Nitrogen Oxide Interferences in the Measurement of Atmospheric Particulate Nitrates

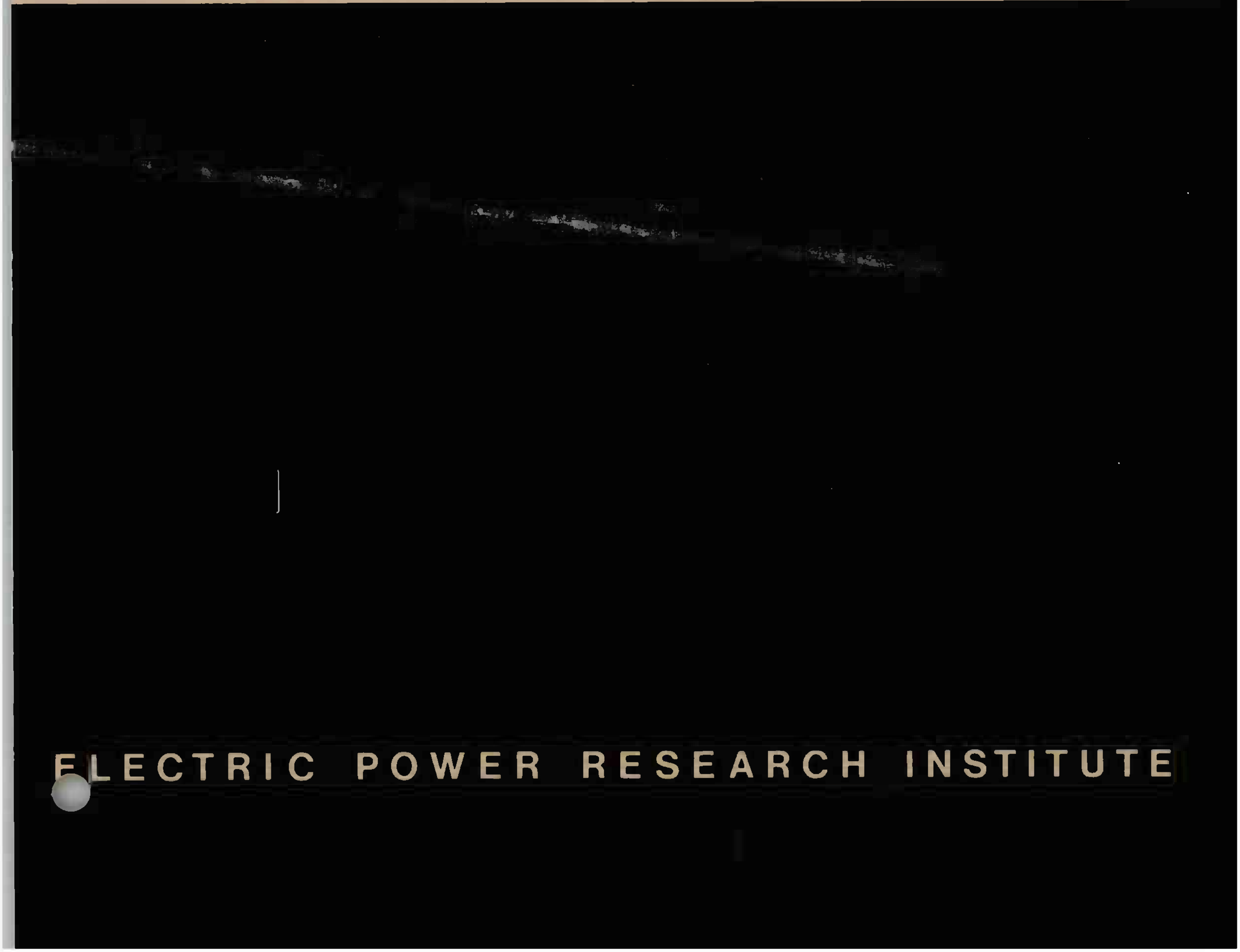
Volume 2

Keywords:
Particulate Nitrates
Artifact Formation
Filter Media
Atmospheric Chemistry

EPRI

EPRI EA-1031
Volume 2
Project 801-1
Final Report
March 1979

Prepared by
Radian Corporation
Austin, Texas



ELECTRIC POWER RESEARCH INSTITUTE

Nitrogen Oxide Interferences in the Measurement of Atmospheric Particulate Nitrates

---

EA-1031, Volume 2
Research Project 801-1

Final Report, March 1979

Prepared by

RADIAN CORPORATION
8500 Shoal Creek Blvd.
Austin, Texas 78766

Program Manager
F. B. Meserole

Project Director
B. F. Jones

Principal Investigators
L. A. Rohlack
W. C. Hawn
K. R. Williams
T. P. Parsons

Prepared for

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 94304

EPRI Project Manager
A. R. Stankunas
Energy Analysis and Environment Division

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ORDERING INFORMATION

Requests for copies of this report should be directed to Research Reports Center (RRC), Box 10090, Palo Alto, CA 94303, (415) 961-9043. There is no charge for reports requested by EPRI member utilities and affiliates, contributing nonmembers, U.S. utility associations, U.S. government agencies (federal, state, and local), media, and foreign organizations with which EPRI has an information exchange agreement. On request, RRC will send a catalog of EPRI reports.

[redacted]

NOTICE

Prepared by
Radian Corporation
Austin, Texas

ABSTRACT

This report presents the results of an experimental program to evaluate the validity of reported atmospheric particulate nitrate concentrations using high-volume (Hi-Vol) sampling techniques. Laboratory and field experiments were conducted to determine the extent of interference that gaseous nitrogen oxides introduce in the atmospheric nitrate determinations.

The formation of artifact nitrate was studied as a function of time, filter type, filter pretreatment, particulate type and loading, temperature, humidity, and nitric oxide, nitrous oxide and ozone concentrations. The highest nitrate values were measured on glass-fiber filters at high nitric oxide and high humidity levels and low temperatures. In fact, the "artifact" nitrate formed during the collection of ambient samples at these worst-case conditions may be the major contributor to measured particulate nitrate values.

The sorption of gaseous nitrogen oxides was reduced from 50 to 100% on teflon, polycarbonate and acid-washed, glass-fiber filters compared to untreated glass-fiber filters.

CONTENTS

APPENDIX A

SUMMARY AND ANALYSIS OF INFORMATION ON NITRATE LEVELS IN AMBIENT PARTICULATE SAMPLES

CONTENTS

Section 1

INTRODUCTION

Nitrate concentrations in ambient air particulates will become increasingly important as the Environmental Protection Agency directs its attention to the severity of the nitrogen oxide problem. Particulate nitrate data gathered in previous years will be reexamined and additional nitrate concentrations will be measured. These data will be used as a basis for regulatory standards.

The primary objectives of this literature search were to determine:

- the volume of nitrate data currently available, and
- the extent that the data have been utilized to draw conclusions about atmospheric chemistry and/or the necessity for NO_x control measures.

The literature was also assessed to determine the sampling methods by which the particulates were collected and the most common filter type used in Hi-Vol sampling. Analytical methods for NO, NO_2, O_3 and particulate nitrate were also noted.

Sources of data are documented in Section 2 and a discussion of the literature and conclusions are presented in Section 3. Section 4 is a tabular summary of literature reviewed and Section 5 contains the bibliography.

Section 2

INFORMATION SOURCES

Information sources included in-house files, open literature, the SAROAD* data compilation, and a telephone survey. In-house literature files were searched and reports containing nitrate information were retrieved and assessed to provide an initial data base.

The SAROAD Branch of the National Aerometric Data Branch was consulted to obtain nitrate data which had been compiled over the past four years from reporting agencies. Nitrate data compiled and reported by quarter were obtained from 1971 to the present for each reporting station across the nation. This source provided data on measured concentrations of suspended nitrate present in the atmosphere throughout the year. A machine-assisted search of Chemical Abstracts was conducted, and reports of work conducted under government contracts were consulted. A telephone survey was also conducted in an attempt to gather data on filter types, analytical methods used, and the frequency of analysis. Participants in the survey were chosen by the amount of work the agency had performed in the field of particulate nitrate collection and analysis.

---

* SAROAD: Storage and retrieval of aerometric data

Section 3

RESULTS OF THE LITERATURE ANALYSIS

A significant amount of ambient nitrate data is available and much of it has been used in studies to determine the sources of nitrates and the chemistry of nitrate formation in the atmosphere.

The majority of the ambient nitrate data available has been provided by the National Air Surveillance Network (NASW). These data indicate that anthropogenic sources, i.e., those sources resulting from the activities of mankind, contribute to the ambient nitrate level. The average suburban and urban nitrate level is 3.0 μg of nitrate per cubic meter, while the level of nitrate in remote areas is 1-2 μg NO_3^{-1}/m^3. On a global basis, it is estimated that less than 6 percent of the total nitrates formed in the atmosphere result from secondary anthropogenic sources of those activities of man which produce NO_2, NO or other precursors to nitrate. The majority of nitrate found in the atmosphere results from the oxidation of biological sources of NO and NO_2 (HI-173).

Twenty-two of the articles reviewed contained either a discussion of the chemistry of the formation of nitrate in the ambient atmosphere or a correlation of ambient nitrate concentration with NO_2, O_3, smog and total suspended particulates. Some correlation was made with temperature, wind direction, peroxyacetyl nitrate, and ammonia.

The following subsections describe the results of the literature analysis. Data on ambient levels of nitrate in particulate samples are presented first. Then a description of sampling and analytical methods reported in a telephone survey of regulatory agencies is given. Finally, a tabular summary of articles describing the atmospheric chemistry of nitrate formation and correlation of particulate nitrate levels with atmospheric parameters is given.

AMBIENT NITRATE DATA

There is a substantial amount of ambient nitrate concentration data available. Data have been collected since 1970. The majority has been measured by local and state agencies comprising the National Air Surveillance Network across the United States. It is submitted to SAROAD (the division of EPA responsible for the storage and retrieval of aerometric data) and then compiled in the National Aerometric Data Bank. Additional nitrate data have also been reported by independent research organizations who have conducted studies whose major or minor objective was the correlation of ambient nitrate data with other atmospheric parameters.

The ambient nitrate data for the years 1970-1974 have been obtained from SAROAD (EN-457). The yearly and quarterly arithmetic means at each sampling site are reported along with the minimum and maximum 24-hour value observed during the year. The location, station type, and population density are listed.

During the period 1970 through 1974, ambient nitrate data were reported to SAROAD for 339 sites with a total of 756 yearly averages. Most of the measurements were made during 1970, 1971, and 1972. In order to be included in the yearly averages, each site had to have made at least five 24-hour nitrate measurements for each of the four quarters.

Over 27,000 ambient 24-hour nitrate measurements were utilized in the computation of the yearly averages. This corresponds to an average of nearly forty nitrate measurements per year at each site. Boston recorded the highest number of 24-hour measurements (172) made within any one year (1970). In Houston, more than one hundred 24-hour nitrate measurements per year were made at 9 sites in 1971.

The highest reported yearly ambient nitrate concentration was 16.71 $\mu g/m^3$ observed in 1971 at Boston. Boston also measured 90 $\mu g/m^3$, the highest 24-hour maximum observed during the five-year time period. San Bernadino, California recorded the second highest yearly average (15.44 $\mu g/m^3$). Hawaii Volcanoes National Park reported .03 $\mu g/m^3$ for the lowest yearly average.

A summary of the ambient nitrate data reported to SAROAD for the years 1970 through 1974 is presented in Table 3-1. The data have been divided according to station location when possible. Arithmetic means of yearly average nitrate concentrations and corresponding standard deviations have been calculated for each of eight station types. Minimum and maximum yearly averages are also given.

The commercial sector of the suburban sites recorded the highest average yearly nitrate concentration, 3.5 $\mu g/m^3$. The residential sector of suburban USA recorded the lowest yearly nitrate concentration (2.7 $\mu g/m^3$) for any of the suburban or

Table 3-1

SUMMARY OF AMBIENT NITRATE DATA OBTAINED FROM SAROAD FOR YEARS 1970-1974

		Yearly Average Nitrate Concentrations $\mu g\ m^{-3}$			
Station Type	Number of Values	Minimum Observed	Maximum Observed	Arithmetic Mean	Arithmetic Standard Deviation
Remote	67	.03	3.86	1.16	.79
Rural	25	.42	3.94	1.62	1.08
Suburban - Residential	42	1.21	5.09	2.70	.90
Suburban - Commercial	78	1.47	9.55	3.46	1.16
Suburban - Industrial	19	1.04	4.54	3.04	1.17
Center City - Residential	30	.81	10.60	2.98	2.35
Center City - Commercial	383	.39	16.7	3.07	2.56
Center City - Industrial	39	1.29	5.40	3.00	.98

urban areas. The remainder of the center city and suburban sites averaged 3.0 $\mu g/m^3$ during the years 1970-1974. A somewhat lower ambient nitrate level of 1.6 $\mu g/m^3$ was reported for the rural stations. The lowest yearly nitrate concentration was observed in the remote areas. This level (1.16 $\mu g/m^3$) is still somewhat higher than would be anticipated if anthropogenic NO_x emissions were the primary source of ambient nitrates.

COLLECTION AND ANALYTICAL METHODS FOR THE DETERMINATION OF AMBIENT NITRATE

The majority of the ambient nitrate data has been acquired using a high volume sampler to collect the ambient particulates and the reduction-diazotization method to analyze for the nitrate ion. The Gelman Type A glass-fiber filter was the filter used most often for high volume sampling. In some cases, the filter type was not reported. These conclusions resulted from a review of literature articles and responses to a telephone survey (Section 4).

The telephone survey of U.S. regulatory agencies was conducted to determine the most common collection method, filter type and nitrate analytical method. Frequency of measurement of ambient nitrate levels was also determined. The responses are summarized in Table 3-2. All the agencies reported that they used the high volume technique to sample from 1500 to 2000 m^3 during a 24-hour period. In over 75 percent of the cases, the Gelman Type A glass-fiber filter was used in the collection of particulates. All of the agencies used the standard EPA technique for the analysis of nitrate (the reduction-diazotization method). Most of the agencies indicated that they were analyzing for nitrate on a routine basis. Two of them replied that they had reinitiated routine nitrate analysis in 1976. The city of St. Louis, Missouri did not have any recent data.

CORRELATION OF NITRATE DATA WITH ATMOSPHERIC PARAMETERS

Twenty-two of the articles reviewed contained either a discussion of the chemistry of the formation of nitrates in the ambient atmosphere or a correlation of ambient nitrate data with atmospheric parameters. Correlations between ambient nitrate concentration and the level of nitrogen dioxide, ozone, smog and total suspended particulates were reported most frequently. Some correlation was made with temperature, wind direction, peroxyacetyl nitrate (PAN), and ammonia. A summary of the twenty-six articles reviewed is presented in Table 4-1 (Section 4).

