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SAMPLING AND ANALYTICAL METHODOLOGY FOR ATMOSPHERIC NITRATES

Interim Report. Evaluation of Sampling Variables



**Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711**

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SAMPLING AND ANALYTICAL METHODOLOGY
FOR ATMOSPHERIC NITRATES
Interim Report. Evaluation of Sampling Variables
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ABSTRACT

The first phase of a study to develop sampling and analytical methodology for atmospheric nitrates is described. Experiments were carried out to determine the effect of nitrogen-containing gases on a number of different filter materials. Gases studied included NO, NO₂, HNO₃, and PAN. Experiments were also conducted to determine the effect of sampling time and sampling rate on atmospheric nitrate collection. Studies of filter storage, and gas-filtrate and gas-soot interactions were also undertaken. In many cases serious interference with the collection of atmospheric nitrate was found.

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INTRODUCTION

It has been known for many years that particulate nitrate is a fundamental constituent of our atmosphere and that the nitrate burden increases considerably as one approaches our major urban centers. Questions as to the physiological impact of particulate nitrates were raised at the time of the Chattanooga epidemiological study and have been asked with increasing frequency since that time. However, it has only been in recent months that the correlations between particulate nitrates and certain types of morbidity have become available. Certainly a strong indication that nitrates cause detrimental health effects is the recent finding⁽¹⁾ that airborne nitrates are associated with aggravation of asthma, even in areas where primary ambient air quality standards are not exceeded.

Particulate nitrate has been determined for many years throughout the United States by standard high volume sampling techniques using glass-fiber filters. Robinson and Robbins⁽²⁾ have estimated the global background nitrate concentration to be on the order of $0.2 \mu\text{g}/\text{m}^3$ in the lower atmosphere. Measurements of nonurban nitrate levels by the National Air Surveillance Network⁽³⁾ generally exhibit a range of annual averages between 0.1 and $1.0 \mu\text{g}/\text{m}^3$, with an overall mean of approximately $0.5 \mu\text{g}/\text{m}^3$. The lowest nitrate values are found in such areas as Glacier National Park in Montana and Black Hills National Forest in South Dakota, well away from industrial and population centers. Nitrate as nitric acid, has been shown⁽⁴⁾ to exist in the stratosphere at concentrations on the order of 0.003 ppm, and is closely associated with the stratospheric ozone layer. There is some evidence⁽⁵⁾ that this stratospheric nitric acid can be transported across the tropopause and thus contribute to the background tropospheric nitrate burden.

The level of particulate nitrate in and around major urban centers can be considerably higher than background levels. Based on an 8-year study⁽⁶⁾ of the mean concentrations of selected particulate contaminants in the atmosphere of the United States, it appears that nitrate on the average contributes somewhat less than 2 percent of the total suspended particulate weight. The figures vary depending on location. Several representative urban areas were Atlanta at $2.0 \mu\text{g}/\text{m}^3$, Chicago at $2.5 \mu\text{g}/\text{m}^3$, and Pittsburgh showing $3.0 \mu\text{g}/\text{m}^3$.

In certain areas, such as the California southcoast basin, the nitrate levels are even higher, averaging nearly $5 \mu\text{g}/\text{m}^3$ in the vicinity of downtown Los Angeles according to NASN results⁽³⁾. It is interesting to note however, that Grodon and Bryan⁽⁷⁾ have reported yearly average nitrate levels in downtown Los Angeles ranging between 9.8 and $15.4 \mu\text{g}/\text{m}^3$. Short-term nitrate levels in the eastern basin have been reported as high as $247 \mu\text{g}/\text{m}^3$ ⁽⁸⁾.

The major source of atmospheric particulate nitrate is thought to be oxidation of natural and anthropogenic NO and NO_2 . The major sinks for particulate nitrate are precipitation scavenging and dry deposition, with the precipitation mechanism estimated⁽²⁾ to be three times as important as dry deposition on a global basis.

Between the emission of gaseous NO or NO_2 and the ultimate scavenging of the particulate nitrate, there is a highly complex series of reactions which may result in a variety of reaction products prior to the ultimate formation of particulate nitrate. In a recent smog-chamber study of nitrogen oxides reactions conducted by Spicer and Miller⁽⁹⁾ at Battelle-Columbus, the major initial products of nitrogen oxides reactions in simulated photochemical smog were peroxyacetyl nitrate (PAN) and nitric acid. Excellent nitrogen mass balances were maintained throughout the experiments and the complex mechanisms leading to the formation of organic and inorganic nitrates were investigated. There is little doubt that in the actual atmosphere several other forms of nitrate exist. For example, we have observed⁽¹⁰⁾ low concentrations of alkyl nitrates and peroxypropionyl nitrate in urban atmospheres. We have also detected low levels of particulate organic nitrate in atmospheric aerosol samples⁽¹¹⁾. Heuss and Glasson⁽¹²⁾ have

observed another organic nitrate, peroxybenzoyl nitrate (PBzN), in smog simulations. There is also reason to suspect important, albeit low, levels of N_2O_5 , a nitrate precursor, in urban atmospheres. It is almost certain that all of these forms of gaseous nitrate ultimately end up as particulate nitrate.

Because of differences likely to be associated with the physiological impact of gaseous and particulate nitrates, it is important to distinguish between the two. The most common means of collecting particulate nitrate is filtration. However, there are a number of known problems involved in filtration sampling of particulate nitrate, and there are also several potentially serious problems which are not so widely recognized. As with any system designed to collect samples by filtration, a most important variable is the filter medium itself. Pate and Tabor⁽¹³⁾ have described the characteristics of a wide variety of glass-fiber filters which have been employed by NASN and other for nitrate collection. The manufacture of such glass-fiber filters required at least six separate steps and usually four participating manufacturers. It is therefore not surprising that substantial variations in the composition and characteristics of these filters often occur. Such variations can affect the accuracy or efficiency of particulate nitrate sampling by

- (1) Changing the nitrate filter blank
- (2) Affecting the efficiency of particulate collection
- (3) Affecting the degree to which particulate nitrate may react with the filter and become unavailable for leaching and analysis
- (4) Affecting the extent of extraneous nitrate formation on the filter by nitrate precursors.

Pate and Tabor⁽¹³⁾ have reported that the nitrate blank can typically comprise up to 10 percent of the nitrate collection in urban areas, and a considerably higher fraction of nonurban filter samples. However, as long as frequent blank determinations are carried out, this should not be a major difficulty except when sampling extremely low levels of particulate nitrate.

A potentially serious problem in the collection of particulate nitrates was pointed out in 1974^(10,14,15). This problem relates to the collection of artifact nitrate on filters due to the interactions of gaseous nitrogen compounds with certain filter materials. Two different studies at Battelle-Columbus have revealed the problem of artifact nitrate collection on certain filter materials. In one study⁽¹⁶⁾ investigating nitrate in auto exhaust, it was found that glass-fiber filters collected almost twice the quantity of nitrate in exhaust as did quartz-fiber filters. Nitrate also appeared on backup filters for both quartz and glass, providing an additional indication of artifact nitrate formation.

In a separate investigation at Battelle, the interaction between nitric acid and a variety of filter materials was studied. The impetus for this study came from the discovery of discrepancies in our atmospheric nitrate data⁽¹⁰⁾ collected on quartz as opposed to glass filters. The results of the study and the implications in terms of atmospheric chemistry and past particulate nitrate data have been reported⁽¹⁰⁾ and presented^(14,15) elsewhere. Briefly we find that both the absolute concentrations and also the assumed size distributions of ambient particulate nitrate from many past studies may be in error, due to gaseous nitric acid interference.

One possible explanation for the different collection efficiencies of gaseous nitric acid by quartz and glass filters involves the filter pH. Studies of filter characteristics at Battelle-Columbus⁽¹⁷⁾ have shown that quartz filters are nearly neutral (100 ml filter extracts yields pH of 5-7) while glass filters are often distinctly alkaline (100 ml filter extract yields pH of 9.4). Thus, neutralization and trapping of nitric acid and other acid gases may occur to a greater extent on glass filters than on quartz.

O'Brien, et al.⁽¹⁸⁾ have described a study of photochemical aerosols in the Los Angeles basin in which high-volume samplers and a cascade impactor were employed to determine concentrations and size distributions for NO_3^- , NH_4^+ , and $\text{SO}_4^{=}$, among other species. The high-volume sampler and each stage of the cascade impactor employed glass-fiber filters as the collection medium. The results of the study yielded very unusual nitrate size distributions which appeared to be dependent on sampling site.

The investigators reported that the strange results could be attributed to formation of artifact nitrate on the glass filters by some gaseous precursor such as nitric acid, and that the true nitrate size distribution was masked in their study by the conversion of gaseous nitrate precursors on the filter.

