New Instrumentation for Airborne Acid Rain Research

Roger L. Tanner[a]; Peter H. Daum[a]; Thomas J. Kelly[a]

[a] Environmental Chemistry Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York, U.S.A.

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ROGER L. TANNER, PETER H. DAUM and THOMAS J. KELLY

Environmental Chemistry Division, Brookhaven National Laboratory, Department of Energy and Environment, Upton, New York 11973, U.S.A.

Instrumental methods have been developed for continuously measuring sulfur dioxide, aerosol sulfur, nitrogen oxides, nitric acid, and ammonia from an aircraft sampling platform. Emphasis has been on modifications to reduce limits of detection to allow sampling at ambient concentrations in the vicinity of clouds. Characterizations based on ambient sampling data, in conjunction with data on cloud water composition and knowledge of the interphase behavior of nitrogen and sulfur oxides and oxyacids, will be used for quantitative evaluation of species contributions to the ionic content of precipitation.

A flame photometric instrument with enhanced sensitivity for airborne measurements of both gaseous and aerosol sulfur compounds has been designed and constructed. Ambient airborne levels of less than 1 ppb may be detected using sensitivity enhancement, and effects of pressure changes on instrumental response have been eliminated.

Sensitive, real-time measurements of NO_x and HNO_3 have been achieved by modified commercial ozone-chemiluminescence detectors. These modifications include: (a) operation at low pressure and large throughput; (b) use of an enlarged, more efficient reaction chamber; and (c) use of a pre-reactor to obtain more stable background. The detection limit for a dual channel instrument for aircraft use is <0.2 ppb (5 second time constant). Nitric acid is determined continuously by difference using a nylon filter in one stream.

An instrument has been constructed for airborne measurements of atmospheric ammonia based on a continuous, fluorescence-derivatization technique. Ammonia is scrubbed into aqueous acid, derivatized and measured in a small filter fluorimeter (HPLC detector). Current detection limit is about 0.25 ppb NH_3 with response time of ~2.5 min.

Data acquired from instrument test flights and preliminary characterization flights with this instrument package are discussed.
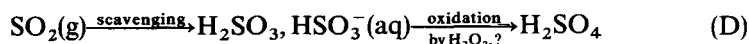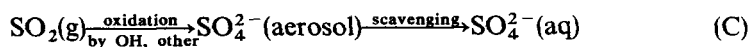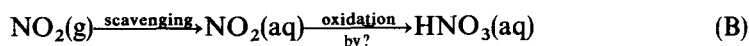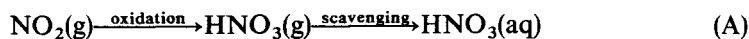
KEY WORDS: Acid rain, aerosol sulfur, flame photometry, HPLC detectors, sulfur oxides, ammonia, nitric acid.

INTRODUCTION

It is now generally recognized that the ionic content of precipitation in eastern North America and Europe consists principally of sulfate, nitrate,

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strong acid (H^+) and, to a lesser extent, ammonium. An important experimental capability required in research efforts to understand the atmospheric processes by which precipitation obtains its ionic content is that of measuring cloudwater composition and relating this composition to concentrations of pertinent gaseous and aerosol species in clear air (below, between clouds) and in interstitial air within clouds. These ambient characterization data, in conjunction with laboratory-derived aqueous kinetic rate and equilibrium data, may then be used to evaluate the importance of processes by which ions are formed or incorporated into precipitation. Potential processes include, at minimum, the following:

$$NO_2(g) \xrightarrow{\text{oxidation}} HNO_3(g) \xrightarrow{\text{scavenging}} HNO_3(aq) \qquad (A)$$

$$NO_2(g) \xrightarrow{\text{scavenging}} NO_2(aq) \xrightarrow[\text{by?}]{\text{oxidation}} HNO_3(aq) \qquad (B)$$

$$SO_2(g) \xrightarrow[\text{by OH, other}]{\text{oxidation}} SO_4^{2-}(\text{aerosol}) \xrightarrow{\text{scavenging}} SO_4^{2-}(aq) \qquad (C)$$

$$SO_2(g) \xrightarrow{\text{scavenging}} H_2SO_3, HSO_3^-(aq) \xrightarrow[\text{by } H_2O_2,?]{\text{oxidation}} H_2SO_4 \qquad (D)$$