Four papers present a general discussion of atmospheric chemistry and include formation and reactions of NO, NO_2, oxidants and hydrocarbons. R. D. Cadle

Table 3-2

RESPONSES OF REGULATORY AGENCIES CONCERNING SAMPLING AND ANALYTICAL METHODS USED FOR NITRATE IN PARTICULATES

Agency	Filter Brand	NO_3^- Analytical Method	Frequency of Analysis
California Air Control Board	Gelman A	Reduction - diazotization	Routine
EPA	Gelman A	Reduction - diazotization	Routine
National Center for Atmospheric Res.	Gelman A	Reduction - diazotization	Routine
Environmental Research Corp.	Gelman A	Reduction - diazotization	Discontinued 1973, restarted 1975
City of Chicago	MSA	Reduction - diazotization	Routine
City of Cincinnati	Gelman A	Reduction - diazotization	Monthly
State of Colorado	Gelman A	Reduction - diazotization	EPA Cases
City of Philadelphia	Gelman A	Reduction - diazotization	Routine
City of St. Louis	Gelman A	Reduction - diazotization	No recent data
California Dept. of Health	MSA	Reduction - diazotization	Routine
Statewide Air Pollution Res. Center	Gelman A/E	Reduction - diazotization	Routine
GCA Technical Division	Gelman A	Reduction - diazotization	Restarted 1976

(CA-154) discusses the formation of photochemical smog when NO_2 is photolyzed and the resulting atomic oxygen reacts with certain organic vapors.

William Chameides and Donald Stedman (CH-345) present a theoretical model discussing reactions of anthropogenic nitrogen oxides with ozone produced in the natural photochemical methane oxidation chain. David Miller and Chester Spicer (MI-215) discuss the formation of nitric acid in smog from reactions involving nitrogen oxides and ozone. One of the most useful discussions was presented by Barbara Finlayson and James Pitts, Jr. (FI-118). Finlayson and Pitts present a discussion of homogeneous and heterogeneous atmospheric chemistry. They state that the hydroxyl radical (OH) is the major oxidizing species in the early states of photochemical smog formation and is an important intermediate in the oxidation of NO to NO_2. They propose that the hydroxyl radical may participate in the early stages of the oxidation of nitrogen dioxide to nitric acid by the three-body reaction:

$$OH + NO_2 \overset{\nu}{\rightarrow} HNO_3 \qquad (3\text{-}1)$$

Later the reaction with O_3 may be important.

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (3\text{-}2)$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad (3\text{-}3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (3\text{-}4)$$

They also cite a reference which states that "the reaction of N_2O_5 with H_2O appears to occur slowly in the gas phase but a more rapid heterogeneous reaction can occur on surfaces. Hence, one role of ambient particulates may be catalysis of such reactions." This may be one explanation for the formation of artifact nitrate on a glass-fiber filter. It also shows the importance of tests done to measure artifact nitrate formation on filters spiked with particulates.

CORRELATION OF NITRATE DATA WITH EMISSION SOURCES

The majority of the papers reviewed indicated that nitrate aerosols result mainly from gaseous sources. R. E. Lee and R. K. Patterson (LE-194) found in their study of three U.S. cities that about 65-68% of the nitrate was associated with particles having an equivalent diameter less than 1 micron, an indication of a gaseous source rather than a wind-erosion source. G. M. Hidy and Associates

(HI-160) found that anthropogenic sources of atmospheric aerosols produce particles in the submicron size range. R. E. Lee, R. K. Patterson, W. L. Crider, J. Wagman (LE-195) conducted a concentration and particle size distribution of particulate emissions in automobile exhaust and found that the particle size of the nitrate produced at all operating conditions was less than .5 micron.

G. M. Hidy and J. R. Brock (HI-078) made an assessment of the global sources of tropospheric aerosols. They evaluated both primary and secondary natural sources, and primary and secondary anthropogenic (resulting from man's activities) sources. Secondary mechanisms are reported to be responsible for almost all of the nitrate found in the atmosphere. The most important source of ambient nitrates is natural secondary sources, primarily from bacterial action in the soil and other biological processes. They state that E. Robinson and R. C. Robbins speculate that 1.2×10^6 tons of nitrate aerosol is produced in one day from the bacterially emitted NO_x. In contrast, Hidy and Brock estimate that the nitrate resulting from secondary anthropogenic sources amounts to only 6×10^4 tons/day. Calculations using these values indicate that less than 6% of the atmospheric nitrate results from anthropogenic emissions such as automobile exhaust, combustion of fuels, and industry.

CORRELATION OF AMBIENT NITRATE WITH HEALTH EFFECTS

No articles were found which specifically correlated ambient nitrate concentration with health effects. One article (SH-225) did study the effects of community exposure to nitrogen dioxide. Carl Shy and Associates found in their "Chattanooga School Children Study" that the ventilatory performance of second grade school children in the high-NO_2 exposure area was significantly lower than that in the control area. Ventilatory performance appeared to be adversely affected only when an NO_2 threshold was exceeded. Above this limit, no further impairment of performance could be detected. The authors measured suspended nitrate, suspended sulfate, total suspended particulates, soiling index, and NO_2 concentration. Suspended nitrates were significantly higher (1.5 x -3.0x) in high-NO_2 areas than in the high particulate and control areas.

Section 4

TABULAR SUMMARY OF LITERATURE REVIEWED

Table 4-1

SUMMARY OF PUBLISHED ARTICLES RELATING NITRATE DATA TO ATMOSPHERIC CHEMISTRY OR THE NECESSITY FOR NO_x CONTROL MEASURES

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
MU-123	EPA	2/76	Ion Chromatography of Sulfate and Nitrate in Ambient Aerosols				Analytical method for determination of water soluble nitrate and sulfate in ambient aerosols utilizing ion chromatographic separation coupled with conductometric detection. Detection limit is .02 μg/ml. No interference from Cl, F, nitrite, sulfite, carbonate or silicate.
SH-225	NAPCA	8/70 Chattanooga	Chattanooga School Children Study: Effects of Community Exposure to NO_2	1/wk x 8 wks 4 in 11/68; 4 in 3/69	NO_3^{-1} - Hi-Vol NO_2 - Jacob-Hochheisser	Reduction to nitrite-Standard EPA technique	Three health effects due to NO_2 and suspended nitrate and sulfate exposure were studied in children: 1) impaired respiration, 2) frequency of acute respiratory illness, and 3) impaired host resistance. High NO_2 concentrations (93 ppb) do negatively affect ventilatory performance when compared to control group (53 ppb). Remainder of results will be presented in another paper. Ventilatory performance was not affected by variations in suspended nitrates (1.6-7.2 μg/m³).

Table 4-1 (Cont)

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
MI-215	Battelle	1974 Los Angeles	Measurement of $HONO_2$ in Smog	1-min intervals for a 5-wk period in 9/73			A sensitive and selective technique has been described for the detection of low concentrations of HNO_3 in air. Sensitivity - 2 ppb HNO_3; estimated accuracy ±5%; no interference from SO_2 (0.5 ppm), NO (1 ppm), PAN (0.2 ppm), H_2SO_4 (0.2 ppm) and CH_2O (0.5 ppm). Evidence is presented which suggests that these reactions $N_2O_5 + H_2O \rightarrow 2HONO_2$; $OH + NO_2(+m) \rightarrow HONO_2(+m)$ may both contribute to $HONO_2$ formation in smog. Atmospheric sampling in L.A. area indicated 24-hr average $HONO_2$ concentration of about 3 ppb and 1-hr maximum concentration of about 10 ppb. N_2O_5 formation is suggested by the following reactions: $O_3 + NO_2 \rightarrow NO_3 + O_2$ $NO_3 + NO_2 \rightarrow N_2O_5$
CU-023	Argonne Lab	Spring 1973 Chicago	Variations in Chemistry of Airborne Particulate Material with Particle Size and Time	3 days - Spring 1973	Lundgren Cascade Impactor	Infrared adsorption	Authors propose that the infrared nitrate band results from chemisorption of NO_2 on the particulate surface.
DE-216	Institute of Nuclear Sciences	9/72	Chemical Analysis of Airborne Particulate Matter During a Period of Unusually High Pollution	24 hr x 7 days	Hi-Vol Whatman 41	Reduction to nitrite	Nitrate particulate levels for 6 consecutive days were 1.8, 3.4, 11.1, 24.2, 17 and 3.3 $\mu g/m^3$ which correspond to 4.1, 4.9, 7.7, 6.6, 8.8 and 3.9% of the total suspended particulate, respectively.

Table 4-1 (Cont)

Page 3

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
KA-219	Aichi Environmental Research Center	10/73-10/74 Nagoya, Japan	Size Distribution of Atmospheric Total Aerosols, Sulfate, Ammonium and Nitrate Particulates in the Nagoya Area	Continuously	Impactor and Gelman A	2,4-xylenol method	Average yearly nitrate concentration was 3 $\mu g/m^3$. Bimodal distribution was observed in the winter with $\approx 2\ \mu g/m^3\ NO_3^{-1}$ in the .4-.6 micron and $\sim 2\ \mu g/m^3\ NO_3^{-1}$ in the 3-5 micron range. The size distribution of summer nitrate concentrations (2.0 $\mu g/m^3$) was primarily limited to the 3-5 micron range.
DU-105	EPA Univ. of Minnesota	11/71 Denver	Comparison of Volume and Mass Distributions for Denver Aerosols	24-hr sampling periods for 4 days	Andersen Cascade Impactor	Reduction to nitrite	Nitrate concentration and its relationship with total suspended particulates was determined during pollution episode in Denver. During the episode they observed the particulate nitrate fraction to be five times the level found on a clear day; the level of total suspended particulates remained fairly constant.
FR-186	California Institute of Technology		Small Particles in Air Pose a Big Control Problem	(EPA data)	Hi-Vol (Gelman A)	Reduction to nitrite	The relationship of small particles either introduced or formed in the atmosphere with ambient air quality is discussed. Annual geometric mean particulate nitrate levels of the eight largest cities in the U.S. were reported.

Table 4-1 (Cont)

Page 4

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
HI-078	N.A. Rockwell Corp.		An Assessment of the Global Sources of Tropospheric Aerosols	NASN - 1966-67	Hi-Vol (Gelman A)	Reduction to nitrite	Authors make projections of production of NO_x from combustion sources in U.S. through year 2000. They estimate it will more than double between 1970 and 2000. They report that the average particulate nitrate concentration in suburban area is 1.1 µg NO_3^{-1}/m^3 or 2.5% of total suspended particulates. Remote areas have average levels of .6 µg NO_3^{-1}/m^3 or 3.1% of total suspended particulates.
HI-157	N.A. Rockwell Corp.		Observation of Aerosols Over Southern California Coastal Waters	Summer and Fall 1970	Hi-Vol (Gelman A)	Colorimetric procedure developed by Snell and Snell (1936)	Nitrate constituted an average of 5.7% of the aerosol, ranging from .4-9.6%. They propose that the enriched nitrate concentrations result from the influence of L.A. pollution.
HI-160	N.A. Rockwell Corp.	7-11/72 12 locations	Summary of the California Aerosol Characterization Experiment				Study of the source and evolution of aerosols in urban air. Observation revealed a relationship between maximum daily O_3 concentration and the light scattering coefficient for aerosols. The suggest that ambient nitrate may be present primarily as NH_4NO_3. Authors suggest that a significant portion of the nitrate found in early morning hours results from absorption of NO_2 on a moist filter.

Table 4-1 (Cont)

Page 5

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
HI-158	N.A. Rockwell Corp.	1969-70	The Nature of the Los Angeles Aerosol	NASN	Hi-Vol (Gelman A)	Reduction to nitrite	L.A. aerosol is unusually rich in nitrates and probably results from a rapid oxidation of NO_x to form nitrate aerosols.
LE-194	NAPCA (EPA)	1965-66 4 cities	Size Determination of Atmospheric Phosphate, Nitrate, Chloride, and Ammonium Particulate in Several Urban Areas	8 and 24-hr samples	Andersen Cascade Impactor	Reduction to nitrite	Average nitrate concentration in Cincinnati was 2.9 µg NO_3^{-1}/m^3. (68% of the nitrate particulates are less than 1 micron in diameter indicating the primary source of nitrate is gaseous as opposed to wind erosion.)
LE-195	NAPCA (EPA)	1969	Concentration and Particle Size Distribution of Particulate Emissions in Automobile Exhaust		Andersen	Reduction to nitrite	Nitrate formation was studied in automobile exhaust. Irradiation produced an increase in particulate nitrate concentration and a decrease in average particle size. The particle size of the nitrate automobile emission was typically submicron and of the same approximate diameter as ambient nitrate.
LU-041	Statewide Air Pollution Research Center	11/68 University of California	Atmospheric Aerosol Composition and Concentration as a Function of Particle Size and of Time	6-4 hr samples over 15 days	Hi-Vol (Gelman A)	Reduction to nitrite	Author states that there is a strong relationship between gaseous peroxyacetyl nitrate, particulate nitrate and aerosol light scattering High concentrations of ammonium nitrate particles, mainly in the 0.5-2µ diameter size range were found in the atmospheric particulate samples collected on days of very high smog. Particulate nitrate levels during November ranges between 0-80 µg NO_3^{-1}/m^3.

Table 4-1 (Cont)

Page 6

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
NO-047	California State Department of Public Health	9/3-4/69	Chemical Composition of Pasadena Aerosol by Particle Size and Time of Day	6-4 hr samples	Lundgren Cascade Impactor	ESCA	Results indicate that the majority of the particulate nitrate occurs in 2-5 micron particle size range. Reported concentrations ranged from .04-.43 $\mu g\ NO_3^{-1}/m^3$.
OB-009	California Air Reservoir Board	9/72	Formation of Photochemical Aerosol from Hydrocarbons, Chemical Reactivity and Products	(Lab study)	Hi-Vol (Gelman A)	IR	NO_2 inhibited formation of organic aerosols.
OB-010	California Air Reservoir Board	9/72	Formation of Photochemical Aerosol from Hydrocarbons, Atmospheric Analysis	8, 24, 48, 72-hr samples at 17 locations, total of 30 ambient samples	Hi-Vol (Gelman A)	IR	Inorganic nitrates of photochemical or at least secondary origin make up 10% of the mass loadings of the samples analyzed. Both $NaNO_3$ and NH_4NO_3 were reported as constituents of the nitrate particulate.
SC-313	University of Washington	9-11/72	Molecular Composition of Secondary Aerosol and Its Possible Origin	Variable	Impactor and Glass Fiber Filter	Mass Spectrometry	The authors discuss the application of mass spectrometry in characterizing ambient air pollution both qualitatively and quantitatively. Organics and inorganic nitrates were identified as secondary pollutants The high particulate nitrate concentrations associated with high smog levels result from the formation of secondary aerosols in the submicron particle size range.

