

THE DEVELOPMENT OF A CONTINUOUS REAL-TIME IN-SITU

AMMONIA MONITOR

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DEDICATION

This thesis is dedicated to the memory of my father, Abdallah Al-Sunaid. Through his loving and patient ways, I learned that hard work and dedication are the main ingredients of success.

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ABSTRACT

The Development of a Continuous Real-Time In-Situ Ammonia Monitor

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A continuous real-time in-situ ammonia monitor has been developed. It utilizes the reaction between ammonia gas and sulfuric acid aerosol to form ammonium sulfate for ammonia measurement. A sensitivity-improved Flame Photometric Detector (FPD) is used with the instrument. The detection limit of the monitor for measuring ammonia is 0.4 ppb NH_3 with a time resolution of five minutes. The detection limit of the FPD for measuring sulfur has been improved by a factor greater than ten. The present detection limit of the FPD is 0.07 ppb S, which is an improvement over the previous detection limit of 1 ppb S.

I. INTRODUCTION

A. Review of Ammonia Measurements and Techniques

Gaseous ammonia plays an important role in atmospheric chemistry. It is the principal basic gas available to neutralize acidic aerosols. It contributes to visibility degradation through the formation of ammonium sulfate in urban areas. Ammonia is a very important component of the nitrogen cycle.

The relative scarcity of ammonia concentration data underlines the difficulty of measuring it. One major problem is the possibility of contamination of samples by ammonia that is emitted by man during handling (Breeding et al., 1973). An additional problem is the propensity of ammonia to sorb on almost any available surface. Air sampling involves differentiating between ammonia and ammonium aerosols, the act of which can give rise to possible degassing of ammonia from the aerosols.

For more than a decade development of an instrument capable of measuring ammonia at atmospheric concentrations has been a major analytical challenge. This study discusses the development of a continuous real-time in-situ gaseous ammonia monitor (CRIAM). A literature review of ammonia-measuring techniques and ammonia data is presented in the following paragraphs.

Although the current measurement techniques vary in their approach, most involve collection and preconcentration before measurement. With the exception of Ferm's method (1979) they all have a Teflon pre-filter to remove aerosols.

Ammonia-measuring methods can be classified into three general categories. Table 1 lists the most recent and common techniques. The impregnated filter method has been criticized for being inaccurate for the reasons given in the table, such as contamination while handling and volatilization of ammonia from aerosol particles (Harrison & Pio, 1983; McClenny et al., 1982; Kamin et al., 1979; Fern, 1979). The diffusion absorption method shares most of the impregnated filter technique disadvantages. The instrumental techniques suffer from amine interference, reduced time resolution, and/or poisoning of the collection medium.

Measured ammonia concentrations in different locations in the world are listed in Table 2. Although the concentration varies, it tends to be mostly under 5 ppb. The time resolved measurements show a diurnal cycle for the gas (McClenny et al., 1982; Abbas & Tanner, 1981; Bos, 1980). Dawson (1977) explained the morning increase in ammonia concentration as an increase of its generation at the surface as a function of ambient ground level temperatures. This leads to evaporation of water and the release of dissolved NH_3 . Mid-day and afternoon decreases may be due to depletion of available ammonia from surface water evaporation and/or ammonia reaction with hydroxyl radical and photochemically generated aerosols (McClenny et al., 1982). Another possibility is the increase of atmospheric mixing as the atmosphere is heated and the inversion layer is lifted.

TABLE 1. Ammonia Measurement Techniques

METHOD/REFERENCES	DESCRIPTION	COMMENTS
Impregnated Filter 4, 7, 9	Air is passed through a Teflon prefilter to remove particles. The NH ₃ is collected on acid (H ₂ SO ₄ , KHSO ₄ , oxalic acid) impregnated filters. The ammonia is dissolved and analyzed by NH ₃ -specific electrode, colorimetric methods, etc.	It gives average NH ₃ concentration (24-hour). It is not accurate due to errors introduced by handling, storage, and contamination. Collected aerosols on the prefilter tend to degas, or gaseous NH ₃ is sorbed on aerosol, depending on weather conditions and type of pollutants present.
Diffusion Absorption 5, 8	Sampled air is passed through a Pyrex tube coated with oxalic acid. At laminar flow conditions NH ₃ diffused to the walls while the ammonium salts get through. The collected ammonia is analyzed with an NH ₃ -specific electrode, indophenol-blue technique, or others.	It has the same disadvantages as the impregnated filter method with the exception of the prefilter effects.
Automated Diffusion Absorption Tube 2	Similar to the above technique. Walls are coated with citric acid. The deposited ammonium salt is dissolved in 2% Nessler reagent in water. After finishing the color reaction, the extinction at 417 nm is measured, and the tube is recoated.	Sampling time varies according to NH ₃ concentration with a minimum of 30 minutes.

TABLE 1 (continued)

METHOD/REFERENCES	DESCRIPTION	COMMENTS
Automated Tungstic Acid Technique 3, 6, 13	NH ₃ and HNO ₃ diffuse and preconcentrate on the walls of Vycor tube coated with tungstic acid, H ₂ WO ₄ . The gases are then thermally desorbed and converted to NO to be monitored by a NO _x monitor. NH ₃ is sorbed on another diffusion stripper to measure HNO ₃ . Ammonia is deduced by difference.	The system is automated to a 1-hour cycle. Detection limit of 0.07 ppb for 20 minutes of sampling at 1 Lpm. The method suffers from poisoning of the diffusion tube during ambient sampling.
GC-Opto-Acoustic Detector 12	Air is sampled through a tube packed with Chromosorb T. The collected ammonia is thermally (100°C) desorbed and detected by opto-acoustic detector and CO ₂ laser.	Sampling time varies from 10 to 60 minutes. Disadvantages are that water vapor absorbs at the same ammonia laser wave length. Amines and HNO ₃ are sorbed by Chromosorb T.
GC-Chemiluminescent Nitrogen Detector 11	Tenax-GC or alkalized Porasil A columns are used to concentrate NH ₃ and amines (100% recovery). The gases are converted to NO over a Pt catalyst and detected by a nitrogen oxide analyzer.	Amine interference.
Remote IR Heterodyne Radiometer 10	The high spectral resolution available from an optical heterodyne instrument is filtered by one or more narrow band pass IR filters to measure the NH ₃ IR spectrum intensity.	Atmospheric ammonia profiles are inferred from IR resolved solar absorption data.

TABLE 1. (continued)

METHOD/REFERENCES	DESCRIPTION	COMMENTS
Automated Fluorescence Derivatization 1	Prefiltered air (5.5 L min^{-1}) is turbulently mixed with $1.6\text{-}2.0 \text{ mL min}^{-1}$ of $10^{-2}\text{N H}_2\text{SO}_4$. The ammonia-containing liquid is separated from the gas and an equal volume of buffered (pH 10.4) O-phthalaldehyde in the presence of a thiol to form an intensely fluorescent 1-alkylthiosoidole product, which is measured by fluorescence spectrometer.	Reproducible NH_3 measurement ≥ 0.1 ppb with less than two minutes time resolution. It needs daily calibration and zeroing. Interference from gases that fluoresce at the excitation and emission wavelengths such as amines.
1	Abbas & Tanner (1981)	
2	Bos (1980)	
3	Braman et al. (1982)	
4	Eggleton (1972)	
5	Ferm (1979)	
6	Gailey et al. (1983)	
7	Gillett & Ayers (1979)	
8	Gras (1983)	
9	Harrison & McCartney (1979)	
10	Hoell et al. (1980)	
11	Kashihira et al. (1982)	
12	McClenny & Bennett (1980)	
13	McClenny et al. (1982)	

TABLE 2. Reported Ammonia Concentrations at Different Locations

NH ₃ CONCENTRATION	LOCATION	COMMENTS	REFERENCES
Range 0.96-0.25 ppb average = 0.45 ppb Range 7.76-0.63 ppb average = 2.17 ppb	Research Triangle Park, NC July 1980. Rural site. Croton, OH. Rural site close to livestock holding area.	Hourly reading	McClenny et al. (1982)
Range 2.0-10 ppb ^a	St. Louis, MO Suburban site.	23-hour averages	Spicer (1977)
Range 2.0-8.0 ppb ^a	West Covina, CA Suburban site.	23-hour averages	
Average 0.08 ppb (STP)	Cape Grim, Tasmania	Ocean air collected on oxalic acid impregnated filters and analyzed with ring oven tech- nique. Sampling period: August 1-14, 1979.	Ayers & Gras (1980)
Range 5.8-0.5 ppb	Cedar Island, NC, Research Triangle Park, NC	Sampling period: July, August, and September 1978.	McClenny & Bennett (1980)
Range 0.05-0.4 ppb	Gothenburg, Sweden	24-hour averages	Ferm (1979)
Range 1.3-2.5 ppb ^a	Harwell, U.K.	Hourly averages	Realy (1974)
0.013-0.039 ppb (STP)	South Pole & Wright Valley (77°31"S, 162°40"E) Antarctica	Diffusion absorption method 24-hour averages. November-December 1980.	Gras (1983)

TABLE 2. (continued)

NH ₃ CONCENTRATION	LOCATION	COMMENTS	REFERENCES
1.4-5.6 ppb ^a	Delft, Netherlands	Hourly averages, August-September 1979	Bos (1980)
1.4-14.1 ppb ^a	Terschelling, Netherlands. Background station.	Hourly averages, October 1979	
0.5-5 ppb	Brookhaven National Lab. Upton, NY	Hourly averages, August 1979	Abbas & Tanner (1981)
129 ppb	Cattle farm	Injected air sample into a GC column.	Kashihira et al.
Range 0.014-0.338 ppb ^a	Petersham, MA	One year of data shows strong seasonal pattern. Weekly av- eraged. Collected filters were analyzed by an NH ₃ specific electrode.	Tjepkema et al. (1981)
4-102 ppb	Riverside, CA	High resolution FT-IR spectrometer used to measure NH ₃ and HNO ₃ . Selective days in July, August, September, and October 1977 were reported.	Doyle et al. (1979)
Range 0.9-5.1 ppb	Hazlerigg, England. A rural site used as grazing for sheep.	KHSO ₄ impregnated filters were collected and analyzed by phenol-hypochlorite colori- metric method. 24-hour averages.	Harrison & Pio (1983)

a: data were reported in $\mu\text{g}/\text{m}^3$ originally; 1 ppb = 0.71 $\mu\text{g}/\text{m}^3$

B. Ammonia Reaction with Sulfuric Acid

The idea for the continuous real-time in-situ ammonia monitor (CRIAM) evolved from the study in our laboratory of the reaction of ammonia with sulfuric acid aerosol (Huntzicker et al., 1980). The study showed that the reaction rate was 21-70% less than the rate calculated by the rate of NH_3 diffusion to the aerosol alone. The reaction coefficient, which is the fraction of gas-particle collisions resulting in a chemical reaction, increased with increased particle size, and the rate of the reaction decreased as the NH_4^+ content of the particle increased. The recent study by McMurry et al. (1983) agrees with the conclusions of Huntzicker et al.

Gaseous ammonia reacts in the presence of excess sulfuric acid aerosol to form NH_4^+ according to the following equation:



The reaction occurs when NH_3 diffuses into sulfuric acid aerosol drops. Ammonia transfer into the drop is governed by the following diffusion equation:

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 1 - \exp[-2 d_p D_{\text{NH}_3} f(\text{Kn}) t] \quad (2)$$

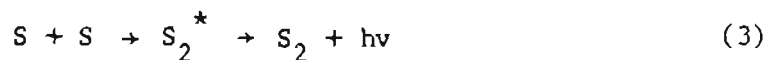
where $[\text{NH}_4^+]$ = the concentration of NH_4^+ in the drop; $[\text{NH}_3]$ = the concentration of the ambient NH_3 ; D = diffusion coefficient of NH_3 into the

air; this equals 0.23 cm sec^{-1} (Andrew, 1955); $f(\text{Kn}) =$ is a function of Knudsen number; $t =$ reaction time.

The Huntzicker et al. (1980) paper gives a detailed derivation of the diffusion equation. The ratio of the diffused ammonia to the gaseous ammonia concentration is exponentially dependent on the particle diameter, total number of aerosol drops, and reaction time, as seen in equation (2) above.

C. The FPD Response to Sulfur-Containing Molecules

Sulfur-containing molecules such as sulfuric acid, ammonium sulfate, sulfur dioxide, and hydrogen sulfide are commonly measured by the flame photometric detector (FPD). The detector measures the chemiluminescence produced when sulfur-containing molecules are burned in a fuel-rich, hydrogen-air flame. Excited state S_2 molecules, which are formed when sulfur-containing species are burned, give off light during their de-excitation process. The light is measured by a photomultiplier. A narrow bandpass filter with a maximum transmittance at around 394 nm is inserted between the flame and the photomultiplier tube to isolate the sulfur emission from most other flame emission sources. The detector response is theoretically proportional to the S_2 as shown in the equation



The intensity of the chemiluminescence is theoretically proportional to the square of the concentrations of mono-sulfur molecules such as sulfur dioxide, sulfuric acid, ammonium sulfate, or ammonium bisulfate, and is linearly proportional to molecules containing two sulfur atoms. In practice, however, the power law for gases such as SO_2 varies from 1.5 to 2, depending on the sulfur compounds being analyzed and the flame conditions (D'Ottavio et al., 1981; Huntzicker et al., 1978; Eckardt et al., 1975).