In addition to interactions between gaseous nitrate precursors and filter media, several other potential interferences with particulate nitrate collection should be considered. For example, certain nitrate precursors may be stable with respect to the filter medium but may be converted by interaction with some component of the aerosol collected on the filter. An example of this type of interaction might be the formation of NaNO_3 by the reaction of NO_2 with NaCl collected on the filter. In addition, there may be certain conditions of relative humidity, temperature, atmospheric composition, etc., under which species such as NH_3 , NO_2 , PAN, N_2O_5 , or N_2O could form and/or react with filters or collected aerosol on the filters. Some precursors may be held on the filter by absorption long enough to be oxidized to artifact nitrate by ozone or some other oxidizing agent.

Another type of interference might involve release of particulate nitrate collected on a filter by conversion to some volatile form. An example might be the reaction of sulfuric acid aerosol with particulate nitrate already collected on the filter to form nitric acid, which could then be lost by volatilization. In the same manner NH_4NO_3 , which has a significant vapor pressure, could be lost from particulate collection filters.

Two recent studies which touch on the kinds of interferences just discussed have been reported by Lovelock and Penkett⁽¹⁹⁾ and Chang and Novakov⁽²⁰⁾. The former investigators found that PAN and PPN do not exist in the clean air over the Atlantic ocean but that clean air has the potential for forming PAN and PPN when exposed to glass surfaces. The potential for PAN formation was greatest on days of high solar intensity, with maximum production during the afternoon hours. An important aspect of this study is the possibility that there are precursors even over the oceans which will form gaseous nitrates given the proper reaction surface.

Since the proper reaction surface was glass, the same material used for filters in most high-volume samplers, the possible importance of this reaction mechanisms for particulate nitrate formation must be considered.

Chang and Novakov⁽²⁰⁾ have studied the formation of particulate nitrogen species due to gas/solid interactions using ESCA. They report the formation of several types of particulate nitrogen due to the reaction of gaseous NO and NH₃ with soot (carbon) particles. Since soot, along with other forms of carbon, is collected on high-volume filter samples, the possibility of forming artifact nitrate from NO and NH₃ reactions exists.

Because of the potentially serious effect of the interferences described above on the accuracy of particulate nitrate data, the U.S. Environmental Protection Agency has initiated a 2-year study at Battelle-Columbus to investigate the impact of these factors on nitrate sampling procedures.

The objectives of this program are threefold:

- (1) To investigate the effects of environmental variables on the sampling and analysis of particulate atmospheric nitrate
- (2) To develop an improved method for the analysis of particulate atmospheric nitrate
- (3) To conceive, develop, validate, and optimize a sampling and analysis methodology for atmospheric nitrate.

The experimental aspects of the program have been broken into four phases. A description of each phase is shown below:

- | | |
|-----------|--|
| Phase I | A laboratory investigation of the factors affecting atmospheric particulate nitrate sampling |
| Phase II | Development of analytical methodology for atmospheric particulate nitrate |
| Phase III | Development and evaluation of a sampling procedure for atmospheric particulate nitrate |

Phase IV Optimization, simplification, and delivery to EPA of a validated sampling and analysis methodology.

The first year of the program has been devoted almost entirely to Phase I. This Interim Report describes the Phase I effort. Subsequent interim reports will describe Phase II and Phase III. At the conclusion of the program a final report will summarize the results of the entire project.

The main tasks that were undertaken in Phase I include investigations into

- Gas-filter interactions
- Gas-filtrate interactions
- Gas-soot interactions
- Effect of sampling time
- Effect of sampling rate
- Effect of storage time.

The remainder of this report will be devoted to a discussion of these tasks.

RESULTS AND DISCUSSION

GAS-FILTER INTERACTIONS

The principal goal of this task is to determine the effect of several nitrogen-containing gases on common filter media and to identify types of filters which might be suitable for particulate nitrate sampling in the atmosphere. The experimental procedure has involved exposing selected filter materials to exaggerated concentrations of nitrogen-containing gases in clean air. Nitrogen-containing gases are first diluted with clean cylinder air in a 500-cu-ft Teflon[®] chamber. The chamber is then evacuated through 47-mm filters of the various materials chosen for study. The pressure and concentration of the nitrogen gas are monitored above and below each filter during the experiment; after exposure the filters are analyzed for NO_3^- , NO_2^- , NH_4^+ , and total N. The experimental apparatus is shown in Figures 1 and 2. A schematic of the apparatus is shown in Figure 3. Each filter is typically exposed to more than 1 cubic meter of the dilute nitrogen-containing gas. The concentration of the nitrogen gas is adjusted (low ppm) so that the filter is exposed to approximately the same mass of nitrogen compound as a standard high-volume filter collected in an urban area. The face velocity is also quite similar to a standard Hi Vol.

The nitrogen-containing gases examined thus far include NO , NO_2 , HNO_3 , PAN, NH_3 , and N_2O . The analytical techniques used for these gases are listed in Table 1. N_2O was not determined directly but was prepared by known dilutions of the pure gas. Both dry and humidified conditions have been employed. We have investigated the effect of these nitrogen-containing gases on artifact nitrate formation on a number of filter types. Most of our experiments were conducted with the following filter types:

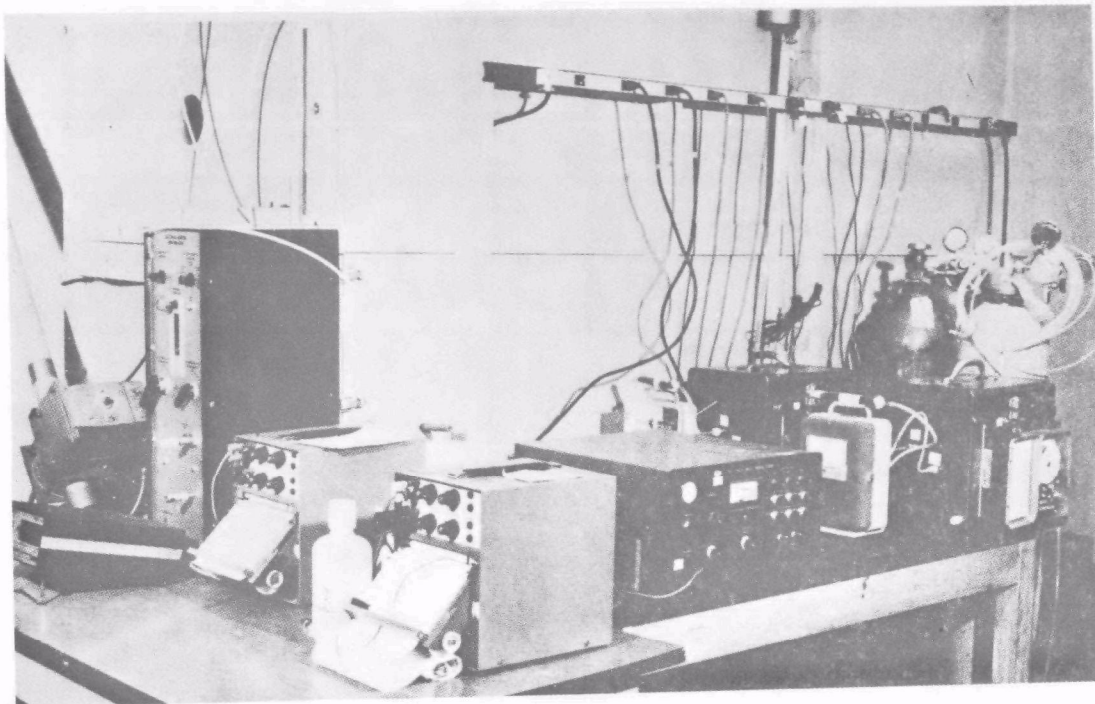


Figure 1. Phase I sampling and analysis apparatus.

