $\text{NO}_3^-$ ) was analyzed with and without Cu-Cd reduction. Without Cu-Cd reduction, the observed signal should be one-half that found with Cu-Cd reduction. The observed instrument response without Cu-Cd reduction was 53% of that observed with Cu-Cd reduction. Furthermore, the response for the above solution with Cu-Cd reduction differed by 0.1% from that obtained with 8  $\mu\text{g/ml NO}_3^-$  (also with Cu-Cd reduction).

#### 6. Silicate

The procedure used is based on the determination of silicates reactive with molybdic acid and is given in Appendix F.

#### 7. Phosphate

Phosphate was measured by a modified molybdenum blue procedure given in Appendix G.

#### 8. Sulfite

Sulfite was determined by the Weste-Gaeke procedure modified for determination of filter samples as given in Appendix H.

Table 6

INTERMETHOD COMPARISON OF NITRATE DETERMINATIONS  
USING 24-HOUR HI-VOL EXTRACTS ( $\mu\text{g}/\text{ml}$ )

<u>Sample ID</u>	<u>Dionex</u>	<u>Technicon</u>
SA0004AT	78.09	80.2
SB0010AT	59.15	50.0
SC0011AT	179.22	185.5
SD0012AT	120.50	123.7
SE0013AT	156.57	137.5
SF0002AT	88.35	91.3
LA0023AT	63.76	67.2
LB0029AT	117.00	121.3
LC0030AT	320.00	330.3
LD0031AT	176.42	183.3
LE0032AT	106.16	107.8
LG0049AT	43.39	38.1
LH0038AT	34.94	29.4
LB0141ST	145.52	143.8
SD0165ST	128.61	130.2
LB0142ST	150.42	152.7
Ratio of Means:	1.00	1.00

9. Calcium and Barium

These were determined by atomic absorption.

#### IV. Characterization of Filter Media

##### A. Introduction

The seven filter media were characterized for the following: filtration efficiency, total carbon and extractable carbon contents (glass fiber only), metals by  $\alpha$ -induced x-ray fluorescence analysis ( $\alpha$ -XRFA) and water extractable ions. The latter included pH, nitrate, sulfate, silica, phosphate, calcium and barium.

Filtration efficiency is of concern for both sulfate and nitrate aerosols because of their typically small particle size. For sulfate, mass median diameters (mmd) in the range 0.2 to 0.5  $\mu\text{m}$  are usually observed while for nitrate, mmd values from 0.3 to 1.7  $\mu\text{m}$  have been reported.<sup>12</sup> In addition, filters for monitoring sulfate and nitrate may also be analyzed for other aerosol constituents existing in principally submicron particle sizes such as lead and carbonaceous material.

The basicity of filters as measured by pH, was determined since it appears to be one of the most important factors controlling the collection of the acidic gases considered in this study.

The concentrations of silica, phosphate, calcium and barium were determined since these may serve as analytical interferences in the determination of sulfate by wet chemical methods.

##### B. Filtration Efficiency Studies

Filtration efficiencies for initially clean filters were determined for room air dust using an Environment One condensation nuclei counter (CNC). The experimental design, detailed in Appendix I, involved sampling pressurized room air so that the air downstream of the filter could be at atmospheric pressure for more reliable CNC performance.

Results obtained are summarized in Table 7. The initial design for field sampling anticipated a flow rate of 3.0 cfm with 47 mm filters. This was later reduced to 0.6 cfm (face velocity 19.4 cm/sec). The filtration efficiencies for the filters studied were determined at 1.0 and 3.0 cfm except for Fluoropore which was measured in the range 0.1-3.0 cfm. With 47 mm filters, a flow rate of 1.32 cfm provides a face velocity equivalent to that for an 8 x 10" filter at 40 cfm (47 cm/sec). Excepting Whatman 41, the filtration efficiencies were > 99 at all flow rates.

13

The previous studies indicated filtration efficiencies  $\geq 99\%$  in the face velocity range 0.3 to ca. 100 cm/sec for Gelman A, MSA 1106BH and a 5  $\mu\text{m}$  pore size cellulose ester filter similar to the Gelman GA-1 filter. Thus, the lack of a measurement of filtration efficiency at 0.6 cfm is not considered significant.

The results given here for Fluoropore filters are similar to those of B.Y.H. Liu and co-workers<sup>14</sup> which indicated > 99.99% efficiency for monodisperse particles in the range 0.03 to 1  $\mu\text{m}$ .

Table 7

## MEASURED FILTRATION EFFICIENCIES

<u>Filter Type</u>	<u>Flowrate cfm*</u>	<u>Number of Filters Tested</u>	<u>Percent Filtration Efficiency for Room Air Dust**</u>
Fluoropore 1 $\mu$ m pore	0.25, 0.38, 0.66	1	> 99.9
	1.0	6	> 99.9
	3.0	6	> 99.9
Gelman GA-1 5 $\mu$ m pore	1.0	5	> 99.1
	3.0	5	> 99.0
Whatman 41	1.0	6	64
	3.0	6	83
Gelman Spectrograde	1.0	6	> 99.8
	3.0	6	> 99.8
Gelman A Glass Fiber	1.0	6	> 99.9
	2.5	6	> 99.9
MSA 1106BH Glass Fiber	1.0	6	> 99.2
	2.5	6	> 99.1
Gelman EPA Grade	1.0	6	> 99.8
	2.5	6	> 99.8

\*Using 47 mm filters. A flow rate of 3.2 cfm provides a face velocity equivalent to that of a high-volume sampler at 40 cfm using an 8 x 10" filter.

\*\*Made with an Environment I condensation nuclei counter.

### C. Water Extractable Ions

The pH and extractable ion concentrations for the seven filter types are summarized in Table 8. Results are shown as  $\mu\text{g}$  per filter for the filter size normally employed. Thus, the results for the glass and cellulose filters are per 8 x 10" sheet while for the cellulose ester and Teflon membrane filters, they are per 47 mm disc.

Whatman 41, Fluoropore, Gelman GA-1 and Gelman Spectrograde all exhibited somewhat acidic pH values. Both MSA 1106BH and the EPA Grade filter exhibited pH values of about 9 which is considered typical for glass fiber filters. Gelman A appears unique in providing a nearly neutral pH without reported use of a surface coating as with Spectrograde. The wetting properties of Gelman A are consistent with the absence of a hydrophobic surface coating.

The nitrate blank values are relatively low in all cases. Only with low volume samples collected on Gelman GA-1 does the nitrate value become significant. In contrast to other filter types, Gelman GA-1 filters from three batches were used in this study as detailed in footnote d. Batch A was used for all field samples and some laboratory exposures. Batches B and C were used for the remaining laboratory exposures. The batch-to-batch variability of the nitrate blank was quite large probably reflecting the fact that cellulose nitrate is a constituent of these filters.

The EPA Grade filter is notable for its low sulfate blank and high phosphate level reflecting the use of phosphoric acid rather than sulfuric acid during manufacture. A high phosphate blank raises some concern about interference in sulfate determinations by the automated methylthymol blue method (MTB). However, filter blank corrections probably eliminate this potential error.

Relatively high silica levels are extractable from the glass fiber filters. For MSA filters, extraction of one-fourth of an 8 x 10" filter into 100 ml water, as used in sulfate analysis by AIHL Method 61, would yield about 450  $\mu\text{g}/\text{ml}$  silica (as  $\text{SiO}_2$ ). Such concentrations would cause positive errors in sulfate measurement by the MTB method. Again, filter blank correction may eliminate this.

### D. Carbon Content

The carbon content of the glass fiber filters is reported in Table 9 as mean results for six filters. Spectrograde exhibited the highest and most variable blank probably reflecting the dimethylsilicone surface coating. Comparing benzene extractable carbon results, except for Spectrograde, all filters were equivalent. Gelman A and EPA Grade exhibited substantially lower soluble polar organic carbon relative to MSA and Spectrograde as measured by methanol-chloroform extraction.

WATER EXTRACTABLE IONS FROM BLANK FILTERS ( $\mu\text{g}/\text{filter}$ )<sup>a</sup>

Filter	pH <sup>b</sup>	Nitrate	Sulfate	Silica <sup>c</sup>	Phosphate	Calcium	Barium
Fluoropore, FALP (Teflon) 47 mm	5.8	3	< 1.5	28.3	< 1	< 0.5	< 5
Gelman GA-1 (cellulose acetate), 47 mm	5.5	d	10	19.9	< 1	4	< 5
Whatman 41 (cellulose), 8 x 10"	4.6 ± .03	< 7	< 23	80 ± 16	< 10	< 8	< 78
Gelman Spectrograde (glass fiber) 8 x 10"	6.2 ± .1	69 ± 8	759 ± 54	85000 ± 5400	< 23	574 ± 20	< 78
Gelman A (glass fiber) 8 x 10"	7.6 ± .4	< 12	1406 ± 239	91200 ± 2100	< 10	96 ± 6	< 78
MSA 1106BH, (glass fiber) 8 x 10"	9.4 ± .1	55 ± 3	3623 ± 170	181,600 ± 2100	< 11	321 ± 24	< 78
EPA Grade (glass fiber) 8 x 10"	9.3 ± .1	19 ± 8	171 ± 36	156,700 ± 9600	2222 ± 77	104 ± 25	< 78

a. For all except pH, results for 8 x 10" filters are means ± 1σ for extraction of six complete filters. With 47 mm filters, 15-47 mm filters were extracted as one batch providing results as the mean of 15 filters but no standard deviation.

b. pH determined following EPA protocol requiring a 9-inch<sup>2</sup> section of filter for hi-vol filters. Results for 8 x 10" filters are the mean of six trials ± 1σ. With 47 mm filters, four filters (total area 10.8-inch<sup>2</sup>) were used as one batch.

c. Calculated as SiO<sub>2</sub>.

d. Results for filters from three separate batches were a, 5.7 ± 1.7; b, 31 ± 5.1; and c, 45.3 ± 2.4 μg/47 mm filter.

Table 9

CARBON BLANKS FOR GLASS FIBER FILTERS<sup>a</sup>  
( $\mu\text{gC}/8 \times 10''$  filter)

<u>Filter</u>	<u>Total C</u>	<u>Benzene Extractable C</u>	<u>Methanol-Chloroform Extractable C<sup>b</sup></u>
Gelman A	510 $\pm$ 150	223 $\pm$ 22	131 $\pm$ 29
EPA Grade	1123 $\pm$ 332	217 $\pm$ 25	128 $\pm$ 42
MSA 1106BH	1857 $\pm$ 220	236 $\pm$ 33	687 $\pm$ 23
Gelman Spectrograde	3812 $\pm$ 981	590 $\pm$ 277	693 $\pm$ 171

a. Mean of six trials  $\pm 1 \sigma$

b. Following benzene extraction.

#### E. Batch-to-Batch Variations

The filter media used in this study are identified by batch or lot number in Table 10. In only one case, Gelman GA-1, was more than one batch used.

It may be inferred from results reported elsewhere together with those in Table 9 that the pH of the filter sold as "Gelman A" can vary widely. Values reported for this filter include from the present work 7.6, compared to 8.8 by Witz and MacPhee<sup>18</sup> and 9.9 by Pierson, et al. While differences in pH measuring techniques may account for some of these variations, the major portion probably reflects batch-to-batch differences.

Table 10

## BATCH NUMBERS FOR FILTER MEDIA EVALUATED

<u>Filter</u>	<u>Batch or Lot No.</u>
Fluoropore, FALP	5
Gelman GA-1	81441 <sup>a, d</sup>
"	80450 <sup>b</sup>
"	80451 <sup>c</sup>
Whatman 41	1576/04
Gelman Spectrograde	8192
Gelman A	8222
MSA 1106BH	J2897
Gelman EPA Grade	8233

- a.  $\text{NO}_3^-$  blank  $5.7 \pm 1.7$   $\mu\text{g}/47$  mm filter.
- b.  $\text{NO}_3^-$  blank  $31.0 \pm 5.1$   $\mu\text{g}/47$  mm filter.
- c.  $\text{NO}_3^-$  blank  $45.3 \pm 2.4$   $\mu\text{g}/47$  mm filter.
- d. The batch used in field sampling and about half of the exposure studies.

## V. Filter Media Comparisons with Atmospheric Samples

### A. Description of Days Sampled

#### 1. San Jose

In general, the concentrations of CO, ozone, NO<sub>2</sub> and particulate matter (COH units) peaked in the afternoons, whereas hydrocarbons and NO<sub>x</sub> peaks occurred in the mornings. The AIHL Meloy SO<sub>2</sub> analyzer registered baseline values (i.e., < 10 ppb) throughout the sampling period. The maximum daytime temperatures were generally in the eighties and nineties (°F), with high fog during the early morning hours. The maximum hourly average pollutant concentrations and the meteorological extremes for the days sampled are given in Table 11.

#### 2. Los Alamitos

Table 12 shows the one-hour average maximum oxidant and SO<sub>2</sub> and meteorological extremes reported by the SCAPCD. The pollution levels were generally moderate (max. oxidant = 0.15 ppm; SO<sub>2</sub> = 0.14 ppm) and the weather warm (max. temperatures 83-96°F) with winds generally from the north and east during the nighttime and early morning hours, and from the south and west during the afternoon hours. By contrast, the peak hourly average SO<sub>2</sub> concentrations, shown in Figures 10 and 11, recorded by the AIHL Meloy SO<sub>2</sub> analyzer monitoring on the hangar roof indicated peak hourly average concentrations as high as 0.50 ppm. The peaks, moreover, all occurred between 1200 and 1600 hour when the winds were predominantly from the direction of the Los Alamitos Power Plant (west). The levels during other hours were at or near background. These differences are consistent with the Southern Zone's past experiences when the District had an SO<sub>2</sub> monitor at this location and are consistent with the significance of a local SO<sub>2</sub> source.

### B. Sulfate Results

#### 1. Comparisons Based on Mean Results

Table 13 summarizes the 24-hour hi-vol and low-volume results for sulfate. In the cases where two values are shown, these represent results for two samplers operated with the same filter medium. From these data we calculate the following:

- a. The precision of hi-vol sampling for sulfate was  $11.5 \pm 9.7\%$ , as measured by the mean coefficient of variation for twelve paired samples collected side-by-side on different samplers but with the same filter type.

Table 11

Pollutant Maximums<sup>☆</sup> and Meteorological Conditions  
During Sampling at San Jose

October 4 - 11, 1976

<u>Pollutant/Episode</u>	10/4-5 (A)	10/5-6 (B)	10/6-7 (C)	10/7-8 (D)	10/8-9 (E)	10/9-10 (F)
CO, pphm	11	12	8	7	10	2
Ox, pphm	10	9	16	10	16	4
NO <sub>2</sub> , pphm	17	13	17	13	12	6
NO <sub>x</sub> , pphm	30	25	24	23	22	4
HC, pphm	5	4	3	6	2	4
COH, units	14	15	13	14	15	3
Max RH, %	81	86	79	96	94	94
Min RH, %	40	36	47	46	55	53
Max Temp, °F	86	94	84	90	86	76
Min Temp, °F	52	57	59	56	58	56
Wind, mph	4	3	3	3	2	4

---

<sup>☆</sup>hourly average

Table 12

Pollutant Maximums and Meteorological Conditions During  
Sampling at Los Alamitos<sup>a</sup>

October 28 - November 5, 1976

<u>Pollutant/Episode</u>	Oct 28-29 (A)	Oct 29-30 (B)	Oct 30-31 (C)	Oct 31- Nov 1 (D)	Nov 1-2 (E)	Nov 2-3 (F)	Nov 3-4 (G)	Nov 4-5 (H)
Ox, pphm	5	9	16	11	7	13	4	9
SO <sub>2</sub> , pphm	3	10	14	6	8	9	9	9
Max RH, %	65	97	90	85	65	63	59	47
Min RH, %	43	50	34	29	29	35	28	30
Max Temp, °F	84	83	83	89	94	96	94	94
Min Temp, °F	60	57	58	47	54	60	59	62
Wind, mph	4	2	3	2	3	3	3	2

<sup>a</sup>One-hour average data.

HOURLY AVERAGE SO<sub>2</sub> CONCENTRATIONS  
AT LOS ALAMITOS

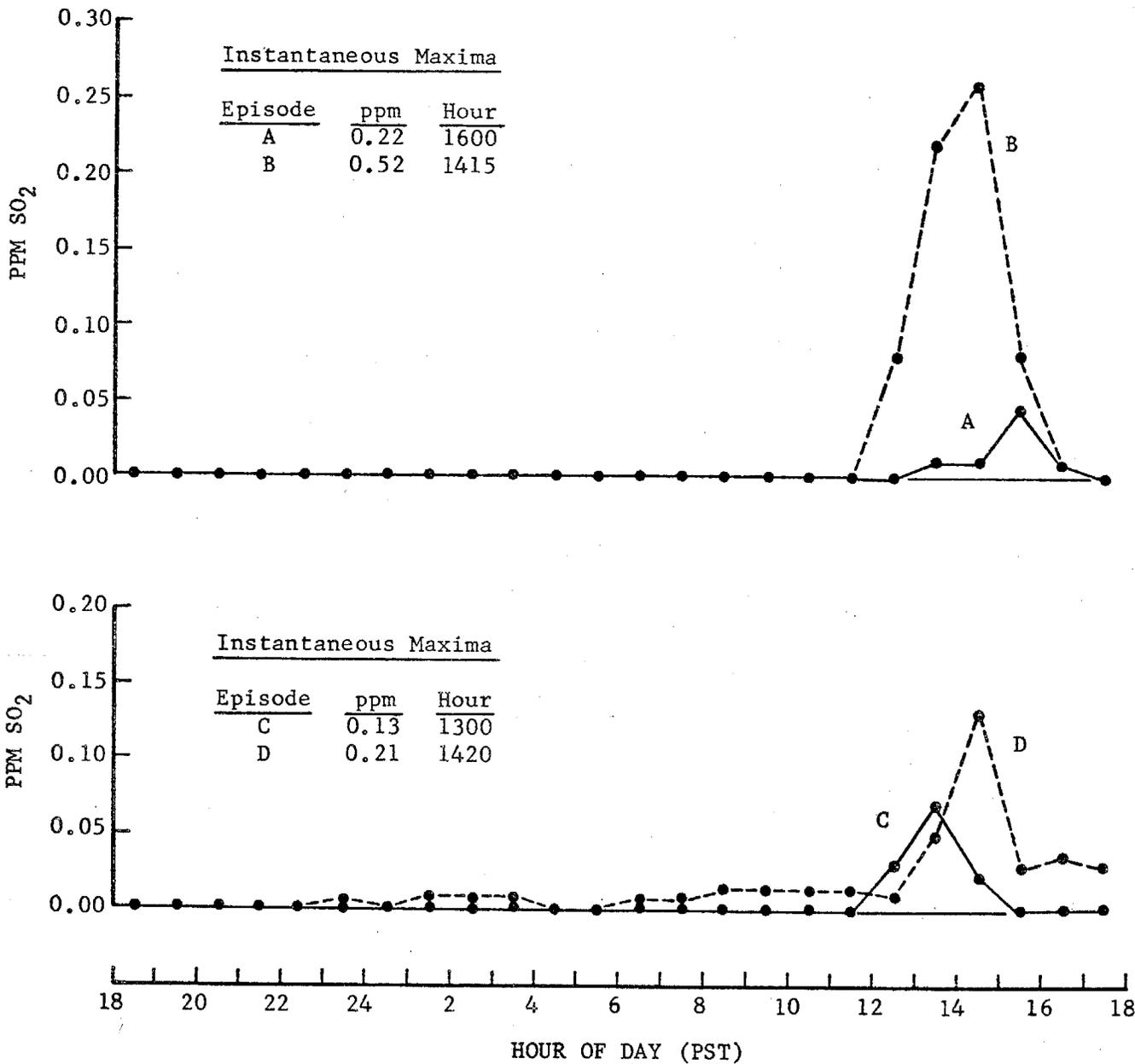


Figure 10

HOURLY AVERAGE SO<sub>2</sub> CONCENTRATION  
AT LOS ALAMITOS

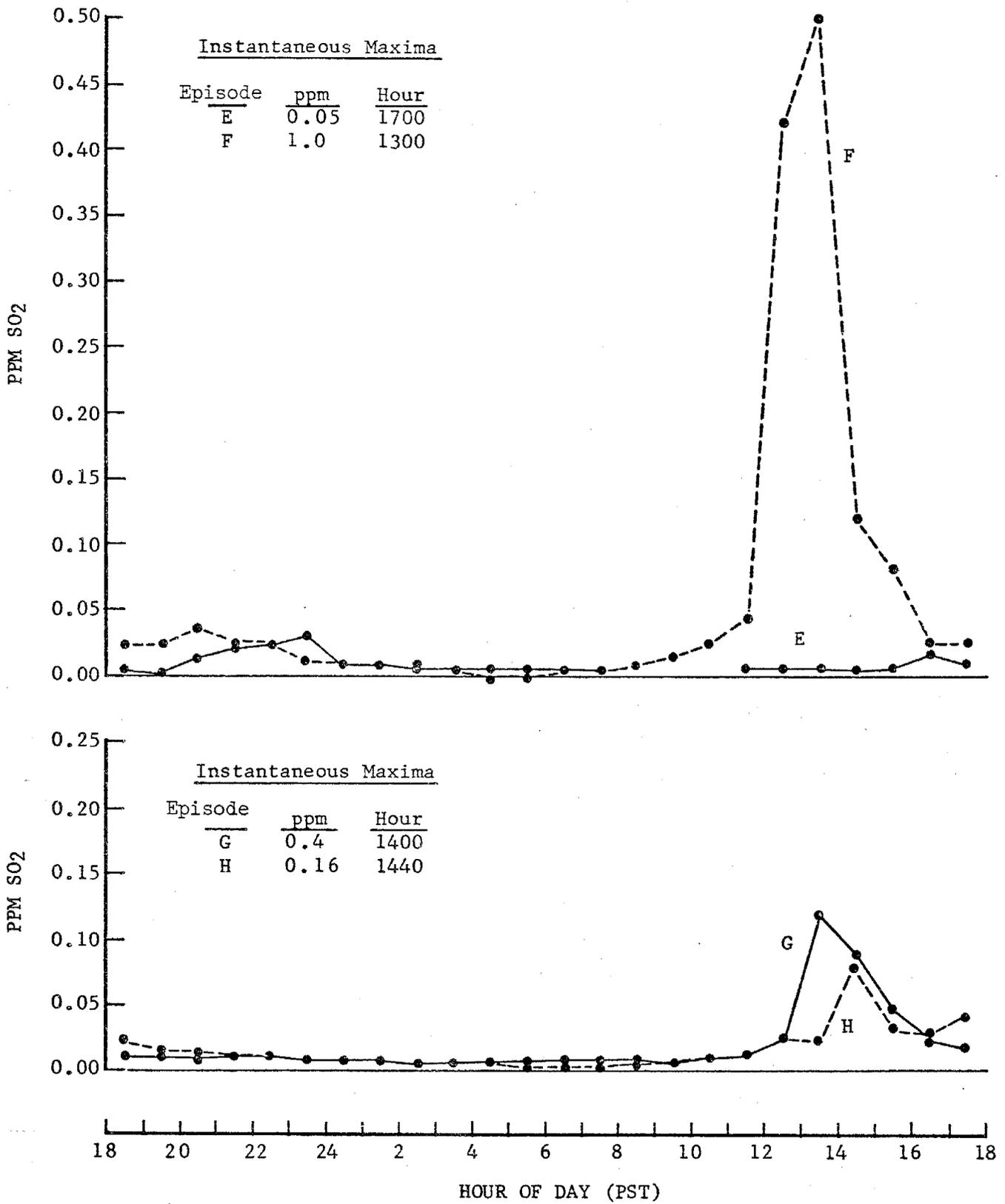


Figure 11

Table 13

Sulfate Results from 24-Hour Samples ( $\mu\text{g}/\text{m}^3$ )<sup>g</sup>

## SAN JOSE

Date (EPISODE)	High-Volume Samples				Low-Volume Samples				
	Gelman A	MSA 1106BH	Whatman 41	Spectro- grade	Gelman A	MSA 1106BH	Spectro- grade	Fluoro- pore	Gelman GA-1
Oct 4-5 (A)	2.9 <sup>b</sup> 3.1 <sup>b</sup>		2.5 <sup>b</sup>	4.6 <sup>b</sup>				2.2	
Oct 5-6 (B)	3.5 <sup>b</sup>	1.7 <sup>b</sup>		4.8 <sup>b</sup> 3.4 <sup>b</sup>					2.3
Oct 6-7 (C)	5.3 <sup>b</sup>		5.7 <sup>b</sup> 5.3 <sup>b</sup>	6.0		10.7			
Oct 7-8 (D)	6.5 <sup>b</sup>	7.8 <sup>b</sup> 8.0 <sup>b</sup>		8.0 <sup>b</sup>	6.4				
Oct 8-9 (E)	5.5		5.0 <sup>b,h</sup>	6.3 <sup>b</sup> 7.5 <sup>b</sup>			9.9		
Oct 9-10 (F)	6.6 <sup>b</sup>			8.0 <sup>b</sup>					6.1

## LOS ALAMITOS

Oct 28-29 (A)	5.0 5.7 <sup>f</sup>		4.1 <sup>b</sup>	7.3 <sup>b</sup>				4.6	
Oct 29-30 (B)	10.9	10.7 <sup>b</sup>		13.2 <sup>b</sup> 12.0 <sup>b</sup>					11.3
Oct 30-31 (C)	11.6		11.3 <sup>b</sup> 13.2 <sup>b</sup>	13.7 <sup>b</sup>		27.6			
Oct 31-Nov 1 (D)	8.7 <sup>b</sup>	12.1 <sup>b</sup> 16.1 <sup>b</sup>		10.9 <sup>b</sup>	9.9				
Nov 1-2 (E)	5.8 <sup>b</sup>		6.1 <sup>b</sup>	8.2 8.1 <sup>b</sup>			10.8		
Nov 2-3 (F)	8.9 <sup>f,h</sup>	11.2 <sup>b</sup> 9.7 <sup>b</sup>		10.0 <sup>b</sup>				5.6	
Nov 3-4 (G)	5.2 <sup>b</sup>	7.9		6.6				3.7	
Nov 4-5 (H)	4.5 <sup>b</sup> 2.8 <sup>b</sup>		2.6 <sup>b</sup>	5.3 <sup>e</sup>					2.7

a. Two values indicate results from separate samplers.

b. Mean of two determinations on the same sample.

c. Shown relative to Gelman A Hi-Vol and, in second line, relative to Fluoropore (Low-Vol).

d. Average of 3 determinations on the sample.

e. Average of 5 determinations on the sample.

f. Average of 4 determinations on the sample.

g. Except as noted, the high-volume samples were analyzed by the Brosset technique and the low-volume samples by the AIHL microsulfate method. The latter values are here corrected to the expected Brosset values using the equation: Brosset = 1.22 (AIHL) + 0.0515, r = 0.976.

h. This sample was analyzed by the AIHL method and corrected as given in footnote g.

- b. In the four cases in which 24-hour hi-vol as well as low-volume results are available for the same filter type run simultaneously (Gelman A, Gelman Spectrograde twice each), low-volume filter results were higher by 6 and 38% for Gelman A and Spectrograde, respectively.

The sulfate results for 6-hour hi-vol and low-volume samples are given in Tables 14 and 15 with separate results listed for respirable and total low-volume samples. The results on the different filters are compared in Table 16 as ratios of arithmetic means  $\pm 1\sigma$ . From these results and comparisons we note:

- a. Based on 24-hour values, the observed sulfate values follow the order, decreasing from top to bottom:

MSA 1106BH (lo-vol)  
Spectrograde (lo-vol)  
Spectrograde (hi-vol)  
MSA 1106BH (hi-vol)  
Gelman A (lo-vol)  
Gelman A (hi-vol)  
Whatman 41 (hi-vol)  
Gelman GA-1 (lo-vol)  
Fluoropore (lo-vol)

The ratio of means for 6-hour results on Gelman A (hi-vol), Spectrograde (lo-vol), Gelman GA-1 and Fluoropore (lo-vol) are quite similar to those for 24-hour samples.

- b. The Spectrograde hi-vol, with a relatively low pH, exhibited sulfate levels nearly equal to the MSA hi-vol filter. If the Fluoropore (low-volume) results are accepted as a true measure of the particulate sulfate level then, on average, artifact sulfate represent about a 70% or  $3 \mu\text{g}/\text{m}^3$  positive error on these filters for the days sampled.

The mean fraction of sulfate in the respirable size range, as obtained with 6-hour low-volume samples, is given in Table 17. If nearly all sulfate resulted from interaction of  $\text{SO}_2$  with the filters then the observed fraction of respirable sulfate would be expected to approach unity, since both respirable and total filters receive the same exposure to  $\text{SO}_2$ . In the case where both particulate sulfate and artifact sulfate occur, the filters providing the least artifact sulfate would be expected to yield the lowest value for the fraction of respirable sulfate. Consistent with this, Fluoropore, which yielded the lowest observed sulfate, shows the lowest respirable fraction. Surprisingly, the highest ratios are observed for Gelman GA-1 and Gelman A which, as noted above, gave other evidence of relatively low levels of artifact sulfate.

Table 14  
SULFATE RESULTS FROM SIX-HOUR SAMPLES AT SAN JOSE ( $\mu\text{g}/\text{m}^3$ )<sup>a</sup>

Date (EPISODE)	Time PST	High-Volume Samples				Low-Volume Samples						
		Gelman A	MSA 1106BH	Whatman 41	Spectrograde	Gelman A T <sup>b</sup>	MSA 1106BH T	Spectrograde T	Fluoropore F	Gelman GA-1 T		
Oct 4-5 (A)	18-24	3.9 <sup>d</sup> 4.5 <sup>d</sup> 4.4 <sup>d</sup> 5.2							1.2 1.4 1.4 3.6			
	24-6										0.4	
	6-12										0.9	
Oct 5-6 (B)	12-18				7.3 <sup>d</sup> 7.8 <sup>d</sup> 7.3 <sup>d</sup> 4.7				5.0 5.5 4.5 5.2	4.4 4.3 4.1 4.2		
	18-24											
	24-6											
Oct 6-7 (C)	6-12			5.9 <sup>c</sup> 4.3 <sup>c</sup> 7.7 6.7								
	12-18											
	18-24											
Oct 7-8 (D)	24-6											
	6-12											
	12-18											
Oct 8-9 (E)	18-24	4.9 <sup>d</sup> 6.9 <sup>d</sup> 6.0 <sup>d</sup> 8.3 <sup>d</sup>			13.4 <sup>d</sup> 12.4 <sup>d</sup> 16.1 <sup>d</sup> 7.4				7.5 5.1 8.6 10.0	7.9 7.2 9.9 11.5		
	24-6											
	6-12											
Oct 9-10 (F)	12-18								5.7 5.2 7.3 12.9	(1.3) <sup>e</sup> (0.6) <sup>e</sup> 5.6 <sup>e</sup> (1.4)		
	18-24											
	24-6											

a. Same as footnote 6, Table  
b. Total filters collecting particles < ca. 20  $\mu\text{m}$ .  
c. Respirable filter sampler collecting particles < 3.5  $\mu\text{m}$ .  
d. Mean of two determinations.  
e. Below working range of method.

Table 15

SULFATE RESULTS FROM SIX-HOUR SAMPLES AT LOS ALAMITOS ( $\mu\text{g}/\text{m}^3$ )<sup>a</sup>

Date (EPIISODE)	Time FST	High-Volume Samples				Low-Volume Samples				
		Gelman A	MSA 1106BH	Whatman 41	Spectrograde	Gelman A T <sup>b</sup> R <sup>c</sup>	MSA 1106BH T R	Spectrograde T R	Fluoropore T R	Gelman GA-1 T R
Oct 28-29 (A)	18-24	5.6 <sup>d</sup>							3.9	2.9
	24-6	3.8 <sup>d</sup>							3.1	2.0
	6-12	4.7 <sup>d</sup>							3.3	2.5
Oct 29-30 (B)	12-18	9.9							9.3	8.8
	18-24				14.1 <sup>d</sup>					6.2
	24-6				13.2 <sup>d</sup>					4.4
Oct 30-31 (C)	6-12				19.1 <sup>d</sup>					10.4
	12-18				23.1 <sup>d</sup>					21.2
	18-24			9.3 <sup>d</sup>						6.2
Oct 31-Nov 1 (D)	24-6			10.3 <sup>d</sup>						4.4
	6-12			13.6 <sup>d</sup>						10.1
	12-18			13.4 <sup>d</sup>						21.0
Nov 1-2 (E)	18-24				28.0 <sup>d</sup>					
	24-6				26.8 <sup>d</sup>					
	6-12				22.0 <sup>d</sup>					
Nov 2-3 (F)	12-18				19.9 <sup>d</sup>					
	18-24	9.2 <sup>d</sup>							17.5	17.6
	24-6	6.8 <sup>d</sup>							18.1	18.3
Nov 2-3 (F)	6-12	5.5 <sup>d</sup>							9.3	8.5
	12-18	4.4 <sup>d</sup>							7.0	4.8
	18-24	7.5 <sup>d</sup>							5.1	4.7
Nov 3-4 (G)	24-6	5.2 <sup>d</sup>							1.8	1.2
	6-12	4.3 <sup>d</sup>							2.6	1.9
	12-18	14.5 <sup>d</sup>							18.3	15.3
Nov 4-5 (H)	18-24	6.8 <sup>d</sup>							3.8	3.0
	24-6	6.9 <sup>d</sup>							2.6	1.8
	6-12	5.1 <sup>d</sup>							1.7	0.5
Nov 4-5 (H)	12-18	8.7							8.4	8.0
	18-24	4.6 <sup>d</sup>								2.8
	24-6	4.0 <sup>d</sup>								3.1
Nov 4-5 (H)	6-12	3.5 <sup>d</sup>								2.5
	12-18	8.8 <sup>d</sup>								8.1
	18-24									8.5

a. See footnote 8, Table

b. Total filters collecting particles < ca. 20  $\mu\text{m}$ .

c. Respirable filter sampler collecting particles < 3.5  $\mu\text{m}$ .

d. Mean of two determinations.

Table 16

## COMPARISON OF SULFATE RESULTS ON DIFFERENT FILTER MEDIA

<u>Sample/Reference</u>	<u>24-Hour Results</u>		<u>Ratio of Means</u>		<u>6-Hour Results</u>		<u>N<sup>a</sup></u>
	<u>Gelman A</u>	<u>Fluoropore</u>	<u>N<sup>a</sup></u>	<u>Gelman A</u>	<u>Fluoropore</u>	<u>N<sup>a</sup></u>	
Gelman A, Hi-vol	1.00	1.39		1.00	1.41		
MSA 1106BH, Hi-vol	1.21 ± .13	1.68	6				
Whatman 41, Hi-vol	0.95 ± .05	1.32	7				
Spectrograde, Hi-vol	1.24 ± .03	1.72	14				
Gelman A, Lo-vol	1.07 ± .08	1.49	2				
MSA 1106BH, Lo-vol	2.27 ± .16	3.15	2				
Spectrograde, Lo-vol	1.83 ± .03	2.54	2	1.60 ± .21	2.25	8	
Gelman GA-1, Lo-vol	0.91 ± .08	1.26	4	0.98 ± .10	1.38	8	
Fluoropore, Lo-vol	0.72 ± .06	1.00	4	0.71 ± .10	1.00	16	

a. Number of filter pairs

Table 17

RESPIRABLE SULFATE AS A FRACTION OF TOTAL PARTICULATE  
SULFATE IN 6-HOUR LOW-VOL FILTER SAMPLES

<u>Filter</u>	<u>Respirable/Total Sulfate</u> <u>(Mean Ratios + 1 <math>\sigma</math>)</u>	<u>N<sup>a</sup></u>
Fluoropore	0.82 $\pm$ .03	16
Spectrograde	0.93 $\pm$ .06	5
MSA 1106BH	0.86 $\pm$ .03	8
Gelman GA-1	1.00 $\pm$ .03	16
Gelman A	1.08 $\pm$ .03	8

---

a. Number of pairs

The ratio of 24-hour sulfate values calculated from four 6-hour samples to those observed directly are given in Table 18. If artifact sulfate results from collection of an acidic gas ( $\text{SO}_2$ ) on a limited number of alkaline sites on a filter, then these ratios should increase for filters producing higher artifact sulfate levels. This follows since in 24-hour sampling, such alkaline sites might easily be saturated after a few hours depending on ambient conditions. Following saturation, sulfate would be collected with relatively little, if any, artifactual sulfate. The observed ratios follow the order: Whatman 41 < Fluoropore = Gelman GA-1 = Spectrograde = Gelman A < MSA. This order differs somewhat from that given above based on side-by-side comparisons. However, in both cases, MSA indicates the highest level of artifact sulfate.

For 14 sampling periods, the mean 24-hour average sulfate on Gelman A hi-vol filters was  $6.5 \mu\text{g}/\text{m}^3$ . For four days on which both Fluoropore and Gelman A filters were run, the mean ratio of results Fluoropore/Gelman A of 0.72 correspondsto a difference of  $1.6 \mu\text{g}/\text{m}^3$ . The hi-vol filter samples exhibited sulfate levels ranging from 30 to 70% higher than on Fluoropore. In the worst case (Spectrograde hi-vol), the mean difference between Spectrograde and Fluoropore corresponded to  $3.1 \mu\text{g}/\text{m}^3$  sulfate. These differences are interpreted to indicate the relative degree of artifact sulfate formation. The cellulose acetate membrane filter, Gelman GA-1, while better than any of the glass fiber hi-vol filters, is calculated to exhibit significantly higher sulfate values compared to Fluoropore and appeared to distort substantially the apparent fraction of respirable sulfate.

## 2. The Efficiency of Conversion of $\text{SO}_2$ to Sulfate on 24-Hour Ambient Filter Samples

At San Jose, the  $\text{SO}_2$  concentrations were below the limit of detection for the Meloy total sulfur analyzer (ca. 7 ppb or  $18 \mu\text{g}/\text{m}^3$ ). The BAAPCD obtains 24-hour bubbler samples (West-Gaeke) at six-day intervals. For the sampling dates September 26, October 2, 8 and 14, the mean 24-hour  $\text{SO}_2$  value was  $4 \mu\text{g}/\text{m}^3$ .<sup>19</sup>

Assuming this mean value is relevant to the days sampled in the current study, the 100% conversion of  $4 \mu\text{g}/\text{m}^3$   $\text{SO}_2$  on a filter would yield  $6 \mu\text{g}/\text{m}^3$  artifact sulfate. Sulfate results on Fluoropore may be used to approximate artifact-free sulfate values.\* As noted above, for four days of sampling, Gelman A and Spectrograde 24-hour hi-vol filters exhibited, on average, 1.6 and  $3.1 \mu\text{g}/\text{m}^3$  higher sulfate values, respectively, compared to Fluoropore. This suggests 27-52% conversion of the assumed  $\text{SO}_2$  level,  $4 \mu\text{g}/\text{m}^3$ .

\*Assuming artifact sulfate formation due to  $\text{SO}_2$ -particulate interactions is negligible.

Table 18

COMPARISON OF CALCULATED<sup>a</sup> AND OBSERVED<sup>b</sup>  
24-HOUR SULFATE VALUES

<u>Filter</u>	<u>Calculated/Observed Ratio of Means</u>	<u>N<sup>c</sup></u>
Gelman A	1.21 ± .09	10
MSA 1106BH	1.85 ± .16	4
Spectrograde	1.20 ± .16	4
Whatman 41	1.00 ± .07	2
Gelman GA-1	1.20 ± .20	4
Fluoropore	1.11 ± .07	4

- 
- a. Calculated as arithmetic mean atmospheric concentrations from four successive 6-hour samples for Hi-vol and Low-vol (total) filter samples.
- b. The sulfate concentration from a filter run continuously for 24 hours.
- c. Number of filter pairs.

### 3. Comparisons Based on Diurnal Variations for Sulfate and Pollutant Gases

As an additional means of evaluating the results, the 6-hour average sulfate data were plotted together with SO<sub>2</sub> concentrations, when the latter were above the detection limit. Figures 12-17 include results for San Jose, and Figures 18-25, for Los Alamitos. The low-volume results show both total and respirable sulfate values.

Diurnal variations for sulfate on different filters will be influenced by the magnitude of the artifact sulfate during each sampling period. This, in turn, will be influenced by such variables as SO<sub>2</sub> concentration and relative humidity (cf. below). Thus, filters differing greatly in potential for artifact sulfate formation might yield significantly different diurnal patterns for sulfate. Filters predicted to produce similar amounts of artifact sulfate should always yield similar diurnal patterns for sulfate.\*

In the present study, distinctly different diurnal patterns were observed in only two cases, involving MSA (lo-vol)-Whatman 41 (hi-vol) and Gelman A (lo-vol)-MSA (hi-vol) in Los Alamitos Episodes C and D (Figures 20 and 21). Results in Table 16 suggest relatively large differences in the degree of artifact sulfate observed on MSA and Whatman 41 filters in 24-hour samples. However, for Gelman A and MSA the difference suggested in 24-hour artifact sulfate in Table 16 is relatively small. Thus, relative results with 24-hour samples cannot be used as a reliable predictor of the degree of similarity in diurnal patterns for sulfate with different filters.

The Los Alamitos sulfate results can be directly compared to SO<sub>2</sub> data since, at least in the afternoons, the SO<sub>2</sub> levels were measurable with a Meloy unit. The diurnal maximum in SO<sub>2</sub> parallels sulfate maxima in most cases, even when Fluoropore filters are used. Notable exceptions are for the MSA (hi-vol) in Episode D and Whatman 41 (hi-vol) in Episode C. Thus, in general, similarity in diurnal patterns between SO<sub>2</sub> and sulfate probably reflect variations in atmospheric concentrations of these species rather than implying the significance of artifact sulfate.

#### C. Nitrate Results

##### 1. Comparisons Based on Mean Results

Table 19 summarizes the 24-hour hi-vol and low-volume results for nitrate. In the cases where two values are shown, these

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\*Even filters differing in filtration efficiency would produce similar diurnal patterns if a constant fraction of sulfate was collected.