Table 4-1 (Cont)

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
LE-227	EPA	1970 Great Britain	The Distribution and Transport of Airborne Particulate Matter and Inorganic Components in Great Britain	24-hr samples at 6 sites for ≈4 months	Hi-Vol (Gelman A)	Reduction to nitrite	Study was divided into two seasons: heating (Jan-April 15) and nonheating (April 15-June). Particulate nitrate levels were correlated with total suspended particulates, sulfate, ammonium and fluoride components. Nitrate concentrations correlated *positively only with the* total suspended particulates and then only during the nonheating season. Total suspended particulates correlated well with wind direction and were significantly higher when the wind direction was from the European continent.
GR-238	Statewide Air Pollution Research Center, U. Calif., Riverside	5-10/75 Riverside, California	The Concentration, Size Distribution and Modes of Formation of Particulate Nitrate, Sulfate and Ammonium Compounds in the Eastern Part of the L.A. Basin	24-hr samples collected daily over a 6-month period	Hi-Vol (Gelman Type A/E)	Cadmium reduction - diazotization method; Selective Ion Electrode	As a result of gas to particle conversion during transport from the western part of the Basin, high sulfate and nitrate levels (up to 48.7 and 70.2 $\mu g\ m^{-3}$) were observed during the 6-month study, with gas-particle distribution factors as high as 77% and 49%, respectively. Six-month averaged $SO_4^=$ and NO_3^- concentrations, calculated from 176 24-hr measurements, were 16.3 and 23.7 $\mu g\ m^{-3}$. Both sulfate and nitrate levels increase markedly with photochemical activity. Sulfate and nitrate aerosols accumulate in the submicron range, and are produced below 0.6μ at rates exceeding 10 $\mu g\ m^{-3} hr^{-1}$ during photochemical episodes.

Table 4-1 (Cont)

Page 8

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
FI-118	California State Univ.		Photochemistry of the Polluted Troposphere				Authors discuss various chemical reactions in the atmosphere between NO, NO_2, O_3, PAN, hydrocarbons, H_2O and ultraviolet radiation. The hydroxyl radical (OH) is an important intermediate in early stages of photochemical smog formation, not only in hydrocarbon oxidation, but also in the oxidation of NO to NO_2. Oxidation by ozone is comparable to that by OH after 2 hrs.
NI-068	Central Laboratory TNO	6-11/72 Delft, Netherlands	Peroxyacetyl Nitrate (PAN) in Relation to Ozone and Some Meteorological Parameters at Delft in the Netherlands	15-min intervals every day			Peroxyacetyl nitrate (PAN) concentration at Delft is a linear function of the time corresponding to ozone concentrations. PAN decomposes more slowly than ozone in the presence of atmospheric pollutants.
CH-345	Univ. of Michigan		Ozone Formation from NO_x in "Clean Air"				Authors present a theoretical model for explaining recent observations of ozone in excess of 80 ppb in relatively rural areas. The proposed mechanism involves the interaction of anthropogenic nitrogen oxides from urban areas with the natural photochemical methane oxidation chain.

Table 4-1 (Cont)

Page 9

Radian No.	Agency	Date and Location	Title of Article	Frequency of Sampling	Collection Media	Analytical Method Employed	Comments
LU-040	Statewide Air Pollution Research Center, Univ. of California	11/68 Riverside	Determination of Particulate Composition, Concentration and Size Distribution Changes with Time	16-hr intervals for each day (4:00 pm - 8:00 am)	Impactor - Teflon Films	Reduction to nitrite	A sampling technique was developed with an elaborate analysis scheme from which determination of particulate composition, concentration and size distribution can be made from a single aerosol. Field data obtained using this technique suggest a strong correlation between peroxyacetyl nitrate, particulate nitrate and smog. Average particulate nitrate levels ranged from 3.7 $\mu g/m^3$ on a low visibility day for an average during the 15-day sampling period of 11.7 $\mu g\ NO_3^{-1}/m^3$. Mean mass diameters of the nitrate particulates ranged from 0.7 microns to 1.8 microns with a mean particle size of 0.8 microns for the entire sampling period.
CA-154	National Center for Atmospheric Research		Formation and Chemical Reactions of Atmospheric Particles				A summary of formation of airborne particles "in situ" by chemical reactions and of the chemical reactions airborne particles may undergo once they are formed.

Section 5

BIBLIOGRAPHY

CA-154 Cadle, R. D., "Formation and Chemical Reactions of Atmospheric Particles", J. Colloid Interface Sc. 39(1), 25 (1972).

CH-345 Chameides, William L. and Donald H. Stedman, "Ozone Formation from NO_x in 'Clean Air'", Env. Sci. Tech. 10(2), 150 (1976).

CU-023 Cunningham, Paul T., Stanley A. Johnson, and Ralph T. Yang, "Variations in Chemistry of Airborne Particulate Material with Particle Size and Time", Env. Sci. Tech. 8(2), 131 (1974).

DE-216 Demuynck, M., et al., "Chemical Analysis of Airborne Particulate Matter During a Period of Unusually High Pollution", Atmos. Env. 10, 21-26 (1976).

DU-057 Dubois, Pierre, "The Reduction of Permanganate by Manganate Sulfate", Compt. Rend. 194, 2213-15 (1932).

DU-105 Durham, J. L., et al., "Comparison of Volume and Mass Distributions for Denver Aerosols", Atmospheric Environment 9, 717-22 (1975).

EN-057 Environmental Protection Agency, Office of Air Programs, Air Quality Data for 1968. APTD 0978. Research Triangle Park, N.C., 1972.

EN-216 Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Air Quality Trends Report, 1973. EPA-450/1-74-007. Research Triangle Park, N.C., Oct. 1974.

EN-457 Environmental Protection Agency, SAROAD, National Aerometric Data Bank, Quarterly Reports, 1970-1974. NA212. Research Triangle Park, N.C., 1976.

FI-118 Finlayson, Barbara J. and James N. Pitts, Jr., "Photochemistry of the Polluted Troposphere", Science 192 (4235), 111 (1976).

FR-186 Friedlander, Sheldon K., "Small Particles in Air Pose a Big Control Problem", Env. Sci. Tech. 7 (13), 1115-18 (1973).

GR-238 Grosjean, Daniel, et al., "Concentration, Size Distribution and Modes of Formation of Particulate Nitrate, Sulfate and Ammonium Compounds in the Eastern Part of Los Angeles Basin", Presented at the 69th Annual APCA Mtg., Portland, Oregon, June 27-July 1, 1976.

HI-078 Hidy, G. M. and J. R. Brock, "An Assessment of the Global Sources of Tropospheric Aerosols", Proceedings 2nd International Clean Air Congress, H. M. Englund and W. T. Berry, eds. N. Y., Academic, 1971, pp.

HI-157 Hidy, G. M., et al., "Observations of Aerosols Over Southern California Coastal Waters", J. Appl. Met. 13, 96 (1974).

HI-158 Hidy, G. M. and S. K. Friedlander, "The Nature of the Los Angeles Aerosol", in Proceedings 2nd International Clean Air Congress, H. M. Englund and W. T. Berry, eds. N. Y., Academic, 1971, pp. 291ff.

HI-160 Hidy, George M., et al., "Summary of the California Aerosol Characterization Experiment", J. APCA 25 (11), 1106 (1975).

HI-173 Hidy, G. M. and J. R. Brock, "Design of the Sulfate Regional Experiment", Env. Research & Tech., Inc. Final Report Project 485, February 1976.

KA-219 Kadowaki, Satoshi, "Size Distribution of Atmospheric Total Aerosols, Sulfate, Ammonium and Nitrate Particulates in the Nagoya Area", Atmos. Env. 10, 39-43 (1976).

LE-194 Lee, Robert E., Jr. and Ronald K. Patterson, "Size Determination of Atmospheric Phosphate, Nitrate, Chloride, and Ammonium Particulate in Several Urban Areas", Atmos. Env. 3, 249-55 (1969).

LE-195 Lee, Robert E., Jr., et al., "Concentration and Particle Size Distribution of Particulate Emissions in Automobile Exhaust", *Atmos. Env. 5*, 225-37 (1971).

LE-227 Lee, Robert E., Jr., et al., "Distribution and Transport of Airborne Particulate Matter and Inorganic Components in Great Britain", *Atmos. Env. 8*, 1095-99 (1974).

LU-040 Lundgren, Dale A., "Determination of Particulate Composition, Concentration and Size Distribution Changes with Time", *Atmos. Env. 5*, 645-51 (1971).

LU-041 Lundgren, Dale A., "Atmospheric Aerosol Composition and Concentration as a Function of Particle Size and of Time", *J. APCA 20* (9), 603 (1970).

MI-215 Miller, David F. and Chester W. Spicer, "Measurement of Nitric Acid in Smog", J. *APCA 25 (9)*, 240 (1975).

MU-123 Mulik, James D., et al., *Ion Chromatography of Sulfate and Nitrate in Ambient Aerosols*. Research Triangle Park, N. C., 1976.

NI-068 Nieboer, H. and J. van Ham, "Peroxyacetyl Nitate (PAN) in Relation to Ozone and Some Meteorological Parameters at Delft in the Netherlands", *Atmos. Env. 10*, 115-120 (1976).

NO-047 Novakov, T., et al., "Chemical Composition of Pasadena Aerosol by Particle Size and Time of Day. Pt. 3", *J. Colloid Interface Sci. 38*(1), 225 (1972).

OB-009 O'Brien, Robert J., John R. Holmes, and Albert H. Bocklan, "Formation of Photochemical Aerosol from Hydrocarbons, Chemical Reactivity and Products", *Env. Sci. Tech. 9* (6), 568-76 (1975).

OB-010 O'Brien, Robert J., et al., "Formation of Photochemical Aerosol from Hydrocarbons, Atmospheric Analysis", *Env. Sci. Tech. 9*(6), 577-82 (1975).

SC-313 Schuetzle, Dennis, et al., "Molecular Composotion of Secondary Aerosol and Its Possible Origin", *Env. Sci. Tech. 9*(9), 838 (1975).

SH-225 Shy, Carl M., et al., "The Chattanooga School Children Study: Effects of Community Exposure to Nitrogen Dioxide. Pt. 1. Methods, Description of Pollutant Exposure, and Results of Ventilatory Function Testing", *J. APCA 20* (8), 539 (1970).

APPENDIX B

DESCRIPTION OF LABORATORY EQUIPMENT AND OPERATING PROCEDURES

CONTENTS

Section 1

INTRODUCTION

The laboratory equipment designed to carry out the experimental portion of this contract is described in this appendix. The equipment consisted of a gas-mixing apparatus, a sampling apparatus, equipment for filter spiking, and a Radian Ambient Air Monitoring trailer. The equipment and its operation will be discussed in the following sequence:

- gas-mixing apparatus, Section 2,
- gas sampling train, Section 3,
- equipment check-out procedures, Section 4,
- operating procedures, Section 5,
- spiking of filters with particulate, Section 6, and
- the Radian Ambient Air Monitoring Trailer, Section 7.

Section 2

GAS-MIXING APPARATUS

The gas-mixing section was designed and built to provide an accurate air stream that could be varied over a wide range of atmospheric parameters. These parameters were temperature, relative humidity, nitric oxide concentration, nitrogen dioxide concentration, and ozone concentration.

A schematic diagram of this apparatus is shown in Figure 2-1. The essential components are:

- an inlet air pretreatment system,
- a water saturator for humidity control,
- nitrogen dioxide and nitric oxide sources,
- an ozone generator,
- flow rate control and monitoring devices, and
- an air stream temperature control device.

INLET AIR PRETREATMENT SYSTEM

Pretreated ambient air was used as the major constituent of the sample gas stream. The pretreatment consisted of removing water vapor, particulate matter, oxides of nitrogen, and ozone from the ambient air. A Gast dual head, oil-free pressure pump was used to provide the required flow of ambient air through the pretreatment system and into the gas-mixing manifold. This pump was installed with a bypass loop and a throttle valve to allow operation over a wide range of flow rates.

The first step in the air pretreatment process was the oxidation of nitric oxide in the ambient air to nitrogen dioxide by pulling room air through a column packed with Chromosorb A resin. The resin was coated with a sulfuric acid/chromium trioxide mixture which performed the oxidation step.

Water vapor was then removed from the sample air by pulling the air through a series of two condensers which were cooled by ice water and then forcing it through a

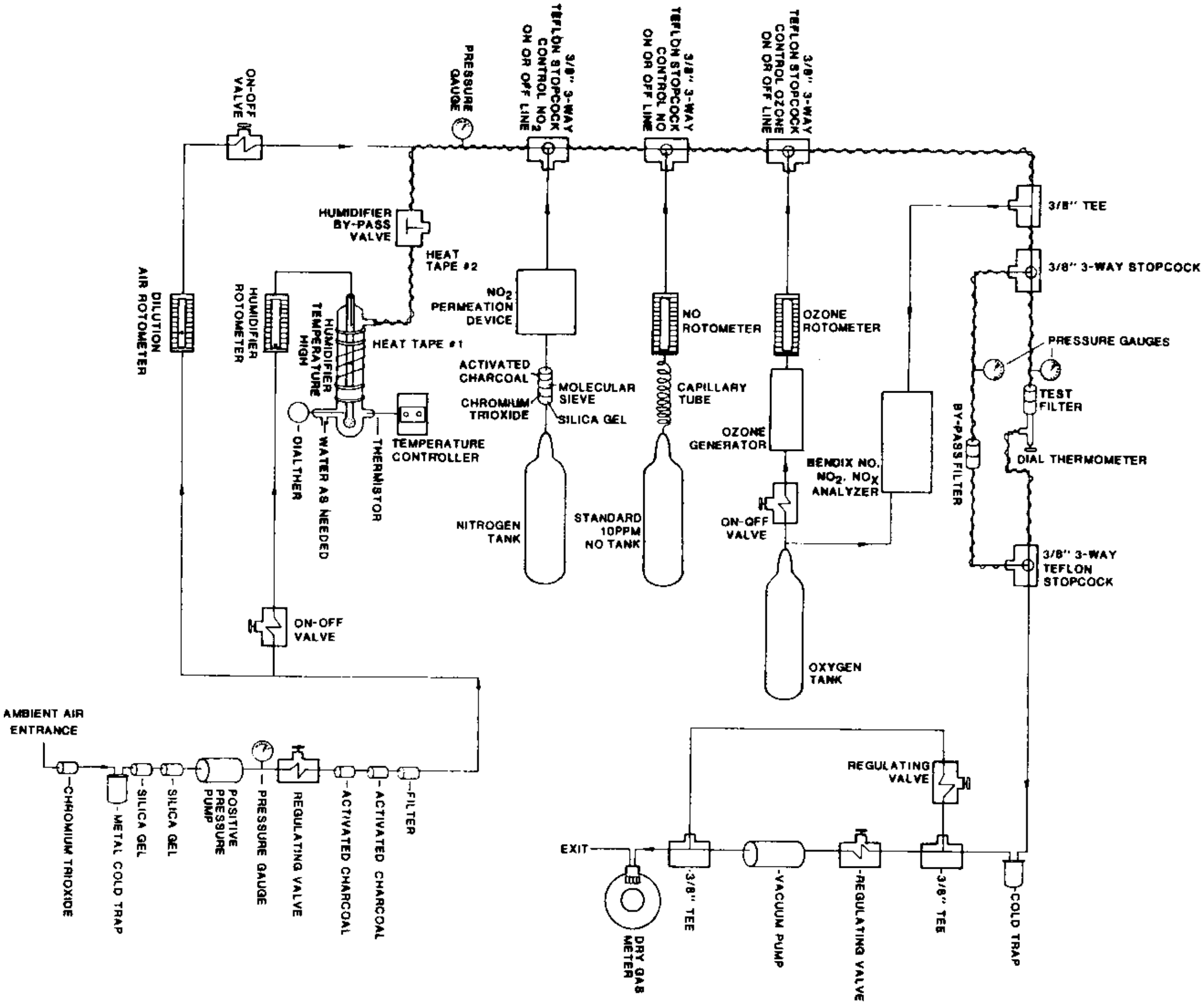


Figure 2-1. Gas-Mixing Apparatus

series of two columns packed with silica gel. The air was then scrubbed free of ozone and nitrogen dioxide by passing it through a series of two columns packed with activated charcoal. The final treatment step was the removal of particulate matter by passing the air stream through a particulate filter.