This paper discusses the development of the experimental capability to directly measure key species in clear air and cloud waters at ambient concentrations using real-time or short-time-duration sampling techniques from an airborne sampling platform, the BNL Atmospheric Sciences research aircraft (twin engine, Britten-Norman Islander).[1] The principal emphasis will be on the clear air measurement techniques for: (a) nitrogen oxides and nitric acid using a commercial ozone chemiluminescence analyzer which has been modified to improve sensitivity and background stability and to provide continuous measurement capability for HNO_3; (b) sulfur dioxide and aerosol sulfur using a dual-channel flame photometric detector employing mass-flow control for altitude stability and sensitivity-enhancement through use of SF_6-doped hydrogen; and (c) ammonia using a continuous fluorescence derivatization technique devised in our laboratory. Recent developments in cloud water sampling and in-situ chemical measurements, and in sampling interstitial air for gaseous and aerosol measurements are briefly mentioned.
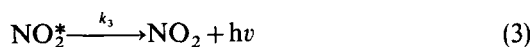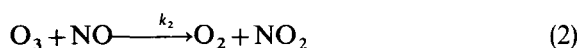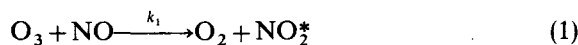
EXPERIMENTAL DESIGN

Cloud liquid water collection

A cloud liquid water collector with gas separator (to produce droplet free air for gas and aerosol sampling) (CWC/GS) has been fabricated

according to the design of the Central Electricity Research Laboratory (CERL), United Kingdom.[2] This device, constructed of Lucite and stainless steel, is mounted inside the airplane cabin, and attached to aluminum tubing which ducts ram air into the cabin. A portion of the air processed by the CWC/GS is then sampled by the BNL filter pack for aerosols and SO_2.[3] A modification of the original CERL-design (enlarging the collection ring) has enhanced coupling of the tangential component of the airflow into the collection ring and extraction ring, thus improving the cloudwater collection efficiency. A second cloudwater collector, of the slotted rod design as developed by the Atmospheric Sciences Research Center (ASRC), State University of New York at Albany[4] has also been installed on the aircraft. Laboratory tests have shown that neither the CERL CWC/GS nor the ASRC cloudwater collector affects the chemical integrity of the collected samples. A cell for continuous conductivity and/or pH measurements of cloudwater samples collected from the ASRC collector has been constructed and tested, and preliminary tests have been successful. Analysis of cloudwater samples for principal ions—H^+, NH_4^+, Na^+, Ca^{2+}, SO_4^{2-}, NO_3^-, Cl^-—is done by conventional techniques.

Modified chemiluminescent analyzer for NO_x and (NO_x-HNO_3).

Ozone chemiluminescence analyzers for oxides of nitrogen are based on the sequence of reactions, (1)–(4);

$$O_3 + NO \xrightarrow{k_1} O_2 + NO_2^* \tag{1}$$

$$O_3 + NO \xrightarrow{k_2} O_2 + NO_2 \tag{2}$$

$$NO_2^* \xrightarrow{k_3} NO_2 + h\nu \tag{3}$$

$$NO_2^* + M \xrightarrow{k_4} NO_2 + M \tag{4}$$

The signal enhancement to be expected[5] from certain modifications can be analyzed by reference to the general response function in Eq. (5):

$$S = Gal = (Ga)\left(\frac{k_1}{k_1 + k_2}\right)\left(\frac{k_3}{k_4}\right)\frac{[NO]F}{P}\left\{1 - \exp-\left(\frac{\tau_r}{\tau_{NO}}\right)\right\} \tag{5}$$

where S = output signal, G = geometric factor, a = PMT sensitivity factor and I = chemiluminescent intensity (photons/sec) within the chamber. I is determined by the fraction of NO_2 formed in the excited state by the O_3-NO reaction, $k_1/(k_1 + k_2)$; the fraction of radiative deactivation of NO_2^*