Figure 12

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE A (OCTOBER 4-5, 1976)

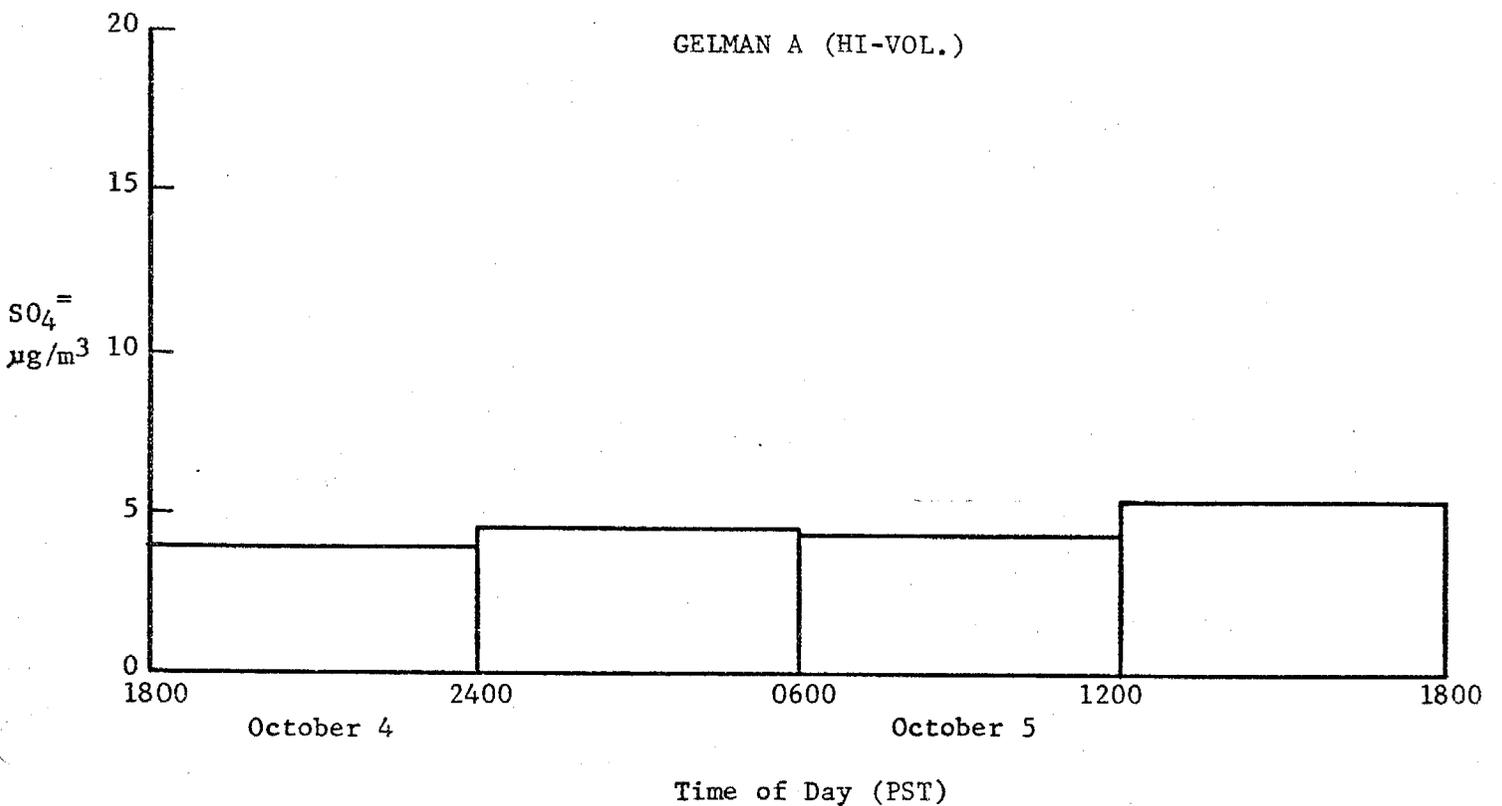
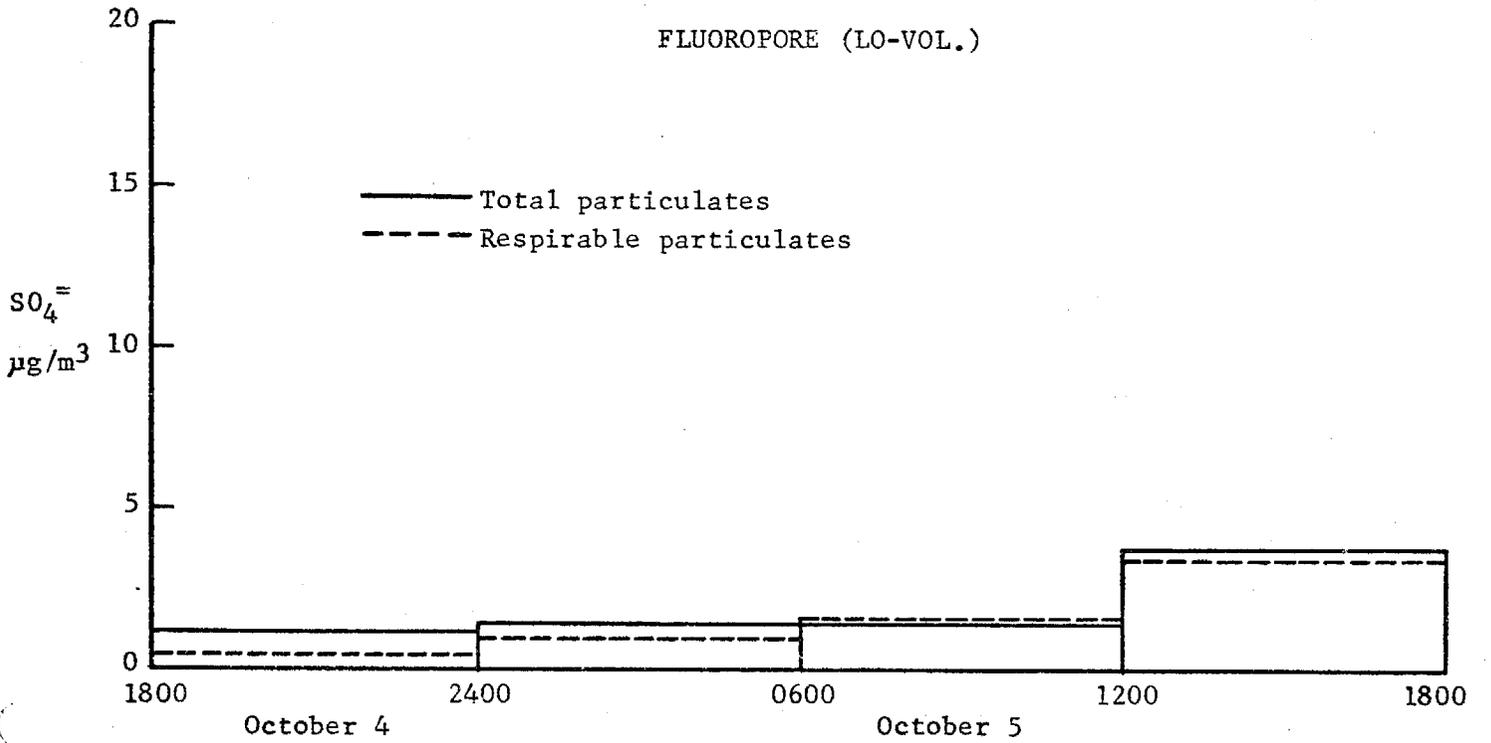


Figure 13

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE B (OCTOBER 5-6, 1976)

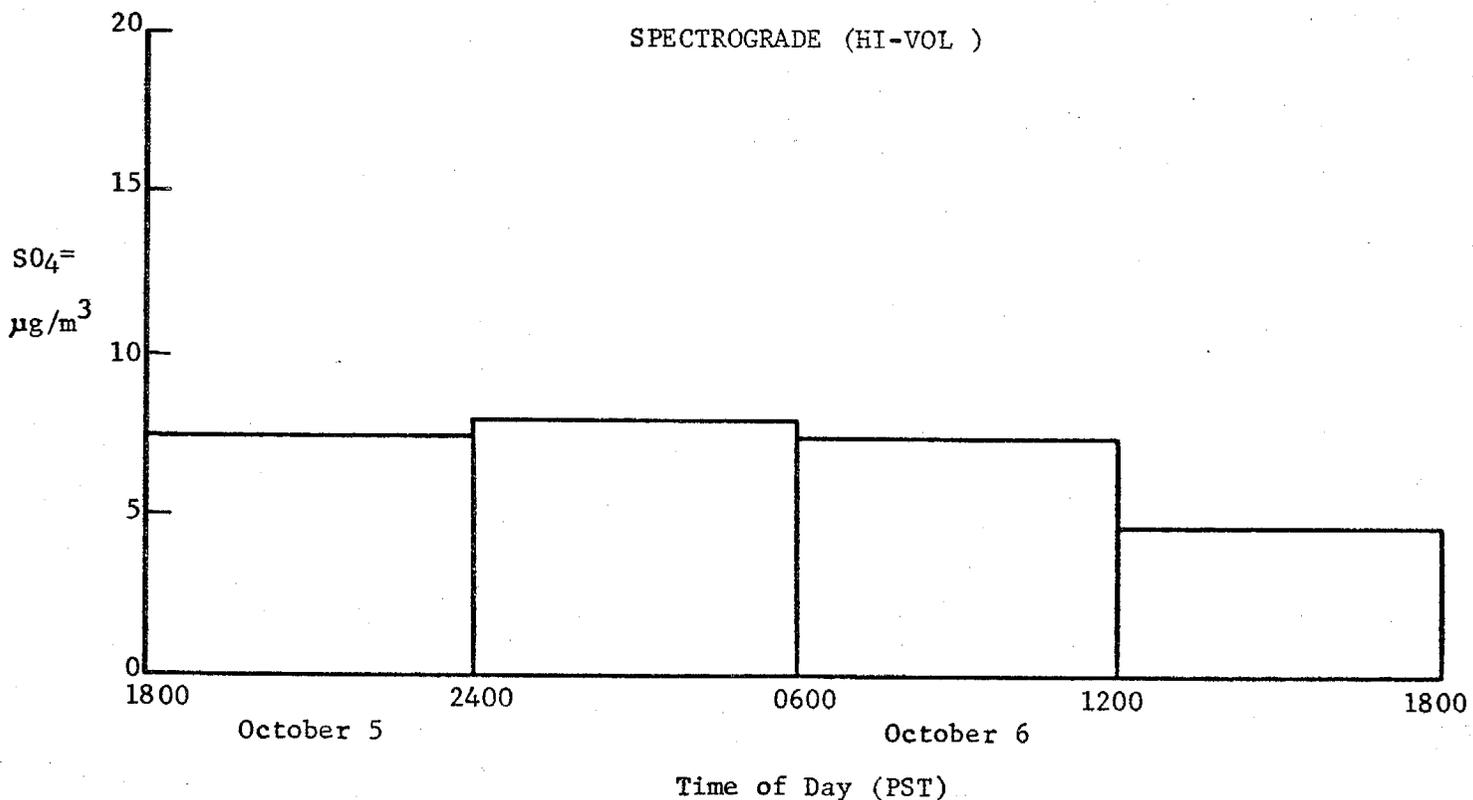
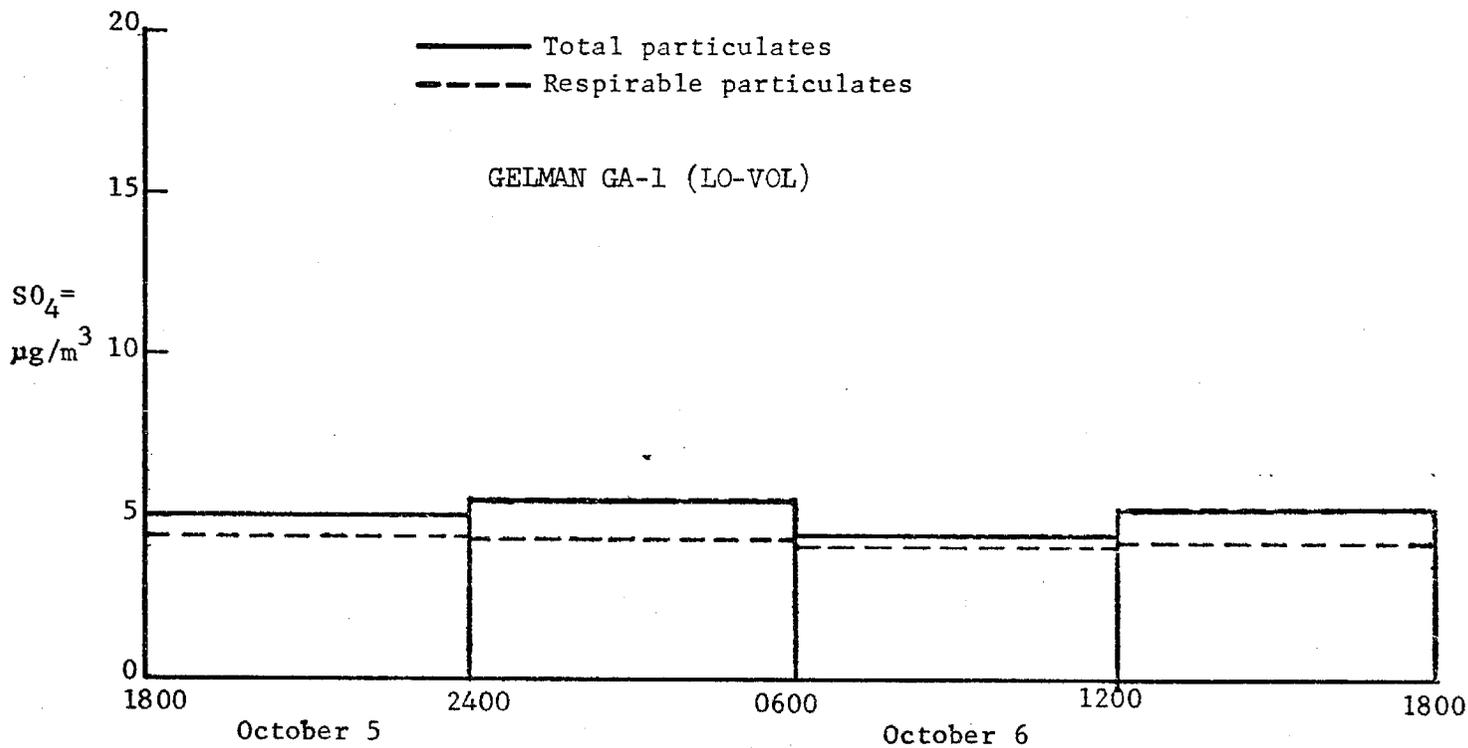


Figure 14

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE C (OCTOBER 6-7, 1976)

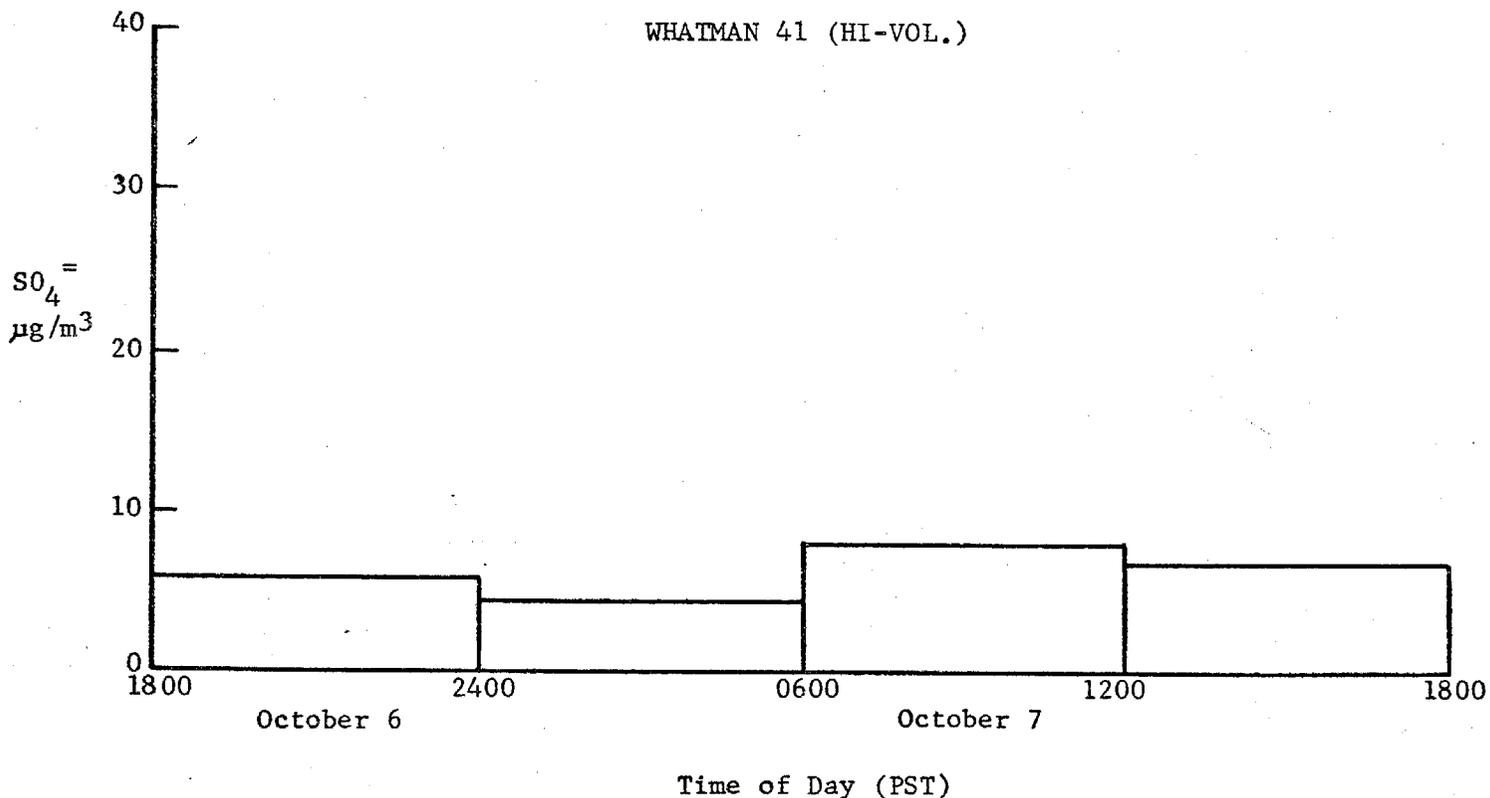
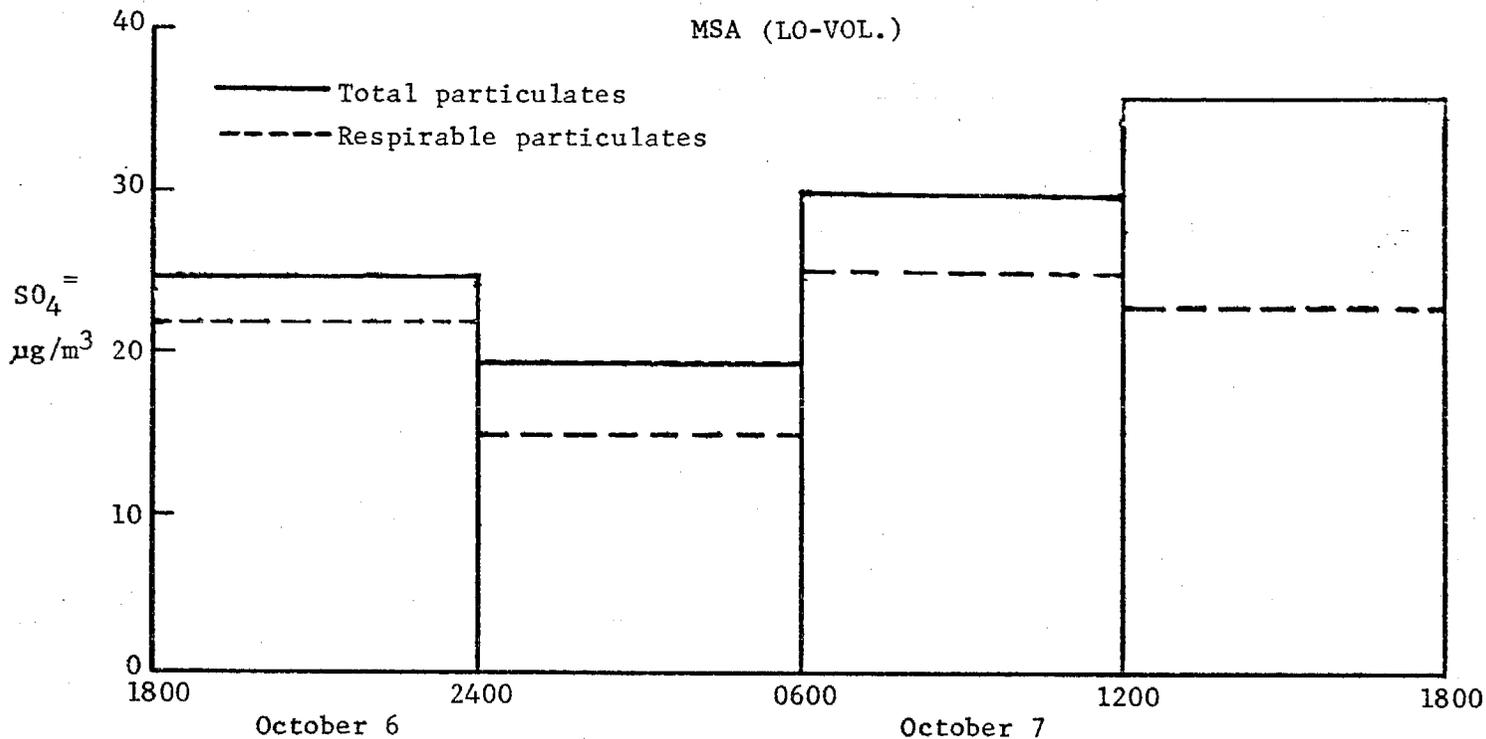


Figure 15

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE D (OCTOBER 7-8, 1976)

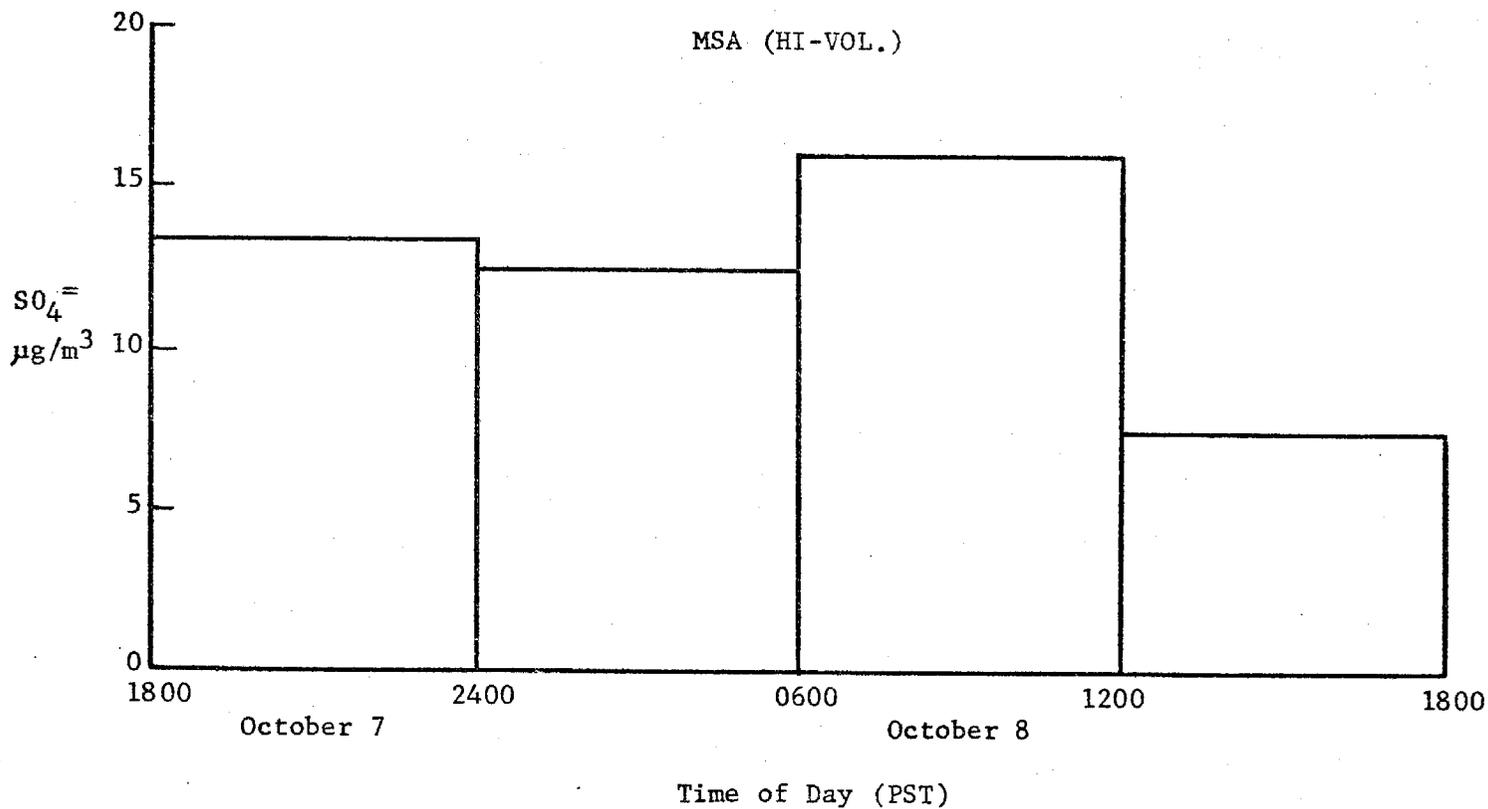
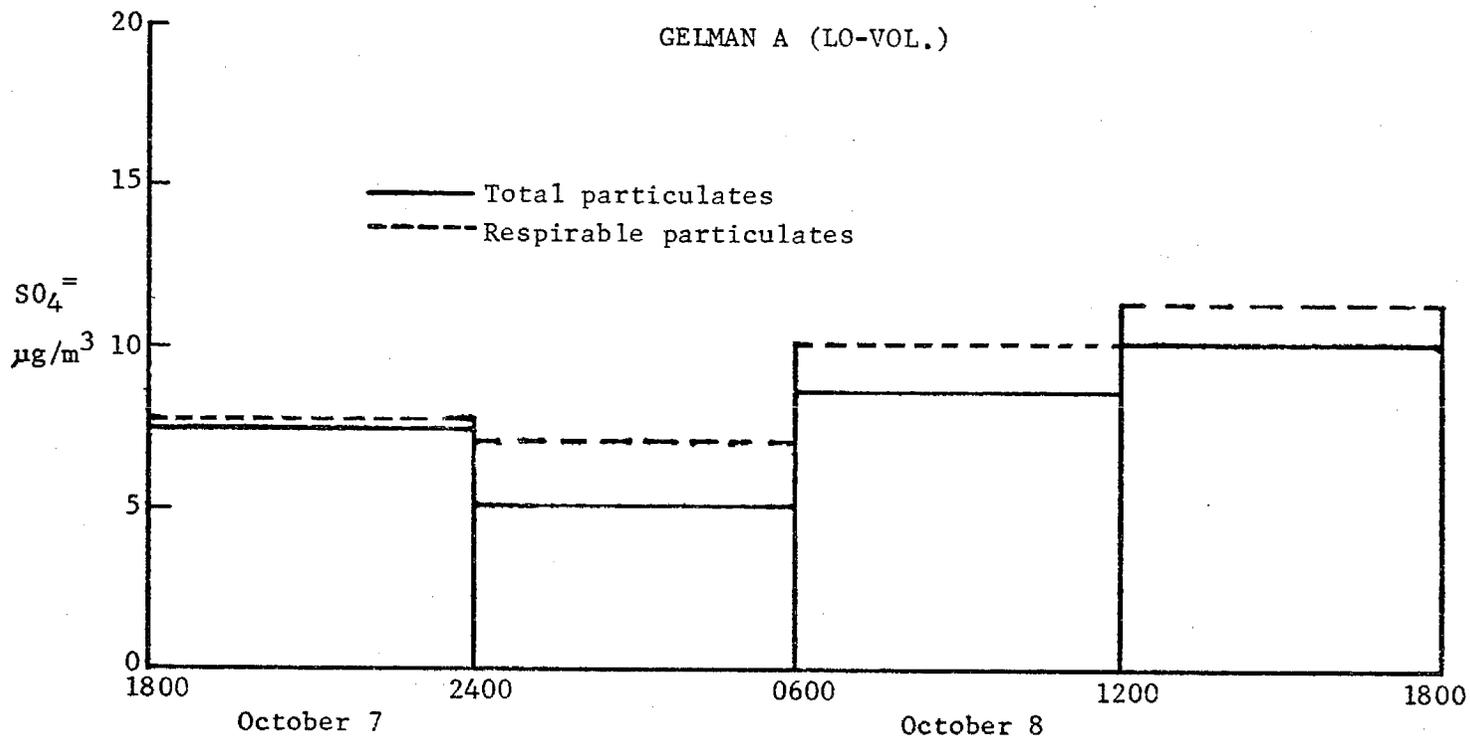


Figure 16

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE E (OCTOBER 8-9, 1976)

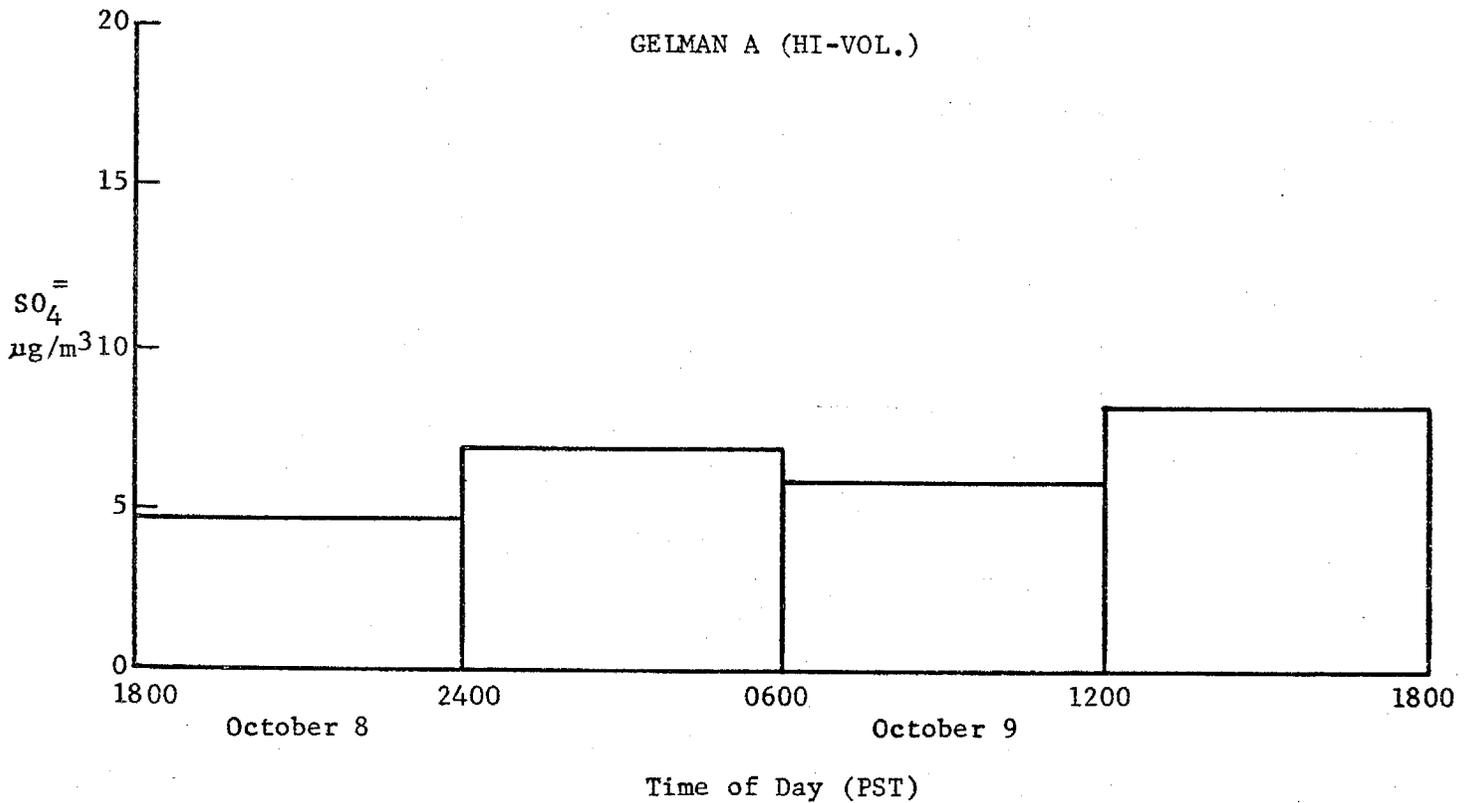
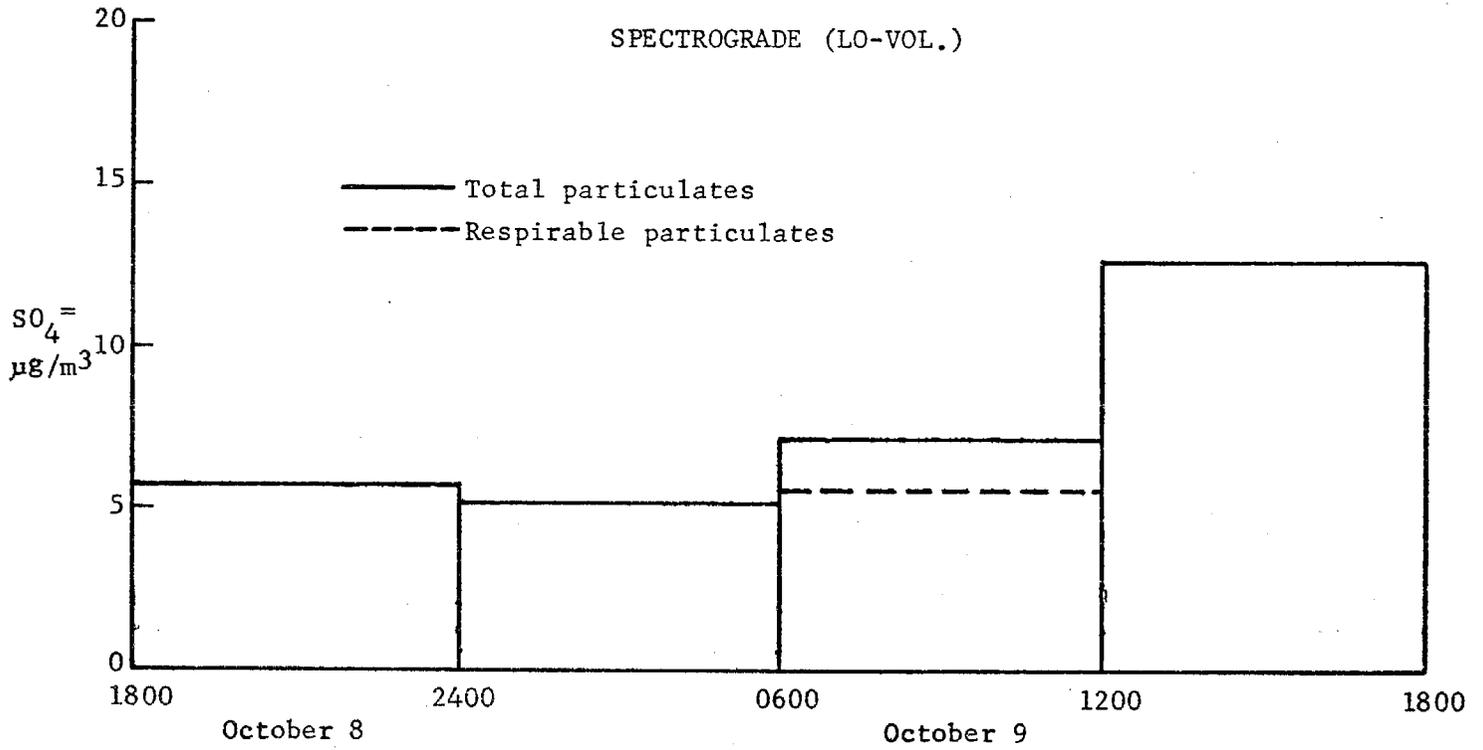
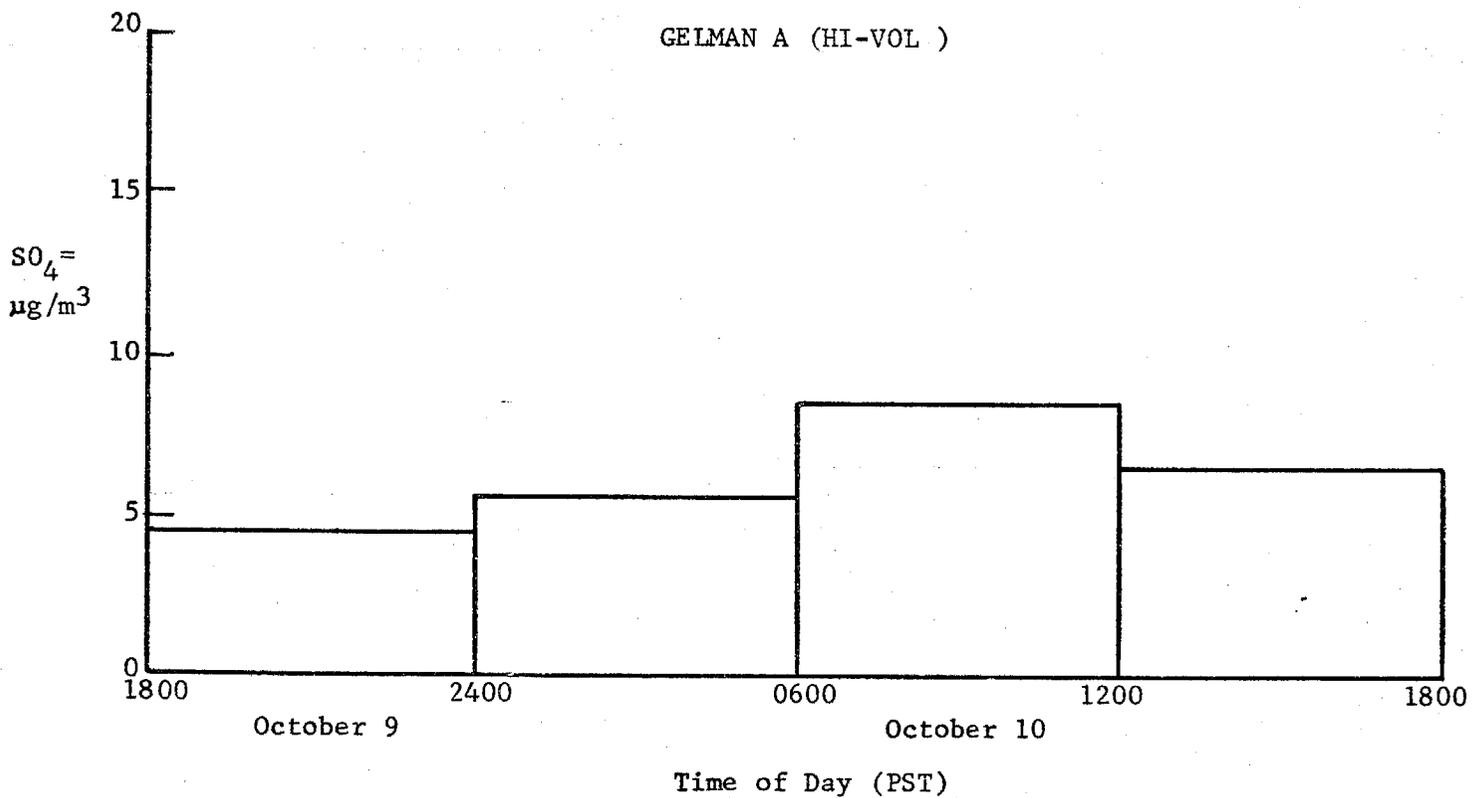
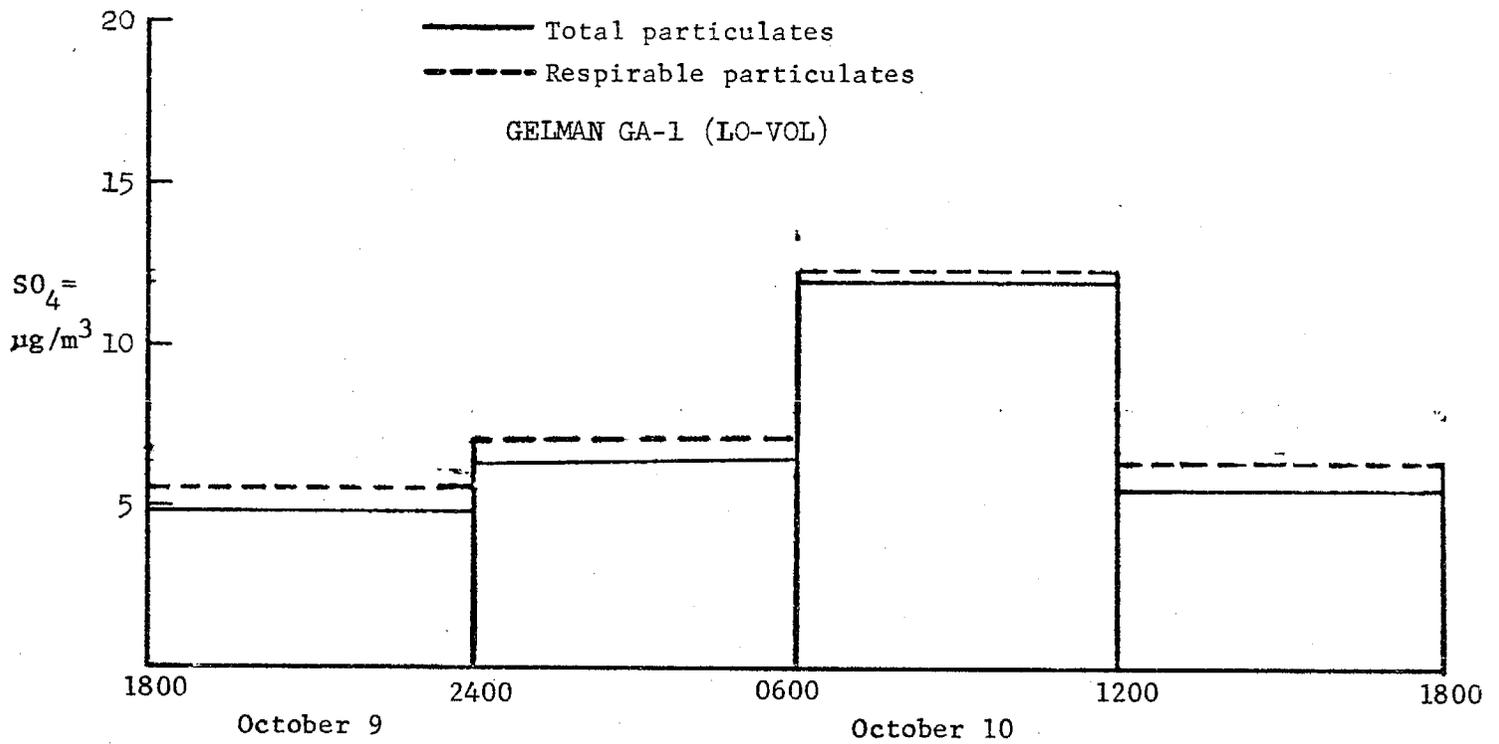


Figure 17

DIURNAL VARIATIONS FOR SULFATE AT SAN JOSE  
EPISODE F (OCTOBER 9-10, 1976)



Time of Day (PST)

Figure 18

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE A, OCTOBER 28-29, 1976

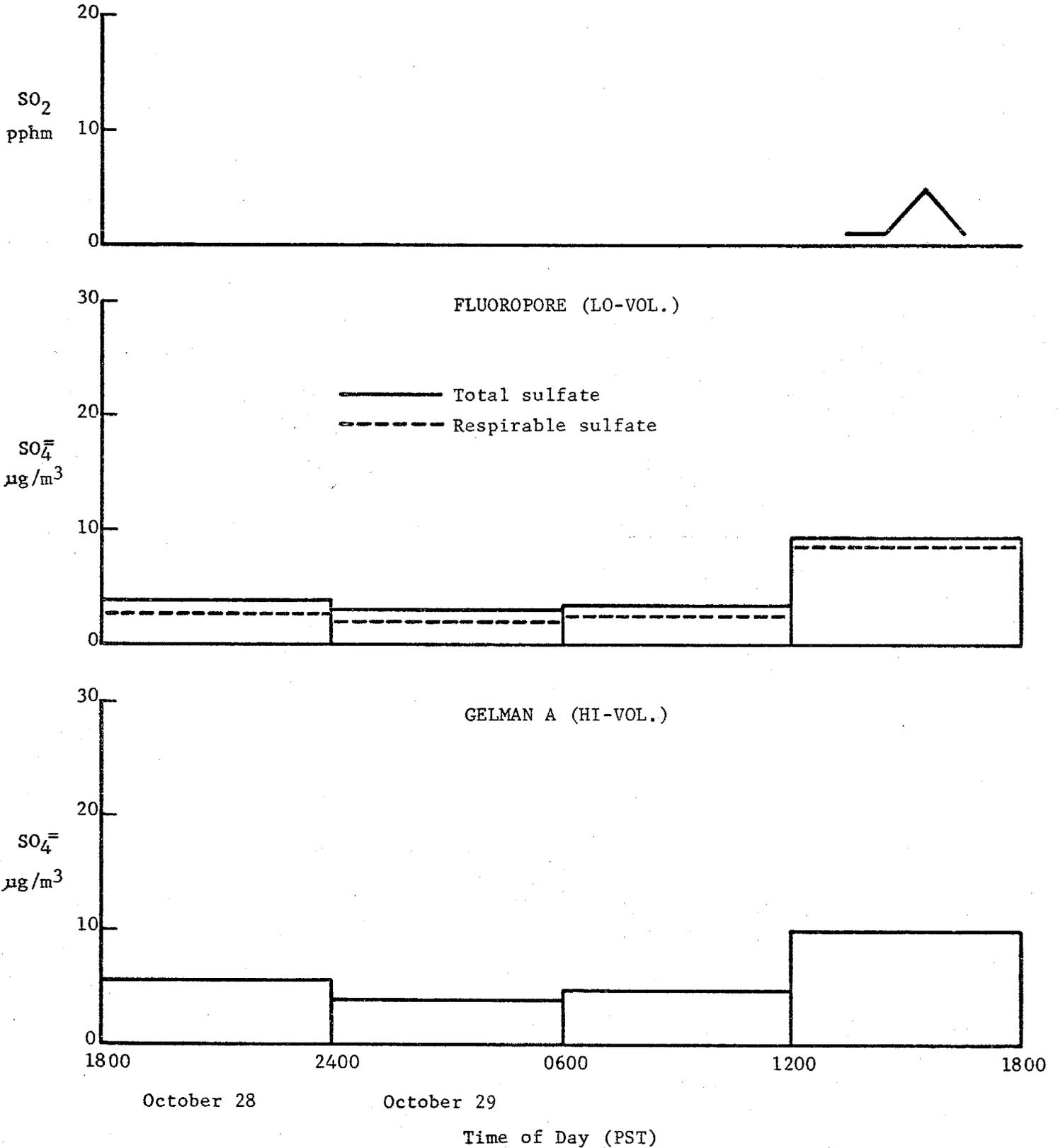


Figure 19

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE B, OCTOBER 29-30, 1976

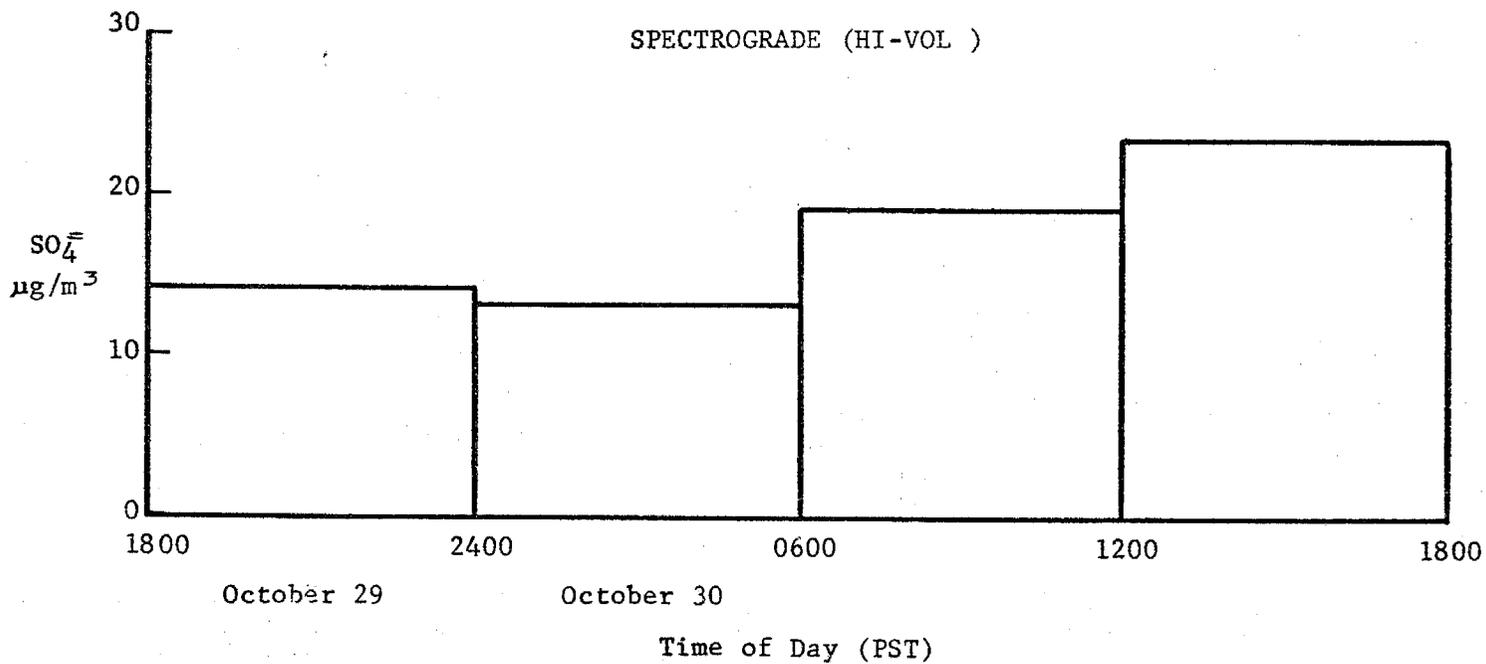
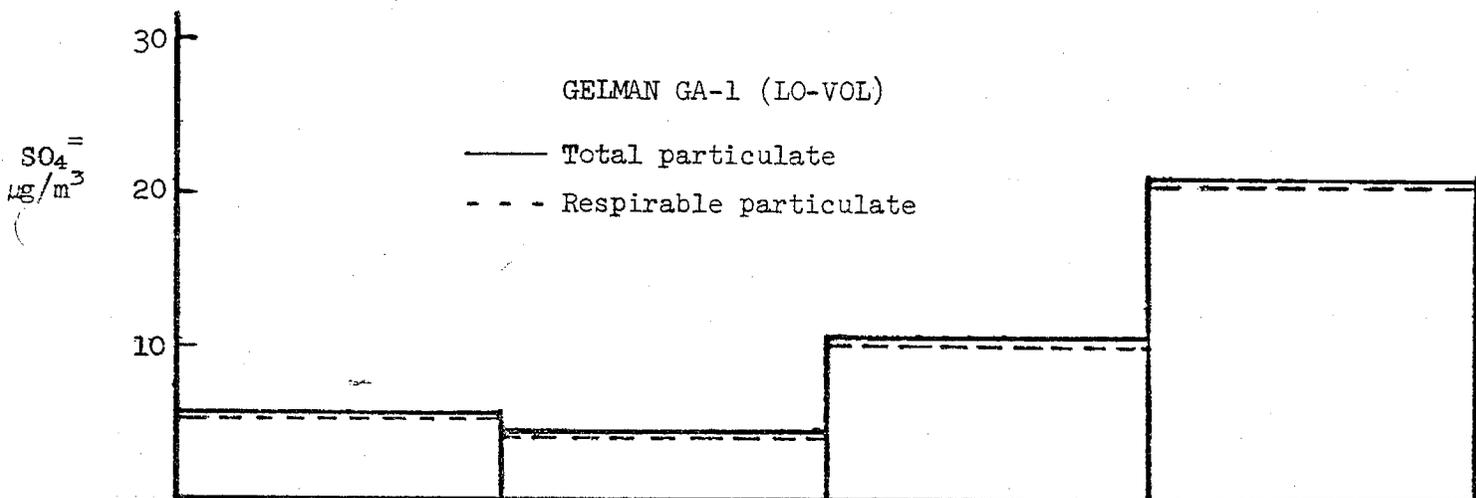
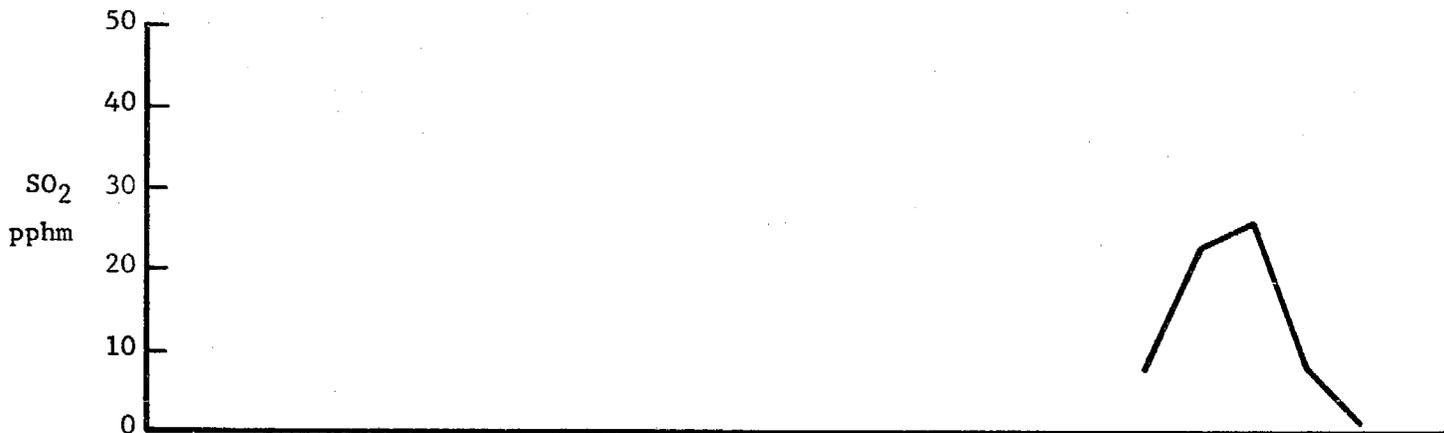