HUMIDITY CONTROL

The desired relative humidity in the sample air stream was obtained by first splitting into two streams the air coming out of the pretreatment section. One stream remained dry and served as dilution air while the other stream was passed through a temperature controlled contact water saturator. Both streams were then metered into the gas-mixing manifold at pre-determined rates. Thus, the relative humidity of the sample gas stream was a function of the water temperature in the saturator, the temperature of the sample gas stream, and the ratio of the flow rate through the saturator to the total flow rate of the sample gas stream.

A heating tape wrapped around the saturator was cycled on and off by a temperature controller in order to maintain the required temperature. To prevent excessive cycling of the temperature controller, the saturator was wrapped with fiberglass insulation. The temperature of the water inside the saturator was visually monitored with a scientific dial thermometer. Water temperature inside the saturator was easily maintained within plus or minus one degree Fahrenheit of the desired value. Liquid-gas contact inside the saturator was achieved by dispersing the gas with a frit fitted in the bottom of the saturator.

CONTROL OF NITROGEN DIOXIDE AND NITRIC OXIDE IN THE SAMPLE STREAM

The inlet air pretreatment section of the gas-mixing apparatus scrubbed oxides of nitrogen from the ambient air before the air was allowed into the gas-mixing manifold. This scrubbing of background "noise" made it easier to maintain the desired concentrations of nitrogen dioxide and nitric oxide in the sample gas stream.

The desired level of nitrogen dioxide in the sample stream was obtained from a temperature regulated nitrogen dioxide permeation unit. This unit, a Tracor Model 410 Mini-Perm, operates under the principle that many liquefied gases, when under pressure, permeate the walls of teflon capsules at a measurable rate. A wide range of stable delivery rates could be had by changing the temperature of the oven which housed the nitrogen dioxide permeation tube. Compressed nitrogen gas, scrubbed to remove oxides of nitrogen, was used as the carrier gas to bring the nitrogen dioxide from the permeation device into the gas-mixing manifold. Carrier gas flow through the nitrogen dioxide permeation device was kept at approximately 100 milliliters per minute during all of the runs.

Nitric oxide for the sample gas stream was provided from a bottle of compressed nitric oxide span gas. This bottle contained approximately ten parts per million of nitric oxide with the balance as nitrogen. By varying the ratio of the nitric oxide span gas flow into the gas-mixing manifold to the total gas flow going through the gas-mixing manifold, the desired level of nitric oxide could be obtained in the sample gas stream.

After the gas stream left the gas-mixing manifold but before it passed through the run filter, the nitric oxide and nitrogen dioxide concentrations were monitored by a Bendix 8101B oxides of nitrogen analyzer.

CONTROL OF OZONE LEVEL IN THE SAMPLE STREAM

Ozone in the sample gas stream was generated by a Pen-Ray #SOG-2 ozone generator. Ozone was produced by passing a purified oxygen stream through a quartz flow tube which paralleled an ultraviolet light source. Ozone production levels could be regulated by adjusting an exposure sleeve which fit over the ultraviolet lamp. When more of the lamp was exposed, there was a greater conversion of the oxygen to ozone. An oxygen gas flow rate of two liters per minute through the quartz flow tube was used in all experimental runs where ozone was used. The ozone produced was metered directly into the gas-mixing manifold.

FLOW RATE CONTROL AND MONITORING

Flow rate control and monitoring were achieved primarily by the use of needle valves and calibrated rotometers. Total flow through the system was monitored by a dry gas meter at the end of the sampling train. Flow through the nitrogen dioxide permeation device was controlled by maintaining a given ΔP between the gas-mixing manifold and the inlet of the permeation device. Three-way teflon valves were used on all the streams entering the gas-mixing manifold to facilitate switching streams in and out of the system.

AIR STREAM TEMPERATURE CONTROL

The temperature of the sample air stream was monitored with a thermometer mounted in-stream directly behind the filter support plate of the run filter. For the moderate temperature and high temperature runs the gas stream temperature could be elevated by increasing the current to the heat tracing around the gas-mixing manifold. The lower temperatures needed for simulation of winter conditions were obtained by incorporating into the system a Forma-Temp Jr. cooling bath along with approximately six extra feet of coiled teflon tubing. The coiled tubing provided the extra surface area needed for effective cooling of the sample gas stream.

Section 3

GAS SAMPLING TRAIN

A schematic representation of the sampling train can be seen in Figure 2-1. The system was designed with a bypass stream set up in the same configuration as the actual sample stream. This provision allowed the system to line out before the run filter was switched in. Switching the bypass filter out and the run filter in was done by two three-way valves.

Other equipment in the sample train included thermometers for measuring the temperatures at the run filter and at the dry gas meter, pressure gauges for monitoring pressures at the run filter and the bypass filter, a moisture condenser, and a Rockwell dry gas meter.

A Forma-Temp Jr. cooling bath was incorporated into the system when making the low temperature runs. Figure 3-1 depicts the equipment utilized in obtaining the low temperatures.

The sampling rate was selected to give a linear gas velocity through the 47 millimeter test filter comparable to the linear velocity through an 8-inch x 10-inch filter typically used in Hi-Vol samplers.

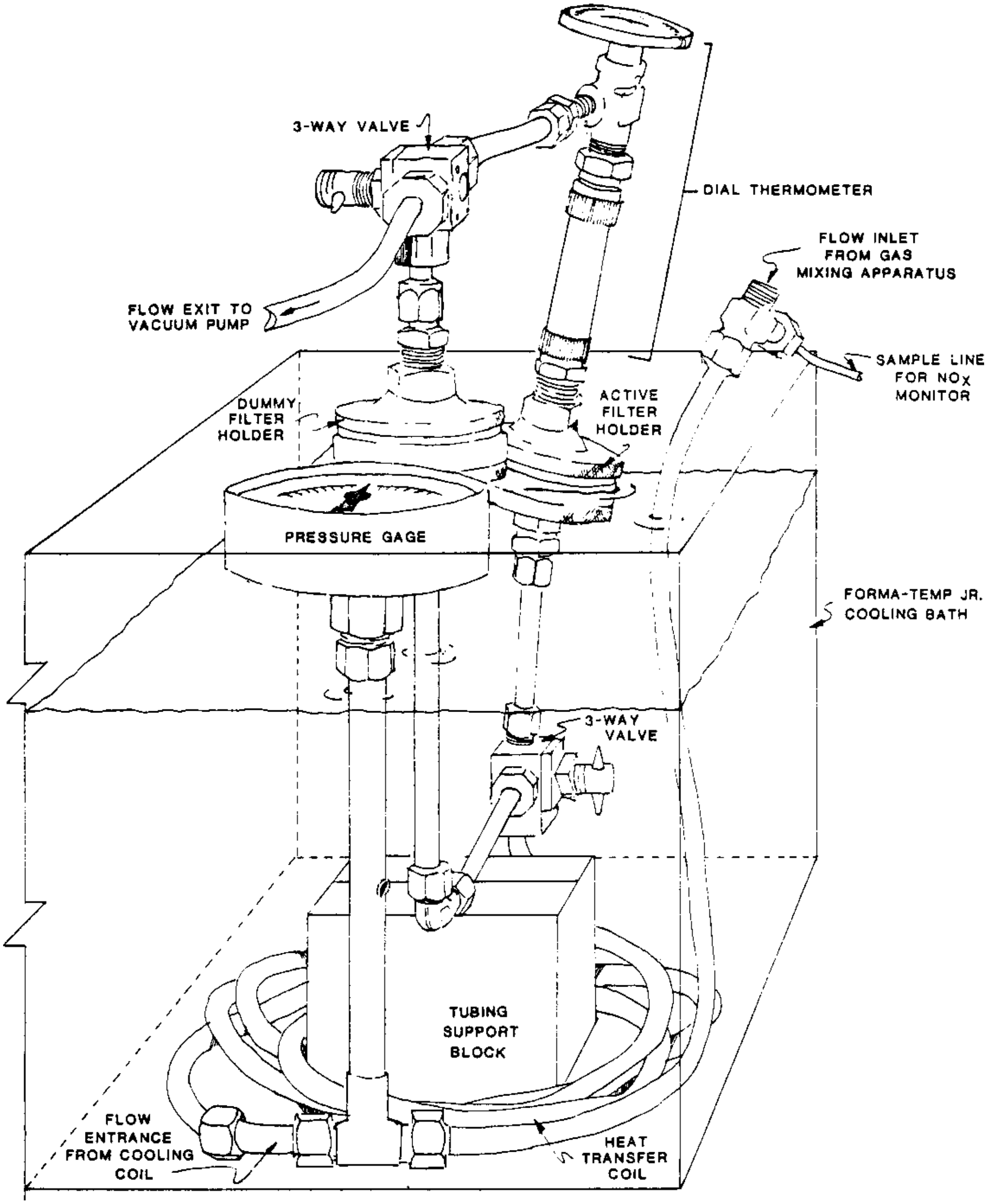


Figure 3-1. Low Temperature Apparatus Used in the Sampling Train.

Section 4

EQUIPMENT CHECK-OUT PROCEDURES

Each of the components which contributed to the accuracy and reproducibility of the experimental system was checked and calibrated. These components were:

- the dry gas meter used to measure total flow through the system,
- the rotometers used to measure individual gas flows into the gas-mixing manifold,
- the nitrogen dioxide permeation device,
- the ozone generator, and
- the water saturator.

CALIBRATION OF THE DRY GAS METER

A Rockwell 175-S dry gas meter was used to measure the total gas flow through the system. This meter was calibrated over a wide range of flows using a wet test meter. The agreement between the two meters was within two percent in all cases.

CALIBRATION OF ROTOMETERS

Selected points on the rotometer calibration curves provided by the manufacturer were checked using the wet test meter. These curves were found to be accurate in most cases. Corrections were made when necessary.

CALIBRATION OF THE NITROGEN DIOXIDE PERMEATION DEVICE

The Tracor Mini-Perm unit was calibrated at different permeation rates by collecting the nitrogen dioxide in a sodium hydroxide/sodium arsenite solution. The nitrite ion concentration was then determined colorimetrically by the addition of a phosphoric acid/sulfanilamide solution, and NEDA. The calibration results at each of the permeation rates verified that the permeation device had excellent reproducibility.

CALIBRATION OF THE OZONE GENERATOR

The Pen-Ray stable ozone generator was calibrated at different operating levels by first collecting the ozone in a buffered potassium iodide solution. This solution was then diluted and the iodine produced was determined colorimetrically. The ozone concentrations produced at different operating levels were found to be reproducible within five percent.

CALIBRATION OF THE SATURATOR

Saturator efficiency was determined by running the saturator at different temperatures and flow rates. The air coming from the saturator was passed through a series of two pre-weighed silica gel columns and then into a dry gas meter. By comparing the increased weight of the silica gel after the calibration run to the volume of dry gas passed through the humidifier, a relative humidity could be determined for a given operating temperature. Calibration runs showed that the saturator performed effectively at most operating flow conditions. However, to obtain high relative humidities at the high temperatures, the saturator had to be operated at disproportionately higher temperatures.

Section 5

OPERATING PROCEDURE

Prior to start-up, the level of water in the saturator was checked and more added if needed. Condensers were emptied of water and packed in ice. Fresh silica gel and Chromosorb cartridges were installed if needed. The particulate filter in the inlet air pretreatment section was checked once a week and changed when necessary.

Start-up was begun with taking the saturator out of the gas-mixing stream until it and the gas temperature in the manifold were lined out. This prevented any danger of water condensing in the gas sample stream. The pump was then turned on, causing dilution air to flow through the gas-mixing manifold. Heat tapes on the saturator, on the line from the saturator, and on the gas-mixing manifold were then turned on. When the saturator and gas manifold were close to operating temperature, the nitric oxide, nitrogen dioxide, and ozone streams were switched into the gas-mixing manifold as run requirements dictated. Gas exiting the gas-mixing manifold first passed through the bypass side of the sampling train. The filter holder in the bypass loop contained a filter of the same type as used in the actual run so that line-out in the bypass mode would approximate line-out in the sample mode. Next, the gas flow through the saturator was switched into the gas-mixing manifold. The vacuum pump on the downstream side of the filter was then turned on and the bypass adjusted in conjunction with the adjustment of the flow rates of the individual gas streams entering the manifold. Adjustment was complete when the desired flow rates were obtained with the manifold pressure gauge registering approximately 5 spig and the pressure gauge on the front side of the filter reading 0.3-1.5 psig. The final step in the line-out procedure was the adjustment of the flow rate through the nitrogen dioxide permeation device so the inlet pressure was 12 psig greater than the pressure on the outlet side.

Approximately fifteen minutes were allowed for the system to equilibrate in the bypass mode once the temperature, flow, and pressure requirements were met. The two three-way valves on the sampling train were then switched, channeling all the flow coming from the gas-mixing manifold through the run filter. An elapsed time clock was started and a reading taken from the dry gas meter in the sampling train.

Upon completion of a run, the sampling train was switched back to the bypass mode so that the run filter could be removed and a fresh one installed. Once the new filter was installed a new run could be started with no additional line-out required if the run conditions were the same as before.