(under conditions where $k_4[M] \gg k_3$ and $[M]$ is expressed as the pressure), k_3/k_4; the nitric oxide concentration, $[NO]$, molecules/cc; the flow rate, F, cc/sec; and the fraction of chemiluminescent photons emitted in the chamber (term in brackets), τ_r and τ_{NO} being the characteristic chamber residence time, (V/F) (V=chamber volume), and NO reaction time, $\{[k_1 +k_2)[O_3]\}^{-1}$, respectively. Improvements in sensitivity are thus expected to accrue from increasing G (light collection efficiency), decreasing P, increasing F(and to some extent V), and increasing $[O_3]$.

A Monitor Labs Model 8840 chemiluminescent NO_x detector has been modified according to the general design indicated in Figure 1 and the instrument installed on the aircraft. A pre-reactor (1.5 L vessel of stainless steel) has been plumbed into the ozone inlet line to the chambers. Mixing of sample air and ozone flow in this chamber results in completion of the O_3–NO reaction away from the chamber, thereby eliminating all signal due to this chemiluminescent reaction. The only background chemiluminescence now occurring in the chambers results from wall reactions, and thus diversion of sample stream through this pre-reactor produces a very stable instrument zero reading.

A larger sampling pump (Alcatel Model 1012A, nominal 300 L/min capacity) has been installed along with glass capillaries in the sample inlet lines, thus reducing the operating pressure in the chambers to 10 torr at a 1.6 L/min flow rate. The original reaction chambers have been replaced by gold-plated stainless steel reaction chambers of much larger volume (150 cc each). A second ozone source has been added to the instrument, increasing the ozone concentration and thus the sensitivity.

Since the instrument is a dual-channel device, NO_x (defined here as NO $+NO_2+HNO_3+PAN$) may be measured in the particulate-filtered air stream to one chamber/detector by passing the air stream through a molybdenum converter. Simultaneously, NO_x less nitric acid may be measured in the airstream to the other chamber/detector by passage through both a nylon filter and a molybdenum converter, since nylon filters have been found to selectively trap HNO_3 at high efficiency while quantitatively passing NO, NO_2 and PAN.[6] NO alone may be measured in one channel by by-passing the converter.