The current generated by the photomultiplier $I(\text{PMT})$ can be expressed by

$$I(\text{PMT}) = I(\text{s}) + I(\text{b}) \quad (4)$$

where $I(\text{s})$ is the current produced by the sample sulfur and $I(\text{b})$ is the background current. The background current $I(\text{b})$ is the photomultiplier current that is produced by the flame with sulfur-free air (zero air). The sulfur current $I(\text{s})$ is expressed as

$$I(\text{s}) = K[\text{S}]^m \quad (5)$$

The FPD sensitivity to sulfur can be expressed as

$$d I(\text{s})/d [\text{SO}_2] = K m [\text{SO}_2]^{(m-1)} \quad (6)$$

For $m > 1$ the detector sensitivity increases with the increase of the sulfur concentration. The sensitivity is equal to $6.2E-11$ amperes/ppb SO_2 for 1.0 ppb SO_2 using the data in Figure 1. Table 3 and Figure 2 show the FPD response to ammonium sulfate. Table 4 and Figure 1 show the FPD response to SO_2 .

D. Doping the FPD with Sulfur Compounds

The FPD has been doped with different sulfur compounds to improve its sensitivity. A common finding in published papers (D'Ottavio et al., 1981; Zehner & Simonaitis, 1976; Crider & Slater, 1969) is that although the sensitivity increases by a factor of five to ten, the noise level increases as well.

Crider and Slater (1969) doped the FPD with SO_2 to improve its sensitivity. The study reports the improvement of the GC-FPD response to sulfur-containing compounds, halogenated compounds, and hydrocarbons. The noise level increased with the increase of the dopant concentration. Thus, the practical sensitivity increase was limited (detection limit = signal/noise = 2) to a factor of five to ten.

Zehner and Simonaitis (1976) doped the flame photometric detector (FPD) with SO_2 (70 ng/min SO_2) to improve the detector response in their gas chromatographic analysis of sulfur-containing compounds. The detection limit (signal-to-noise ratio = 2) was improved by a factor of eight

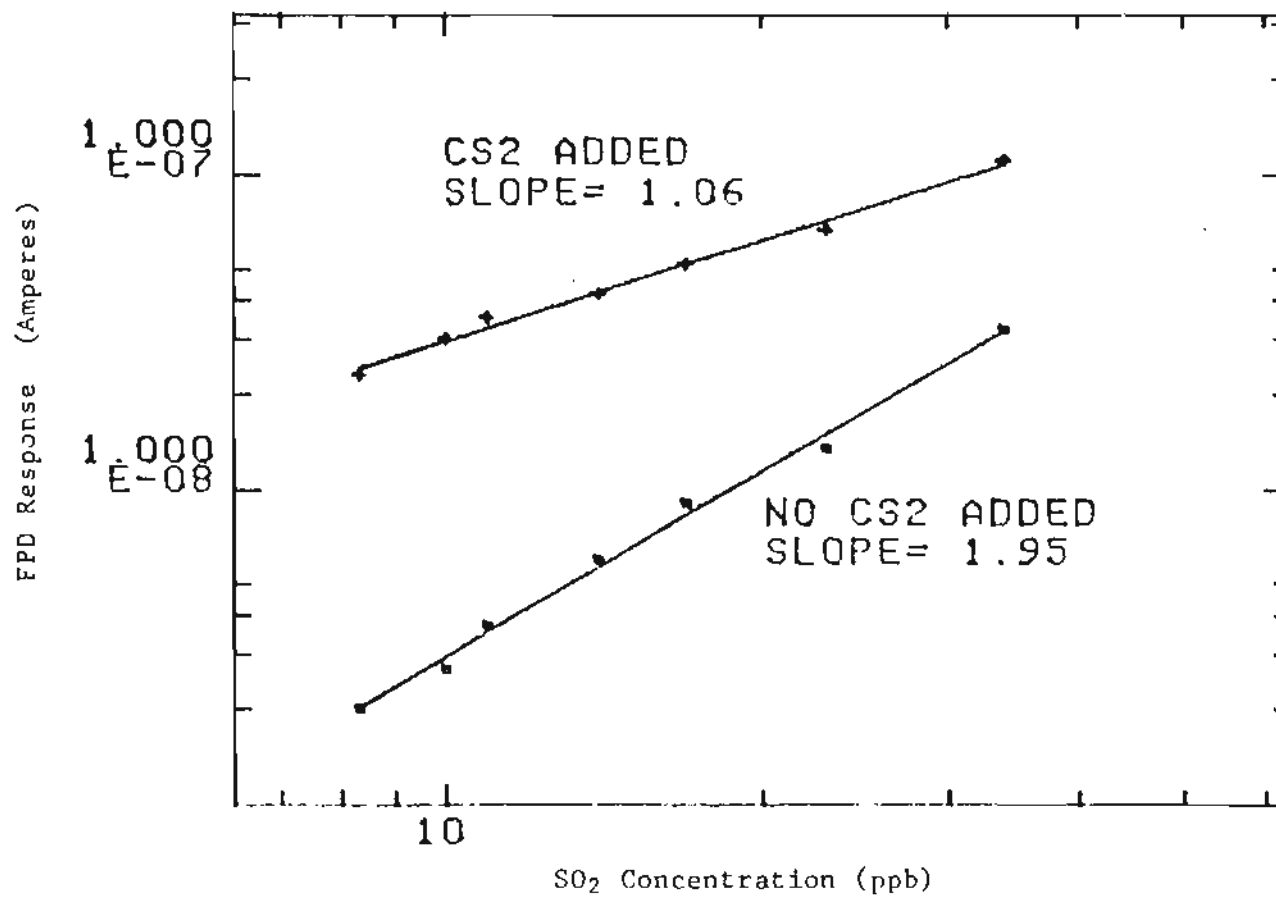


Figure 1. FPD response to SO₂ before and after the addition of CS₂.

TABLE 3. FPD Response to $(\text{NH}_4)_2\text{SO}_4$ Aerosol Without CS_2 Addition

Ammonium Sulfate Aerosol Concentration $\mu\text{g}/\text{m}^3 \text{SO}_4$	ADC Response (counts)	ADC Response-Blank (counts)
Blank	163	0
2.0	507	344
3.6	1,386	1,223
7.6	3,282	3,119
9.8	4,442	4,279
16.5	12,664	12,501
23.6	20,664	20,418
30.9	29,151	28,988
33.1	48,318	48,155

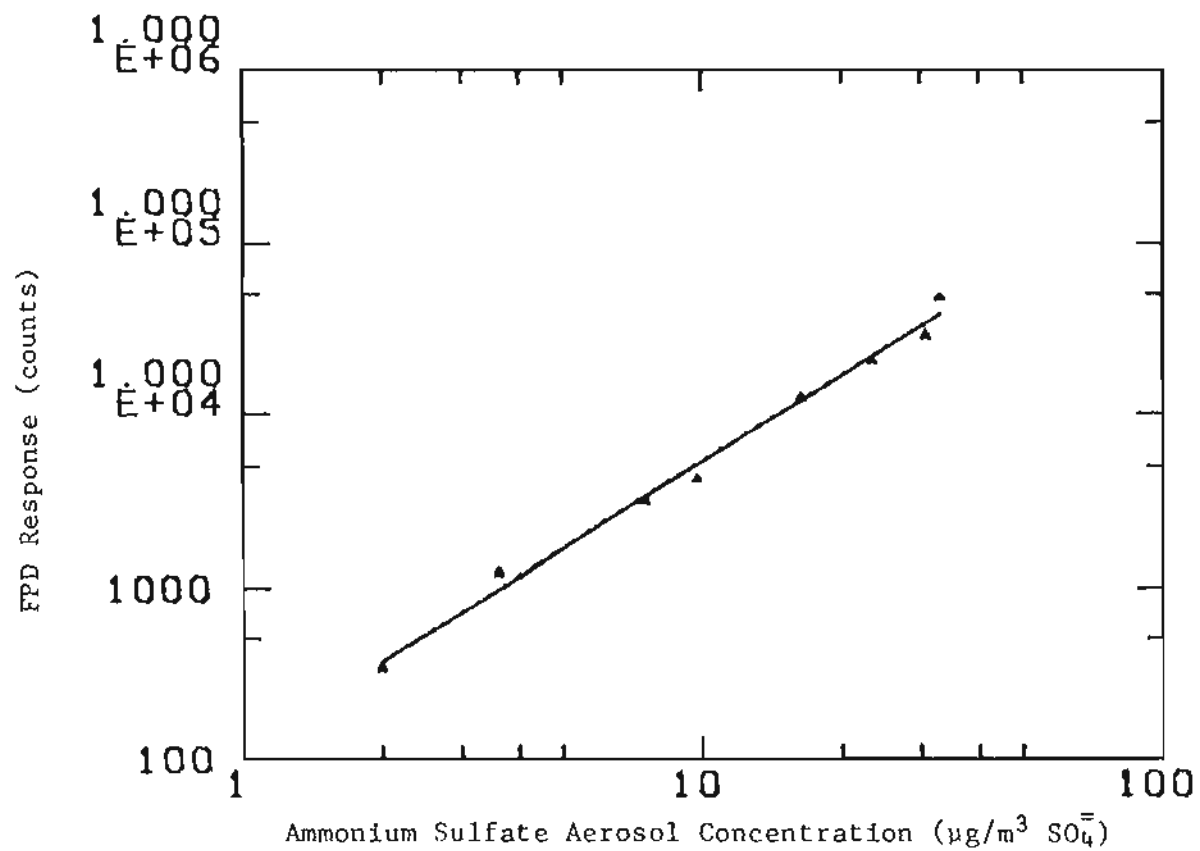


Figure 2. Ammonium sulfate calibration before the addition of CS_2 to the flame. Slope = 1.65 ± 0.06 .

TABLE 4. FPD Calibration with SO₂ Before and After the Addition of CS₂ to the Hydrogen Fuel

SO ₂ Concentration (ppb)	FPD Response (amperes)
8.3	2.3E-8 ^a
10.0	3.0E-8
11.0	3.5E-8
14.0	4.1E-8
17.0	5.1E-8
23.0	6.6E-8
34.0	1.1E-8
8.3	2.0E-9 ^b
10.0	2.7E-9
11.0	3.7E-9
14.0	6.0E-9
17.0	9.0E-9
23.0	1.3E-8
34.0	3.2E-8

^a FPD response to SO₂ after the addition of CS₂ (23.5ng/min) to the hydrogen fuel. Background current (6.3E-8) is subtracted.

^b FPD response to SO₂ before the addition of CS₂ to the hydrogen fuel. Background current (2.0E-8) is subtracted.

for aldicarb, which is (2-(methyl-2-(methylthio)propionaldehyde α -(methylcarbamoyl)oxime)). The study also reported an increase in the noise level with the increase of the dopant concentration.

D'Ottavio et al. (1981) doped the FPD hydrogen fuel with 66 ppb SF_6 , which produced a flame signal equivalent to 28 ppb SO_2 , in their study of low level atmospheric sulfate and sulfuric acid. They reported a detection limit (signal-to-noise ratio = 2) of 0.1 ppb.

The response of the FPD after doping with a constant amount of sulfur compound (such as CS_2) can be theoretically derived in the following manner.

The sulfur current $I(s)$ is expressed in equation (5) as

$$I(s) = K[S]^m \quad (5)$$

where $[S]$ is the concentration of sulfur in the flame. If x is the concentration of the added sulfur compound and s is the concentration of the sulfur to be measured, then:

$$[S]^m = [x + s]^m \quad (7)$$

For $m = 2$:

$$[x + s]^2 = x^2 + 2xs + s^2 \quad (8)$$

For $x \gg s$, $s^2 \ll 2xs$ and $x = \text{constant}$, then

$$[S]^2 = [x + s]^2 \approx x + 2xs \quad (9)$$

and

$$I(s) \approx K(x + 2xs) \quad (10)$$

For $x = 40$ ppb SO_2 , which was the equivalent concentration of our dopant CS_2 in the flame, then the FPD response is proportional to $[1 + (S/40)]^2$. A theoretical value of m can be estimated by plotting $\log [1 - R]$ vs. $\log [S]$, where $R = [1 + S/40]$ and $[S]$ is the sulfur dioxide concentration in parts per billion. The FPD response is proportional to $S^{1.03}$ as shown in Figure 3.

II. FEASIBILITY STUDY OF AMMONIA MEASUREMENT BY FLAME PHOTOMETRY

The instrument operating principle is based on the conversion of ammonia gas to ammonium bisulfate via the reaction of ammonia with artificially generated sulfuric acid aerosol. The instrument, however, must remove ammonium salts and particles from the sampled air stream before the reaction and remove excess sulfuric acid before measuring the ammonium bisulfate reaction product.

This chapter is divided into six sections in order to facilitate the understanding of how the instrument works. The first part contains the physical description. The second explains how the instrument works.