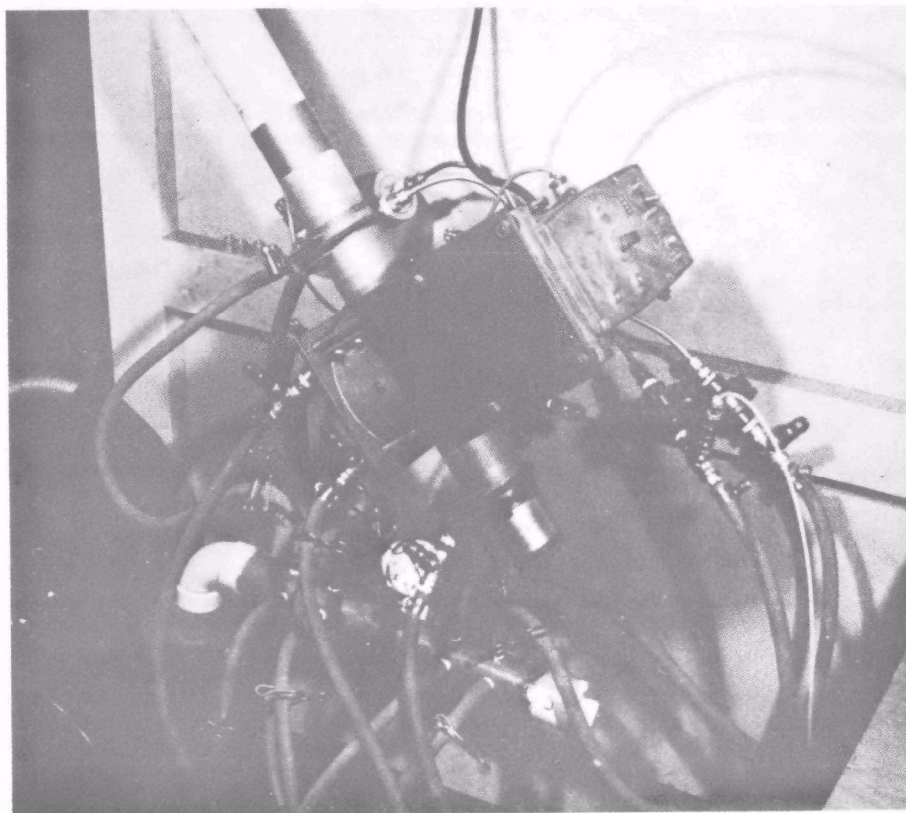


Figure 2. Close-up of sampling manifold and filter holders.

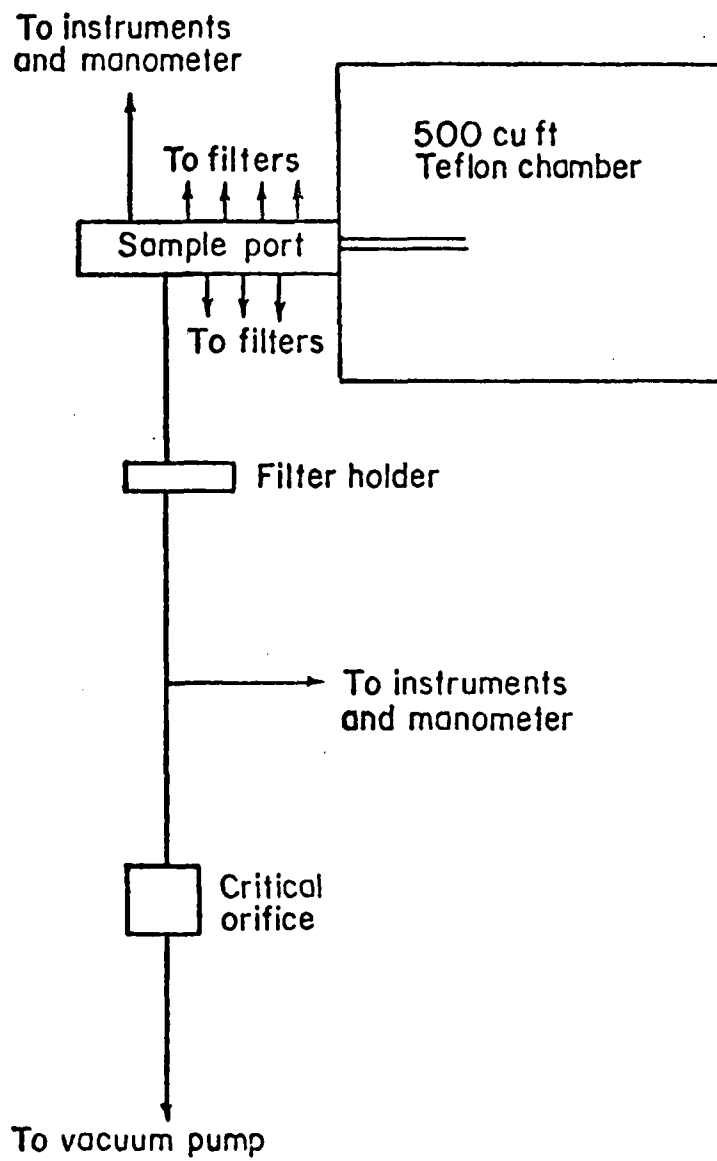


Figure 3. Schematic of sampling systems for eight simultaneous filters.

Glass Fiber - Gelman A
 Glass Fiber - Gelman E
 Glass Fiber - Gelman AE
 Teflon - Millipore Mitex
 Polycarbonate - Nuclepore
 Nylon - Millipore Duralon
 Cellulose Acetate - Millipore Celotate
 Quartz Fiber - ADL.

TABLE 1. GAS ANALYSIS INSTRUMENTATION

Gas	Analysis Method
NO, NO ₂	Chemiluminescence (low temperature carbon converter for NO ₂)
HNO ₃	Microcoulometry
PAN	Electron Capture Gas Chromatography
NH ₃	Chemiluminescence (dual temperature catalytic converter)

Toward the end of the Phase I effort a limited number of experiments with some additional filters were conducted. These experiments involved

Quartz Fiber - Pallflex QAST
 Glass Fiber - Gelman AA
 Glass Fiber - Gelman Spectrograde
 Cellulose-Backed Quartz - Pallflex E 70-2075 W.

A brief description of each of these filter types is shown in Table 2. The procedures employed for analysis of the filter samples are summarized in Table 3.

TABLE 2. PHYSICAL/CHEMICAL PROPERTIES OF PHASE I FILTER MEDIA

Filter Type	Pore Size ^(a)	pH ^(b)	Alkalinity ^(c)	NO ₃ ⁻ Blank ^(d)	Supplier
Cellulose Acetate	1.0	6.65	(1.8 x 10 ⁻³)	<0.005	Millipore
Polycarbonate	0.8	6.0	(9 x 10 ⁻⁴)	≤0.006	Nuclepore
Teflon-Mitex	5.0	7.0	0.0	<0.005	Millipore
Glass-AA	NA	8.9	3.24 x 10 ⁻²	<0.005	EPA/Gelman
Glass-A	NA	8.3	4.2 x 10 ⁻³	<0.005	Gelman
Glass-AE	NA	9.4	4 x 10 ⁻²		Gelman
Glass-E	NA	8.5	3.8 x 10 ⁻³	<0.005	Gelman
Glass-Spectro	NA	7.2	1 x 10 ⁻⁴	<0.005	Gelman
Nylon	1.0	5.3	(3.6 x 10 ⁻³)	≤0.007	Millipore
Quartz-ADL	NA	8.1	1 x 10 ⁻⁴	<0.005	EPA/ADL
Quartz-QAST	NA	8.1	3.8 x 10 ⁻³	<0.005	Pallflex
Quartz-E 70-2075 W	NA	6.2	(7.6 x 10 ⁻³)	<0.005	Pallflex

(a) Pore size in micrometers where applicable.

(b) ASTM-D-202; pH of 100 ml H₂O extract.

(c) Milliequivalents of acid or base required to titrate to neutral point per gram of filter. Parentheses indicate acidic filter.

(d) mg/47 mm filter.

TABLE 3. METHODS OF ANALYSIS

Specie	Method of Analysis
NH_4^+	Gas sensing electrode
NO_2^-	Diazotiazation-colorimetric
NO_3^-	Brucine sulfate colorimetric/ Ion chromatographic
Total Nitrogen	Modified Kjeldahl digestion

All of the filters exposed thus far have been analyzed for nitrate and total nitrogen and many have also been analyzed for ammonium and nitrite, depending on the gas being studied. Out of all the filters analyzed to date, none have shown any significant increase in the nitrite concentration under any circumstance. Out of all the filters exposed to gaseous NH_3 , only the nylon filters have shown substantial increases in particulate ammonium levels.

The results of the nitrate analyses conducted to date are shown in Figures 4 and 5. These figures show in bar-graph format the quantity of artifact nitrate found on the filter after exposure to ppm concentrations of the gases shown on the left side of the figure. The experiment number shown at the left of the figure is keyed to a complete tabulation of the experimental conditions contained in the Appendix. In most cases, two or more different concentrations of the nitrogen-containing gas have been employed, and frequently both dry and humidified conditions have been examined.