Figure 20

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE C, OCTOBER 30-31, 1976

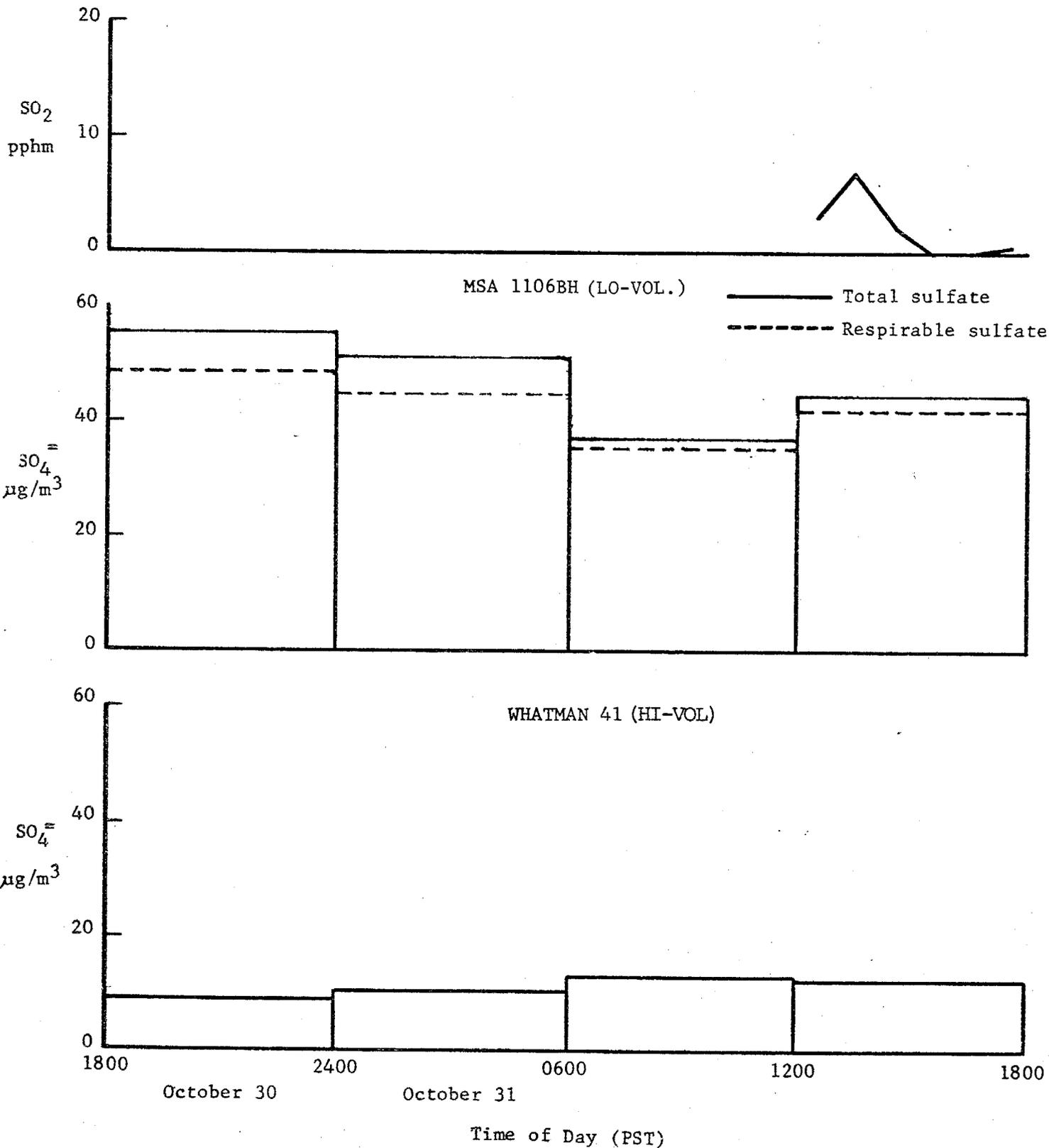


Figure 21

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE D, OCTOBER 31-NOVEMBER 1, 1976

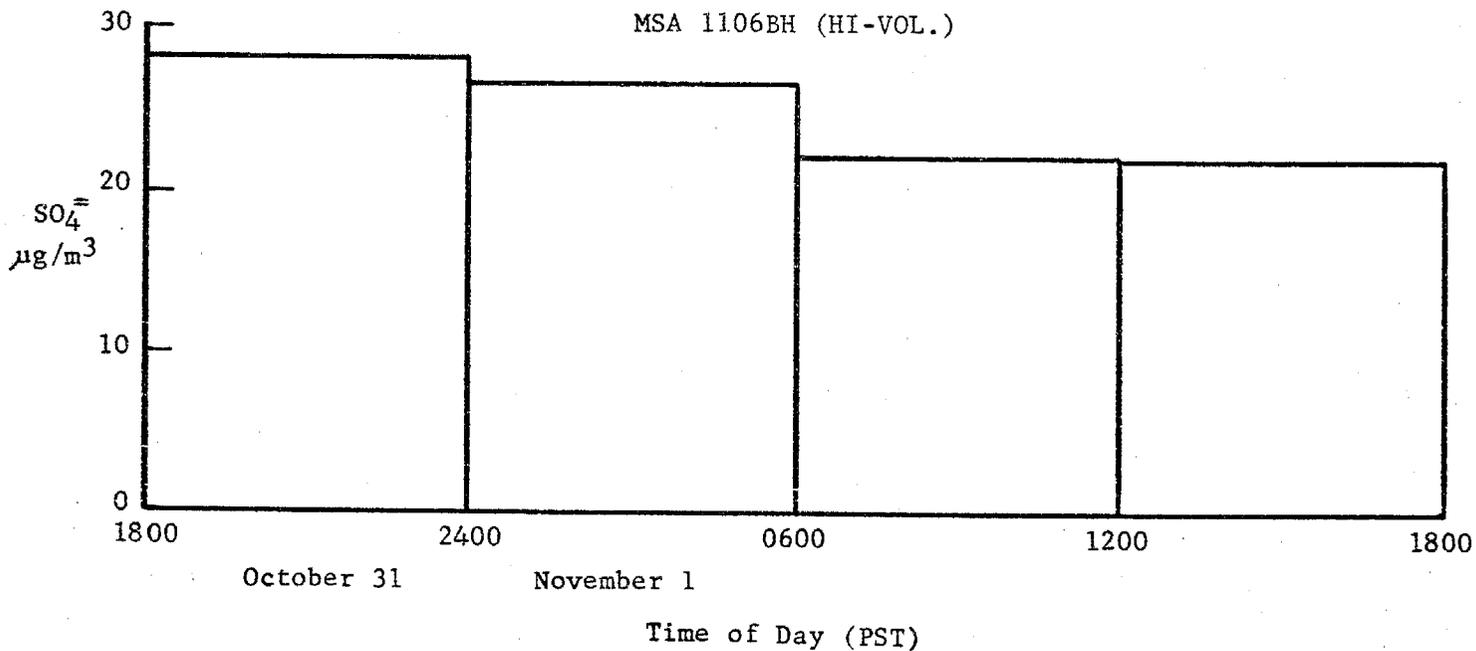
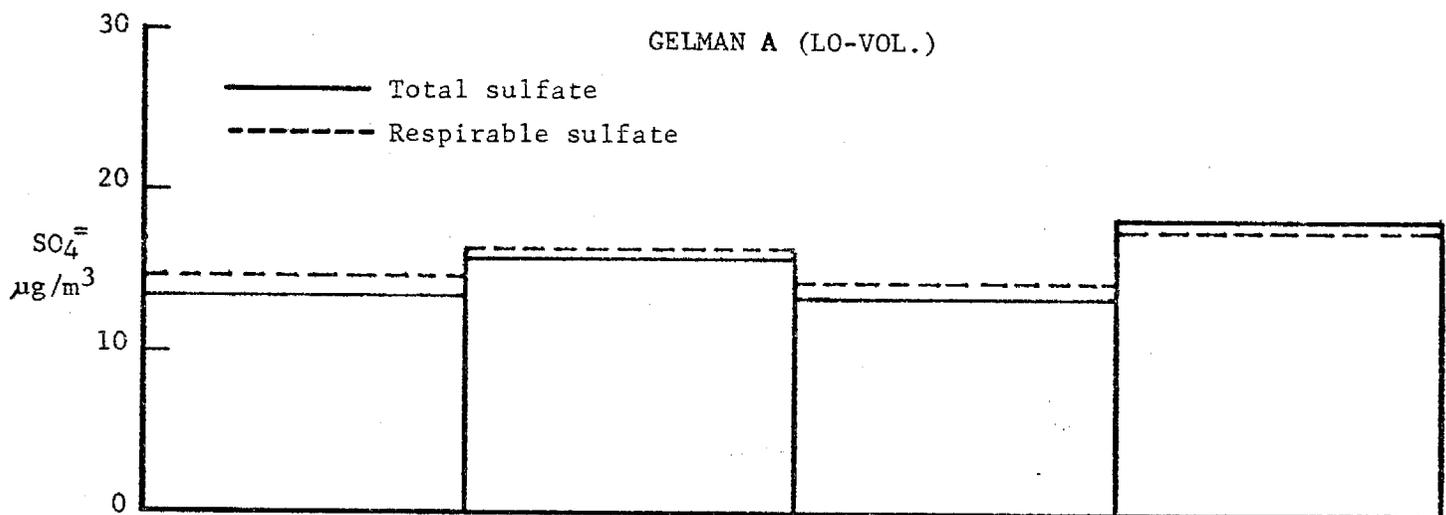
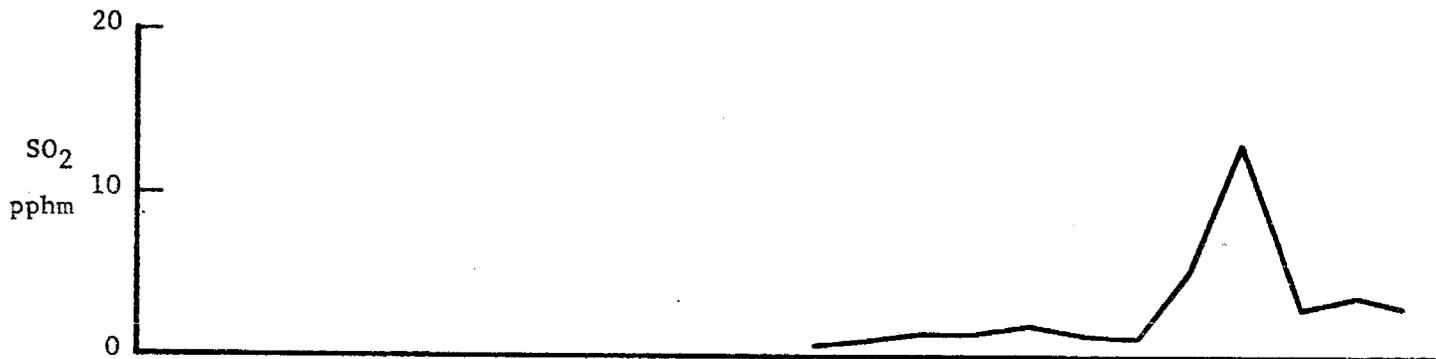


Figure 22

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE E, NOVEMBER 1-2, 1976

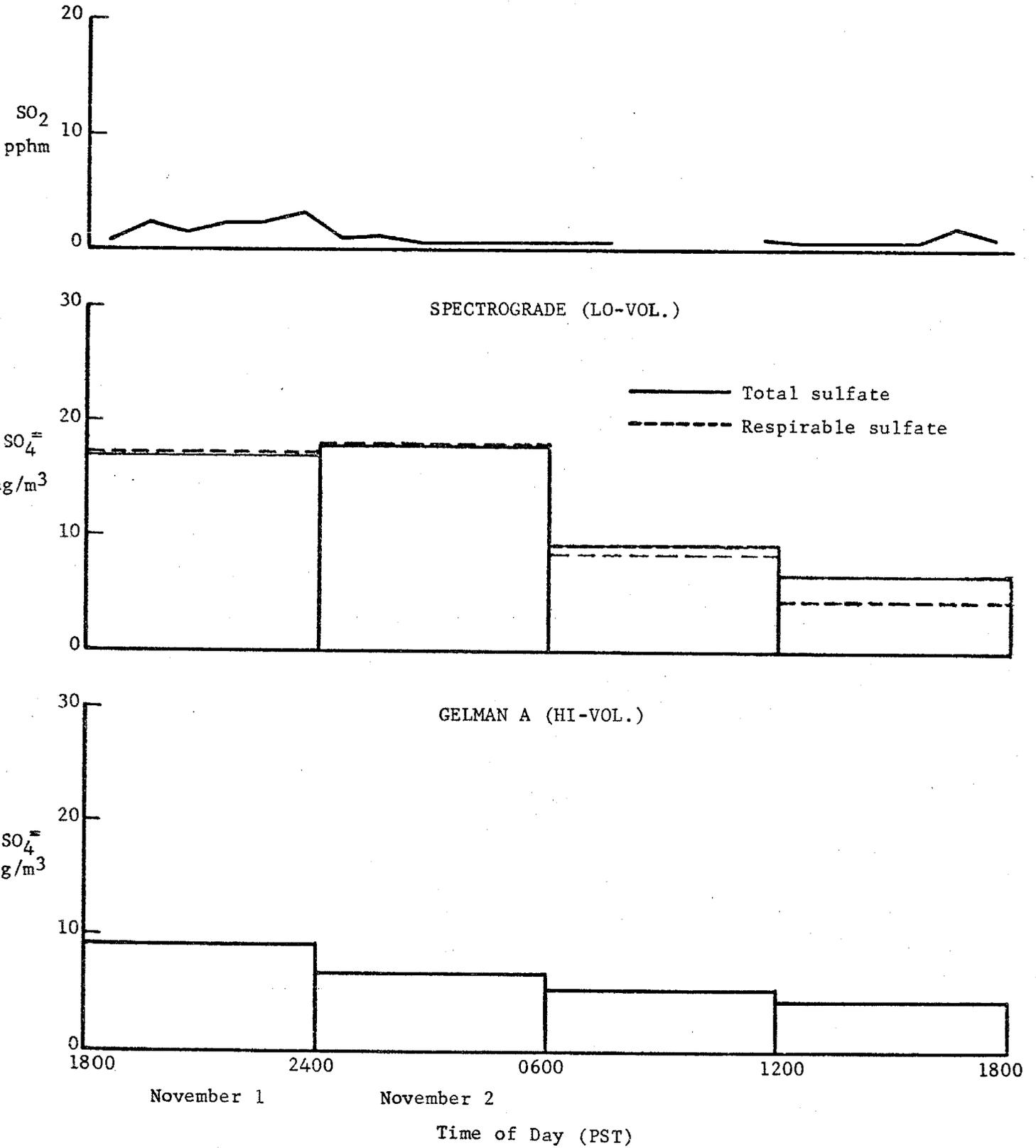


Figure 23

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE F, NOVEMBER 2-3, 1976

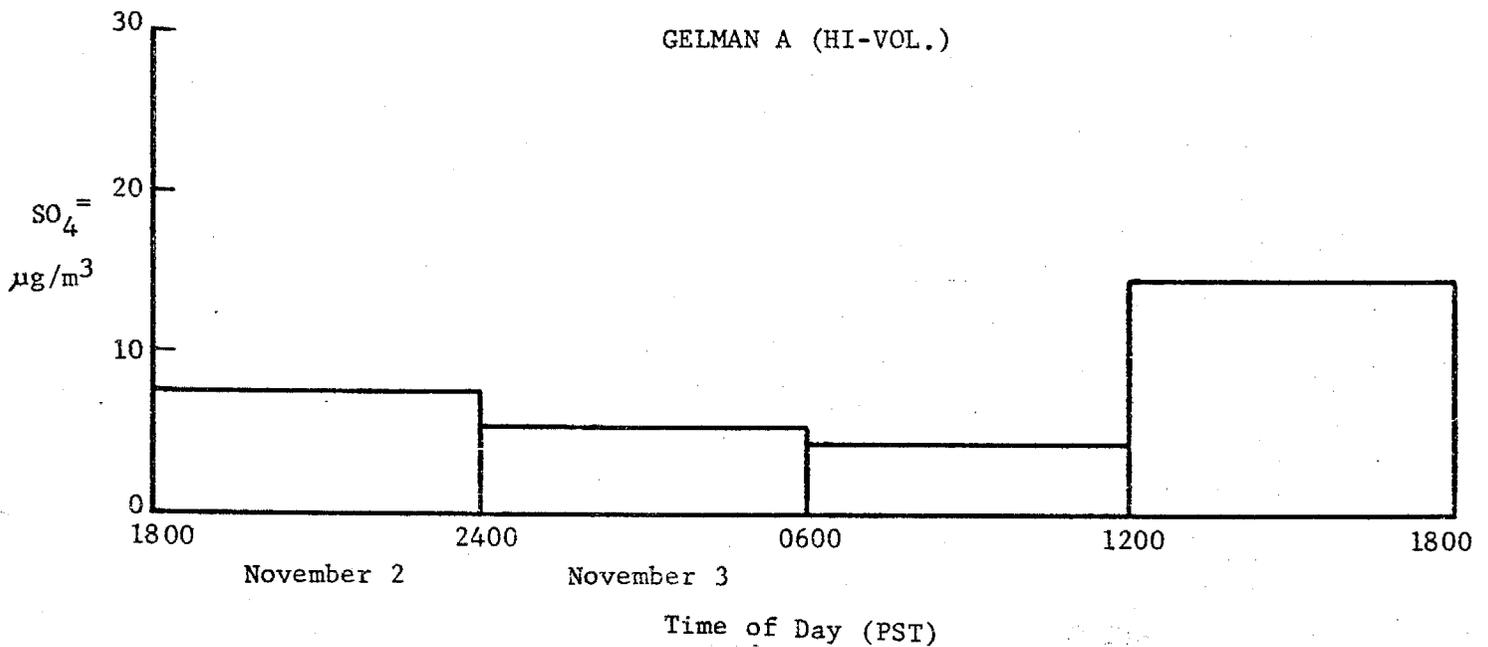
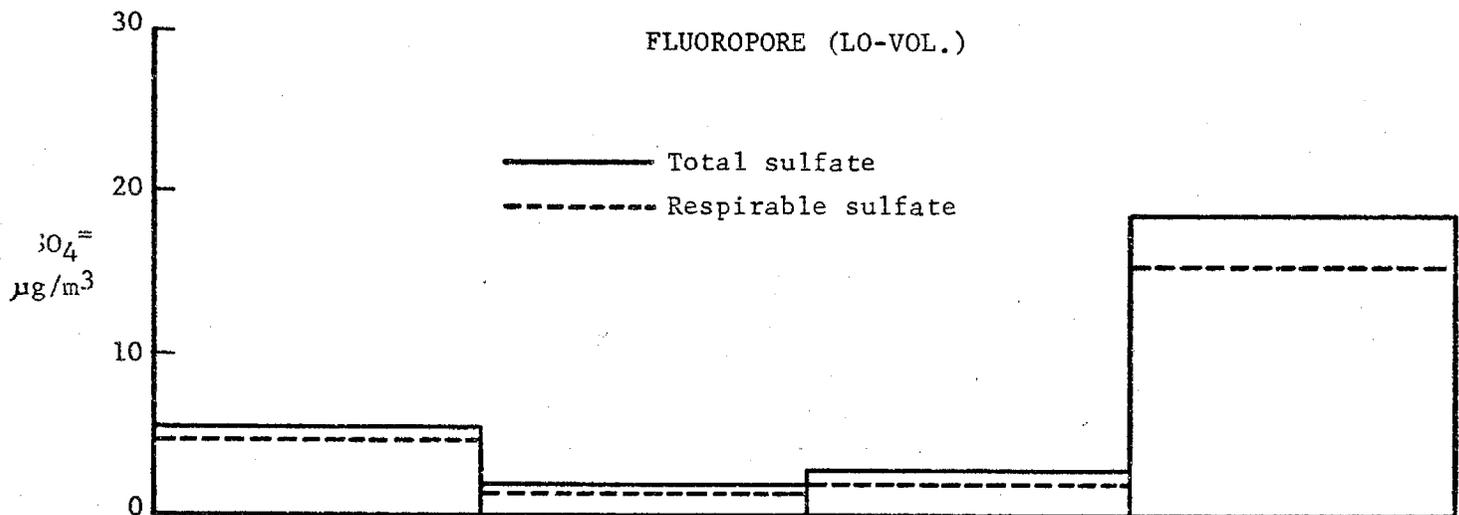
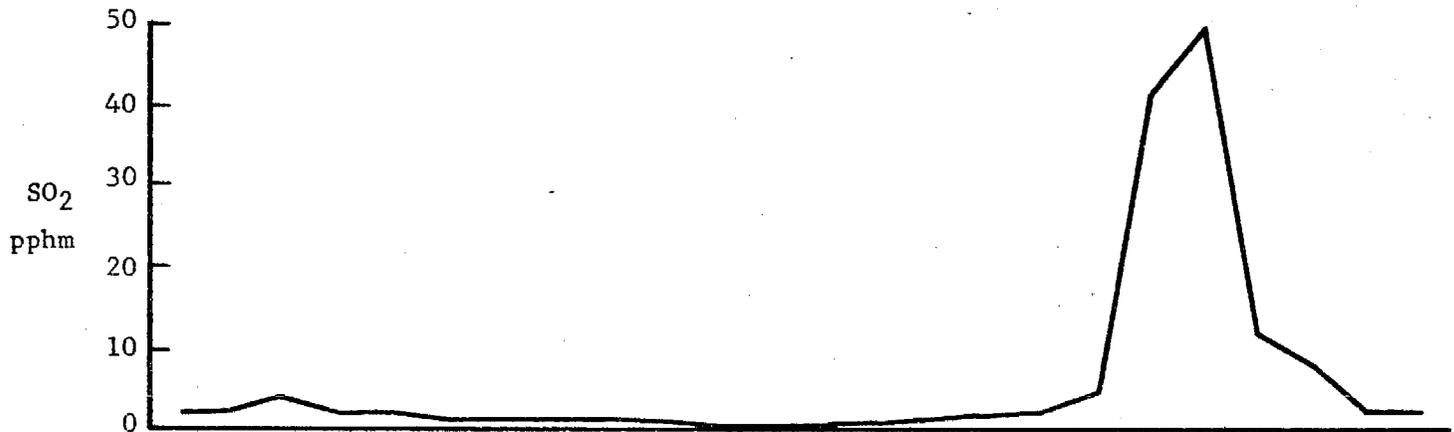


Figure 24

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE G, NOVEMBER 3-4, 1976

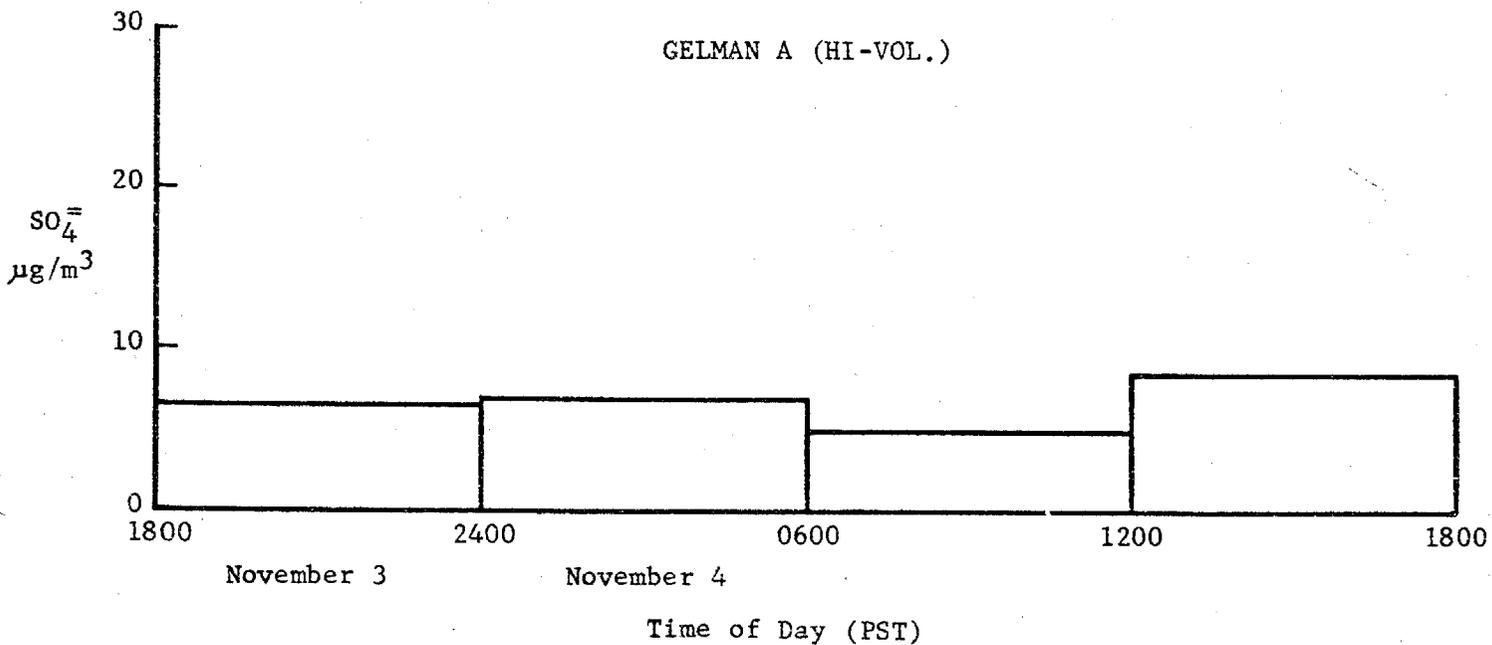
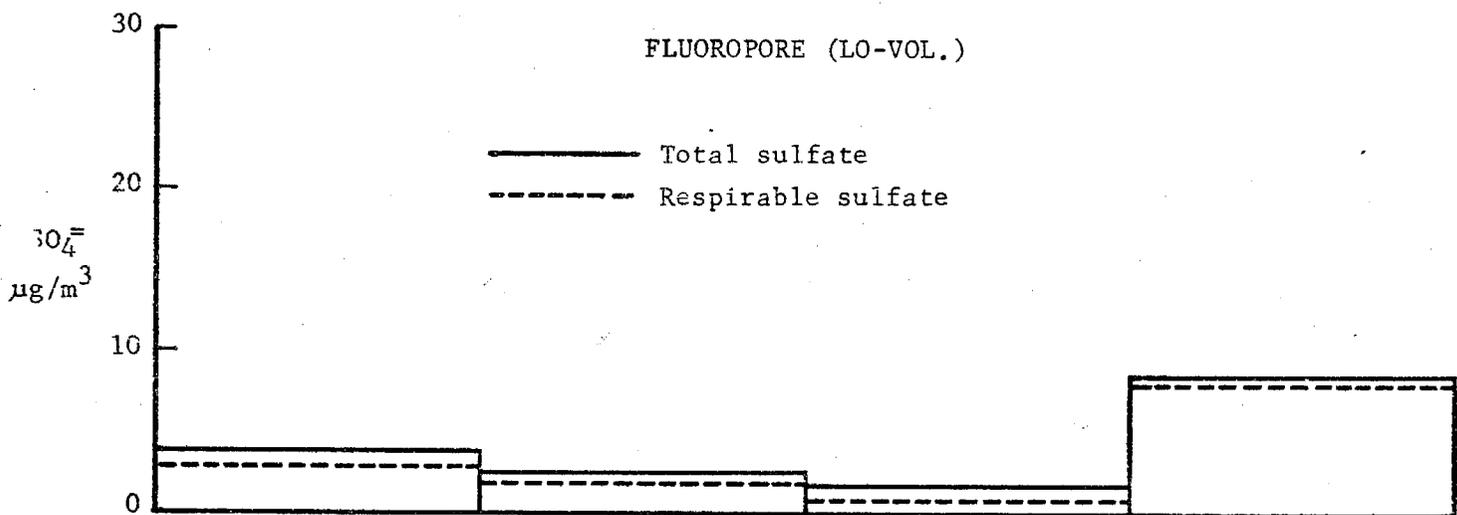
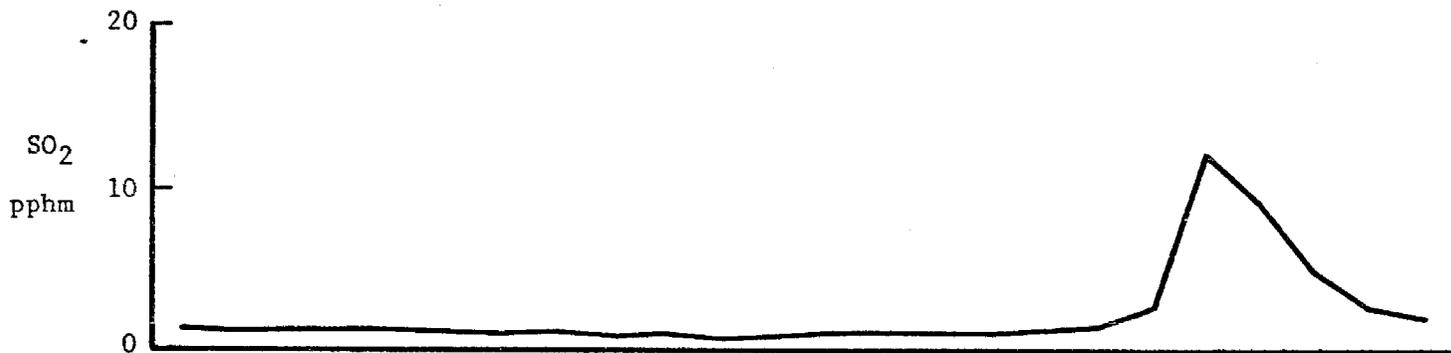
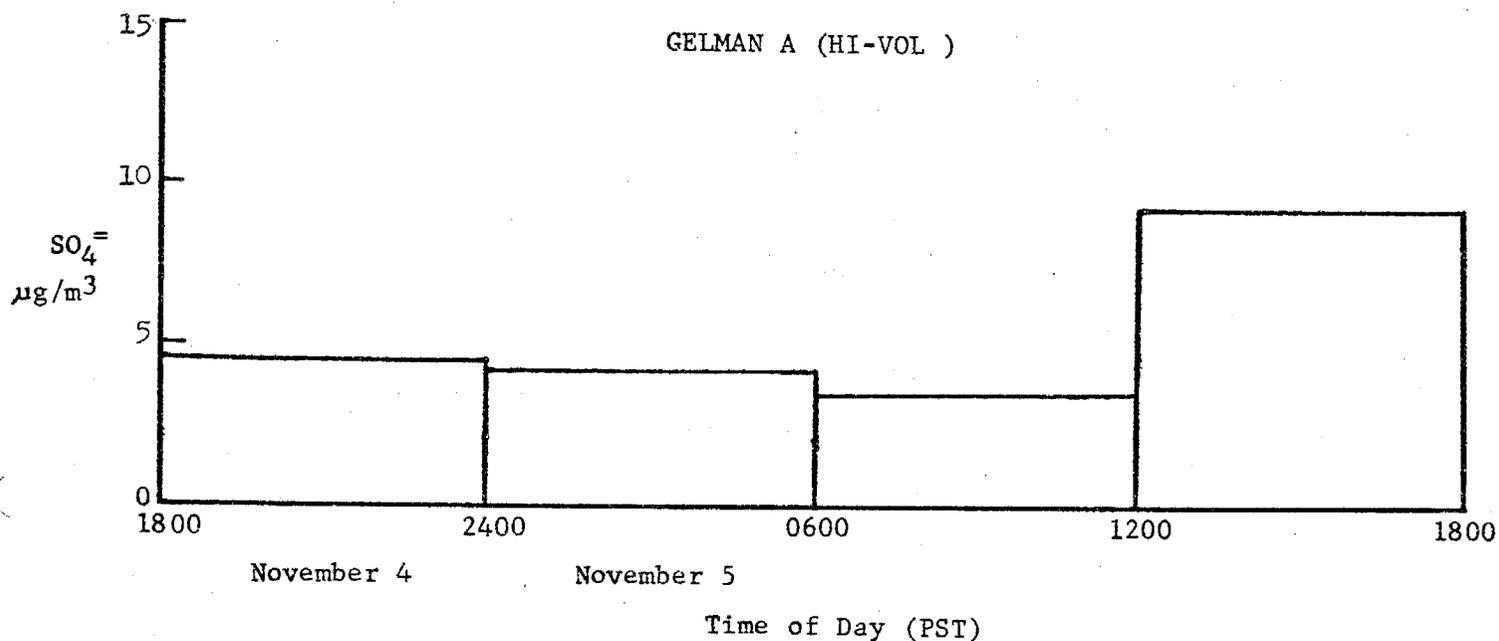
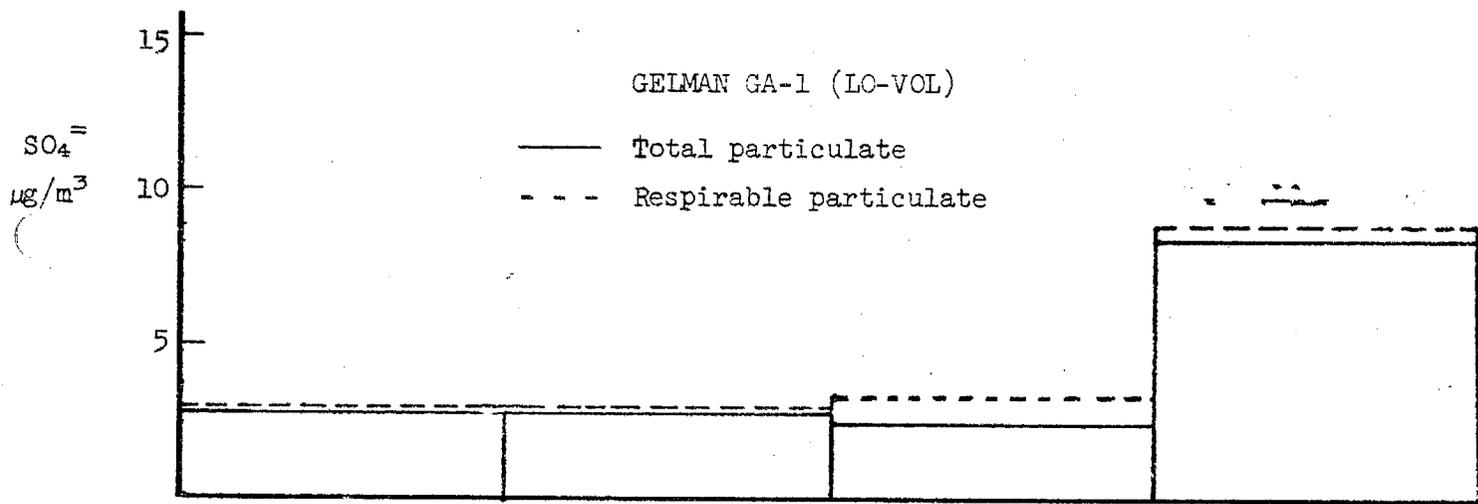
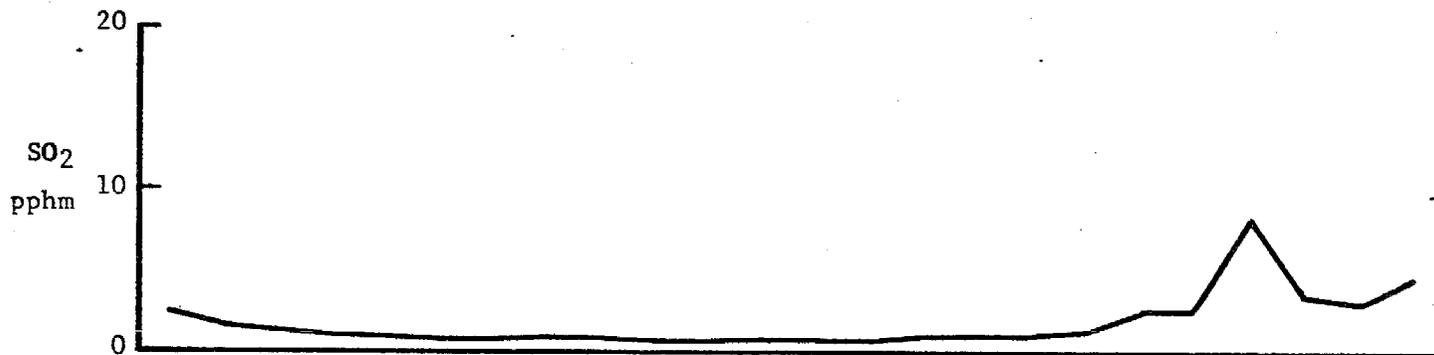


Figure 25

DIURNAL VARIATIONS FOR SULFATE  
LOS ALAMITOS, EPISODE H, NOVEMBER 4-5, 1976



NITRATE RESULTS FROM 24-HOUR SAMPLES ( $\mu\text{g}/\text{m}^3$ )

## SAN JOSE

Date (EPISODE)	High-Volume Samples				Low-Volume Samples			
	Gelman A	MSA 1106EH	Whatman 41	Spectro- grade	Gelman A	MSA 1106EH	Spectro- grade	Fluoro- pore
Oct 4-5 (A)	9.9 <sup>a</sup> 11.1		12.4	16.5				7.3
Oct 5-6 (B)	6.3	12.3 <sup>b</sup>		13.7 10.6				
Oct 6-7 (C)	22.0		15.9 25.5	25.0		27.2		
Oct 7-8 (D)	14.5	15.6 15.5		15.0	14.8			
Oct 8-9 (E)	15.7 <sup>b</sup>		21.3	22.6 21.2			21.2 <sup>b</sup>	
Oct 9-10 (F)	10.6 <sup>b</sup>		11.1	12.1 <sup>b</sup>				

## LOS ALAMITOS

Oct 28-29 (A)	7.8 <sup>b</sup> 7.6 <sup>b</sup>		7.6	10.5				3.5
Oct 29-30 (B)	14.1	14.5		17.2 <sup>b</sup> 17.5				
Oct 30-31 (C)	39.0		42.7 41.7	43.5		60.6		
Oct 31-Nov 1 (D)	24.8	25.8 28.2		27.8	24.2 <sup>b</sup>			
Nov 1-2 (E)	13.9 <sup>b</sup>		18.1 <sup>b</sup>	20.5 18.3			20.2	
Nov 2-3 (F)	10.7 <sup>b</sup>	17.5 <sup>b</sup> 15.7		13.4 <sup>b</sup>				6.1
Nov 3-4 (G)	4.7	10.2		8.7				3.4
Nov 4-5 (H)	4.3 3.5		6.6	8.0 <sup>b</sup>				

a. Two values indicate results from separate samplers.

b. Mean of two determinations on the same sample.

represent results for two samplers operated with the same filter medium. From these data we calculate the following:

- a. The precision of hi-vol sampling for nitrate was 8.6%, as measured by the mean coefficient of variation for twelve paired samples collected side-by-side on different samplers but with the same filter type. The poorest precision was observed for Whatman 41 which, at times, exhibited large flow changes with increased loading.\* This poor precision resulted, in part, from the uncertainty in using the average of initial and final flow rates and from the imprecision of final flowmeter readings  $\leq 20$  cfm.
- b. In the four cases in which 24-hour hi-vol as well as low-volume results are available for the same filter type run simultaneously (Gelman A, Gelman Spectrograde twice each), the results agree within 4%.
- c. Comparing hi-volume filter samples, the nitrate results follow the order Gelman A < Whatman 41 < MSA 1106BH = Gelman Spectrograde.
- d. Fluoropore (low-volume) results for nitrate are, on average, almost half of those obtained on Gelman A.

The nitrate results for 6-hour hi-vol and low-volume samples are given in Tables 20 and 21, with separate results listed for respirable and total low-volume samples. The results on the different filters are compared in Table 22. From these results and comparisons we note the following:

- a. In spite of its lower initial filtration efficiency, observed nitrate levels on Whatman 41 were invariably greater than on some of the glass fiber filters. Accordingly, particle collection efficiency effects are not the dominant factor in controlling observed nitrate levels.
- b. Both with 6- and 24-hour samples, Fluoropore low-vol nitrate results are about half of those with Gelman A hi-vol filter samples.

\*The samplers available for this study were not equipped with constant flow controllers.

TABLE 20

NITRATE RESULTS FROM SIX-HOUR SAMPLES AT SAN JOSE ( $\mu\text{g}/\text{m}^3$ )

## High-Volume Samples

## Low-Volume Samples

Date (EPIS DE)	Time PST	High-Volume Samples			Low-Volume Samples				
		Gelman A	MSA 1106BH	Whatman 41	Spectrograde	Gelman A <sup>a</sup>	MSA 1106BH	Spectrograde	Fluoropore
						T <sup>d</sup>	R	T	R
Oct 4-5 (A)	18-24	10.0						5.5	1.5
	24-6	7.2						4.1	- <sup>d</sup>
	6-12	21.9						12.1 <sup>c</sup>	10.8
	12-18	15.6						5.0	2.4
Oct 5-6 (B)	18-24				10.5				
	24-6				9.0				
	6-12				25.8				
	12-18				25.3				
Oct 6-7 (C)	18-24			31.7					
	24-6			13.3		29.3	20.6		
	6-12			11.5		12.9	10.1		
	12-18			29.0 <sup>c</sup>		33.7	27.0		
Oct 7-8 (D)	18-24								
	24-6		8.4						
	6-12		7.5						
	12-18		30.2						
Oct 8-9 (E)	18-24	18.4							
	24-6	12.7 <sup>c</sup>						16.4 <sup>c</sup>	9.7
	6-12	20.4						18.3	9.7
	12-18	30.5 <sup>c</sup>						13.9	14.5
Oct 9-10 (F)	18-24	9.7						31.0	19.6
	24-6	10.5							
	6-12	20.7							
	12-18	11.0							

a. Total filters collecting particles < ca. 20  $\mu\text{m}$ .b. Respirable filter sampler collecting particles < 3.5  $\mu\text{m}$ .

c. Mean of two determinations.

d. Below working range of method.