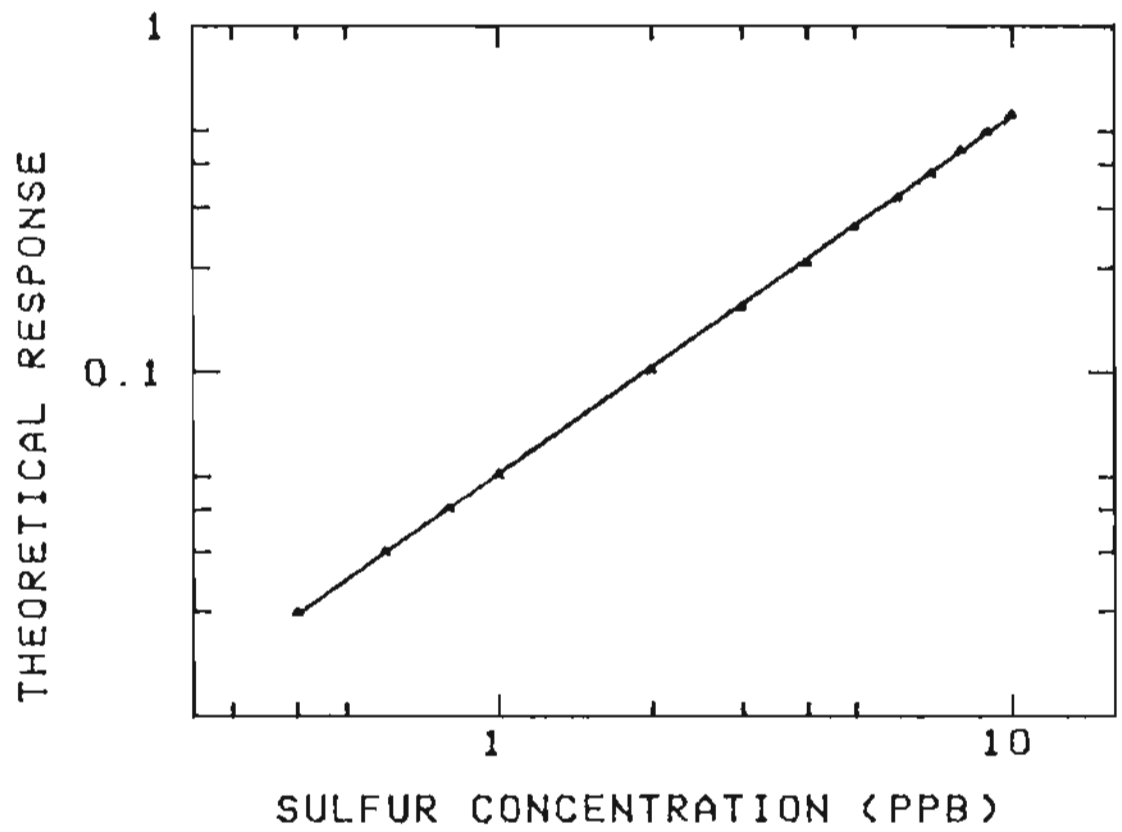


Figure 3. Theoretical response of the FPD after the addition of CS₂.
Slope = 1.03 ± 0.03.

The third and fourth show the improvement in the FPD sensitivity after the introduction of the CS₂ dopant. The fifth describes ammonia calibrations. And the final section discusses the ammonia reaction with sulfuric acid.

A. System Description

The in-situ ammonia analyzer is shown in Figure 4. The instrument discussed here shows the system used in the evaluation study, which was later simplified for ambient measurements (Figure 15). The modifications will be discussed in the third chapter. The instrument consists of three parts: the reactor unit, the aerosol separation and measurement section, and the microprocessor control system.

1. Reactor Unit

The ammonia reaction with sulfuric acid takes place in the reactor. The main part of the reactor unit is the reaction tube. It is a 150-cm long vertically mounted Pyrex glass tube. The inlet is 14 mm O.D. and is gradually expanded to its full diameter (9 cm) at a 39° angle. The bottom is sealed with a rubber stopper. A vacuum pump is connected to the bottom. The aerosol sampling probe is placed 40 cm from the bottom in the middle of the tube (see Figure 4).

Sorption of ammonia on the reactor walls is a problem for real-time measurements. It takes from one to two hours for the walls to equilibrate with ammonia depending on its concentration. The sorption

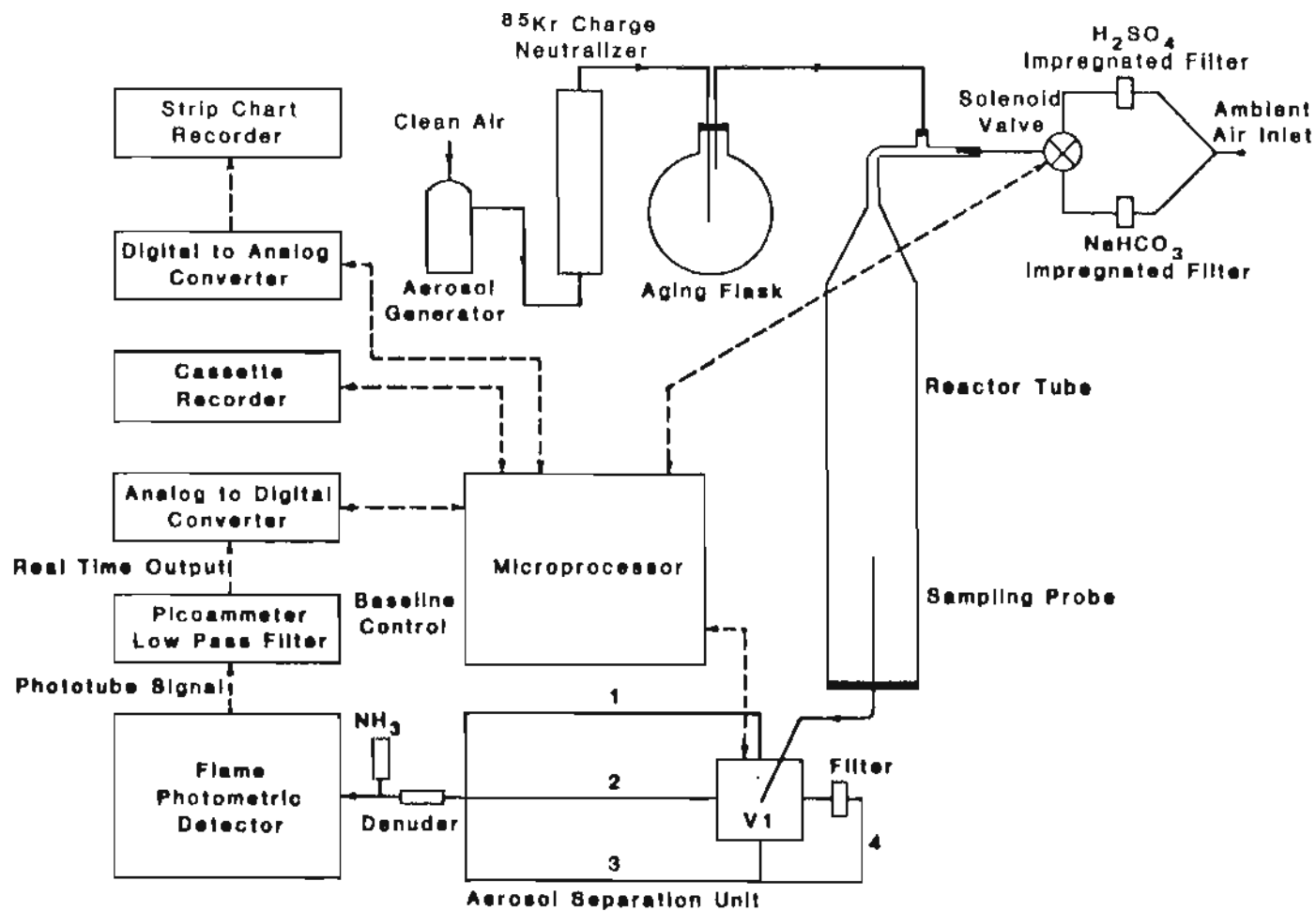


Figure 4. Ammonia measuring system for feasibility study.

and desorption process introduces error in ammonia measurement. This problem was solved by coating the reactor walls with sodium carbonate. The sodium carbonate made the walls more basic and reduced the ammonia sorption. The instrument reaches over 80% of its maximum response within 5 minutes. This is acceptable because the CRIAM is programmed to wait 15 minutes before taking the first ambient measurement. Figure 6 shows the improvement in response time after coating the reactor walls with sodium bicarbonate.

The top of the reactor tube has two inlets. The first is connected to a three-port Teflon solenoid valve (12 VDC, Mace Corp., South El Monte, California). The valve is connected to two Teflon filter holders (Mace Corp.). One contains a sulfuric acid impregnated quartz filter (47 mm, Pallflex Products Corp., Putnam, Connecticut), and the other contains a sodium carbonate impregnated quartz filter. The valve directs sample ambient air through either filter. The sulfuric acid impregnated filter removes the ammonia and the aerosols from the sample air stream, while the sodium carbonate impregnated filter removes the aerosols only. The sodium carbonate increases the basicity of the filter and hence minimizes the sorption of ammonia.

Teflon and aluminum filter holders were tested for their sorption of ammonia. The Teflon holder did not absorb any ammonia. The aluminum holder, on the other hand, was very absorbent. It took over eight hours for the aluminum holder to reach the saturation level for an ammonia concentration of 60 ppb.

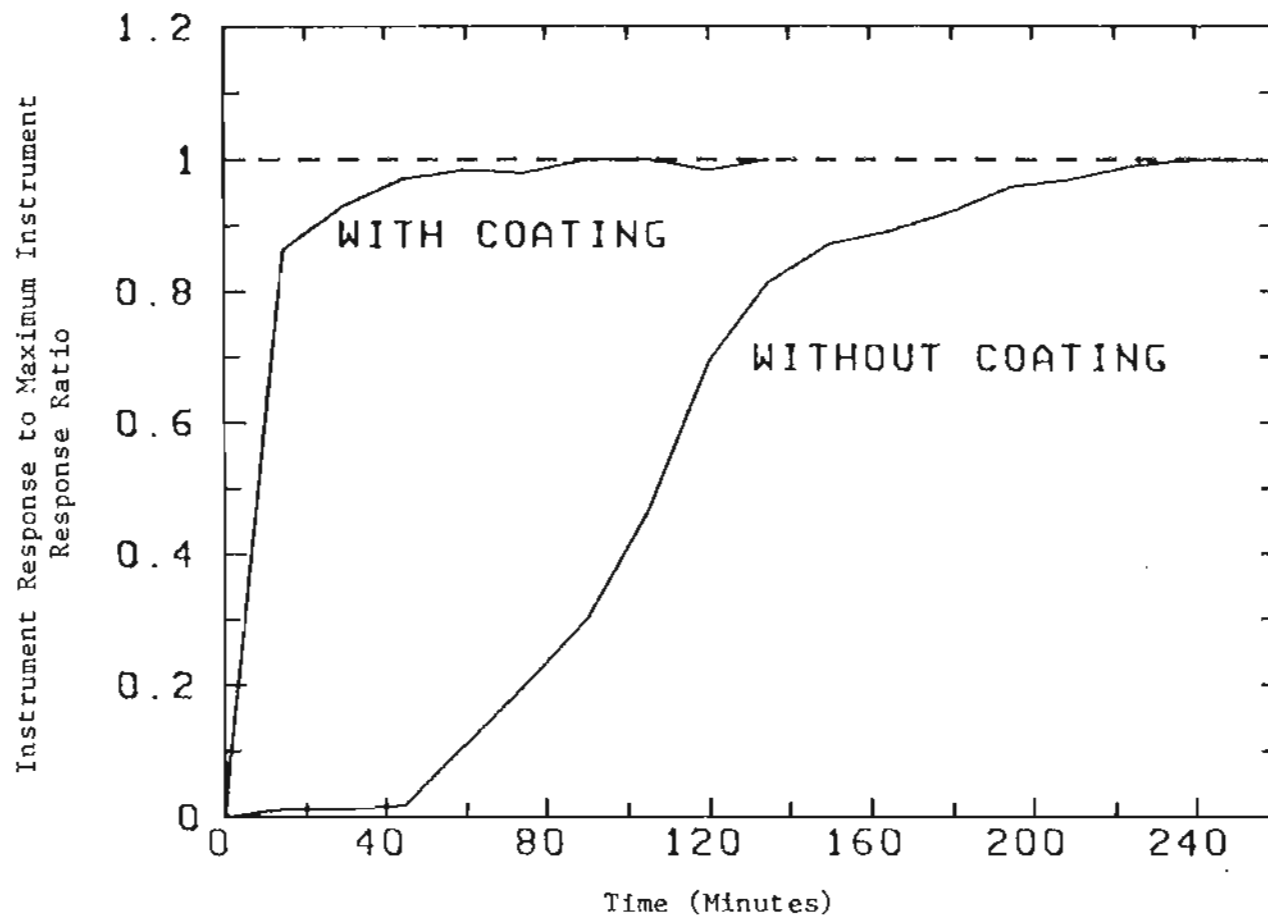


Figure 5. Instrument response time improvement after coating the reactor walls with NaHCO_3 .

Two types of filter materials were tested. The Fluoropore Teflon filter (47 mm, 0.5 μm pore size) did not absorb any ammonia. The other filter was a quartz fiber filter (47 mm, Pallflex Products Corp.), which absorbed ammonia. The quartz filter coated with either sodium carbonate or sodium bicarbonate, however, did not absorb ammonia.

In this study we used a Teflon filter holder and a 2 μm Teflon filter backed up with a quartz fiber filter coated with either sodium carbonate or sodium bicarbonate. The pressure drop in the system without filters is 8 mm Hg at our operating conditions (aerosol flow = 6.4 Lpm, and sample air flow = 14.7 Lpm). The system pressure drop with impregnated quartz filters is 20 mm Hg. The 2 μm Teflon filter is placed in front of the sodium carbonate impregnated filter to prevent ammonium-containing particles from coming into contact with the highly basic quartz filter surface. This is because Brosset (1979) has theoretically shown that ammonia release from the particle phase could occur if fine particles, which contain NH_4^+ , come into contact with coarse alkaline particles. The H_2SO_4 impregnated filter was also preceded by a Teflon filter to maintain constant pressure drop in the system. The instrument response was not affected by the addition of the Teflon filters. Table 5 shows the data collected with the Teflon filter holder containing sodium bicarbonate coated quartz fiber filter.

