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Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts

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CURRENT METHODS TO MEASURE ATMOSPHERIC NITRIC ACID
AND NITRATE ARTIFACTS

edited by

Robert K. Stevens
Inorganic Pollutant Analysis Branch
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina   27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA   27711

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FOREWORD

The Environmental Sciences Research Laboratory (ESRL) of the U.S. Environmental Protection Agency at Research Triangle Park, North Carolina (EPA-RTP) conducts an intramural and extramural research program to detect, define, and quantify the effects of air pollution on urban, regional, and global atmospheres (and the subsequent impact on water quality and land use). Within ESRL, the Inorganic Pollutant Analysis Branch develops and conducts research in chemistry, physics, and engineering related to development of instrumentation for field measurement and characterization of atmospheric contaminants.

In performance of this role, the Inorganic Pollutant Analysis Branch conducted a workshop on "Measurement of Atmospheric Nitrates" in Southern Pines, North Carolina, on October 3 and 4, 1978. This report represents one important product of that meeting.

Aubrey P. Altshuller, Director
Environmental Sciences Research
Laboratory

ABSTRACT

Presentations given at a workshop on "Measurement of Atmospheric Nitrates" (Southern Pines, North Carolina, October 3-4, 1978) are documented. The authors consider various analytical methods to measure ambient concentrations of nitric acid and artifact nitrate formation.

In an Introduction, R. Stevens and W. McClenny summarize the workshop presentations and outline a proposed field experiment to evaluate and compare nitric acid and particulate nitrate measurement methods. E. Tuazon and colleagues discuss measurements of nitric acid in the California South Coast Air Basin by Fourier transform long path infrared spectrometry. C. Spicer describes measurement of nitric acid by coulometric, chemiluminescence, and ion chromatographic techniques. Chemiluminescence measurements of nitric acid at Boulder, Colorado are reported by T. Kelly and D. Stedman. A. Lazrus and colleagues describe reduction to ammonium ion of fixed inorganic nitrogen collected on nylon filters, followed by the indophenol ammonia test. Collection of nitric acid on sodium chloride impregnated filters at high volume flow rates is discussed by J. Forrest and coworkers. R. Hare and colleagues describe electron capture gas chromatographic techniques for analysis of nitric acid. J. Tesch and R. Sievers report particulate nitrate and gaseous nitric acid measurements by electron capture gas chromatography. Use of the Denuder Difference Experiment to obtain separate determinations of particulate nitrate and gaseous nitric acid without interference of positive or negative nitrate artifacts is discussed by R. Shaw and coworkers.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

approx.	— approximately
ARB	— Air Resources Board
ASTM	— American Society for Testing and Materials
atm	— atmosphere
BNL	— Brookhaven National Laboratory
°C	— degree Celsius
cm	— centimeter
DDE	— Denuder Difference Experiment
ECGC	— electron capture gas chromatography
EPA	— U.S. Environmental Protection Agency
ESRL	— Environmental Sciences Research Laboratory
°F	— degree Farenheit
FEP	— fluorinated ethylene propylene
ft	— foot
FTS	— Fourier transform spectrometry
g	— gram
hi-vol	— high-volume
hr	— hour
i.d.	— inside diameter
in	— inch
IR	— infrared
K	— thousand
km	— kilometer
LPIR	— long path infrared
m	— meter
mi	— mile
µg	— microgram

μm	— micrometer
min	— minute
ml	— milliliter
mm	— millimeter
N	— normality
NCAR	— National Center for Atmospheric Research
nm	— nanometer
NOAA	— National Oceanic and Atmospheric Administration
NSF	— National Science Foundation
PDT	— Pacific Daylight Time
pH	— negative logarithm of hydrogen ion concentration
ppb	— part per billion
ppb_v	— part per billion by volume
ppm	— part per million
RTP	— Research Triangle Park, North Carolina
QAST	— light transmission cutoff
SAPRC	— Statewide Air Pollution Research Center
USP	— U.S. Pharmacopoeia

SYMBOLS

Ar	— argon
C	— carbon
CH_4	— methane
CO	— carbon monoxide
CO_2	— carbon dioxide
$C_6H_5NO_2$	— nitrobenzene
C_6H_6	— benzene
C_7H_8	— toluene
Cu	— copper
CuCl	— cuprous chloride
EDTA	— ethylenediaminetetraacetic acid
$FeSO_4$	— iron sulfate
H^+	— hydrogen ion
HCHO	— formaldehyde
HCOOH	— formic acid

HCl	— hydrochloric acid
HNO_2	— nitrous acid
HNO_3	— nitric acid
H_2O	— water
H_2O_2	— hydrogen peroxide
HO_2NO_2	— per(oxy)nitric acid
H_2SO_4	— sulfuric acid
HgCdTe	— mercury cadmium telluride
InSb	— indium antimonide
K_2CO_3	— potassium carbonate
M	— third body molecule (usually N_2 or O_2) in a three-body atmospheric collision
NH_3	— ammonia
NH_4^+	— ammonium ion
^{63}Ni	— radioactive isotope of nickel (beta transmitter)
NH_4NO_3	— ammonium nitrate
NMHC	— total nonmethane hydrocarbons
NO	— nitric oxide
NO_2	— nitrogen dioxide
NO_2^-	— nitrite ion
NO_3^-	— nitrate ion
NO_x	— total oxides of nitrogen
N_2O_5	— nitrogen pentoxide
NaCl	— sodium chloride
$Na_2Fe(CN)_5NO$	— sodium nitroprusside
NaOH	— sodium hydroxide
O_3	— ozone
PAN	— peroxyacetyl nitrate
SO_2	— sulfur dioxide
$SO_4^{=}$	— sulfate ion
Zn	— zinc
e	— 2.718

INTRODUCTION

Robert K. Stevens

William A. McClenny

Inorganic Pollutant Analysis Branch
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

A workshop entitled "Measurement of Atmospheric Nitrates" was held at
Southern Pines, North Carolina, on October 3 and 4, 1978, to discuss analytical
methods to measure ambient concentrations of nitric acid (HNO_3) and artifact
nitrate formation. Attending the workshop were scientists directly involved
in the development of methods to measure HNO_3, including representatives from
the academic, private, and public sectors. The first day was devoted to
discussions of measurement methods and factors causing formation of nitrate
artifacts on a variety of collection surfaces. On the second day, a field
sampling experiment was designed to test HNO_3 measurement methods and to
determine factors that cause positive and negative nitrate artifacts.

OVERVIEW OF METHODS

Methods described in the workshop sessions included the use of continuous
(real-time) and semi-continuous monitors as well as integrative collection
of HNO_3 on adsorbing materials. The continuous methods were the following:
(1) microcoulometry (Spicer, Battelle Columbus Labs); (2) chemiluminescence
(Spicer, Battelle Columbus Labs; Stedman, University of Michigan); (3) Fourier
transform long path infrared spectrometry (FTS-LPIR) (Winer, University of
California at Riverside). Methods involving preconcentration were: (1)

collection of HNO_3 on nylon or cotton followed by extraction, conversion to
nitrobenzene ($C_6H_5NO_2$), and analysis by gas chromatography (Hare, Monsanto
Research; Sievers, University of Colorado); (2) reduction to ammonium ion
(NH_4^+) of fixed inorganic nitrogen collected on nylon filter, followed by the
indophenol ammonia test (Lazrus, National Center for Atmospheric Research);
(3) collection of HNO_3 on sodium chloride (NaCl) impregnated filters, followed
by extraction and hydrazine reduction-diazotization analysis of nitrate (New-
man, Brookhaven National Labs).

A tabulated summary of these techniques is presented in Table 1. Each
technique is associated with a procedure consisting of a number of experimental
steps. "Sampling" refers to the transport of ambient air to the place of
measurement; as used in Table 1, the term includes prefiltering to eliminate
particulates. "Scrubbing" is the elimination of some interfering gaseous
component of the ambient air; "conversion" occurs in those cases when the HNO_3
is thermally converted to nitric oxide (NO) prior to measurement. "Collection"
and "extraction" refer to sampling onto a filter followed by a wet chemical
extraction in which HNO_3 is changed in form. "Measurement" is by the tech-
nique stated, whereas "subtraction" refers to the identification of a signal
increment contributed by HNO_3. "Minimum detectable levels" are taken from the
investigators' reports (this volume) or are estimated from available informa-
tion.

Each technique has unique features. FTS-LPIR is ideal for detection of
HNO_3, since measurement takes place in the atmosphere and identification is
made unambiguously by the recognition of characteristic infrared absorptions.
However, the equipment is not portable, and the method has a minimum detection
level of 5 ppb. Chemiluminescence has the inherent sensitivity of a rate
sensor, but involves the measurement of small differences in a signal that is
frequently large and time-varying due to interferences (e.g., total oxides of
nitrogen, NO_x; peroxyacetyl nitrate, PAN; and organic nitrates).

Collection techniques involve tedious documentation of collection and
release efficiencies, maximum loading, and interferences; preconcentration, of
course, reduces the requirements for sensitivity. The formation of nitrate

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TABLE 1. SUMMARY OF HNO$_3$ DETECTION TECHNIQUES

Technique	Procedure					Minimum Detectable Level (ppb$_v$)	Temporal Status	Tested Interference(s)	Reference(s)
chemiluminescence (Spicer)	sample	scrub	convert	measure	subtract	5.0	cyclic	NO, NO$_2$, PAN, organic nitrates	Joseph and Spicer, 1978
chemiluminescence (Stedman)	sample	scrub	convert	measure	subtract	0.3	cyclic	NO, NO$_2$, PAN, organic nitrates	Kelly and Stedman, this volume; Likens, 1976
FTS-LPIR (Winer)				measure	subtract	5.0	real-time	most gaseous species in normal ambient air	Tuazon *et al.*, this volume
microcoulometry (Spicer)	sample	scrub		measure	subtract	5.0	cyclic	SO$_2$, NO$_2$, PAN H$_2$SO$_4$, CH$_2$O	Miller and Spicer, 1975; Spicer *et al.*, 1978b
colorimetry (Lazrus)	sample	scrub		measure	subtract	<0.1	periodic	NH$_4^+$, particulate nitrate	Lazrus *et al.*, 1968
colorimetry (Newman)	sample	collect	extract	measure		0.1	periodic	NO$_2$, particulate nitrate	Okita *et al.*, 1976
ECGC (Hare, Sievers)	sample	collect	extract	measure		0.1	periodic	NO$_2$, particulate nitrate	Ross *et al.*, 1975
ion chromatography (Spicer)	sample	collect	extract	measure		0.1	periodic	bromide	Spicer *et al.*, 1978a

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artifacts during collection of nitrates on filter media can occur because:
(1) filters may collect HNO_3 and nitrogen dioxide (NO_2), producing a nitrate
ion (NO_3^-) artifact; (2) nitrate present as ammonium nitrate (NH_4NO_3) may evapo-
rate during collection; and (3) nitrate may be lost from the filter if acid
aerosols react with solid nitrate on the filter to release HNO_3. Shaw *et al.*
(this volume) describe the Denuder Difference Experiment in which — assuming
the nylon collection surface quantitatively collects only HNO_3 — the positive
and negative artifact nitrate on a variety of filter media is measured. This
technique is considered to be the best proposal for quantifying the "negative
nitrate artifact" — the effect of acid gases (especially sulfuric acid, H_2SO_4)
reacting with particulate nitrate on the filter surface to release HNO_3.

PLANNED FIELD EXPERIMENT

On the second day of the workshop, the participants divided into three
groups to consider the protocol for a field experiment to evaluate and compare
methods to measure HNO_3 and nitrates. Group I considered the pollutant gases
that need to be measured, Group II considered HNO_3 methods and testing pro-
cedures, and Group III designed experiments to determine nitrate artifact
levels.

It was decided that a 7-day field study should be conducted at Harvey
Mudd College in the Los Angeles Basin during early June, 1979, for the purpose
of intercomparing methods to measure HNO_3 and particulate nitrate. This site
was selected because an FTS-LPIR instrument is located there. (FTS-LPIR
equipment is not portable; therefore, it is necessary to conduct the initial
comparison study at an FTS-LPIR site.) The group also recommended that a
second study be conducted in the eastern part of the United States to evaluate
methods to measure HNO_3 and nitrates in an environment in which nitrate and
HNO_3 levels are relatively low and in which other acid aerosols (H_2SO_4) are
proportionately higher.

A final discussion among the three groups produced the following outline
for the proposed experiment:

Objectives

(1) To test and compare measurement systems for HNO_3 vapor and nitrate aerosol; and

(2) To determine the extent to which measurement systems are susceptible to artifact nitrate formation or loss and, if possible, to determine the cause of artifacts.

Methods and Rationale

(1) The various measurement systems are now available; their comparison can best be achieved by side-by-side evaluation under field conditions, similar to the EPA Charleston Aerosol Sampler Comparison Study (see Camp *et al.*, 1978).

(2) In order to determine the *absolute* reliability of the instruments, each must be run side-by-side with FTS-LPIR, which is the only technique established at this time to be interference-free.

(3) In order to determine the cause of nitrate artifacts, the following possible parameters (in addition to nitrate and HNO_3) should be monitored simultaneously with the instrument study:

carbon monoxide (CO)   ammonia (NH_3)

hydrogen ion (H^+) ammonium ion (NH_4^+)

hydrochloric acid (HCl)   nitrogen pentoxide (N_2O_5)

water (H_2O) ozone (O_3)

hydrogen peroxide (H_2O_2) PAN

NO   sulfur dioxide (SO_2)

NO_2 sulfate ion $(SO_4^=)$

Because of the large number of interested participants who already possess equipment, it seems that all (or nearly all) of these can be measured.

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(4) In order to eliminate possible confusion concerning the role of large aerosol particles, all participants making aerosol measurements will use 15 μm cutoff inlets.

(5) Long- and short-term sampling will be performed to investigate possible artifact-time relationships and diurnal patterns.

(6) The Denuder Difference Experiment (Shaw *et al.*, this volume) is expected to provide unambigious values for HNO_3 vapor and measurements of nitrate losses (negative artifacts).

To summarize, this is an ambitious project that will require considerable work to arrive at a fruitful conclusion. We believe, however, that such an effort can bring to an end the aerosol nitrate ambiguity that plagues evaluation of air monitoring data. The experiment will establish the best techniques for HNO_3 and nitrate measurements, and the conditions under which the remaining techniques yield valid results.

The balance of this report consists of workshop presentations relating to HNO_3 measurement techniques.

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MEASUREMENTS OF AMBIENT HNO$_3$ IN THE CALIFORNIA SOUTH COAST AIR BASIN BY KILOMETER PATHLENGTH FOURIER TRANSFORM INFRARED SPECTROMETRY

Ernesto C. Tuazon

Arthur M. Winer

Richard A. Graham

James N. Pitts, Jr.

Statewide Air Pollution Research Center
University of California
Riverside, California 92521

INTRODUCTION

The current lack of systematic and reliable data on ambient concentrations of a host of nitrogenous and oxygenated compounds, known or suspected to be present in polluted urban atmospheres, is generally recognized. To address this problem, EPA has supported an ambient air monitoring program based on FTS-LPIR. In this program the Statewide Air Pollution Research Center (SAPRC) of the University of California has operated a kilometer pathlength FTS-LPIR instrument, originally designed and assembled by Hanst (EPA-RTP). This system provides an *in-situ* ppb detection capability for many oxygenated and nitrogenous pollutants for which reliable, alternative analytical methods are presently unavailable. A description of the FTS-LPIR instrument and the initial measurements made in Riverside during the fall of 1976 have been reported (Tuazon *et al.*, 1977, 1978); these earlier results included the first spectroscopic detection of HNO$_3$ and formaldehyde (HCHO) in the polluted troposphere. The present paper briefly describes the SAPRC experimental facility, its specific application to ambient measurements of HNO$_3$, and some results obtained from monitoring carried out in the California South Coast Air Basin

during the smog seasons of 1977 at Riverside (a downwind receptor site) and 1978 at Claremont (a mid-basin site). A more comprehensive account of this program and the data it has produced is currently in press (Tuazon *et al.*, 1979).

INSTRUMENTATION AND METHODS

Kilometer Pathlength Cell and FTS-LPIR Instrument

Figure 1 illustrates the eight-mirror multiple reflection cell employed in this study. The details of its design have been described by Hanst (1971). The in-focus (nesting) mirror assembly consists of four rectangular mirrors, while the out-of-focus assembly (collecting mirrors) consists of four 30-cm diameter mirrors and is 22.5 m (the eight-mirror average radius of curvature) from the nesting mirror assembly. All mirrors are optically polished and gold-coated for maximum reflectivity in the infrared (IR).

The prime consideration in the choice of the operating pathlength is signal attenuation accompanying an increased number of reflections. The average reflectivity coefficient of the cell mirrors was determined to be ~0.98. The 47 mirror reflections at a pathlength of 1080 m correspond to a transmitted intensity of 0.39 times the incident radiation. This value is slightly greater than 1/e (0.37), which has been established as the criterion for maximizing the signal-to-noise ratio for IR systems that are detector noise limited (Stephens, 1958, 1961).

The cell consists of a sectional rectangular aluminum frame (total dimensions: 0.81 x 0.84 x 23 m) with a lining of 50 μm fluorinated ethylene propylene (FEP) Teflon film. Teflon provides a relatively inert, replaceable surface and transmits solar radiation efficiently when the cell is used as a reaction chamber for synthetic systems.