TABLE 21

NITRATE RESULTS FROM SIX-HOUR SAMPLES AT LOS ALAMITOS ( $\mu\text{e}/\text{m}^3$ )

Date (EPISODE)	Time PST	High-Volume Samples				Low-Volume Samples				
		Gelman A	MSA 1106RH	Whatman 41	Spectrograde	Gelman A T <sup>a</sup> R <sup>b</sup>	MSA 1106RH T R	Spectrograde T R	Fluoropore T R	
Oct 28-29 (A)	18-24	5.6							2.3	1.1
	24-6	6.2							3.7	2.2
	6-12	16.3							5.6	3.1
	12-18	9.2							2.6	d
Oct 29-30 (B)	18-24				8.3					
	24-6				7.9					
	6-12				28.4					
	12-18				24.7					
Oct 30-31 (C)	18-24			27.1			23.7	16.0		
	24-6			37.6			43.9	40.2		
	6-12			84.1			77.4	78.6		
	12-18			30.4			35.0 <sup>c</sup>	26.3		
Oct 31-Nov 1 (D)	18-24		20.8			17.4				
	24-6		21.1			27.4				
	6-12		62.3			57.5				
	12-18		34.0			19.9				
Nov 1-2 (E)	18-24	22.6							15.7	
	24-6	20.0							16.9	
	6-12	24.2							20.6	
	12-18	12.6							8.7	
Nov 2-3 (F)	18-24	14.8								4.4
	24-6	7.0							5.5	3.4
	6-12	19.1							8.9	7.8
	12-18	14.6							6.6	3.6
Nov 3-4 (G)	18-24	22.1 <sup>c</sup>								12.6
	24-6	12.7								11.2
	6-12	7.3								2.2
	12-18	3.8 <sup>c</sup>								d
Nov 4-5 (H)	18-24	7.8								
	24-6	1.1								
	6-12	11.4								
	12-18	6.9								

c. Mean of two determinations.

d. Below working range of method.

a. Total filters collecting particles < ca. 20  $\mu\text{m}$ .b. Respirable filter sampler collecting particles < 3.5  $\mu\text{m}$ .

Table 22

## COMPARISON OF NITRATE RESULTS ON DIFFERENT FILTER MEDIA

<u>Sample/Reference</u>	<u>Ratio of Means</u>					
	<u>24-Hour Results</u>			<u>6-Hour Results</u>		
	<u>Gelman A</u>	<u>Fluoropore</u>	<u>N<sup>a</sup></u>	<u>Gelman A</u>	<u>Fluoropore</u>	<u>N<sup>a</sup></u>
Gelman A, Hi-Vol	1.00	1.67		1.00	2.00	
MSA 1106BH, Hi-Vol	1.29 ± .14	2.15	6			
Whatman 41, Hi-Vol	1.14 ± .06	1.90	8			
Spectrograde, Hi-Vol	1.27 ± .06	2.12	14			
Gelman A, Lo-Vol <sup>b</sup>	0.99 ± .02	1.65	2			
MSA 1106BH, Lo-Vol <sup>b</sup>	1.44 ± .15	2.40	2			
Spectrograde, Lo-Vol <sup>b</sup>	1.39 ± .05	2.32	2	1.01 ± .06	2.02	8
Gelman GA-1, Lo-Vol <sup>b</sup>	1.29 ± .21	2.15	4	1.00 ± .07	2.00	8
Fluoropore, Lo-Vol <sup>b</sup>	0.60 ± .06	1.00	4	0.50 ± .04	1.00	15

a. Number of filter pairs.

b. Total filter samples.

- c. Spectrograde low-vol (total filter) results for 6 hours are about equal, on average, to Gelman A hi-vol results. However, with 24-hour samples Spectrograde yielded substantially higher values. Spectrograde low-vol results, relative to Fluoropore low-vol, are about equal for 6-hour and 24-hour samples. Since minimal artifact nitrate formation is likely for Fluoropore, these results imply that the level of artifact nitrate formation on 6-hour Gelman A filters is somewhat greater than on 24-hour Gelman A filters.

The mean fraction of nitrate in the respirable size range, as obtained with 6-hour low-volume samples is summarized in Table 23. If nearly all observed nitrate resulted from artifact formation by interaction of the filter with  $\text{HNO}_3$  or  $\text{NO}_2$  (which would not be influenced by a cyclone), then the observed fraction of respirable nitrate would always be about 1.0. Filters providing the least artifact nitrate would be expected to show the lowest value for the fraction of respirable nitrate.

The results indicate about equal values for Fluoropore and Spectrograde filters. MSA 1106BH and Gelman A results are also about equal but somewhat higher than for Fluoropore and Spectrograde. The results for Fluoropore are consistent with findings in the preceding tables which indicated that Fluoropore invariably yielded lower nitrate values. However, the results with Spectrograde appear anomalous considering the relatively high nitrate yields found from this filter. The variability in this ratio is especially large, however.

The ratios of observed 24-hour values to those calculated from four 6-hour values is given in Table 24. In contrast to expectations, results for Spectrograde, Whatman 41, Fluoropore and MSA are similar and close to 1.0. Since artifact nitrate may involve interaction between a limited number of basic sites on a filter and acidic  $\text{NO}_x$  species (i.e.,  $\text{HNO}_3$  or  $\text{NO}_2$ ), for filters exhibiting significant artifact nitrate, a ratio  $> 1.0$  would be expected. The results with Gelman A (ratio 1.3) are unexpected since this filter gave evidence of relatively low artifact nitrate level, as previously discussed.

For 14 sampling periods, the mean 24-hour average nitrate on Gelman hi-vol filters was  $13.5 \mu\text{g}/\text{m}^3$ . For the four days on which both Fluoropore and Gelman A filters were run, the mean ratio of results Fluoropore/Gelman A of 0.60 corresponds to a difference of  $3.4 \mu\text{g}/\text{m}^3$ . Considering one of the worst filters, the mean difference between Spectrograde (hi-vol) and Fluoropore for four days of parallel sampling corresponded  $7.2 \mu\text{g}/\text{m}^3$  nitrate. As with sulfate, these differences are interpreted to indicate the relative extent of artifact nitrate formation.

Table 23

RESPIRABLE NITRATE AS A FRACTION OF TOTAL  
PARTICULATE NITRATE IN 6-HOUR LOW-VOL FILTER SAMPLES

<u>Filter</u>	<u>Respirable/Total Nitrate</u> <u>(Overall Ratios <math>\pm 1 \sigma</math>)</u>	<u>N<sup>a</sup></u>
Fluoropore	0.68 $\pm$ .06	12
Spectrograde	0.71 $\pm$ .05	8
MSA 1106BH	0.85 $\pm$ .06	8
Gelman A	0.87 $\pm$ .05	8
Gelman GA-1	0.77 $\pm$ .03	16

---

a. The number of pairs of respirable and total particulate samples.

Table 24

COMPARISON OF CALCULATED<sup>a</sup> AND OBSERVED  
24-HOUR NITRATE VALUES (OVERALL RATIO  $\pm 1\sigma$ )

<u>Filter</u>	<u>Calculated/Observed</u>	<u>N</u>
Gelman A	1.33 $\pm$ .07	10
MSA 1106BH	0.95 $\pm$ .14	4
Spectrograde	1.07 $\pm$ .09	4
Whatman 41	1.05 $\pm$ .01	2
Fluoropore	1.29 $\pm$ .30	4
Gelman GA-1	1.08 $\pm$ .06	4

---

a. Calculated from four successive 6-hour samples for Hi-Vol and Low-Vol (total) filter samples.

In summary, differences up to a factor of two were observed among 24-hour nitrate samples collected simultaneously with five filter types. Nitrate results followed the order MSA 1106BH  $\approx$  Spectrograde  $\approx$  Gelman GA-1 > Whatman 41 > Gelman A > Fluoropore. While filter type was important, little difference was observed between hi-vol and low-volume filter results. This suggests that artifact nitrate formation is independent of sampling rate per unit area of filter. Evidence of greater artifact nitrate formation with 6-hour compared to 24-hour samples was obtained with some filters. The observed ratio respirable/total nitrate was substantially lower on Fluoropore relative to the other filter types. This is consistent with a mechanism for artifact nitrate formation involving interactions of gaseous  $\text{NO}_x$  species with the filter media. However, respirable/total nitrate results for Spectrograde filters imply more complex mechanisms.

## 2. Comparisons Based on Diurnal Variations of Nitrate and Pollutant Gases.

Figures 26-31 compare the diurnal variations for particulate nitrate to those for  $\text{NO}_2^*$  and  $\text{O}_3^*$  at San Jose. The ozone maxima typically occurred in the afternoon and that for  $\text{NO}_2$ , in the morning. One of the most interesting observations is seen in Figure 28 (Episode C, San Jose) where the diurnal nitrate maximum on MSA low-volume filters parallels that for  $\text{NO}_2$  but for Whatman 41 (hi-vol), the nitrate maximum occurs in the succeeding 6-hour period. As noted in Table 22, Whatman 41 (hi-vol) 24-hour samples exhibit substantially lower nitrate results than MSA (lo-vol) presumably indicating lower artifact nitrate formation on Whatman 41.\*\* These results suggest that  $\text{NO}_2$  or other pollutant peaking during this period may contribute to the artifact nitrate observed on MSA 1106BH filters. At Los Alamitos (Figures 32-39) the local district's  $\text{NO}_x$  monitor was not functioning so only  $\text{O}_3$  data are shown.\*\*\* In all the cases, the diurnal variations obtained on the low-volume and high-volume filters are similar.

It should be noted that similarities in diurnal patterns between  $\text{NO}_2$  and observed nitrate do not necessarily imply formation of artifact nitrate from  $\text{NO}_2$  because  $\text{HNO}_3$  may have a similar diurnal pattern but it was not measured.

\*Data provided by the BAAPCD.

\*\*Lower filtration efficiency for Whatman 41 may also be involved.

\*\*\*Provided by the South Coast Air Quality Management District's Los Alamitos Station.

Figure 26

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
SAN JOSE, EPISODE A, OCTOBER 4-5, 1976

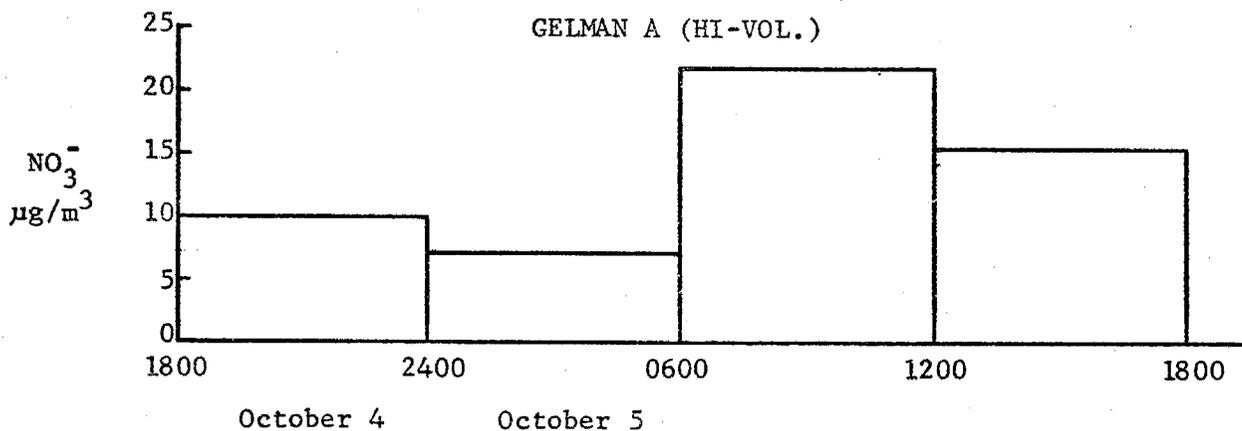
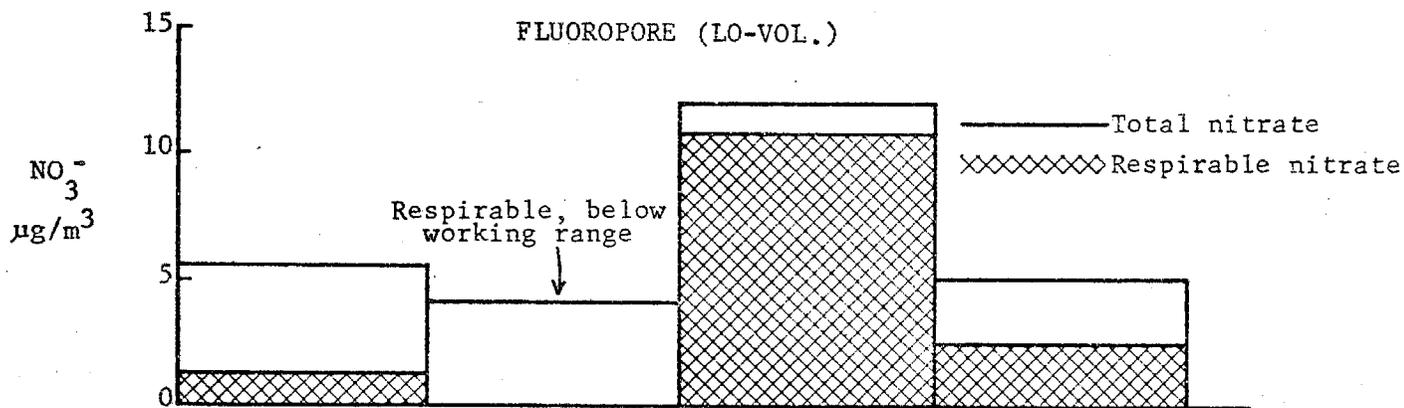
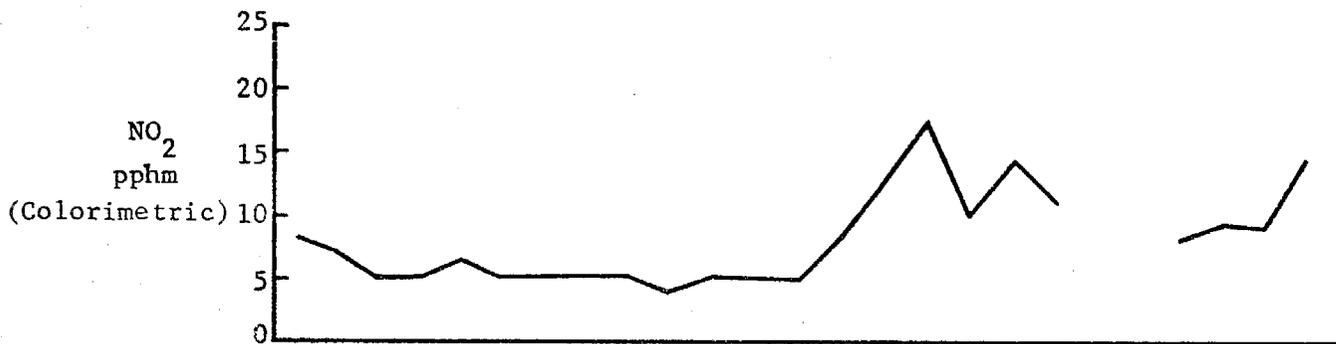
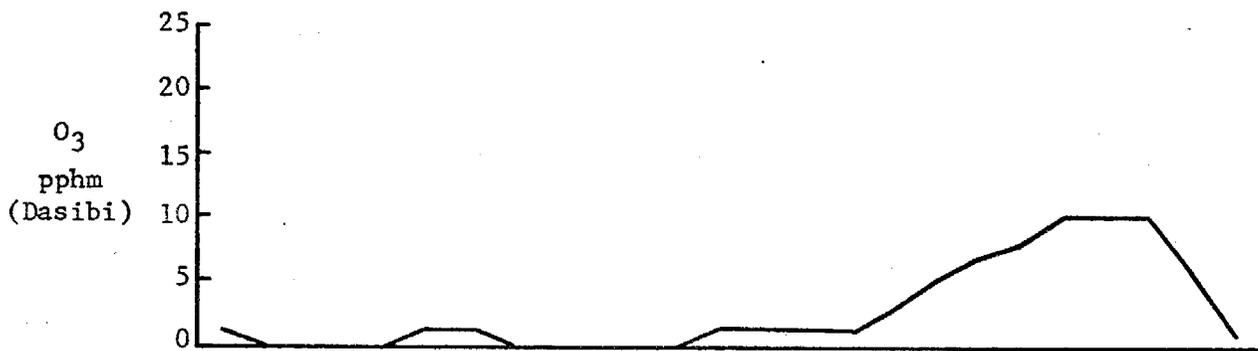


Figure 27

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
SAN JOSE, EPISODE B, OCTOBER 5-6, 1976

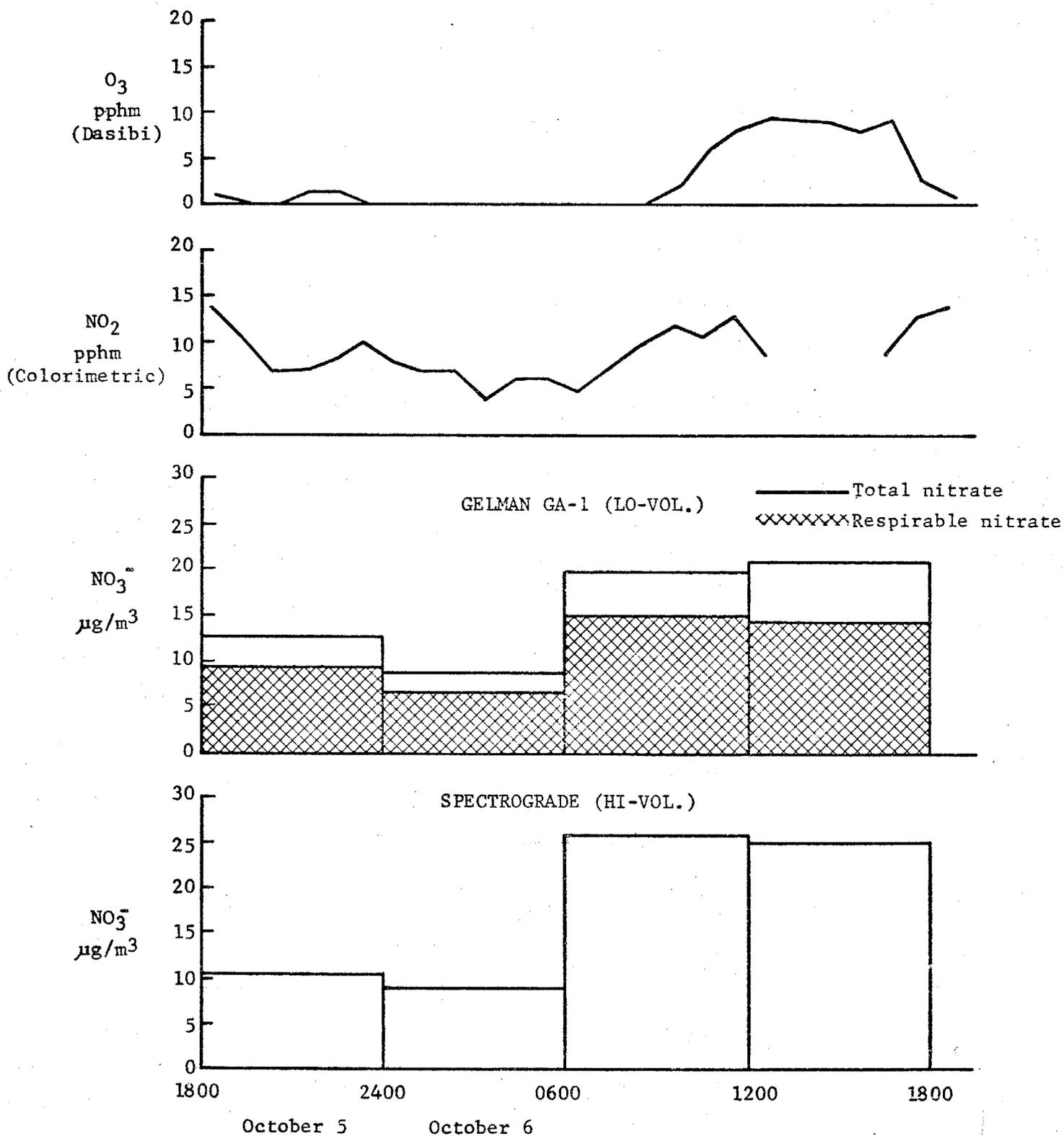


Figure 28

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
SAN JOSE, EPISODE C, OCTOBER 6-7, 1976

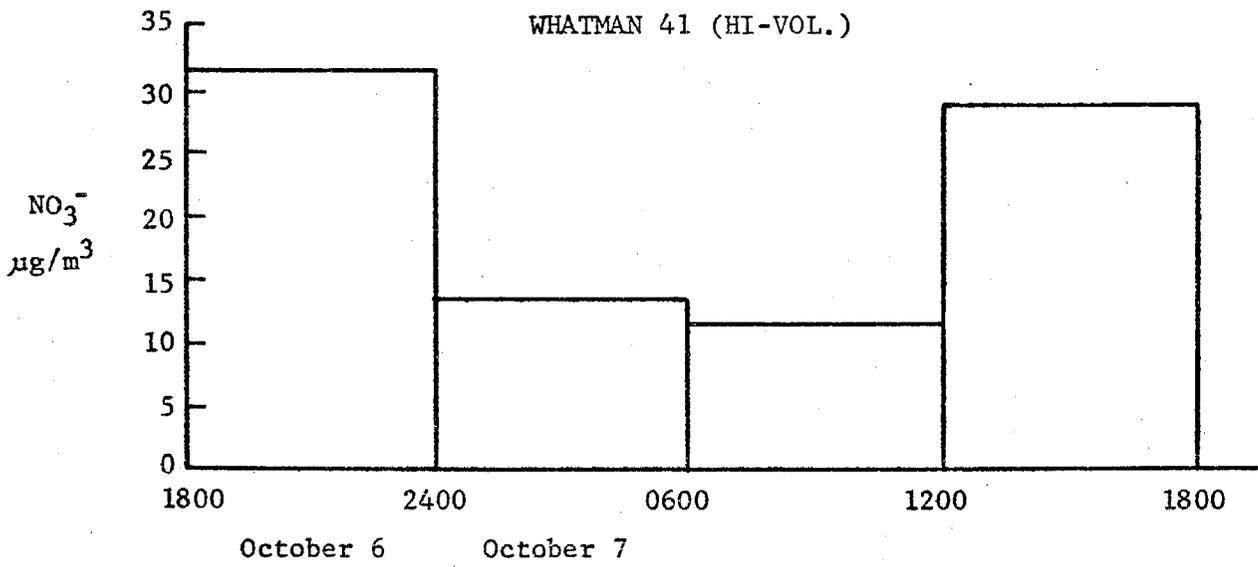
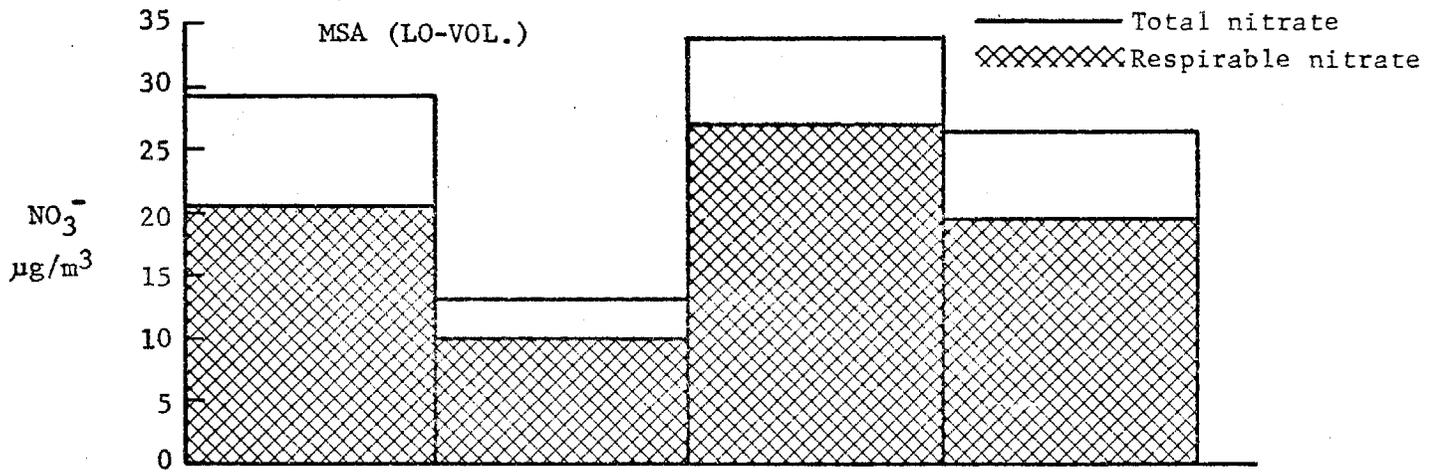
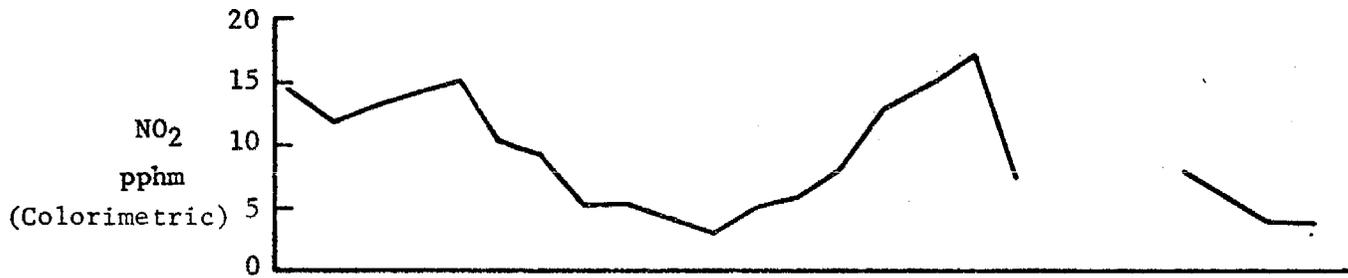
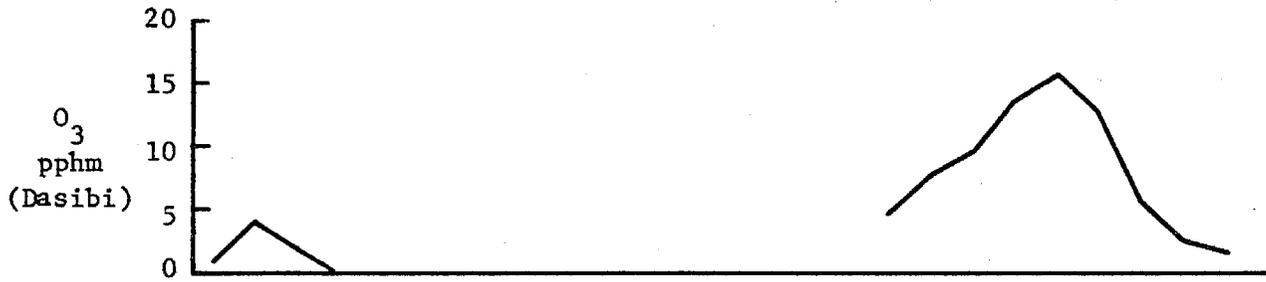


Figure 29

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
 SAN JOSE, EPISODE D, OCTOBER 7-8, 1976

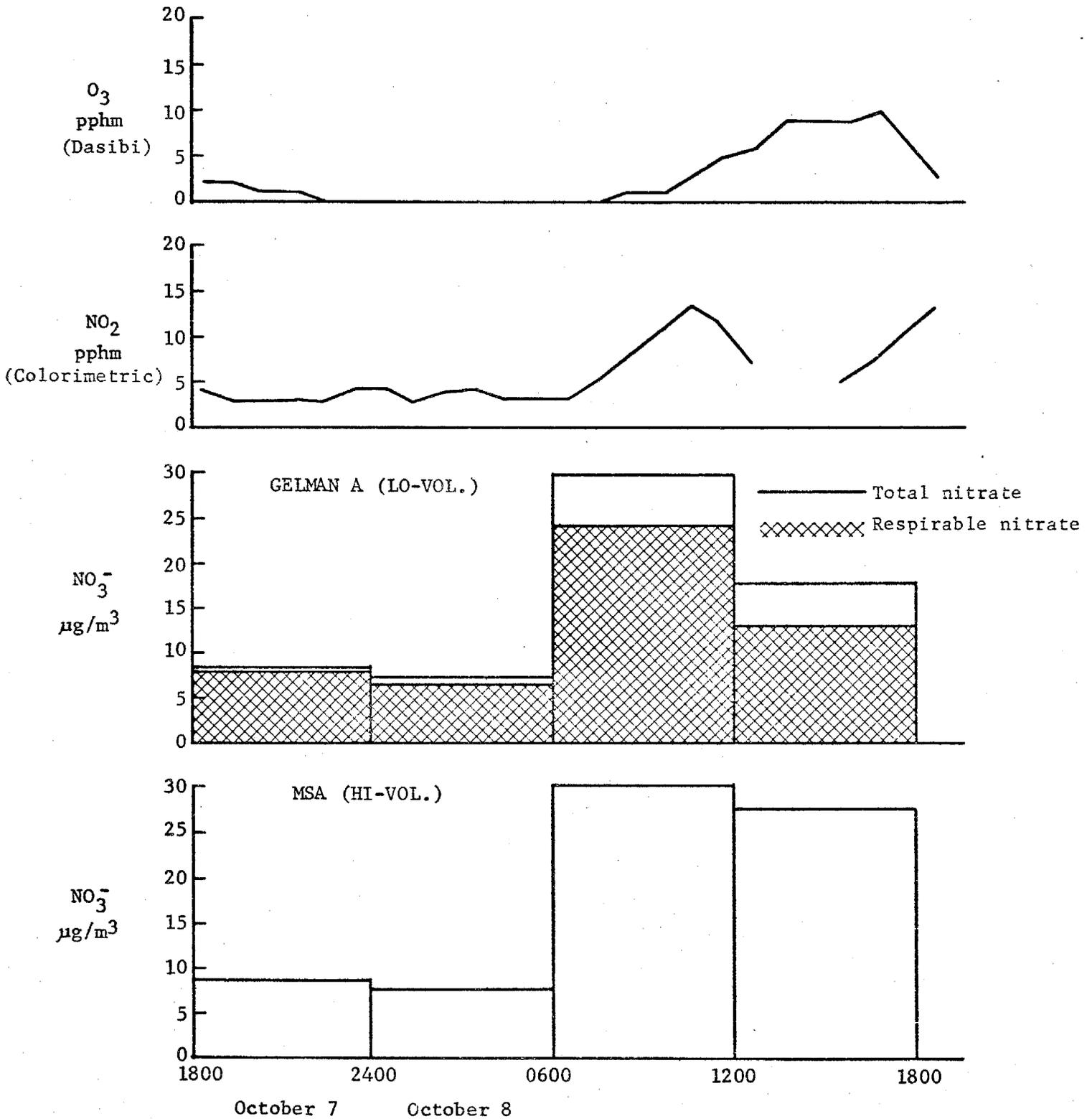


Figure 30

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
SAN JOSE, EPISODE E, OCTOBER 8-9, 1976

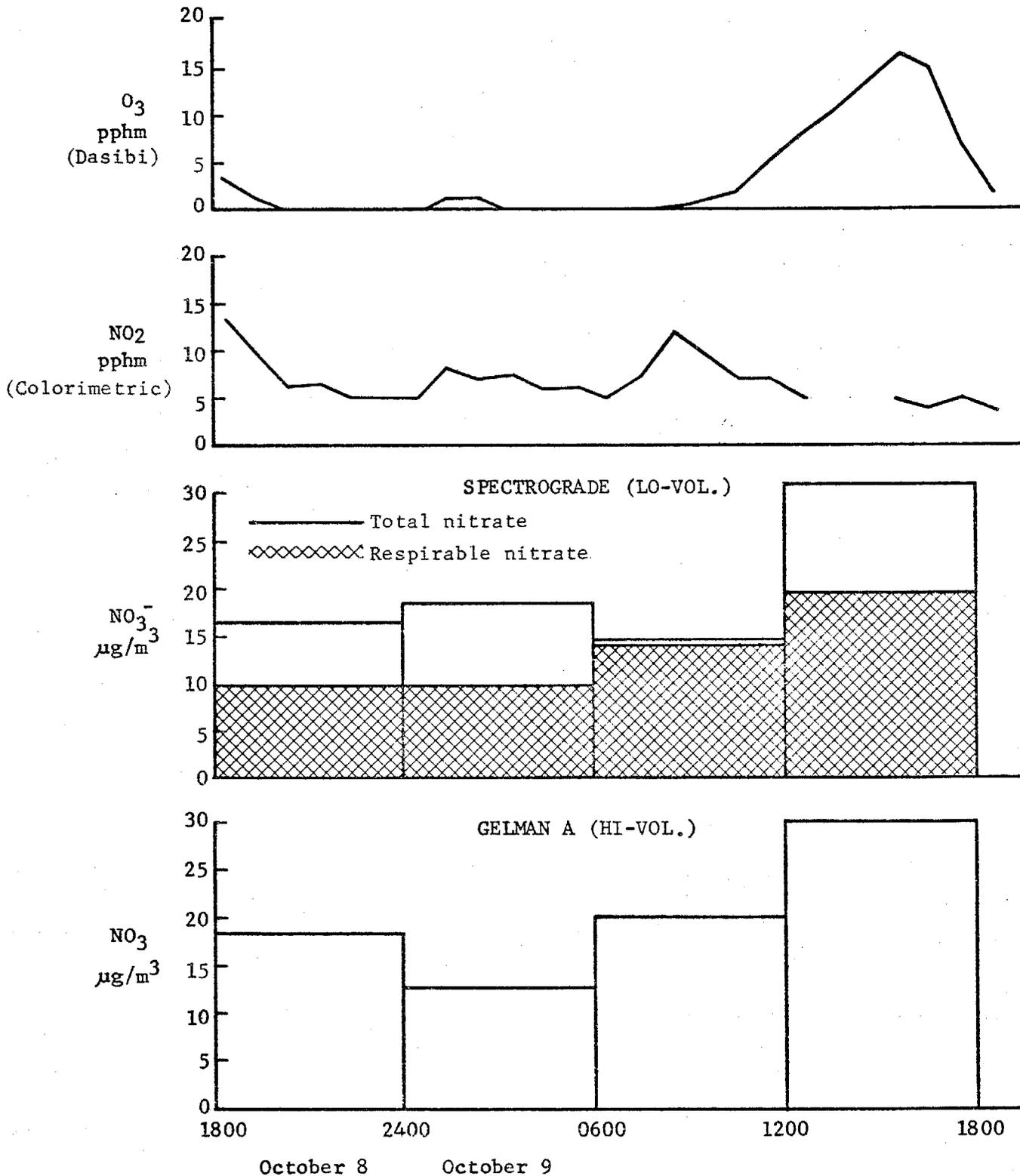


Figure 31

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
 SAN JOSE. EPISODE F, OCTOBER 9-10, 1976

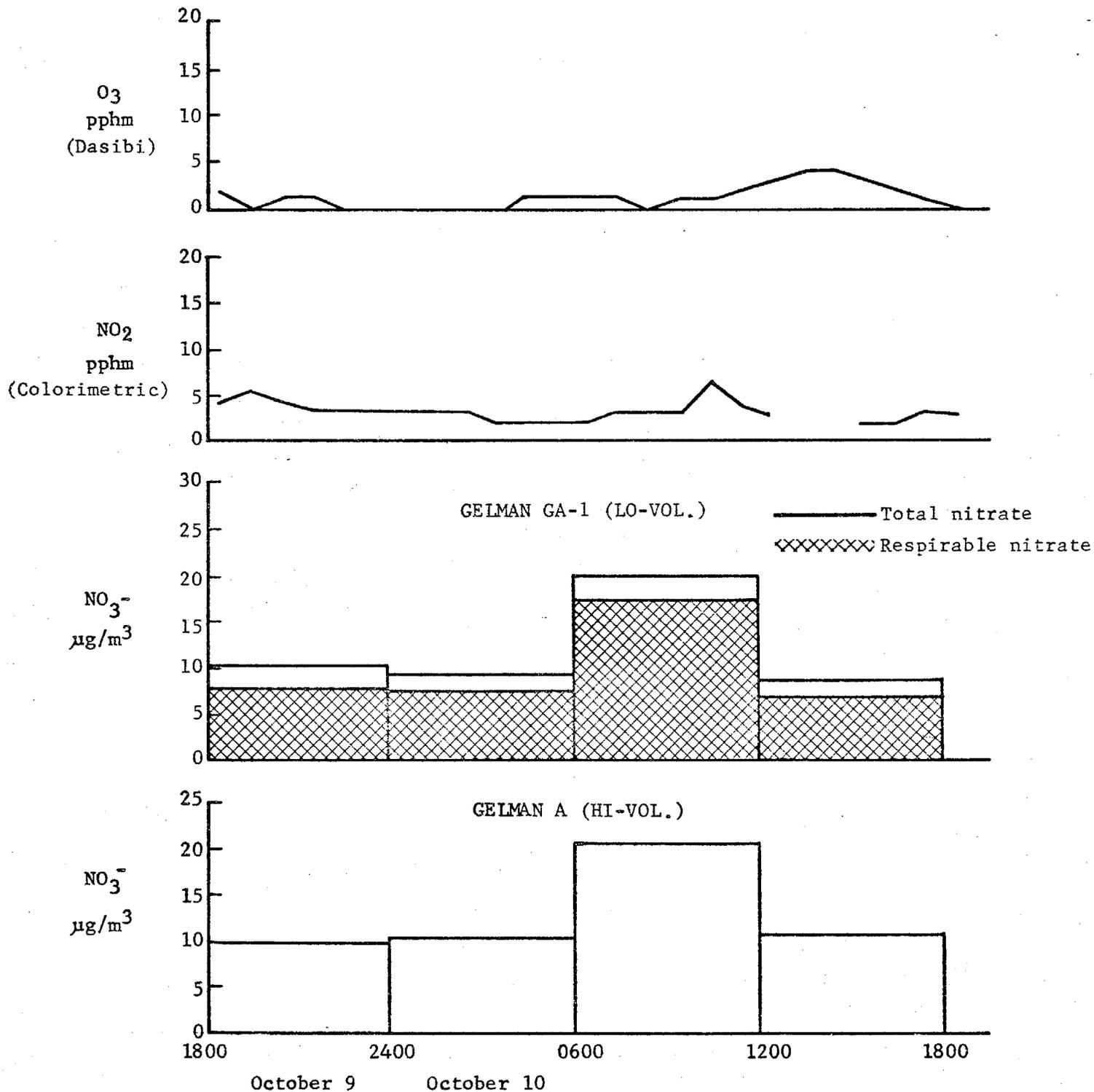


Figure 32

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
LOS ALAMITOS, EPISODE A, OCTOBER 28-29, 1976

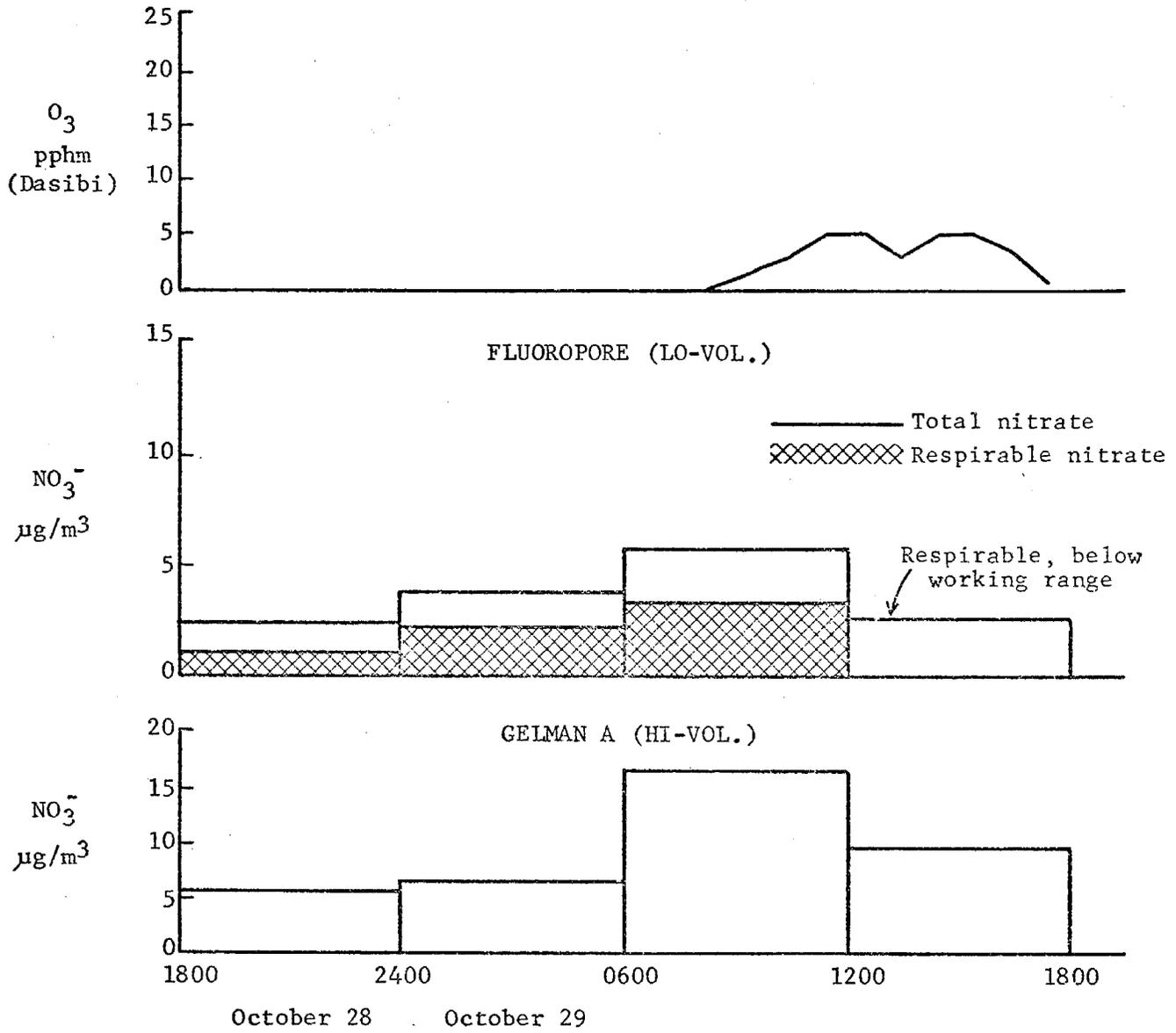


Figure 33

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
 LOS ALAMITOS, EPISODE B, OCTOBER 29-30, 1976

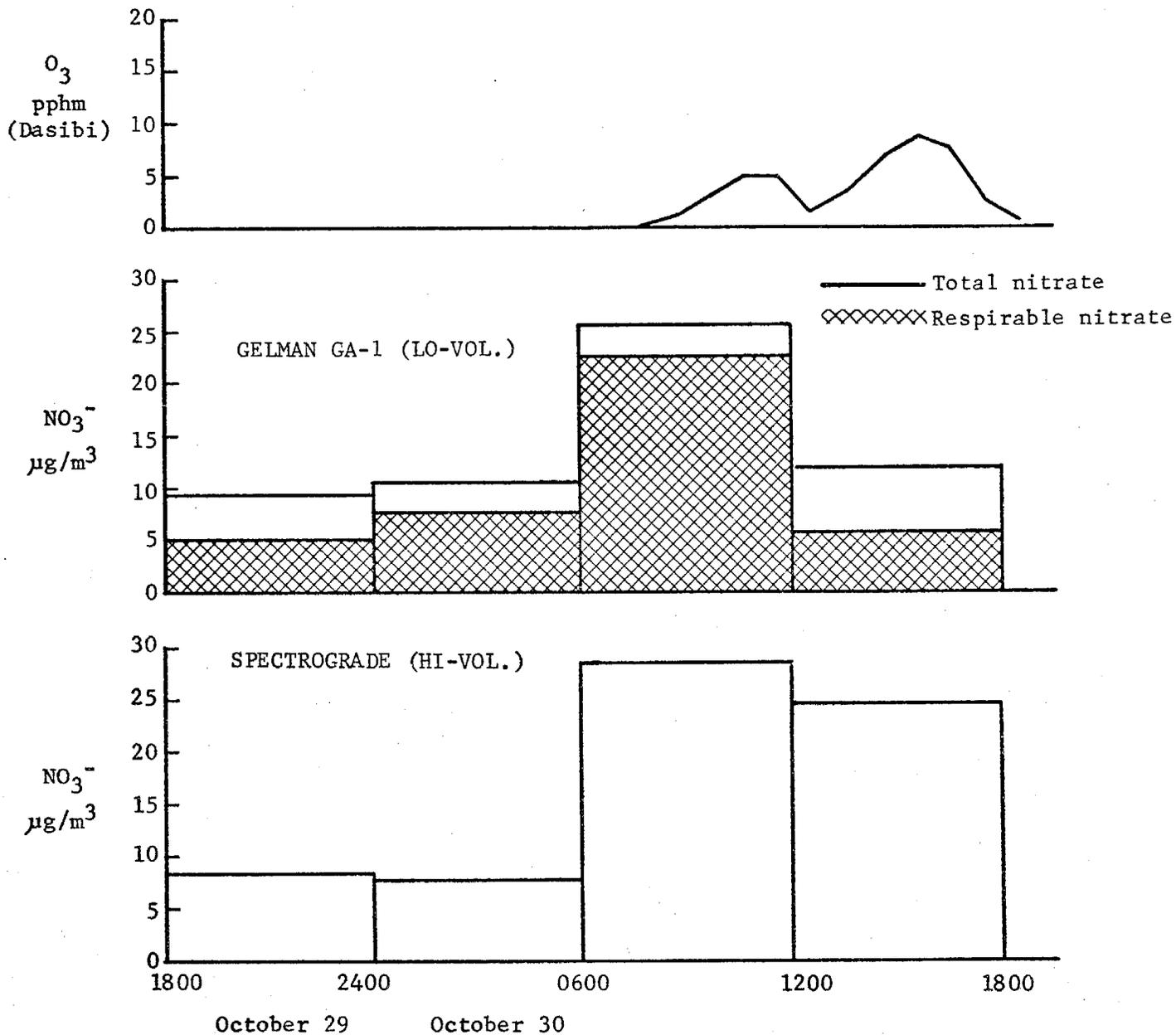


Figure 34

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
LOS ALAMITOS, EPISODE C, OCTOBER 30-31, 1976