The second inlet at the top of the reactor is connected successively to a five-liter aging flask, a ^{85}Kr charge neutralizer, and an aerosol nebulizer.

TABLE 5. The Effect of Aerosol Prefiltering on Ammonia Measurements

Measured Ammonia Concentration Without Filter (ppb)	Measured Ammonia Concentration With Filter ^a (ppb)
4.6	4.9
6.1	5.8
7.9	8.5
9.0	9.3
13.9	13.1

^a Teflon filter holder with 47 mm quartz fiber filter coated with sodium bicarbonate.

2. Aerosol Separation and Measurement Sections

The aerosol separation and measurement section is used to differentiate between the ammonium bisulfate product and excess sulfuric acid. The aerosol sampling probe is connected to a five-port valve (Whitey SS-43ZF2). The valve routes sampled air to one of four channels. All channels are thermally controlled at 120°C with three Omega Model 49 Proportioning Control Heaters (Omega Eng., Stamford, Connecticut). In channel four the sample goes through a quartz fiber filter before entering channel three. All particles are removed, and the resultant FPD signal is used for baseline measurement. The thermal speciation columns (heaters) are 0.64 cm O.D., 60 cm long stainless steel tubes. All the channels lead to an SO₂-H₂S diffusion stripper (denuder) before connecting to the FPD. The diffusion stripper is a 0.95 cm O.D., 23 cm long stainless steel tube into which is inserted a cylinder of Whatman 41 paper impregnated with lead acetate, Pb(CH₃CO₂)₂. Between the denuder and the FPD, ammonia is added. The ammonia addition converts all unneutralized sulfuric acid to ammonium sulfate. This ensures an equal FPD response to sulfuric acid and ammonium sulfate aerosols. The ammonia is produced by an NH₃ permeation tube. The ammonia tube is enclosed in a 0.95 cm O.D. stainless steel tube that is capped at one end such that NH₃ enters the sample stream by diffusion.

The instrument utilizes the thermal speciation principle to distinguish between the acidic and the ammonium fractions of the aerosol. The excess acid is removed before measuring the ammonium bisulfate produced by the gaseous ammonia reaction with the sulfuric acid.

The principle of thermal speciation is based upon the difference of volatilization and decomposition temperatures of sulfuric acid, the ammonium sulfates, and refractory sulfates. The volatilization temperature range is 50-110°C for sulfuric acid, 120-200°C for the ammonium sulfates, and >200°C for refractory sulfur species. The volatilized sulfur is removed by the heater walls or by the lead acetate coated diffusion tube.

The ammonia reaction with sulfuric acid produces an internally mixed aerosol in which sulfuric acid and ammonium salts are mixed in the same droplet. The FPD signal produced by such aerosol corresponds to the amount of ammonium bisulfate (as sulfur) present. Figure 6 shows thermograms for internally mixed sulfuric acid and ammonium sulfate aerosols.

Although the oven temperature is set to 120°C, traces of the sulfuric acid aerosol managed to get through the columns. This is attributed to the presence of some ammonium sulfate impurities in the original sulfuric acid aerosol and traces of sulfuric acid that are not effectively removed by the heater. Figure 7 shows a thermogram of the sulfuric acid aerosol. The sulfuric acid aerosol signal is subtracted from the signal produced by ammonia reaction with acid aerosol to deduce the signal due to reacted ammonia alone.

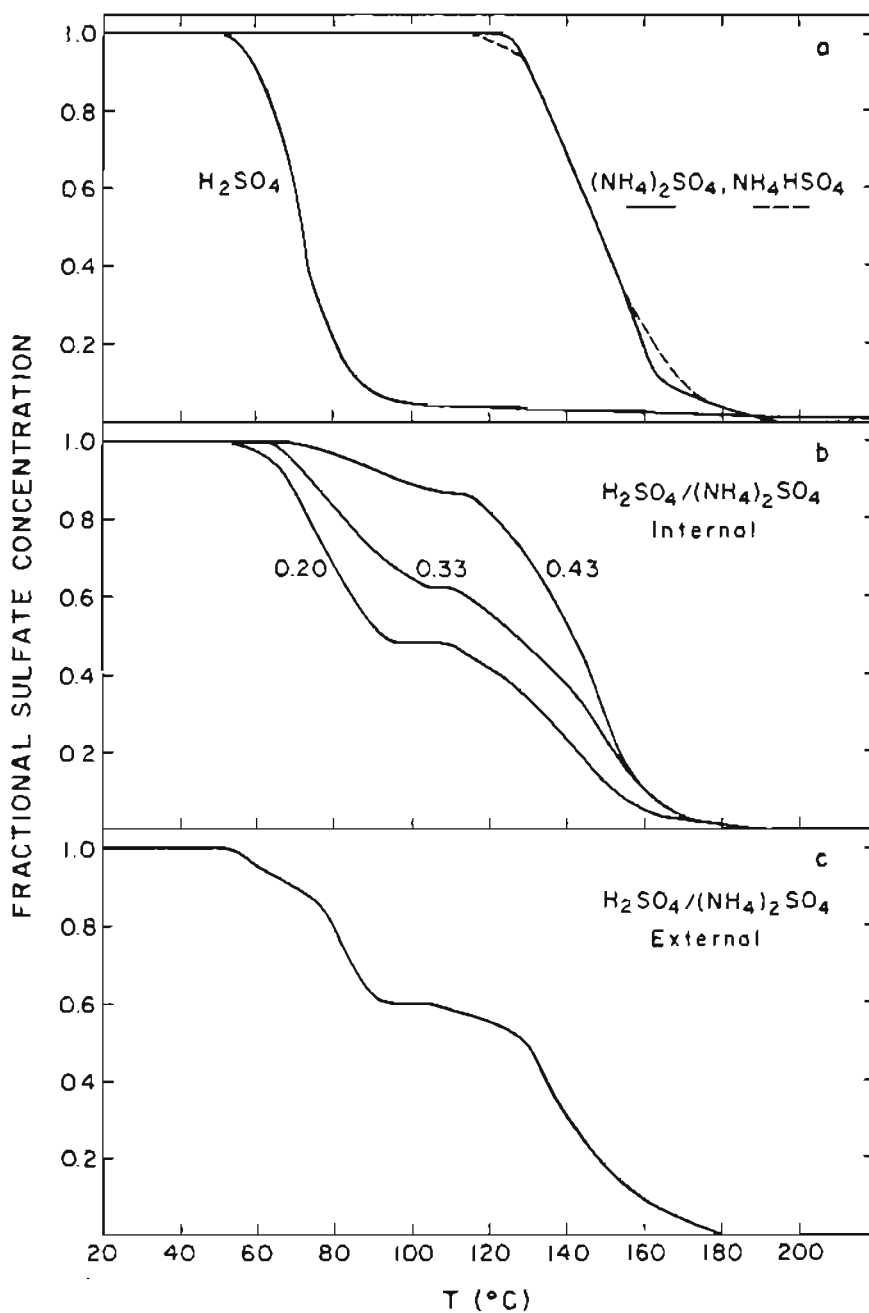


Figure 6. Thermograms for sulfate aerosols (Huntzicker et al., 1978).

- (a) H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ (—), and NH_4HSO_4 (- - -);
- (b) homogeneous H_2SO_4 - $(\text{NH}_4)_2\text{SO}_4$ aerosols with $\frac{b}{a} = 0.25, 0.50, 0.75$ where \underline{b} and \underline{a} are the molar fractions of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 in the particles;
- (c) heterogeneous mixture of H_2SO_4 droplets and $(\text{NH}_4)_2\text{SO}_4$ particles with the H_2SO_4 constituting 53% of the total sulfate and $(\text{NH}_4)_2\text{SO}_4$ 47%.

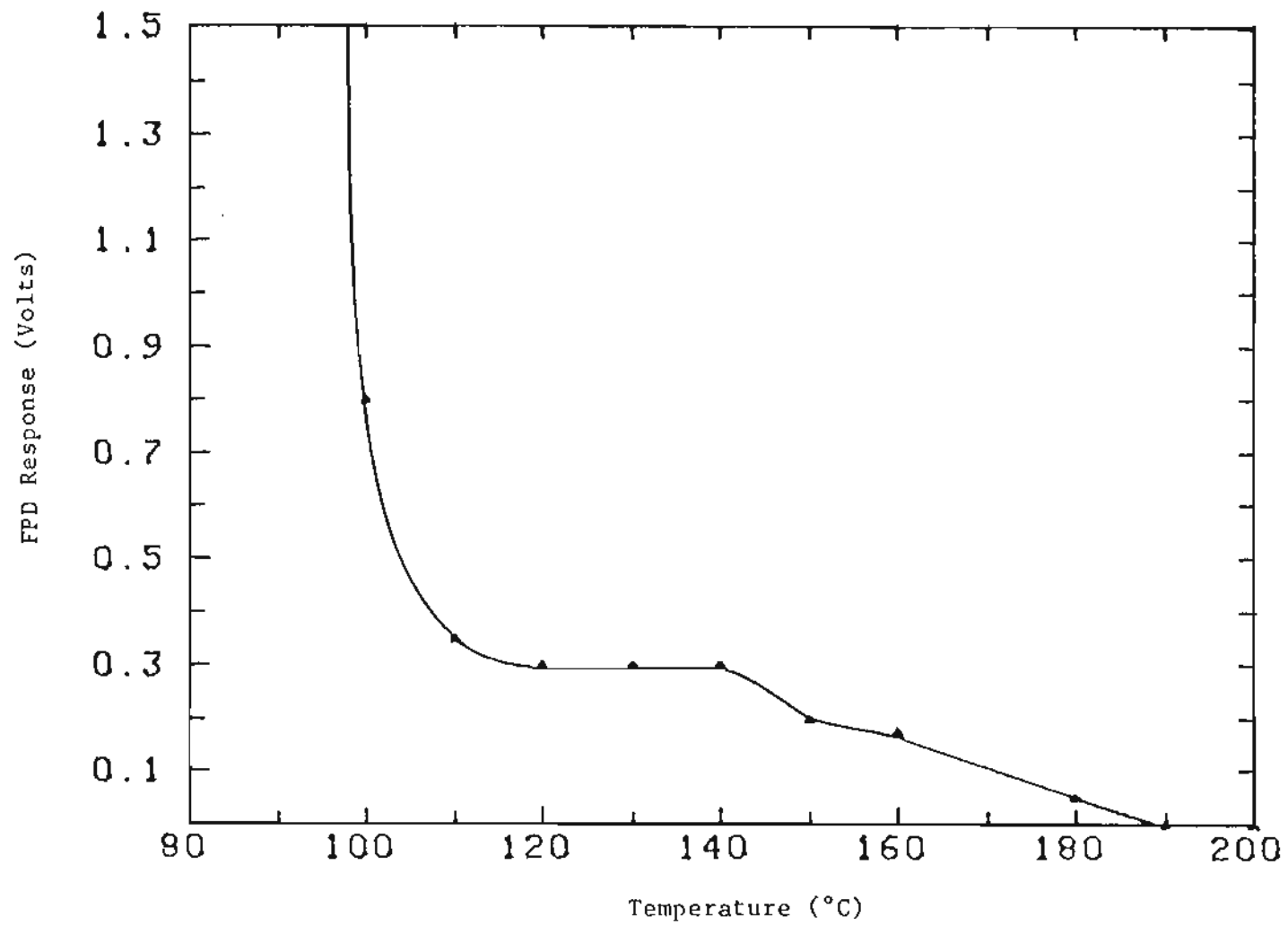


Figure 7. Sulfuric acid and $(\text{NH}_4)_2\text{SO}_4$ aerosol thermogram.

The flame photometric detector is housed in a modified Meloy SA 285E Sulfur Analyzer. The instrument is modified to improve its sensitivity and stability in the following manner. First, the inlet sample was re-plumbed to improve aerosol transmission into the flame. The sample inlet was shortened, and the number of right angle bends was minimized. Second, the signal processing electronics of the Meloy were replaced by a microprocessor system discussed below (Huntzicker et al., 1984). And finally, the sensitivity was increased by doping the hydrogen fuel with carbon disulfide. The hydrogen is passed into a 50°C container that contains a carbon disulfide permeation tube whose permeation rate was about 23.5 ng/min.

3. The Microprocessor Control Unit

The third part of the in-situ ammonia analyzer system is the computer control unit. It is built around a Motorola 6802 microprocessor and can be operated in either an automatic or a manual mode. The latter is used to check the instrument response. In the automatic mode the microcomputer controls the solenoid valve, the five-port valve, data acquisition, data processing, and data output to a strip chart recorder (Model 7100B, Hewlett Packard/Moseley Division) and a cassette recorder (Model 815, Datacassette, Techtran Industries, Inc.).

B. Instrument Operation

When the microprocessor is in the automatic mode, it sends a signal to the five-port valve orienting it for ammonia measurement (channel #1), and at the same time it sets the solenoid valve so that the sample air goes through the sodium carbonate impregnated quartz filter. The sample air is mixed with sulfuric acid aerosol at the top of the flow reactor. It stays in this position for 4.5 minutes to allow the FPD response to stabilize. Then the microprocessor starts accumulating data for thirty seconds. The data are temporarily stored in a buffer until the cycle ends. At the end of the first five minutes the processor shifts the five-port valve to channel #2 and waits five minutes before it takes an additional ammonia measurement. The five-port valve is switched to channel #3, and the solenoid valve is switched back to route sample air through the sulfuric acid impregnated filter. At this position the air sample is free of ammonia, and the FPD gives a measure of the nebulized sulfuric acid aerosol that is not efficiently removed by the thermal speciation process. After taking a reading, the five-port valve is switched to channel #4 in which particles are removed by this channel filter, and a measure of the baseline signal is obtained. This cycle repeats itself every twenty minutes. The instrument takes one measurement in every channel position at five-minute intervals.