Figure 2 depicts the multiple-reflection cell coupled to the FTS-LPIR system, which is housed in an air-conditioned building (3.7 x 3.7 m). The collimated IR beam from a Nernst glower is modulated by a Digilab Model 296
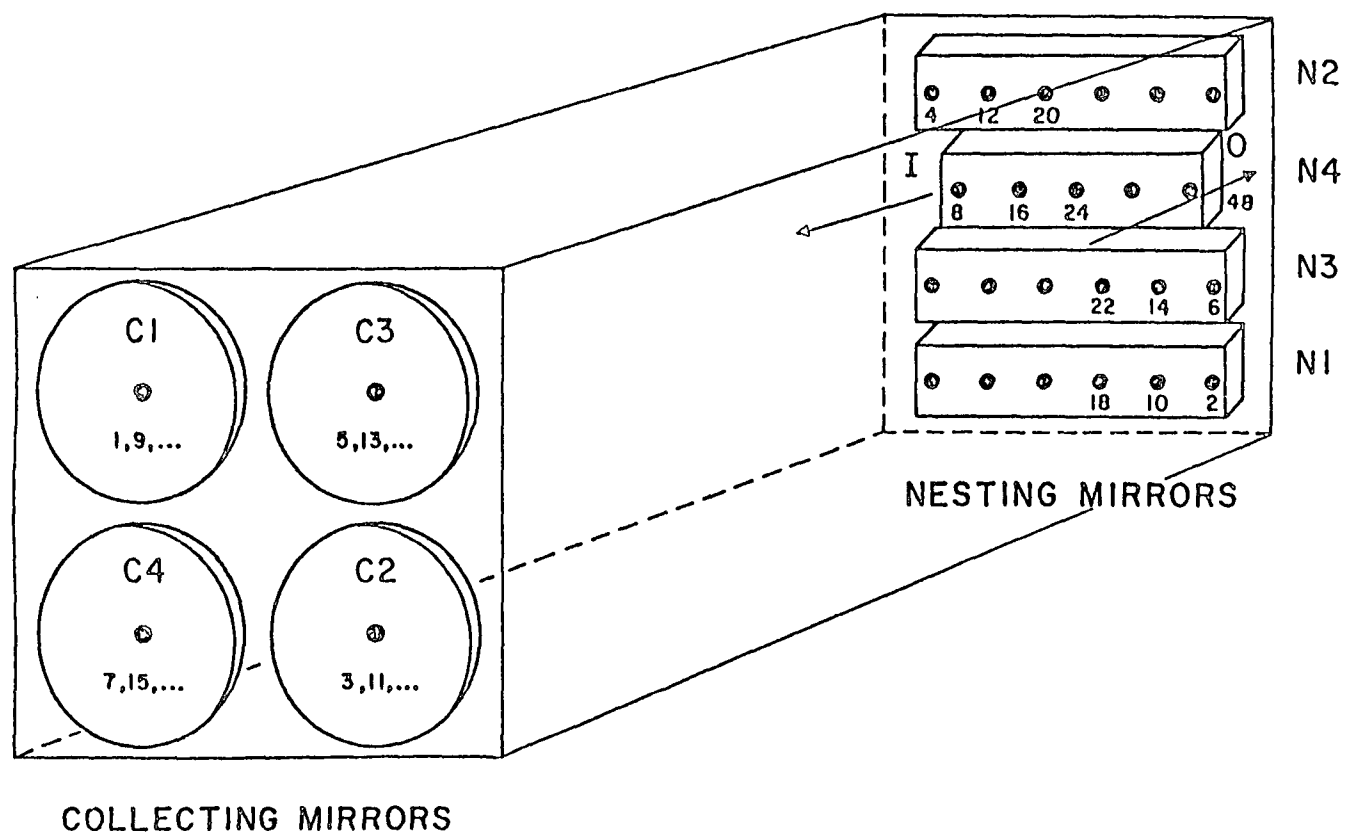
Figure 1. Eight-mirror multiple reflection system. Numbered dots indicate sequence of reflections during six complete passes through the cell; I = entrance aperature; O = exit aperature.

EXHAUST
BLOWER

AIR INTAKE

EIGHT MIRROR MULTIPLE REFLECTION OPTICS

22.5 meters

MAGNETIC TAPE
DATA STORAGE

PLOTTER

COMPUTER

In Sb
DETECTOR

Hg Cd Te
DETECTOR

SOURCE

MICHELSON
INTERFEROMETER
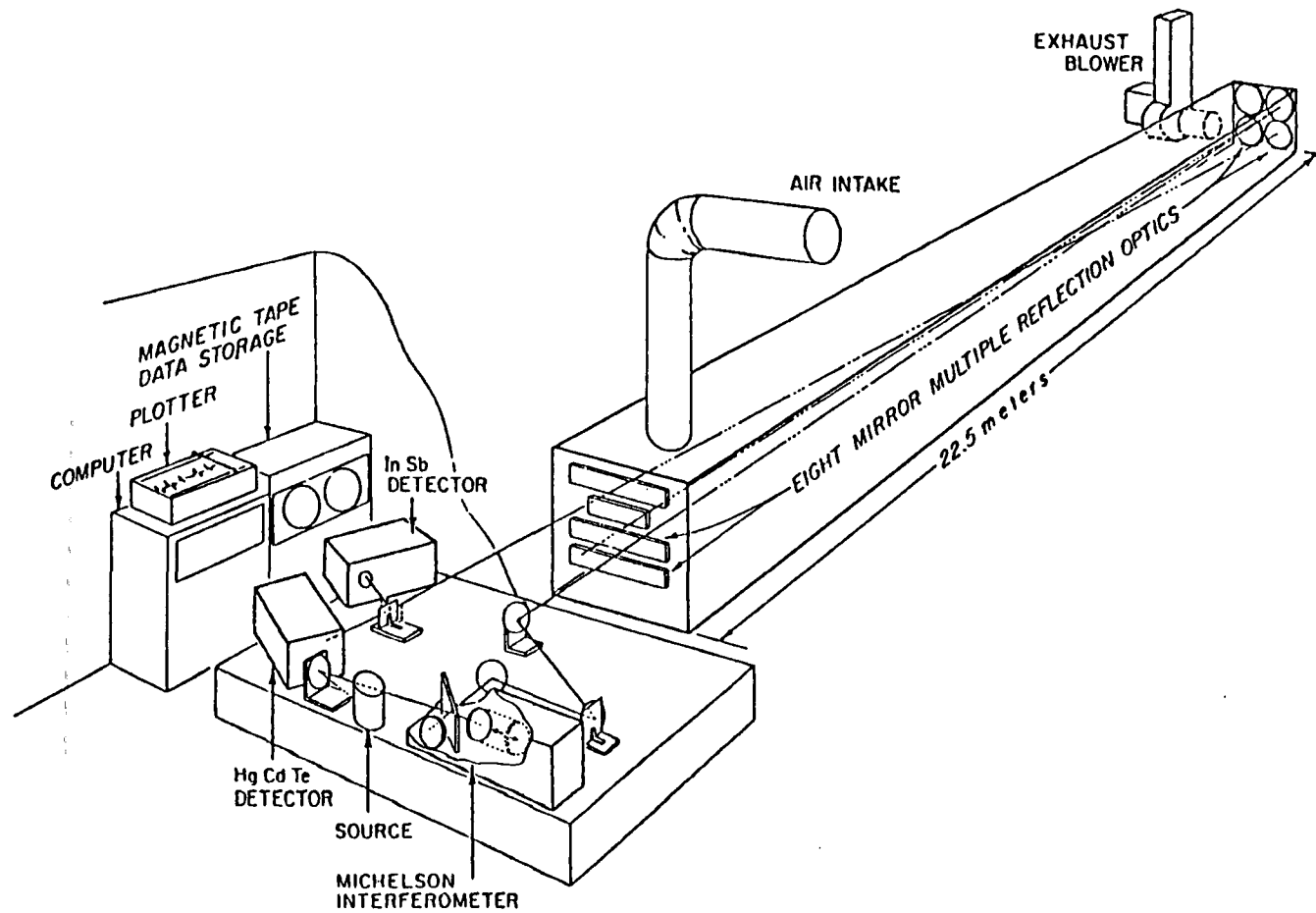
Figure 2. Kilometer pathlength FTS-LPIR system.

Michelson IR interferometer (resolution ≥ 0.5 cm^{-1}). The beam exiting from the cell is sent to either of two liquid nitrogen cooled detectors: a photovoltaic indium antimonide (InSb) detector for the 2000-3900 cm^{-1} range or a photoconductive mercury cadmium telluride (HgCdTe) detector for the 600-2000 cm^{-1} region.

Data collection and processing are performed by a Data General Nova 1200 computer with 4096 16-bit words of core. A disk unit (128 K words) is used for software storage and partial data storage. Archival data is stored on a Kennedy Model 9700 magnetic tape unit. The Digilab system is also equipped with a pen plotter, an oscilloscope, and a teletype.

Routine data collection is carried out at pathlengths of 900 and 1080 m. Data collection, transform computation, routine plotting of a portion of the spectrum, and magnetic tape storage can be accomplished within 10 min for each detector. Hence, a time resolution of three complete spectra (600-4000 cm^{-1}) per hour is available to characterize moving smog fronts.

To measure the best performance of the system, experiments are conducted at night (when thermal effects and vibrations are minimal) and with the cell purged to low relative humidities with dry nitrogen gas. At pathlengths near 1 km, a signal to peak-to-peak noise ratio of 400 is attained. This corresponds to a signal-to-noise ratio of approximately 1000 for a single mirror reflection. From the analysis of Hanst *et al.* (1973), a theoretical detection sensitivity of 0.8 ppb has been calculated for a compound with an absorptivity of 30 cm^{-1} atm^{-1} (e.g., PAN). In practice, the theoretical detection sensitivity is not usually achieved due to effects such as vibrations, concentration fluctuations with time, interfering absorptions, and variations in the refractive index of the air caused by temperature gradients in the cell. Additional details of optical alignment procedures, multiple reflection cell operation, and signal-to-noise considerations can be found elsewhere (Tuazon *et al.*, 1979).

Data Collection and Processing

Strong absorptions due to the H_2O and carbon dioxide (CO_2) content of the atmosphere render certain regions of the IR unsuitable for detection of pollutant molecules. At pathlengths of 1 km and longer, the spectral windows for IR detection are generally limited to the 760-1300 cm^{-1}, 2000-2230 cm^{-1}, and 2390-3000 cm^{-1} regions. Fortunately, the majority of pollutant molecules have "fingerprint" absorptions in the accessible IR regions. For data analysis the spectra are retrieved from storage and ratioed against a clean background spectrum with the same H_2O content in order to eliminate the majority of interfering water absorptions.

The sampling procedure consisted of drawing air through the cell at a rate of 330 liters sec^{-1} for a minimum of 4 min before the start of an interferogram averaging. This corresponded to a displacement of the previous air sample by a minimum of five volumes of fresh sample. Total pathlengths of 900 or 1080 m and a spectral resolution of 0.5 cm^{-1} were employed. Actual data collection of 30 co-added interferograms took no more than 6 min. Several experiments were performed in which spectra of smoggy air were recorded; alternately for air being drawn continuously through the cell and for the system in the stopped flow mode. These experiments established that key pollutant species (e.g., HCHO, HNO_3, formic acid [HCOOH]) were not significantly lost to or off-gassed from the cell walls during the brief scanning period.

FTS-LPIR Absorptivities and Detection Limits

Initial estimates of pollutant concentrations in the 1976 study (Tuazon *et al.*, 1977, 1978) were based on literature values of absorptivities measured at lower spectral resolutions (≥ 2 cm^{-1}) than those employed in this program. New measurements (Tuazon *et al.*, 1979) of absorptivities for HCOOH, HCHO, NH_3, and HNO_3 have since been made in the SAPRC evacuable chamber, and in some cases significant disagreements with the literature values were found.

Table 1 gives the newly measured absorptivities for HCOOH, HCHO, NH_3, and HNO_3, as well as their estimated detection levels in the present system at

TABLE 1. CALCULATED DETECTION LIMITS FOR SEVERAL POLLUTANT SPECIES

Compound	Measurement Frequency (cm^{-1})	Absorptivity* $(cm^{-1} atm^{-1},$ RTP[†]$)$	Resolution (cm^{-1})	Reference	Approximate Detection Limit at 1 km Pathlength
O_3	1055	9.7	1-2	Pitts et al., 1976 McAffee et al., 1976	10
PAN	1162	32	2-4	Stephens, 1964	3
NH_3	931	27	0.5	Tuazon et al., 1979	4
	967.5	35	0.5	Tuazon et al., 1979	3
	993	21	0.5	Tuazon et al., 1979	4
HNO_3	896	12[‡]	0.5	Tuazon et al., 1979	6
HCHO	2779 2781.5	16[‡]	0.5	Tuazon et al., 1979	6
HCOOH	1105	70[‡]	0.5	Tuazon et al., 1979	2
HNO_2	791 (trans)	~30	0.5	Chan et al., 1976	$10^{[§]}$ (cis + trans)
	853 (cis)	71	0.5	Chan et al., 1976	
H_2O_2	1251	9±3	2	Hanst et al., 1975	$40^{[§]}$
HO_2NO_2	803	27	0.5-1	Graham et al., 1977	$8^{[§]}$

*Absorptivity = $\log e(I_o/I)/pl$ where p is the concentration (atm) of the compound, l is the pathlength (cm) and I and I_o are the transmitted intensities with and without the compound present, respectively.
[†]23°C, 760 torr.
[‡]Measured from the intensity of the Q branch only. (See text.)
[§]See text for discussions of atmospheric interferences for the spectral analysis of HNO_2, H_2O_2, and HO_2NO_2 concentrations.

a 1-km pathlength. Nominal uncertainties in measured concentrations are one
half of the detection limits. For the analytical bands of HCOOH at 1105 cm^{-1}
and HCHO at 2780 cm^{-1}, no more than 10% difference exists between the absorp-
tivity value of the Q branch height alone and that of the total value as
measured from the true baseline. For HNO_3, however, the total absorptivity at
896 cm^{-1} is approximately twice that of the value for the Q feature alone due
to the significant contribution of the broad P and R branches. Nevertheless,
only the Q branch height absorptivities were used for all of the above com-
pounds; this procedure minimized baseline interferences caused by possible
absorptions from unidentified species. These Q branches were verified by
experiment to obey Beer's law for our program's specific conditions.

The detection limits given in Table 1 are, in most cases, based on a 1%
absorption. For the 993 cm^{-1} line of NH_3 and the 896 cm^{-1} Q branch of HNO_3,
however, the detection sensitivities are slightly better (~0.75% absorption)
because these features are virtually free of atmospheric H_2O and CO_2 absorp-
tions. Moreover, spectra analyses made in 1977 (Tuazon et $al.$, 1979) facili-
tated the establishment of operational minimum signal levels at which H_2O_2,
HNO_2, and per(oxy)nitric acid (HO_2NO_2) can be positively detected.

RESULTS

Table 2 summarizes the maximum concentrations of NH_3, HNO_3, HCOOH, HCHO,
O_3, and PAN measured in 1977 in Riverside between 1 a.m. and 7 p.m. (PDT)
during 10 episode days in July, August, and October. Detailed pollutant
concentrations as a function of time are presented in Tables 3 and 4 for
representative 1977 air pollution episodes in Riverside on July 21 and 25,
respectively. Figure 3 shows time concentration profiles for nine species
observed on October 14, 1977.

Included in the data for July 21 are the corresponding 5-min concentra-
tion averages for NO, NO_2, total nonmethane hydrocarbons (NMHC, expressed as
total carbon [C]), and CO, obtained by SAPRC staff using the California Air
Resources Board (ARB) mobile laboratory located adjacent to the km cell facil-
ity. In this SAPRC-ARB facility, $NO/NO_2/NO_x$ were measured with a Bendix

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TABLE 2. MAXIMUM POLLUTANT CONCENTRATION (PPB) MEASURED
IN RIVERSIDE AIR IN 1977

Date	O_3	PAN	NH_3	HNO_3	HCOOH	HCHO
Jul. 21	264	11	41	12	5	20
25	291	10	47	20	4	19
Aug. 10	234	10	40	*	8	19
11	287	13	39	13	10	27
12	249	11	46	16	11	25
Oct. 3	241	10	57	13	8	29
4	195	10	37	15	8	25
11	242	18	132	12	9	38
14	260	17	102	9	13	36
17	240	14	81	11	11	38

*Below detection limit.

TABLE 3.   POLLUTANT CONCENTRATIONS* (PPB) IN RIVERSIDE AIR,
JULY 21, 1977

Time[†]	O_3	PAN	NH_3	HNO_3	HCOOH	HCHO[‡]	NO_2	NO	NMHC (ppmC)	CO (ppm)
1140	173	10	—	—	3	15	40	1	0.3	1.2
1202	180	8	—	—	3	12	36	1	0.3	1.4
1231	176	4	—	—	4	11	35	1	0.2	1.1
1258	161	3	4	—	2	13	28	2	0.2	0.8
1336	152	—	25	—	2	13	23	2	0.2	0.7
1423	198	3	41	—	2	11	36	2	0.1	1.0
1444	216	3	38	—	—	13	43	2	0.1	0.9
1507	214	6	29	—	2	15	35	2	0.3	1.1
1534	245	5	24	10	2	15	37	3	0.3	1.2
1552	229	8	19	7	3	19	53	3	0.4	1.4
1610	253	9	13	9	5	20	37	2	0.4	1.5
1632	264	10	11	10	4	19	54	2	0.5	1.4
1653	238	9	5	—	4	19	65	2	0.5	1.5
1711	239	9	6	10	3		49	2	0.6	1.6
1743	239	9	6	—	4	18	66	2	0.4	1.3
1800	225	11	—	—	3	18	59	2	0.4	1.3
1818	200	9	9	12	4	17	55	2	0.4	1.3
1835	206	9	8	—	2	19	64	2	0.4	1.3
1857	181	9	8	—	2		83	2	0.4	1.3

*Dashes indicate below detection limit.   Blanks indicate no measurement.
[†]PDT.
[‡]HCHO measurements were made with the InSb detector approx. 10-15 min after
the times listed in the table for the HgCdTe detector spectra.