With the above modifications a significant reduction in background noise has been attained, and the limit of detection has been reduced from about 4 ppb to 0.2 ppb, based on a signal/peak-to-peak noise ratio (S/N) of 2 at an instrumental time constant of 5 sec. The detection limit for HNO_3 measurement by difference is ~0.3 ppb; the most sensitive range is ~9 ppb full scale. Calibrations with NO as low as 1.8 ppb have been performed and direct HNO_3 calibrations with a low-level capillary source are in progress.
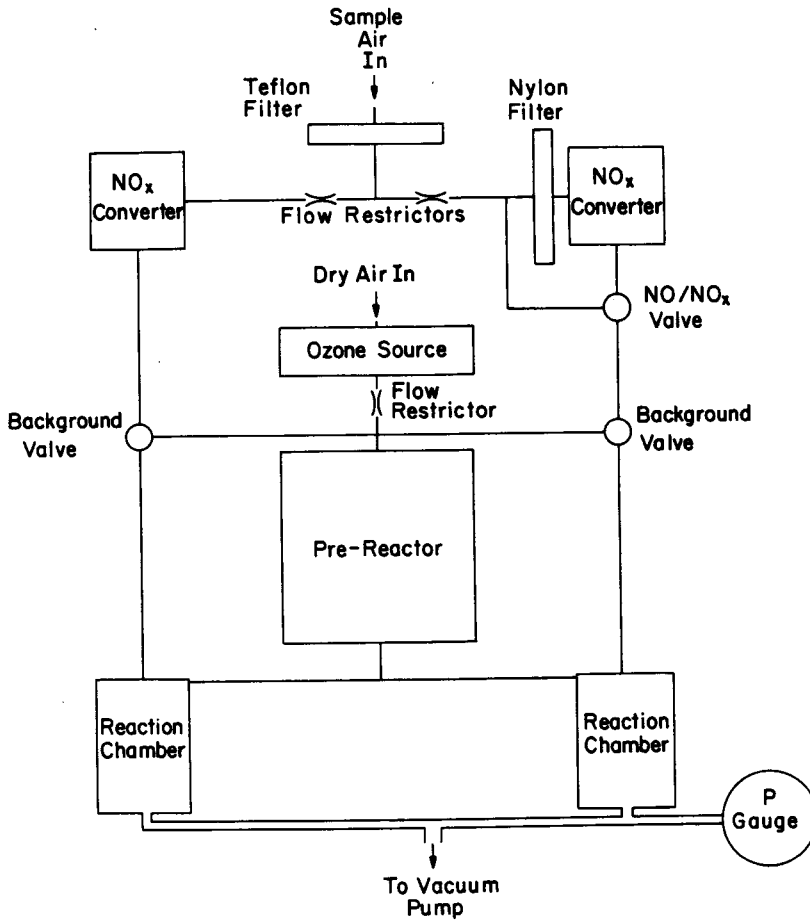
FIGURE 1 Design for ozone chemiluminescence oxides-of-nitrogen, nitric-acid detector with enhanced sensitivity.

Dual Flame Photometric Detector (FPD) for SO$_2$ and Aerosol S.

A Meloy Model 260 sulfur analyzer has been used as the basis for a dual-channel flame photometric instrument for airborne measurements of both gaseous and aerosol sulfur. The details of the construction and testing of this device will be reported elsewhere,[7] but the pertinent elements for airborne measurements in and about clouds are given below. Based on previous work with ground-based FPD instruments,[8,9] an instrument with two inlets was constructed, one with an inert filter in line

for measurements of gaseous sulfur (principally SO_2), and one with a lead(II) oxide-glycerol-coated denuder to remove SO_2 and H_2S for measurements of aerosol sulfur (principally sulfate). Calibrations are done for both channels by direct admission of SO_2, based on previously demonstrated equivalence of response to SO_2 and aerosol ammonium sulfate in this instrument. To avoid the complications of zero drift affecting the accuracy of sulfur response,[9] output sulfur current is recorded directly without linearization.

Two major problems in using an FPD technique for determination of low ambient levels of SO_2 and aerosol S from an airborne platform have been overcome in our design. One is the major changes in background current and the more modest changes in sulfur response curves that occur when the sample inlet pressure is changed during flight. This so-called altitude effect is due to the sensitivity of background current and sulfur response to both the H_2/O_2 ratio and total mass flow of H_2+air in the burner. This effect is largely eliminated[7] by controlling the mass flow of H_2 entering the burner block and of combustion gas exiting the burner block (the latter after removal of condensable water), using Tylan mass flow controllers. The mass flow of sample air is thus controlled by difference, independent of inlet pressure, down to at least 0.65 atm.

The second problem is the limited sensitivity of the conventional FPD, in that non-urban SO_2 concentrations are sometimes below, and aerosol sulfur concentrations frequently below even the optimistic limit of detection ($\sim$1 ppb) of the instrument reported by Coburn et al.[10] However, a sensitivity-enhancement technique is suggested by the semiquadratic nature of the FPD response to sulfur given in Eq. 6:

$$I_{pmt} = I_B + I_S = I_B + K(C_S)^m \qquad (6)$$

where I_{pmt} = PMT current, I_B = background current, I_S = sulfur current, C_S = concentration of sulfur to be measured, and K and m are constants ($m \sim 1.6-1.9$). Since $m > 1$, sensitivity increases with S concentration and addition of a stable gaseous sulfur compound to the flame gases should result in enhanced sensitivity to low levels of sulfur in the sample airstream:

$$\frac{d(\Delta I)}{dC_S} = mKC_s^{(m-1)} \text{ (undoped } H_2) \qquad (7)$$

$$\frac{d(\Delta I)}{dC_S} = KC_d \text{ (doped } H_2) \qquad (8)$$

where C_d = concentration of dopant, and $C_d \gg C_s$.