At the end of each cycle the data are processed. The baseline is updated by interpolating between channel #4 readings of the current cycle and the previous one. The baseline contribution to every data

point is subtracted, and a histogram is plotted on the chart recorder. At this stage the processor stores all raw data in the cassette recorder and clears its buffer memory before recording the next cycle.

The difference between channels #3 and #4 is a measure of the nebulized sulfuric acid that managed to get through the heater. This serves as a check on the degree of ammonium contamination of the nebulizer solution and the efficiency of the thermal speciation process. The gaseous ammonia signal is obtained by subtracting the channel #3 measurement from the readings of channels #1 and #2.

The raw data stored on the cassette are processed in the main computer (Prime Computer, Inc., Framingham, Massachusetts). A Fortran program is used for baseline updating and data analysis.

C. The FPD Response After the CS₂ Addition

The adaptation of the FPD technique to measure gaseous ammonia at concentrations less than 1 ppb necessitated its sensitivity improvement. Carbon disulfide was chosen for this purpose for the following reasons. First, previously published papers (Crider et al., 1969; Zehner et al., 1976; D'Ottavio et al., 1981) have shown that the addition of any sulfur compound would improve the FPD sensitivity. Second, the carbon disulfide molecule contains two sulfur atoms. Hence, a linear FPD response for carbon disulfide concentration is expected. Crider et al. (1969) observed this linear relationship in their study of carbon disulfide. Third, it is desirable to have the FPD response to the dopant molecule

(i.e., CS_2) be linear so that any fluctuation in flame condition, noise, or carbon disulfide permeation tube emission will not be magnified (i.e., by a square power law response).

The addition of carbon disulfide to the flame changed the response for ammonium sulfate to $S^{1.04}$ from $S^{1.65}$ before the addition (Figure 2). (The carbon disulfide permeation rate is about 23.5 ng/min^{-1} , which is equivalent to 40 ppb sulfur dioxide (Figure 8).) In the case of sulfur dioxide, it changed the response to $S^{1.06}$ from $S^{1.95}$ without the addition of carbon disulfide (Figure 1). Table 6 shows the data used for the calibration. Table 4 shows the data for the sulfur dioxide current calibration, and Table 7 shows the microprocessor- SO_2 calibration. The FPD response to ammonium sulfate and sulfur dioxide is similar to the theoretically calculated response ($S^{1.03}$) derived in Chapter I.

The improvement in the FPD sensitivity is evident in the increase of the sulfur current $I(s)$ after the addition of carbon disulfide in Figure 1. The detector sensitivity is essentially constant and is equal to $2.5\text{E-}9$ ampere/ppb SO_2 . This is a factor of 40 larger than the original sensitivity. Figure 8 shows that the FPD responds essentially linear to ammonium sulfate aerosol over a wide range from $0.2 \mu\text{g/m}^3 \text{SO}_4$ to $80 \mu\text{g/m}^3 \text{SO}_4$ or from 0.05 to 20 ppbS.

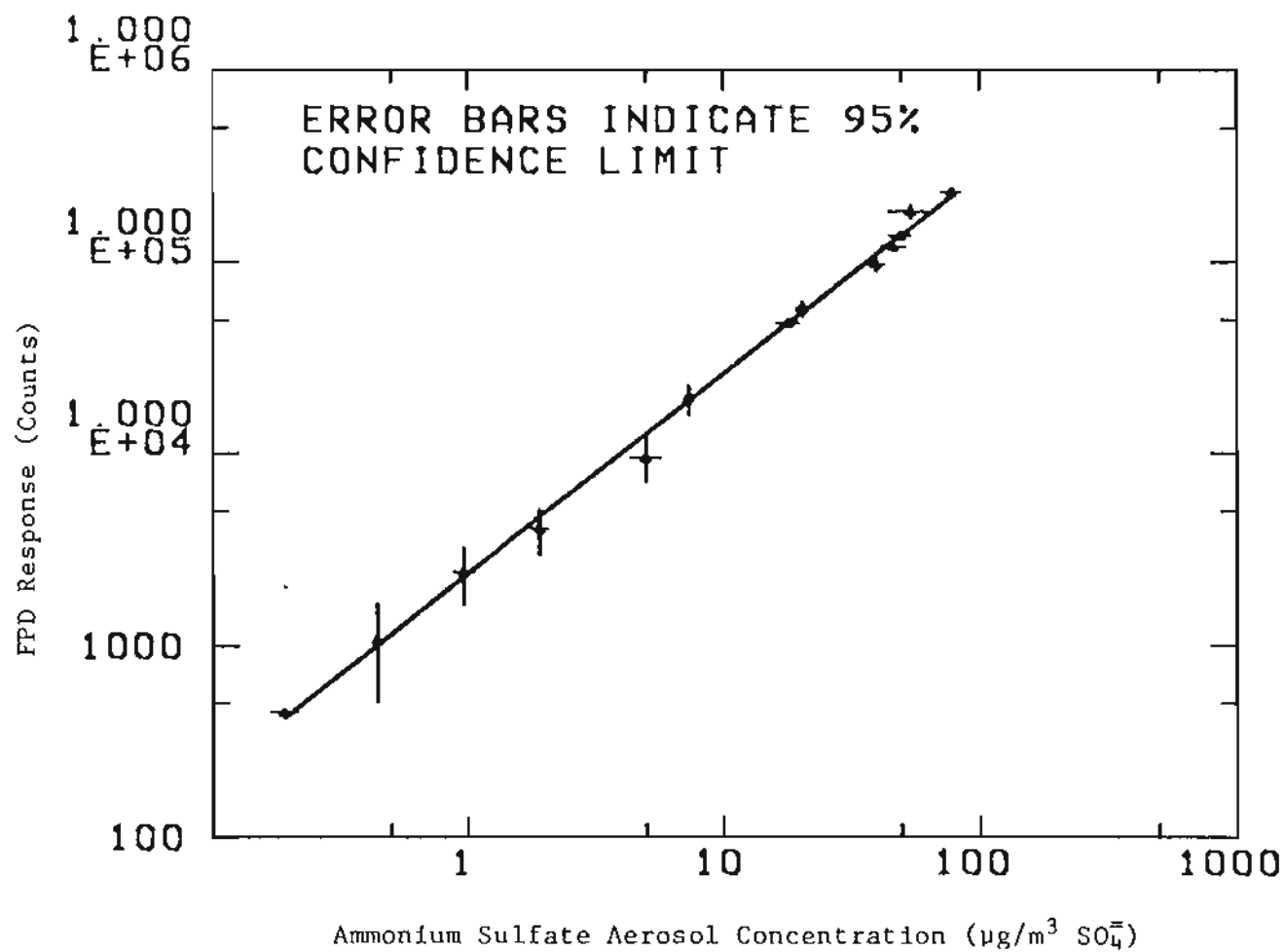


Figure 8. Ammonium sulfate calibration after the addition of CS₂ permeation tube. Slope = 1.04 ± 0.02.

TABLE 6. FPD Response to $(\text{NH}_4)_2\text{SO}_4$ Aerosols After the Addition of CS_2 to the Hydrogen Fuel. (1)

Ammonium sulfate aerosol concn. $\mu\text{gm}^{-3} \text{SO}_4$	Ammonium sulfate ⁽²⁾ solution concn. mg/L SO_4	Average ADC response (counts)	Average ADC response-blank (counts)
0.0 (n=3)	Blank	25 ± 199 (n=57)	0.0
0.19 ± 0.01 (n=3)	0.25	477 ± 791 (n=61)	452
0.44 ± 0.01 (n=3)	0.5	1,102 ± 287 (n=52)	1,077
0.97 ± 0.04 (n=3)	1.0	2,460 ± 390 (n=57)	2,435
1.91 ± 0.07 (n=3)	2.0	4,039 ± 530 (n=58)	4,014
4.98 ± 0.32 (n=3)	5.0	9,588 ± 1,200 (n=71)	9,563
7.3 ± 0.15 (n=3)	10.0	19,360 ± 1,628 (n=12)	19,335
18.1 ± 0.95 (n=3)	20.0	48,081 ± 673 (n=6)	48,056
20.4 ± 0.49 (n=3)	25.0	57,728 ± 2,606 (n=11)	57,703
39.9 ± 1.5 (n=3)	40.0	97,956 ± 3,965 (n=12)	97,931
46.7 ± 2.6 (n=3)	50.0	121,690 ± 2,356 (n=10)	121,665
49.7 ± 2.5 (n=3)	60.0	136,545 ± 2,266 (n=10)	136,520
53.9 ± 4.5 (n=4)	70.0	184,460 ± 7,437 (n=10)	184,435
77.9 ± 2.9 (n=3)	80.0	229,428 ± 5,143 (n=10)	229,403
120.8 ± 2.2 (n=3)	150.0	The ADC response is >300,000 counts, which is the maximum.	
178.5 ± 7.2 (n=4)	200.0		

(1) CS_2 is added to the hydrogen fuel at 23.5 ng/minute.

(2) This is the concentration of the solutions used to generate the aerosols at an aspirator flow of 4.2 Lpm and a dilution flow of 23.1 Lpm.

TABLE 7. FPD Calibration with SO₂ After the Addition of CS₂ to the Hydrogen Fuel

SO ₂ Concentration (ppbv)	FPD Response (ADC Counts)
8.3	77,321 ^a
10	89,671
11	108,300
14	132,700
17	171,042
23	219,814

^aZero air response (64,267 counts) is subtracted.

D. The Limit of Detection

A model for determining the limit of detection (LOD) was adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1975 and was reaffirmed by the ACS Subcommittee on Environmental Analytical Chemistry in 1980 (Long and Winefordner, 1983). The IUPAC definition states that "the limit of detection, expressed as a concentration C_L (or amount, q_1), is derived from the smallest measure, X_L , that can be detected with reasonable certainty for a given analytical procedure." The definition states that

$$X_L = X_B + k S_B$$

where X_B is the mean blank signal, S_B is its standard deviation, and k is a numerical factor chosen in accordance with the desired confidence level. A value of $k = 3$, which gives a confidence level of 99.86%, was chosen by the IUPAC (Long and Winefordner, 1983) and the ACS Committee on Environmental Improvement in its most recent revision, which appeared in the December issue of Analytical Chemistry, 1983 (Volume 55, pp. 2210-2218). The ACS Committee defined the limit of detection as the lowest concentration level that can be determined to be statistically different from the blank.

The statistical detection limit of the FPD after the addition of carbon disulfide is 0.06 ppbS. The blank signal is 25 ± 199 counts.

The F-test and t-test show that the difference between the zero air signal and the 0.05 ppbS signal is significant at a 95% confidence limit.

E. Calibration

1. Ammonium Sulfate Calibration

Initially we hoped to use an ammonium sulfate calibration to measure the absolute amount of the NH_4^+ ion in the reacted sulfuric acid aerosol in order to deduce the ammonia concentration. As the instrument developed, it became necessary to use a different calibration procedure. This was due to the fact that the system was slightly pressurized during the ammonium sulfate calibration, but in the final CRIAM design the FPD was operating under a slight vacuum. Such pressure differences have a profound effect on the FPD response.

The ammonium sulfate calibration was used during the feasibility study to evaluate (1) the extent of the ammonia reaction with H_2SO_4 aerosol, (2) wall losses, and (3) the optimization of the operating conditions of the instrument.

The procedure for ammonium sulfate calibration was as follows: a polydisperse ammonium sulfate aerosol was generated by nebulization with an aspirator flow of 4.2 Lpm and dilution air of 23.1 Lpm. Different aerosol concentrations ($0-180 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$) were produced by using different ammonium sulfate solution concentrations ($0-200 \text{mg}/\text{L} \text{SO}_4^{=}$) (Figure 9). The aerosol was passed through a ^{85}Kr charge neutralizer and an