TABLE 4. POLLUTANT CONCENTRATIONS* (PPB) IN RIVERSIDE AIR, JULY 25, 1977

Time	O_3	PAN	NH_3	HNO_3	HCOOH	HCHO	NO_2
1058	137	3	—	8	2	11	
1128	145	—	—	8	3	11	
1210	158	—	8	8	—	12	
1229	142	—	7	9	2	16	
1308	130	—	29	—	—	15	
1350	193	—	47	—	—	13	
1500	51	—	14	—	—	9	
1542	189	—	24	9	—		
1603	256	9	13	15	3	16	51
1623	291	10	18	20	3	19	31
1642	247	8	19	17	4	16	55
1704	197	5	13	15	3	13	85
1722	191	5	14	12	2	19	59
1755	184	3	13	14	2	13	42

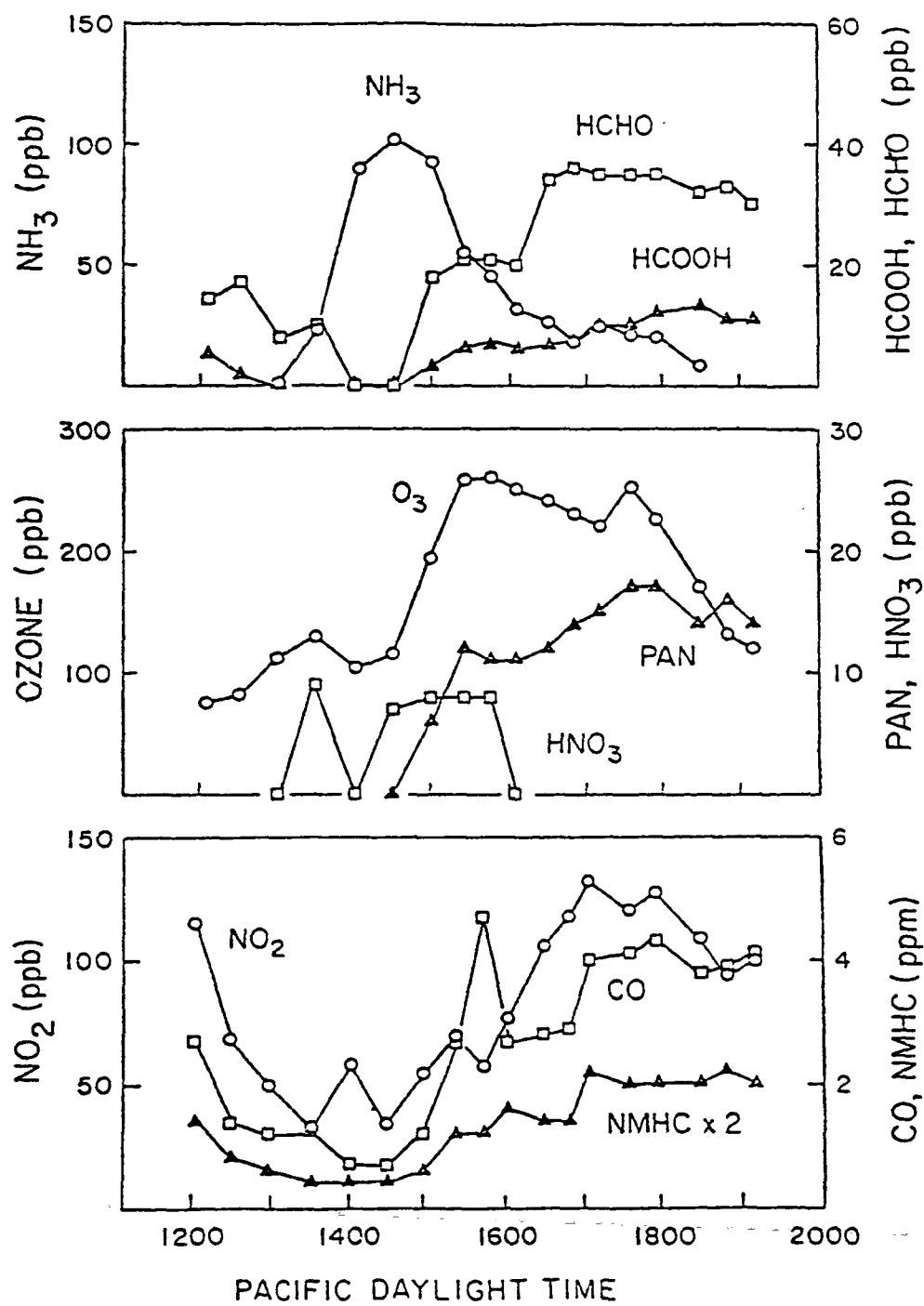*Dashes indicate below detection limit. Blanks indicate no measurement.

Figure 3. Time-concentration profiles obtained from 900-m pathlength FTS-LPIR spectra of Riverside ambient air on October 14, 1977.

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chemiluminescent analyzer, and CO and total NMHC were measured with a Beckman 6800 gas chromatograph. The NO_2 concentrations have been corrected for inter- ferences due to PAN and HNO_3 (Winer *et al.*, 1974; Spicer and Miller, 1974).

DISCUSSION

Reliable data on the ambient concentrations of HNO_3 are essential in understanding the fate of nitrogen oxides emitted into the atmosphere and in establishing an adequate nitrogen balance for photochemical smog. The impor- tant reactions for the formation of HNO_3 are

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{1}$$

and

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \text{ (heterogeneous)} \tag{2}$$
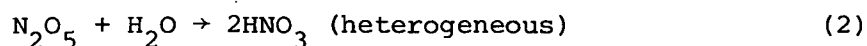
Since HNO_3 has a low photolysis rate in the lower atmosphere, it serves as a sink for gas phase nitrogen oxides.

The first detection of HNO_3 in polluted urban air was reported by Spicer and Miller (1974) and Miller and Spicer (1975). Using a modified Mast micro- coulomb meter adapted for sensing acids rather than oxidants, the authors reported a daily average concentration of 3 ppb and an average hourly peak of 10 ppb HNO_3 in West Covina, California, during the period August to September in 1973. A later report (Spicer, 1977) detailed the results of the West Covina study and the July-August 1973 measurements in St. Louis, in which both the continuous Mast analyzer and an integrated analysis by a modified chroma- tropic acid method were used. Their tabulated data showed the highest 1-hr maximum HNO_3 concentration to be 80 ppb for St. Louis and 40 ppb for West Covina. The West Covina results contrast sharply with the almost concurrent FTS-LPIR study in Pasadena by Hanst *et al.* (1975). Hanst and co-workers did not observe HNO_3, even in severe smog episodes (i.e., oxidant ~0.6 ppm), and they reported a detection limit of approximately 10 ppb for their FTS-LPIR system. A subsequent FTS-LPIR study reported the first spectroscopic

detection of HNO_3, at concentrations up to 6 ppb, in Riverside during the fall of 1976 (Tuazon *et al.*, 1977, 1978).

As seen in Figure 4(c), the absorption band of HNO_3 at ~880 cm^{-1} is characterized by three distinct Q branches at 879, 885 and 896 cm^{-1}. Improvements in operating parameters provided spectra of higher quality during our 1977 and 1978 studies, and they verified conclusively our previously reported detection of HNO_3 (Tuazon *et al.* 1977, 1978). Figure 5 is a portion of a spectrum recorded at 12:32 p.m. on August 12, 1977. Although the atmospheric H_2O absorptions are not exactly cancelled in this ratio spectrum, the three Q branches mentioned above clearly appear in their proper intensity ratios and establish the presence of HNO_3 in this sample at a 16 ppb concentration.

The maximum HNO_3 concentration observed in our monitoring studies was 20 ppb and occurred during an episode in Riverside on July 25, 1977, in which the O_3 concentration reached 300 ppb. Measured NH_3 levels were low during this episode (<30 ppb most of the time). Smog chamber (Spicer and Miller, 1976) and ambient air (Spicer and Miller, 1974; Miller and Spicer, 1975) data indicate that O_3 and PAN levels are strong predictors of HNO_3 concentrations. Indeed, our data indicate that HNO_3 concentrations of 10-20 ppb coincide with high O_3 levels (200-300 ppb) for several cases, particularly when the NH_3 levels are low (≤30 ppb). Unusually high concentrations of NH_3 were recorded on October 11, 14, and 17, 1977, with maxima of 80-130 ppb. Shortly after these maxima occurred, the HNO_3 levels dropped below the detection limit of 6 ppb, even though the O_3 levels remained near or above 200 ppb. During the earlier hours of these episodes, when the NH_3 concentrations were low, 8-12 ppb HNO_3 levels were recorded at oxidant levels of 110-140 ppb. In general, the HNO_3 concentration was near or below our detection limit when high NH_3 concentrations were present.

CONCLUSIONS

The data cited above, as well as those reported elsewhere in more complete form (Tuazon *et al.*, 1979), support the current view on the NH_3 role in stabilizing HNO_3 by forming particulate nitrates. However, the observation in
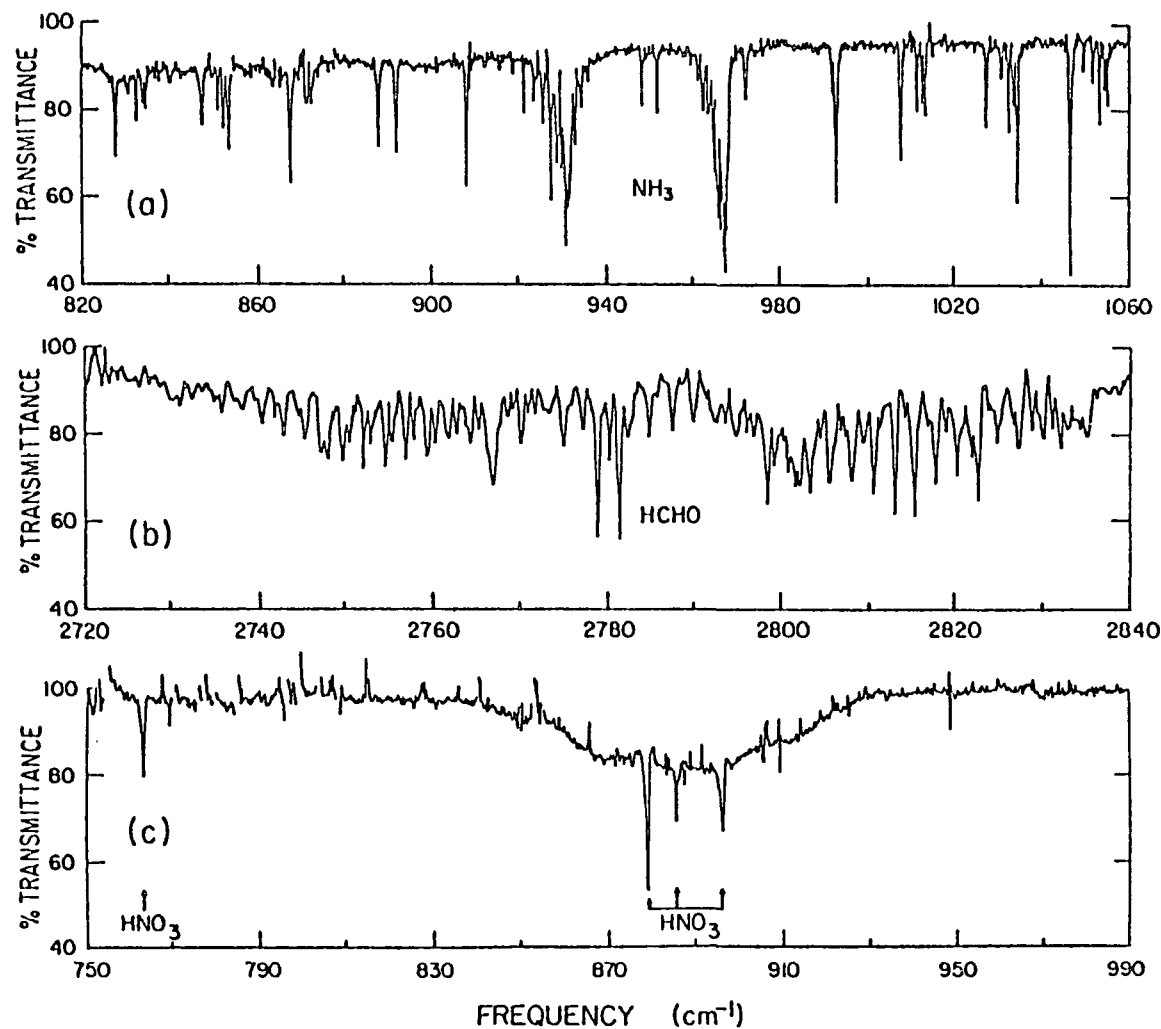
Figure 4. Reference spectra at 0.5 cm^{-1} spectral resolution and 1080-m pathlength: (a) NH_3 ~200 ppb; (b) HCHO ~270 ppb; (c) HNO_3 ~150 ppb.
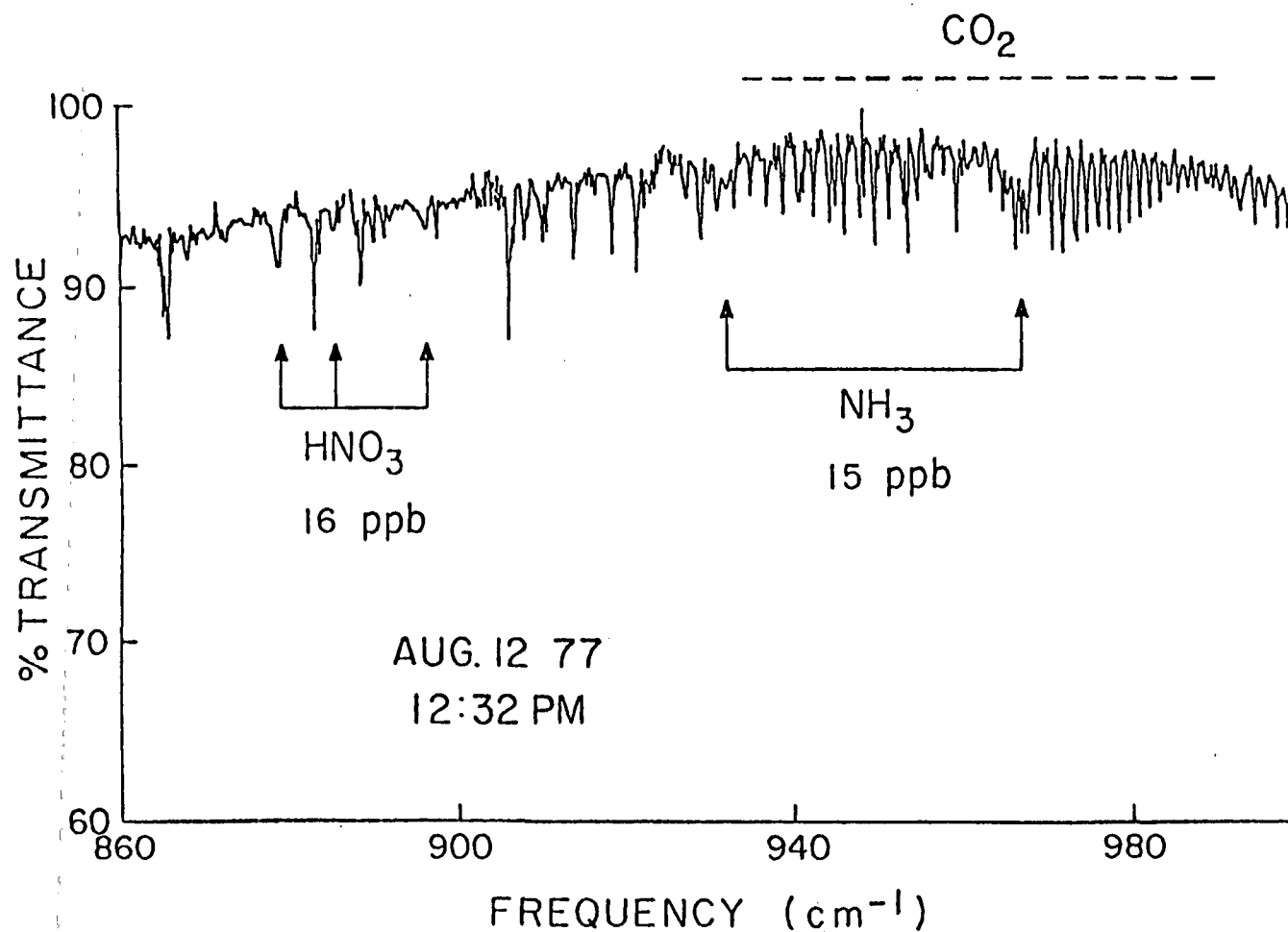
Figure 5. Riverside ambient air spectrum (August 12, 1977 at 12:32 p.m.) at 0.5 cm^{-1} spectral resolution, 900-m pathlength, with HgCdTe detector. HNO_3 concentration = 16 ppb; NH_3 concentration = 15 ppb.

this study of the HNO_3 and NH_3 coexistence, with HNO_3 present in concentrations of ~10-20 ppb simultaneously with NH_3 levels as high as ~50 ppb, provides potentially important data in quantitatively elucidating the relationship between NH_4NO_3 aerosol and gaseous HNO_3 and NH_3 in the atmosphere. Further studies of this relationship are thus being carried out in our laboratory (Doyle *et al.*, in preparation).