The choice of SF_6 to be added to the H_2 supply was based on the stability of SF_6 in pressurized gas mixtures and the ability to add SF_6 at precise concentrations over long periods of time.[8] About 100 ppb SF_6/H_2 was obtained in six 1A-cylinder lots from Scott Environmental Technology, Inc. As described in more detail elsewhere,[7,9] the enhancement predicted from Eq. 8 is realized and results in a LOD for aerosol S or SO_2 of less than 1 ppb during aircraft sampling employing no signal averaging (time response ~ 5 sec.).

Continuous fluorescence derivatization technique for NH_3

The method for continuous determination of atmospheric ammonia by a fluorescence derivatization technique has been described[11] in detail elsewhere and ground-level data using this technique have been reported.[12] Ammonia is scrubbed from the filtered sample air by dilute sulfuric acid, and subsequently reacted with o-phthalaldehyde and mercaptoethanol in buffered aqueous solution. The product formed is detected by its emission at 440 nm upon excitation at 340 nm in a filter fluorimeter. Current detection limit is 0.25 ppb NH_3 in ambient air, with a response time of 2.5 min.

Several modifications have been made in the original design to permit sampling from an instrumented aircraft. The components have been packaged to fit into a small $(20\,cm \times 33\,cm \times 43\,cm)$ dual chassis framework with only the gas sampling pump, the fluorimeter and recorder external to the chassis. A dual filter inlet is used and filters are changed during zero checks to avoid filter desorption peaks. The calibration scheme shown in Figure 2 was developed using elements of a Monitor Labs 8500 Calibrator. It employs a cold trap, Drierite, charcoal and an ammonia denuder ($KHSO_4$-coated glass tube) to produce zero air and a low-level ammonia permeation source to generate NH_3 standards in the 4–12 ppb range. Calibration curves typically exhibit correlation coefficients, $r > 0.99$, day-to-day slope variance of $\sim \pm 10\%$ and intercept values of -0.3 to $+0.7$ ppb.

RESULTS AND DISCUSSION

The principal goal of this section is to illustrate that the instrumentation designs detailed above have been demonstrated to operate in actual ambient sampling missions. The cloud water collectors have been evaluated on several scoping flights to date, and as noted above, the CERL-design CWC/GS has been subjected to laboratory tests to establish that sample integrity is maintained in the sampler. For initial flights conducted in
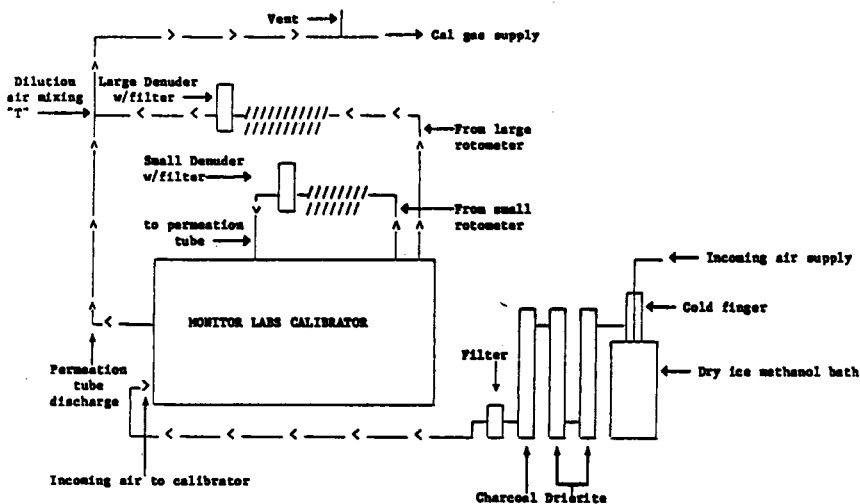
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FIGURE 2 Calibration system for ammonia at ambient levels used with continuous, fluorescence-derivatization instrument.