O<sub>3</sub>  
pphm  
(Dasibi)

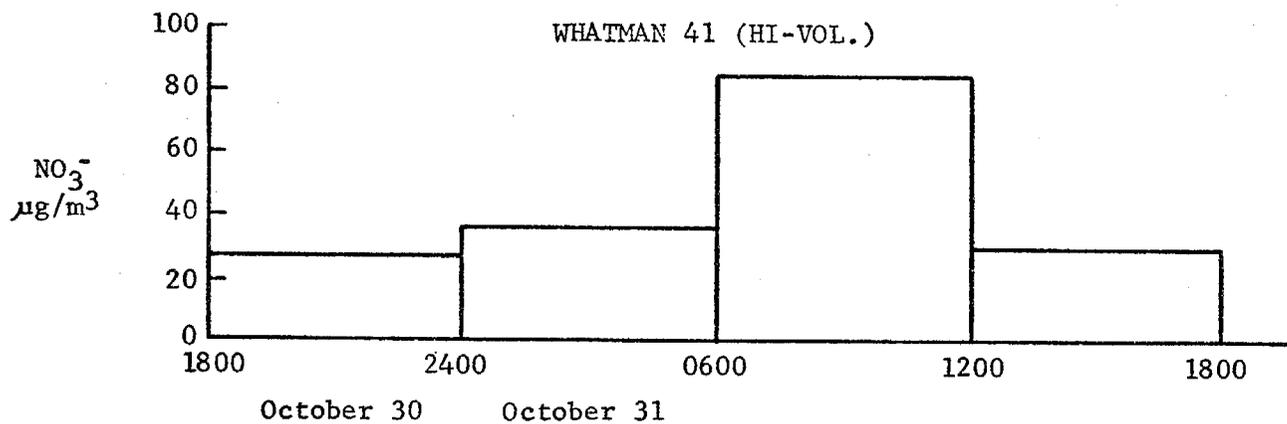
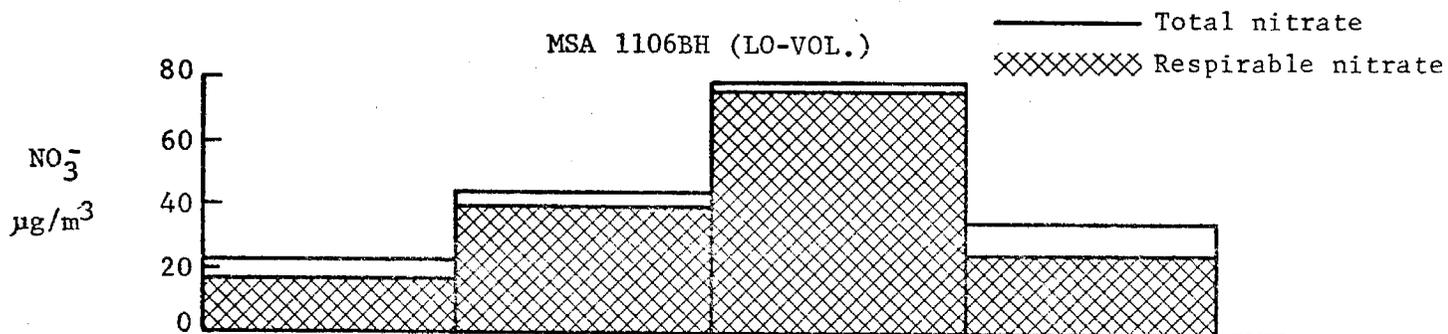
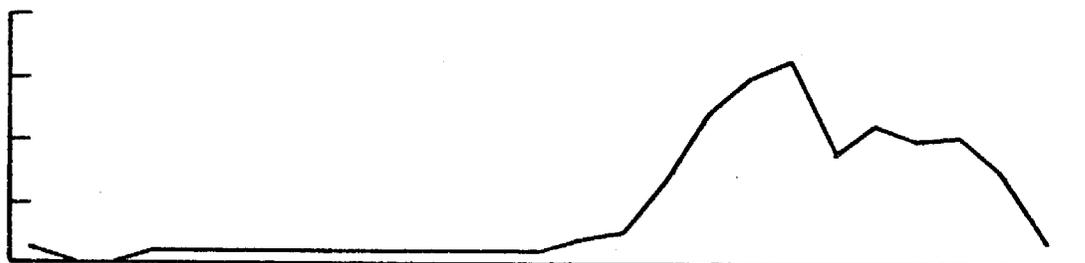


Figure 35

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
LOS ALAMITOS, EPISODE D, OCTOBER 30-NOVEMBER 1, 1976

O<sub>3</sub>  
pphm  
(Dasibi)

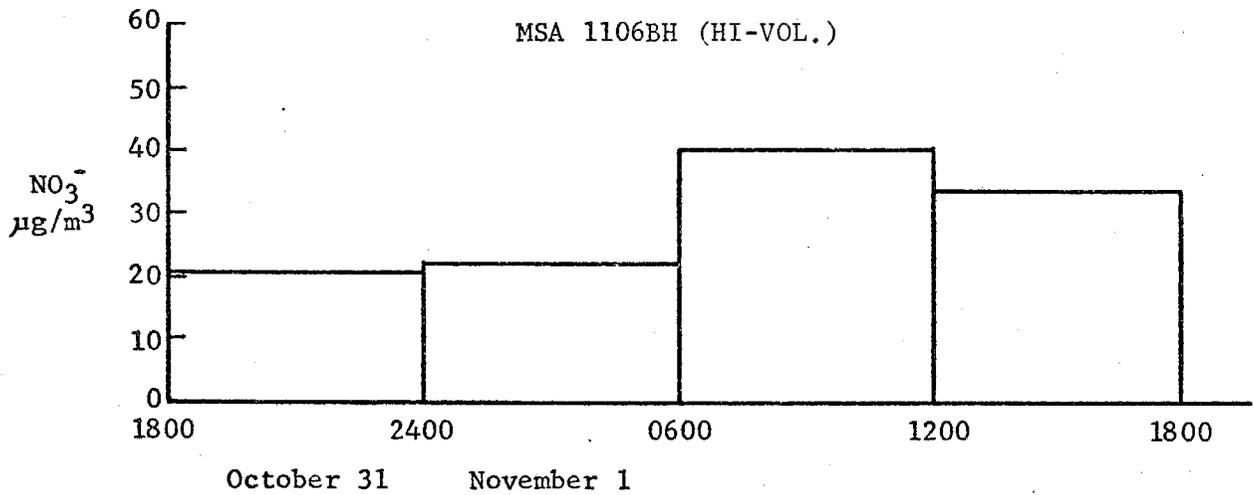
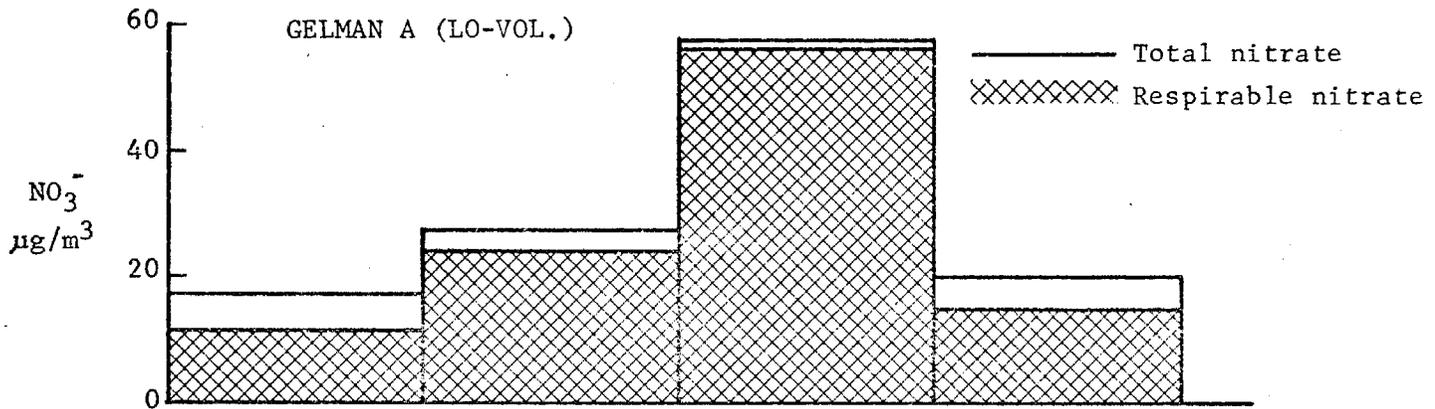


Figure 36

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
LOS ALAMITOS, EPISODE E, NOVEMBER 1-2, 1976

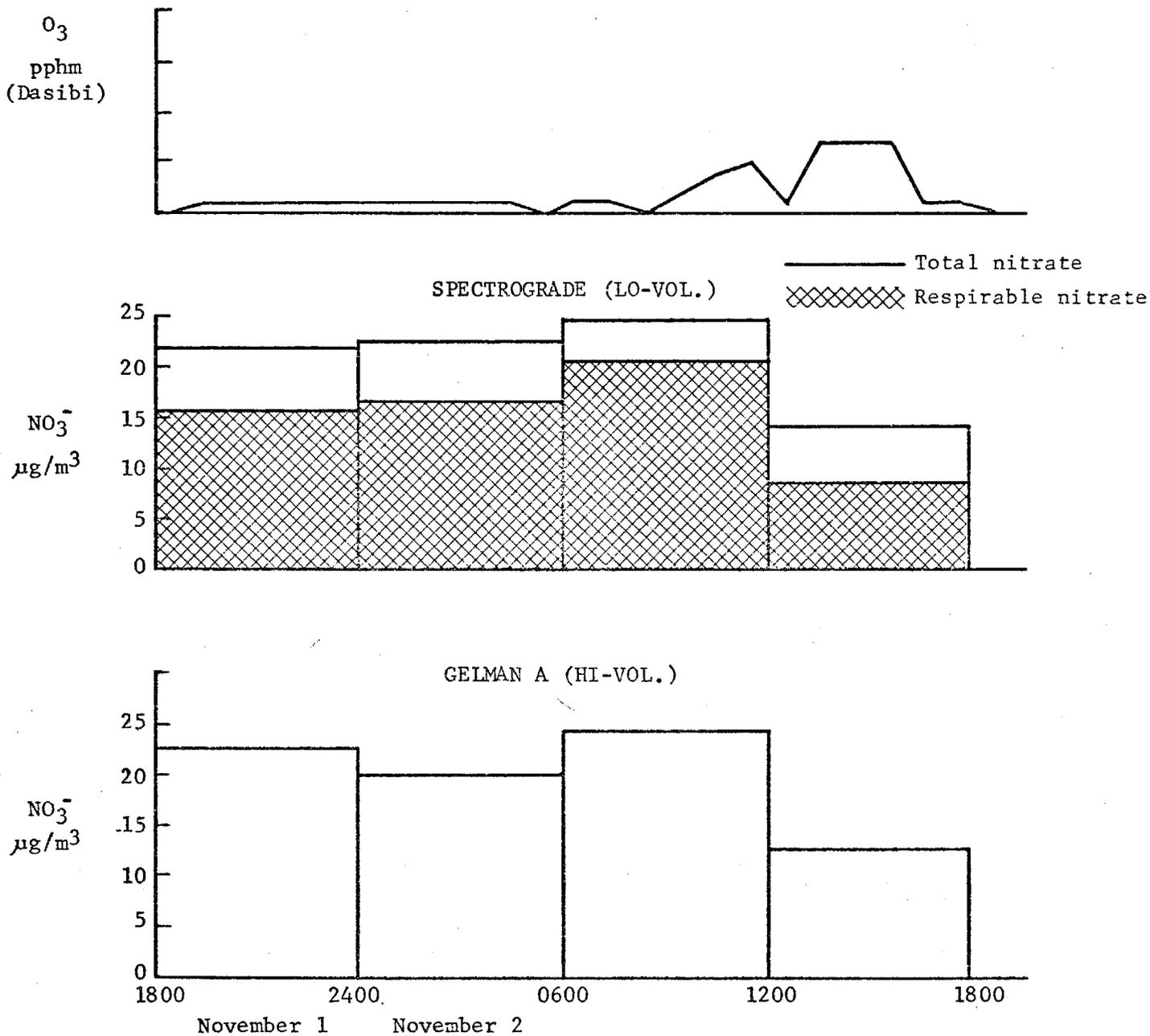


Figure 37

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
LOS ALAMITOS, EPISODE F, NOVEMBER 2-3, 1976

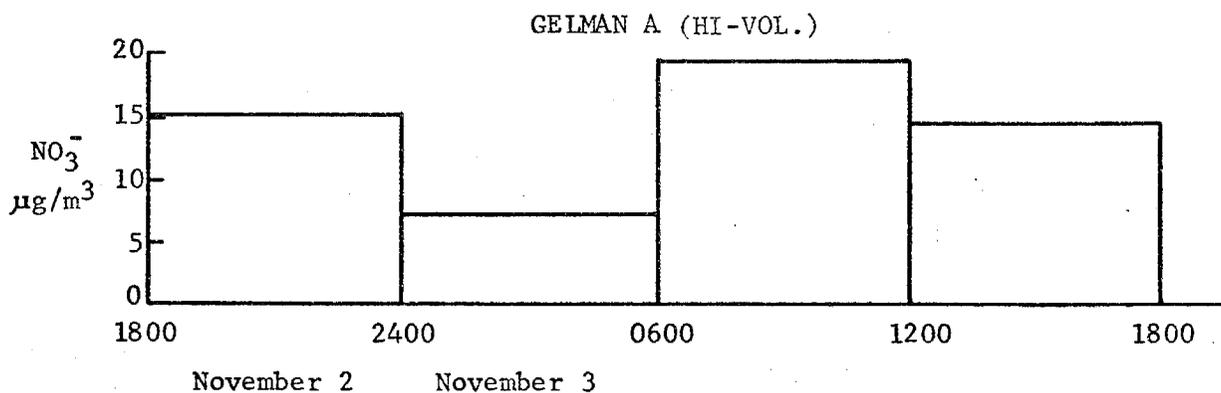
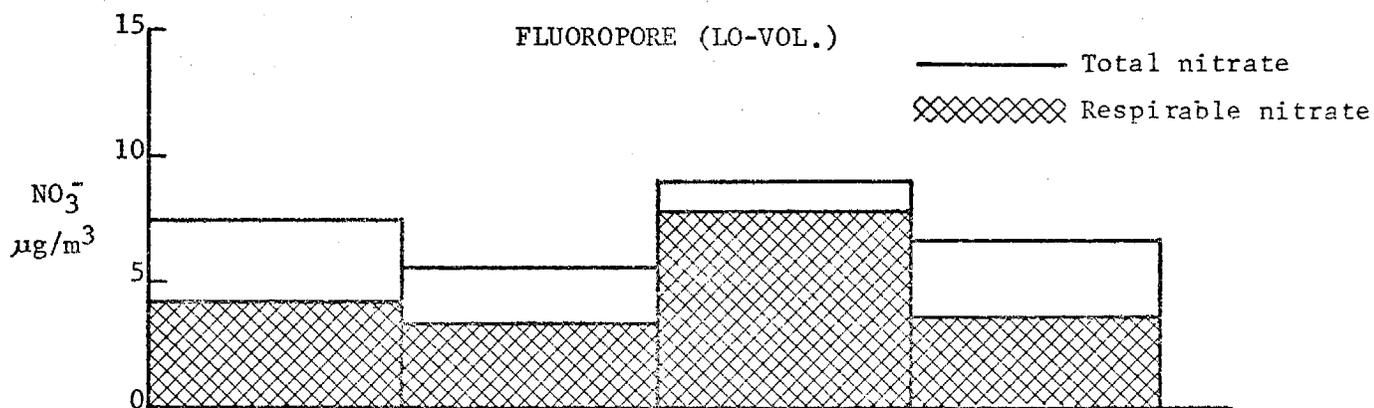
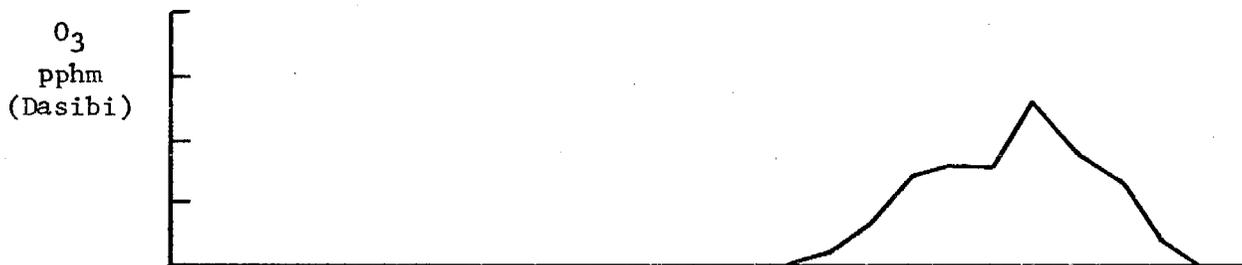


Figure 38

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
 LOS ALAMITOS, EPISODE G, NOVEMBER 3-4, 1976

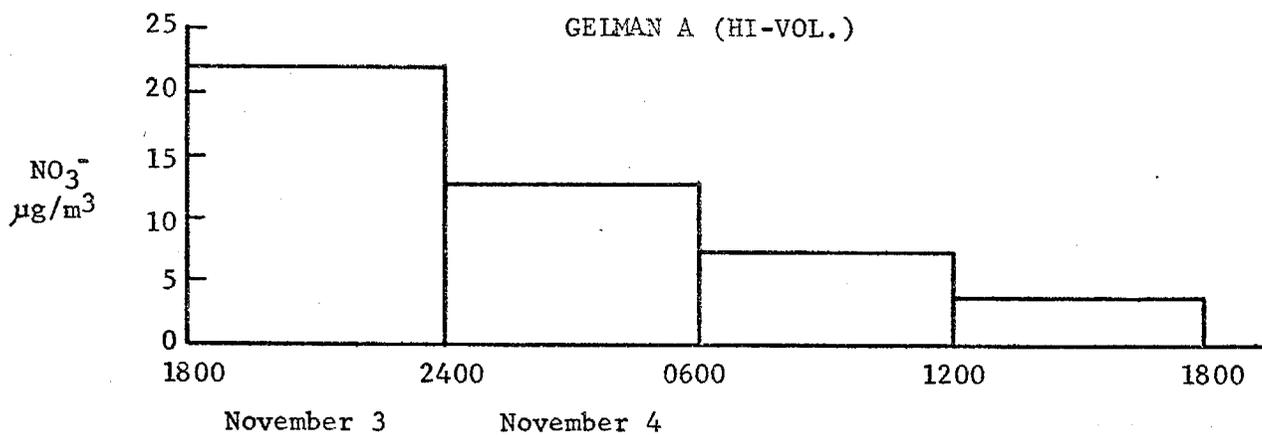
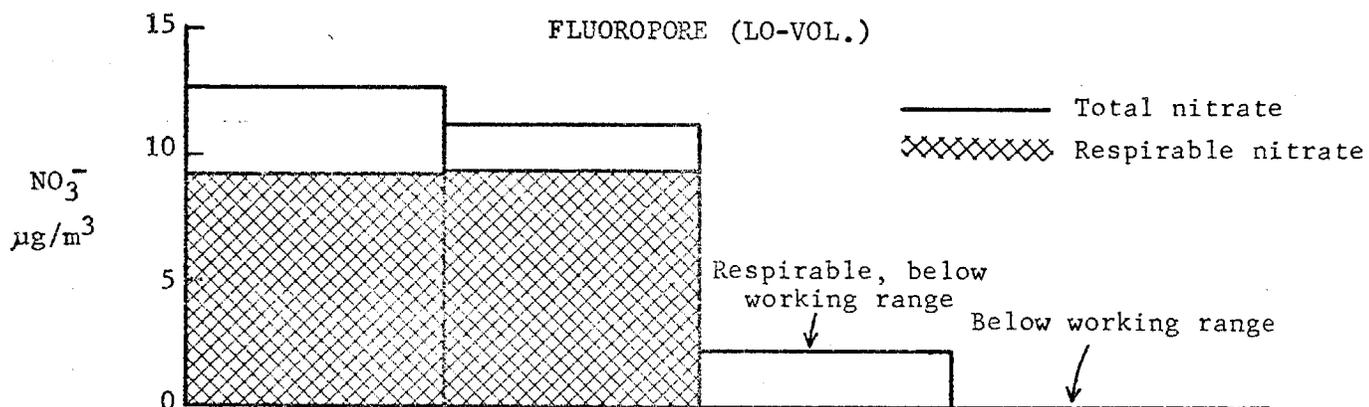
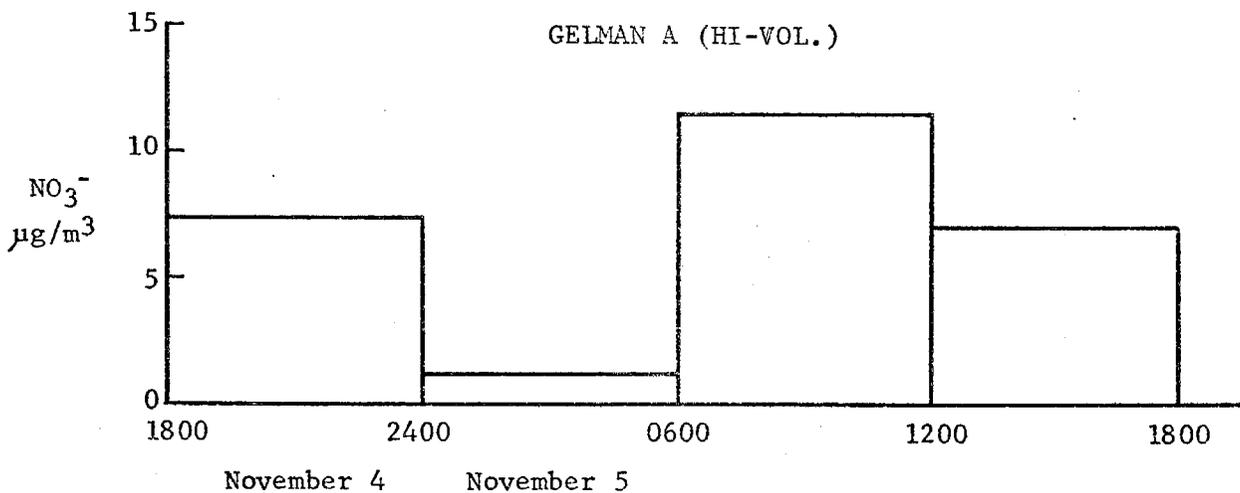
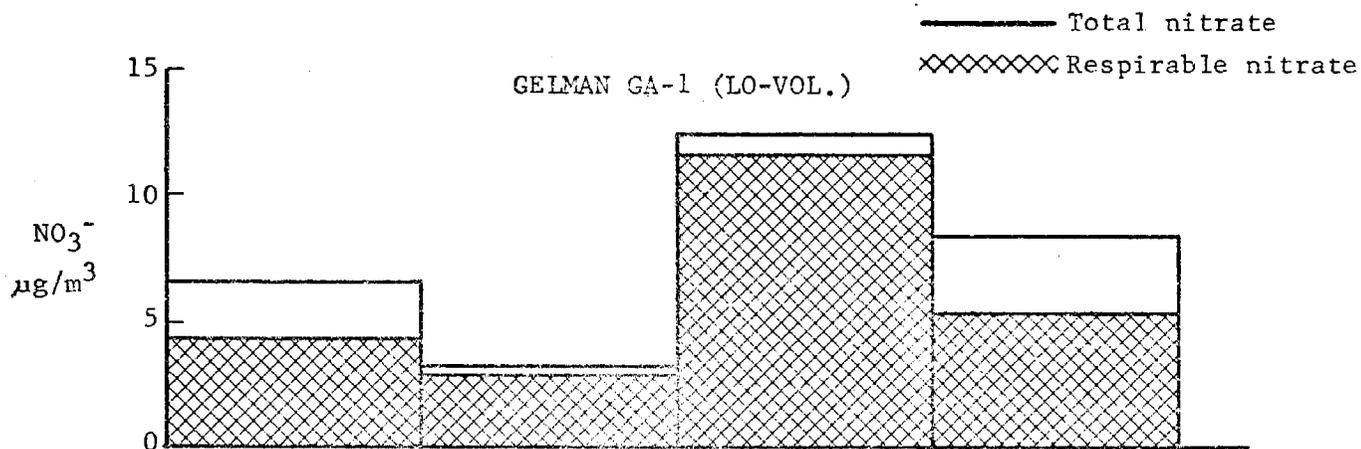
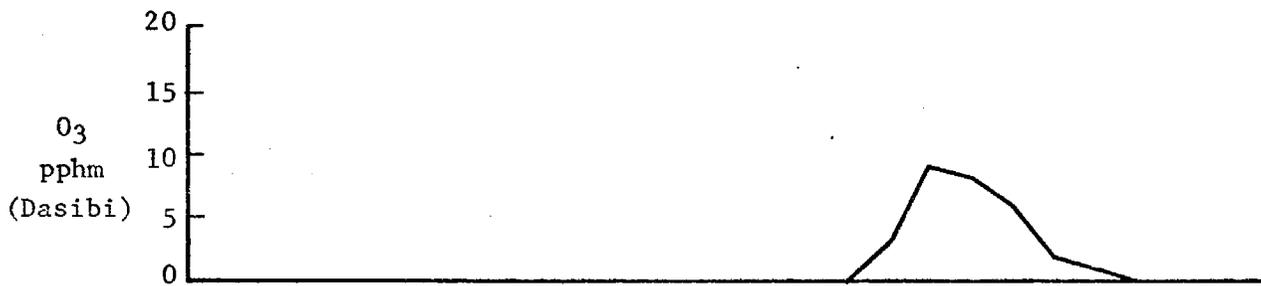


Figure 39

DIURNAL VARIATIONS OF NITRATE AND POLLUTANT GASES  
 LOS ALAMITOS, EPISODE H, NOVEMBER 4-5, 1976



#### D. Carbonaceous Material Results

Twenty-four hour high volume samples collected on Gelman A and MSA 1106BH filters were extracted and analyzed for carbon solubilized by successive extractions in benzene and methanol-chloroform as a means of estimating total organic carbon. The data are given in Table 25. These results together with the total carbon values (Table 26) determined in each sample permit estimation of elemental carbon as the carbon remaining insoluble in the above extractions. Correlation between these data and 24-hour average sulfate results were sought for two reasons. Firstly, elemental carbon might be a significant catalyst for oxidation of  $\text{SO}_2$  to sulfate. Secondly, the degree of interaction between  $\text{SO}_2$  and atmospheric particulate matter has been shown in one case to vary inversely with the amount of organic carbon.<sup>20</sup>

Regression equations between sulfate and total organic carbon and elemental carbon are shown separately for each filter type in Table 27. The highest correlation coefficient seen was +0.5 between organic carbon and sulfate on MSA filters. A positive correlation here contrasts with prior results for model systems.<sup>20</sup> No correlation between elemental carbon and sulfate is seen.

Total carbon values for 6-hour samples are given in Tables 28 and 29.

#### E. Metals Determination of Atmospheric Samples

Atmospheric samples collected on Fluoropore and Spectrograde filters were analyzed by Prof. T. Cahill and co-workers using alpha particle-induced x-ray fluorescence ( $\alpha$ -XRFA). Analytical values were obtained for sulfur as well as various metals. The objective of these determinations were:

1. To assess the level of metals which might accelerate (i.e., catalyze) the oxidation of  $\text{SO}_2$  to sulfate during laboratory exposures using both total filter and respirable particulate samples.
2. To seek correlations between catalytic metals and sulfate levels in the atmospheric particulate as indicators of mechanism of sulfate formation.
3. To seek correlations between observed sulfate levels and metals typically found in fuel oil fly ash and presumably emitted by the Los Alamitos power plant.
4. To provide an intermethod comparison between wet chemical sulfate and total sulfur (as sulfate) determinations.
5. To provide a comparison of metals concentrations obtained with Spectrograde (hi-vol) and Fluoropore (low-vol) filters in simultaneous sampling.

Table 25

TOTAL ORGANIC CARBON<sup>a</sup> AND ELEMENTAL CARBON<sup>b</sup>  
 RESULTS FROM 24-HOUR HIGH-VOLUME SAMPLES ( $\mu\text{g}/\text{m}^3$ )

<u>Date</u> <u>(EPISODE)</u>	<u>Gelman</u> <u>A</u>	<u>MSA</u> <u>1106BH</u>
SAN JOSE		
Oct 4-5 (A)	11.9 (8.4)	
Oct 5-6 (B)		11.2 (9.3)
Oct 6-7 ( )	14.7 (7.1)	
Oct 7-8 (D)		7.4, 7.6 (6.1), (5.8)
Oct 8-9 (E)	11.8 (6.1)	
Oct 9-10 (F)	4.0 (1.6)	
LOS ALAMITOS		
Oct 28-29 (A)	6.4 (4.7)	
Oct 29-30 (B)		7.4 (5.2)
Oct 30-31 (C)	16.9 (5.9)	
Oct 31-Nov 1 (D)		17.9, 17.2 (9.4), (8.3)
Nov 1-2 (E)	21.3 (8.9)	
Nov 2-3 (F)		15.8, 17.0 (9.7), (8.7)
Nov 3-4 (G)		13.0, 12.2 (8.7), (8.9)
Nov 4-5 (H)	10.7 (6.7)	

a. The sum of benzene and methanol-chloroform soluble carbon.

b. Shown in brackets. Approximated as carbon insoluble in determining total organic carbon.

Table 26

TOTAL CARBON RESULTS FROM 24-HOUR SAMPLES  
( $\mu\text{g}/\text{m}^3$ )<sup>a</sup>

## SAN JOSE

Date (EPISODE)	<u>High-Volume Samples</u>		<u>Low-Volume Samples</u>		
	Gelman A	MSA 1106BH	Gelman A	MSA 1106BH	Spectro- grade
Oct 4-5 (A)	20.3				
Oct 5-6 (B)		20.5			
Oct 6-7 (C)	21.9			27.4	
Oct 7-8 (D)		13.5 <sup>b</sup> 13.5	16.7		
Oct 8-9 (E)	17.9				22.6
Oct 9-10 (F)	5.6				

## LOS ALAMITOS

Oct 28-29 (A)	11.1				
Oct 29-30 (B)		12.5			
Oct 30-31 (C)	22.8			26.3	
Oct 31-Nov 1 (D)		27.3 25.4	30.8		
Nov 1-2 (E)	30.2 <sup>b</sup>				31.1
Nov 2-3 (F)		25.4 25.8			
Nov 3-4 (G)		21.6 21.1			
Nov 4-5 (H)	17.4				

a. Two values indicate results from separate samplers.

b. Mean of two determinations on the same sample.

Table 27

CORRELATION BETWEEN ATMOSPHERIC SULFATE  
AND CARBONACEOUS MATERIAL

$$\text{SO}_4^{2-} = a + bx$$

<u>Filter</u>	<u>x</u>	<u>a</u>	<u>b</u>	<u>r</u>	<u>N***</u>
Gelman A	Elemental C*	7.89	-0.33	-0.29	8
Gelman A	Organic C**	4.36	0.12	0.26	8
MSA 1106BH	Elemental C	9.14	0.02	0.01	10
MSA 1106BH	Organic C	3.48	0.46	0.54	10

\*Estimated as total C less benzene plus methanol-chloroform soluble C.

\*\*Estimated as benzene plus methanol-chloroform soluble carbon.

\*\*\*Number of data pairs.





In the relatively few cases in which vanadium levels were measurable, these ranged from 0.07 to 0.2  $\mu\text{g}/\text{m}^3$  and displayed no apparent correlation with sulfate (Figure 40). Nickel, however, does show slight correlation with observed atmospheric sulfate levels (Figure 41). Since nickel is a constituent of fuel oil fly ash, this would be consistent with a sulfate contribution from the Los Alamitos power plant. However, the absence of correlation between sulfate and vanadium, which, in general, is present in higher abundance than nickel in fuel oil fly ash, suggests the correlation with nickel is not meaningful. Nickel has not been reported to be an oxidation catalyst for sulfur dioxide.

Table 30 summarizes the results obtained for four additional elements on 24-hour Fluoropore and Spectrograde samples. The mean ratio of results Fluoropore/Spectrograde from side-by-side sampling indicates, on average, 10-15% higher results on Fluoropore. However, for copper the high volume samples contain about three times the level found on Fluoropore, suggesting contamination with copper particles generated by the hi-vol motor.

The fraction of the potential catalysts observed in the respirable size range is given in Table 31, based on samples collected at both sites. Values for copper and vanadium were below limits of detection in all cases with the low volume samples. Only 20% of the observed iron appears in the respirable fraction. However, while iron is a significant fly ash constituent, soil and automobile emissions probably contribute to the iron in larger particles. In these cases, the iron may be less catalytically active for effecting  $\text{SO}_2$  oxidation. Thus, no estimate can be made of the potential of respirable and total filters for contributing to iron-catalyzed  $\text{SO}_2$  oxidation.

A comparison of sulfur (by  $\alpha$ -XRFA) and sulfate results is given in Appendix J. The analyses were both done on Fluoropore and indicate generally poor agreement. As discussed in Appendix J, the error appears to be in the  $\alpha$ -XRFA values.

In summary, of the metals demonstrated to accelerate  $\text{SO}_2$  oxidation under laboratory conditions (usually as ions in aqueous solution) only iron and copper are present at levels permitting their determination by  $\alpha$ -XRFA in a majority of the samples analyzed. Observed sulfate levels at Los Alamitos do not correlate strongly with fuel oil combustion indicator elements, suggesting important sources of sulfate in addition to the Los Alamitos Power Plant.

## F. Mass Results

### 1. Introduction

While mass results were not required for this program, it appeared desirable to obtain such data, where practical, for quality assurance, for an additional filter media comparison,

Figure 40

SULFATE vs. VANADIUM LEVELS

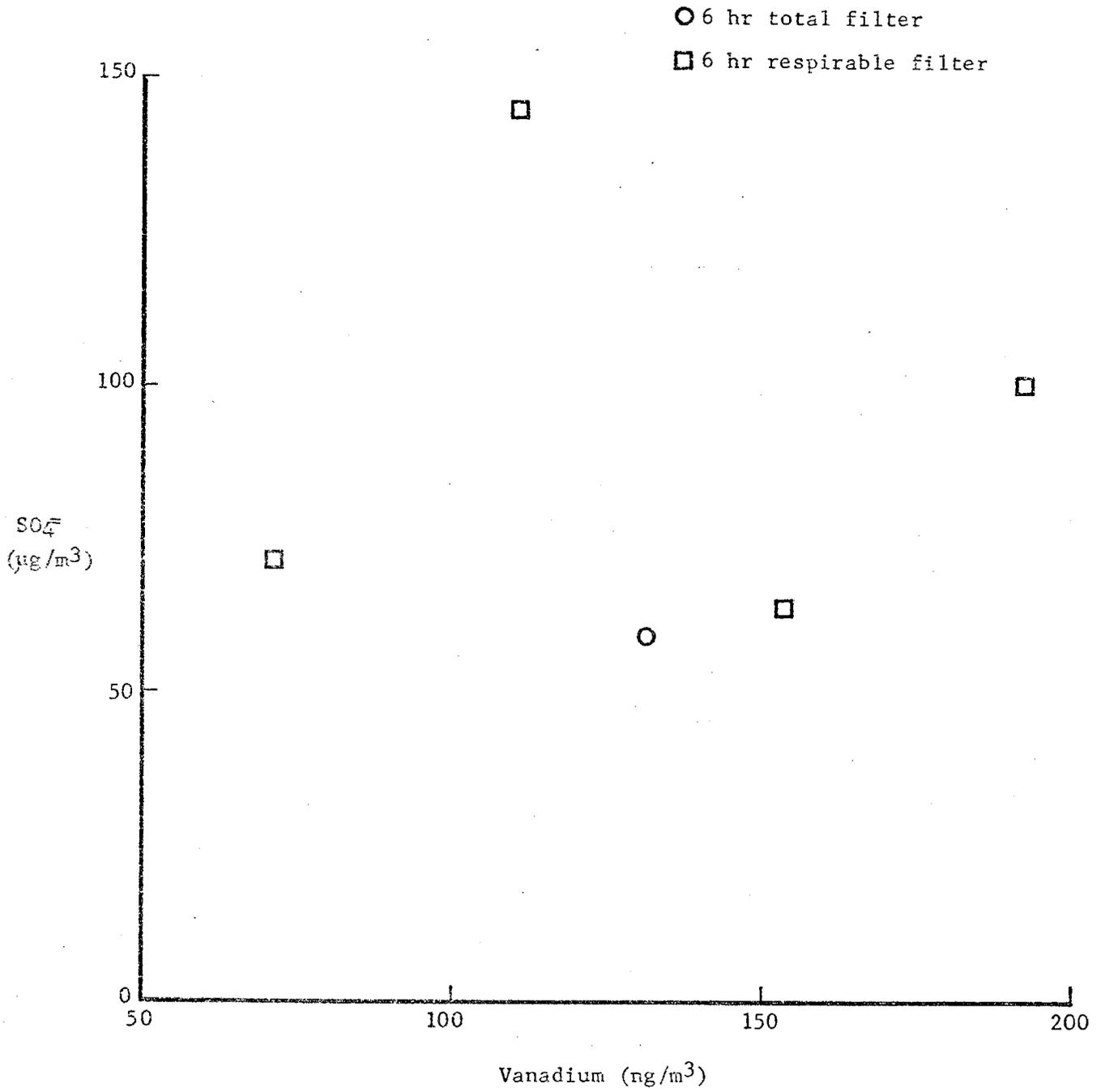


Figure 41

SULFATE vs. NICKEL LEVELS

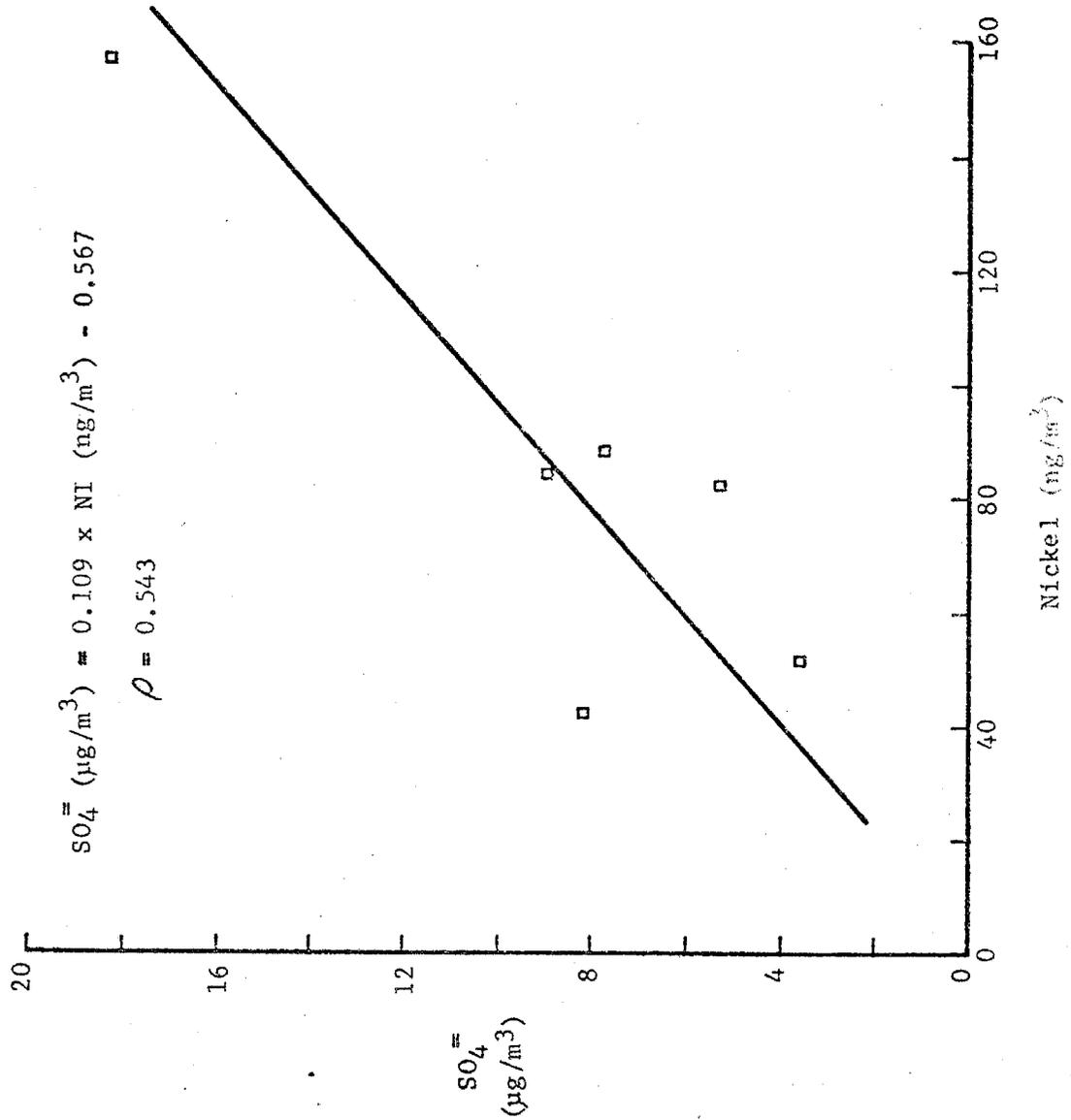


Table 30

CONCENTRATIONS OF METALS OBSERVED IN 24-HOUR ATMOSPHERIC SAMPLES ( $\mu\text{g}/\text{m}^3$ )

<u>Episode</u>	<u>Spectrograde</u>				
	<u>Pb</u>	<u>Br</u>	<u>Fe</u>	<u>Cu</u>	
SA	2.35	0.82	2.18	0.10	
LA	2.16	0.85	0.88	--	
LF	7.14	2.26	3.03	0.12	
LG	5.64	1.88	2.54	0.14	
	<u>Fluoropore</u>				
SA	3.44	1.15	2.51	0.049	
LA	3.06	1.01	1.63	--	
LF	6.61	2.28	2.72	0.029	
LG	4.57	1.41	1.66	0.028	
Ratio	$\frac{\text{Fluoropore}}{\text{Spectrograde}}$	$1.15 \pm .33$	$1.09 \pm .28$	$1.14 \pm .52$	$.31 \pm .16$

Table 31

## FRACTION OF METALS IN RESPIRABLE SIZE RANGE

<u>Metal</u>	<u>Ratio Respirable/Total Particulate Values</u>	<u>N<sup>a</sup></u>
Fe	0.19 ± 0.09	15
Cu	---	0
V	---	0
Zn	0.64 ± 0.23	12
Ni	0.99	1

a. Number of paired samples.

and for evaluation of the field sampling techniques. Because of the hygroscopicity of the filters and low sampling rates, reliable mass data were not obtained with Gelman GA-1 cellulose acetate and Whatman 41 cellulose filters.

## 2. Results

Table 32 summarizes the 24-hour hi-vol and low-volume results for mass, excepting for those from Gelman GA-1 and Whatman 41 filters. In the cases where two values are shown, these represent results for two samplers operated with the same filter medium. From these data, we calculate the following:

- a. The precision of hi-vol sampling for mass was 5.9%, as measured by the mean coefficient of variation for eleven paired samples collected side-by-side on different samplers but with the same filter type.
- b. In the four cases in which 24-hour hi-vol as well as low-volume results are available for the same filter type run simultaneously (Gelman A, Gelman Spectrograde twice each) high-volume and low-volume filter results agreed within 5% in three of four cases and within 20% for the remaining case.

3. The mass results for 6-hour hi-vol and low-volume samples are given in Tables 33 and 34, with separate results listed for respirable and total low-volume samples. The results on the different filters are compared in Table 35 as ratios of arithmetic means  $\pm 1 \sigma$ . From these results and comparisons we note:

- a. Mass results on 24-hour Fluoropore are significantly lower than those of other filter types with both low- and high-volume samplers consistent with the reduced artifact sulfate and nitrate levels expected for the Teflon filters. The mass results on other filters are equal within experimental uncertainty.
- b. The relatively good agreement in mass found for filters such as MSA 1106BH low-vol with glass fiber hi-volume filters, in contrast to results for sulfate and nitrate may reflect, in part, the restriction of the low-volume filters to particles  $< 20 \mu\text{m}$  (i.e., enhanced artifact sulfate and nitrate on low-vol filters may be offset by the exclusion of soil particles  $> 20 \mu\text{m}$ ).

Table 32

MASS RESULTS FROM 24-HOUR SAMPLES ( $\mu\text{g}/\text{m}^3$ )

## SAN JOSE

Date (EPISODE)	High-Volume Samples			Low-Volume Samples			
	Gelman A	MSA 1106BH	Spectro- grade	Gelman A	MSA 1106BH	Spectro- grade	Fluoro- pore
Oct 4-5 (A)	103.7 101.4		113.7				101.3
Oct 5-6 (B)	112.4	111.7	116.3 72.1				
Oct 6-7 (C)	138.4		133.5		141.3		
Oct 7-8 (D)	90.6	91.6 91.8	91.2	92.0			
Oct 8-9 (E)	99.7		122.8 106.2			120.6	
Oct 9-10 (F)	53.4		58.7				

## LOS ALAMITOS

Oct 28-29 (A)	65.5 65.5		77.6				61.1
Oct 29-30 (B)	77.0	77.5	84.1 81.3				
Oct 30-31 (C)	147.5		150.4		67.0		
Oct 31-Nov 1 (D)	139.0	148.7 146.1	143.4	134.7			
Nov 1-2 (E)	134.0		147.5 139.8			119.2	
Nov 2-3 (F)	136.3	138.7 137.4	146.1				115.7
Nov 3-4 (G)	109.6	126.0 119.1	126.0				91.5
Nov 4-5 (H)	97.9 90.7		99.8				

Table 33

MASS RESULTS FROM SIX-HOUR SAMPLES AT SAN JOSE ( $\mu\text{g}/\text{m}^3$ )

Date (EPISODE)	Time PST	High-Volume Samples				Low-Volume Samples						
		Gelman A	MSA 1106BH	Spectrograde	Gelman A T <sup>a</sup>	R <sup>b</sup>	MSA 1106BH T	R	Spectrograde T	R	Fluoropore T	R
Oct 28-29 (A)	18-24	87.0									81.6	40.5
	24-6	75.9									81.8	27.5
	6-12	161.3									151.3	68.2
	12-18	111.1									107.4	41.7
Oct 29-30 (B)	18-24			138.0								
	24-6			120.6								
	6-12			184.6								
	12-18			158.6								
Oct 30-31 (C)	18-24						145.2	56.8				
	24-6						100.6	36.0				
	6-12						222.4	107.2				
	12-18						155.7	98.3				
Oct 31-Nov 1 (D)	18-24											
	24-6			53.2	58.7	32.8						
	6-12			55.0	42.8	37.5						
	12-18			161.7	162.5	85.5						
Nov 1-2	18-24				57.8	40.5						
	24-6											
	6-12											
	12-18											
Nov 2-3 (F)	18-24	103.8										
	24-6	112.6										
	6-12	105.6										
	12-18	120.5										
Nov 2-3 (F)	18-24	49.2										
	24-6	37.3										
	6-12	68.6										
	12-18	62.2										



Table 35

COMPARISON OF MASS RESULTS ON DIFFERENT FILTER MEDIA

	Ratio of Means			
	24-Hour Results		6-Hour Results	
	Ratio to Gelman A, Hi-Vol	Normalized to Fluoropore (N)	Ratio to Gelman A, Hi-Vol	Normalized to Fluoropore (N)
Gelman A, Hi-Vol	1.0	14	1.0	8
MSA 1106BH, Hi-Vol	1.04 ± .02	6		
Spectrograde, Hi-Vol	1.05 ± .02	14		
Gelman A, Lo-Vol	0.99 ± .02	2		
MSA 1106BH, Lo-Vol	0.73 ± .28	2		
Spectrograde, Lo-Vol	1.03 ± .16	2	0.81 ± .21	2
Fluoropore, Lo-Vol	0.89 ± .04	4	0.89 ± .03	4

a. The value for MSA for October 30-31 appears anomalous.