ACKNOWLEDGMENTS

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MEASUREMENT OF GASEOUS HNO_3 BY
ELECTROCHEMISTRY AND CHEMILUMINESCENCE

Chester W. Spicer

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

INTRODUCTION

Gaseous and particulate nitrates are important constituents of the atmosphere due to their potential impact on health, visibility, and precipitation chemistry. This report describes three methods we have employed for measurement of atmospheric HNO_3. The first method to be discussed involves coulometry, the second employs chemiluminescence, and the last is a filtration technique.

MEASUREMENT OF HNO_3 BY COULOMETRY

Instrumentation and Methods

A schematic of the microcoulometric monitor is shown in Figure 1. Table 1 presents a list of potential interferences we have investigated. At atmospheric concentrations, none of the species studied will significantly interfere with the HNO_3 measurement.
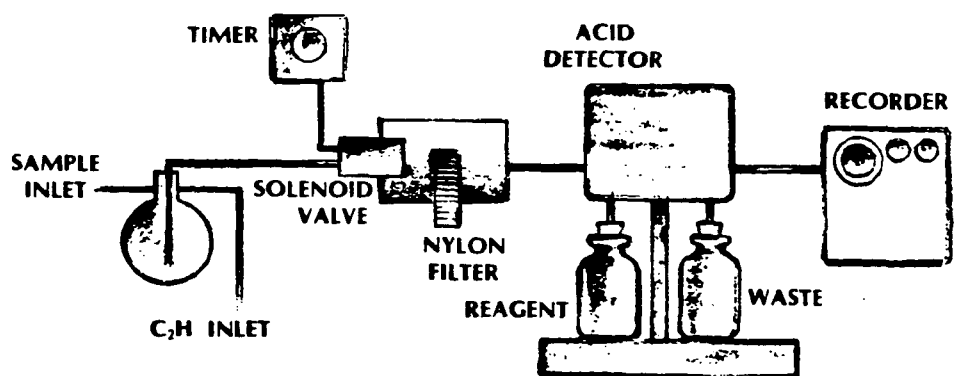
Figure 1.   Microcoulometric monitor.
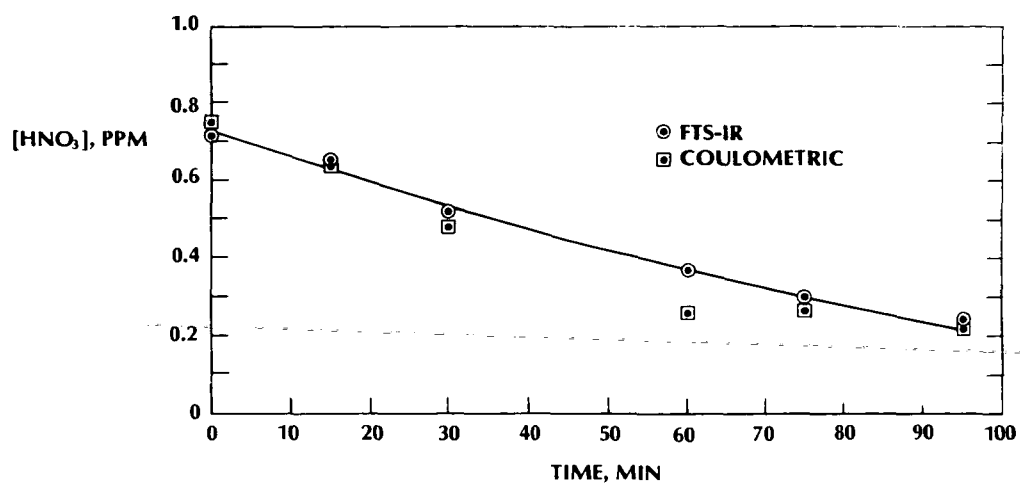
Figure 2.   Comparison of HNO$_3$ analysis by FTS-LPIR and coulometric methods.

TABLE 1.   EVALUATION OF INTERFERENCES TO COULOMETRIC HNO_3 MONITORING

Species	Comment
O_3	No interference up to 0.8 ppm
NO_2	No interference up to 1 ppm
SO_2	No interference up to 1.1 ppm
H_2SO_4	No interference up to 100 $\mu g/m^3$
HCl	No interference up to 0.4 ppm
HCHO	No interference up to 0.5 ppm
PAN	No interference up to 0.2 ppm
HCOOH	Variable interference between 0-10% of HCOOH concentration
HNO_2	No interference up to 0.4 ppm

Results

A comparison of the coulometric instrument with FTS-LPIR for gaseous HNO_3 is shown in Figure 2.   Agreement between the two methods is quite good.   A similar comparison under simulated smog conditions (in the EPA smog chamber) also showed good agreement, even in the presence of high concentrations of potential interferences such as SO_2, H_2SO_4, NO_2, O_3, PAN, and HCOOH.   This comparison is shown in Figure 3.

MEASUREMENT OF HNO_3 BY CHEMILUMINESCENCE

Instrumentation and Methods

While the coulometric instrument can be used for many HNO_3 monitoring applications, it is not well suited for all sampling requirements.   Its detection limit (~5 ppb) and relatively long response time make it particularly unsuited for either clean air measurements or aircraft sampling in plumes.   To accommodate these situations we have developed two other methods
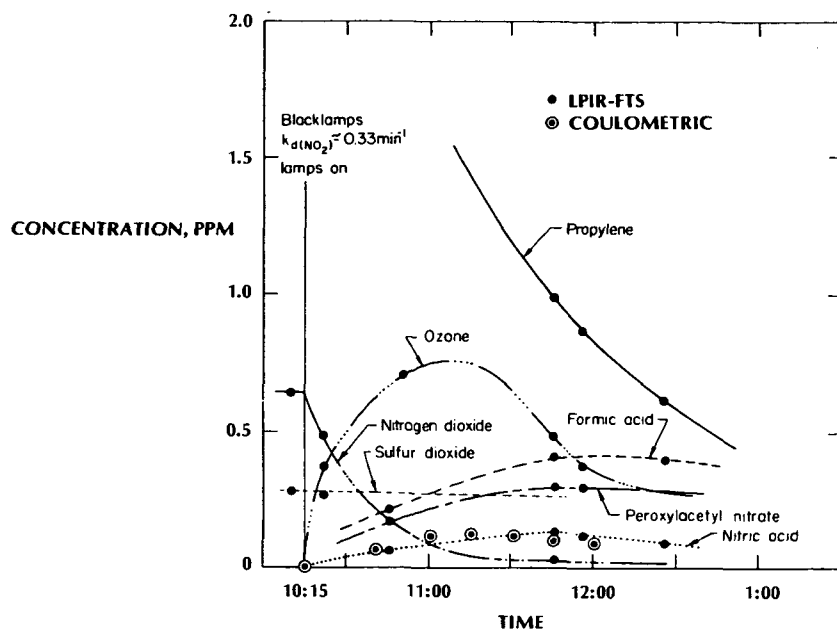
Figure 3. Photooxidation of propylene/nitrogen dioxide/sulfur dioxide in FTS-LPIR chamber.
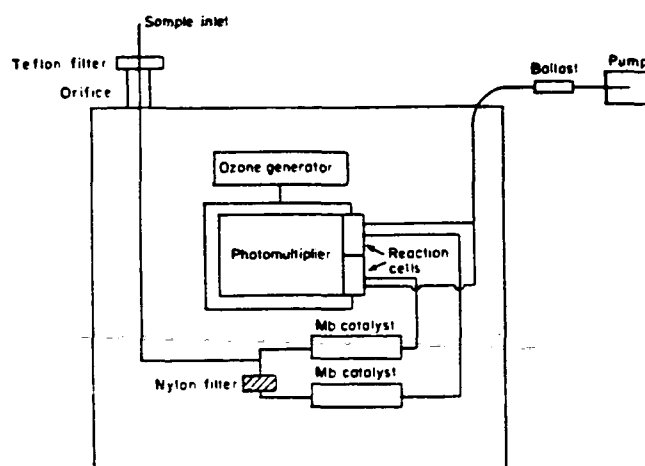
Figure 4. Schematic of chemiluminescent instrument modified for simultaneous NO_x/HNO_3 monitoring.

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for measuring HNO_3. One of these methods is a simple modification of the chemiluminescence procedure used for monitoring NO. A schematic of the instrument is shown in Figure 4.

Results

The chemiluminescence instrument agrees quite well with the coulometric for gaseous HNO_3, as seen in Figure 5. The performance of the chemiluminescence monitor when exposed to NO, NO_2, and HNO_3 is shown in Figure 6.

A study of the response of the instrument to varying converter temperature is shown in Figure 7. For molybdenum converters, 300-325° C is the optimum operating range. At these temperatures, complete conversion of NO_x and HNO_3 is obtained without conversion of NH_3.

Some actual atmospheric data from our recent study of NO_x reactions in urban plumes are shown in Figures 8 and 9. A traverse of the Boston urban plume approximately 40 km downwind of the city (east over the ocean) is pictured in Figure 8. Both the HNO_3 and O_3 concentrations are shown. Figure 9 shows the vertical profiles of several variables downwind of Philadelphia during inversion conditions. These data demonstrate the utility of the chemiluminescence instrument for airborne studies.

MEASUREMENT OF HNO_3 BY FILTRATION

Low concentrations of gaseous HNO_3 can be quantitatively collected on nylon filters without significant interference from other atmospheric constituents. Analysis of the nylon filter for nitrate provides an integrated measure of the HNO_3 concentration. We employ Teflon prefilters to separate particulate nitrate from gaseous HNO_3. Thus the analysis of the two filters yields a simultaneous estimate of the particulate nitrate and HNO_3 concentrations.

The dual filter procedure has been tested in the laboratory and recently used during a field study. The results of the field test are not available.

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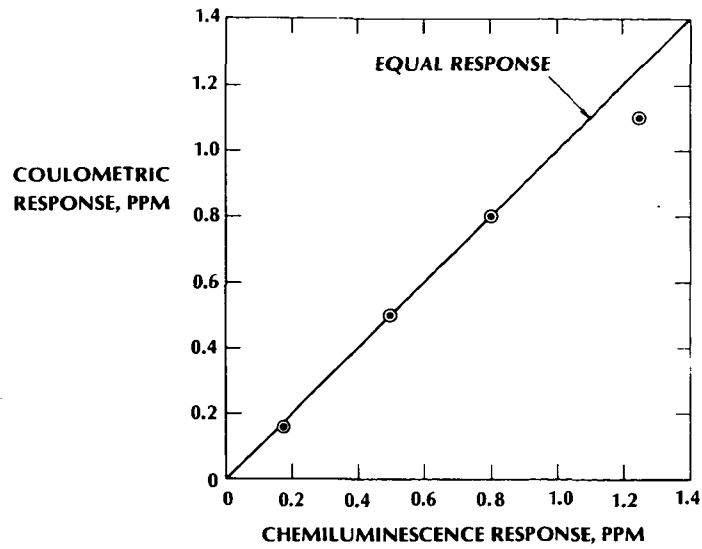
Figure 5. Coulometric vs. chemiluminescent response to gaseous HNO_3.
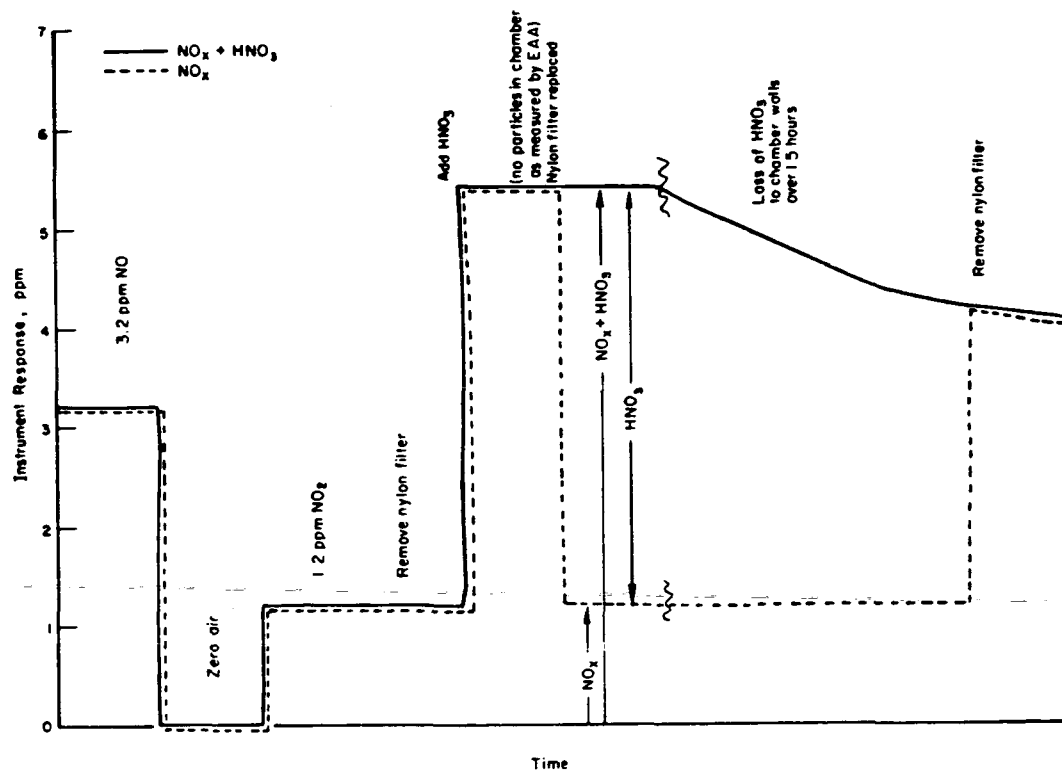
Figure 6. Chemiluminescence response.
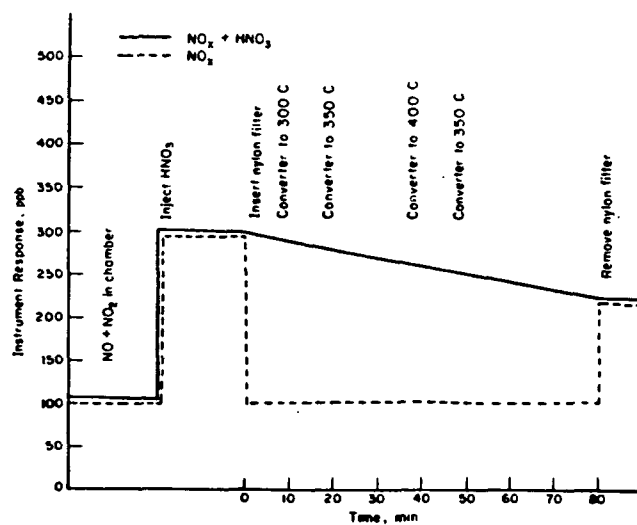
Figure 7.   Chemiluminescence response under varying conditions.
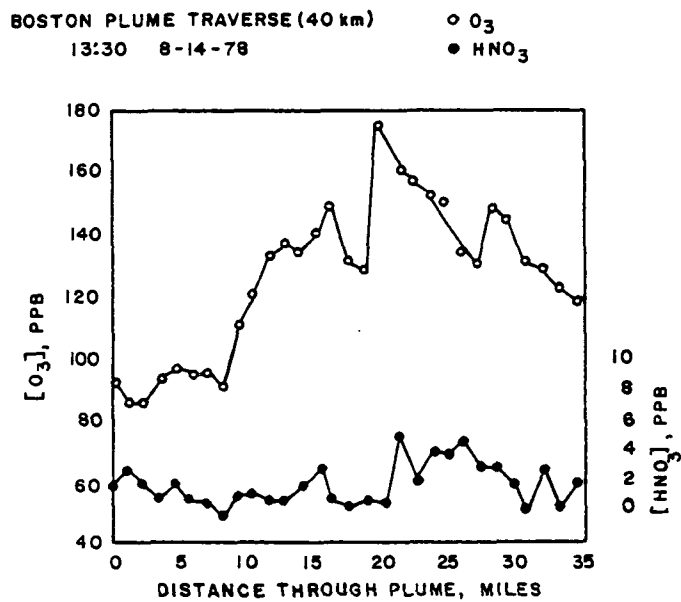
Figure 8. O_3 and HNO_3 during urban plume traverse.