September, 1981 on Long Island, NY, cloudwater pH values in the range of 3.2 to 5.2 were observed, only slightly more acidic than rainwater pH values typically observed at the BNL site. A subset of these data, shown in Table I, illustrates the usually good ionic balances obtained with the ASRC collector. The details of the cloudwater collection and analysis procedures and the analysis of ion composition data will be presented elsewhere.[13] This synopsis was presented to illustrate the value of sampling and measurement capabilities for both ambient levels of acidic

TABLE I

Analysis of cloud water samples

Date of collection	pH	Sample concentrations, μeq/L[a]				
		H^+	NH_4^+	NO_3^-	SO_4^{2-}	Ion balance[b]
06/15/81	3.01	977.0	196.0	435.0	642.0	+96
09/03/81	3.37	427.0	137.0	182.0	404.0	−22
09/09/81	4.02	95.5	26.3	40.2	85.8	−4.2
09/17/81	3.76	174.0	36.3	27.3	118.0	+65

[a] 1 μeq $= 10^{-6}$ equivalent.
[b] Ion balance $= \Sigma$(cations) $- \Sigma$(anions), neq/m³.

precursor gases and aerosols and for cloudwater composition on the same instrumented aircraft.

The results for real-time gaseous and aerosol measurements shown in Table II and Figures 3 and 4 were obtained during a two-week sampling period in February, 1982 using the aircraft sampling platform near Charleston, SC. The summary in Table II was obtained by averaging real-time data over the period indicated during conditions of stable gaseous and aerosol conditions; it illustrates that NO_x and O_3 may be determined under ambient airborne conditions with $\pm 10\%$ precision, sulfur dioxide and aerosol sulfur with better than $\pm 20\%$ precision, and that nitric acid is clearly detectable at < 0.5 ppb even using a two-channel difference scheme. During this experiment ammonia was not present at concentrations greater than the detection limit of about 0.25 ppb.

TABLE II

Real-time airborne concentrations Charleston, SC, 2/25/82, 1730-1750 EST

Species	Sample reading, ppb $(\pm s)$[a]	Zero reading, ppb $(\pm s)$	Net concentration, ppb $(\pm s)$
Ozone[b]	44 (± 3)	2 (± 2)	42 (± 3.6)
NO_x	3.4 (± 0.3)	-0.1 (± 0.2)	3.5 (± 0.35)
HNO_3	0.35 (± 0.2)	0.0 (± 0.1)	0.35 (± 0.25)
SO_2	12 (± 1.5)	2 (± 0.5)	10 (± 1.6)
Aerosol S	7 (± 0.5)	2.5 (± 0.3)	4.5 (± 0.6)

[a] s = standard deviation of observed air concentrations during sampled period.
[b] Ozone measured by AID ethylene–chemiluminescence instrument.

In Figures 3 and 4 we show real-time data from another mission during the Charleston sampling period. The nitric acid information is a continuous recording of the *difference* in the two output channels, NO_x and NO_x-HNO_3, for air sampled identically except for insertion of an HNO_3-removing nylon filter in one air stream. Zero air was sampled with all instruments from 1901:30 to 1905 hr, and with the dual FPD (SO_2 and aerosol sulfur) instrument from 1850 to 1852:30. It is noteworthy that the zero air levels and precision for all instruments were maintained even under these conditions of varying gaseous and aerosol concentrations.