- c. Relative results for 6-hour samples with Spectrograde low-volume filters are lower than those on Fluoropore but the large uncertainty prevents conclusions.

In Table 36 the mean mass results calculated from four 6-hour samples are compared to the 24-hour value for each filter type. The filters exhibiting the lowest artifact sulfate and nitrate, Fluoropore and Gelman A, have values closest to 1.0 while Spectrograde and MSA show higher mean results.

The mean fraction of the total mass in the respirable size range, as obtained with 6-hour low-volume samples, is given in Table 37. In the preceding sections, it was shown that the fraction of respirable sulfate and nitrate on Fluoropore was the lowest of any filter type, a finding consistent with minimal artifact sulfate and nitrate. Fluoropore and Gelman A show the highest respirable particulate fraction. Such differences between results for mass and those for sulfate and nitrate may relate, in part, to the ability of filter media to retain large particle agglomerates on their surfaces when turned upside down during handling. Fluoropore filters would probably retain such agglomerates less well than the fibrous glass fiber media, leading to losses in mass primarily from the total particulate sample and, therefore, a higher respirable fraction would be observed. This provides no explanation for Gelman A glass fiber, however.

In summary, mass results with all filter media agree within 30%. Fluoropore, the filter providing the lowest levels of artifact sulfate and nitrate, exhibited the lowest 24-hour mass results and good agreement between short-term and 24-hour samples. The fraction of respirable particulate mass ranged from 0.4 to 0.6 for the different filter types with results for Fluoropore and Gelman A higher than with the other types.

Table 36

COMPARISON OF CALCULATED<sup>a</sup> AND OBSERVED<sup>b</sup>  
MASS VALUES

<u>Filter</u>	<u>Calculated/Observed Ratio of Means</u>	<u>N</u>
Gelman A	1.06 ± .02	10
MSA 1106BH	1.44 ± .40	4
Spectrograde	1.10 ± .18	4
Fluoropore	1.07 ± .03	4

a. Calculated mass is the mean of the four six-hour mass values for lo- and hi-vol samples.

b. Observed is the 24-hour mass value for lo- and hi-vol samples.

Table 37

RESPIRABLE MASS AS A FRACTION OF  
TOTAL PARTICULATE MASS IN SIX-HOUR  
LOW-VOL FILTER SAMPLES

<u>Filter</u>	<u>Respirable/Total Mass</u> <u>(Mean ratio <math>\pm</math> 1 <math>\sigma</math>)</u>	<u>N<sup>a</sup></u>
Fluoropore	0.58 $\pm$ 0.12	16
Spectrograde	0.44 $\pm$ 0.07	8
MSA 1106BH	0.49 $\pm$ 0.12	8
Gelman A	0.63 $\pm$ .06	8

a. Number of pairs.

## VI. Laboratory Study of Artifact Sulfate Formation on Clean Filter Media

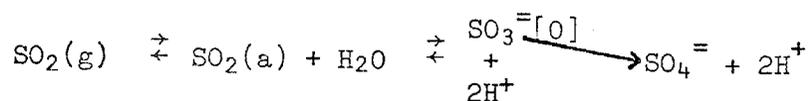
### A. Introduction

Artifact sulfate formation can, in principle, relate to interactions of gaseous sulfur species with either or both the filter media and the particulate matter. The first phase of our laboratory studies attempting to simulate artifact sulfate formation evaluated the interaction of SO<sub>2</sub> with clean filter media.

In principle, artifact sulfate formation could involve fixation and oxidation of atmospheric hydrogen sulfide (H<sub>2</sub>S) as well as SO<sub>2</sub>. To our knowledge, no studies of the interaction of H<sub>2</sub>S with filter media have been made. However, the low level of H<sub>2</sub>S relative to SO<sub>2</sub> in ambient air makes such studies of doubtful value, at least for ambient air sulfate monitoring.

It is highly desirable to monitor continuously the adsorption of acidic gases such as SO<sub>2</sub> on filter media since their degree of adsorption can be expected to decrease as alkaline sites on the filter become neutralized. Accordingly, adsorption of SO<sub>2</sub> on filters was monitored continuously by passing an air stream containing the pollutant through a filter (one filter at a time) and monitoring the SO<sub>2</sub> concentration upstream and downstream as a function of time. Based on previously reported studies with glass fiber filters, substantial removal of SO<sub>2</sub> by such filters was expected, initially, the fraction retained on the filter decreasing with time. The downstream/upstream concentration against time at constant temperature is referred to as adsorption isotherm. The construction of such isotherms is detailed in Appendix J.

Figure 42 illustrates an isotherm for SO<sub>2</sub> adsorption on MSA 1106BH. The area above the curve in the figure is proportional to the SO<sub>2</sub> adsorbed. The collection of SO<sub>2</sub> on filter media probably involves a series of steps such as the following:

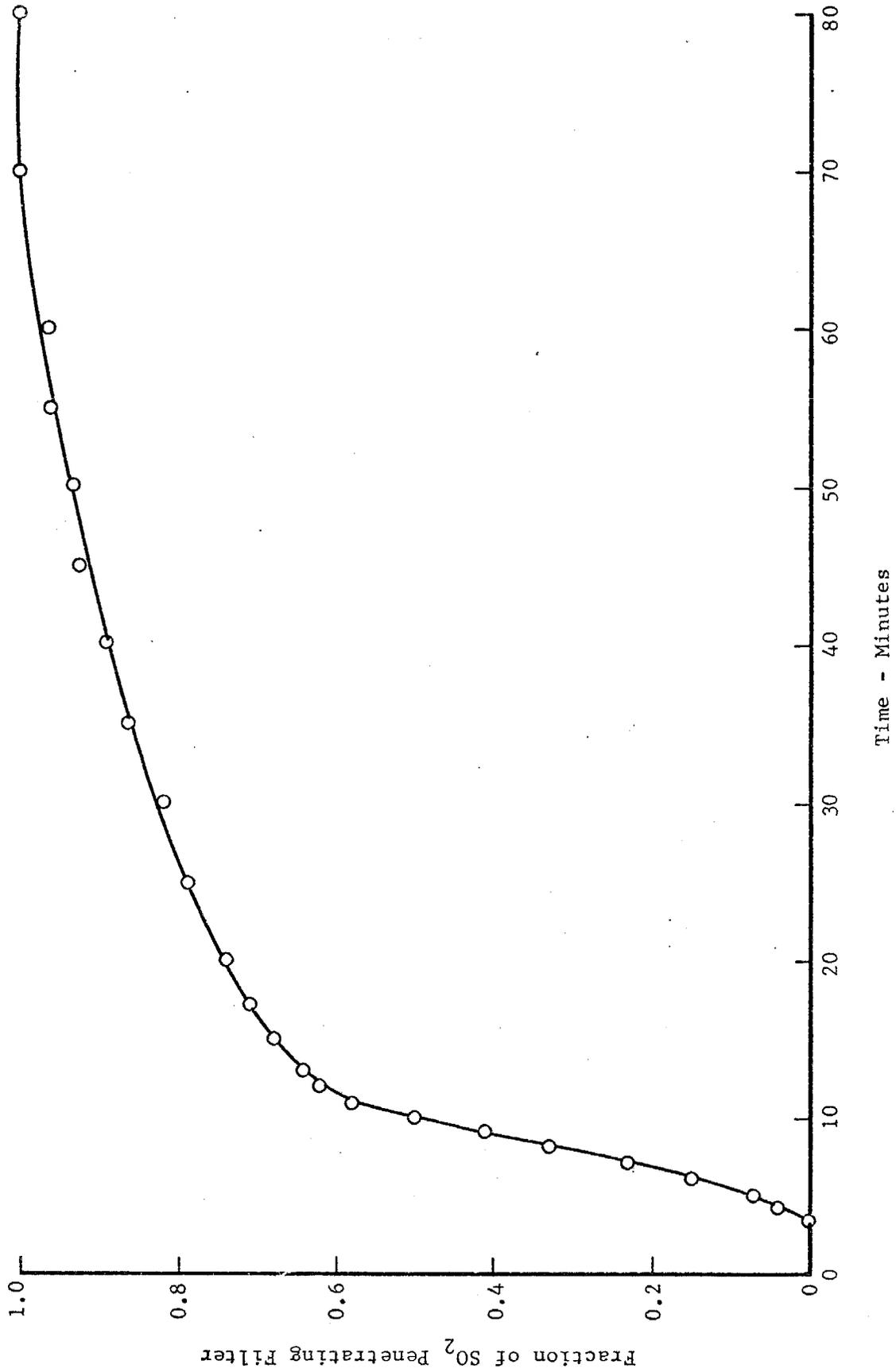


where SO<sub>2</sub>(g) = gas phase SO<sub>2</sub>

SO<sub>2</sub>(a) = adsorbed SO<sub>2</sub>

Oxidation of sulfur from the +4 state (as in SO<sub>2</sub> and sulfite, SO<sub>3</sub><sup>−</sup>) to the +6 state in sulfate probably occurs as a separate and discrete step from the initial adsorption of SO<sub>2</sub>. It was noted previously that under usual extraction and analysis conditions, sulfite is indistinguishable from sulfate. However, since sulfite formation is probably reversible with respect to gaseous SO<sub>2</sub>, the SO<sub>2</sub> adsorbed, as measured by a decrease in SO<sub>2</sub>(g), may not be equivalent to the sulfate observed after aqueous extraction.

FIGURE 42 - CORRECTED ADSORPTION ISOTHERM FOR MSA FILTER WITH SO<sub>2</sub>



## B. Adsorption Isotherm Results

Adsorption isotherms for SO<sub>2</sub> were determined for conditions relevant to the current program. Flow rates were 0.56 and 1.32 cfm which provided flow rates, in m<sup>3</sup>/cm<sup>2</sup>, equal to those used with the low-volume and high-volume filters in field sampling. SO<sub>2</sub> concentrations were 0.1 and 0.5 ppm and relative humidities either 50-60 or 90-95%.

Table 38 summarizes results obtained for all of the SO<sub>2</sub> isotherms. The isotherms are characterized by lag time (i.e., the time, in minutes, for which penetration is negligible) and times to 95 and 100% SO<sub>2</sub> penetration. Also shown are the expected sulfate levels, obtained by integration of the isotherms in all cases where this was feasible, the observed sulfate, and the ratio of observed to expected sulfate. A value of 1.0 in this ratio implies that all SO<sub>2</sub> adsorbed is analyzed as water soluble sulfate. A value < 1.0 suggests that some of the adsorbed SO<sub>2</sub> was lost, presumably by desorption following the filter exposure. From this table we note the following.

1. At the higher flow rate and lower humidity, the time required to saturate filters with SO<sub>2</sub> is reduced.
2. The time required to saturate filters, in general, followed the order Fluoropore = Gelman GA-1 < Whatman 41 < Gelman A < EPA Grade < MSA. The position of Gelman Spectrograde appears variable being either immediately before or after Gelman A.

This pattern is similar to that found for atmospheric sulfate and nitrate on these filter types.

3. The ranking of the different filters by order of increasing observed artifact sulfate generally paralleled that for time to saturation. The results for EPA Grade, 50% R.H., 0.56 cfm, 0.1 ppm SO<sub>2</sub> appear anomalous.
4. Higher artifact sulfate levels, in ug/filter, were observed at lower flow rates.
5. Fluoropore and Whatman 41 results suggest that SO<sub>2</sub> adsorption is largely reversible on these filters with much of the SO<sub>2</sub> being lost before aqueous extraction. With MSA and Gelman A, the SO<sub>2</sub> adsorbed was apparently converted irreversibly to a material analyzed as sulfate. Results with the EPA Grade filters resemble those with MSA and Gelman A at 0.5 ppm SO<sub>2</sub> but correspond more closely to the behavior of Fluoropore and Whatman 41 with respect to reversibility at 0.1 ppm SO<sub>2</sub>. The results with Spectrograde filters are also variable. Since the expected sulfate levels for exposed Gelman GA-1 were insufficient to permit calculation, no conclusions on the degree of reversibility of SO<sub>2</sub> sorption can be reached for this filter.

Table 38

SUMMARY OF SO<sub>2</sub> ADSORPTION ISOTHERM RESULTS

Filter Type	I.D.	Response, min			SO <sub>4</sub> <sup>=</sup>	SO <sub>4</sub> <sup>=</sup>	Observed Expected	SO <sub>4</sub> <sup>=</sup>
		lag	to 95%	to 100%	Expected µg	Observed µg		
		Conditions: 90% R.H.			1.32 cfm		0.5 ppm SO <sub>2</sub>	
Spectrograde	0201S	0.1	2.5	5	-- <sup>a</sup>	57.3		
EPA Grade	4001E	0.1	3.5	6	243	286	1.18	
		Conditions: 60% R.H.			1.32 cfm		0.5 ppm SO <sub>2</sub>	
Whatman 41	0602W	0.2	1.5	ca. 2	--	4.7		
Gelman A	0002A	0.1	1	2	--	57.6		
EPA Grade	4002E	0.2	4.5	5	189	223	1.18	
MSA	0402M	(1.5)	6	7	--	334		
		Conditions: 90% R.H.			0.56 cfm		0.5 ppm SO <sub>2</sub>	
Fluoropore	1001F	0.5	2	ca. 4	65.7	< L.D.	< 0.06	
Gelman GA-1	2001G	0.1	0.5	0.5	--	11.3		
Spectrograde	0202S	0.5	16	30	106	89.8	0.85	
MSA	0403M	0.6	30	50	315	390	1.24	
		Conditions: 50% R.H.			0.56 cfm		0.1 ppm SO <sub>2</sub>	
Fluoropore	1002F	0.1	0.5	0.5	--	< L.D.		
Gelman GA-1	2002G	0.05	0.1	0.5	--	6.2		
Spectrograde	0203S	0.1	33	48	67.5	43.3	0.64	
Gelman A	0003A	0.5	25	55	33.9	46.3	1.36	
EPA Grade	4003E	5	125	160	197	27	0.14	
MSA	0404M	6.5	150	250	262	308	1.18	
		Conditions: 50% R.H.			1.32 cfm		0.1 ppm SO <sub>2</sub>	
Whatman 41	0604W	0.1	0.5	4	11.6	< L.D.	< 0.34	
Spectrograde	0204S	0.5	25	50	90.2	18.6	0.21	
Gelman A	0004A	0.2	4	10	29.7	40.7	1.37	
EPA Grade	4004E	2.5	65	90	246	125	0.51	
MSA	0405M	3.5	55	70	262	206	0.78	

<sup>a</sup> A dash indicates that no calculation of expected sulfate was possible since integration of the isotherm was unfeasible due to an insignificant difference from the system blank.

6. No quantitative conclusions can be drawn from these data on the influence, individually, of relative humidity and SO<sub>2</sub> concentration on artifact sulfate formation. However, simultaneously decreasing both relative humidity and SO<sub>2</sub> concentration consistently decreased the observed artifact sulfate.

#### C. Sulfite vs. Sulfate Formation

While it may be of little practical significance to distinguish sulfite and sulfate because of subsequent oxidation during extraction and analysis, it is of substantial interest in efforts to understand the nature of SO<sub>2</sub>- filter media interactions. Accordingly, a brief study was made evaluating sulfite vs. sulfate formation in simultaneous sampling of 0.1 ppm SO<sub>2</sub> at 50% R.H. in 6-hour exposures with the seven filter types. Sulfite was determined as described in Appendix H. The results are given in Table 39. Where measurable, the results indicate that the proportion of sulfite is highest for the high pH filters; the correlation between the proportion of sulfite (S<sup>IV</sup>) and pH is illustrated in Figure 43. Only Whatman 41 appears to have higher than expected S<sup>IV</sup> levels.

The sulfate results cited in this report are to be considered the sum of sulfate and any sulfite present.

The filter pH reasonably controls the extent of fixation of SO<sub>2</sub> as either SO<sub>2</sub> (adsorbed) or SO<sub>3</sub><sup>=</sup>. If the rate of subsequent oxidation to sulfate is comparatively slow and independent of the concentration of the SO<sub>2</sub> (adsorbed) or SO<sub>3</sub><sup>=</sup>, then increasing pH would lead to an increasing proportion of sulfite. Further studies are needed to confirm this inference.

#### D. Artifact Sulfate Formation in Side-by-Side Exposures of Filters to SO<sub>2</sub> in Clean Air

##### 1. Compilations of Results

Tables 40 and 41 compile the artifact sulfate results obtained under a variety of conditions. In general, the results are means for two independent trials. In addition to results in µg/filter, results are expressed relative to those obtained by the EPA Grade material. MSA 1106BH and the EPA Grade filters exhibit the highest levels of artifact sulfate, consistent with their high pH. Fluoropore and Gelman GA-1 filters exhibit negligible or slight artifact sulfate levels in all cases.

Artifact sulfate results for some of the data given are shown again in µg per m<sup>3</sup> of air sampled at a flow rate equivalent to a hi-volume (Table 42) and low-volume (Table 43) sampler. The results for 6-hour sampling at the hi-vol flow rate indicate positive errors up to 31 µg/m<sup>3</sup> (for the EPA Grade and MSA filter). For 24-hour sampling, the maximum error observed was about 8 µg/m<sup>3</sup> (for the MSA filter). Lo-vol sample errors up to 74 µg/m<sup>3</sup> and 13 µg/m<sup>3</sup> were noted for 6-hour and 24-hour sampling, respectively, again, with the MSA 1106BH filters.

Table 39

SULFITE vs. SULFATE FORMATION FROM  
SO<sub>2</sub>-CLEAN FILTER INTERACTION

<u>Filter</u>	$\text{SO}_3^=$ (as $\mu\text{g S}^{\text{IV}}$ /filter)	$\text{SO}_3^= + \text{SO}_4^=$ (as $\mu\text{g S}^{\text{IV}} + \text{S}^{\text{VI}}$ /filter)	$\frac{\text{S}^{\text{IV}}}{\text{S}^{\text{IV}} + \text{S}^{\text{VI}}}$	$\frac{\text{S}^{\text{IV}}}{\text{S}^{\text{VI}}}$
Fluoropore	0.1 ± .1	0.1 ± .1	_a	_a
Gelman GA-1	0.1 ± 0	2.8 ± .4	0.0 ± .1	0.0
Whatman 41	0.6 ± .3	2.3 ± .4	0.3 ± .1	0.3 ± .3
Spectrograde	0.9 ± .4	20.5 ± 2.1	0.0	0.0
Gelman A	1.8 ± .6	15.6 ± 1.1	0.1 ± .04	0.1 ± .03
MSA 1106BH	38.1 ± 2.2	79.8 ± 18.6	0.5 ± .1	0.9 ± .4
EPA Grade	34.8 ± 2.4	55.2 ± 8.4	0.6 ± .1	1.7 ± .7

Conditions: 0.1 ppm SO<sub>2</sub>  
50% R.H.  
1.32 cfm  
6 hours  
20°C

a. Not reliably determinable

Figure 43

SCATTER DIAGRAM OF SULFITE FRACTION AGAINST FILTER pH

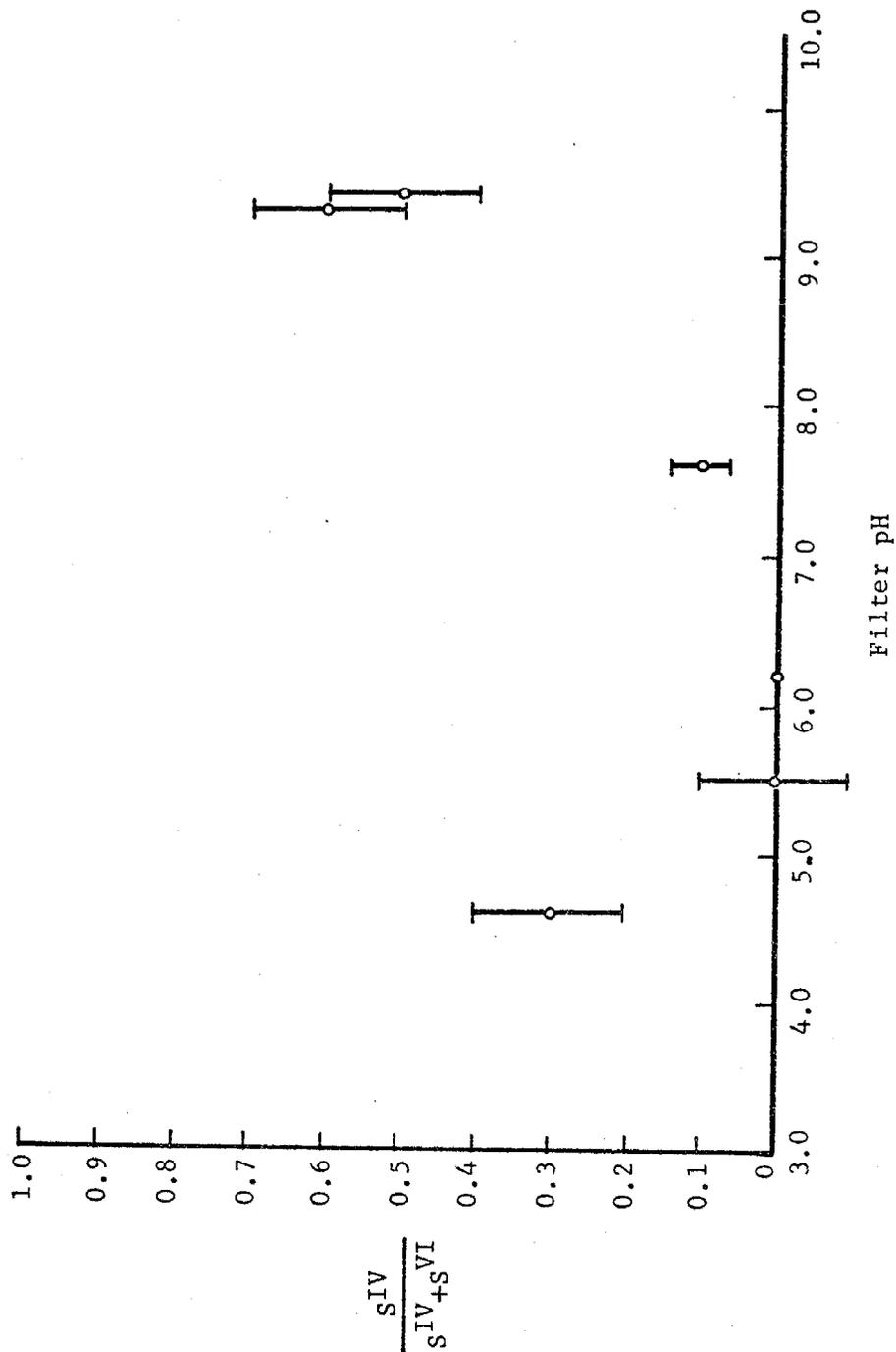




Table 41

SO<sub>2</sub>-CLEAN FILTER EXPOSURES AS A FUNCTION OF TEMPERATURE  
AND RELATIVE HUMIDITY AT HI-VOL FLOW RATE <sup>a</sup>  
( $\mu\text{g}/\text{filter}$ )

Conditions	7°C 90% RH 0.1 ppm (SO <sub>2</sub> ) 2 hour	6°C 90% RH 0.5 ppm (SO <sub>2</sub> ) 2 hour	5°C 50% RH 0.1 ppm (SO <sub>2</sub> ) <sup>d</sup>	7°C 50% RH 0.5 ppm (SO <sub>2</sub> ) 2 hour	21°C 35% RH 0.5 ppm (SO <sub>2</sub> ) 2 hour	21°C + 0.6 35% RH 0.1 ppm (SO <sub>2</sub> ) 2 hour
Fluoropore	- b	- b	- b	- b	- b	- b
Gelman GA-1	11.1 ± 1.2	9.7 ± 1.9	5. ± 0.8	5.4 ± 0.1	13.6 ± 2.0	8.7 ± 0.4
Whatman 41	- b	- b	- b	- b	- b	- b
Spectrograde	33.6 ± 16.5	35.4 ± 11.7	14.5 ± 2.1	30.6 ± 1.9	4.1 <sup>c</sup>	13.5 <sup>c</sup>
Gelman A	49.9 ± 2.5	47.4 ± 0.8	41.4 ± 3.1	42.0 ± 0.6	36.4 ± 3.0	29.9 ± 3.1
MSA 1106BH	239.3 ± 3.7	264.0 ± 35.6	163.7 ± 13.0	175.5 ± 12.8	160.2 ± 15.2	147.5 ± 6.4
EPA Grade	234.6 ± 0.8	241.9 ± 1.2	104.1 ± 11.4	109.5 ± 9.5	63.1 ± 5.2	64.1 ± 6.1

Table 41 (continued)

SO<sub>2</sub>-CLEAN FILTER EXPOSURES AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY AT HI-VOL FLOW RATE <sup>a</sup>

(µg/filter)

Conditions	35°C 15% RH 0.1 ppm (SO <sub>2</sub> ) 2 hour	35°C 15% RH 0.5 ppm (SO <sub>2</sub> ) 2 hour	35°C 50% RH 0.1 ppm (SO <sub>2</sub> ) 2 hour	35°C 50% RH 0.5 ppm (SO <sub>2</sub> ) 2 hour
Fluoropore	- b	- b	- b	- b
Gelman GA-1	6.6 ± 0.5	14.3 ± 0.5	7.3 ± 0.7	9.7 ± 1.5
Whatman 41	- b	- b	- b	- b
Spectrograde	15.2 ± 2.1	15.5 ± 2.8	28.1 ± 2.0	26.1 ± 2.8
Gelman A	28.7 ± 4.2	31.6 ± 1.6	35.7 ± 3.8	35.0 ± 0.9
MSA 1106BH	123.3 ± 14.2	128.8 ± 15.7	186.8 ± 8.6	195.9 ± 7.0
EPA Grade	30.9 ± 4.5	36.4 ± 5.6	97.2 ± 5.3	126.4 ± 1.6

a. Flow rate 1.32 cfm providing face velocity of 47 cm/sec, equivalent to an 8 x 10" filter at 40 cfm. Results are for two independent trials except as noted.

b. Results are below the limit of detection: 2.5 µg/filter (before correction for blank).

c. Results are from 1 trial. The error is the precision for replicate analyses of the same filter extract.

d. Average ± 1 σ of one 2-hour and one 3-hour run in each case.

Table 42

SUMMARY OF ARTIFACT SULFATE RESULTS ( $\mu\text{g}/\text{m}^3$ )  
AT HI-VOL FLOW RATE<sup>a</sup>

	24-Hour Sampling		6-Hour Sampling		
	0.1 ppm SO <sub>2</sub> 50% RH	0.5 ppm SO <sub>2</sub> 90% RH <sup>b</sup>	0.1 ppm SO <sub>2</sub> 50% RH	0.1 ppm SO <sub>2</sub> 90% RH	0.5 ppm SO <sub>2</sub> 90% RH <sup>b</sup>
Fluoropore	- <sup>c</sup>	- <sup>c</sup>	0.02 ± 0.01 <sup>d</sup>	0.22 ± 0.04	- <sup>c</sup>
Gelman GA-1	- <sup>c</sup>	- <sup>c</sup>	0.63 ± 0.09 <sup>d</sup>	1.40 ± 0.18	- <sup>c</sup>
Gelman A	1.03 ± 0.10	1.98 ± 0.02	3.50 ± 0.26	5.04 ± 0.41	9.54 ± 3.4
Spectrograde	1.17 ± 0.20	3.03 ± 0.06	4.58 ± 0.48	8.76 ± 0.77	4.39 ± 0.11
Whatman 41	0.44 ± 0.04	1.77 ± 0.01	0.52 ± 0.08	1.73 ± 0.40	1.07 ± 0.03
MSA 1106BH	5.27 ± 0.38	7.92 ± 0.63	17.8 ± 4.2	30.7 ± 1.0	29.0 ± 1.0
EPA Grade	3.48 ± 0.41	6.71 ± 0.52	12.3 ± 1.9	25.9 ± 0.7	30.8 ± 2.2

a. Flow rate 1.32 cfm providing face velocity of 47 cm/sec, equivalent to an 8 x 10" filter sampling at 40 cfm. Results are for two independent trials except as noted.

b. Results are for one trial. The error is the precision for replicate analysis of the same filter extract.  
c. No sample taken.

Table 43

SUMMARY OF ARTIFACT SULFATE RESULTS ( $\mu\text{g}/\text{m}^3$ )  
AT LO-VOL FLOW RATES<sup>a</sup>

	24-Hour Sampling		6-Hour Sampling
	0.1 ppm SO <sub>2</sub> 50% RH	0.5 ppm SO <sub>2</sub> 90% RH	
Fluoropore	< 0.05 <sup>c</sup>	< 0.03 <sup>c</sup>	< 0.02 <sup>c</sup>
Gelman GA-1	0.61 ± 0.10	0.76 ± 0.08	2.65 ± 0.83
Gelman A	2.33 ± 0.14	5.40 ± 0.26	16.7 ± 1.8
Spectrograde	2.89 ± 0.33	7.39 ± 1.6	4.37 ± .06 <sup>b</sup>
Whatman 41	0.63 ± 0.05	1.53 ± 0.04	0.88 ± 0.02 <sup>b</sup>
MSA 1106BH	13.4 ± 0.9	19.1 ± 0.7	74.4 ± 2.1 <sup>b</sup>
EPA Grade	8.20 ± 0.43	21.6 ± 1.9	65.6 ± 8.3

- a. Flow rate 0.56 cfm. Results are for two independent trials except as noted.
- b. Results are for one trial. The error is the precision for replicate analysis of the same filter extract.
- c. Below or near the minimum detection level of ~0.05  $\mu\text{g}/\text{m}^3$  (before correction for blank). Results below minimum detection level of ~0.1  $\mu\text{g}/\text{m}^3$  (before correction for blank).
- d. Results near or below minimum detection level of ~0.04  $\mu\text{g}/\text{m}^3$  (before correction for blank).

In subsequent sections, these results are further examined for the influence of specific variables on observed sulfate levels.

## 2. The Effect of Time in Side-by-Side Exposures of Filters to SO<sub>2</sub>

The results of the isotherm studies imply that exposing filters for more than four hours may be unnecessary since saturation is achieved before this with all of the filters. However, since SO<sub>2</sub> sorption can be reversible, it is difficult to predict if the observed sulfate value would remain constant after increased exposure times.

The influence of exposure time, shown in Figures 44 and 45 for 50 and 90% R.H., respectively, indicates that for MSA and the EPA Grade, the level of observed sulfate remains constant within  $\pm 10\%$  at 400  $\mu\text{g}/47$  mm filter over a 6- to 24-hour period when exposed to 0.5 ppm SO<sub>2</sub> at 90% R.H. Similarly for Gelman A, the level remained constant. However, at 90% R.H. with Spectrograde and Whatman 41, the observed sulfate continued to increase. At 50% R.H., increase was seen only with the hygroscopic Whatman 41. It was concluded from these studies that 24-hour exposures were essential to adequately assess levels of artifact sulfate formation expected on 24-hour samples due to SO<sub>2</sub>-filter interactions.

It may be noted that the filters which showed increasing sulfate with time also showed ratios of observed/expected sulfate substantially below 1.0 in the isotherm studies and sulfite/sulfite + sulfate ratios  $\ll 1.0$  (6-hour exposures). It appears that with these filters a slow oxidation of sulfite and/or adsorbed SO<sub>2</sub> occurs yielding sulfate irreversibly. The higher the proportion of sulfur as sulfate, the lower can be the loss of sulfur by desorption following removal of the filter from the exposure system.

## 3. The Effects of Flow Rate and SO<sub>2</sub> Concentration

An increase in flow rate for a constant sampling time and SO<sub>2</sub> concentration can influence artifact sulfate in two ways: The quantity of SO<sub>2</sub> collected might increase assuming that the alkaline sites were not completely neutralized during sampling at the lower rate. Secondly, since the total air volume sampled increases in proportion to the flow rate, the calculated sulfate concentration, in  $\mu\text{g}/\text{m}^3$ , may decrease.

The effect of flow rate was explored at both 50 and 90% and with 6-hour and 24-hour samples (Figure 46). In general, little effect was seen, calculating results as  $\mu\text{g}$  sulfate per filter. If calculated as  $\mu\text{g}/\text{m}^3$  sulfate, a sharp decrease in sulfate concentration with increased flow rate would have been seen.

Increasing the SO<sub>2</sub> concentration from 0.1 to 0.5 ppm is seen to have a negligible or small influence on artifact sulfate in 6-hour exposures (Figure 47). This is consistent with substantially complete neutralization of alkaline sites on the filters at the lower concentration.

Figure 44  
SULFATE OBSERVED VS. SO<sub>2</sub> EXPOSURE TIME

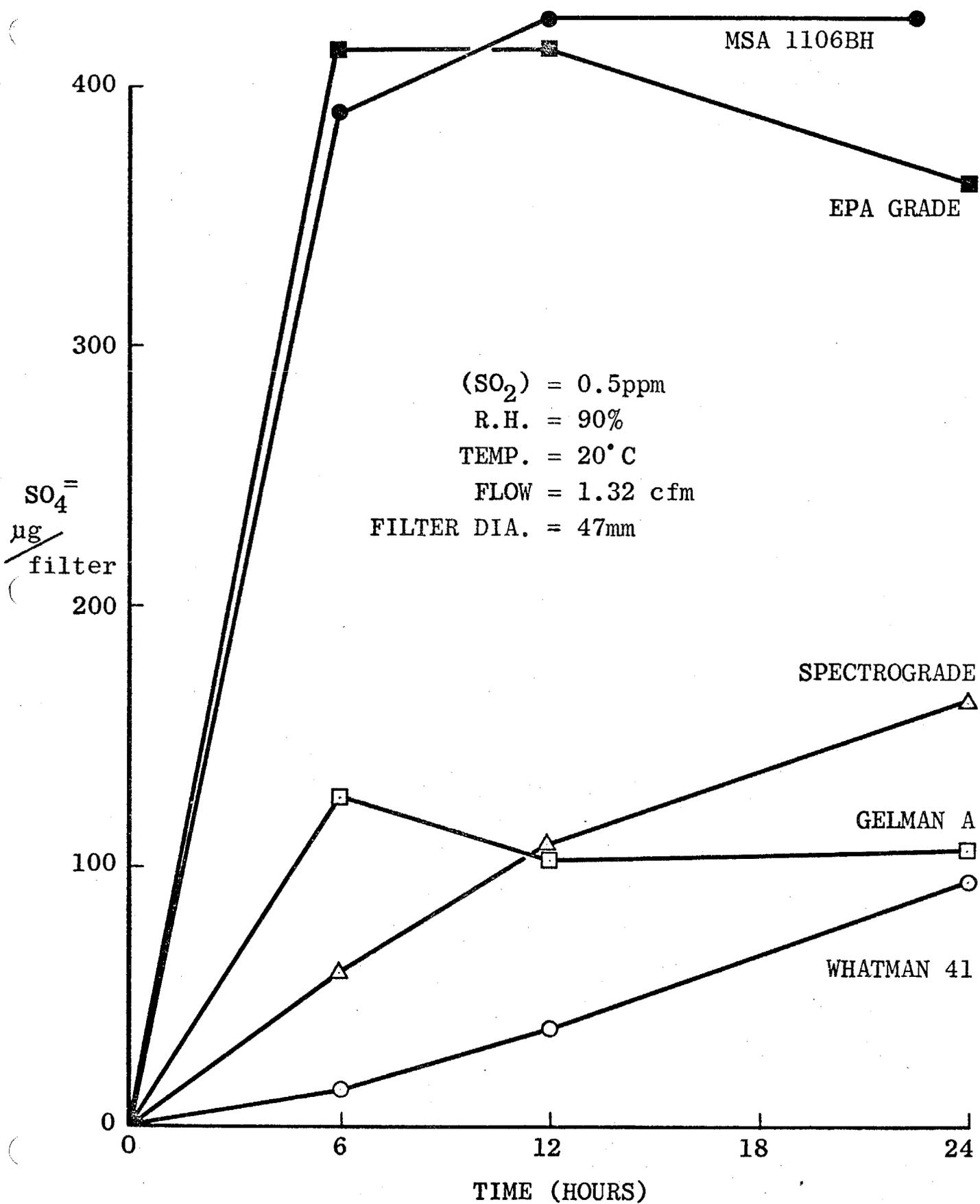


Figure 45

SULFATE OBSERVED vs. SO<sub>2</sub> EXPOSURE TIME

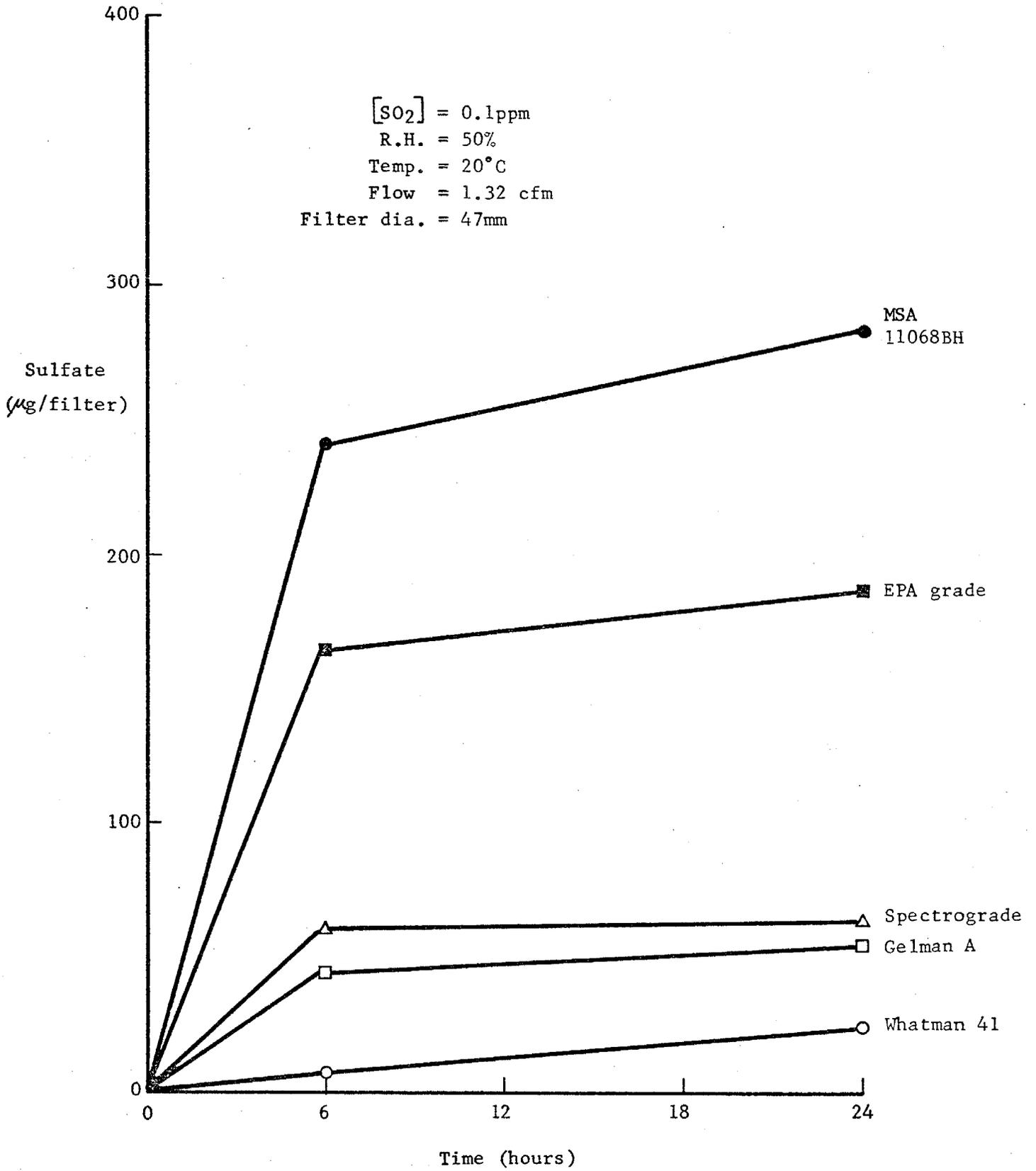


Figure 46

THE EFFECT OF FLOW RATE ON ARTIFACT SULFATE

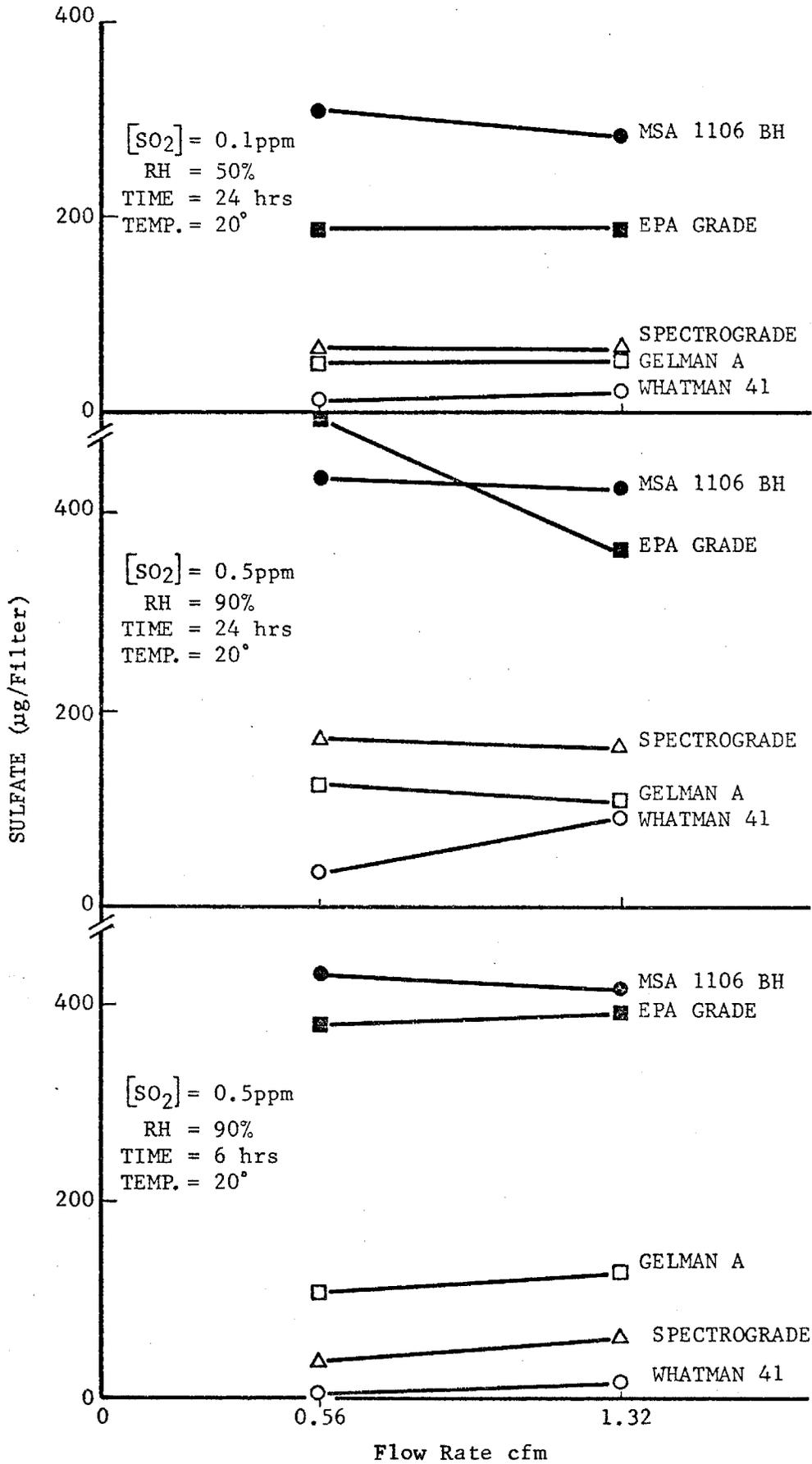
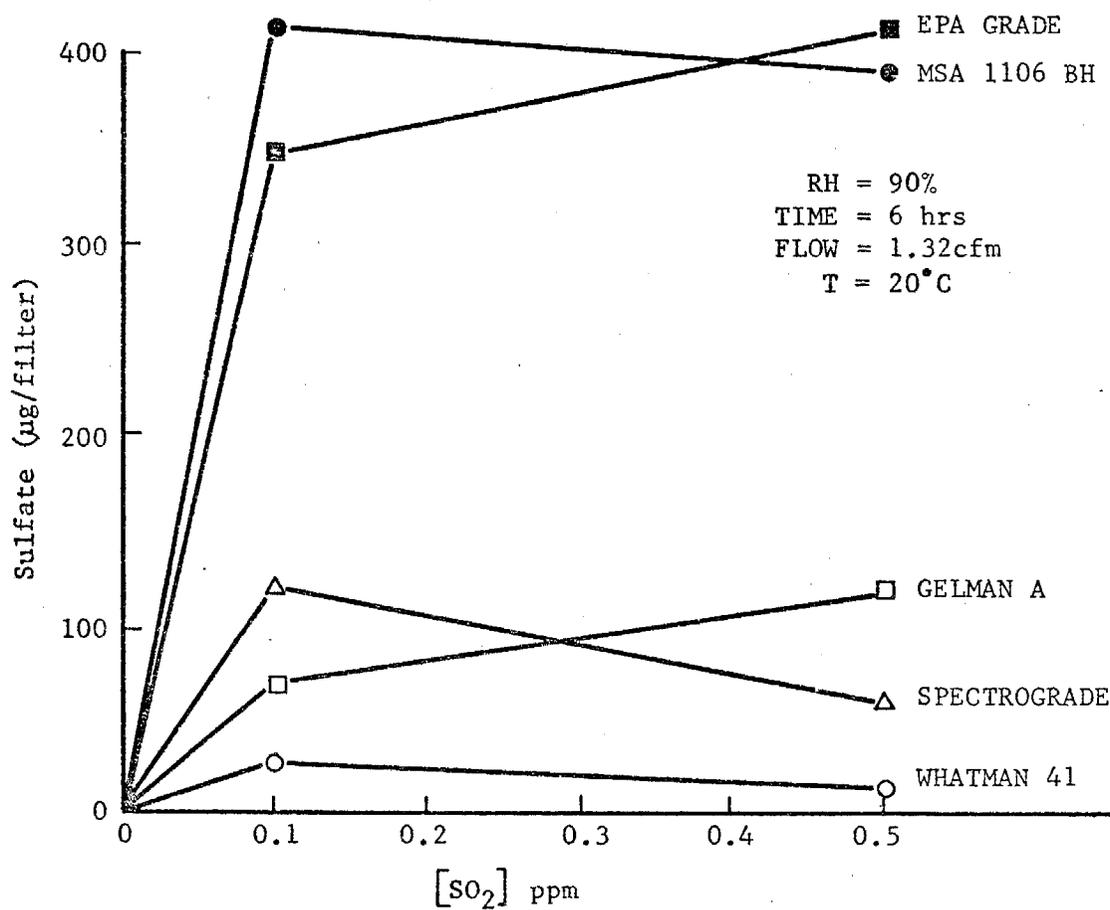


Figure 47

THE EFFECT OF SO<sub>2</sub> CONCENTRATION  
ON ARTIFACT SULFATE



#### 4. The Effect of Relative Humidity and Temperature on Artifact Sulfate

The effect of changing from 50 to 90% relative humidity at constant temperature can be seen in the data obtained with 6-hour exposures with 0.1 ppm SO<sub>2</sub> (Figure 48). In all cases, a pronounced increase is observed, approaching or exceeding a factor of two with high pH filters.