At the end of each experimentation day, at least one calibration run was made to verify the output of the nitrogen dioxide permeation device. This was done by switching all streams out of the gas-mixing manifold, the exceptions being the nitrogen dioxide stream and the dilution air stream. Before the streams were switched out of the system, the bypasses on the sample train vacuum pump and on the inlet air pressure pump were fully opened simultaneously to prevent water backup in the humidifier rotometer. The sample train vacuum pump was then shut off and the unneeded streams were switched out of line. The dilution air stream was then adjusted so that the combined flow of the dilution air stream and the nitrogen dioxide stream was approximately two liters per minute.

To calibrate, the run filter was replaced by a length of teflon tubing. The air stream was run for thirty minutes through the tubing into a series of two gas-sorption bubblers, each containing approximately 75 milliliters of sodium hydroxide/sodium arsenite solution.

Section 6

SPIKING OF RUN FILTERS WITH SOLID PARTICULATE OR MIST

As part of the overall research program, a study was undertaken to determine what effect, if any, the presence of selected particulates would have on artifact nitrate formation. Particulates selected for evaluation were those commonly found in ambient air. These included both solid particulate matter such as fly ash and aerosol mists such as sulfuric acid. The method of deposition of these particulates onto the filter media is discussed below.

PRELIMINARY PREPARATION OF FILTERS TO BE SPIKED

A supply of forty-seven millimeter diameter filters, in excess of projected needs, were cut from the same eight-inch by ten-inch sheet. These were allowed to equilibrate for one day in a desiccator. Prior to spiking with particulate, the filters were weighed on an analytical balance.

SPIKING FILTERS WITH SELECTED MISTS

The mists selected for study were sulfuric acid, nitric acid, and ammonium chloride. Sulfuric acid mist was obtained by passing a stream of clean, dry argon over the surface of sulfuric acid heated to 90°C and through a holder containing a 47 mm diameter filter. The apparatus used in this procedure is shown in Figure 6-1. The nitric acid mist was spiked onto filters in the same way except that heating of the nitric acid was unnecessary.

Ammonium chloride was obtained using a flask of ammonium hydroxide and a flask of hydrochloric acid. Argon was passed over the surfaces of these two reagents and the two streams were then manifolded together into the flask shown in Figure 6-1. The ammonium chloride thus formed was then spiked onto a filter in the same way as the nitric acid and sulfuric acid mists.

SPIKING FILTERS WITH SELECTED SOLID PARTICULATES

The two solid particulates deposited onto filters were fly ash and charcoal. In both cases the solids were ground prior to use. The charcoal or fly ash solids

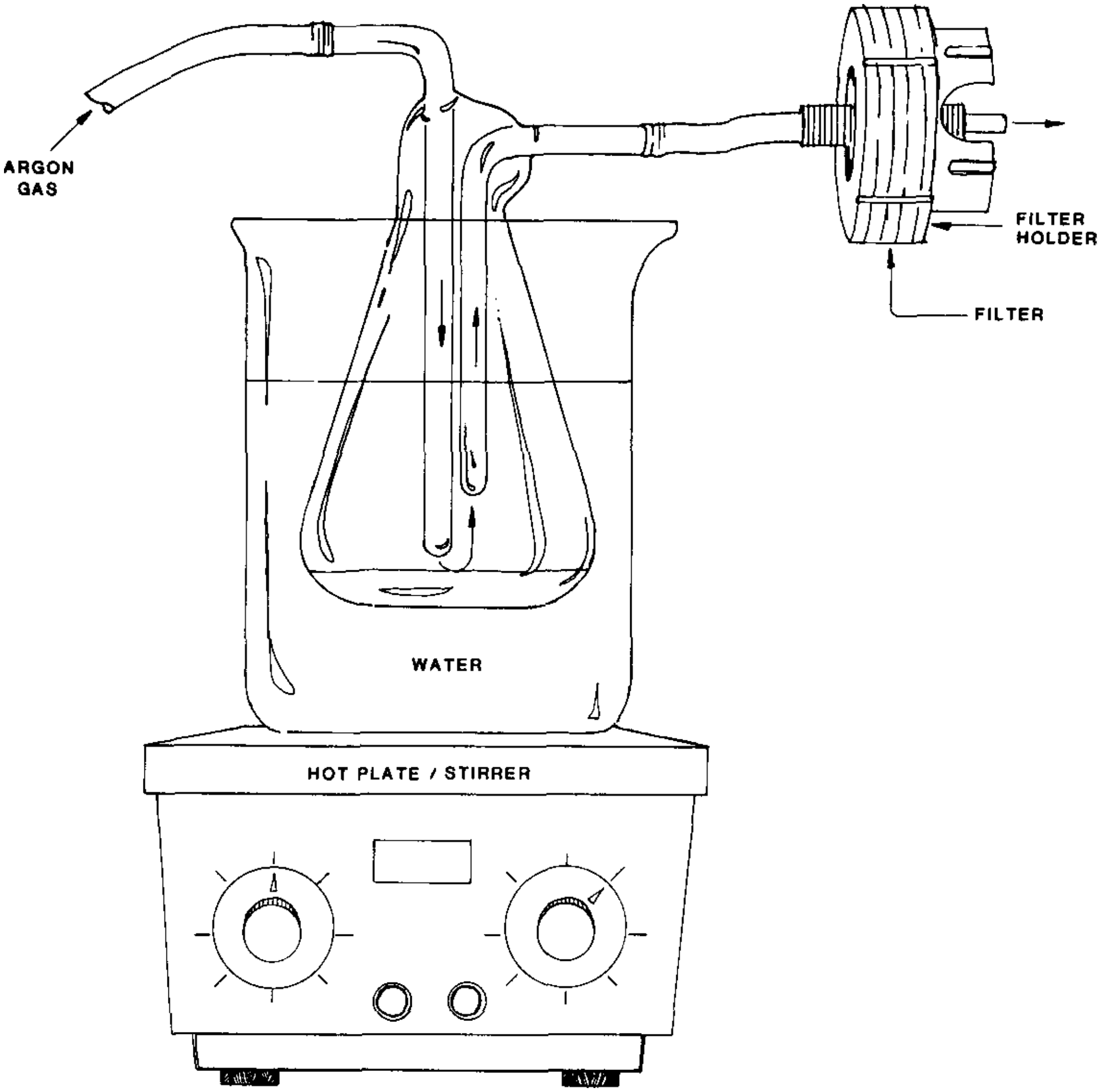


Figure 6-1. Apparatus for Mist Deposition

were deposited using an apparatus similar to that shown in Figure 6-2. A vibrator was used in place of a hot plate. The vibrator insured the presence of an airborne cloud of particulates inside the flask. Argon gas carried the particulate into the filter holder where it was deposited onto a filter.

FINAL PREPARATION OF SPIKED FILTERS

The filters were weighed after they were spiked with particulate. If the weight increase fell within the desired range they were put in a desiccator and weighed again the next day. Filters with more than the desired amount were discarded. Filters containing less than the required amount of particulate matter were respiked to bring them in range and then desiccated until they were used.

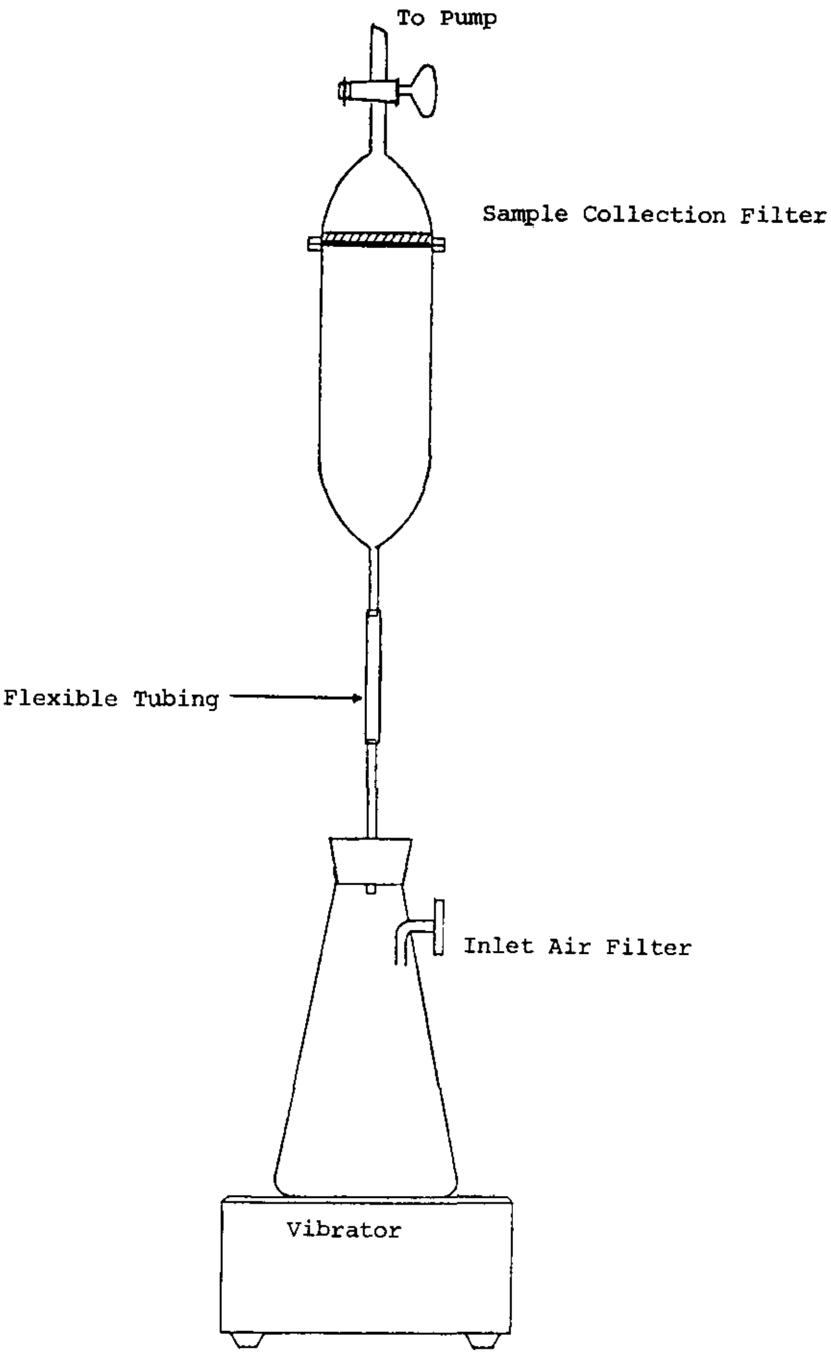


Figure 6-2. Apparatus for Deposition of Small Particulates.

Section 7

AMBIENT HI-VOL SAMPLING

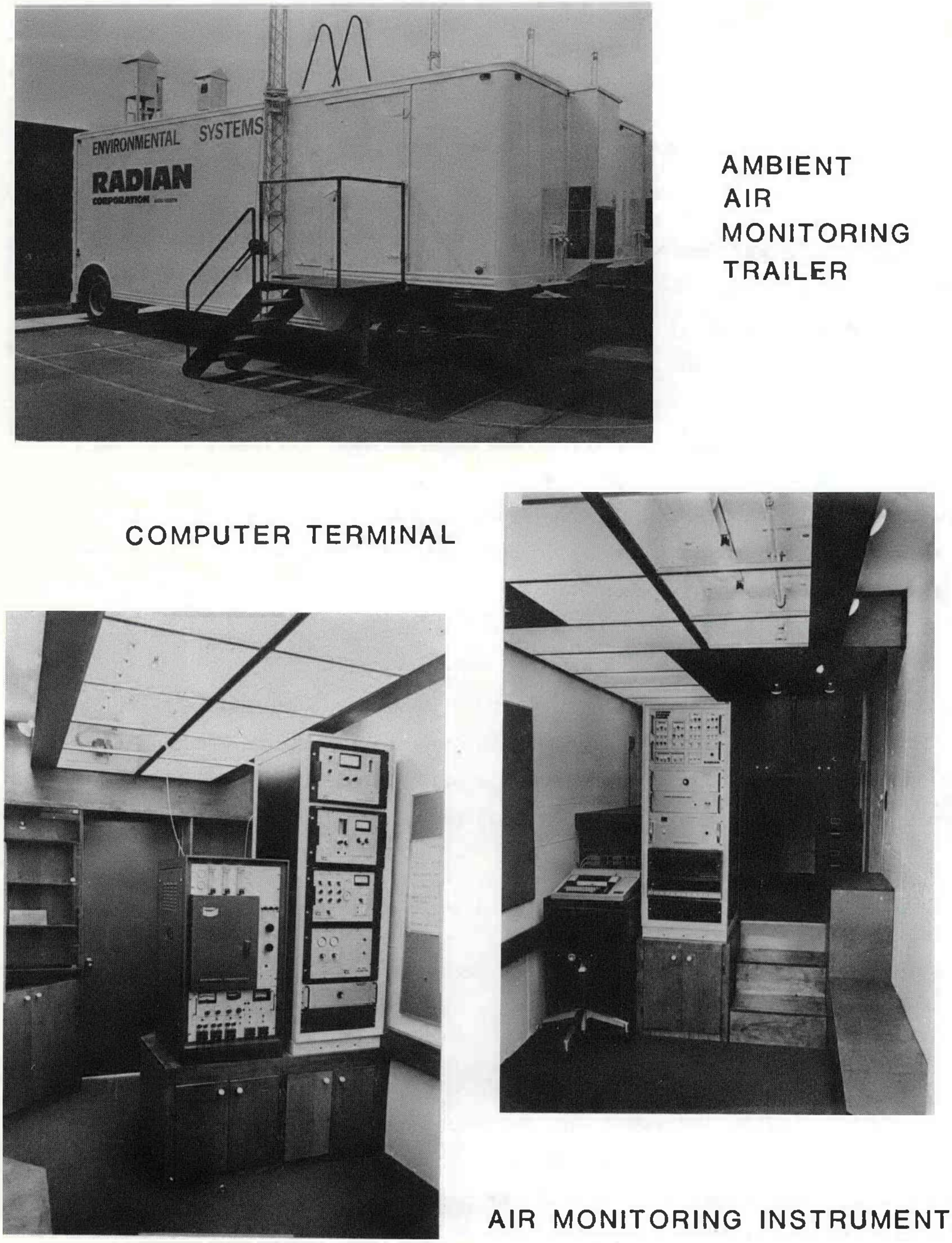
A series of experiments was designed to partially determine if the results of this project can be used in predicting the amount of artifact nitrate that will form on various filters under various ambient conditions. A Radian Ambient Air Monitoring Trailer was set up to monitor the atmospheric concentrations of NO, NO_2, O_3, and SO_2 while two Hi-Vol samplers on top of the trailer collected particulates. By comparing the nitrate formed on two filters incorporated in each Hi-Vol sampler, the amount of artifact nitrate formed on the first filter can be approximated. Then the validity of previous results can be checked by comparing the artifact nitrate formed during Hi-Vol sampling with the predicted artifact nitrate. The equipment used to fulfill the requirements of this project are described in this segment of Appendix B.