For purposes of this discussion, we will arbitrarily set the level of significant nitrate interferences as $\geq 100 \mu\text{g}$. Since we are dealing with a surface effect and a standard 8" x 10" Hi-Vol. filter has 40 times the effective collecting area of the 47-mm filters used in this study, a standard Hi-Vol. filter might be expected to collect about 40 times as much artifact nitrate as our filters. If our filters collect 100 g of

bogus nitrate, a standard Hi-Vol. might collect 4000 μg of artifact. Assuming a 24-hour sample volume of 2000 m^3 for a standard Hi-Vol. filter, the level of nitrate interference would be 2 $\mu\text{g}/\text{m}^3$. This concentration approaches the average NO_3^- concentration measured in many urban areas and thus constitutes a major interference.

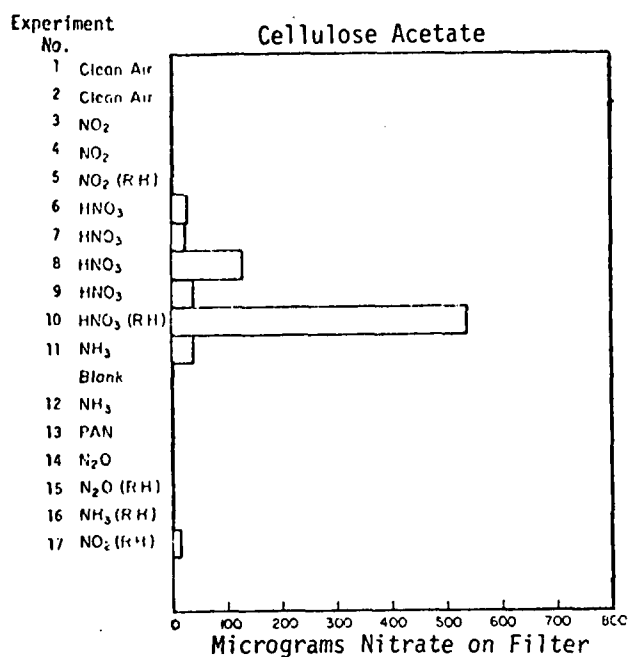
Figure 4a shows the results of our experiments with cellulose acetate filters. Two different experiments with nitric acid exhibit substantial interferences on this filter type, thus precluding its use as a particulate nitrate sampling medium.

The results of our studies of polycarbonate filters are shown in Figure 4b. It is clear from this figure that none of the gases studied to date yield significant artifact nitrate on polycarbonate filters.

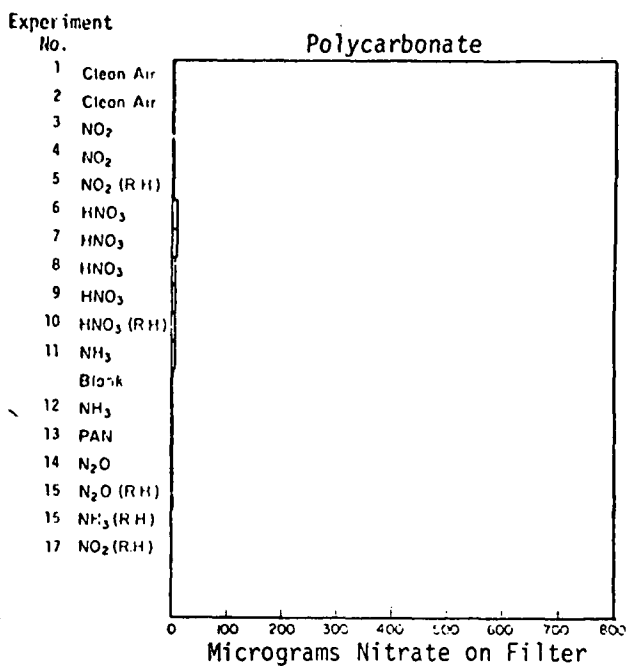
The results with Teflon filters, pictured in Figure 4c, are similar to the polycarbonate results in that no important interferences are apparent from any of the gaseous species studied to date.

The results of our investigation of nylon filters are shown in Figure 4d. Nylon was chosen for study in the hopes that it might provide quantitative collection of gaseous nitrates and thus serve as a gaseous nitrate sampling technique. It is clear from the figure that large quantities of nitric acid are collected by the nylon media. Judging from the final experiment, high levels of NO_2 (30 ppm) at high humidity also lead to very high levels of artifact nitrate. The first NH_3 experiment indicates formation of considerable artifact NO_3^- , while the second and third NH_3 runs show no such effect. We suspect that some NH_4NO_3 may have formed in our Teflon chamber during this experiment from trace quantities of HNO_3 remaining in the chamber from the previous experiment. Thus the results of the first NH_3 experiment are probably in error.

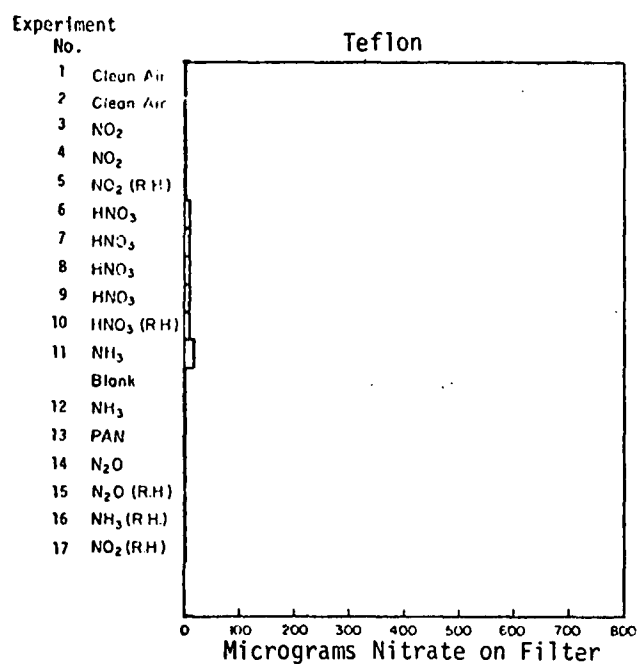
The results of our investigations of two types of glass-fiber filters (Gelman A and E) are shown in Figures 4e and 4f. Both filter materials show substantial interferences from nitric acid and also from high concentrations of NO_2 at high relative humidity. The interference by NO_2 is extremely important due to the high concentrations of NO_2 which frequently occur in urban areas. The interferences with particulate nitrate collection on these alkaline-surfaced glass filters makes them rather poor choices for nitrate sampling in the atmosphere.



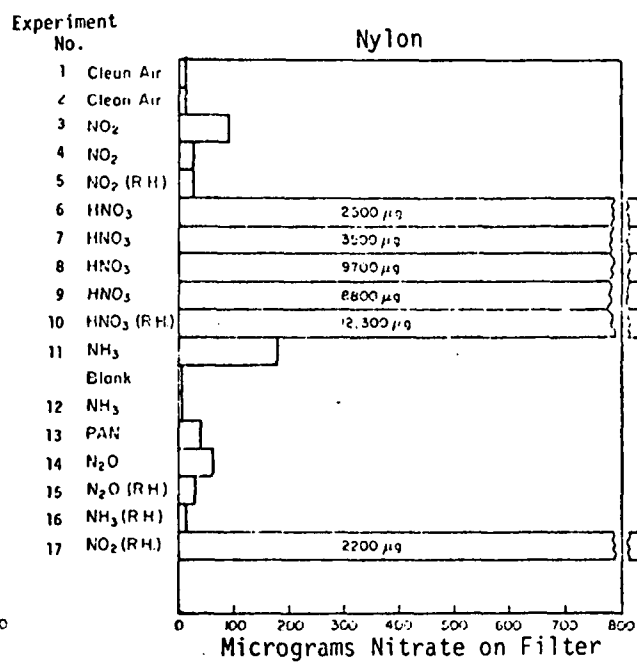
4a.



4b.

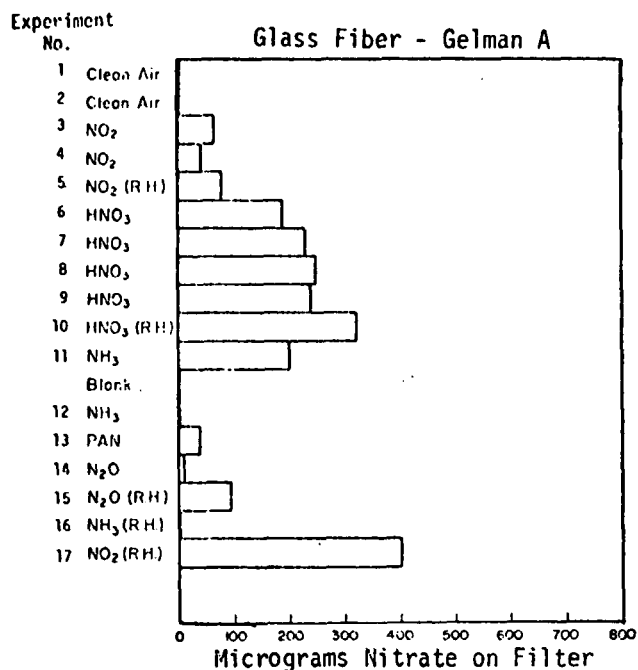


4c.