Varying relative humidity at constant temperature is done by changing the absolute humidity of the air stream. Thus, either or both relative and absolute humidity may be the cause of the observed change in artifact sulfate.

An alternative experiment is to vary relative humidity while maintaining absolute humidity constant. This requires variation in temperature leading, again, to possible ambiguity in interpretation. The effects of changing relative humidity at constant absolute humidity was studied with both 0.1 and 0.5 ppm SO<sub>2</sub> (Figure 49). The results parallel those obtained at constant temperature; excepting for Gelman GA-1, all filters showed increasing artifact sulfate at higher R.H. with the effect especially pronounced for the high pH filters, MSA 1106BH and EPA Grade.

Finally, the effect on artifact sulfate formation of changing temperature at constant relative humidity is shown in Figure 50. Increasing temperature leads to generally increasing artifact sulfate with the high pH filters (MSA and EPA Grade) as well as Gelman GA-1. Results are not shown for Fluoropore or Whatman 41 filters since observed sulfate levels in these two-hour exposure studies were below limits of detection. For Spectrograde and Gelman A filters, sulfate either decreased or remained constant within experimental uncertainty.

If the extent of adsorption of SO<sub>2</sub> were the limiting factor in artifact sulfate formation and if this adsorption involved relatively weak bonding (e.g., physical adsorption) increased temperature should decrease artifact sulfate. The opposite trend with the high pH filters suggests either that bonding is not weak and/or the rate of a subsequent step (e.g., oxidation to SO<sub>4</sub><sup>VI</sup>) may determine the extent of artifact sulfate observed.

#### E. The Effect of Ammonia on Artifact Sulfate Formation

Ammonia was introduced into the exposure system at two concentrations considered relevant to ambient air levels, 40 and 90 ppb.<sup>12</sup> A Lear-Siegler (SM 1000) second derivative spectrometer, calibrated for ammonia immediately before use against an NH<sub>3</sub> permeation tube of known emission rate, was used to continuously monitor NH<sub>3</sub> levels.

Figure 48

EFFECT OF RELATIVE HUMIDITY  
ON ARTIFACT SULFATE AT CONSTANT TEMPERATURES

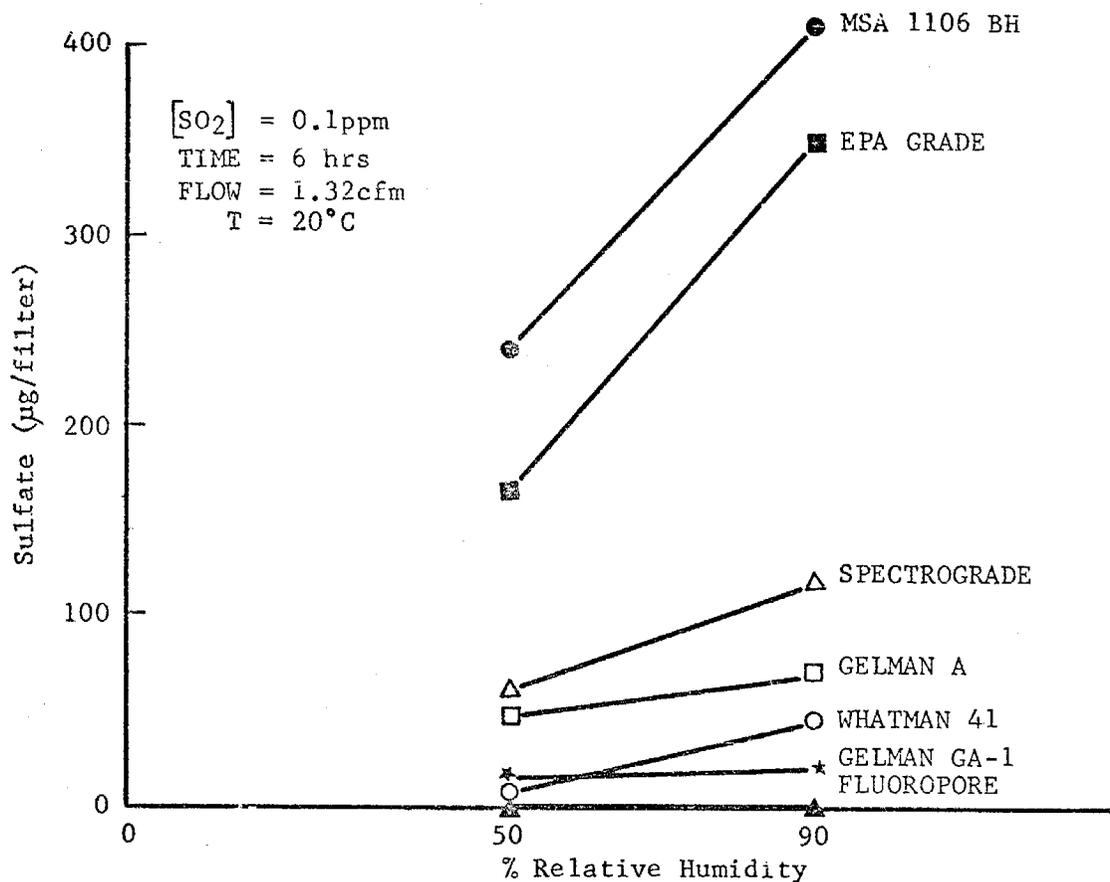


Figure 49

THE EFFECT OF CHANGE IN RELATIVE HUMIDITY (AT CONSTANT ABSOLUTE HUMIDITY)  
ON ARTIFACT SULFATE FORMATION

MSA 1106BH

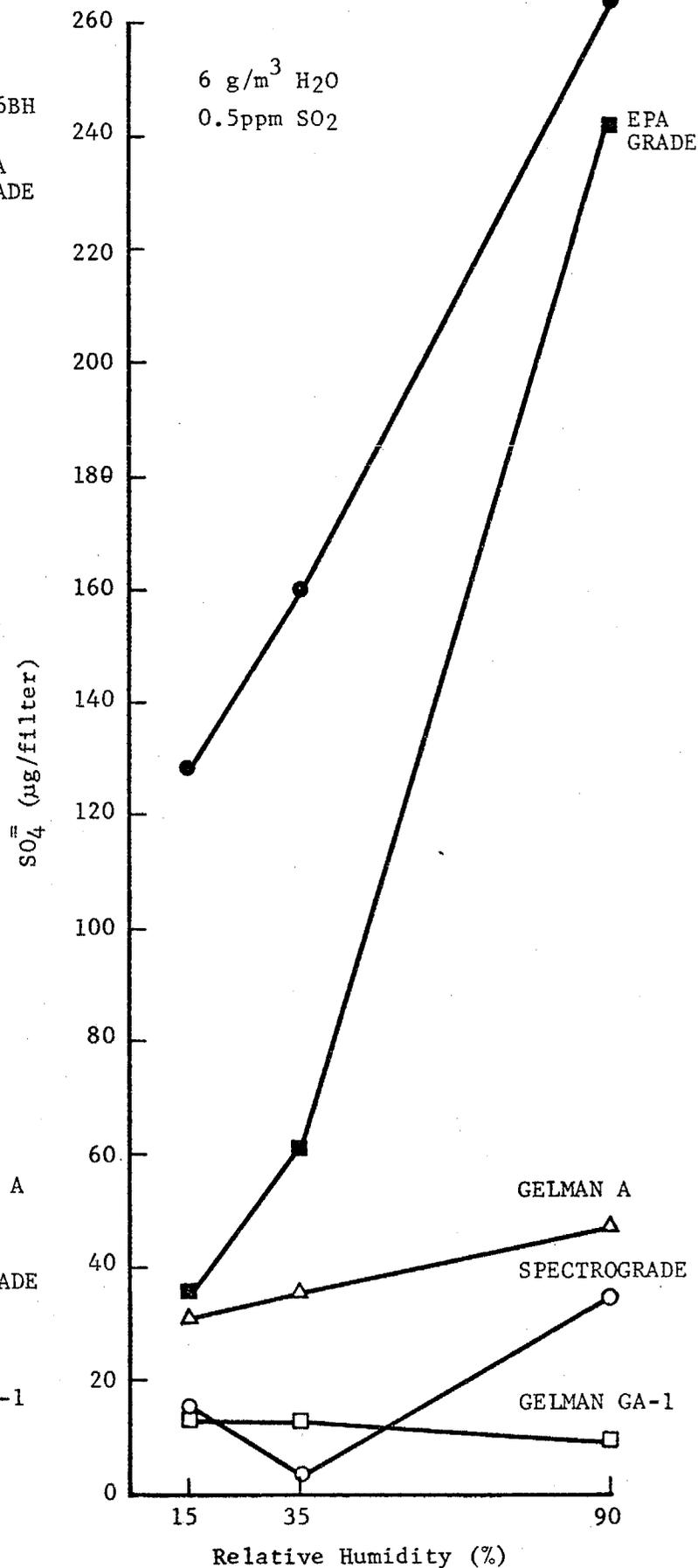
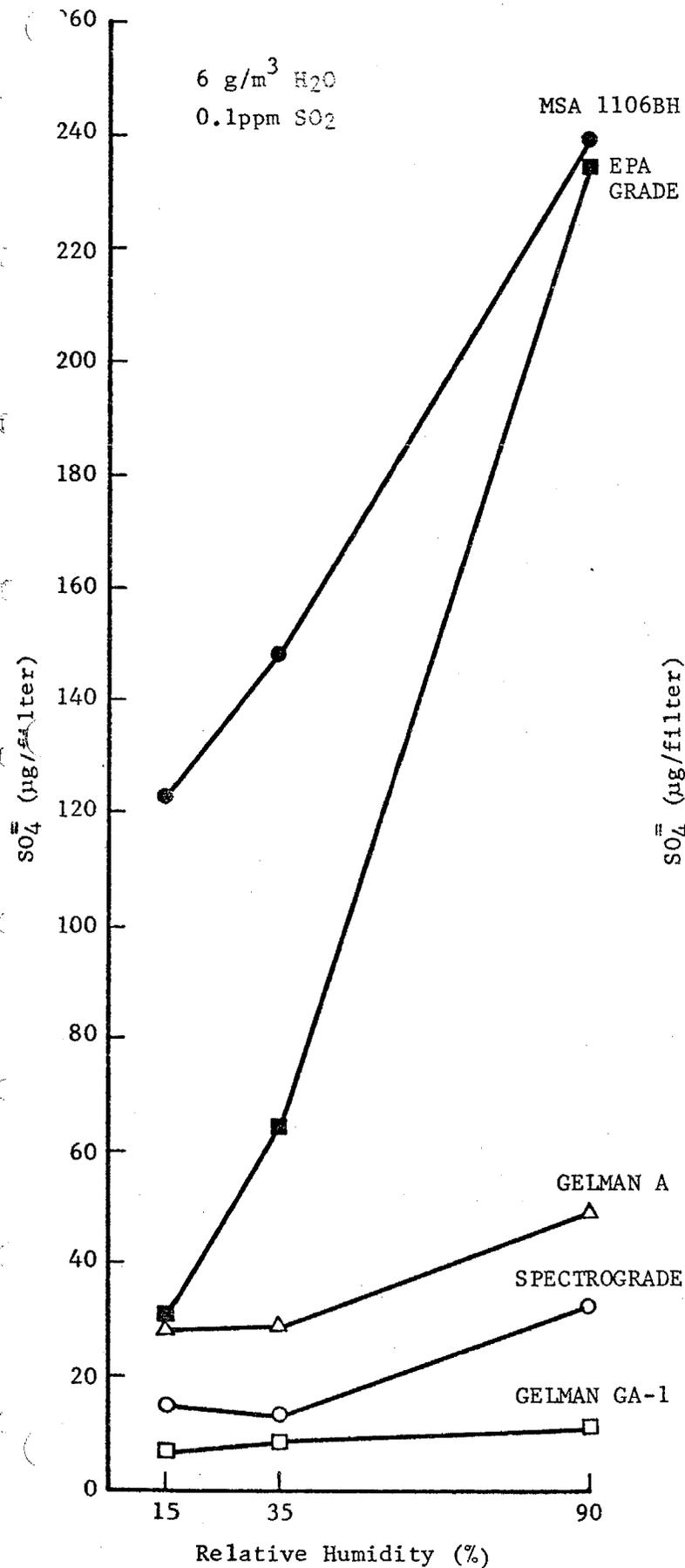
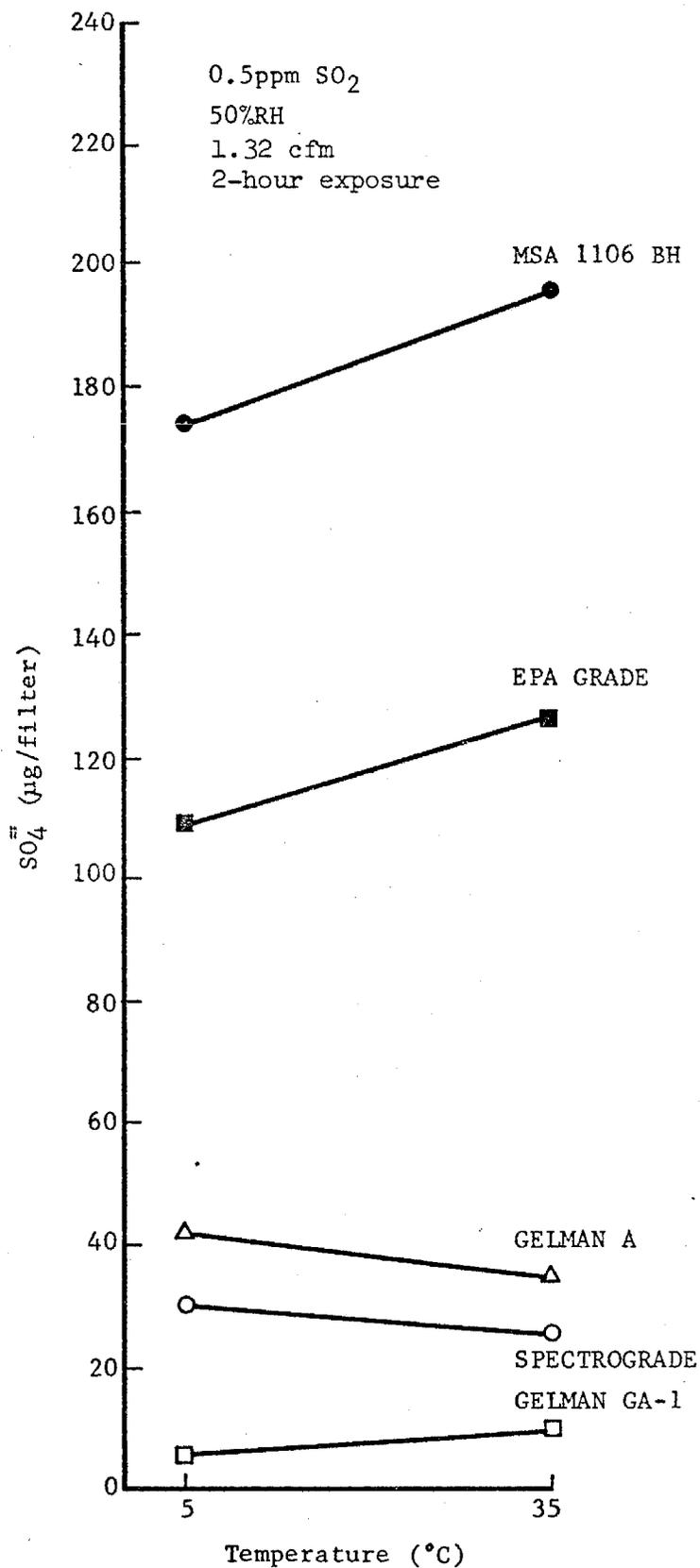
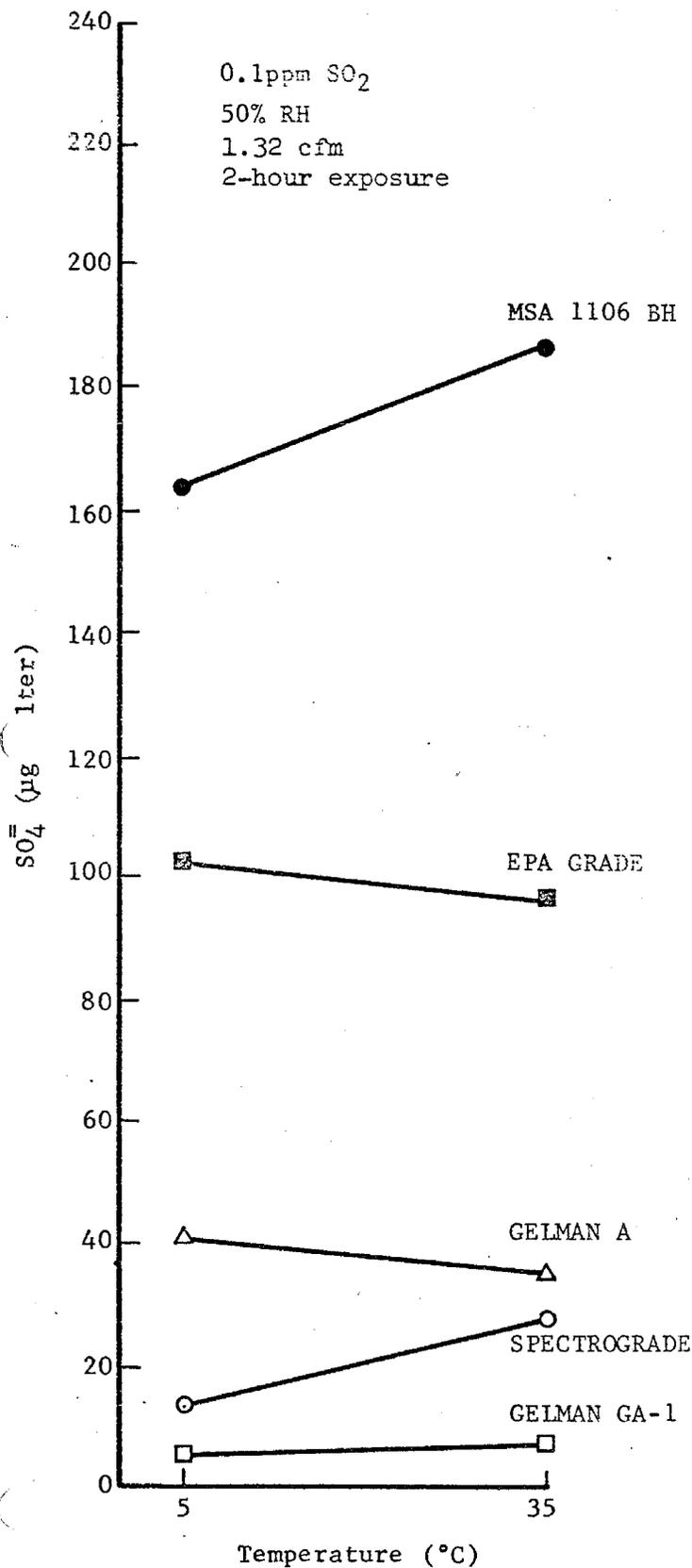


Figure 50

THE EFFECT OF TEMPERATURE CHANGE ON ARTIFACT SULFATE FORMATION



Sulfur dioxide gave a 100% positive interference in the NH<sub>3</sub> measurement. Since SO<sub>2</sub> was monitored independently (using a Meloy flame photometric total sulfur analyzer) no difficulty was encountered in accurately measuring NH<sub>3</sub> levels.

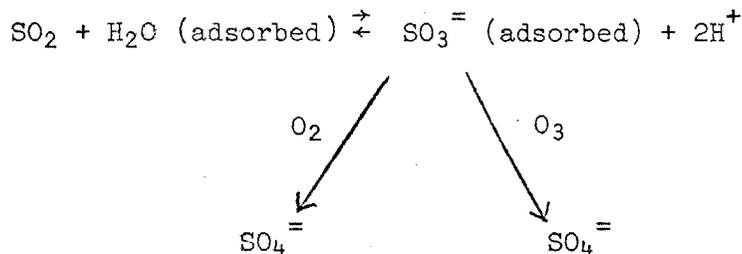
Mean results for two runs at 0, 40 and 90 ppb NH<sub>3</sub> are given in Table 44. Ammonia is seen to cause a slight enhancement in artifact sulfate with the low pH filters, Fluoropore, Gelman GA-1 and Whatman 41. With the other filters the effect of ammonia is, within experimental error, negligible.

#### F. The Effect of Ozone on Artifact Sulfate Formation

Ozone was generated by an Hg arc source and introduced into the exposure system to provide 0.5 ppm O<sub>3</sub>. This level was selected to represent close to the expected upper limit of urban ambient concentrations. Ozone levels were monitored using a Bendix chemiluminescent analyzer with calibration referenced against the UV procedure.

The effect of 0.5 ppm ozone on SO<sub>2</sub> absorption by filter media was evaluated at both 50% and 90% relative humidity. The results are summarized in Table 45. Ozone clearly enhanced the observed sulfate in all cases. The increase was generally higher for the filters of higher pH.

The enhancement of observed sulfate suggests either (or both) oxidation of SO<sub>2</sub> to SO<sub>3</sub> in gas phase and hydration to H<sub>2</sub>SO<sub>4</sub> or oxidation of SO<sub>2</sub> following its absorption on filters. However, direct gas phase oxidation of SO<sub>2</sub> by ozone apparently occurs at too low a rate to be significant.\* A more likely mechanism is the following:



The oxidation of dissolved SO<sub>2</sub> by O<sub>3</sub> has been studied by Erickson and Yates<sup>22</sup> who evaluated the rates of oxidation of H<sub>2</sub>SO<sub>3</sub>, HSO<sub>3</sub><sup>-</sup>, and SO<sub>3</sub><sup>-2</sup> with O<sub>3</sub>. At pH values > 4, the oxidation of dissolved SO<sub>2</sub> was shown to proceed via oxidation of SO<sub>3</sub><sup>-2</sup>. At pH values < 1.7, only H<sub>2</sub>SO<sub>3</sub> and HSO<sub>3</sub><sup>-</sup> were involved.

\*J. Pitts and co-workers report an SO<sub>2</sub> oxidation rate of 1% per hour for gas phase ozone and SO<sub>2</sub>.<sup>21</sup>

Table 44

THE EFFECT OF AMMONIA ON ARTIFACT SULFATE FORMATION  
( $\mu\text{g}/\text{filter sulfate}$ )<sup>a</sup>

<u>Filters</u>	<u>0 ppb-NH<sub>3</sub><sup>a</sup></u>	<u>40 ppb NH<sub>3</sub><sup>a</sup></u>	<u>90 ppb NH<sub>3</sub><sup>a</sup></u>
Gelman A	46.9 ± 3.4	38.4 ± 5.7	40.2 ± 5.6
EPA	165 ± 25	167 ± 8.6	187 ± 13
Fluoropore	0.3 ± 0.2	1.9 ± 1.3	2.5 ± 0.5
Gelman GA-1	8.5 ± 1.2	13.4 ± 1.8	12.8 ± 4.2
MSA	239 ± 56	218 ± 12	233 ± 11
Spectrograde	61.4 ± 6.4	54.3 ± 1.9	65.7 ± 4.0
Whatman 41	7.0 ± 1.1	14.1 ± 3.1	10.5 ± 1.1

a. Exposure conditions: 0.1 ppm SO<sub>2</sub>, 50% R.H., 1.32 cfm, 22°C, 6 hours exposure.

Table 45

THE EFFECTS OF OZONE ON ARTIFACT SULFATE FORMATION  
IN SIX-HOUR SO<sub>2</sub> EXPOSURES (µg/FILTER APPARENT SULFATE) a, b

Filter	50% Relative Humidity		90% Relative Humidity	
	No O <sub>3</sub>	0.5 ppm O <sub>3</sub>	No O <sub>3</sub>	0.5 ppm O <sub>3</sub>
Fluoropore FALP	0.3 ± 0.2	4.4 ± 0.3	2.9 ± 0.5	8.4 ± 7.4
Gelman GA-1	8.5 ± 1.2	48.3 ± 0.5	18.8 ± 2.4	39.8 ± 3.0
Whatman 41	7.0 ± 1.1	27.7 ± 0.2	23.2 ± 5.4	26.7 ± 4.2
Gelman A	46.9 ± 3.4	86.6 ± 1.8	67.6 ± 5.4	96.9 ± 5.9
Spectrograde	61.4 ± 6.4	76.7 ± 7.7	117.5 ± 10.1	112.9 ± 3.7
EPA Grade	165 ± 25	312 ± 8.1	347 ± 7.6	471 ± 4.1
MSA 1106BH	239 ± 56	344 ± 24	412 ± 12	474 ± 5.9

a. Flow rate 1.32 cfm.

b. Values shown are means ± 1σ for two separate trials.

To illustrate the effect of O<sub>3</sub> on apparent atmospheric sulfate concentration, the 147 µg/filter enhancement at 50% R.H. for the EPA Grade filter represents a positive sulfate error of about 11 µg/m<sup>3</sup> for the 6-hour exposure. Extrapolation of these findings to 24 hours would generally be unwarranted since ozone concentrations usually decrease to ca. 0 during nighttime hours. If one assumes a constant O<sub>3</sub> concentration of 0.5 ppm for 6 hours and 18 hours of sampling with zero ozone, then the enhancement of 11 µg/m<sup>3</sup> for 6 hours decreases to about 3 µg/m<sup>3</sup> when averaged over 24 hours.

#### G. The Effect of NO<sub>2</sub> on Artifact Sulfate Formation

In ambient air, it is likely that all acidic gases (e.g., SO<sub>2</sub>, HNO<sub>3</sub>, HCl, NO<sub>2</sub>) compete for adsorption on the alkaline or polar sites of filter media. As a result, the extent of artifact sulfate observed in the laboratory from adsorption of SO<sub>2</sub> from mixtures in clean air might significantly overestimate its importance in ambient air. Table 46 summarizes results of a brief evaluation of the influence of NO<sub>2</sub> on artifact sulfate under conditions likely to maximize the impact of such an effect. With 0.5 ppm NO<sub>2</sub> and 0.1 ppm SO<sub>2</sub>, the observed artifact sulfate values are, in all cases, substantially decreased. On a percentage basis, the effect of NO<sub>2</sub> is higher for the low pH filters compared to the MSA and EPA Grade materials.

Conclusions on the effect of NO<sub>2</sub> are weakened in this study by the presence of a contaminant source of nitrate in the exposure system. The observed nitrate values on these samples, excepting for Fluoropore, ranged from 112 to 170 µg/filter both with and without added SO<sub>2</sub>, or about four times the level established for NO<sub>2</sub> collection with a clean system (see Table 47). Contamination of the system by nitric acid desorbing from the glass walls is the probable cause. Accordingly, the decreased artifact sulfate may reflect the influence of NO<sub>2</sub> plus an unknown quantity of nitric acid. Nevertheless, the results are consistent with the model described above.

#### H. Comparison of Artifact Sulfate Results with Other Studies

R. Coutant's results on artifact sulfate are summarized in Figure 51. The alkalinity of the filter media is expressed as microequivalents of acid required to achieve neutrality per cm<sup>2</sup> of filter. Coutant reported that alkalinities of 0.3 corresponded to filter pH values of 9.2 to 9.4. Thus, the results shown at A = 0.3 are comparable to those for EPA Grade and MSA 1106BH in the present study. Flows (F) are expressed in m<sup>3</sup>/cm<sup>2</sup>. For a 24-hour 8 x 10" high-volume sample, this is about 4. Coutant's results indicate that under "normal" conditions of SO<sub>2</sub> concentration and relative humidity an artifact sulfate (or sulfate error) level of  $\leq 1 \mu\text{g}/\text{m}^3$  can be expected.

Results from the present study are shown in Figures 52 and 53. While in general data are insufficient to test linearity, the results reveal trends similar to those found by Coutant. Specifically, artifact sulfate follows  $P_{\frac{1}{2}}\text{SO}_2/(1-\text{RH})^{\frac{1}{3}}$ , and decreasing the flow (in m<sup>3</sup>/cm<sup>2</sup>)

Table 46

THE EFFECT OF NO<sub>2</sub> ON ARTIFACT SULFATE FORMATION<sup>a</sup>

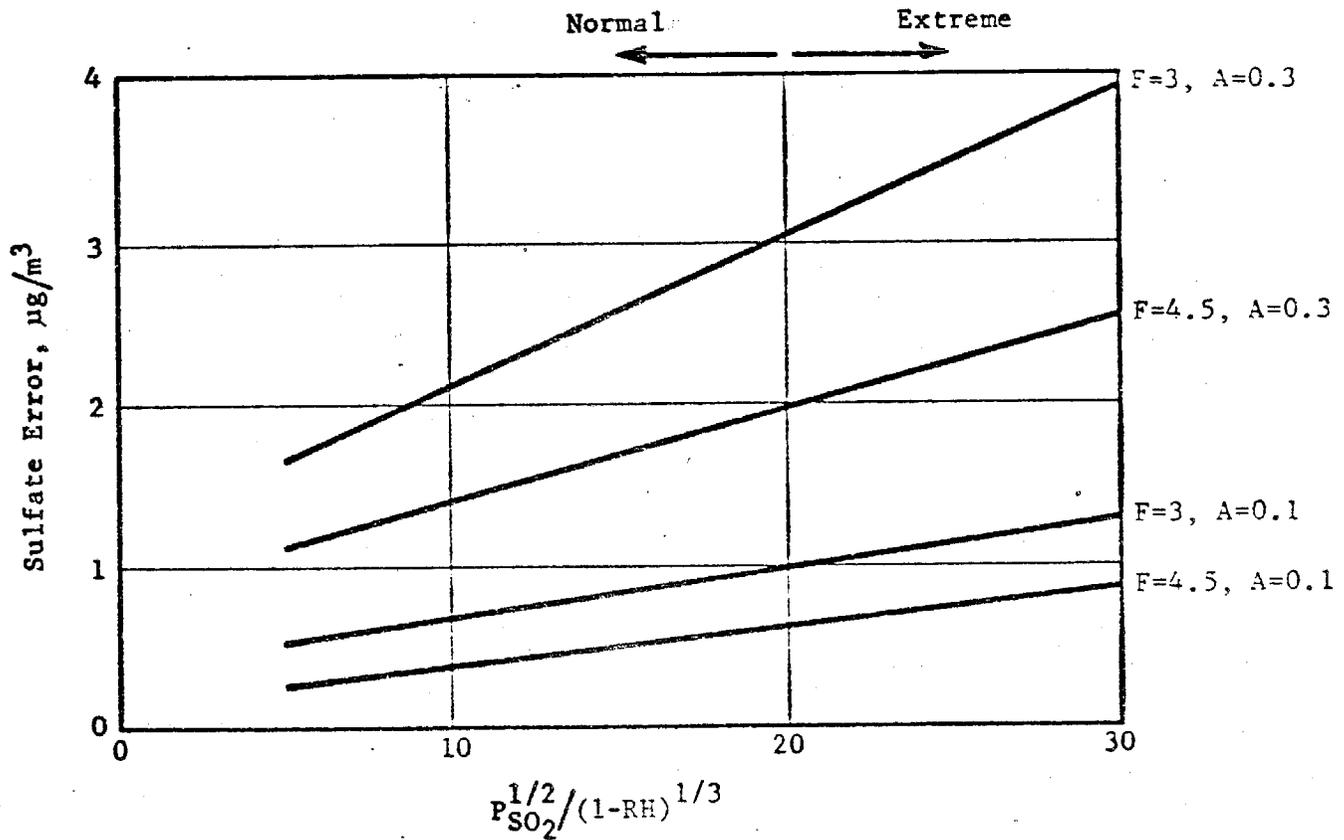
<u>Filter</u>	<u>SO<sub>4</sub><sup>=</sup> (μg/filter)</u>	
	<u>0 ppm NO<sub>2</sub></u>	<u>0.5 ppm NO<sub>2</sub></u>
Fluoropore	2.9 ± 0.5	None detected
Gelman GA-1	18.8 ± 2.4	4.8 ± 0.6
Whatman 41	23.2 ± 5.4	None detected
Spectrograde	118 ± 10	51.7 ± 4.6
Gelman A	67.6 ± 5.4	37.7 ± 4.7
MSA 1106BH	412 ± 12	324 ± 26
EPA Grade	347 ± 8	298 ± 12

Conditions: (SO<sub>2</sub>) = 0.1 ppm  
 R.H. = 90%  
 Temp. = 20°C  
 Time = 6 hours  
 Flow Rate = 1.32 cfm

a. The results are mean values + 1 σ for two trials.

Figure 51

ARTIFACT SULFATE IN FILTER SAMPLING



Data of R. W. Coutant, Reference 1.

F = flow,  $m^3/cm^2$

A = alkalinity,  $\mu eq/cm^2$  of filter

$P_{SO_2}$  = ppb  $SO_2$

R.H. = relative humidity expressed as a fraction

Figure 2

ARTIFACT SULFATE FORMATION WITH EPA GRADE FILTERS (pH = 9.3)

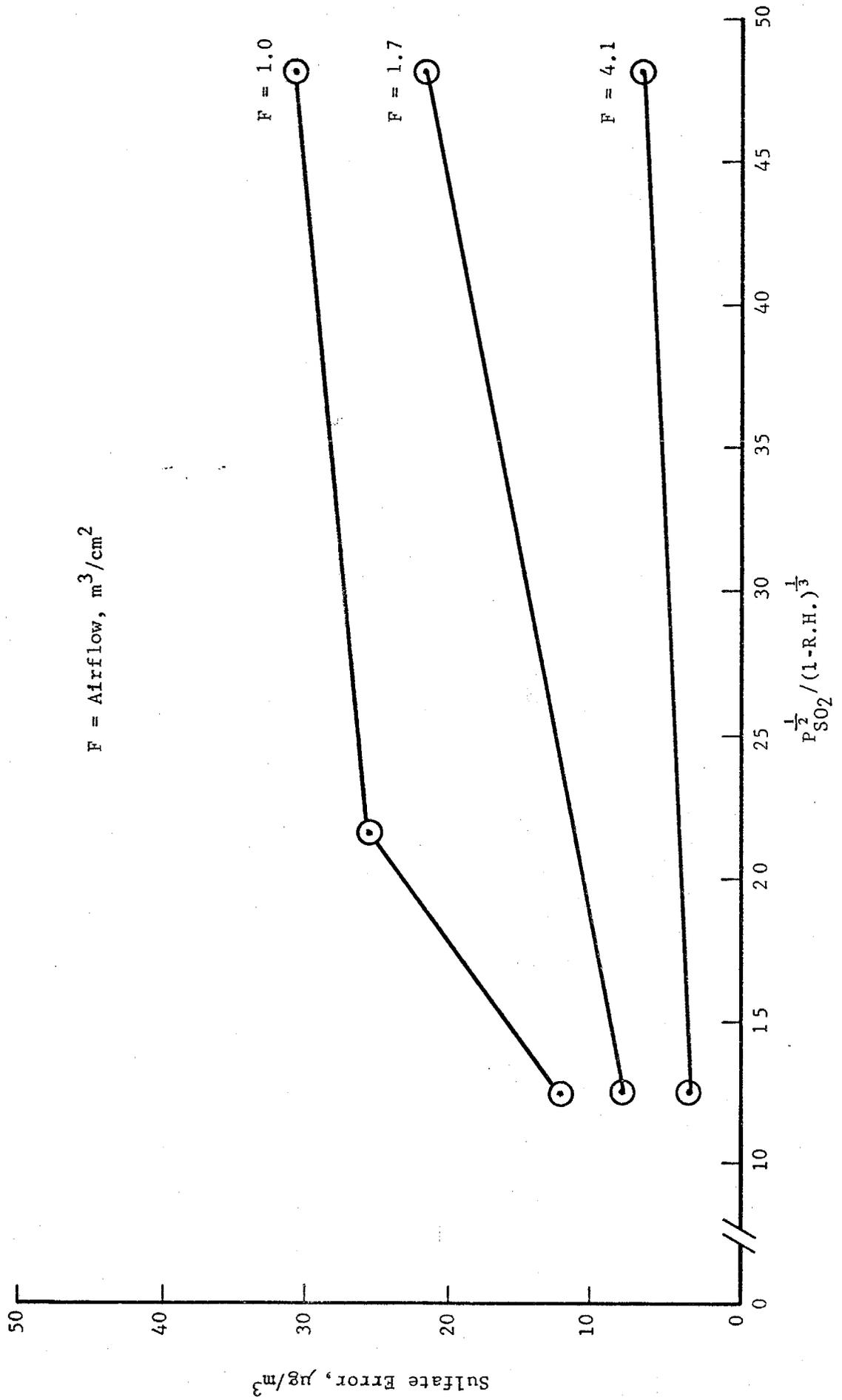
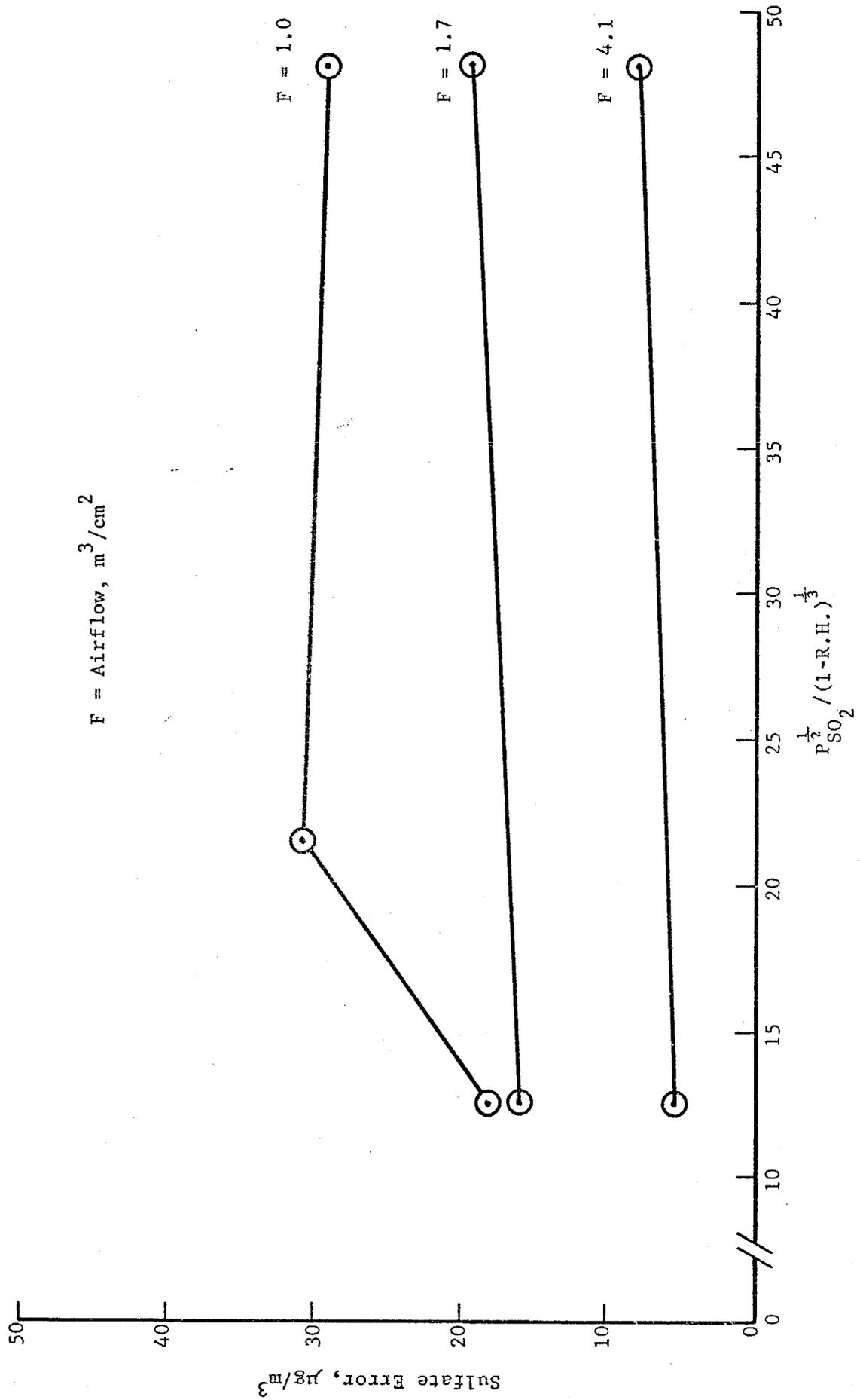


Figure 53

ARTIFACT SULFATE FORMATION WITH MSA 1106BH FILTERS (pH = 9.4)



does increase artifact sulfate. However, in the cases where three data points are available, the increase in artifact sulfate is not linear with the function of SO<sub>2</sub> and R.H. employed.

The most significant difference in results between the two studies is the substantially higher levels of artifact sulfate observed in the present work. The present laboratory studies may also be compared to the field sampling observations (Section V., B.) which, by comparison to Fluoropore results, lead to artifact sulfate values up to 3.1 µg/m<sup>3</sup> for a 24-hour hi-vol filter sample.

## VII. Laboratory Study of Artifact Nitrate Formation on Clean Filter Media

### A. Introduction

As with artifact sulfate, artifact nitrate formation on filter media can, in principle, relate to interactions of gaseous nitrogen oxides with either or both the filter media and the particulate matter. However, Okita, et al., found<sup>26</sup> that untreated glass fiber filters (Gelman A) collected gaseous  $\text{HNO}_3$  with an efficiency up to 56%. In the current study, principal emphasis was given to evaluating clean filter interactions with nitrogen oxides. Results from such laboratory work are then compared to those in ambient sampling potentially involving both routes.

The two most probable nitrogen oxides involved in artifact nitrate formation were chosen for evaluation: nitrogen dioxide ( $\text{NO}_2$ ) and nitric acid ( $\text{HNO}_3$ ). As with  $\text{SO}_2$ , absorption isotherms were determined for  $\text{NO}_2$  at 0.1 and 0.5 ppm  $\text{NO}_2$  at 50 and 90% relative humidity and 0.56 and 1.32 cfm. However, in no case was a measurable isotherm obtained; the ratio of downstream/upstream  $\text{NO}_2$  concentration was never measurably different from the system blank without a filter in place.

Attempts were also made to determine absorption isotherms with nitric acid exposures of clean filters. However, the pressure drop across the filters made sampling of the downstream concentration using the modified Mast meter unfeasible. In lieu of isotherms, studies of nitric acid collection as a function of time in side-by-side exposures were included.

### B. Artifact Nitrite and Nitrate from $\text{NO}_2$ -Clean Filter Interaction

The analytical method used for nitrate determination involves reduction of nitrate to nitrite followed by azo dye formation. Accordingly, the method does not distinguish nitrate from nitrite in the sample, and, except as noted, nitrate values are understood to include nitrite.

The nitrite concentration observed in side-by-side exposures of filters to  $\text{NO}_2$  was determined (Table 47). Only high pH filters show significant nitrite levels. The corresponding nitrate levels for this exposure ranged from 0 to 30  $\mu\text{g}/\text{filter}$  or 0 to 2  $\mu\text{g}/\text{m}^3$ . The highest proportions of nitrite were observed on the two filters of highest pH, MSA 1106BH and EPA Grade. These results parallel those found for sulfite vs. sulfate as reported in Section VI.