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DOWNWIND PHILADELPHIA, 8-14-78
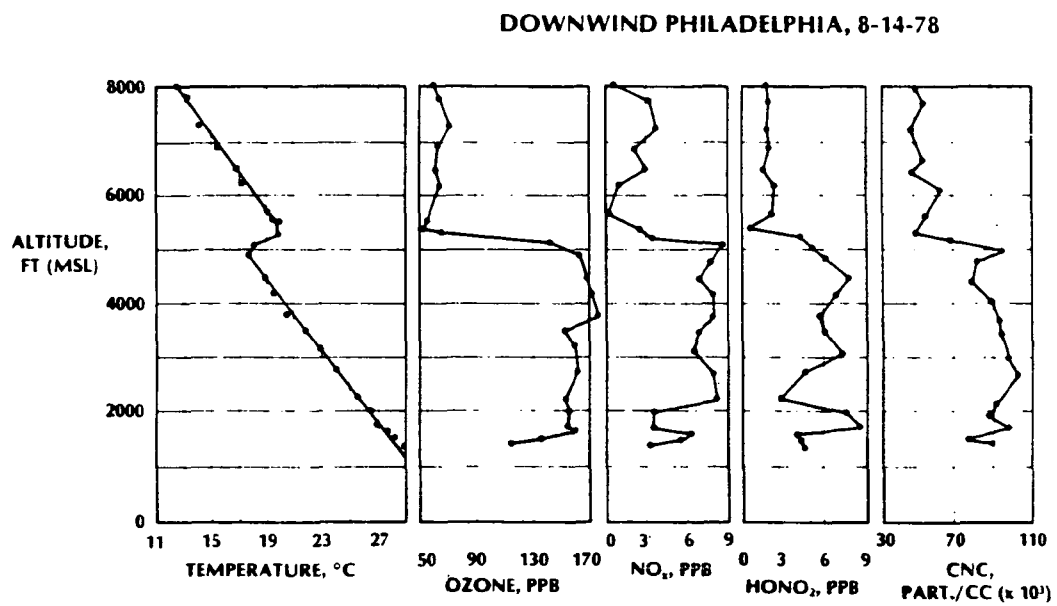
Figure 9. Vertical profiles downwind of Philadelphia.

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Manufacture of nylon filters has been discontinued by Millipore Corporation. However, similar nylon filters will soon be available from Ghia Corporation (7071A Commerce Circle, Pleasanton, California 94566).

CHEMILUMINESCENCE MEASUREMENTS OF HNO$_3$ IN AIR

Thomas J. Kelly

Donald H. Stedman

Departments of Chemistry and Atmospheric and Oceanic Science
University of Michigan
Ann Arbor, Michigan 48109

INTRODUCTION

Knowledge of the concentration of HNO$_3$ in the atmosphere is important for an understanding of the chemistry of both polluted and unpolluted air. HNO$_3$ is the major end product in the tropospheric photochemical transformation of NO$_x$. In regions of high emissions, HNO$_3$ formation results in increased acidity of precipitation, causing economic and ecological damage.

HNO$_3$ has been measured in polluted air by a coulometric technique (Miller and Spicer, 1975) and by an LPIR method (Tuazon *et al.*, 1978), and in the clean troposphere by a selective filter technique (Huebert and Lazrus, 1978). Drawbacks of these methods include poor sensitivity and/or long analysis time. The chemiluminescence method of Joseph and Spicer (1978) does not distinguish the components of NO$_x$ (other than HNO$_3$).

We have measured HNO$_3$ by adaptation of a sensitive chemiluminescence NO$_x$ monitor described elsewhere (Ritter *et al.*, 1978). Measurements were made at the site of the National Oceanic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory 300-m tower, in a rural area about 15 mi east of Boulder, Colorado. All measurements were made near ground level, during the last two weeks of February 1978. The site is sufficiently far from local

sources that, though it is often heavily polluted, the pollutants are well mixed. In addition to the measurements of HNO_3, NO and NO_2 were measured by the same chemiluminescence instrument used for HNO_3, CO was measured by infrared absorption, and O_3 was measured by chemiluminescence with ethylene.

INSTRUMENTATION AND METHODS

A schematic diagram of the HNO_3 detection system is presented in Figure 1. The single sample inlet point is a glass frit connected to a glass and Teflon plumbing system. The detector has four sample flow channels corresponding to four solenoid valves in the inlet plumbing that are controlled automatically by the detector electronics. When V1 is opened, sample air passes directly into the reaction chamber where any NO in the sample is detected. Alternatively, a background reading can be taken by diverting the sample flow to a prereactor where it is mixed with the O_3 flow and the chemiluminescent reaction completed before passage into the detection chamber. Opening V2 passes the sample air through a pot of granular iron sulfate ($FeSO_4$), which converts NO_2 to NO. Thus, the signal from Channel 2 indicates the sum of NO + NO_2, and NO_2 is obtained by subtraction of the Channel 1 NO signal. Channel 3 passes the sample air through a trap of loose cotton or nylon fiber, selectively removing HNO_3 from the sample (Miller and Spicer, 1975). The stream then passes through the HNO_3 converter. Channel 4 goes directly into the converter (a quartz tube at 350° C packed with 4 mm diameter Pyrex beads), which quantitatively converts HNO_3 to NO_2. The $FeSO_4$ completes the conversion to NO. The quartz tube is hot enough to also cause detection of organic nitrates or PAN, but does not oxidize organic amines or ammonia. Any difference in signal between Channels 2 and 3 is a measure of the "total organic nitrate" present, though the individual compounds in that total are not identified. HNO_3 is thus seen as the difference in signal between Channels 3 and 4.

The detector electronics switch sequentially through the four channels and a background reading in 1 min. The system has been calibrated directly with ppb quantities of HNO_3 in air as well as with standard mixtures of NO or NO_2. We have found no loss of HNO_3 in the inlet plumbing, and have shown
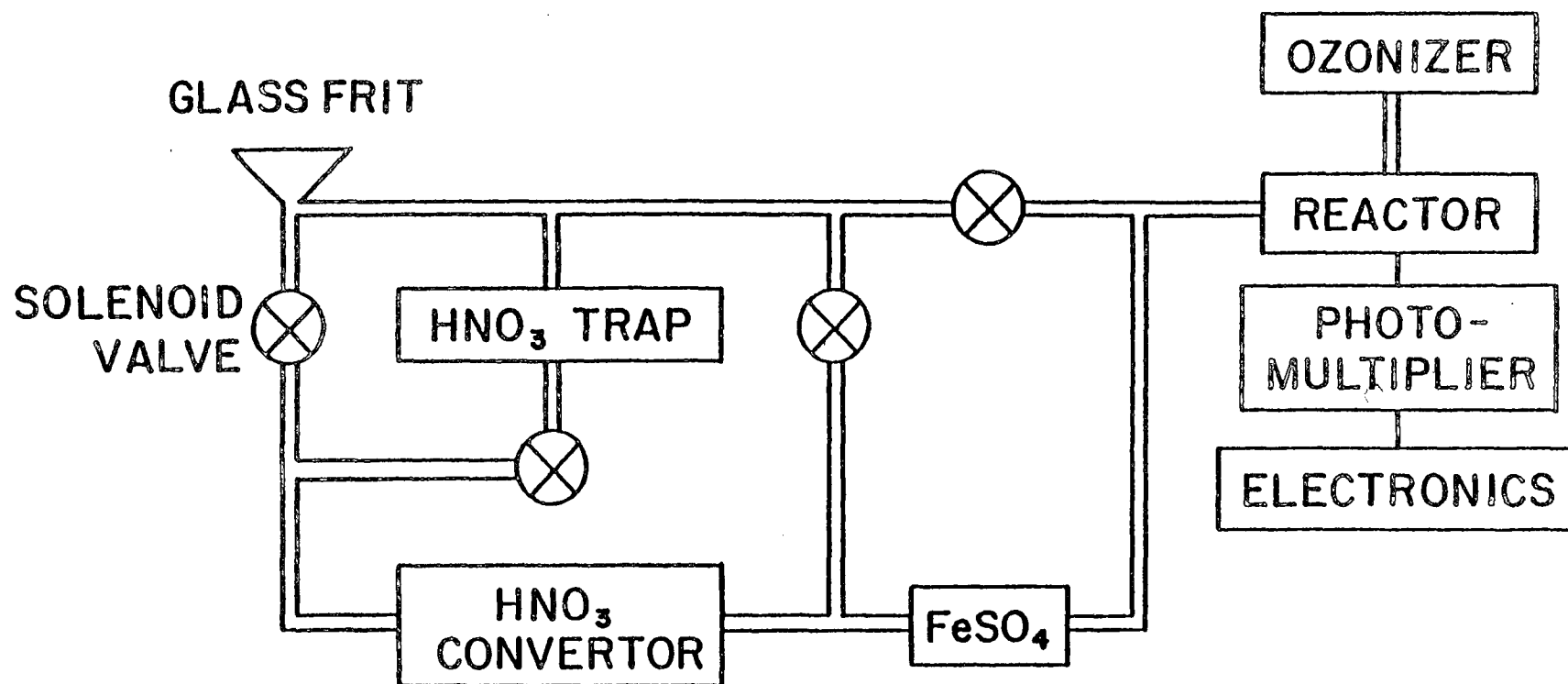
Figure 1. Instrumentation for measurement of NO_x by chemiluminescence.
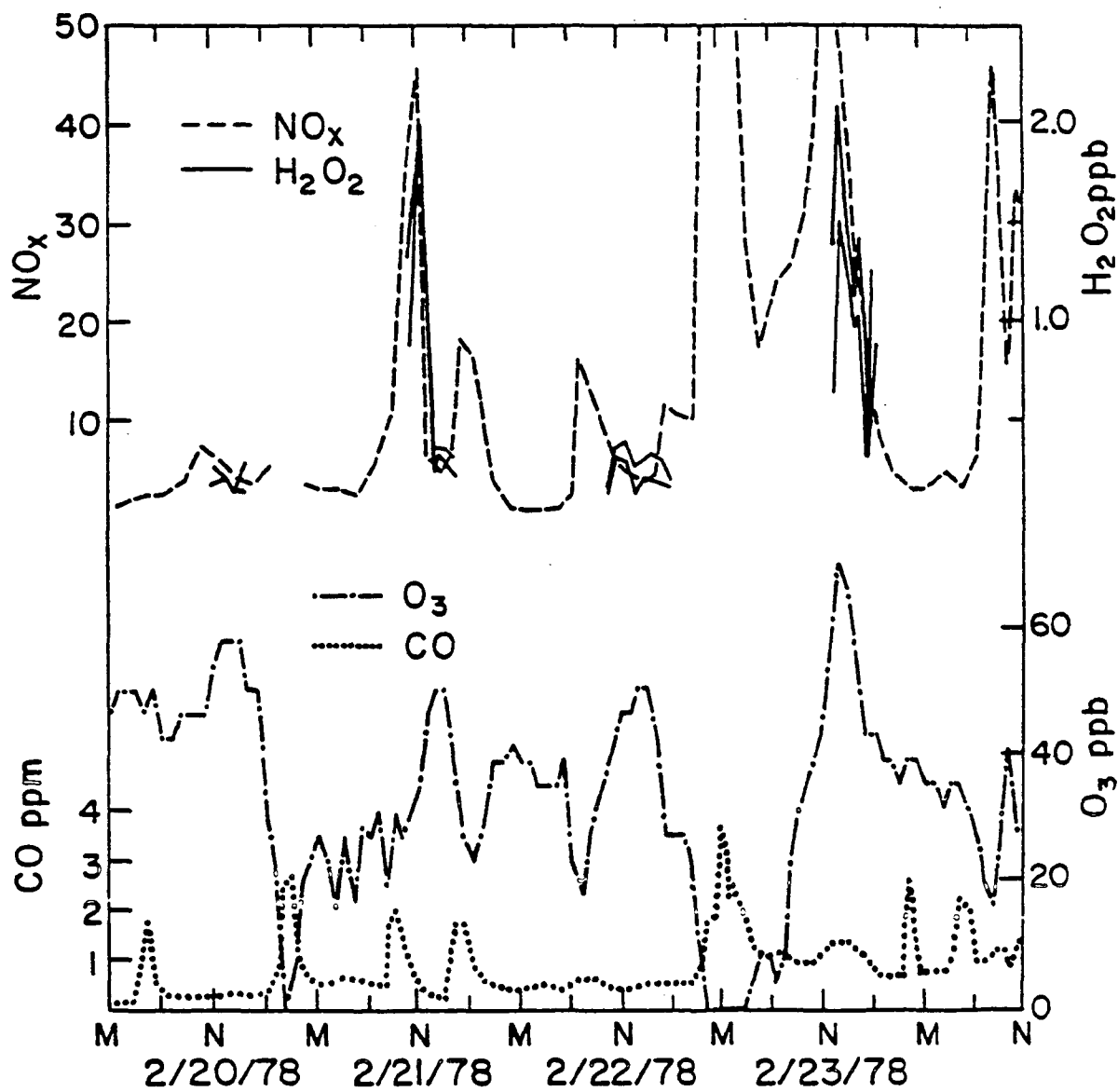
Figure 2. O_3, CO, NO_x, and H_2O_2 levels at Boulder, Colorado, February 20-23, 1978, as measured by chemiluminescence.

HNO₃ − NOₓ DATA   2/17−2/26/78   ERIE TOWER
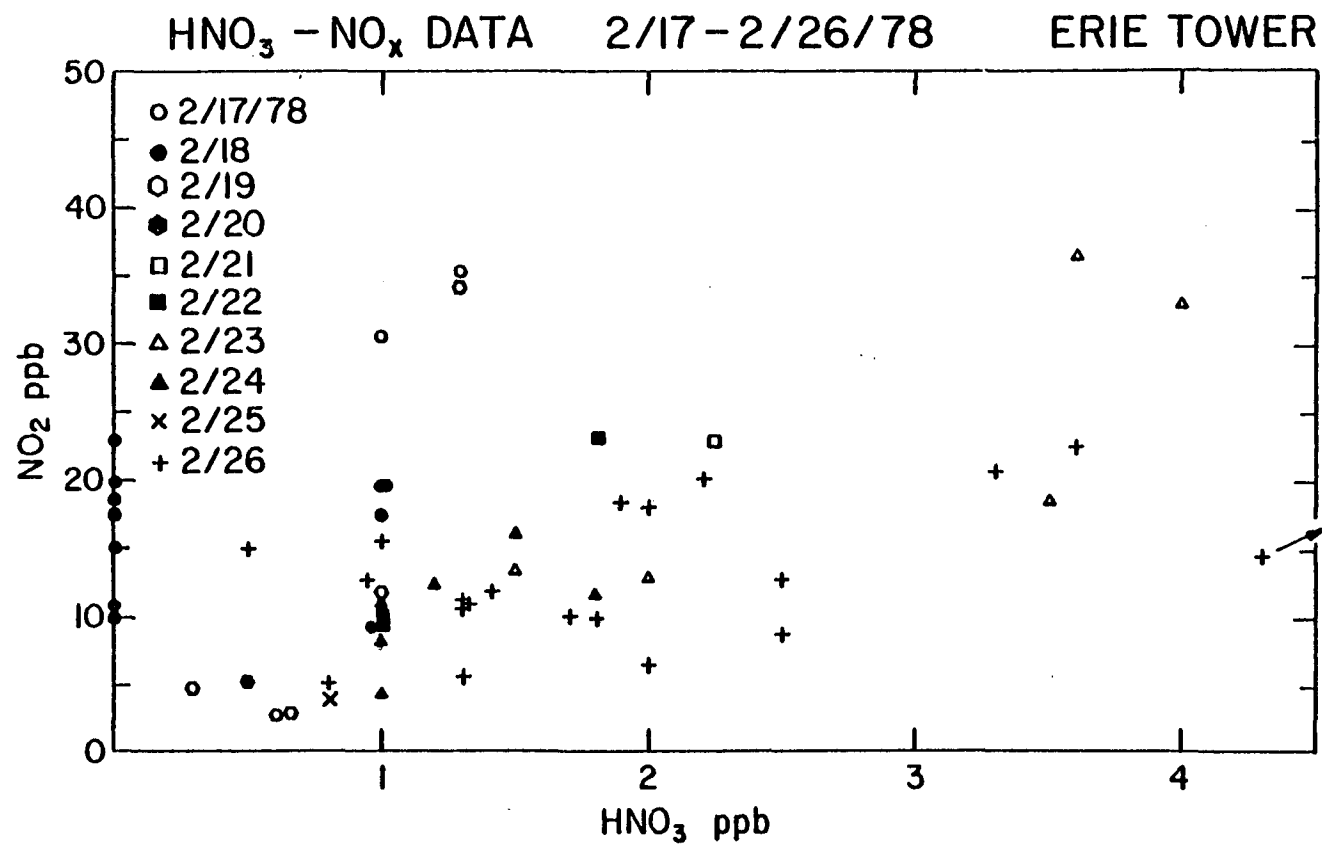
Figure 3. HNO₃ and NO₂ levels at Boulder, Colorado, February 17-26, 1978, as measured by chemilumines-cence.

HNO_3 to be efficiently converted by the quartz tube and trapped by the fiber trap. The detection limit of the system is presently about 0.3 ppb.

RESULTS AND DISCUSSION

Figure 2 shows data for O_3, CO, NO_x (NO + NO_2), and H_2O_2 for several days in February 1978. During this period, concentrations of HNO_3 were frequently below the detection limit. Figure 3 shows HNO_3 and simultaneous NO_2 data for those periods when HNO_3 was relatively constant for half an hour or more. In general, higher NO_2 levels correlated with higher HNO_3, with HNO_3 values of 0.5 to 5 ppb. NO_x was always much greater than HNO_3. Our NO_x/HNO_3 ratios were mostly greater than 10, with some readings of >20 ppb NO_2 with no detectable HNO_3 present. The NO_x levels clearly indicate tropospheric pollution, since background NO_x levels are less than 0.5 ppb in the Boulder area (Ritter et al., 1978). These NO_x/HNO_3 ratios are in agreement with those of other investigators for the polluted troposphere (Spicer, 1977; personal communication, 1978). In clean air, HNO_3 is expected to be greater than NO_x by as much as a factor of 10 (Liu, 1977; Fishman and Crutzen, 1977; Chameides, 1978), but measurements to test this prediction have not been accomplished. "Total organic nitrate" levels of a few ppb were commonly observed.