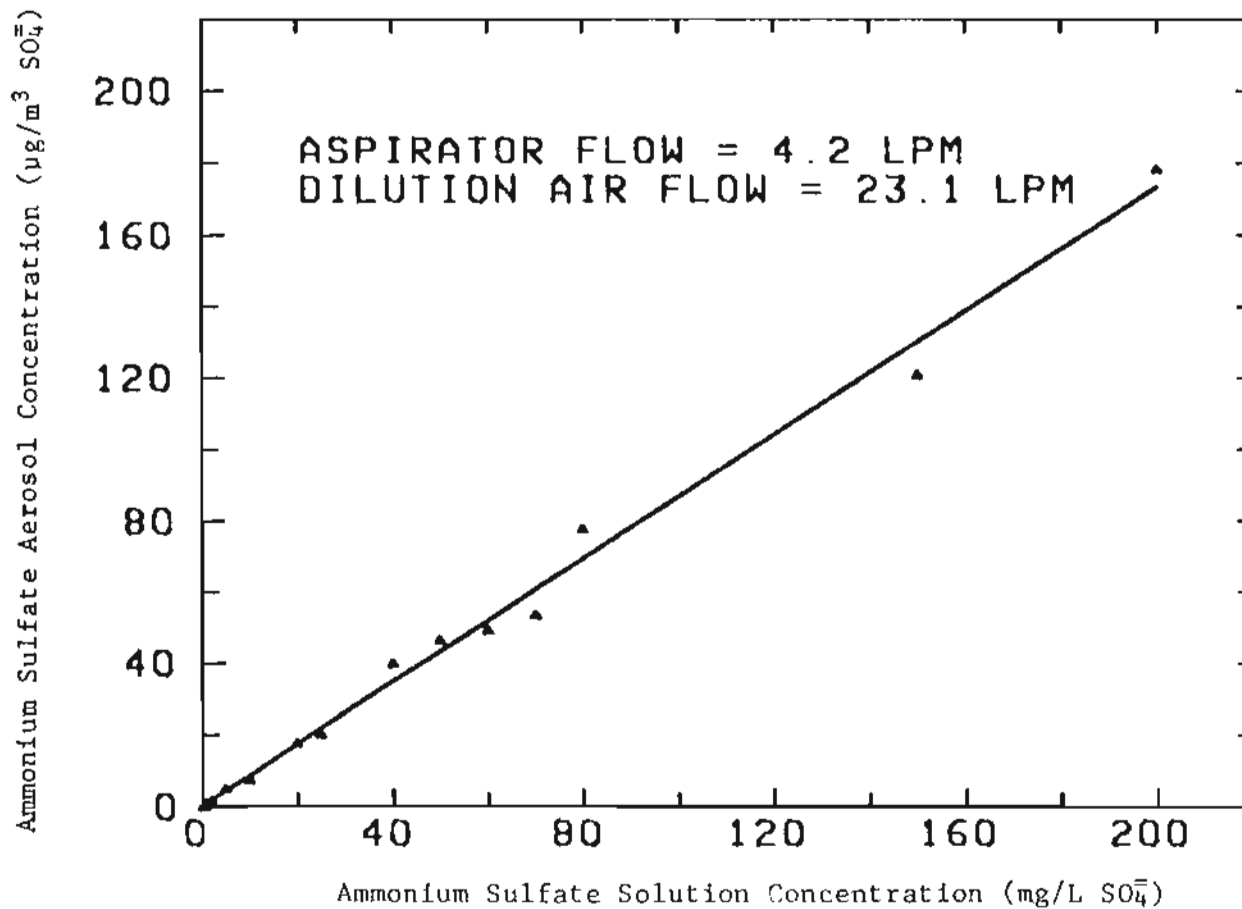


Figure 9. Aerosol concentration as a function of $(\text{NH}_4)_2\text{SO}_4$ solution concentration
 $(\mu\text{g SO}_4/\text{m}^3) = 0.28 + 0.86 (\text{mg SO}_4/\text{L})$

aging flask before entering the flow reactor. The aerosol was sampled by the instrument and simultaneously collected on a 0.5 μm pore size Fluoropore Teflon filter. The filtration flow rate was 15.6 Lpm. The filtering time was variable, depending on the aerosol concentration. The filter-collected ammonium sulfate particles were dissolved in deionized water.

The solutions were analyzed by our laboratory version of the flash volatilization method. The reader can find a detailed discussion on the method in papers published by Huntzicker et al. (1978), Roberts and Friedlander (1976), and Husar et al. (1975).

A diagram of the flash-volatilization apparatus and its associated circuitry is shown in Figure 10. A 0.015 cm diameter Pt wire is mounted on molybdenum posts using molybdenum nuts and washers. A dc power supply continuously charges the capacitors. When the dc circuit is closed, the capacitors discharge through the Pt wire. The apparatus connects to the FPD sampling inlet.

A 4 μL drop containing either an ammonium sulfate standard or a collected sample solution is hung on the Pt wire just below the cone. The drop is then slowly evaporated by about a 1.5 amp ac current, and the sulfate is deposited on the wire. The capacitors are charged to about five volts and then discharged through the wire. The Pt wire is rapidly heated to greater than 1000°C, converting any deposited sulfur to sulfur dioxide. The sulfur dioxide is measured as a sharp pulse by the flame photometer. Figure 11 shows the calibration of the flash-vaporization apparatus.

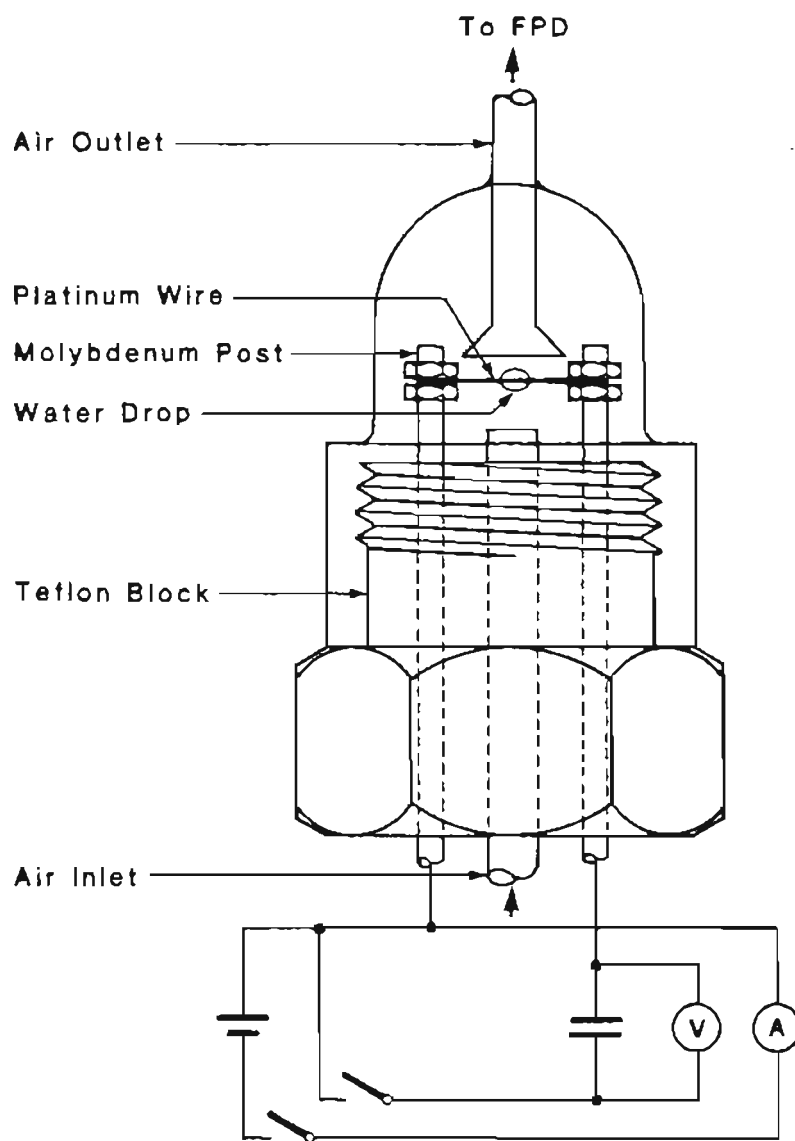


Figure 10. Flash-volatilization cell and its associated electrical circuit.

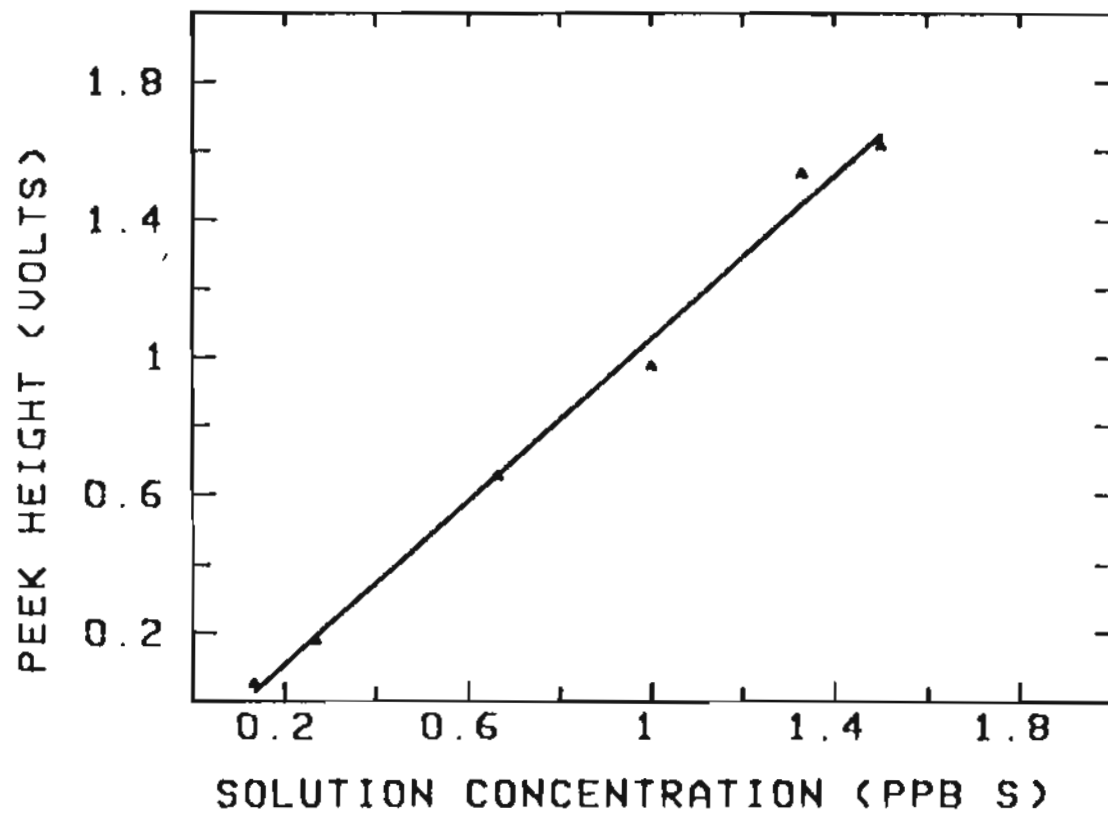


Figure 11. The calibration of the flash-volatilization apparatus.

2. Permeation Tube Calibration

A calibrated ammonia permeation tube was used to generate the various gaseous ammonia concentrations. The tube is housed in a constant temperature bath (50°C), which is a part of the gas calibrator (8500 CALIBRATOR, Monitor Labs., Inc.). The resultant permeation rate was 162 ng/minute NH_3 at 50°C. The permeation rate was determined by weighing the tube with a five-place balance at different time intervals over 103 days. Figure 12 shows the calibration equation.

F. Ammonia Reaction with Sulfuric Acid Aerosol

The ammonia-sulfuric acid reaction study was limited to the understanding of the operating parameters, which were needed in the monitor design. Detailed studies of the reaction had been done by Huntzicker et al. (1980) and McMurry et al. (1983). The study of ammonia reaction with sulfuric acid was accomplished in two steps. First, the FPD response to ammonium sulfate aerosol was established. The resultant calibration equation was then used to deduce the concentration of reacted ammonia.

The second step in the ammonia reaction study was to establish the fraction of the reacted ammonia to the actual ammonia concentration entering the reactor for different experimental conditions (e.g., flow rate and sulfuric acid aerosol concentration).

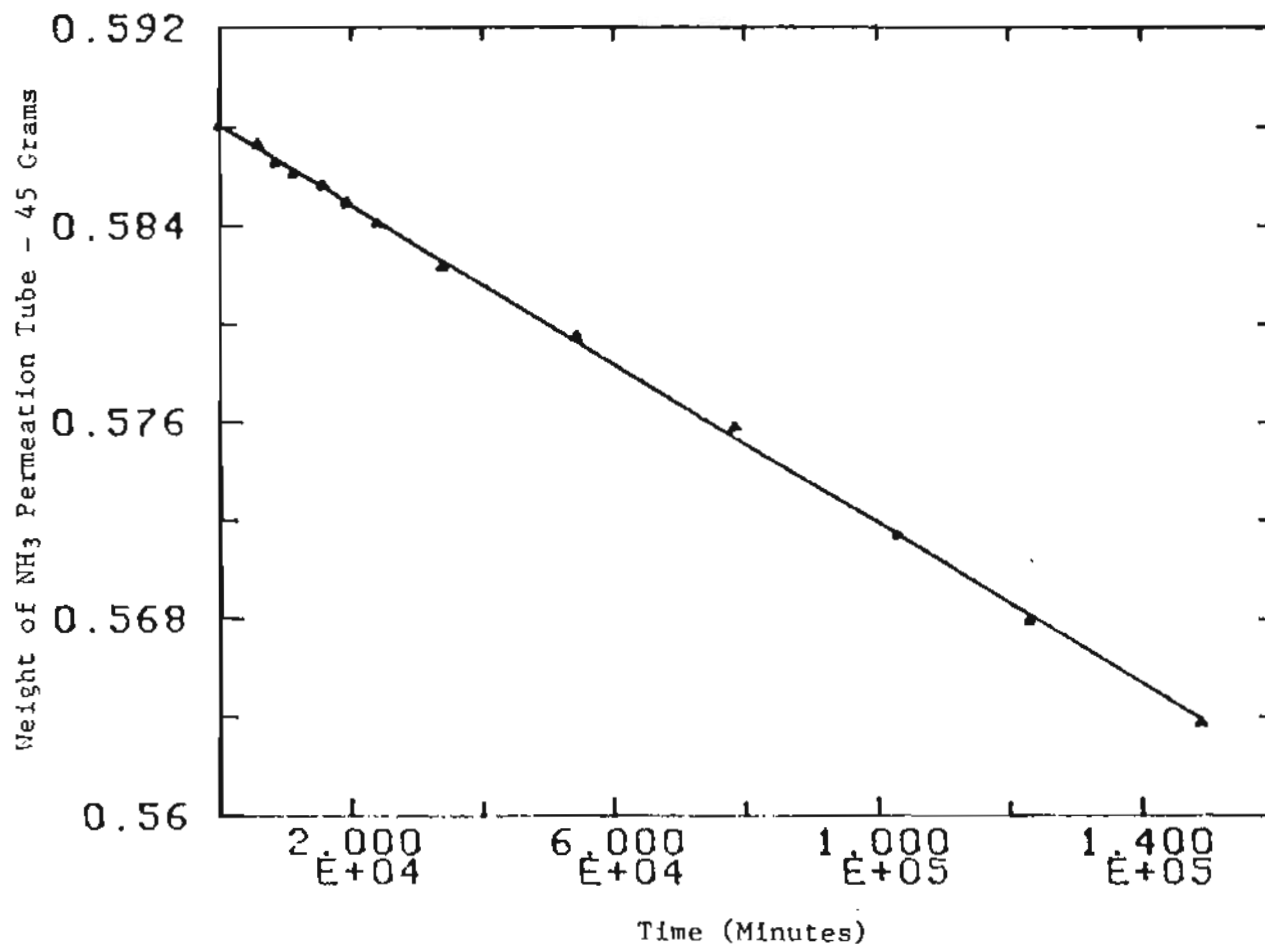


Figure 12. Calibration of the ammonia permeation tube.
 $(W_{\text{NH}_3} - 45) = 0.59 - 1.62 \times 10^{-7} t$