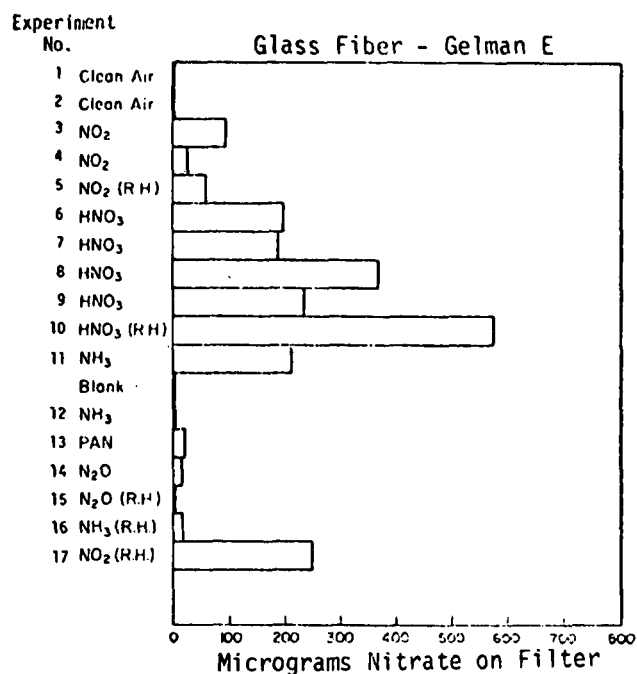


4d.

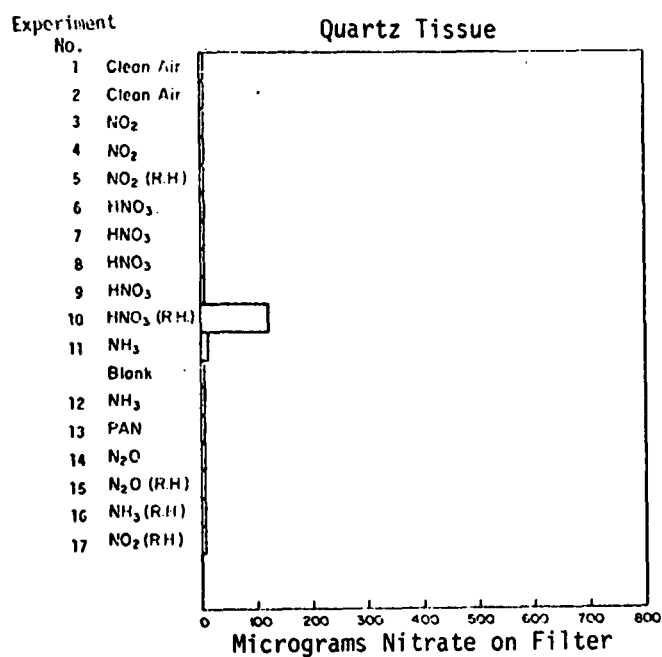
Figure 4. Gas-filter interactions.



4e.



4f.



4g.

Figure 4. Gas-filter interactions

The results of our investigations using quartz-fiber filters are pictured in Figure 4g. In terms of artifact nitrate collection, the quartz filters look quite good. Only one experiment, at high nitric acid and high relative humidity, shows any significant interference. However, the results from this one experiment are suspect since the total nitrogen analysis indicated no artifact nitrogen collection by the filter.

The results of a limited number of experiments with four additional filter materials compared with the ADL quartz filters are shown in Figure 5. The Pallflex quartz filters show no evidence of serious interference. However, the three remaining materials were all influenced by nitric acid, and the Gelman AA filter by nitrogen dioxide. The interference with particulate nitrate collection on Gelman AA filters is particularly significant since the material is widely employed in the NASN program. We strongly suspect that the surface coating of the Spectrograde filter is attacked by nitric acid, the interaction with the exposed surface resulting in very high levels of bogus nitrate.

All of the experiments described above have involved sampling about 1 cubic meter of air containing ppm quantities of some nitrogenous gas through individual filters. While the results of these experiments will only be used to indicate types of filters suitable for particulate nitrate sampling, still it would be useful to understand the relationships among artifact nitrate formation, sample concentration and sample volume. The results of a preliminary investigation of these relationships are listed in Table 4. The experiment (No. 22) shown in this table was designed to investigate the effect on filters of sampling low nitric acid concentrations over longer exposure times. Approximately 4 m^3 of the sample mixture (350 ppb nitric acid in air) passed through the filters. Based on the $100 \text{ } \mu\text{g}$ interference criterion put forward earlier, the glass filter shows significant artifact nitrate. The ADL microquartz was unaffected by the dilute gaseous nitric acid, while the Pallflex tissuequartz collected artifact nitrate at levels approaching the $100 \text{ } \mu\text{g}$ interference criterion. We plan to investigate these relationships further at the conclusion of the Phase III field study.

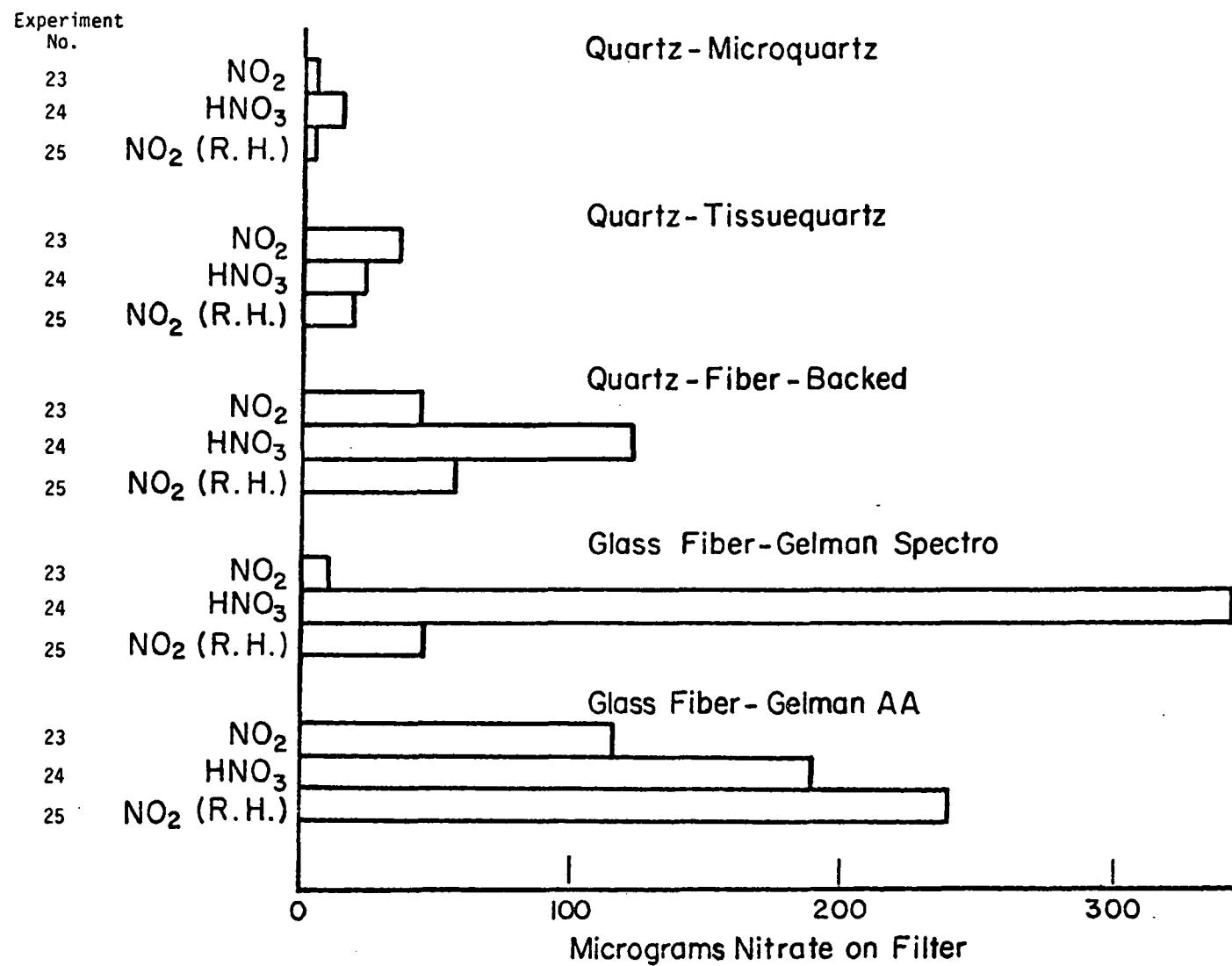


Figure 5. Gas-filter interactions

TABLE 4. RESULTS OF LOW CONCENTRATION
NITRIC ACID EXPERIMENT (350 ppb HNO₃)