ACKNOWLEDGMENTS

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INDOPHENOL AMMONIA TEST IN MEASUREMENT OF HNO_3 AND NO_3^-

Allen L. Lazrus

B. W. Gandrud

J. P. Greenberg

The National Center for Atmospheric Research
Post Office Box 3000
Boulder, Colorado   80307

INTRODUCTION

Lazrus *et al.* (1968) described a technique for a total inorganic fixed nitrogen test utilizing a rapid reduction of NO_3^- and nitrite ion (NO_2^-) to NH_4^+ by a zinc-copper (Zn-Cu) reduction column, followed by an indophenol ammonia test. Since then, many improvements in the indophenol NH_3 test (Harwood and Huyser, 1970a,b) have been incorporated. The test, in automated form, is performed on the Auto-Analyzer II, and is capable of yielding total inorganic fixed nitrogen and NH_4^+ separately, depending on whether the sample passes through the reduction column. Using the selectivity of the sampling system, the analysis may be used to measure HNO_3 vapor and NO_3^- aerosol. A combination of a Teflon prefilter and nylon filter is suitable for this purpose.

INSTRUMENTATION AND METHODS

Reagents

Sodium Phenate—

Dissolve 85.4 g phenol and 200 ml 5 N sodium hydroxide (NaOH) in deionized H_2O, diluting to 1 liter.

Nitroprusside—

Dissolve 1.32 g sodium nitroprusside $(Na_2Fe(CN)_5NO) \cdot 2H_2O$ in deionized H_2O, diluting to 500 ml.

Sodium Hypochlorite—

Dilute 62.8 ml commercial bleach (with 3.5% available chlorine) to 500 ml with deionized H_2O.

Ethylenediaminetetraacetic Acid—

Dissolve 37.4 g tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) in 1 liter deionized H_2O. Do not heat.

Electrolyte—

Dissolve 262.5 g NaCl in deionized H_2O. Add 40 ml of 1 N HCl and dilute to 1 liter.

Zn-Cu (Lazrus *et al.*, 1968)—

Dissolve 1.0 g cuprous chloride (CuCl) $\cdot$ $2H_2O$ in 80 ml H_2O containing 12 drops of 1 N HCl. To 40 g 20-mesh Zn granules add 40 ml concentrated HCl (diluted 1 to 5 with H_2O), and etch the Zn for 1 min. Pour out the acid and wash the An four or five times with H_2O. Quickly add the CuCl solution to the Zn, and shake vigorously until the blue color just disappears. Immediately swirl the alloy into a filter in a buchner funnel under suction. Wash once with water and then once with methyl alcohol. Let air be drawn past the granules until they no longer stick together; spread the Zn on a large piece of filter paper to dry. Place the dry alloy in a glass-stoppered test tube, and shake vigorously to remove loosely adhering Cu. Separate the Cu powder from the alloy granules. (A sieve to eliminate the fines works nicely.) Fill a glass tube (4-mm i.d., 5-in length) with the alloy, and put a glass wool plug on each end of the tube to contain the granules.

Manifolds

The procedure requires a manifold that satisfies the conditions determined by Harwood and Huyser (1970a,b) and the reduction of Lazrus *et al.* (1968).

The manifold schematic is shown in Figure 1. Removal of the Zn-Cu reducing column allows the determination of NH_4^+. With the reducing column in place, NO_3^- and NO_2^- are reduced to NH_4^+, and the color developed is proportional to $NO_3^- - NH_4^+$, $NO_2^- - NH_4^+$ and $NH_4^+ - NH_4^+$. (The convention $NO_2^- - NH_4^+$ signifies that the nitrogen is in the form of a nitrite ion but is expressed as NH_4^+)

Interference filters that transmit 630 µm light are used in the colorimeter. The reference side of the colorimeter uses only air in the sample path.

Ghia nylon membrane filters, 47-mm diameter, 1.2-µm pore size, are used in the procedure. The filters are extracted with 0.1 N NaOH in a nonionic detergent (5 ppm Brij 35). The extracting solution and filter are subjected to ultrasonic treatment for 15 min, neutralized with HCl using an automatic pipette, and analyzed for NO_3^- and NH_4^+.

The detection limit of the test in its present configuration is 5 ppb N in H_2O, utilizing 0.6 ml H_2O at a rate of 30 samples per hour.

RESULTS AND DISCUSSION

In measuring NH_4^+, the test is effective between pH 2 and pH 8.5. NH_3 begins to disappear from solutions more basic than this (D'Elia *et al.*, 1977). Samples containing only nitrate nitrogen show no variability between pH values 2 and 10. Since the automated system is closed and the sample is acidified during reduction, no NH_3 can be lost. At pH 1, the test results are erratic. As shown in Table 1, the precision of the test appears to be a function of concentration.

The test appears to be free of interferences from organically-bound nitrogen at concentrations in which they typically occur. The flight interferences occur in the indophenol NH_3 test, and they appear to be unaffected by the presence of the reduction column. The interferences may result from NH_3

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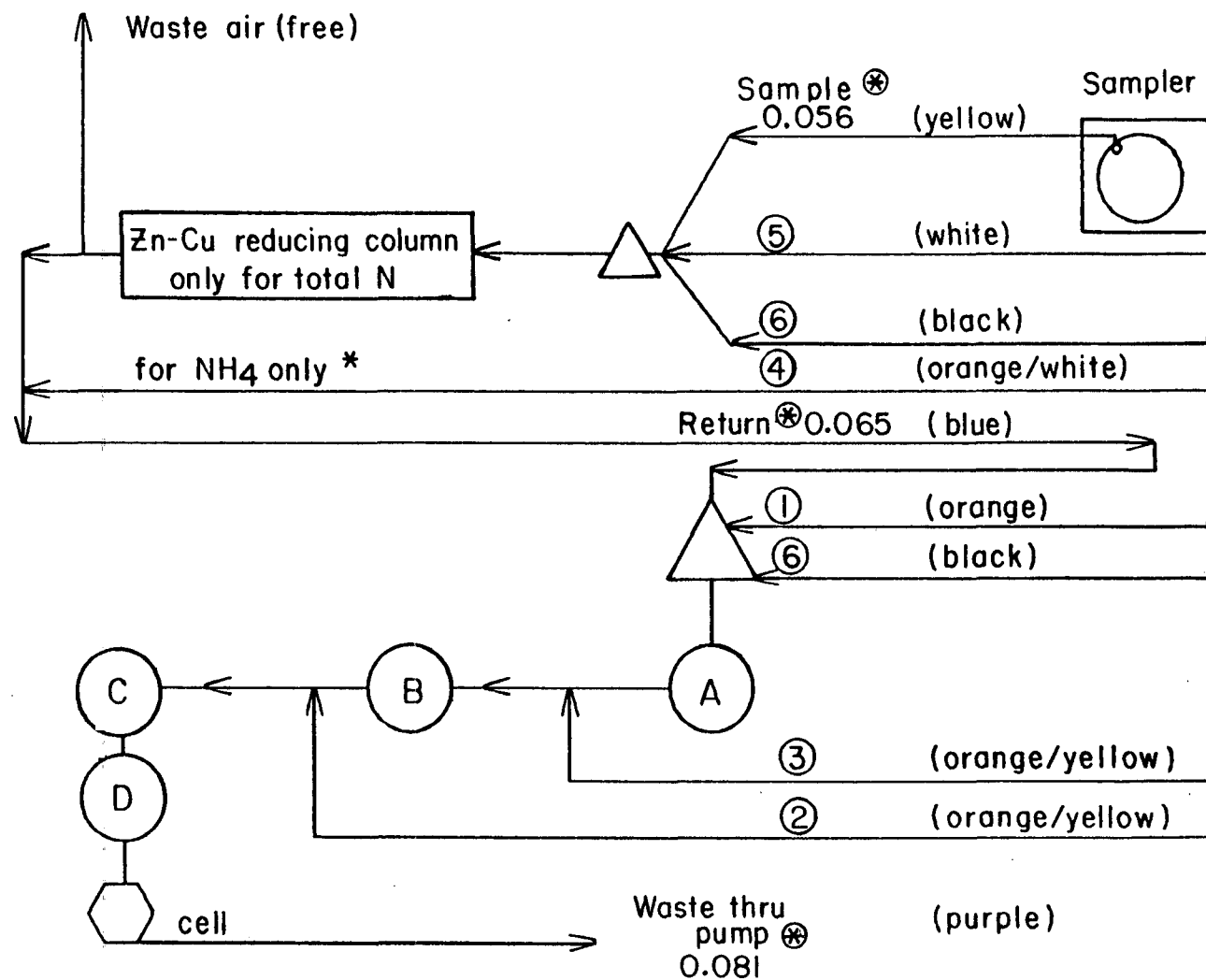
Figure 1. NH_4^+ and total inorganic fixed N manifold. Range: 0.05-2 ppm for NH_4^+; after dilution, 0.05-10.0 ppm NH_4^+. Wavelength: 610-18 nm. Sample rate: 20/hr. A, B, C: Five-turn mixing coils. D: 15-20 min delay coil. ⊛: Solvaflex tubing. Reagents: (1) Sodium phenate 0.035, (2) nitroprusside 0.020, (3) sodium hypochlorite 0.02, (4) EDTA tetrasodium salt 0.025, (5) electrolyte 0.040, (6) air bubbled through 50% H_2SO_4, 0.030. Tubing size is color-coded.

TABLE 1. PRECISION AS A FUNCTION OF CONCENTRATION

Concentration as NH_4^+ (ppm)	Coefficient of Variance (1%)		
	NH_4^+	NO_2^-	NO_3^-
0.05	5.9	2.0	2.1
0.10	3.13	2.4	2.7
0.25	0.46	1.1	1.6
0.50	0.66	0.69	0.54
5.0	0.36	0.22	0.43

TABLE 2. ORGANIC NITROGEN COMPOUND ANALYSIS FOR NH_4^+

Solution (100 ppm NH_4^+)	Response as NH_4^+
ethyl amine HCl	0.94
diethylamine HCl	0.1
hydrazine 2HCl	0.1
aminophenol	1.1
alanine	0.1
aniline sulfate	4.3
dl-phenylalanine	0.15
dl-valine	0.08
glycine	0.06
urea	0.02

contamination of the organic reagents. Solutions of organic compounds equiv-alent to 100 ppm NH_4^+ were analyzed. The NH_4^+ response is shown in Table 2. Hydroxylamine reacts as an inorganic constituent.

The Ghia nylon membrane filters efficiently collect HNO_3 vapor. No NH_4^+ blank was observed.

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DETERMINATION OF ATMOSPHERIC HNO$_3$
WITH NaCl-IMPREGNATED FILTERS AT HIGH VOLUME FLOW RATES

Joseph Forrest

Roger L. Tanner

Daniel Spandau

Ted D'Ottavio

Leonard Newman

Brookhaven National Laboratory
Upton, New York 11973

INTRODUCTION

The existence in the atmosphere of gaseous nitrates, particularly HNO$_3$, has been well documented (Spicer, 1977; Okita *et al.*, 1976; Okita and Ohta, 1978). Moreover, it appears that the concentration in some localities of gaseous nitrates exceeds that of particulate nitrates. Any attempt to understand the formation mechanisms, transformations, and relationships with acid precipitation of nitrogen oxides must necessarily involve the accurate determination of atmospheric HNO$_3$.

INSTRUMENTATION, METHODS, AND RESULTS

Experiments were conducted to explore the possibility of extending the standard Brookhaven National Laboratory (BNL) 5-in diameter high-volume (hi-vol) SO$_2$ and SO$_4^=$ filter pack to permit measurement of plume HNO$_3$ concentrations. The nylon filters described by Spicer were no longer commercially available (and in all probability would not have had the proper flow characteristics for hi-vol employment). Efforts were therefore concentrated on the NaCl-impregnated

cellulose paper technique of Okita, using Schleicher and Schuell Fast Flow 2W filters to achieve maximum flow rates. Sampled papers were extracted in warm H_2O and nitrate measured by a hydrazine reduction-diazotization auto analyzer technique.

When placed downstream from acid-pretreated quartz particulate filters in a hi-vol sampler, single NaCl-impregnated filters collected HNO_3 vapor at efficiencies of about 90%. By combining two filters on a single screen, efficiency was improved to >95% with negligible decrease in flow rate.

Some adsorption of NO_2 on impregnated filters with retention as nitrate had been observed by Okita et $al.$ (1976). This possible interference was evaluated by loading the hi-vol with a quartz prefilter, a double NaCl filter, and a backup double NaCl filter downstream. Upon introducing NO_2 to the sampler at concentrations of 0.5-2 ppm above ambient air, no indication of adsorbed NO_2 as nitrate was detected on the backup filters (Table 1).

NO_2 may react with active catalytic sites on the quartz particulate pre-filters to (a) form retained nitrate, and/or (b) to disproportionate in the presence of moisture to HNO_3 subsequently released and collected as artifact on the NaCl filters. Reaction "b" was evaluated as follows: Ambient air with and without added NO_2 was passed through a filter pack consisting of quartz and NaCl filters to remove atmospheric particulate and gaseous nitrates, followed by an additional quartz filter supplying "reactive sites" and NaCl filters to absorb artifact HNO_3. At NO_2 concentrations of 0.005-2 ppm and relative humidities of 70-100%, less than 1% of incident NO_2 was removed (Table 2). The extent of reaction "a" was assessed by analyzing the second quartz filter for retained artifact nitrate. Again, less than 1% of incident NO_2 was retained by the quartz (Table 3).

Retention capability of 5-in diameter NaCl filters (two sheets) was determined by passing varying amounts of HNO_3 through the hi-vol sampler and measuring collection efficiency by means of backup filters. Absorption capacity was 11 mg HNO_3 before breakthrough occurred.

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TABLE 1.   ADSORPTION OF NO_2 BY NaCl FILTERS IN QUARTZ-NaCl-NaCl FILTER PACK*

Date	Sampling Time, min	NO_2 Concentration, ppm	Total NO_2, mg	Flow Rate, $ft^3\ min^{-1}$	Temperature, °F	Relative Humidity, %	NO_3^- in NaCl Backup Filter, µg
4/20	60	0.91	41	14	70	52	3
4/20	60	0.91	41	14	50	95-60	5
4/24	60	0.91	41	14	70	52	3
4/26	90	0.53	36	14	70	52	4
4/26	90	0.53	36	14	45	70	7
7/5	60	1.0	16	5	70	52	3
7/11	60	2.0	32	5	70	52	3

*Double 4-in diameter NaCl filters on each screen.

TABLE 2. CONVERSION OF NO_2 TO VOLATILE HNO_3 BY QUARTZ FILTERS IN QUARTZ-NaCl-QUARTZ FILTER PACK

Date	Sampling Time, hr	NO_2 Concentration, ppm	Total NO_2, mg	Temperature, °F	Relative Humidity, %	Artifact HNO_3 in Third NaCl Filter, µg	NO_2 Converted to HNO_3 %	Artifact HNO_3/ Total HNO_3,* %
6/27-28	16	ambient	—	72	97	77	—	3.6
6/28	2	ambient	—	84	60	6.8	—	3.0
6/28	2	ambient	—	84	60	7.9	—	5.9
7/27-28	16	ambient	—	72	98	35	—	7.3
7/5-6	16	0.010	6.3	61	86	50	0.57	7.9
8/7-8	16	0.0053	4.4	74	100	13	0.15	11.6
7/11	1	1.0	16	72	70	3.4	0.02	—
7/11	1	2.0	33	72	70	2.3	0.007	—

*HNO_3 concentration range = 0.10-2.9 ppb.

TABLE 3. CONVERSION OF NO_2 TO RETAINED NO_3^- BY QUARTZ FILTERS IN QUARTZ-NaCl-NaCl-QUARTZ-NaCl FILTER PACK

Date	Sampling Time, hr	NO_2 Concentration, ppm	Total NO_2, mg	Temperature, °F	Relative Humidity, %	Artifact NO_3^- in Second Quartz Filter, μg	NO_2 Converted to NO_3^-, %	Artifact NO_3^-/ Total Particulate NO_3^-,* %
6/27-28	16	ambient	—	72	97	21	—	10
6/28	2	ambient	—	84	60	3	—	5.0
6/28	2	ambient	—	84	60	8	—	4.8
7/27-28	16	ambient	—	72	98	22	—	4.0
7/5-6	16	0.010	6.3	61	86	31	0.37	3.6
8/7-8	16	0.0053	4.4	74	100	28	0.47	8.9
7/11	1	1.0	16	72	70	2	0.01	—
7/11	1	2.0	33	72	70	4	0.01	—

*Particulate NO_3^- concentration range = 0.7-4.4 $\mu g/m^3$.

At high humidities, adsorption of HNO_3 on the quartz prefilter became significant, suggesting that relative retention varies inversely with HNO_3 concentration and directly with relative humidity (Figure 1). However, adsorption losses could be minimized by desorption in a post-collection, 10-min sampling period in which drier air is provided by a heat gun.