### C. The Effect of Ammonia on Artifact Nitrate Formation from $\text{NO}_2$

The effect of ammonia on artifact nitrate formation from  $\text{NO}_2$  absorption by filter media is shown in Table 48. The levels of ammonia used represent values ranging up to the maximum likely to be encountered in ambient air. The results for  $\text{NO}_2$  without ammonia are shown as a single trial reflecting the difficulty subsequently

Table 47

OBSERVED NITRITE AND NITRATE IN SIDE-BY-SIDE  
SAMPLING OF NO<sub>2</sub> WITH CLEAN FILTERS

<u>Filter</u>	<u>NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> <sup>a</sup></u>		<u>NO<sub>2</sub><sup>-</sup></u>	<u>N<sup>III</sup> / N<sup>III</sup>+N<sup>V</sup></u>
	<u>μg/filter</u>	<u>μg/m<sup>3</sup></u>	<u>μg/filter</u>	
Fluoropore	< 3	< 0.2	< 0.2	-
Gelman GA-1	26.0	1.9	1.2	0.062
Whatman 41	27.4	2.0	< 0.2	< .01
Spectrograde	19.1	1.4	1.8	0.13
Gelman A	29.6	2.2	< 0.2	< 0.01
MSA 1106BH	30.5	2.3	13.1	0.58
EPA Grade	31.4	2.3	3.5	0.15

Conditions: 0.5 ppm NO<sub>2</sub>

50% R.H.

1.32 cfm

Temp: 20°C

6 hours

- a. Expressed as nitrate. Under our analytical conditions, nitrite provided a 100% positive interference, on a molar basis.

Table 48

Effect of  $\text{NH}_3$  on Artifact Nitrate Formation from  $\text{NO}_2$   
 ( $\mu\text{g NO}_3^-$ /filter)

<u>Filter</u>	<u>0<sup>a</sup></u>	<u><math>\text{NH}_3</math> (ppb)</u>	
		<u>40<sup>b</sup></u>	<u>90<sup>b</sup></u>
Fluoropore	0.0	6.1 <u>+2.7</u>	8.4 <u>+1.0</u>
Gelman GA-1	26.0	33.7 <u>+0.8</u>	27.1 <u>+1.2</u>
Whatman 41	27.4	48.1 <u>+2.0</u>	41.3 <u>+0.6</u>
Spectrograde	19.1	41.3 <u>+6.6</u>	36.9 <u>+4.3</u>
Gelman A	25.6	48.4 <u>+1.8</u>	39.0 <u>+3.1</u>
MSA 1106BH	30.5	49.7 <u>+7.0</u>	40.6 <u>+8.5</u>
EPA Grade	31.4	47.2 <u>+0.4</u>	42.1 <u>+0.2</u>

Conditions: 50% RH  
 20°C  
 0.5 ppm  $\text{NO}_2$   
 1.32 cfm flowrate

a. Results for a single filter of each type.

b. Mean results for two trials.

encountered with contamination of the exposure system probably with nitric acid yielding elevated nitrate values. Contamination problems and the rate of desorption of the contaminant nitrate are discussed in Appendix L. The effect of ammonia addition is, in all cases, small with enhancements of observed nitrate of less than 20 µg/filter. These results are similar to those found with ammonia additions to SO<sub>2</sub>.

#### D. The Effect of Ozone on Artifact Nitrate Formation from NO<sub>2</sub>

To evaluate the effect of ozone under worst case conditions, 0.5 ppm ozone was added to an equal concentration of NO<sub>2</sub> at 90% R.H. The results are presented in Table 49 showing the increase in observed nitrate. Absolute nitrate values are not shown because the system apparently remained contaminated with nitric acid from the NO<sub>2</sub>-O<sub>3</sub> run leading to elevated nitrate levels for the runs without added ozone. As a result, the values shown represent minimum values. The results indicates substantial increases in observed nitrate on the high pH filters (EPA Grade and MSA 1106BH). It is notable that no increase was detectable with Spectrograde filters.

If the mechanism for enhanced NO<sub>2</sub> absorption involved gas phase oxidation of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> by ozone followed by gas phase hydration to HNO<sub>3</sub>, the results in the presence of ozone should parallel those obtained with HNO<sub>3</sub>. As discussed below, this was not observed, and we infer that the effect of ozone involves reactions occurring on the filter surfaces.

#### E. The Effect of SO<sub>2</sub> on Artifact Nitrate Formation from NO<sub>2</sub>

As discussed in Section VI., G., it is likely that acidic gases compete for alkaline or polar sites on filter media. It was shown there that 0.5 ppm NO<sub>2</sub> (plus an undetermined nitrate contaminant) could substantially reduce artifact sulfate formation with 0.1 ppm SO<sub>2</sub>. The same samples were also analyzed for nitrate permitting evaluation of the influence of 0.1 ppm SO<sub>2</sub> on artifact nitrate formation from 0.5 ppm NO<sub>2</sub>.

As previously indicated, the observed nitrate levels with and without added SO<sub>2</sub> were substantially elevated indicating contamination of the system, probably by nitric acid. Accordingly, the results given in Table 50 indicate only observed changes in nitrate produced by the addition of 0.1 ppm SO<sub>2</sub>. Such changes are not significantly different from zero. Accordingly, 0.1 ppm SO<sub>2</sub> has a negligible effect on the observed nitrate. Since, as discussed in Section VI., G., most of the observed nitrate apparently resulted from a contaminant (HNO<sub>3</sub>) formed on the walls of the exposure system the results may not be representative of the effect of SO<sub>2</sub> on NO<sub>2</sub> fixation.

Table 49

THE EFFECT OF 0.5 ppm OZONE ON 0.5 ppm NO<sub>2</sub> ADSORPTION  
ON CLEAN FILTER MEDIA (90% R.H.)<sup>a</sup>

<u>Filter</u>	<u>Observed Increase in NO<sub>3</sub><sup>-b</sup></u>	
	<u>µg/filter</u>	<u>µg/m<sup>3</sup></u>
Fluoropore	- 5.8	-
Gelman GA-1	3.3	0.3
Whatman 41	- 9.9	-
Gelman A	3.3	0.3
Spectrograde	- 3.7	-
MSA 1106BH	91	6.8
EPA Grade	48	3.6

a. Flow rate = 1.32 cfm. T = 22°C, 6-hour exposures.

b. Mean of two trials.

Table 50

THE EFFECT OF 0.1 ppm SO<sub>2</sub> ON ARTIFACT NITRATE FORMATION FROM NO<sub>2</sub><sup>a</sup>

<u>Filter</u>	<u>Change in Observed Nitrate (<math>\mu\text{g}/\text{filter}</math>)</u>
Fluoropore	0
Gelman GA-1	1.7 $\pm$ 2.7
Whatman 41	2.5 $\pm$ 1.2
Spectrograde	32 $\pm$ 35
Gelman A	-12 $\pm$ 10
MSA 1106BH	8.9 $\pm$ 21
EPA Grade	7.2 $\pm$ 25

Conditions: (NO<sub>2</sub>) = 0.5 ppm  
 R.H. = 90%  
 Temp. = 20°C  
 Time = 6 hours  
 Flow Rate = 1.32 cfm

a. The results are mean values  $\pm$  1  $\sigma$  for two trials.

#### F. Artifact Nitrate Formation from Nitric Acid

The system used for feeding nitric acid into the filter exposure systems permitted operation under constant  $\text{HNO}_3$  concentrations for 6-hour runs but was not feasible for 24-hour exposures. Side-by-side filter exposures were conducted for both 2 and 6 hours to permit some assessment of the influence of time. Other variables considered include the influence of flow rate, nitric acid concentration, relative humidity and temperature.

The results for all trials are summarized in Table 51. As with  $\text{NO}_2$  the adsorption of nitric acid on Fluoropore filters was negligible. However, with the other filters adsorption greatly exceeded that found with  $\text{NO}_2$ . While high levels of nitric acid are collected on the high pH filters (EPA Grade and MSA 1106BH), the level on Spectrograde (pH = 6.2) is still greater.

#### G. The Effect of Time, Relative Humidity and Temperature on Nitric Acid Collection by Filter Media

The effect of time is shown graphically in Figure 54. In all cases, the filters exposed for 6 hours exhibit greater levels than those for 2-hour exposures although with Fluoropore the increase is slight.

The ability of the different filters to form artifact nitrate from nitric acid can be expressed in terms of the percent removal of nitric acid from the air stream (Table 52). The results indicate a range from 1% (for Fluoropore) to 53% for Spectrograde in 2-hour exposures. The average efficiency for filters removing > 20%  $\text{HNO}_3$  in two hours is seen to decrease substantially in 6-hour exposures implying saturation may be achieved in < 6 hours. Thus, extrapolation of results given in Figure 54 to 24-hour exposures is not generally feasible.

The study of influence of relative humidity on gaseous  $\text{HNO}_3$  collection was restricted to lower R.H. values since  $\text{HNO}_3$  forms an aerosol above ca. 70% R.H. Figure 54 shows the effect of changing from 35 to 50% R.H.; absorption of  $\text{HNO}_3$  increases with all filters except Gelman GA-1.

Nitric acid collection was studied in the temperature range from 7 to 35°C at constant relative humidity as is also shown in Figure 54. Increasing temperature is seen to cause reduced  $\text{HNO}_3$  collection except with Spectrograde filters for which the observed nitrate remained relatively constant. If nitric acid collection is due to physical adsorption or relatively weak chemical bonding on the filters, then a decreased level of  $\text{HNO}_3$  collection with increasing temperature would be expected as was, indeed, observed with all filters except Spectrograde. The unusual temperature dependence with this filter suggests a different mechanism for  $\text{HNO}_3$  collection, for example, chemical reaction with the silicone resin coating. Any such reaction must lead to products from which nitrate and/or nitrite is still recovered during aqueous extractions.

Table 51

SUMMARY OF HNO<sub>3</sub> EXPOSURE RESULTS<sup>a</sup>  
( $\mu\text{g}/\text{filter} + 1\sigma$ )

Conditions:	6 hours		6 hours		6 hours		2 hours		2 hours		2 hours		2 hours	
	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade	Obs. NO <sub>3</sub> <sup>-</sup>	Rel. to EPA Grade
	0.5 ppm HNO <sub>3</sub> 50% R.H. 22°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 50% R.H. 22°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 50% R.H. 22°C 0.56 cfm	0.2 ppm HNO <sub>3</sub> 50% R.H. 22°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 35% R.H. 22°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 56 + 6% R.H. 7°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 15% R.H. 35°C 1.32 cfm	0.2 ppm HNO <sub>3</sub> 50% R.H. 35°C 1.32 cfm						
Fluoropore	23.7 (0.3)	0.01	74.3 (42.2)	24.3 (2.0)	3.1 (4.1)	69.4 (43.8)	0.0	0.005	0.05	0.0	0.0	-	0.0	-
Gelman GA-1	1,653 (1,315)	0.60	1,064 (539)	278 (1)	300 (16)	980 (+69)	0.47	0.32	0.75	181 (27)	0.37	0.37	225 (25)	0.29
Whatman 41	1,152 (442)	0.42		505 (39)	400 (10)	1,313 (+206)	0.62	0.59	1.01	133 (15)	0.27	0.27	282 (12)	0.36
Spectrograde	1,982 (419)	0.72		1,222 (106)	807 (44)	1,319 (+229)	1.26	1.42	1.01	1,018 (237)	2.07	2.07	1,484 (52)	1.89
Gelman A	1,653 (1,315)	0.60		223 (13)	151 (1)	591 (+125)	0.24	0.26	0.45	140 (4)	0.28	0.28	207 (27)	0.26
MSA 1106BH	1,055 (8)	0.38		817 (67)	614 (18)	1,070 (+294)	0.96	0.95	0.82	634 (72)	1.29	1.29	736 (5)	0.94
EPA Grade	2,750 (1,311)	1.00		858 (88)	641 (9)	1,306 (+23)	1.00	1.00	1.00	492 (8)	1.00	1.00	784 (4)	1.00

a. Values shown in brackets represent 1 $\sigma$  for two independent trials.

Figure 54

HNO<sub>3</sub> EXPOSURE STUDY

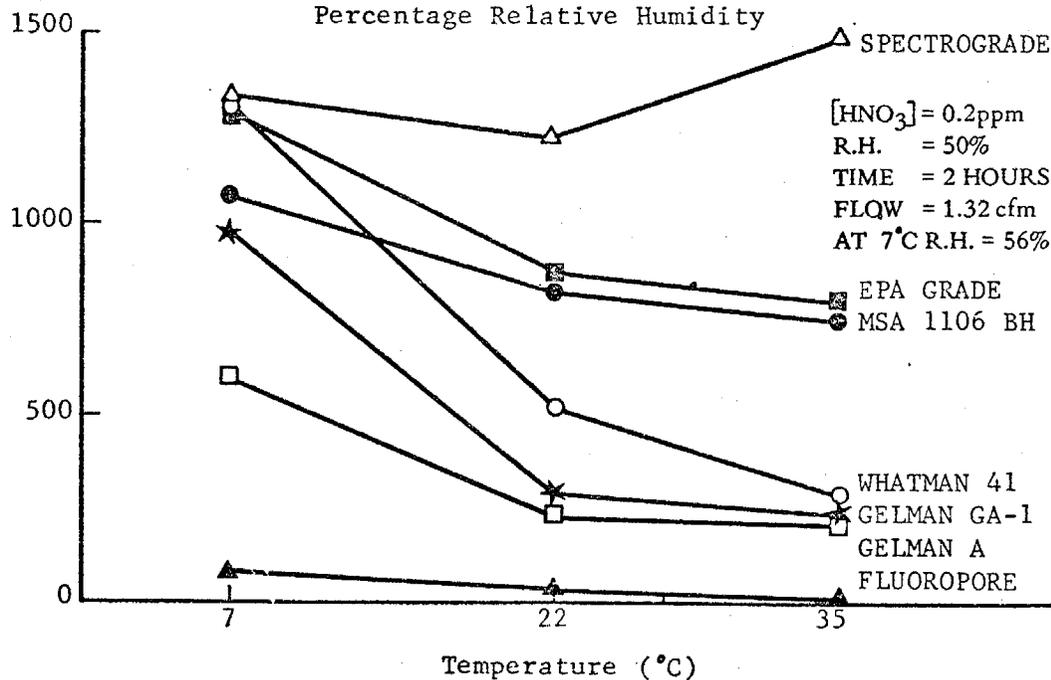
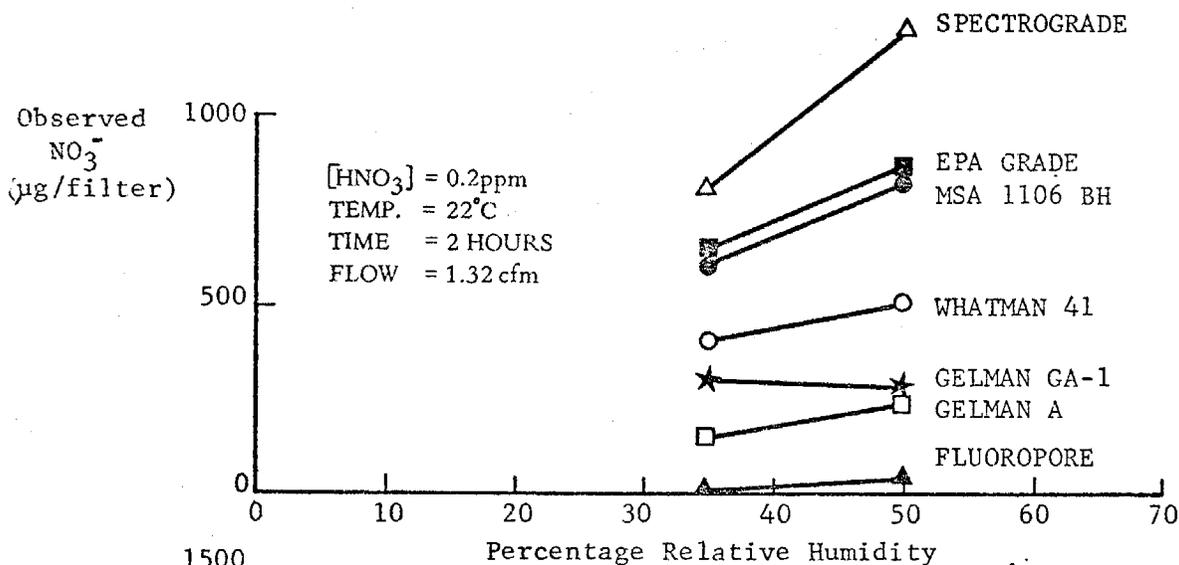
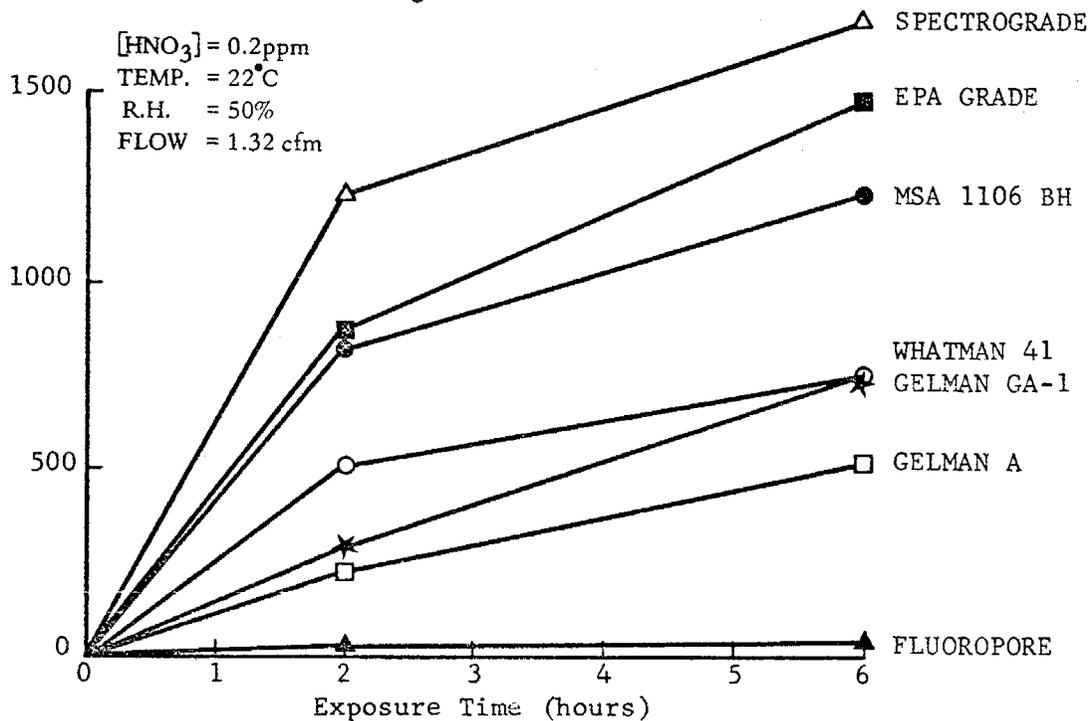


Table 52

AVERAGE EFFICIENCY FOR HNO<sub>3</sub> COLLECTION (%)

<u>Filter</u>	<u>Two-Hour Exposures</u>	<u>Six-Hour Exposures</u>
Fluoropore	1.1 ± .1	0.5 ± .3
Gelman GA-1	12.0 ± .04	10.6 ± 1.3 <sup>a,b</sup>
Gelman A	9.7 ± .6	7.4 ± 1.3
Whatman 41	21.9 ± 1.7	10.7 ± .8
MSA 1106BH	35.4 ± 2.9	17.6 ± 1.1
EPA Grade	37.1 ± 3.8	21.3 ± .6
Spectrograde	52.9 ± 4.6	24.3 ± 1.9

Conditions: 0.2 ppm HNO<sub>3</sub>  
 50% R.H.  
 22°C  
 37.4 lpm (face velocity 47 cm/sec)

- a. Increases to 36 ± 18% at a 15.9 lpm flow rate (face velocity 20 cm/sec).
- b. At 0.5 ppm HNO<sub>3</sub>, the efficiency was 9.5 ± 7.6%.

Since reduction of nitrate to nitrite by reaction with the Spectrograde filter's surface coating was one possible reaction pathway, filters exposed to nitric acid were analyzed for both nitrite and nitrate. However, no nitrite was detectable from Spectrograde or any other filters. Thus, reaction with Spectrograde filters involving oxidation-reduction reactions can probably be ruled out.

## VIII. Laboratory Studies of Artifact Sulfate Formation on Filters Loaded with Potential SO<sub>2</sub> Oxidation Catalysts

### A. Introduction

Various materials have been suggested or demonstrated to be effective in accelerating the conversion of SO<sub>2</sub> to sulfate. Some materials (e.g., Fe<sup>III</sup> salts) appear to do so without, themselves, being chemically changed and thusly may be termed "catalysts" in the proper sense. A second class of materials (e.g., Cu<sup>II</sup> salts) appear to serve as oxidizing agents for sulfite to sulfate conversion, with reduction to a lower oxidation state. If such materials were present and active in atmospheric particulate matter with respect to oxidation of adsorbed SO<sub>2</sub> (or SO<sub>3</sub><sup>-</sup>) then the level of artifact sulfate might be enhanced over that due only to interactions between the filter media and SO<sub>2</sub>. The present study included a relatively brief evaluation of several materials possibly active in yielding enhanced sulfate by either or both mechanisms, including combustion derived carbon, vanadium dioxide, manganese dioxide, ferric oxide and cupric oxide. It should be emphasized that the choice of the specific metal compounds for study was made without knowledge of the correct oxidation states and compounds actually present in ambient particulate matter.

Filters were loaded with, in general, realistic levels of the above metal oxides as described in Appendix M. Except with carbon, both Fluoropore and MSA 1106BH filters were used as supports for the catalysts so the influence of such catalysts could be evaluated with widely varying filter pH values.

The study of carbon was extended to include evaluation of SO<sub>2</sub> oxidation occurring on airborne carbon particles as well as those already collected on filters.

### B. Carbon as a Catalyst for SO<sub>2</sub> Oxidation

Experiments were conducted in cooperation with Dr. T. Novakov and co-workers of the Lawrence Berkeley Laboratory, to evaluate the efficiency of combustion-derived carbon ("soot") in converting SO<sub>2</sub> to sulfate with the carbon supported on filters. In addition, the extent of sulfate formation on freshly generated, airborne carbon particles was also determined. In no case was the extent of sulfate formed measurably above the experimental uncertainty. Details are given in Appendix N.

### C. Iron, Vanadium, Manganese and Copper Oxides as SO<sub>2</sub> Oxidation Catalysts

The technique used to produce filters loaded with vanadium, copper and iron hydroxide or oxide particles resulted in the formation of ammonium nitrate on the filters as well (see Appendix M). Filters loaded with manganese oxide particles were produced by initially loading filters with KMnO<sub>4</sub> particles and then reducing the permanganate to MnO<sub>2</sub> and/or Mn<sub>2</sub>O<sub>3</sub> with gas-phase formaldehyde. Thus, the

filters may also contain potassium formate. Because ammonium nitrate is hygroscopic, metal oxide-NH<sub>4</sub>NO<sub>3</sub> particles were observed to grow. It is expected that on MSA filters, the aqueous phase will wet the surface leaving behind the relatively insoluble metal hydroxide.

The effects of the metal oxides on artifact sulfate formation were studied in a series of laboratory exposures at both 50 and 90% R.H. Each run evaluated one metal oxide loaded on four 47 mm filters, two Fluoropore and two MSA 1106BH filters. The remaining three positions in the exposure system were used for blank filters. The observed artifact sulfate with the catalyst loaded filters was evaluated by comparison to the levels observed with the corresponding blank filter in the same run (Table 53).

The results for the iron and vanadium oxides indicate lower artifact sulfate values compared to the blank filters. This decrease is consistent with partial masking of absorption sites on the filter by either the metal oxide or ammonium nitrate. These results indicate that neither these metal oxides nor ammonium nitrate enhance artifact sulfate under the conditions studied.

With CuO, a small enhancement was seen except with the MSA filter at high R.H. For MnO<sub>2</sub>, an increase in observed sulfate up to 263 µg per filter is seen. Relative humidity increases caused higher sulfate levels with both filters. However, in this case, the possible formation of an alkaline co-product, potassium formate (hydrolysis would produce KOH and the weak acid, formic acid) might be the cause of increased retention of SO<sub>2</sub>.

To evaluate the extent of formation of alkaline co-products during preparation of manganese oxide-loaded filters, Gelman A (pH = 7.6) and MSA 1106BH (pH = 9.4) filters were spotted with an aqueous solution of KMnO<sub>4</sub>, air dried in particle-free air and reduced with formaldehyde. The pH values for the resulting samples are compared to those prior to formaldehyde as detailed in Appendix O. The results indicate a slight increase ( $\Delta$  pH  $\leq$  0.2) in alkalinity ascribable to preparation of the manganese oxide which could produce as much as 34 µg artifact sulfate. Accordingly, most of the enhanced sulfate levels, at least with MSA filter samples, may reasonably be ascribed to the presence of the manganese oxide.

Possible reaction products from reaction of MnO<sub>2</sub> plus Mn<sub>2</sub>O<sub>3</sub> with SO<sub>2</sub> include MnSO<sub>4</sub> and MnS<sub>2</sub>O<sub>6</sub> (manganese dithionate). The latter is thought to be comparatively unstable with decomposition to the sulfate. Assuming only sulfate formation, an average of 91 µg Mn would yield a maximum of 159 µg sulfate as MnSO<sub>4</sub>. Allowing an additional 34 µg sulfate for that produced by increased alkalinity, the total calculated value, 193 µg, is about 73% of the observed maximum sulfate, 263 ± 7 (on MSA 1106BH). Thus, a small degree of catalysis of sulfate formation is possible. Considering the likelihood of formation of other sulfur-containing products, catalysis is considered unlikely, however. On Fluoropore, the average observed

Table 53

SO<sub>2</sub>-CATALYST INTERACTION STUDIES ( $\mu\text{g SO}_4^{=}/47 \text{ mm FILTER}$ )<sup>a</sup>

Catalyst	Filter	Catalyst Loading ( $\mu\text{g}/47 \text{ mm Filter}$ ) <sup>b</sup>	No. Filters	R.H. (%)	Observed Sulfate With Catalyst	Observed Sulfate With Blank Filter	Sulfate Due to Catalyst
Fe(OH) <sub>3</sub> <sup>c</sup>	Fluoropore	275 + 91	1	50	< 2.5	< 2.5	ca. 0
	MSA 1106BH	228 + 17	1	50	91.6 ± 3.2 <sup>d</sup>	167.3 ± 1.8	- 75.7 ± 3.7
Fe(OH) <sub>3</sub> <sup>c</sup>	Fluoropore	275 + 91	4	90	< 2.5	< 2.5	ca. 0
	MSA 1106BH	228 + 17	4	90	180.6 ± 26.0	273.7 ± 8.0	- 93.1 ± 27
V <sub>2</sub> O <sub>5</sub>	Fluoropore	36.7 + 10	1	50	< 2.5	< 2.5	ca. 0
	MSA 1106BH	31.7 + 10	1	50	143.6 ± 1.9	167.3 ± 1.8	- 23.7 ± 2.6
V <sub>2</sub> O <sub>5</sub>	Fluoropore	36.7 + 10	4	90	< 2.5	< 2.5	ca. 0
	MSA 1106BH	31.7 + 10	4	90	215.6 ± 4.2	277.0 ± 18.5	- 61.4 ± 19
Cu(OH) <sub>2</sub> <sup>c</sup>	Fluoropore	81.8 + 20	2	50	4.7 ± 0.2	< 2.5	3.5 ± 1.8
	MSA 1106BH	84.4 ± 29	2	50	150.2 ± 7.0	144.2 ± 14.3	6.0 ± 16
Cu(OH) <sub>2</sub> <sup>c</sup>	Fluoropore	81.8 + 20	2	90	12.8 ± 0.8	< 2.5	11.6 ± 1.8
	MSA 1106BH	84.4 ± 29	2	90	250.1 ± 10.9	284.4 ± 7.0	- 34.3 ± 13
MnO <sub>2</sub> <sup>e</sup>	Fluoropore	61.5 ± 21	2	50	37.3 ± 0.6	< 2.5	36.1 ± 1.8
	MSA 1106BH	91.1 ± 21	2	50	291.4 ± 8.4	157.3 ± 19.6	134.1 ± 21
MnO <sub>2</sub> <sup>e</sup>	Fluoropore	61.5 ± 21	2	90	71.6 ± 3.3	< 2.5	70.4 ± 3.3
	MSA 1106BH	91.1 ± 21	2	90	528.3 ± 5.5	265.1 ± 3.6	263.2 ± 7

a. Exposure conditions: 0.1 ppm SO<sub>2</sub>, 2 hours, 1.32 cfm.

b. Based on weight of metal.

c. Probably a mixture of the hydroxide and oxide.

d. Where one metal loaded filter was used, errors cited are standard deviations for the sulfate analysis.

e. Probably a mixture of MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub>.

sulfate at 90% R.H., 70 ug is substantially less than that corresponding to a stoichiometric reaction consuming all manganese.

These results with manganese oxides are consistent with the model shown in Section VI.,A., viz., the alkaline sites of the glass fiber filter yield relatively high equilibrium concentration of  $\text{SO}_3^-$  and the manganese oxide accelerates conversion of  $\text{SO}_3^-$  to sulfate by chemical reaction consuming the oxidizing agent. The relevance of these observations with manganese and copper to results in ambient air remains questionable, however, since 1) the chemical states of the metals in ambient particulates are unknown, 2) correlation between observed sulfate and manganese or copper levels in atmospheric samples cannot be tested because of low metals concentrations, and 3) the metal loadings are higher (by up to a factor of 10) than those observed in ambient air.

The results, however, do justify additional studies to clarify the role that such metals may play not only in artifact sulfate formation but in atmospheric conversion of  $\text{SO}_2$  as well. The use of manganese as a fuel oil additive to control fly ash particle size<sup>23</sup> requires careful evaluation for enhanced sulfate formation.

## IX. Laboratory Studies of Artifact Sulfate Formation from Atmospheric Particulate Plus Filter Media-SO<sub>2</sub> Interactions

### A. Introduction

Previous studies of artifact sulfate formation have unsuccessfully sought evidence that interactions between SO<sub>2</sub> and particulate matter could produce positive errors in observed particulate sulfate values.<sup>1,2</sup> Nevertheless, such studies remained inconclusive, in part, because the aerosol was of ill-defined composition. There remained the possibility that filters loaded with particulate matter collected at sites likely to be enriched with SO<sub>2</sub>-oxidation promoting metal salts or oxides might contribute to artifact sulfate formation.

Accordingly, in the present work, the atmospheric particulate matter collected in Los Alamitos was used for study of particulate-SO<sub>2</sub> interaction as it was enriched, at least during the afternoon with particulates from the plume from the nearby Los Alamitos Power Plant. Such particulate matter was demonstrated to have enhanced levels of nickel and, at times, vanadium. It was also probably enriched in small-particle iron oxides from fuel oil fly ash. Manganese levels were below detectable limits, however.

An additional complication in such studies is the fact that the particulate matter might already be saturated with SO<sub>2</sub> during field sampling and thus be unresponsive to additional SO<sub>2</sub> exposures. It was reported recently that water washing of certain materials (e.g., clay, cement) increased their SO<sub>2</sub> absorbing properties and, if done after SO<sub>2</sub> exposure, restored the SO<sub>2</sub> absorbing capability of the material.<sup>26</sup> Accordingly, in the present study, the effect of water washing particulate matter was also studied.

Particulate matter samples collected on both Gelman GA-1 cellulose ester, and MSA 1105BH filter media were studied to evaluate any interactive effect between particulate matter and filter pH.

Finally, the influence of storage time following SO<sub>2</sub> exposure on observed sulfate was evaluated with several filter types. This study was done since collection of SO<sub>2</sub> (as adsorbed SO<sub>2</sub> or sulfite) is conceptually reversible. Thus, if enhanced artifact sulfate were observed (possibly due to sulfite) it might decrease with time.

### B. Results

Table 54 summarizes results of the SO<sub>2</sub> exposure study in which samples were analyzed within 48 hours of the exposure. Samples for SO<sub>2</sub> exposure from Gelman GA-1 47 mm samples were obtained by cutting one 25 mm disc from the filter, analyzing the overage for "Before SO<sub>2</sub>" sulfate and exposing the 25 mm discs to SO<sub>2</sub>. The flow rate used, 0.15 cfm, provided a face velocity equivalent to that of an 8 x 10" filter at 40 cfm.

The results for the Gelman GA-1 samples, expressed as mean values for the samples used, indicate little or no change in observed sulfate after exposure to either 0.1 or 0.5 ppm SO<sub>2</sub>.

The water washing of samples collected on Gelman A and MSA 1106BH had the effect of eliminating nearly all the atmospheric sulfate initially in the sample. After SO<sub>2</sub> exposure of the filter disc and remaining particulate matter, the observed sulfate was not significantly different from that prior to the exposure.

The sulfate observed on the water washed filters may be roughly compared to the levels found with clean filter-SO<sub>2</sub> interaction in 6-hour exposures since, as shown earlier, saturation of filters with SO<sub>2</sub> occurred in less than two hours. The value 11.9 ± 9.3 for Gelman A (per 25 mm disc) compares to 12.0 ± 1.0 for the clean filter. The value 5.9 ± 3.1 for MSA 1106BH compares to 73.4 ± 2.1 calculated from Table 40 for a 25 mm disc.\* We conclude that, in contrast to the low pH Gelman A filter, water washing a high pH MSA 1106BH filter loaded with atmospheric particulate does not restore the SO<sub>2</sub> absorbing capacity of the clean filter. This may relate to the presence of water-insoluble organics coating the glass fibers providing at least a short-term barrier to SO<sub>2</sub> contact with alkaline sites. Further work is needed to explain this phenomenon.

Since no enhancement in observed sulfate following SO<sub>2</sub> exposure was observed in this study, no changes with time in observed sulfate would be expected. Table 55 details results of the storage time study conducted over a two-month period. The results with samples collected on four filter types, suggest an effect of storage in the case of the MSA sample with 0.5 ppm SO<sub>2</sub> initial exposure. It was previously shown that the sulfite/sulfate ratio is maximal for high pH filters (such as MSA 1106BH). Thus, loss of some sulfite (as SO<sub>2</sub>) may be involved. However, the failure to observe increased sulfate with a water-washed MSA 1106BH sample vitiates this conclusion.

### C. Conclusions

No evidence of artifact sulfate formation was found which can be ascribed to particulate-SO<sub>2</sub> interactions. The presence of particulate matter and/or atmospheric exposure of filter media to acidic gases decreases the artifact sulfate formed due to SO<sub>2</sub>-filter interaction. This decrease may relate to partial masking of alkaline sites by particulate matter or partial neutralization by acidic gases during field sampling.

\*The SO<sub>2</sub>-exposed areas for 47 and 25 mm filters were 13.2 and 2.35 cm<sup>2</sup>, respectively.

SUMMARY OF PARTICULATE-SO<sub>2</sub> INTERACTIONS ( $\mu\text{g}/25$  mm FILTER) AT 90% RH<sup>a,b</sup>

Sample	N <sup>e</sup>	(SO <sub>2</sub> ) ppm	Observed Sulfate		$\Delta^d$
			Before SO <sub>2</sub>	After SO <sub>2</sub>	
Gelman GA-1 total <sup>a</sup> particulate (6-hour)	8	0.1	10.6	9.4	- 1.2
			$\pm 2.9$	$\pm 3.0$	$\pm 1.9$
Gelman GA-1 refined <sup>a</sup> particulate (6-hour)	8	0.5	17.7	14.3	- 3.4
			$\pm 11.6$	$\pm 9.8$	$\pm 3.6$
Gelman GA-1 total <sup>a</sup> particulate (24-hour)	8	0.1	11.8	9.4	- 2.5
			$\pm 2.7$	$\pm 2.7$	$\pm 2.6$
Gelman GA-1 total <sup>a</sup> particulate (24-hour)	8	0.5	$\pm 15.3$	$\pm 13.0$	- 3.1
			$\pm 12.2$	$\pm 10.0$	$\pm 2.2$
Gelman GA-1 total <sup>a</sup> particulate (24-hour)	2	0.1	58.3	44.2	- 14.1
			$\pm 51.0$	$\pm 29.6$	$\pm 12.1$
Gelman A Hi-Vol <sup>b</sup> (24-hour), H <sub>2</sub> O washed	2	0.5	39.3	31.7	- 7.6
			$\pm 20.1$	$\pm 12.5$	$\pm 4.0$
Gelman A Hi-Vol <sup>b</sup> (24-hour), H <sub>2</sub> O washed	- <sup>c</sup>	0.1	< 5	11.9	
			< 5	$\pm 9.3$	
MSA 1106BH Hi-Vol <sup>b,f</sup> (24-hour), H <sub>2</sub> O washed	- <sup>c</sup>	0.1	< 5	5.9	
			< 5	$\pm 3.1$	

a. Conditions for Gelman GA-1 sample SO<sub>2</sub> exposure: 25 mm discs exposed at 0.15 cfm for 2 hours, 20°C.

b. Conditions for Gelman A and MSA 1106BH sample exposures: 47 mm discs exposed at 1.32 cfm for 2 hours, 20°C.

c. Sulfate results prior to SO<sub>2</sub> exposure are for one disc, and after SO<sub>2</sub>, results are means  $\pm 1\sigma$  for two discs from the same 8x10" filter.

d. These values are the averages  $\pm 1\sigma$  of the  $\Delta$ 's for each filter

e. The number of filter samples studied.

f. Samples are dried at room temperature with SO<sub>2</sub>-free air after water washing.

THE EFFECT OF STORAGE TIME FOLLOWING SO<sub>2</sub> EXPOSURE OF PARTICULATE-LOADED SAMPLES<sup>a</sup>  
( $\mu\text{g SO}_4/25$  mm filter)

Sample	No. Samples (Episode)	(SO <sub>2</sub> ) ppm	Storage Time (Month)		
			0.0 <sup>b</sup>	1.0 <sup>b</sup>	2.0 <sup>b</sup>
Whatman 41 (24-hour)	1 (H)	0.1	36.5 ± 0.5	34.5 ± 0.5	39.0 ± 7.1
	1 (H)	0.5	36.0 ± 1.0	35.0 ± 0.5	35.0 ± 3.0
Gelman A (24-hour)	1 (F)	0.1	124.6 ± 3.0	119.6 ± 0.5	122.6 ± 1.5
	1 (F)	0.5	117.6 ± 2.5	119.8 ± 2.0	119.1 ± 0.5
MSA 1106BH (24-hour)	1 (G)	0.1	154.5 ± 3.5	150.0 ± 3.0	166.2 ± 4.1
	1 (G)	0.1	167.7 ± 3.0	153.0 ± 3.5	152.0 ± 0.5
Spectrograde (24-hour)	1 (F)	0.1	132.2 ± 0.5	135.3 ± 16.2	130.2 ± 6.1
	1 (F)	0.5	136.8 ± 4.1	130.7 ± 1.0	133.3 ± 3.0

a. Exposure conditions: 47 mm discs exposed at 1.32 cfm for 2 hours at 25°C, 90% RH.

b. Results from the analysis of one 15 mm circular portion of the filter. Error is obtained from replicate analyses of the same filter extract.

c. All samples were collected at Los Alamitos.

## X. Comparison of Atmospheric and Laboratory Sulfate and Nitrate Results

### A. Sulfate

Table 56 compares 24-hour mean sulfate results for atmospheric samples on six filter media to those obtained in laboratory studies of artifact sulfate due to clean filter-SO<sub>2</sub> interaction. As previously discussed, EPA Grade filters were not available for the field sampling. The laboratory results selected for comparison were obtained at 50 and 90% R.H. and 0.1 ppm SO<sub>2</sub>, conditions which were considered the most relevant to ambient conditions of those studied.

Since the atmospheric results include both genuine particulate sulfate as well as artifact sulfate, quantitative agreement between atmospheric and laboratory results cannot be expected. However, comparing the atmospheric and laboratory results, excepting for Spectrograde, the ranking of observed sulfate is identical. Thus differences in the extent of possible artifact sulfate formation due to SO<sub>2</sub>-clean filter interactions provides at least a qualitative explanation for the atmospheric sulfate results.

Based upon the laboratory results obtained, atmospheric sampling results for EPA Grade filters are expected to be similar to those for MSA 1106BH.

Fluoropore filters displayed both negligible artifact sulfate in the laboratory and the lowest mean atmospheric sulfate level. Based on these observations and the lack of measurable artifact sulfate ascribable to SO<sub>2</sub>-particulate interactions, we conclude that the atmospheric results on Fluoropore samples provide a close approximation to the true atmospheric particulate sulfate (plus sulfite).

### B. Nitrate

Atmospheric nitrate results are compared to nitrate results from exposure of clean filters to NO<sub>2</sub> and to HNO<sub>3</sub> in Table 57. Comparing relative results, the atmospheric values generally parallel the artifact nitrate from HNO<sub>3</sub> exposures rather than from NO<sub>2</sub> exposure. The mean atmospheric results calculated for MSA 1106BH represent about 9 µg/m<sup>3</sup> more than obtained on Fluoropore. This may be used as an upper limit to the artifact nitrate found in field sampling. The corresponding range of NO<sub>3</sub><sup>-</sup> from exposing clean filters to HNO<sub>3</sub> for six hours was 119.5 µg/m<sup>3</sup>. As noted previously this value cannot be extrapolated to 24 hours. However a lower limit estimate of the 24 hour average artifact nitrate from nitric acid exposure (0.2 ppm) can be made by assuming that after six hours no further collection of nitric acid on the filters occurs. This leads to a 24-hour value of  $\geq 30$  µg/m<sup>3</sup> artifact nitrate.

The efficiency of collection of nitric acid on filter media at levels close to those observed in ambient air (e.g.  $\leq 10$  ppb or 26 µg/m<sup>3</sup>)<sup>10</sup> cannot be estimated from the current studies which were restricted, to concentrations above 200 ppb (520 µg/m<sup>3</sup>) by limitations in available analytical techniques. As an upper limit, filters collecting 100%

Table 56

COMPARISON OF ATMOSPHERIC TOTAL SULFATE AND LABORATORY ARTIFACT  
SULFATE RESULTS<sup>a</sup>

<u>Filter</u>	<u>Atmospheric (24-hr)</u>	<u>Results Relative to Gelman A</u>	
		<u>Laboratory with 0.1 ppm SO<sub>2</sub></u>	
		<u>50% R.H. (24-hr)</u>	<u>90% R.H. (6-hr)</u>
Fluoropore, lo-vol	0.72 ± .06 <sup>b</sup>	< 0.02 <sup>b</sup>	0.04 <sup>e</sup>
Gelman GA-1, lo-vol	0.91 ± .08 <sup>b</sup>	0.26 <sup>b</sup>	0.28 <sup>e</sup>
Whatman 41, hi-vol	0.95 ± .05	0.43	0.34
Gelman A, hi-vol	1.00 <sup>c</sup>	1.00 <sup>d</sup>	1.00 <sup>f</sup>
Spectrograde, hi-vol	1.24 ± .03	1.13	1.74
EPA Grade, hi-vol	----	3.4	5.1
MSA 1106BH, hi-vol	1.21 ± .13	5.1	6.1

a. Except as noted, results at hi-vol flow rate (face velocity @ 47 cm/sec)

b. Results at 0.56 cfm (face velocity 20 cm/sec)

c. Mean concentration 6.5 µg SO<sub>4</sub><sup>=</sup>/m<sup>3</sup> for 14 episodes

d. Mean loading 55.5 µg SO<sub>4</sub><sup>=</sup>/filter or 4.1 µg SO<sub>4</sub><sup>=</sup>/m<sup>3</sup>

e. Only results at hi-vol flow rate (face velocity 47 cm/sec) available

f. Mean loading 67.6 µg SO<sub>4</sub><sup>=</sup>/filter or 5.0 µg SO<sub>4</sub><sup>=</sup>/m<sup>3</sup>

Table 57

COMPARISON OF ATMOSPHERIC TOTAL NITRATE AND LABORATORY ARTIFACT  
NITRATE RESULTS<sup>a</sup>

Filter	Observed Nitrate Results Relative to Gelman A		
	Atmospheric (24-hr)	0.2 ppm HNO <sub>3</sub> 50% R.H. 6-hr	0.5 ppm NO <sub>2</sub> 50% R.H. 6-hr
Fluoropore, lo-vol	0.60 ± .06 <sup>e</sup>	0.14 <sup>e</sup>	0 <sup>f</sup>
Gelman A, hi-vol	1.00 <sup>b</sup>	1.00 <sup>c</sup>	1.00 <sup>d</sup>
Whatman 41, hi-vol	1.14 ± .06	1.44	0.93
Spectrograde, hi-vol	1.27 ± .06	3.26	0.65
Gelman GA-1, lo-vol	1.29 ± .21 <sup>e</sup>	2.06 <sup>e</sup>	0.88 <sup>f</sup>
EPA Grade, hi-vol	---	2.86	1.06
MSA 1106BH, hi-vol	1.29 ± .14	2.37	1.03

- a. Except as noted all results obtained at hi-vol flow rate (face velocity @ 47 cm/sec)
- b. Mean concentration on Gelman A 13.5 µg NO<sub>3</sub><sup>-</sup>/m<sup>3</sup> for 14 episodes.
- c. Mean loading on Gelman A 516 µg NO<sub>3</sub><sup>-</sup>/filter or 38.3 µg NO<sub>3</sub><sup>-</sup>/m<sup>3</sup>
- d. Loading on Gelman A 29.6 µg NO<sub>3</sub><sup>-</sup>/filter or 2.2 µg NO<sub>3</sub><sup>-</sup>/m<sup>3</sup>
- e. Results at 0.56 cfm (face velocity 20 cm/sec)
- f. Only results at hi-vol flow rate (face velocity 47 cm/sec) available

of the gaseous nitric acid approximated by a 24-hour mean concentration of 3 ppb\* would show about  $3 \mu\text{g}/\text{m}^3$  artifact nitrate. Improved estimation of the artifact nitrate formation due to nitric acid in ambient air requires both ambient nitric acid concentration data and filter collection studies extended to lower nitric acid levels.

In contrast to  $\text{HNO}_3$ , adsorption of  $\text{NO}_2$  does not appear to provide sufficient nitrate to result in a range between filter extremes equivalent to that in observed atmospheric nitrate results. As noted in Section VII, the addition of ozone greatly increases artifact nitrate in the system  $\text{NO}_2\text{-O}_3$  with the high pH filters. The maximum increase in artifact nitrate observed with 0.5 ppm ozone added to 0.5 ppm  $\text{NO}_2$  at 90% R.H. was about  $7 \mu\text{g}/\text{m}^3 \text{NO}_3^-$  (for MSA 1106BH). While this mechanism may account for a portion of the observed artifact nitrate, it is probable, considering the more usual atmospheric levels of  $\text{NO}_2$  and  $\text{O}_3$ , that it is generally a minor contributor.

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\*This is about one third of the mean maximum reported by Spicer, West Covina.

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