Filter Material	NO ₃ ⁻	NH ₄ ⁺	Total N
Glass (Gelman AE)	0.23	<0.003	0.04
Quartz (ADL Microquartz)	<0.005	<0.003	0.01
Quartz (Pallflex Tissuequartz)	0.086	<0.003	0.03

The interaction of the gaseous nitrates PAN and nitric acid with filter materials is of particular concern in this study because (1) we have observed these gases at relatively high concentrations (50 ppb) in urban atmospheres and (2) they could easily form artifact nitrate by simple adsorption on filters. In addition to the experiments already reported with these two gases, we have carried out several experiments using a different technique. In these experiments either PAN or nitric acid was generated at low (sub-ppm) concentrations in a 200 liter glass smog chamber. The mixture was then pulled through the filters under study. The concentration of PAN or nitric acid in the chamber was determined at the start of the experiment, and then the concentration was monitored down stream of the filters. After an initial induction period during which the gaseous nitrates were removed by the filter, breakthrough occurred and the concentration downstream of the filter slowly increased to the level in the chamber. The breakthrough response curve was integrated and used to calculate the mass of gaseous nitrate removed by the filter. A system blank (same apparatus but filter holders empty) was run for each gas and subtracted from the filter results.

The results of the filter adsorption experiments for nitric acid are shown in Table 5. These data are in substantial agreement with the nitric acid results presented earlier, i.e., nitrate interference due to nitric acid adsorption on Teflon, quartz and polycarbonate filters is negligible. Interference due to adsorption on the two types of glass filters can be serious.

TABLE 5. FILTER ADSORPTION RESULTS FOR
NITRIC ACID

Filter Material	Nitrate Removed by 47-mm Diameter Filter, μg
Teflon	0.13
Quartz	0.11
Polycarbonate	2.8
Glass (Gelman E and AE)	Very large (no breakthrough after 8 hours of sampling)

PAN was generated at ambient concentrations for the breakthrough experiments by the photolysis of ethyl nitrite in dry air. A gas chromatograph equipped with an electron capture detector was used to monitor the PAN. The mass of PAN removed by the various filters is shown in Table 6, along with a list of the potential artifact nitrate which might be expected under actual ambient sampling conditions for each filter type. These data indicate, as did the results from experiment 13, that nitrate interference due to PAN adsorption is unimportant for the filters studied.

TABLE 6. PAN-FILTER INTERACTION STUDY RESULTS

Filter Material	PAN Adsorbed, μg	Potential Hi-Vol. Nitrate Interference, μg
Quartz - Microquartz	0.003	.065
Quartz - Pallflex 2500 QAST	0.006	.13
Quartz - Pallflex E 70-2075 W	0.009	.20
Glass - Gelman AA	0.35	7.6
Glass - Gelman A	0.010	.22
Glass - Gelman E	0.012	.26
Glass - Gelman AE	0.18	3.9
Glass - Gelman Spectrograde	0.020	.43
Nylon - Duralon	0.008	.17
Cellulose Acetate	0.007	1.3
Polycarbonate	0.007	.15
Teflon	0.005	.11

A check of the filter nitrogen balance for nylon, Gelman A and Gelman E filters was carried out using the results of experiment numbers 6, 7, 8, 9, 10 and 17. These experiments were chosen because the quantity of artifact nitrate found on the filters was well above the filter blank. The percentage of the total filter nitrogen which could be accounted for as nitrate-nitrogen has been calculated for these three filter types,

taking both the nitrate and total nitrogen blank into account. The average accountability for the six experiments was

Nylon - 71 percent

Gelman A - 127 percent

Gelman E - 93 percent.

The value shown for nylon is probably not very accurate due to the large total nitrogen blank correction. The Gelman A percentage is unexpectedly high. The high percentage seems to result from low total nitrogen analyses of Gelman A filters for two of the experiments. The reason for the low analytical results is unknown.

With the laboratory data obtained in the Phase I effort, it is extremely dangerous to attempt to quantitate the impact of artifact nitrate formation on filters under actual ambient sampling conditions. The greatest danger lies in extrapolating directly from our laboratory results—obtained under high concentration/low sample volume conditions, to ambient (low concentration/high volume) conditions. The Phase I study was not designed to quantitate the interference so much as to screen prospective filter materials in terms of their suitability for particulate nitrate sampling. A subsequent phase of this program will investigate the impact of artifact nitrate formation under actual ambient conditions and should provide a much more accurate estimate of the extent of nitrate interference. Additional laboratory studies are also underway with the objective of defining the relationships between nitrate interference and precursor concentration/sample volume. Indications from our laboratory data suggest that we saturated the surface sites of many of the filters early in our experiments by using ppm quantities of precursor gases. Under such conditions the apparent artifact collection efficiency is lower than expected under ambient sampling conditions. In other words, we believe that the percentage of artifact nitrate interference reported here may only be the lower limit to that expected under ambient sampling conditions.

GAS-FILTRATE INTERACTIONS

As mentioned in the introductory section of this report there are several possible interactions between gases or aerosols in ambient air and the particulate matter (filtrate) collected on high volume filters, which could result in either positive or negative interference with particulate nitrate determinations. The interaction between gases or aerosols passing through a filter and the collected filtrate was investigated by exposing actual ambient filter collections to exaggerated concentrations of several potential interferences. The concentration of nitrate on the filters was determined both before and after exposure, so that a simple comparison should reveal any significant interferences. In terms of experimental procedure, ambient Columbus aerosol was collected by Hi Vol sampling on several 142-mm filter media. 47-mm circles were cut from these filters and exposed to candidate gases in the same apparatus used for the gas-filter interaction studies. The results of nitrate analyses of these filters are shown in Table 7. The lack of consistent changes in NO_3^- levels upon exposure indicates that interactions between candidate substances and the collected particulate are not significant.

GAS-SOOT INTERACTIONS

The potential role of soot collected on Hi Vol filters in converting gases such as NO_2 and NH_3 to nitrate has been discussed by Chang and Novakov⁽²⁰⁾. The importance of gas-soot interactions was investigated in this study by loading 142-mm Gelman A filters with 4 mg of finely dispersed carbon-black and then passing approximately 2 m^3 of air containing ppm levels of NH_3 or NO_2 through several 47-mm diameter circles cut from these filters. Analysis of these filters gave the results shown in Table 8. The nitrate level increased after exposure to NO_2 , however, the magnitude of the increase is below the level of artifact nitrate formed during exposure

TABLE 7. PRESOILED FILTER ANALYSES (mg/FILTER)

Filter Material	NO_3^-	NH_4^+	Total N
<u>Presoiled Filters (Before Exposure)</u>			
Glass-Gelman AE (1) ^(a)	0.36	0.007	0.10
Glass-Gelman AE (2)	0.26	0.006	0.10
Cellulose Acetate (3)	0.037	0.014	0.06
Cellulose Acetate (4)	0.047	0.027	0.09
Quartz-Microquartz (5)	0.038	0.028	0.06
Quartz-Tissuequartz (8)	0.12	0.072	0.15
<u>Exposed Filters</u>			
<u>Experiment No. 18 - 11.5 ppm NH_3</u>			
Glass-Gelman AE (1)	0.35	0.005	0.13
Cellulose Acetate (3)	0.033	0.016	0.10
Quartz-Microquartz (5)	0.025	0.026	0.07
<u>Experiment No. 19 - 97 $\mu\text{g}/\text{m}^3$ H_2SO_4</u>			
Glass-Gelman AE (1)	0.28	0.068	0.17
Cellulose Acetate (3)	0.030	0.045	0.14
Quartz-Microquartz (5)	0.055	0.10	0.14
Quartz-Tissuequartz (8)	0.12	0.19	0.20
Quartz-Microquartz (unsoiled) ^(b)	<0.005	0.092	0.11
<u>Experiment No. 20 - 3.4 ppm HNO_3</u>			
Glass-Gelman AE (1)	0.40	0.011	0.13
Cellulose Acetate (3)	0.26	0.028	0.22
Quartz-Microquartz (5)	0.037	0.025	0.06
<u>Experiment No. 21 - 19.5 ppm NO_2</u>			
Glass-Gelman AE (1)	0.22	0.013	0.10
Cellulose Acetate (4)	0.043	0.021	0.07
Quartz-Microquartz (5)	0.028	0.020	0.05
Quartz-Tissuequartz (8)	0.11	0.072	0.14

(a) Numbers in parentheses identify ports used during presoiling.