The experimental observation of simultaneous increases of all species (O_3, NO_x, HNO_3, SO_2, aerosol S) for a brief period about 1854 hr, probably indicates the presence of a local plume interacting with background levels of these pollutants. Although the apparent "plume widths" were not identical ($NO_x \approx HNO_3 > SO_2 \approx$ aerosol S > ozone), this
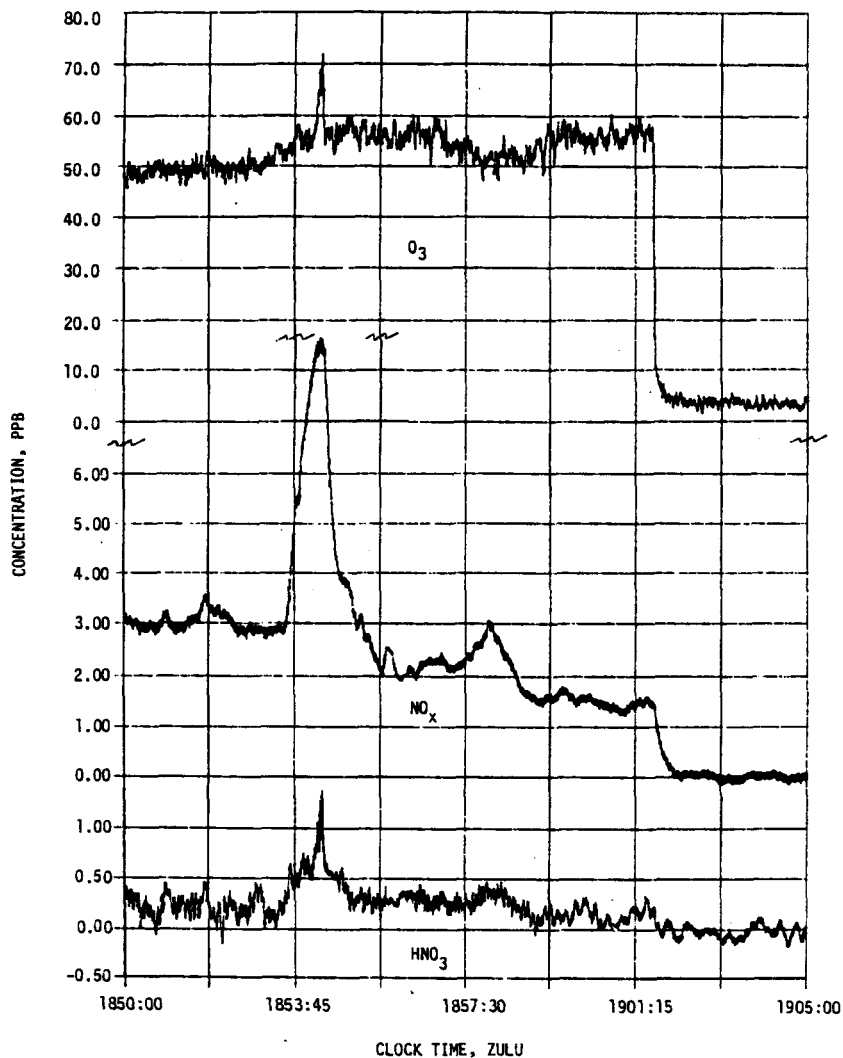
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FIGURE 3 Real-time concentration data for ozone, NO_x ($NO + NO_2 + PAN$), and nitric acid, obtained by airborne sampling near Charleston, SC, February 23, 1982, altitude $= 610$ m (MSL).