A Radian Ambient Air Monitoring Trailer (Figure 7-1) was set at the rear of the Radian facilities in Austin, Texas. The trailer was set up to continuously monitor the atmospheric concentrations of NO, NO_2, O_3, and SO_2. The equipment used to determine the atmospheric concentration of the pollutants in question were:

- a Meloy Laboratories Model NA520 oxides of nitrogen analyzer,
- a Meloy Laboratories Model OA350-2R ozone analyzer, and
- a Meloy Model SA185-2A sulfur dioxide analyzer.

The Meloy Laboratories Model NA520 oxides of nitrogen analyzer was used to monitor NO, NO_2, and NO_x. This instrument uses the chemiluminescent principle of analysis, and has dual channels to continuously monitor NO and NO_x. NO_2 is obtained continuously by difference. This instrument is calibrated with NO span gas (NBS certified), and the converter and NO_2 circuit are checked via an NO_2 permeation tube.

The Meloy Laboratories Model OA350-2R ozone analyzer was used to monitor ozone. This continuous analyzer works on the chemiluminescent principle and is EPA-



AMBIENT
AIR
MONITORING
TRAILER

COMPUTER TERMINAL

AIR MONITORING INSTRUMENTATION

Figure 7-1. Radian Ambient Air Monitoring Trailer approved as an equivalent method for ozone. Radian has found this analyzer to be extremely reliable, and to contribute to a high percentage of data capture.

The Meloy Model SA185-2A sulfur dioxide analyzer is an EPA-designated equivalent method for the measurement of ambient sulfur dioxide concentration. It employs a flame photometric detector to continuously monitor NO and NO_x. NO_2 is obtained continuously by difference. This instrument is calibrated with NO span gas (NBS certified), and the converter and NO_2 circuit are checked via an NO_2 permeation tube. A high detection specificity and sensitivity of the analyzer are achieved by the use of a special geometric arrangement that optically shields the photo-multiplier tube from the primary flame and a 394 nm narrow band pass filter.

Data generated by the above instruments were processed using a data acquisition system that is based on a minicomputer NOVA 1200 system. This system permits real-time data processing, on-site generation of data summaries, and automatic decision making and control of the entire system.

Particulates were collected daily using two Hi-Volume particulate samplers situated on top of the trailer. Each sampler was constructed by Radian following guidelines recommended by the EPA. The samplers meet or exceed all federal performance and dimensional specifications including those in Federal Register, Vol. 36, No. 84, dated April 30, 1971.

APPENDIX C

ANALYTICAL PROCEDURES

CONTENTS

Section 1

ANALYTICAL PROCEDURES

During this project, the following analytical procedures were used:

- the Reduction-Diazotization Method for determining total nitrate,
- the Modified Christie Technique for measuring nitrogen dioxide, and
- the EPA reference method for ozone determination.

These methods were adopted by Radian because of their widespread use by the EPA, Texas Air Control Board (TACB), and other regulatory agencies. Each analytical technique was evaluated for accuracy and applicability for this program.

A reevaluation of the Reduction-Diazotization Method was performed later in the project and the results of the evaluation are given in a section of this appendix.

Section 2

SUMMARY OF METHODS

In this section of the appendix, a brief description of the analytical procedures used in this program will be presented.

The Reduction-Diazotization Method for determining total nitrate is performed by refluxing a filter in deionized water. Refluxing of the filter extracts any nitrate that has absorbed onto the filter. Once extracted, the nitrate is reduced to nitrite by the addition of hydrazine solution. Next, a diazotizing reagent and the color developing compound NEDA are added. The concentration of the resulting color formation is determined spectrophotometrically.

The procedure used to determine NO_2 in this program was the Modified Christie Technique. First, the nitrogen dioxide is absorbed in a sodium hydroxide/sodium arsenite solution where it forms sodium nitrite. The concentration of nitrite ion is measured colorimetrically by the addition of phosphoric acid/sulfanilamide solution and NEDA. The intensity of the color is proportional to the concentration of nitrite ion present.

In the EPA reference method for the determination of ozone, the gas is bubbled through fritted bubblers containing a buffered potassium iodide solution. Ozone oxidizes the iodide to iodine, producing a blue color. The color intensity is proportional to the amount of sorbed ozone. The concentration of ozone is determined by comparing the absorbance of the sample with the absorbance of known standards.

The following sections of the appendix will give a detailed description of each analytical procedure.

Section 3

NITRATE DETERMINATION

This section describes the experimental procedure used to determine the amount of nitrate on filters.

INTERFERENCES

There were no serious interferences encountered in using this method. But, when sulfite ion is present in all concentrations up to 10 mg/ℓ it causes random variations of about 10 percent in both the nitrate and nitrite concentration.

REAGENTS

Stock Copper Reagent

Dissolve 1.25 g of $CuSO_4 \cdot 5H_2O$ in deionized water and dilute to 500 ml in a volumetric flask.

Working Copper Reagent

Place 10 ml of stock copper reagent in a 1000 ml volumetric flask and dilute to the mark with deionized water.

Stock Hydrazine Sulfate Reagent

Dissolve 6.8 g of hydrazine sulfate in deionized water and dilute to 500 ml in a volumetric flask.

Working Hydrazine Sulfate Reagent

Place 50 ml of stock hydrazine sulfate reagent in a 1000 ml volumetric flask and dilute to the mark with deionized water.

Sodium Hydroxide (0.3 N)

Dissolve 12 g of NaOH pellets in deionized water and dilute to 1 liter.

Acetone: Water Mixture

Dilute 25 ml of acetone to 250 ml with deionized water.

Sulfanilamide Reagent

Dissolve 5 g of sulfanilamide in 95 ml of 85% phosphoric acid (commercial strength). Rinse into a 250 ml volumetric flask and dilute to the mark with deionized water.

NEDA Reagent (NEDA: N-(1-Naphthyl)-ethylenediamine Dihydrochloride)

Dissolve 0.1 g of NEDA in deionized water and dilute to 100 ml in a volumetric flask. Prepare fresh daily.

Stock Nitrate Solution

Accurately weigh out 0.1630 g of KNO_3. Place in a 1000 ml volumetric flask, dissolve, and dilute to the mark with deionized water. This solution contains 100 µg NO_3^-/ml.

Working Nitrate Solution

Dilute 10 ml of stock nitrate solution to 100 ml in a volumetric flask with deionized water. This solution is stable for only 24 hours and must be prepared daily. It contains 10 µg NO_3^-/ml.

LABORATORY EQUIPMENT

Gelman Type A glass-fiber filter, 47 mm diameter
Reflux columns (water condenser)
1-100 ml Erlenmeyer suction flask
2-60 ml Erlenmeyer filtering funnels
1-Funnel
1-1000 ml Erlenmeyer volumetric flask
1-250 ml Erlenmeyer volumetric flask
6-100 ml Erlenmeyer volumetric flask
6-50 ml Erlenmeyer volumetric flask
1-50 ml pipette
1-25 ml pipette
1-10 ml pipette
1-8 ml pipette

1-6 ml pipette
1-5 ml pipette
1-4 ml pipette
1-3 ml pipette
1-2 ml pipette
1-1 ml pipette
1-Test tube rack
1-Spectrophotometer capable of handling 10 mm cells and operating at 540 nm
1- Constant temperature bath
Test Tubes sufficient for the number of samples to be analyzed
1-1000 ml micro pipette

REDUCTION-DIAZOTIZATION METHOD

To determine nitrate by this method, first place the used filter into a 125 ml flask equipped with a water condenser. Add 50 ml of deionized water and reflux gently for one hour (Figure 3-1). Filter the solution into a 100 ml volumetric flask and bring to volume with deionized water.

A standard solution containing 10 μg NO_3^-/ml is then prepared by diluting 10 ml of the stock nitrate solution to 100 ml in a volumetric flask using distilled water. Additional standard solutions are then prepared by pipetting 0, 1, 2, 3, 4, and 5 ml of the 10 μg NO_3^-/ml standard into separate 50 ml volumetric flasks and diluting with deionized water. These standards now contain 0, 0.2, 0.4, 0.6, 0.8, and 10 μg NO_3^-/ml, respectively. 10 ml of each of the standard solutions are then placed into separate test tubes using a volumetric pipette. A total of 1.0 ml of copper reagent, 1.0 ml of 0.3N NaOH, and 1.0 ml of hydrazine reagent is then added to each standard and sample. After thoroughly mixing the contents of the test tubes, each test tube is then placed in a 38°C constant temperature water batch (refer to Figure 3-2). After 30 minutes, 2.0 ml of the acetone-water solution is added to each test tube to stop the reduction reaction. Then, 1.0 ml of the sulfanilamide solution and 1.0 ml of the NEDA reagent are added to each test tube. The test tubes are then thoroughly mixed and the color is allowed to develop for 10 minutes. The absorbances of the samples are then measured against a blank at 540 nm using a 10 mm cuvette. A calibration curve (refer to Figure 3-3) is then constructed using the absorbance values of the standards. The concentration (μg NO_3^-/ml) of nitrate in each sample is then determined using the standard curve.

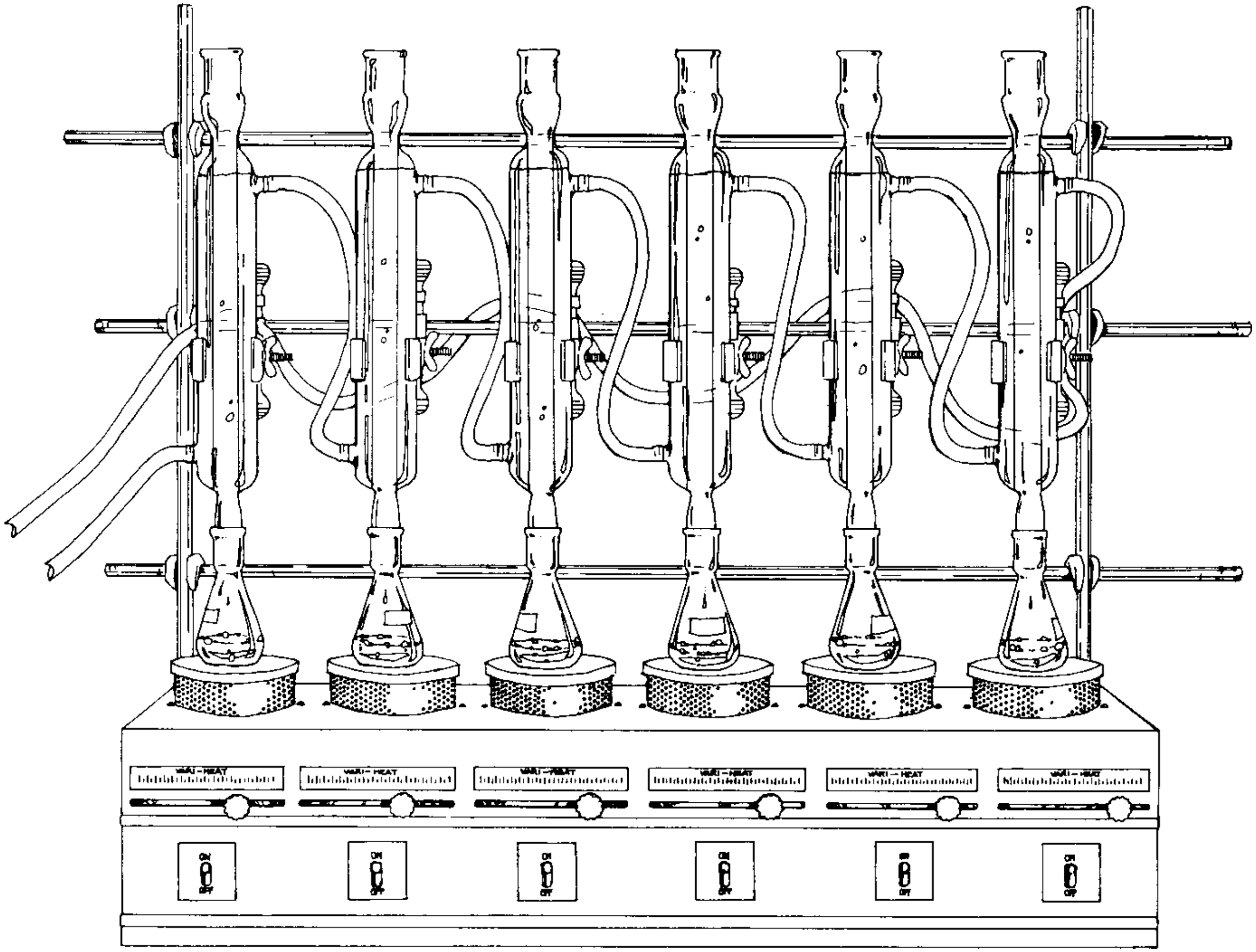


Figure 3-1. Reflux Apparatus for Nitrate Determination by the Reduction-Diazotization Method