(b) SO_4^{2-} was 0.087 for this filter.

TABLE 8. SOOT INTERACTION STUDY RESULTS^(a)
(mg/FILTER)

Exposure Conditions	NO ₃ ⁻	NH ₄ ⁺
Filter before exposure	0.008	<0.003
11.5 ppm NH ₃	0.010	<0.005
19.5 ppm NO ₂	0.017	<0.003

(a) Filter medium used was Gelman A with 4-mg carbon-black loaded on a 142-mm circle.

of clean Gelman A filters alone. Thus the gas-soot interaction does not appear to contribute significant quantities of artifact nitrate.

EFFECT OF SAMPLING RATE

To examine the effect of sampling rate on nitrate collection efficiency and artifact nitrate formation, ambient Columbus aerosol was collected simultaneously over 24 hours on two groups of four Gelman AE 142-mm filters, each at two flowrates. The results of this study are included in Table 9. The average nitrate collected on the four filters run at 38.2 μ /min flow rate was 2.65 ± 0.16 , $\mu\text{g}/\text{m}^3$ while the average for the 99.3 μ /min rate was 2.45 ± 0.20 $\mu\text{g}/\text{m}^3$. Since this difference is not statistically significant, nitrate collection is not affected by moderate variation of sampling rate.

EFFECT OF SAMPLING TIME

The effect of sampling time has been examined by simultaneous collection of atmospheric aerosol samples on parallel samplers. During the collections, the sample stream is split in half, with each half passing through an identical set of three filter types. One set of filters continuously sampled the atmosphere for a 48-hour period, while the second

TABLE 9. SAMPLING RATE STUDY (mg/FILTER)

Filter Material	NO_3^-	NH_4^+	Total N	m^3	$\frac{\mu\text{g}/\text{NO}_3^-}{\text{m}^3}$
Gelman AE (1)	138	29	70	56	2.46
" " (2)	380	82	160	142	2.68
" " (3)	146	29	70	54	2.70
" " (4)	360	89	170	150	2.40
" " (5)	153	42	70	54	2.83
" " (6)	315	97	200	143	2.20
" " (7)	146	29	70	56	2.61
" " (8)	345	124	200	137	2.52

set of filters was changed after the first 24 hours of the sampling period. Comparison of the amount of nitrate collected by the 48-hour filter with the sum of nitrate collected by the two 24-hour filters will indicate whether sampling time affects the collection of particulate nitrate. The three filter types included quartz tissue (ADL), glass fiber (Gelman AE), and a compound filter consisting of a quartz (ADL) and a nylon (Duralon) filter inserted in the same filter holder. This compound filter was used to investigate whether particulate and gas-phase nitrate could be separated and determined simultaneously by a filtration technique. The quartz filter has been shown to remove particulate nitrate but not gaseous nitrate, while the nylon filter quantitatively removes gaseous nitric acid. Thus the dual filter might make the simultaneous separation and determination of the two nitrate types feasible.

The results of the total mass determinations and the aerosol nitrogen analyses for these experiments are presented in Table 10. If sampling time has no effect on the aerosol collections, then the sum of the two 24-hour filter collections should approximate the 48-hour filter sample. The data in Table 10 indicates that within the estimated experimental uncertainty, the total mass, NH_4^+ , NO_3^- , and total nitrogen values

TABLE 10. RESULTS OF THE SAMPLING TIME STUDY

	Filter Type	Total Mass, mg	NH_4^+ , mg	NO_3^- , mg	Total N, mg
48-hour filter	Quartz	23.53	1.11	0.56	0.97
Sum of 24-hour filters		26.44	1.21	0.64	1.30
48-hour filter	Glass Fiber	27.92	0.74	1.92	0.85
Sum of 24-hour filters	(Gelman AE)	35.03	0.93	1.44	0.94
48-hour filter	Quartz and Nylon	30.63	1.91	1.24	0.94 ^(a)
Sum of 24-hour filters		30.03	2.11	1.28	1.08 ^(b)

(a) Total nitrogen values for quartz filter only.

are the same (no sampling time effect) for the 48-hour versus 24-hour comparisons, with two possible exceptions. The total mass collected by the two 24-hour glass-fiber filters is considerably greater than the 48-hour filter mass. We suspect a weighing error has caused this discrepancy. In addition, the 48-hour glass filter collected more nitrate than the two 24-hour glass filters. This discrepancy cannot be readily explained but is not significant enough to cause great concern.

Of major interest is the fact that the glass-fiber filters collected much more nitrate than the quartz filters, almost four times as much for the 48-hour filters. This additional nitrate must be artificial and result from collection of gaseous nitrogen compounds on the alkaline glass surface. These actual atmospheric data tend to confirm our laboratory results and show the potential impact of artifact nitrate formation on glass filters.

The glass filters collected less NH_4^+ than either the quartz or the quartz + nylon. This is understandable in the case of the dual filter, since nylon was shown earlier to collect some NH_3 as NH_4^+ . The lower levels of NH_4^+ collected on glass as opposed to quartz may be due to the alkaline nature of the glass filter. Such filters may tend to reject alkaline substances such as NH_3 or NH_4^+ compounds.

Table 11 shows the analyses of the individual quartz and nylon filters which made up our compound filter. Again, the sum of the 24-hour filters compared to the 48-hour filters indicates no dramatic sampling time effect. The quartz prefilter results from Table 11 compare quite well with the single quartz filter results shown in Table 10, serving as a check of our precision. The observation of NH_4^+ and NO_3^- on the nylon backup filter indicates that gaseous ammonium and nitrate precursors are penetrating the quartz filter and are adsorbed by the nylon backup. Thus, both the nylon and the glass-fiber filter results suggest that a gaseous nitrate precursor can strongly influence the apparent particulate nitrate concentrations. This is completely consistent with our earlier Phase I experimental findings.

TABLE 11. COMPOUND FILTER RESULTS

Filter Type		NH_4^+ , mg	NO_3^- , mg	Total N, mg
48-hour filter	Quartz (compound)	1.11	0.36	0.94
Sum of 24-hour filters		1.13	0.48	1.08
48-hour filter	Nylon (Backup)	0.80	0.88	-
Sum of 24-hour filters		0.98	0.80	-

EFFECT OF FILTER STORAGE ON PARTICULATE NITRATE

Filters collected in the field for particulate nitrate determination must frequently be stored for days, weeks, or even months before the actual analyses are performed. The effect of this storage period on particulate nitrate is uncertain. Therefore, a brief investigation of storage-time effects was added to the Phase I effort.

The results of several storage-time experiments are shown in Table 12. The filters were analyzed, stored for either 2 or 7 months in

TABLE 12. RESULTS OF THE STORAGE-TIME STUDY

Filter Materials	NO_3^-		Storage Time, Mos.
	Before Storage	After Storage	
Gelman AE	0.26	0.31	2
Celotate	0.047	0.016	2
Quartz (Pallflex QAST)	0.12	0.14	2
Duralon (Two 24-hr collections)	0.80	0.68	7
Duralon (One 48-hr collection)	0.88	0.69	7

glassine envelopes within sealed plastic bags, and then reanalyzed. There does not appear to be any decay of nitrate on Gelman AE or Pallflex quartz (QAST) during a 2-month storage period. Loss of nitrate from the Cellotate filter is indicated; however, the precision of the analysis at such low levels is not good. This may account for part of the apparent decay. A loss of nitrate was detected on the Duralon filters. This loss may be related to the longer storage of the Duralon filter samples.

The results of this brief study suggest that storage of quartz and glass (Gelman AE) filters for periods of at least 2 months prior to analysis should have a minimal effect on particulate nitrate results.

SUMMARY

A great deal has been learned about particulate nitrate sampling during this investigation, even though some of the individual studies are not yet complete. Our investigation of the interaction between gaseous nitrogen compounds and filter substrates indicates that nylon filters, cellulose acetate filters and many glass fiber filters are subject to significant particulate nitrate interference due to the formation of artifact nitrate on the filter. Teflon, polycarbonate and quartz fiber filters showed only minimal interferences from gases studied. Considering other factors such as cost, handling characteristics, pressure drop, efficiency for submicron particle collection and mass loading considerations, the quartz filters appear most appropriate for particulate nitrate sampling, especially for large sampling networks.

Studies of the possible interaction between gases or aerosols being pulled through a filter and the particles already collected on the filter indicated no major interferences, either positive or negative, with particulate nitrate determination. The interaction between NO_2 or NH_3 and soot collected on filters was also shown to result in negligible artifact nitrate formation under the conditions studied.