may be in part due to differences in response times of the real-time instruments. Nevertheless, the ability of the instrumentation to track rapidly fluctuating concentrations of the measured species about their ambient levels is readily evident.
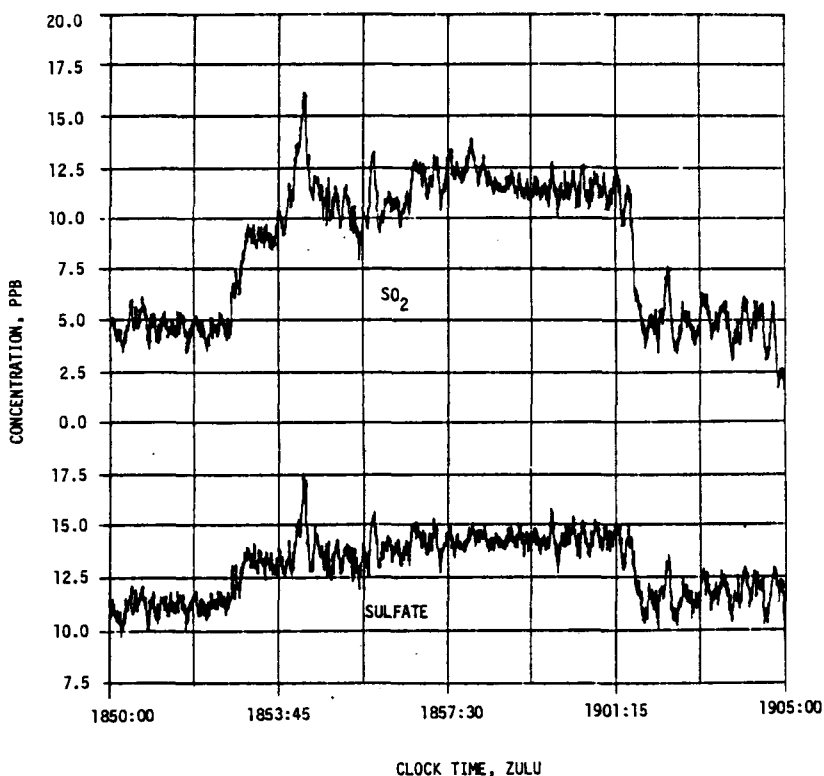
FIGURE 4 Real-time concentration data for sulfur dioxide and aerosol sulfur, obtained by airborne sampling near Charleston, SC, February 23, 1982, altitude = 610 m (MSL). Zero readings are offset from "recorder zero" by arbitrary amounts; actual zero reading determined by zero air sampling in flight.

Again, for the 23 February mission, no ammonia concentrations were observed greater than the instrumental detection limit of ~ 0.25 ppb. In fact, for the mission in Charleston, SC only for one sampling day *on the ground* was any ammonia observed. Ammonia levels have previously been measured on a few missions on Long Island, NY using the same apparatus. These results are summarized in Table III, and indicate that on one sampling day (31 July) no vertical stratification of ammonia levels were observed, but on a second day (21 August), [NH$_3$] decreased from ~ 1.5 ppb at 160 m (MSL) to below the detection limit above ~ 650 m MSL. Further vertical profiles of ammonia are required along with temperature spirals and other meteorological data to understand the implications of the data reported here.

TABLE III

Ammonia levels sampled from the BNL aircraft

Date	Approx. time EDT	Altitude m, MSL[a]	[NH$_3$] ppb
7/31/81	1153–1216	150	1.0 ±0.1
	1226–1240	455	1.1 ±0.1
	1258–1307	760	1.1 ±0.1
	1326–1337	455	0.84±0.25
8/21/81	1108–1122	150	1.54±0.07
	1142–1154	610	~0.25±0.1
	1212–1220	1220	<LOD[b]

[a]Indicates sampling altitude in meters above mean sea level.
[b]LOD = Limit of Detection ~0.25 ppb for these samples.

CONCLUSION

The experimental design and operation of an instrumentation package capable of measuring cloud water composition and ambient levels of aerosol and gaseous nitrogen and sulfur pollutants sampled from an aircraft sampling platform has been presented. It is anticipated that extensive use of this airborne package will provide important new information from which the vertical profiles of pollutants and the extent of interphase transfer of gases, aerosols and cloud liquid water in the ambient atmosphere may be deduced. In addition, this characterization data may be combined with laboratory data on equilibria and oxidation kinetics involving sulfur and nitrogen oxides to quantitatively evaluate the major routes of incorporation of ionic species into precipitation.

Acknowledgement

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