Loss of collected particulate nitrate during sampling by on-filter reaction with ambient H_2SO_4 to form volatile HNO_3 has long been suspected. The extent of such loss was evaluated by preloading quartz filters with atmospheric particulates (16-hr hi-vol sampling). Opposite quarters of the filters were masked and the remaining areas exposed to generated H_2SO_4 aerosol. Circles (1-in diameter) were cut from each quarter and analyzed for NO_3^- and $SO_4^=$. Differences between exposed and covered sections ranged from 10 to 25 µg NO_3^- per mg of collected H_2SO_4 or (for 16-hr samples of ~1 µg/m^3 NO_3^-) from 4 to 16% of the particulate nitrate per mg of H_2SO_4 (Table 4). Some or all of the NO_3^- losses may possibly have arisen from the reaction of H_2SO_4 with adsorbed HNO_3. After deposition of the aerosol H_2SO_4, the permitted reaction time prior to extraction and analysis of the filters was not carefully controlled. Both of these factors will require further consideration in future experiments.

Cellulose filters impregnated with potassium carbonate (K_2CO_3) were placed in series downstream from quartz and NaCl papers and the filter pack subjected to 0.07 to 1 ppm SO_2 atmospheres. No losses of SO_2 were detected on the preceding filters, indicating the integrated filter pack could be safely used for $SO_4^=$, SO_2, and HNO_3 analyses (Table 5).

Ambient measurements of particulate NO_3^- and HNO_3 concentrations were made over 2- to 16-hr periods. In only 1 of 13 periods was the particulate NO_3^- level decidedly greater than that of HNO_3; in 2 cases, the levels were approximately equal (Table 6). In the remaining 10 periods, the fraction of gaseous nitrate to total nitrate ranged from 0.59 to 0.92, with an average ratio of 0.71 for the 13 measurements (Table 6). Standard deviation for eight duplicate analyses (including errors in hi-vol flow measurements) at HNO_3 levels of
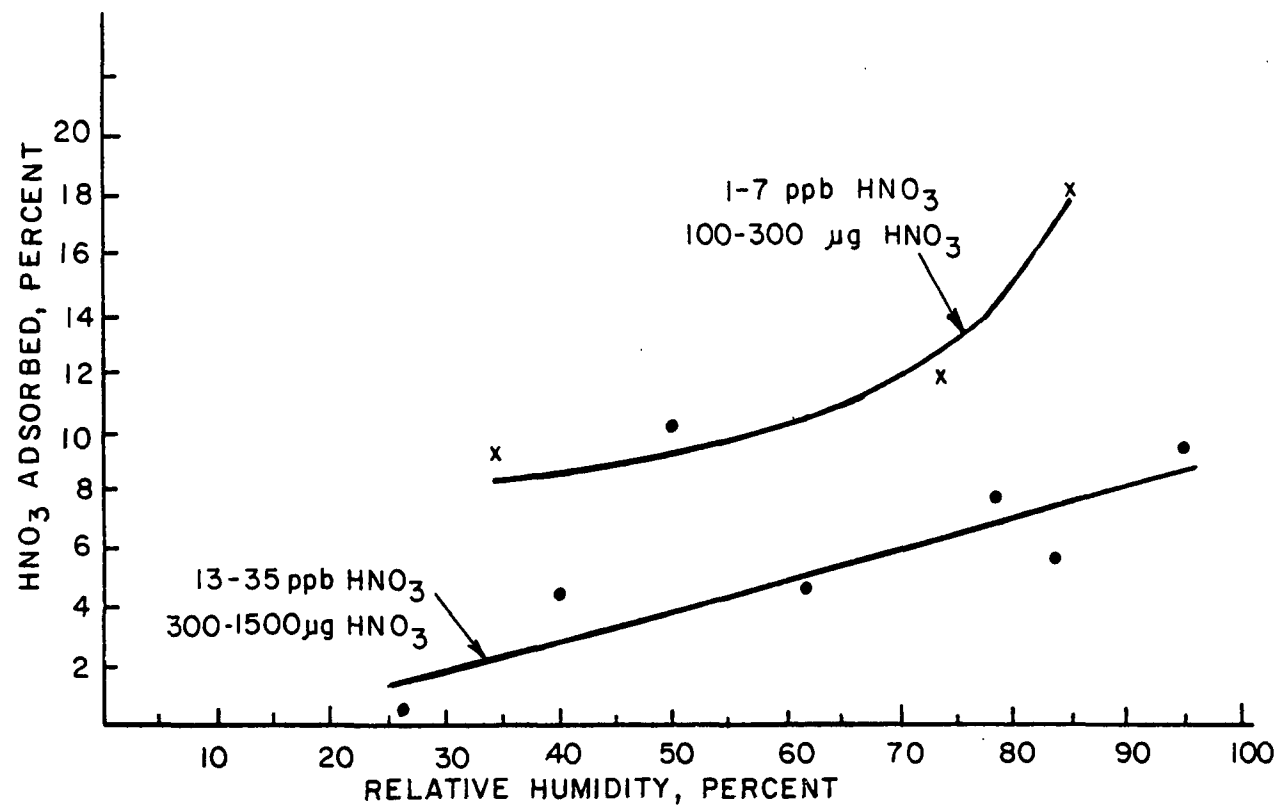
Figure 1. Adsorption of HNO_3 by quartz filters.

TABLE 4. LOSS OF PARTICULATE NO_3^- BY REACTION WITH
AEROSOL H_2SO_4 ON PRELOADED QUARTZ FILTERS

No.	NO_3^-, μg	H_2SO_4 Added, mg	NO_3^-, Lost, %	NO_3^-, Lost per mg H_2SO_4, μg
1	231	3.14	12.9	9.6
2	235	1.00	0.90	2.5
3	241	1.70	17.6	24.9
4	182	1.94	10.5	9.5
5	217	2.54	20.9	17.6
6	365	2.31	14.1	22.0
7	127	1.56	24.8	21.5
8	123	4.06	39.5	11.6

TABLE 5. ADSORPTION OF SO_2 BY K_2CO_3 AND NaCl FILTERS

No.	Sampling Time, min	SO_2 Concentration, ppm	SO_2 Adsorbed, mg K_2CO_3 Filter	NaCl Filter
1	30	0.07	2.14	0.042
2	30	0.30	11.0	0.029
3	7	0.80	6.69	0.050
4	15	1.07	19.0	0.051

TABLE 6. COMPARISON OF PARTICULATE AND GASEOUS NITRATES

Concentration, $\mu g/m^3$		
Particulate NO_3^-	Gaseous HNO_3	Gaseous HNO_3/NO_x*
1.16	1.21	0.34
0.28	1.62	0.85
0.82	1.74	0.68
2.27	3.27	0.59
0.55	5.07	0.90
2.24	5.94	0.73
3.94	1.99	0.34
0.55	4.25	0.89
0.66	7.69	0.92
1.30	5.76	0.82
0.88	3.89	0.82
2.63	2.48	0.49
3.59	16.0	0.82

*Average = 0.71.

TABLE 7. PRECISION OF HNO$_3$ ANALYSES*

| Date | Sampling Time, hr | HNO$_3$ Concentration, ppb | |
		Sample A	Sample B
6/14	18	0.68	0.68
6/19	17	1.97	2.17
6/26	16	1.66	1.28
6/27	16	2.88	2.99
7/5	16	0.74	0.96
7/10	2	2.28	2.24
7/11	2	1.39	1.51
7/18	2	5.86	6.29

*Relative standard deviation = 12%.

0.7-6 ppb was ~12% (Table 7). Minimum detectable concentration (defined as 3 x blank) for a 2-hr sample at flows of 20 ft^3 min^{-1} was ~0.1 ppb HNO_3.

ACKNOWLEDGMENTS

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SELECTIVE COLLECTION AND MEASUREMENT OF GASEOUS HNO_3 IN AMBIENT AIR

Richard J. Hare

M. T. Wininger

William D. Ross

Monsanto Research Corporation
Post Office Box 8, Station B
Dayton, Ohio   45407

INTRODUCTION

Nitrates were found to accumulate on glass fiber filters when hi-vol air samplers were used to collect particulates; these accumulations were caused by interactions of gaseous nitrogen compounds with the filters. NO_2 and HNO_3 vapor are both capable of interacting with the glass fiber filter under sampling conditions normally used for determination of particulate nitrate in air. Consequently, most earlier measurements of particulate nitrate are probably in serious error.

Several techniques have been used to determine atmospheric HNO_3. One such technique is chemiluminescence monitoring; another is the Mast coulometric method, which requires exacting control of conditions, is expensive, and is therefore impractical as a widespread monitoring program.

In the present study, an automated sampling technique was developed for the collection of HNO_3 vapor. In this technique, ambient air is analyzed for HNO_3 vapors by quantitatively collecting the HNO_3 on nylon fibers, extracting the fibers with an NaOH solution, and converting the nitrate in an acid solution of benzene (C_6H_6) to form $C_6H_5NO_2$. The $C_6H_5NO_2$ is then measured by electron capture gas chromatography (ECGC).

TABLE 1. HOUSTON FIELD STUDY MEASUREMENTS OF HNO_3 (PPB, BY VOLUME) AUGUST 1978

Date Sample Time, Flow Rate	Tube Position							
	1	2	3	4	5	6	7	8
Thursday 8/24 35 min @ 3 liter/min	2.8	3.3	2.9	2.4	5.3	10.1	14.9	*
Friday 8/25 35 min @ 3 liters/min	14.4	9.6	2.9	8.1	5.8	2.9	7.7	15.4
Saturday 8/26 65 min @ 4.9 liters/min	2.6	1.0	2.5	2.3	2.5	2.3	3.4	3.4
Monday 8/28 65 min @ 4.9 liters/min	2.3	1.5	2.1	2.0	3.4	2.9	3.7	3.4
Tuesday 8/29 65 min @ 4.9 liters/min	4.6	0.9	2.6	5.8	3.4	4.0	3.1	4.3
Wednesday 8/30 65 min @ 4.9 liters/min	1.8	†	†	0.8	†	1.5	†	†

*Sample lost.
†Sample equal to blank level.

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INSTRUMENTATION AND METHODS

Nitric acid vapors in air are collected on 100 mg of nylon fiber stretched out in a 6 in x 1/4 in Teflon tube. All HNO_3 is retained at concentrations as low as 0.5 ppb with air flows up to 10 liters/min. There are no interferences from exaggerated concentrations of NO and NO_2, even at elevated temperatures and humidity. A Teflon particulate filter, 5 μm pore size, is required in advance of the nylon fiber to remove particulate nitrates which, if unscreened, can interfere with chemical analysis. Laboratory research has indicated no retention of HNO_3 on Teflon filters.

Desorption of HNO_3 from the nylon fiber is accomplished by passing a 1% aqueous solution of NaOH through the filter tube, opposite the direction of air flow sampling. Complete removal of as little as 0.1 μg HNO_3 can be achieved. Reacting the desorbing solution with C_6H_6 and concentrated H_2SO_4 quantitatively converts the HNO_3 to $C_6H_5NO_2$ for ECGC analysis. Minimum detectability of $C_6H_5NO_2$ is 1×10^{-12} g with a linear response range covering five orders of magnitude.

RESULTS AND DISCUSSION

The sampling system and analysis method described above were recently field tested during August 1978 in Houston, Texas. The results of the test are shown in Table 1. The HNO_3 ranged from 1.4 to 14.9 ppb during the course of the study. Collection time for the first 2 days was 35 min; thereafter it was 65 min.

The gas chromatographic method for measuring HNO_3 is highly selective and has excellent sensitivity. The field test measurements of HNO_3 were reasonable and within expected limits. In addition, the instrumentation needed to perform the analysis is widely available and not highly specialized.

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SELECTIVE COLLECTION AND MEASUREMENT OF PARTICULATE NITRATE AND GASEOUS HNO_3 IN AMBIENT AIR

John Tesch

Robert Sievers

Department of Chemistry
University of Colorado
Boulder, Colorado   80309

INTRODUCTION

The ever increasing use of fossil fuels is accompanied by an increase in the emission of NO into the air. The fate of NO involves a number of products, including NO_2, HNO_3 vapor, and particulate nitrate. NO_2 and particulate nitrate have been measured for years, while measurement of HNO_3 vapor has frustrated investigators and is only now beginning to be accomplished. These new measurements give evidence that HNO_3 vapor is a more important member of this family of pollutants than previously believed; this evidence also suggests that a large number of earlier measurements of particulate nitrate might be positively biased by accidental HNO_3 vapor collection. This bias is confirmed by Spicer *et al.* (1974) and by studies in this laboratory.

Chemiluminescence appears to be a highly reliable method for the analysis of NO_2 and NO. Recently, Joseph and Spicer (1978) reported the use of a chemiluminescence monitor for the determination of atmospheric HNO_3. Precise control of conditions is needed for the Mast coulometric method for HNO_3 measurements; this technique is therefore probably unreliable for any extensive monitoring program. A method described by Lazrus and Gandrud (1974) for the determination of HNO_3 vapor in the stratosphere was based on the collection of HNO_3 vapor by IPC-1478 filters impregnated with tetrabutyl ammonium hydroxide

and bis-2-butoxy ethyl phthalate. Okita *et al.* (1976) have collected partic-
ulate nitrate on Fluoropore filters and HNO_3 vapor on a second stage cellulose
filter impregnated with NaCl. The nitrate collected was extracted with warm
water and measured by a hydrazine reduction-diazotization colorimetric tech-
nique (Okita *et al.*, 1976; Newman, this volume).

In the present study, we developed a sampling technique for serial col-
lection of particulate nitrate, HNO_3 vapor, and/or NO_2. The species collected
was analyzed by a modification of the technique described in our earlier paper
(Tesch *et al.*, 1976) with the important difference that Teflon filters were
substituted for the previously used glass fiber filters. The technique in-
cludes conversion of the collected species to a nitroaromatic compound, which
is separated and measured readily, even in very small amounts by ECGC. Hare
et al. (this volume) recently used a partially automated modification of this
technique, substituting nylon sorbent for cotton with excellent success. Used
in an EPA field test in Houston, this technique was sufficiently sensitive to
permit measurement of particulate nitrate and of gaseous HNO_3 every 30 min.
No potentially interfering peaks were seen in the chromatograms.

INSTRUMENTATION AND METHODS

Collection of Particulate Nitrate

Air samples are drawn through a series of a filter and two sorbents by a
vacuum pump. Flow rates vary from 8 to 15 liters of air per min. Typically,
a 1000 liter volume of air is sampled; however, samples as small as 100 liters
are analyzed with acceptable sensitivity and precision for both particulate
nitrate and HNO_3 vapor. Particulate nitrate is collected on 25 mm diameter
Fluoropore filters.

Collection of HNO_3

The determination of HNO_3 vapor in air is based on selective collection
by cotton. Interference from particulate nitrate is eliminated by removing

particulate matter with a Fluoropore filter before passing the air through the cotton. The cotton filter consists of cotton fiber loosely packed to a depth of 3 cm in 0.8-mm i.d. glass tube. Collection studies indicate that >95% of the first 7 µg of HNO_3 vapor passing through this type of cotton filter is collected on the first 0.05 g (~15 mm) of cotton. The amount collected is sufficient to allow accurate determination of HNO_3 vapor in air.

A mixture of concentrated HNO_3 and H_2SO_4 (1 to 3, by volume) recommended by Fehsenfeld et al. (1975) is placed in a 1-cm bulb blown at one end of a heavy-walled capillary tube (2.0-mm i.d., 15-cm length). HNO_3 diffuses from this source at ~1 µg/min at 25° C. Nitrogen gas is passed at 60 ml/min through copper coils in a constant temperature bath and through a constant temperature chamber containing the HNO_3 diffusion tube. The system is allowed to equilibrate overnight to saturate the sites on the glass walls of the tubing.

NO_2 and NO from standard sources are passed through cotton filters; <5% is retained. When a cotton filter is placed in the inlet of a chemiluminescence detector, the concentrations of NO_2 and NO read by the detector are virtually unchanged from those measured without the cotton filter. Repetitions of the experiment at several NO_2 concentrations have indicated little or no detectable retention of NO_2 or NO by cotton filters.

Analysis of Collected Sample

For each nitrogen species collected, analysis begins with conversion to a nitroaromatic compound such as $C_6H_5NO_2$ (Ross et al., 1976; Tesch et al., 1976). The nitroaromatic is separated and quantitated by ECGC. Investigations carried out after completion of the present study indicate that toluene (C_7H_8) can be substituted for the more toxic C_6H_6 satisfactorily, so long as account is taken of nitrotoluene isomers (Wizner and Sievers, unpublished data).

For determination of particulate nitrate, the Fluoropore filter is rolled and placed directly into a 2-dram borosilicate glass reaction vial; 0.20 ml H_2O, 1.00 ml C_6H_6, and 1.00 ml concentrated H_2SO_4 are added. The vial is

capped and shaken for 10 min to allow the nitration reaction to proceed to essential completion. The upper C_6H_6 layer is removed, and a 1-μl aliquot is injected into the ECGC instrument. The peak height of the $C_6H_5NO_2$ generated is compared with a calibration plot generated from injection of standard concentrations of $C_6H_5NO_2$ in C_6H_6. Chromatographic conditions are described below.

The first 0.05 g (~4 mm) of cotton are removed from the inlet of the cotton fiber filter, placed directly into a vial, and analyzed by the same method as earlier described for the Fluoropore filters. A second 0.05-g portion of the sampled cotton and an unsampled portion also are analyzed to assure complete collection by the first piece of cotton and to allow for measurement of a blank concentration due to contaminant nitrate on the cotton. If more than 0.08 g cotton is placed in the reaction vial, incomplete nitration results.