Sampling time and rate were investigated in this study and were found to have no effect on particulate nitrate collection over the range of rates and times studied. The effect on nitrate determinations of storing filter samples up to 2 months prior to analysis was found to be negligible for glass (Gelman AE) and quartz filters.

The results of this laboratory investigation will ultimately be combined with data on the comparison of many of the same filter materials under actual field sampling conditions. Those data, which will complement and augment these Phase I results, will be collected and reported in the third phase of this program.

REFERENCES

1. "Summary Report on Atmospheric Nitrates", U.S. Environmental Protection Agency, Research Triangle Park, N.C., July 31, 1974.
2. Robinson, E., and Robbins, R.C., J. Air Poll. Control Assoc., 20 (5), 303 (1970).
3. Air Quality Data for 1967 from the National Air Surveillance Networks (Revised 1971) PB 203 546, National Technical Information Center.
4. Murcray, D.G., Kyle, T.G., Murcray, F.H., and Williams, W.J., Nature, 218, 78 (1968).
5. Lazrus, A.L. and Gandrud, B.W., Proceedings of Third Conference on Climatic Impact Assessment Program, p. 161, Feb. 26, 1974.
6. Public Health Service Publ. No. 978, U.S. Dept. of Health, Education, and Welfare, Washington, D.C. (1962).
7. Gordon, R.J. and Bryan, R.J., Environ. Sci. and Tech., 7 (7), 645 (1973).
8. Hidy, G.M., et al., "Characterization of Aerosols in California", Final Report (Vo. IV), California Air Resources Board, Sept., 1974.
9. Spicer, C.W., and Miller, D.F., "Nitrogen Balance in Smog Chamber Studies", presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado (1974).
10. Spicer, C.W., "The Fate of Nitrogen Oxides in the Atmosphere", Battelle-Columbus Laboratories Final Report to EPA/CRC, 1974.
11. Miller, D.F., Schwartz, W.E., Jones, P.E., Joseph, D.W., Spicer, C.W., Riggle, C.J., and Levy, A., "Haze Formation: Its Nature and Origin — 1973", Battelle-Columbus Laboratories report to EPA and CRC, June, 1973
12. Heuss, J.M. and Glasson, W.A., Environmental Sci. Tech., 2, 1109 (1968).
13. Pate, J.B. and Tabor, E.C., Ind. Hyg. Jour., March-April, 1962, p. 145.
14. Spicer, C.W., Gemma, J., Joseph, D., and Levy, A., "The Fate of Nitrogen Oxides in Urban Atmospheres", presented at the American Chemical Society Meeting, Atlantic City, New Jersey, Sept., 1974.

15. Spicer, C. W., "Non-regulated Photochemical Pollutants Derived from Nitrogen Oxides", presented at EPA Symposium on Automotive Pollutants, Washington, D. C., Feb. 12, 1975.
16. Pierson, W.R., Butler, J.W., and Trayser, D.A., Environ. Letters, 7 (3), 267 (1974).
17. Trayser, D.A., Blosser, E.R., Creswick, F.A., and Pierson, W.A., "Sulfuric Acid and Nitrate Emissions from Oxidation Catalysts", paper presented at SAE Congress and Exposition, Feb. 25, 1975.
18. O'Brien, R.J., Holmes, J.R., Reynolds, R.J., Remoy, J.W., and Bockian, A.H., Paper No. 74-155, presented at 67th APCA Meeting, Denver, Colorado, (1974).
19. Lovelock, J.E. and Penkett, S.A., Nature, 249, 434 (1974).
20. Chang, S.G. and Novakov, T., "Formation of Pollution Particulate Nitrogen Compounds by NO-Soot and NH₃-Soot Gas-Particle Surface Reactions", pre-print of paper submitted to Atm. Environ. (1974).

APPENDIX A

EXPERIMENTAL CONDITIONS

TABLE A-1. EXPERIMENTAL CONDITIONS AND SAMPLE VOLUMES
(VOLUMES IN m³)

Experiment No.:	1	2	3	4	5	6	7	8	9
Experimental Conditions:	Clean Air	Clean Air	2.6 ppm NO ₂	2.0 ppm NO ₂	1.8 ppm NO ₂ 40% RH	1.4 ppm HNO ₃	1.5 ppm HNO ₃	8.0 ppm HNO ₃	3.0 ppm HNO ₃
<u>Filter Materials</u>									
Nylon (Duralon)	1.08	1.00	1.02(1.02)	0.99	0.87	0.76	0.99	1.29	1.32
Teflon (Mitex)	0.98	0.93(0.93)	0.92	0.91	0.79	0.69	0.89	1.22	1.22
Cellulose Acetate (Celotate)	0.95(0.95)	0.89	0.89	0.89	0.68	0.68	0.85	1.17	1.18
Glass (Gelman A)	1.12	1.05	1.02	1.02	0.79	0.79	1.00(1.01)	1.35	1.34
Glass (Gelman E)	1.12	1.03	1.03	1.03	0.79(0.79)	0.79(0.79)	1.00	1.35	1.37
Polycarbonate (Nuclepore)	1.07	1.00	1.00	0.97	0.75	0.75	0.96	1.31	1.28
Quartz (ADL)	1.12	1.04	1.05	1.01(1.03)	0.78	0.78	1.02	1.35	1.35
Experiment No.:	10	11	12	13	14	15	16	17	18
Experimental Conditions:	3.0 ppm HNO ₃ 30% RH	80 ppm NH ₃	5.5 ppm NH ₃	0.3 ppm PAN	15.6 ppm N ₂ O	18 ppm N ₂ O ~100% RH	1.7 ppm NH ₃ 40% RH	30 ppm NO ₂ 70% RH	11.5 ppm NH ₃
<u>Filter Materials</u>									
Nylon (Duralon)	0.73	1.35	1.15	0.93	1.61	1.33	1.45	0.99(1.01)	—
Teflon (Mitex)	0.98	0.98	1.07(1.05)	0.82	1.52	1.25	1.34(1.36)	0.84	—
Cellulose Acetate (Celotate)	0.96	1.27	1.05	0.85(0.82)	1.45	1.17	1.29	0.91	1.29
Glass (Gelman A)	1.13	1.39	1.18	0.97	1.66	1.41	1.47	1.04	—
Glass (Gelman E)	1.13	1.39	1.20	0.97	1.67(1.64)	1.39	1.52	1.03	2.36
Polycarbonate (Nuclepore)	1.00	1.31	1.12	0.92	1.61	1.31(1.33)	1.40	0.89	—
Quartz (ADL)	1.13	1.41	1.20	0.96	1.64	1.41	1.50	1.03	2.37

TABLE A-2. EXPERIMENTAL CONDITIONS AND SAMPLE VOLUMES

Experiment No.	Experimental Conditions	Filter Material	Volume Sampled, m ³
19	0.024 ppm H ₂ SO ₄	Glass (Gelman AE)	2.24
		Quartz (ADL)	2.29
		Cellulose Acetate	1.22
		Quartz (Pallflex)	2.30
		Quartz (ADL), clean	2.25
20	3.4 ppm HNO ₃	Quartz (ADL)	3.68
		Glass (Gelman AE)	3.71
		Cellulose Acetate	2.24
21	19.5 ppm NO ₂	Glass (Gelman AE)	2.14
		Cellulose Acetate	1.87
		Quartz (ADL)	2.10
		Quartz (Pallflex)	2.10
22	0.35 ppm HNO ₃	Quartz (Pallflex)	4.15
		Quartz (ADL)	4.18
		Glass (Gelman AE)	4.09
23	21 ppm NO ₂	Quartz (Pallflex)	0.95
		Quartz/Cellulose	0.98
		Glass (Gelman AA)	0.97
		Quartz (ADL)	0.98
		Glass (Spectrograde)	0.96
24	17.5 ppm HNO ₃	Quartz (ADL)	1.25
		Glass (Gelman AA)	1.28
		Quartz/Cellulose	1.28
		Glass (Spectrograde)	1.28
		Quartz (ADL)	1.25
25	16.5 ppm NO ₂ 17% RH	Glass (Spectrograde)	1.26
		Quartz (ADL)	1.29
		Quartz (Pallflex)	1.29
		Quartz/Cellulose	1.30
		Glass (Gelman AA)	1.27

TECHNICAL REPORT DATA
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The first phase of a study to develop sampling and analytical methodology for atmospheric nitrates is described. Experiments were carried out to determine the effect of nitrogen-containing gases on a number of different filter materials. Gases studied included NO, NO₂, N₂O, HNO₃, NH₃, and PAN. Experiments were also conducted to determine the effect of sampling time and sampling rate on atmospheric nitrate collection. Studies of filter storage, and gas-filtrate and gas-soot interactions were also undertaken. In many cases serious interference with the collection of atmospheric nitrate was found.

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