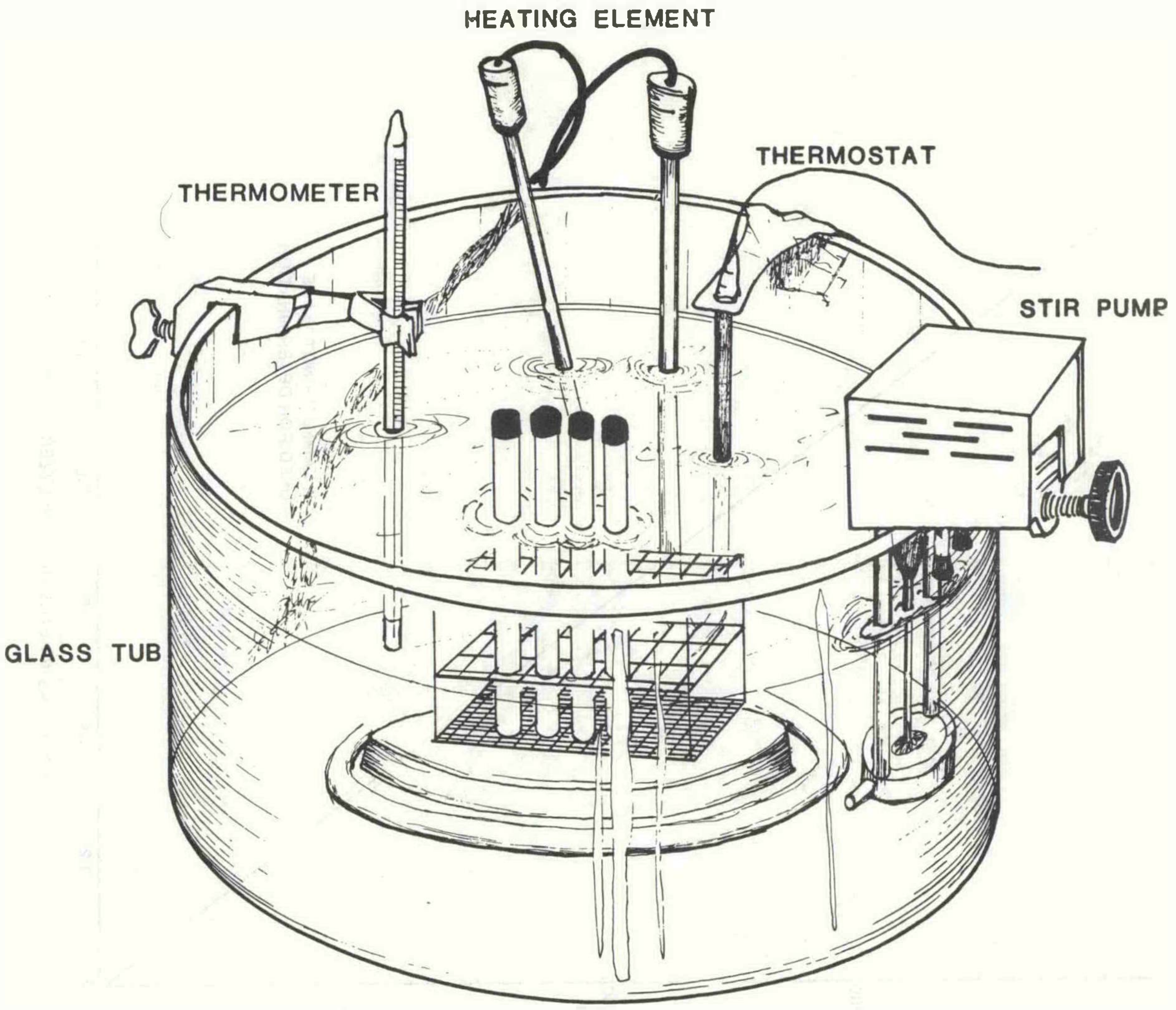


Figure 3-2. Constant Temperature Bath for Nitrate Determination by the Reduction-Diazotization Method

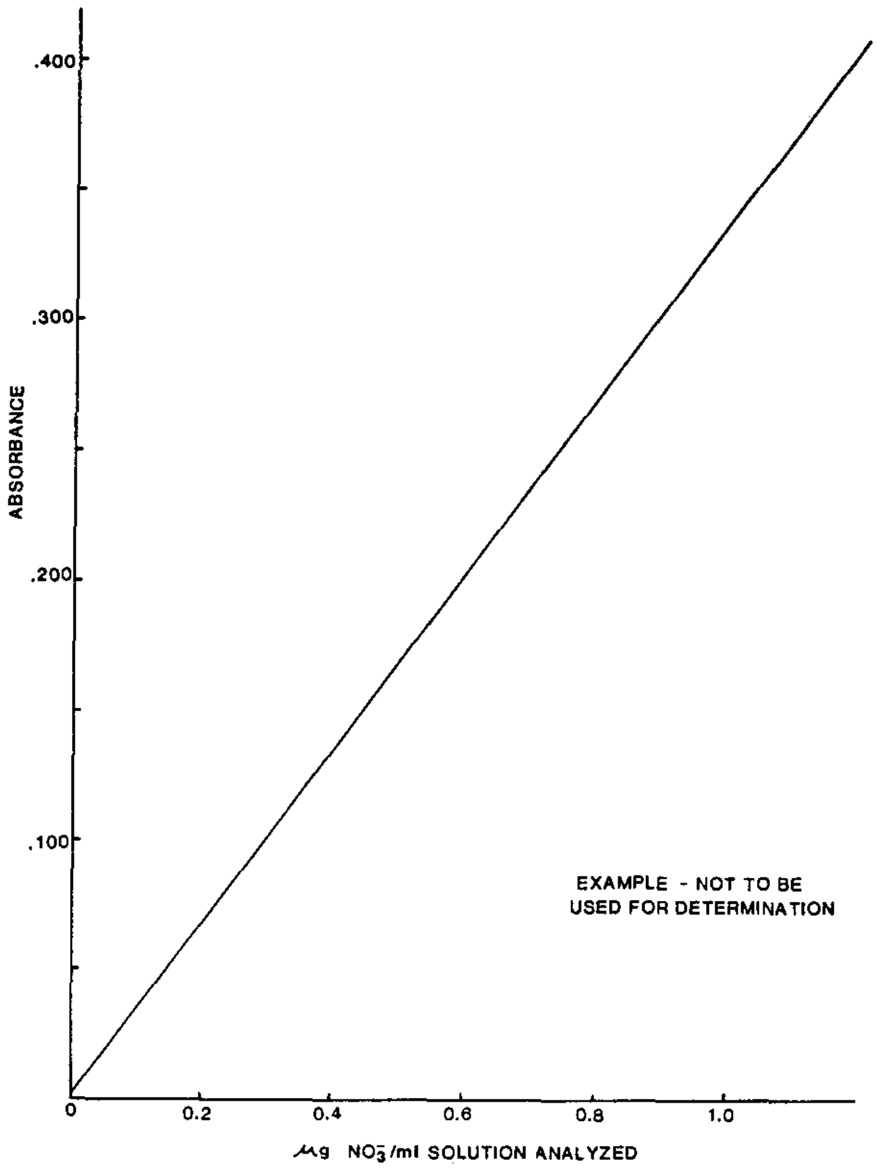


Figure 3-3. Standard Curve for Determination of Nitrate by the Reduction-Diazotization Method.

During this project, temperature and pH were found to be important parameters in determining nitrate using the Reduction-Diazotization technique. The reduction of nitrate to nitrite occurs at 38°C. Lower temperatures yield incomplete reduction while higher temperatures cause nitrite to be reduced. A pH of 1.7 must be maintained during the color develop step or the color will not develop properly.

CALCULATIONS

$$\text{Total } \mu\text{g } NO_3^- = \mu\text{g } NO_3^-/\text{ml} \times \text{original volume of sample} \qquad (3\text{-}1)$$

Section 4

NITROGEN DIOXIDE DETERMINATION

Modified Christie Technique used to determine the concentration of nitrogen dioxide present in gas streams is described in this section.

INTERFERENCES

The literature reports that nitric oxide is not a significant interference. 100 $\mu g/m^3$ SO_2 gives a slight negative response considered acceptable for ambient bubbler sampling. Due to the strong reducing properties of the absorbing solution, ozone and peroxide do not affect this method. Radian had no interference problems.

REAGENTS

All reagents should be ACS reagent grade.

Absorbing Solution

Place 20 g of sodium hydroxide (NaOH) and 1 g of sodium arsenite ($NaASO_2$) in a 1000 ml volumetric flask and dilute to the mark with distilled water. This solution is highly toxic and should be washed off if spilled on the skin.

Phosphoric Acid/Sulfanilamide Solution

Place 4.0 g sulfanilamide in approximately 100 ml of distilled water in a 200 ml volumetric flask. Add 75 ml of 85% phosphoric acid, mix, and dilute to the mark with distilled water.

NEDA: (0.1%)

Dilute 0.10 g of N-(1-Naphthyl)-ethylenediamine dihydrochloride to 100 ml with distilled water in a volumetric flask. This solution should be prepared fresh daily.

Stock Standard Nitrate Solution

Accurately weigh out 0.1500 g NaNO and dilute to 1000 ml in a volumetric flask with distilled water. This stock solution contains 100 µg NO_3^-/ml.

LABORATORY EQUIPMENT

2-1000 ml volumetric flasks
4-100 ml volumetric flasks
6-50 ml volumetric flasks
1-10 ml volumetric pipette
1-5 ml volumetric pipette
1-4 ml volumetric pipette
1-3 ml volumetric pipette
1-2 ml volumetric pipette
1-1 ml volumetric pipette
Sufficient test tubes for the number of analyses
Cuvette (10 mm) for reading absorbance in the spectrophotometer
Spectrophotometer capable of operating at 540 nm.
1-1000 ml micro pipette

MODIFIED CHRISTIE TECHNIQUE

To determine the amount of nitrogen dioxide concentration in samples, the Modified Christie Technique is employed. A standard solution containing 10 µg NO_3/ml is first prepared by diluting 10 ml of the stock nitrite solution to 100 ml in a volumetric flask with distilled water. Into separate 50 ml volumetric flasks pipette 0, 1, 2, 3, 4, and 5 ml of the standard solution and dilute with absorbing solution. These standards now contain 0, 0.2, 0.4, 0.6, 0.8, and 10 µg NO_3/ml, respectively.

Now place 10 ml of each of the standard solutions and sample solutions into separate test tubes using a volumetric pipette. Add 2 ml of phosphoric acid/sulfanilamide solution, mix, add 1 ml of NEDA solution, and mix again. Allow ten minutes for color to develop. Read standards and samples against the blank in a 10 mm cell at 540 nm for absorbance. Plot a curve of absorbance <u>vs</u> concentration of final standards (Figure 4-1).

There were no problems encountered in using this method.

CALCULATIONS

$$\mu g\ NO_2/ml \times \text{volume of absorber in ml} = \text{total } \mu g\ NO_2 \qquad (4\text{-}1)$$

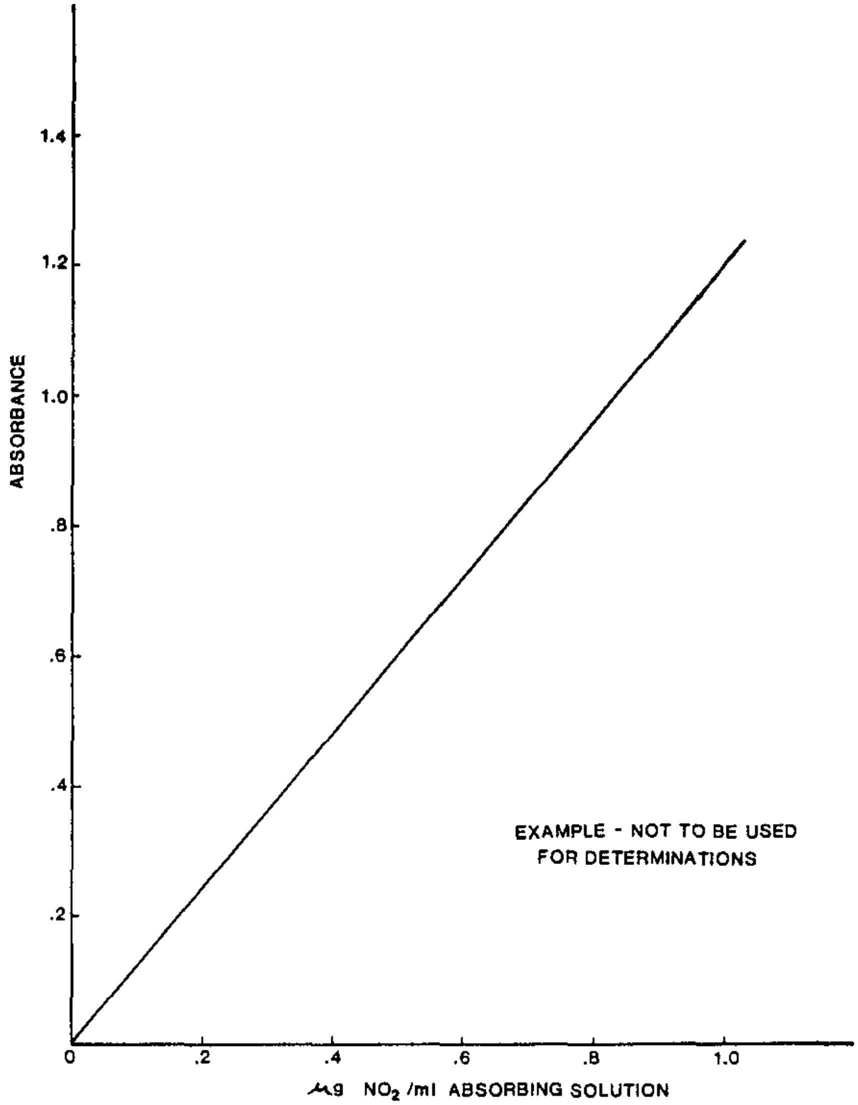


Figure 4-1. Standard Curve for the Determination of Nitrogen Dioxide by the Modified Christie Technique.

Section 5

OZONE DETERMINATION

The EPA method for the Federal Register of Rules and Regulations was used for the calibration of the ozone generator.

INTERFERENCES

Pure oxygen gas was used in the ozone calibrations and no interferences were encountered.

LABORATORY EQUIPMENT

1-100 ml volumetric flask
1-funnel
1-250 ml fritted bubbler
1-spectrophotometer
1-set of 10 mm cells

REAGENT

Absorbing Reagent

Dissolve 13.6 g potassium dihydrogen phosphate (KH_2PO_4), 35.8 g disodium hydrogen phosphate dodecahydrate salt ($Na_2HPO_4 \cdot 12\ H_2O$), and 10.0 g potassium iodide (KI) in deionized water and dilute to 1000 ml. The pH should be 6.8. The solution is stable for several weeks.

EPA METHOD FOR OZONE DETERMINATION

Ozone is determined by first placing 75 ml of absorbing solution into a 250 ml fritted bubbler. Bubble the ozone containing gas through the fritted bubbler for ten minutes at a flow rate of $\sim$2 liters per minute. Rinse the bubbler content into a 100 ml volumetric flask, dilute to the mark using absorbance solution. Read the absorbance against the blank on a spectrophotometer at 352 nm in 100 mm cells.

A curve is plotted to determine the amount of ozone produced (Figure 5-1).