Known ammonia concentrations were reacted with excess polydisperse sulfuric acid aerosols, and the resultant NH_4HSO_4 were measured by the FPD. The different concentrations were generated by diluting the generated ammonia with ammonia-free air. Lower ammonia concentrations were obtained by increasing the total air flow in the reactor. Therefore, the reactor (residence time) was shortened as lower ammonia concentrations were generated. This led to a reduction in the amount of ammonium sulfate produced. Table 8 shows the results based upon the ammonium sulfate calibration, and Figure 13 shows a graphical representation of the data. The regression equation is

$$[\text{NH}_3]\text{Reacted} = -0.7 + 0.97 [\text{NH}_3]\text{Total} \quad (11)$$

$$(r = 0.985)$$

where $[\text{NH}_3]\text{Reacted}$ is the concentration of ammonia measured by the FPD using the ammonium sulfate calibration (Figure 8), and $[\text{NH}_3]\text{Total}$ is the ammonia concentration entering the reactor tube.

The negative intercept in Eq. 11 is an artifact of the measurement procedure. The lowest NH_3 concentrations were produced by dilution with NH_3 -free air, which resulted in a reduced residence time in the reactor as noted above. The reduction in residence time resulted in a smaller net conversion of NH_3 to NH_4^+ during the transit through the reactor. Figure 14 shows a plot of reacted ammonia as a function of residence time.

TABLE 8. Gaseous Ammonia Measurements

Total Ammonia Concentration (ppb)	Reacted Ammonia Concentration (ppb)
1.3	0.7
1.4	0.7
1.7	1.5
1.9	1.2
2.0	1.4
2.5	2.1
3.1	2.5, 2.6
3.3	2.2
3.5	2.9
3.6	3.8
4.0	3.1, 2.5
4.1	3.6
4.2	3.0
4.8	4.4
5.1	4.2
5.6	4.8
6.5	4.9, 5.9
6.8	5.8, 5.3
7.3	5.3
7.5	6.4
7.8	6.2, 6.5, 7.3
8.3	6.4, 6.4
9.0	7.4
9.7	8.9
10.5	9.2, 10.3
11.5	10.6, 11.0
12.7	12.9

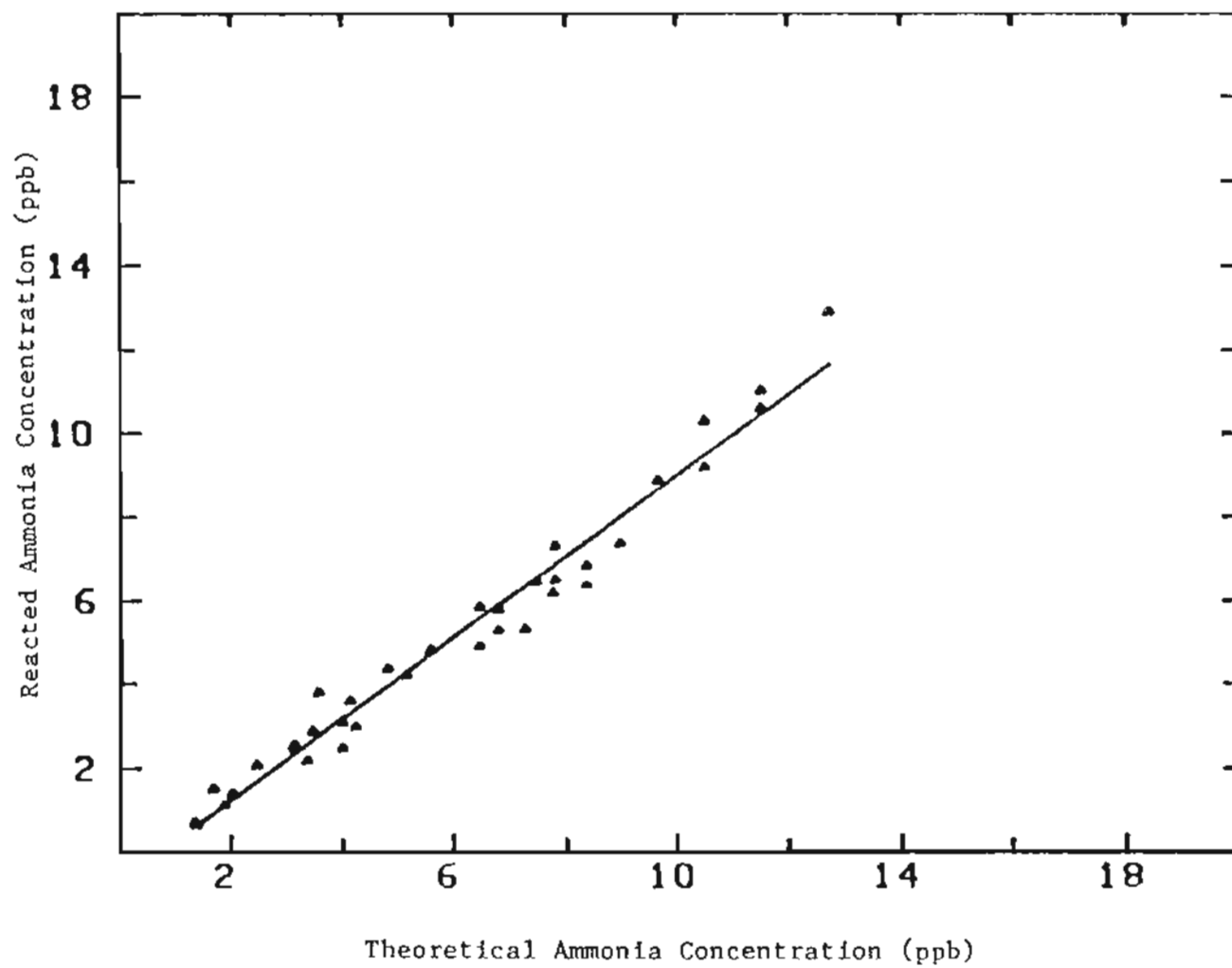


Figure 13. Instrument response to gaseous NH_3 .
Slope = 0.968.

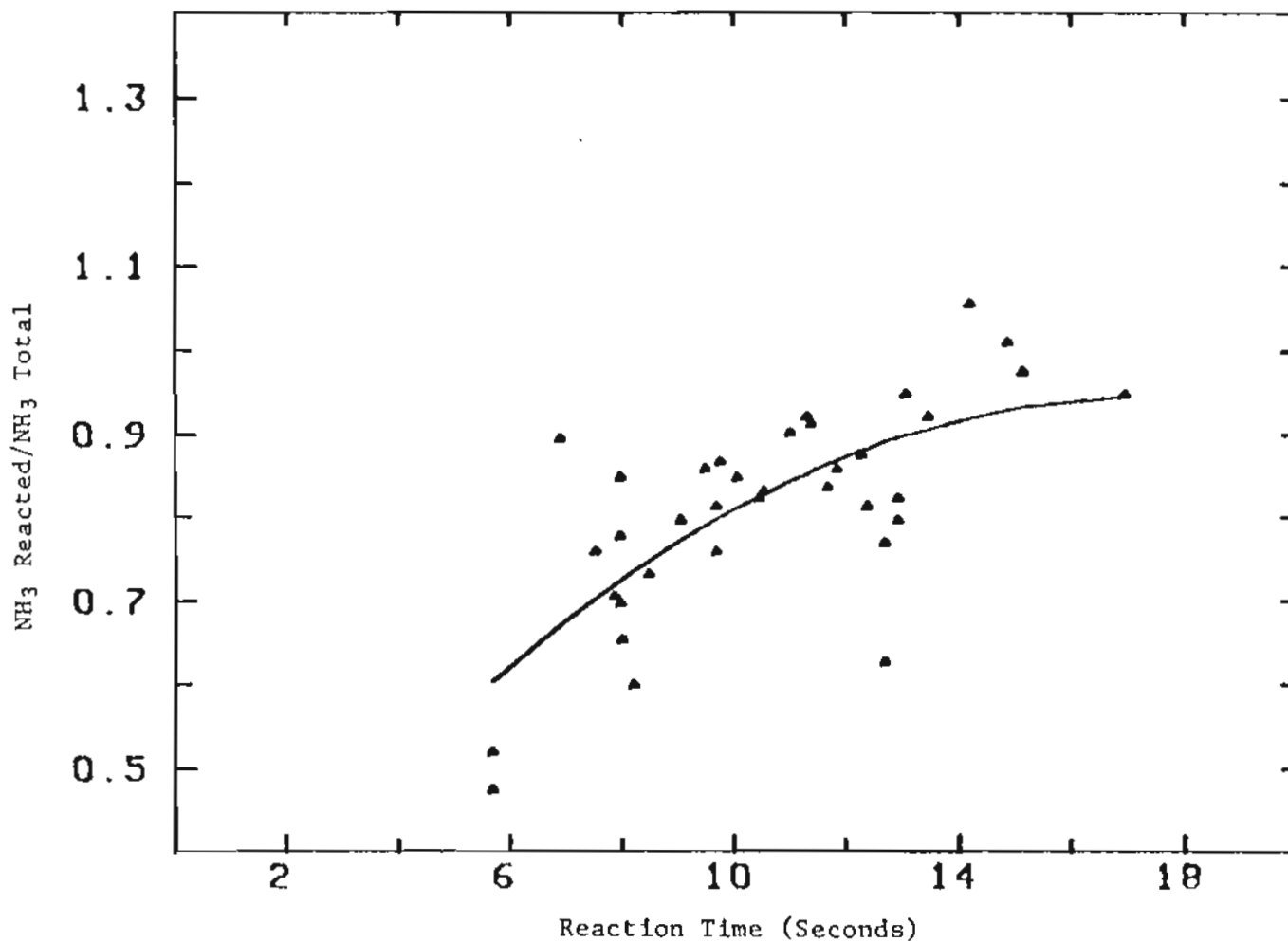


Figure 14. Reaction time effects on the extent of ammonia reaction with H₂SO₄ aerosol.

III. FINAL INSTRUMENT DESIGN AND EVALUATION EXPERIMENTS

An instrument that utilizes the FPD to measure ambient ammonia must meet the following conditions. First, it has to separate gaseous ammonia from ammonium salts. Second, it must be capable of removing sulfur dioxide and hydrogen sulfide from sampled air. This is done by using a denuder coated with lead acetate. Third, excess sulfuric acid used in the reaction must be removed. Fourth, it should be capable of detecting ammonia at about a 1 ppb level. And finally, it should have a reasonable time resolution between measurements.

A. Ambient Ammonia Instrument

The instrument is simplified for ambient measurements. The five port valve and all the heated columns but one are removed. A 2 μm Teflon filter is placed in front of the sulfuric acid and sodium carbonate impregnated filters to remove particles. The sodium carbonate impregnated filter is used to maintain the same pressure drop in the system when air is passed through either of the two filter holders. The instrument operates in the following manner (see Figure 15).