The larger volume of the molecular sieves requires that they be analyzed in a 50-ml Erlenmeyer flask with a ground glass stopper. Reagent amounts were increased tenfold; H_2O is replaced by 0.1 N H_2O_2. Addition of H_2O_2 is a necessary oxidizing process because NO_2 is disproportionated in H_2O to form equal amounts of NO_3^- and NO_2^-, and the latter would not be converted to $C_6H_5NO_2$. Occasionally, up to 5 ml H_2O is added after the reaction is complete to displace the C_6H_6 from the molecular sieves for analysis. Because of the larger amount of reagents required, sensitivity is significantly decreased. For this reason, chemiluminescence detection is probably a preferred method for NO_2 measurement.

Apparatus and Reagents

Gas Chromatographic Conditions—
  Chromatographic analyses are performed on Hewlett-Packard Models 402 and 5750 gas chromatographs equipped with [63]Ni and titanium tritide electron capture detectors (fixed frequency, variable current), respectively. The columns contain 1.5% SE-30 polydimethylsiloxane coated on 80-100 mesh acid-washed Chromosorb G, packed in glass tubing (76 cm x 4-mm i.d.) or heavy-walled

Teflon tubing (51 cm x 3-mm i.d.). Isothermal column temperatures between 100° and 190° C are used for various experiments, and carrier gas flow rates of 40 and 60 ml/min of 90/10 Ar/CH_4 are employed. The detector temperature most commonly is 180° C; the injection port temperature is 200° C.

Hi-Vol Air Sampler—

Airborne particulate samples are collected over 24-hr periods with a Precision Scientific hi-vol sampler meeting American Society for Testing and Materials (ASTM) standard D2009.

Chemiluminescent Analyzer—

Chemiluminescent measurements of NO and NO_2 are made using a Model 14D dual chamber $NO-NO_2-NO_x$ analyzer from Thermo Electron Corporation, 85 First Avenue, Waltham, Massachusetts 02154.

Reagents—

Reagent grade H_2SO_4 and thiophene-free, reagent grade C_6H_6 are available from both Fisher Scientific and J. T. Baker, Inc. Precautions noted by Ross *et al.* (1976) with regard to H_2SO_4 purity should be observed. Both the C_6H_6 and the H_2SO_4 may be used without additional purification. Other liquid organic reagents are supplied by commercial sources and are purified by fractional distillation at least once prior to use. All other reagents are used without further purification.

Filters—

Glass fiber filters (8 in x 10 in) meeting ASTM D2009 requirements are supplied by Fisher Scientific Company (Catalog No. 1-037-048). Quartz filters (8 in x 10 in, 2500 QAST) are obtained from Pallflex Products Corporation, Kennedy Drive, Putnam, Connecticut 06260. U.S. Pharmacopoeia (USP) sterilized absorbent cotton (1 lb. roll, seamless, No. 96-9116) is available from Swansdown Corporation, New Haven, Connecticut 06503. Nylon fiber wool is a product of Atlas Electric Company. Pyrex wool filtering fiber (Catalog No. 3950) and porous glass beads may be obtained from Corning Glass Works, Corning, New York.

Uni-Pore polycarbonate membrane filters (25-mm diameter, 0.8-μm pore size, Catalog No. 312-0059) are supplied by Bio-Rad Laboratories, 2200 Wright Avenue, Richmond, California 94804. Duralon (nylon, 25-mm diameter, 1.0-μm pore size, Catalog No. NRWPO2500), Mitex (Teflon, 25-mm diameter, 5.0-μm pore size, Catalog No. LSWPO2500), and Fluoropore (reinforced Teflon, 25-mm diameter, 0.5-μm pore size, Catalog No. FHLPO2500) filters are available from Millipore Corporation, Bedford, Massachusetts 01730.

Molecular sieves, Linde Type 5A calcium aluminosilicate (pore size 5 angstroms, 40-60 mesh) may be obtained from Matheson, Coleman, and Bell, Inc., Norwood, Ohio.

Zeolon 200H molecular sieve particles have physical dimensions of 1/16-in diameter x 1/4- to 1/2-in length and a bulk density of 47 lb/ft^3. The material is a synthetic crystalline aluminosilicate with a 10 to 1 ratio of silica to alumina, and is very resistant to acid attack. The crystalline material has an effective pore size of 8-9 angstroms.

Precision Wet Test Meter—

A Precision Scientific wet test gas meter (Catalog No. 63125) meeting ASTM D1071 is used for measuring high gas flow rates and volumes when samples are collected with other than the hi-vol sampler. Mallinckrodt $C_6H_5NO_2$ (Chem Services, West Chester, Pennsylvania) is employed to prepare calibration standard solutions.

DISCUSSION

When standard sources of HNO_3 vapor and NO_2 are passed through the Fluoropore filters, not more than 5% (the detection limit under the conditions tested) of each is collected, even when extended sampling times and slow flow rates (60 ml/min) are employed. In general, collection efficiencies of particulates on these filters are reported (Okita et al., 1976) >95% at flow rates up to 20 liters/min., but the collection efficiency of nitrate salts is difficult to estimate owing to the low but significant volatility of NH_4NO_3. It

should be borne in mind, however, that the suspended particles being collected are already bathed in the same air which is being drawn through the filters over the collected particles. Consequently, provided that sampling times are kept short, losses due to volatilization of NH_4NO_3 will be minimal. Furthermore, the air being drawn through contains some gaseous HNO_3, and sometimes significant concentrations of NH_3. Therefore, loss of NH_4NO_3 from the filter is much less than would be predicted from the vapor pressure, assuming perfectly clean air is being drawn through the filter.

Filter/Sorbent Comparison for HNO_3 Vapor and NO_2 Collection

Several filters and sorbents were tested for collection efficiency with both HNO_3 vapor and NO_2. Filters tested were 25-mm in diameter and held in a polycarbonate aerosol filter holder (Bio-Rad No. 342-0004). Nitrogen streams containing HNO_3 vapor and NO_2 at concentrations varying from a few ppb to 1 ppm were passed through the filters at flow rates from 30 ml/min to 15 liters/min. Filter analysis was accomplished by placing the entire filter into the reaction vial prior to adding the H_2O, C_6H_6, and H_2SO_4. To insure complete recovery of $C_6H_5NO_2$ with the filters present, samples containing various concentrations of NO_3^- in H_2O were added to unsampled filters and reacted. Percent recoveries were computed for HNO_3 by bubbling the gas through a frit into 50 ml of 0.1 N NaOH. The NaOH was analyzed by the general microanalysis procedure described in an earlier paper (Tesch *et al.*, 1976). Percent recoveries for NO_2 were calculated, based on the weight loss of the permeation tube.

The results of these studies are listed in Table 1. Teflon filters did not retain detectable amounts of HNO_3 vapor or NO_2, and therefore were selected as the material for the first stage of the collection system. Nitric acid vapor was collected on several of the other filters and sorbents, but the amount collected varied greatly with flow rate and concentration. These data also show that a significant error is introduced when collecting particulate nitrate on glass fiber filters. We attribute the high collection efficiency of the IPC-1478 filter to its high cotton content. It should be noted that both cotton and nylon collected HNO_3 vapor selectively and quantitatively over

a wide range of flows and concentrations. This remained true even when air and nitrogen were bubbled through H_2O prior to passing through the HNO_3 or NO_2 sources, indicating that NO_2 was not converted to HNO_3 and collected in the presence of H_2O vapor when passed through nylon or cotton at these concentration levels.

TABLE 1. COLLECTION EFFICIENCY OF FILTERS AND SORBENTS* FOR HNO_3 VAPOR AND NO_2

Substance	Percent HNO_3	Percent Recovered NO_2
Fluoropore filter	†	†
Mitex filter	†	†
Duralon filter	47-66	†
Unipore filter	6-30	†
Quartz filter	56	‡
Glass fiber filter	38-92	0-22
IPC-1478 filter	89-94	1-5
Whatman-41 filter	10-81	†
Porous glass	35-95	32-64
Cotton	95-100	†
Nylon	95-100	†
Molecular sieves	‡	55
Drierite	75	‡

*Based on 3-cm collection path.
†No data.
‡Not tested.

Sampling Problems and Differentiating Particulate Nitrate and Gaseous HNO_3

If the air contains high concentrations of H_2SO_4 aerosols, some particulate nitrate may be displaced from the filter and collected as HNO_3 on the second stage cotton sorbent. Although perhaps less likely, the opposite effect might be seen if basic sites exist in the particulates on the Teflon

filter. If large volumes of air are passed thorugh particulates already collected, the particulate matter may collect some HNO_3 vapor by reaction with basic constituents or by adsorption. For this reason, the volume of air passed over particles already on the filter must be kept to a minimum. It seems clear, however, that removal of gaseous HNO_3 on collected particulates on Teflon filters is not nearly as great as that unavoidably collected on glass fiber filters, which appear to have basic sites on the glass fiber surfaces. Even relatively acidic quartz fiber filters retain some gaseous HNO_3. To minimize possible artifacts, one must shorten sample times and/or reduce linear velocities of air drawn through the filters.

Measurements of particulate nitrate and HNO_3 vapor in air sampled at the University of Colorado campus were made intermittently during the spring of 1977 using a combined two-stage filter. Sampling time was in general from 30 min to 2 hr at 8 to 15 liters/min air flow rate. Each filter was analyzed as previously described. Results of these analyses are listed in Table 2. As can be seen, HNO_3 vapor is a significant contributor to air pollution, even in relatively clean areas. These values are about a factor of 10 higher than those found at Fritz Peak, Colorado, in a remote area high in the mountains near the Continental Divide (Wizner and Sievers, unpublished data).

Nylon fibers have been shown by a number of workers to collect HNO_3 vapor (Spicer *et al.*, 1974; Hare *et al.*, this volume). Although no significant advantages are apparent for its use in preference to cotton, tests were conducted to insure that recovery of HNO_3 and its conversion to $C_6H_5NO_2$ could be accomplished quantitatively when nylon was the collection medium. No interferences were found with nylon; however, the cotton fibers were finer, giving more surface area, and total collection requied less fiter material with cotton than nylon. Consequently, it would appear that nylon fibers can be substituted for cotton without any compromise in the efficacy of the in-tegrated selective measurement method described here.

Short sampling times and reduced volume throughout can be achieved only with a highly sensitive method, such as that described here based on ECGC. In

TABLE 2.   REPRESENTATIVE MEASUREMENTS OF PARTICULATE NITRATE
AND HNO_3 IN AMBIENT AIR*

| Date | Time | Concentration ($\mu g/m^3$) | |
		Particulate Nitrate	HNO_3 Vapor
10 May	1013-1113	2.56	0.57
	1150-1330	2.07	1.22
12 May	1230-1350	0.82	0.80
13 May	0830-0930	0.92	0.49
16 May	1944-2109	0.30	0.51
17 May	0825-0910	0.63	0.74
	0925-0956	0.43	0.30
	1258-1333	0.75	0.27
	1549-1632	0.49	0.98
23 May	1415-1628	0.29	0.31
24 May	1352-1609	0.23	0.13
2 June	1055-1456	0.90	0.42
3 June	1340-1545	0.48	0.63
7 June	1055-1210	0.32	0.30
8 June	1348-1518	0.19	0.20
14 June	1003-1203	1.05	0.79

*All measurements were made at the University of Colorado, Boulder, Colorado, in 1977.

the EPA field test (Hare *et al.*, this volume), samples were taken every 30 min, and the signal to noise (and blank) ratio was sufficient to allow measurements to be taken with much lower volumes of sampled air than required for other methods of analysis.

ACKNOWLEDGMENTS

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THE DENUDER DIFFERENCE EXPERIMENT

Robert W. Shaw

Thomas G. Dzubay

Robert K. Stevens

Inorganic Pollutant Analysis Branch
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina   27711

INTRODUCTION

Nitrates in the atmosphere may occur as solids (e.g., ammonium or metal nitrates in particles) or as gases (e.g., HNO_3), and a difficulty has existed in distinguishing between them because of possible nitrate artifact formation during sampling. The problems of atmospheric nitrate artifacts are now thought to be of two kinds: (1) the formation of particulate nitrates from gaseous nitrates on a collection filter (positive artifacts), and (2) the loss of particulate nitrates as gaseous nitrates due to chemical reactions on the filter (e.g., H_2SO_4 aerosol and particulate nitrates reacting to particulate sulfates and gaseous HNO_3) or evaporation. The occurrence of positive nitrate artifacts has been reported by Stevens *et al.* (1978a) and Spicer *et al.* (1978), and the loss of particulate nitrate by chemical reaction on the collecting filter has been demonstrated in the laboratory by Harker *et al.* (1977). The objective of the Denuder Difference Experiment (DDE) is separately to determine particulate nitrate and gaseous HNO_3 without influence of either type of artifact.

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INSTRUMENTATION AND METHODS

The DDE requires two sampling assemblies. Both assemblies consist of a Teflon particle filter followed by an HNO_3 collection tube (Hare *et al.*, this volume). For one of the assemblies, however, the particle filter is preceded by an acid gas diffusion denuder (Stevens *et al.*, 1978b) coated with a strong base; under typical operating conditions, the residence time of a particle in the denuder is approximately 0.4 seconds. This denuder will remove acid gases (in particular, HNO_3) and pass aerosol particles. Thus, the difference between the amounts of nitrate collected by the two assemblies is due only to the removal of gaseous HNO_3 in one assembly. The measured quantities are expressed as follows:

Quantities of Interest

N_T = total atmospheric nitrate (particulate nitrate and gaseous HNO_3)

N_P = particulate nitrate

N_H = gaseous HNO_3

Observed Quantities

F_D = nitrate measured on filter behind denuder

F = nitrate measured on filter in assembly without denuder

T_D = nitrate measured on collection tube behind denuder

T = nitrate measured on collection tube in assembly without denuder

Thus

N_H = $N_T - N_P$

N_T = $F + T$

N_P = $F_D + T_D$

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Therefore

$$N_H = (F + T) - (F_D + T_D)$$

Notice that the experiment depends on the following characteristics of the apparatus:

(1)   The diffusion denuder removes all gaseous HNO_3 and passes all particles;

(2)   The combination of particle filter and HNO_3 collection tube collects all gaseous HNO_3 and particulate nitrate; and

(3)   The two assemblies sample equal amounts of air.

DISCUSSION

The results of the DDE are not affected by artifacts due to loss of particulate nitrate as HNO_3 from the filter or gain of particulate nitrate from reactions of HNO_3 on the filter. In fact, the DDE results may be used to determine the amount of nitrate loss or gain due to artifacts. From the definitions above, we see that T_D is equal to the amount of nitrate lost as HNO_3 from the filter, since the diffusion denuder prevents gaseous HNO_3 from entering the filter-collector assembly. On the other hand, particulate nitrate gain from HNO_3 is given by the difference $F - F_D$. Since nitrate formation from HNO_3 is negligible for Teflon filters (Spicer *et al.*, 1978), any measurable gain would presumably be due to gaseous conversion on the collected aerosol.

In this discussion it has been assumed that amounts of gaseous nitrates, other than HNO_3, are negligible. If amounts of other gaseous nitrates are significant, their effect on the DDE can be determined by considering the event matrix:

Collector Efficiency	Denuder Efficiency 100%	0%
100%	$T_D = 0$ $T = X$	$T_D = X$ $T = X$
0%	$T_D = T = 0$	$T_D = T = 0$

Here X is the amount of gaseous nitrate (not HNO_3) that enters the system; T and T_D have been previously defined. For simplicity, we assume that no particulate nitrates are present. If the diffusion denuder removes the gaseous nitrate and the tubes are capable of collecting it, the amount of gaseous HNO_3 determined will be too high by the amount X. This is demonstrated by the relation

$$N_H = (F + T) - (F_D + T_D)$$

In this case (as represented by the upper left matrix element)

$$N_H = T - T_D = X$$

In all other cases, the values of N_H are not affected. If the denuder does not remove the gaseous nitrate and the tube collects it (as represented by the upper right matrix element), the value N_P will be too high by the amount X. For all other cases, the values of N_P are not affected.

As mentioned above, loss of particulate nitrate may occur by evaporation from the collecting filter. Significant losses of NH_4NO_3 have been observed in the laboratory in an extreme experiment — loading a filter with pure NH_4NO_3 aerosol and subsequently passing clean air through it (D. Reutter, private communication). Because of their much lower vapor pressures, metal nitrates are expected to show much lower evaporative losses than NH_4NO_3.

Losses of NH_4NO_3 by evaporation from urban aerosols may be suppressed by: (1) presence of gaseous NH_3 and HNO_3 in the atmosphere in equilibrium with the particles, and (2) reduction of vapor pressure of the particles due to the presence of other materials. If evaporative loss from the filter occurs, however, we expect the NH_4NO_3 to decompose according to

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$
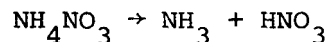
Because the HNO_3 collection tubes follow the particle filters, DDE results are not affected by evaporative loss. If more than one artifact process becomes significant, however, interpretation of the DDE may become complicated.

To summarize, the DDE provides the following measures of atmospheric nitrates:

N_H = gaseous HNO_3

N_P = particulate nitrate

N_T = total atmospheric nitrate

T_D = artifact due to loss of particulate nitrate by reaction on the filter

$F - F_D$ = artifact due to gain of particulate by transformation of gaseous nitrate

ACKNOWLEDGMENTS

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16. ABSTRACT

Presentations given at a workshop on "Measurement of Atmospheric NItrates" (Southern Pines, N.C. October 3-4, 1978) are documented. The authors consider various analytical methods to measure ambient concentrations of nitric acid and artifact nitrate formation.

17. KEY WORDS AND DOCUMENT ANALYSIS

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