CALCULATIONS

Equation:

$$\frac{(\mu g/ml)(\text{total vol. in ml})}{\#\text{ of min. bubbled}} = \mu g/min \qquad (5\text{-}1)$$

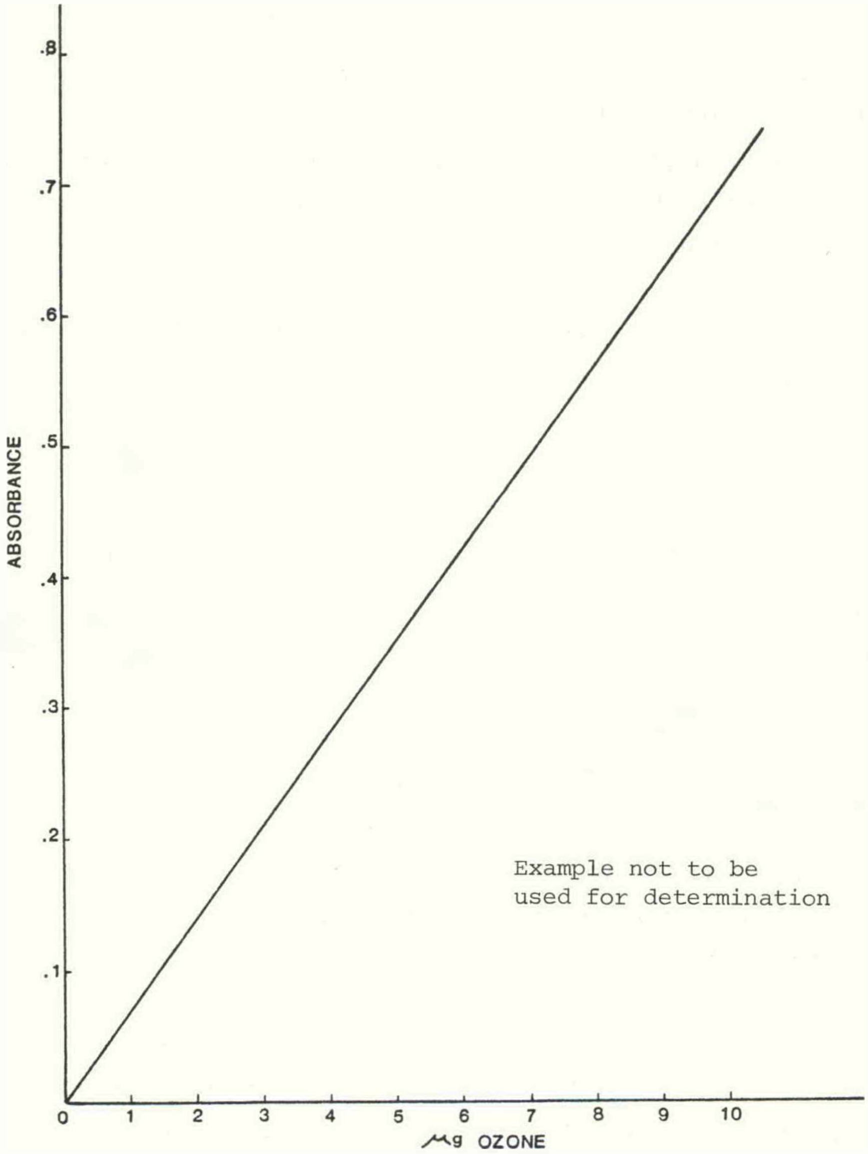


Figure 5-1. Standard Curve for Determination of Ozone by EPA Reference Method.

Section 6

EVALUATION OF THE REDUCTION-DIAZOTIZATION METHOD

It was necessary to reevaluate the Reduction-Diazotization Method because of discrepancies between duplicate nitrate absorbance values from corresponding runs performed at the same conditions. In order to determine whether the analytical procedure was contributing to these variations, several factors which influence the determination of nitrate as nitrite were investigated.

The factors investigated in the reevaluation of the analytical procedure were:

- effect of temperature in the reduction step,
- effect of pH on the reduction step, and
- effect of pH on color development.

This section will deal with the results and details of the evaluation and the changes that were made.

EFFECT OF TEMPERATURE

Temperature is an important factor in the reduction of nitrate to nitrite when hydrazine sulfate is used as the reducing agent. An article written by L. J. Kamphake in Water Research, 1 (1967) pp. 205-216, shows that nitrate reduction occurs at temperatures as low as 20°C but does not become quantitative until within the range of 35°C-38°C. At temperatures above 38°C, the reduction goes one step further, resulting in the reduction of nitrite.

The water bath used was thought to be at a constant temperature of 38°C, but in checking several sections of the bath, it was found that the temperature was not constant throughout and varied ±2°C. Therefore, the samples being analyzed were at a different temperature, which possibly accounted for some variations in nitrate values.

The temperature bath was modified (see Figure 3-2) by adding a circulating water pump to assure a constant temperature of 38°C throughout and to cover that section of the sample containing the solution for analysis.

EFFECT OF pH ON THE REDUCTION OF NITRATE TO NITRITE

For a while during this project (Screening Studies Run 21-1 through Day and Night Run 24-1), a sodium hydroxide solution instead of deionized water was added to the reflux step to help preserve the sample. The procedure for refluxing the sample filters was to add 50 ml of 0.1N NaOH to each sample and reflux for one hour. Once refluxed, the samples were filtered and diluted to 100 ml in volume.

The reduction of nitrate to nitrite begins at pH 11 and reaches a maximum at pH 12.0-12.2. There was nothing found in the literature to indicate that a pH higher than 12.2 is detrimental to the reduction of nitrate to nitrite. The use of sodium hydroxide during the reflux step insured that the pH of the solution during the reduction was always greater than 12.0 and there was no obvious impairment of the reduction process.

EFFECT OF pH ON THE COLOR DEVELOPMENT STEP

Unlike the reduction step which occurs in a basic solution, the color development step only occurs in an acid (pH 1.7) solution. If the pH of the solution is not maintained at strongly acid conditions, the color development will be incomplete and will result in low nitrate absorbance values. Because the samples were refluxed in 50 ml of 0.1N NaOH instead of deionized water, there was some concern that the color development was occurring at a higher pH than 1.7. The standards were not refluxed; therefore, the only sodium hydroxide added to them was 1 ml of 0.3N NaOH and maximum color development took place at a pH of 1.7. Because the standards were used to obtain the concentration of nitrate in the samples, a study was initiated to determine the effect of 50 ml of 0.1N NaOH on the standards.

In determining the effects of NaOH on the standard, three sets of standards were prepared, each with various amounts of NaOH added during preparation. The first set was prepared using only deionized water, while the second set was prepared using 50 ml of 0.1N NaOH, and the third set was prepared by using 80 ml of 0.1N NaOH. Six standards varying in concentrations from 0.2 μg/ml NO_3^- to 1.0 μg/ml NO_3^- were prepared in each set. The results of the test are presented in Figure 6-1.

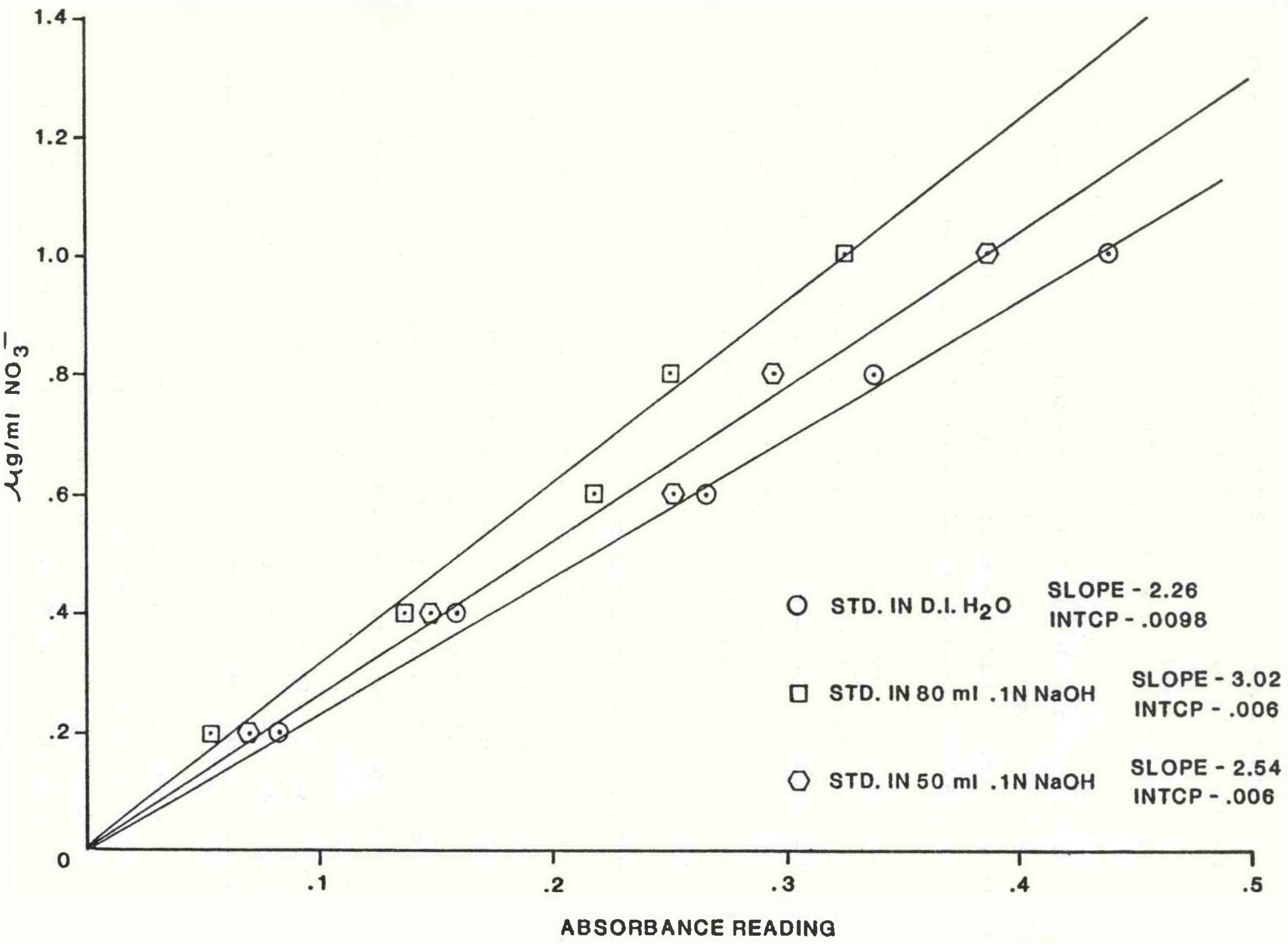


Figure 6-1. Comparison of Sets of Nitrate Standards with Various Amounts of NaOH.

The results indicate that NaOH has a definite effect on the absorbance values of the standards. The measured concentrations differ by 10-11% when using 50 ml of 0.1N NaOH as compared to deionized water. There is about a 30% decrease in measured concentration when using 80 ml of 0.1N NaOH instead of deionized water. Further samples were refluxed in deionized water and refrigerated to minimize desorption and to preserve the sample. All values for samples that were refluxed in 50 ml of 0.1N NaOH were increased by about 10% in order to correct for the effect of the NaOH on the color development.

RESULTS

The use of deionized water instead of NaOH in the reflux step gave variations in the values of the standards of only 3 to 8 percent from day to day. The temperature in the water bath varied ±1% after addition of the circulating pump.

CONCLUSIONS

The reevaluation of the analytical procedure indicates that the method may have contributed to some of the discrepancies between runs and analyses but the large discrepancies are still unaccounted for.

APPENDIX D

CALCULATIONS

TABLE OF CONTENTS

Section 1

INTRODUCTION

A description of the calculations utilized in the data analysis of the experimental runs is presented in this appendix. Those calculations that were of primary interest in this program were of:

- the volumetric flow rate at the filter,
- the concentration of the gaseous species NO_2, NO, and O_3 at the filter, and
- the equivalent atmospheric nitrate concentration.

Each of the above calculations is described in the following sections.

Section 2

VOLUMETRIC FLOW RATE AT THE FILTER

For the calculation of volumetric flow rate at the filter, the flow rate at the dry gas meter was corrected for the temperature, pressure, and moisture content at the filter. In equation form,

$$F_f = F_m \frac{T_f}{T_m} \cdot \frac{P_m}{P_f} \cdot \frac{DGF_m}{DGF_f} \qquad (2\text{-}1)$$

where,

F_f = volumetric flow rate of filter, m/min
F_m = flow rate at dry gas meter, m/min
T_f = absolute temperature at filter, $^{\circ}$Rankin
T_m = absolute temperature at meter, $^{\circ}$Rankin
P_f = pressure at filter, psig
P_m = pressure at meter, psig
DGF_f = dry gas fraction at filter
DGF_m = dry gas fraction at meter

The gas temperature was monitored continuously on the back side of both the filter and the dry gas meter. The average temperature at each location was then used in flow calculations. A pressure gauge on the front side of the filter holder was used in controlling and monitoring the gas pressure in front of the filter. Because of the negligible pressure drop across the dry gas meter, the pressure at the meter was assumed to be ambient. A pre-weighed silica gel trap was used to determine the efficiency of the cold trap. The dry gas fraction at the filter was obtained from the moisture content of the gas flowing through the humidifier and the fraction of total flow passing through the humidifier.

Section 3

FILTER CONCENTRATIONS OF NO_2, NO_x, and O_3

The concentration of the gaseous species NO_2, NO, and O_3 at the filter were determined from calibration data and the volumetric flow rate at the filter.

An NO_2 permeation device was used to generate NO_2 at specified rates (μg NO_2/minute) depending on its temperature. The NO_2 permeation rate was determined on a daily basis in order to obtain accurate NO_2 concentration data and check the reproducibility of the device. After the NO_2 permeation rate and the volumetric flow rate at the filter were determined, the NO_3 concentration at the filter was determined using the following equation:

$$NO_2 \text{ concentration } (\mu g/m^3) = \frac{NO_2 \text{ permeation rate } (\mu g/min)}{\text{Volumetric flow rate } (m^3/min)} \qquad (3\text{-}1)$$

Desired levels of nitric oxide (NO) were obtained by diluting gas from a certified gas bottle. A rotometer calibrated with the NO gas was used to determine the actual flow rate. The formula for the NO concentration at the filter is:

$$NO\ (\mu g\ NO/m^3) = \frac{\text{Original NO concentration } (\mu g/m^3) \times \text{NO flow } (m^3/min)}{\text{Volumetric flow rate } (m^3/min)} \qquad (3\text{-}2)$$

A Pen-Ray stable ozone generator using purified oxygen was used to provide an accurate concentration of ozone to the test stream. Early in the program, the ozone generator was calibrated over a range of quartz tube exposure lengths. Concentration checks were made periodically to monitor the reproducibility of the instrument.

Section 4

EQUIVALENT ATMOSPHERIC NITRATE CONCENTRATION

After the amount of artifact nitrate formed on a 47 mm filter had been determined, the equivalent atmospheric nitrate concentration was calculated using the following formula:

$$\text{EAN } (\mu g/m^3) = N_F \cdot \frac{A_{\text{Hi-Vol}}}{A_F} \cdot \frac{1}{T_{vs}} \qquad (4\text{-}1)$$

where

EAN = equivalent atmospheric nitrate concentration, $\mu g/m^3$
N_F = nitrate collected on test filter, μg
$A_{\text{Hi-Vol}}$ = effective surface area of 8" x 10" Hi-Vol filter (430 cm^2)
A_F = effective surface area of 47 mm diameter test filter (10.8 cm^2)
T_{vs} = volume of gas sampled during 24 hours at a sampling rate of $1.4 \text{ m}^3/\text{min}$.

The equations presented above represent the bulk of the calculations performed in the data analysis of the experimental runs.