At the beginning, the valve is oriented to measure gaseous ammonia. Ambient air is drawn through the filter holder containing the Teflon and sodium carbonate impregnated filters. The microprocessor waits fifteen minutes before taking the first NH_3 reading. Two additional ammonia measurements, which are five minutes apart, are taken in

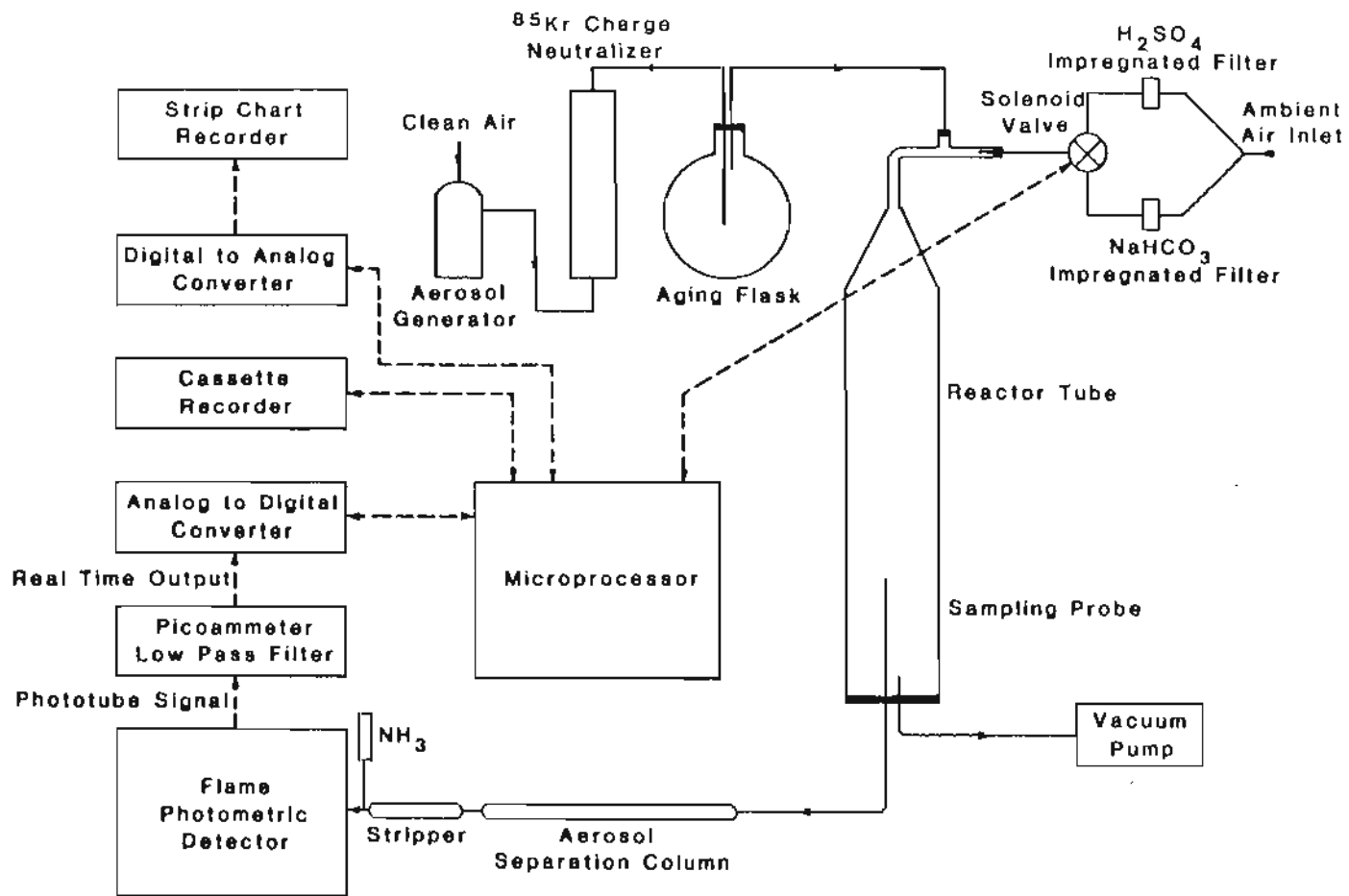


Figure 15. Ambient ammonia measuring system.

the next ten minutes. At this point 25 minutes have elapsed since the start of the cycle, and the valve is switched to pass sampled air through the sulfuric acid impregnated filter to remove gaseous ammonia from sample air. The processor waits 15 minutes before it takes the baseline reading. The reason for the fifteen minute wait is that on days of high humidity the instrument response time is considerably slowed. We have found that the response time is slowed by 10 to 12 minutes during high humidity experiments (>90% relative humidity). This finding agrees with the D'Ottavio et al. (1981) and Luis (1978) observations of positive correlation between high humidity and response time. Each cycle is 40 minutes long, and at the end of every cycle the baseline is updated as explained above.

B. Limit of Detection

The ammonia detection limit is 0.4 ppb. The detection limit is defined according to the 1983 ACS Committee on Environmental Improvement recommendation, which appeared in the December 1983 issue of Analytical Chemistry. The limit of detection is defined as the lowest concentration level that can be determined to be statistically different from the blank. The blank signal was 34 ± 508 counts for the calibration during the ambient ammonia measurement period of October 7 through October 19, 1983 (Table 9). In February 1984 another calibration was taken to extend the calibration to sub-1 ppb level, using a new CS₂ permeation tube. Table 10 shows the data and Figure 16 shows a plot of the data.

TABLE 9. Instrument Calibration for Ambient Ammonia Measurements

NH ₃ Concentration (ppbv)	Instrument Response (counts)
zero air	34 ± 508 (n = 46)
1.7	14,631 ± 312 (n = 4)
2.0	17,862 ± 869 (n = 51)
3.2	32,460 ± 1,531 (n = 4)
3.6	36,601 ± 1,658 (n = 40)
4.3	44,730 ± 1,466 (n = 5)
5.9	66,395 ± 2,378 (n = 49)
8.0	83,358 ± 1,670 (n = 4)
10.4	114,656 ± 1,683 (n = 4)

TABLE 10. February 1984 Instrument Ammonia Calibration with a New CS₂ Tube

Ammonia Concentration (ppbv)	Instrument Response (counts)
zero air	23 ± 443 (n = 23)
0.45	2,045 ± 967 (n = 18)
0.71	3,105 ± 1,044 (n = 45)
1.2	4,741 ± 807 (n = 63)
2.3	10,538 ± 785 (n = 7)
4.0	25,524 ± 1,027 (n = 4)
4.5	25,372 ± 2,820 (n = 69)
5.7	33,016 ± 1,072 (n = 50)
7.1	44,444 ± 737 (n = 6)
8.7	52,235 ± 956 (n = 9)
11.0	67,314 ± 748 (n = 5)

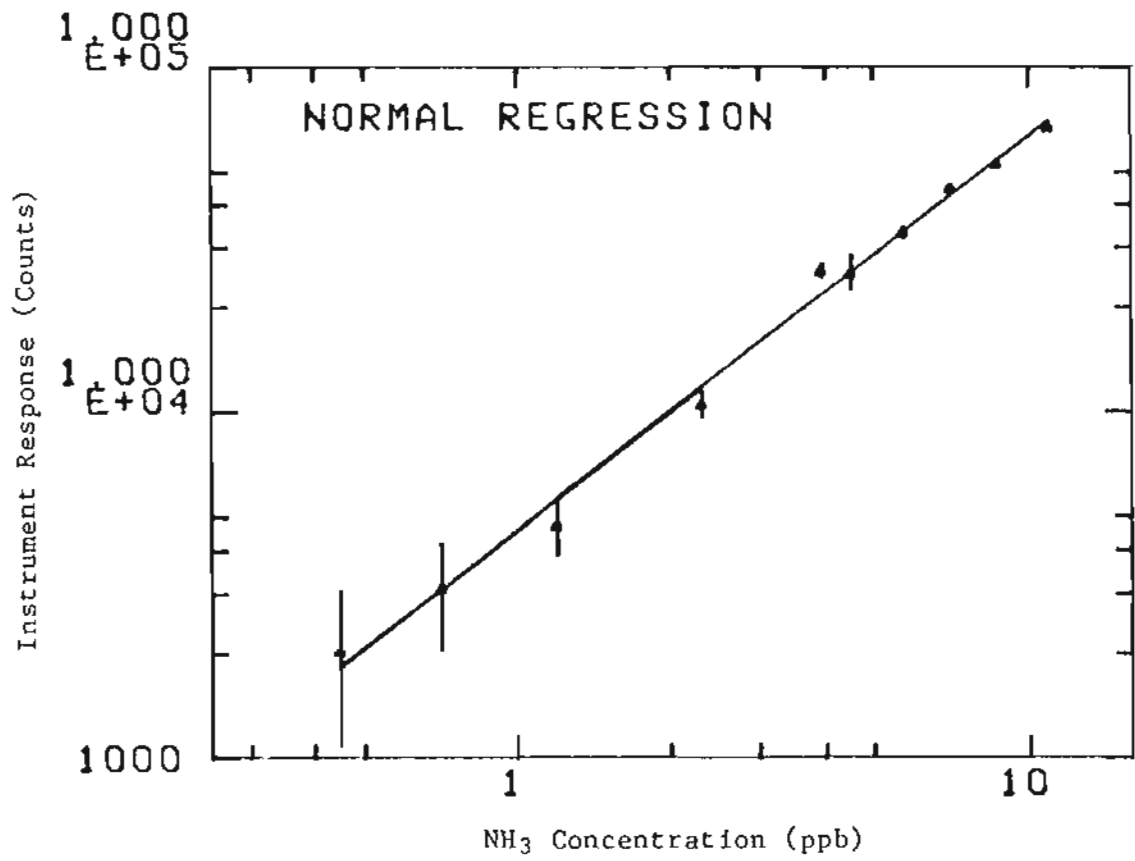


Figure 16. Instrument calibration during February 1984. The regression equation is $\log[\text{counts}] = 3.66 + 1.14 \log[\text{NH}_3]$.

This calibration gave a blank signal of 23 ± 443 counts. In calculating the limit of detection the February calibration blank signal of 23 ± 443 counts was used. The October calibration gave a detection limit of <0.3 ppb.

C. Ambient Ammonia Measurements

Ambient ammonia measurements were taken outside our laboratory at the Oregon Graduate Center during the period of October 7-20, 1983. The site is rural surrounded by houses and farms.

The CRIAM was calibrated for ambient ammonia measurement by generating different concentrations into a polyethylene bottle. The monitor sucks in air containing different NH_3 concentrations simulating actual sampling conditions. Table 9 shows the calibration data, and Figure 17 shows the calibration line and equation taken during the field measurement period of October 7 to October 19, 1983.

The data show that the maximum NH_3 concentration was 7.3 ppb, the minimum was 0.2 ppb, and the average was 1.7 ppb for the sampling period. Figure 18 shows the instrument response to ammonia-free ambient air. It gave an average of 280 counts, which is equivalent to 0.06 ppb NH_3 . The ammonia data (see Figures 19 to 26) show a diurnal cycle in which the ammonia concentration peaks in the late morning hours, usually between nine and twelve. Another but usually weaker peak is sometimes observed between 5 and 9 P.M. The figures show periods in which filters were changed and no data were collected. The morning high is caused by

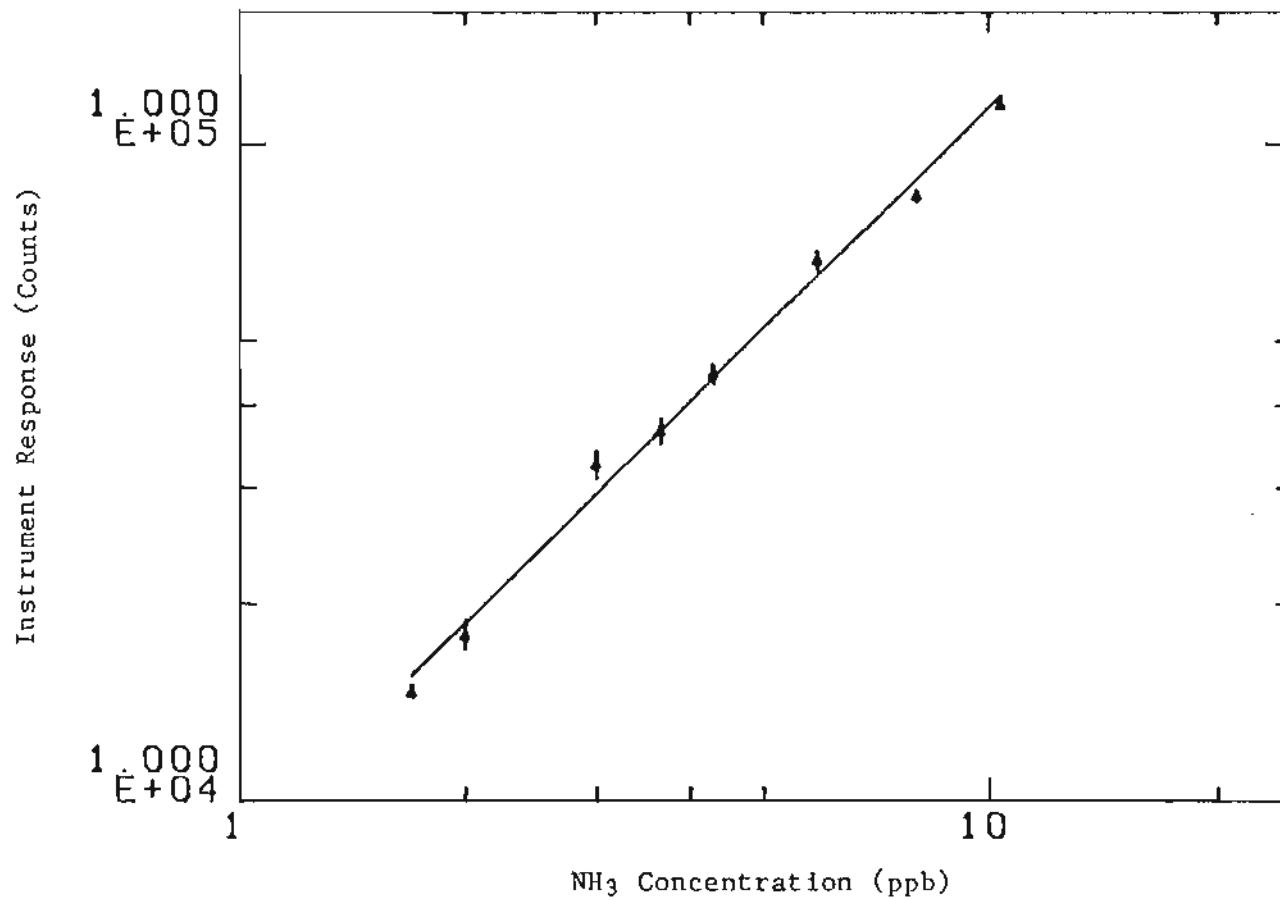


Figure 17. October 1983 instrument calibration for ambient measurements.
The regression equation is $\log[\text{counts}] = 3.93 + 1.13 \log[\text{NH}_3]$.

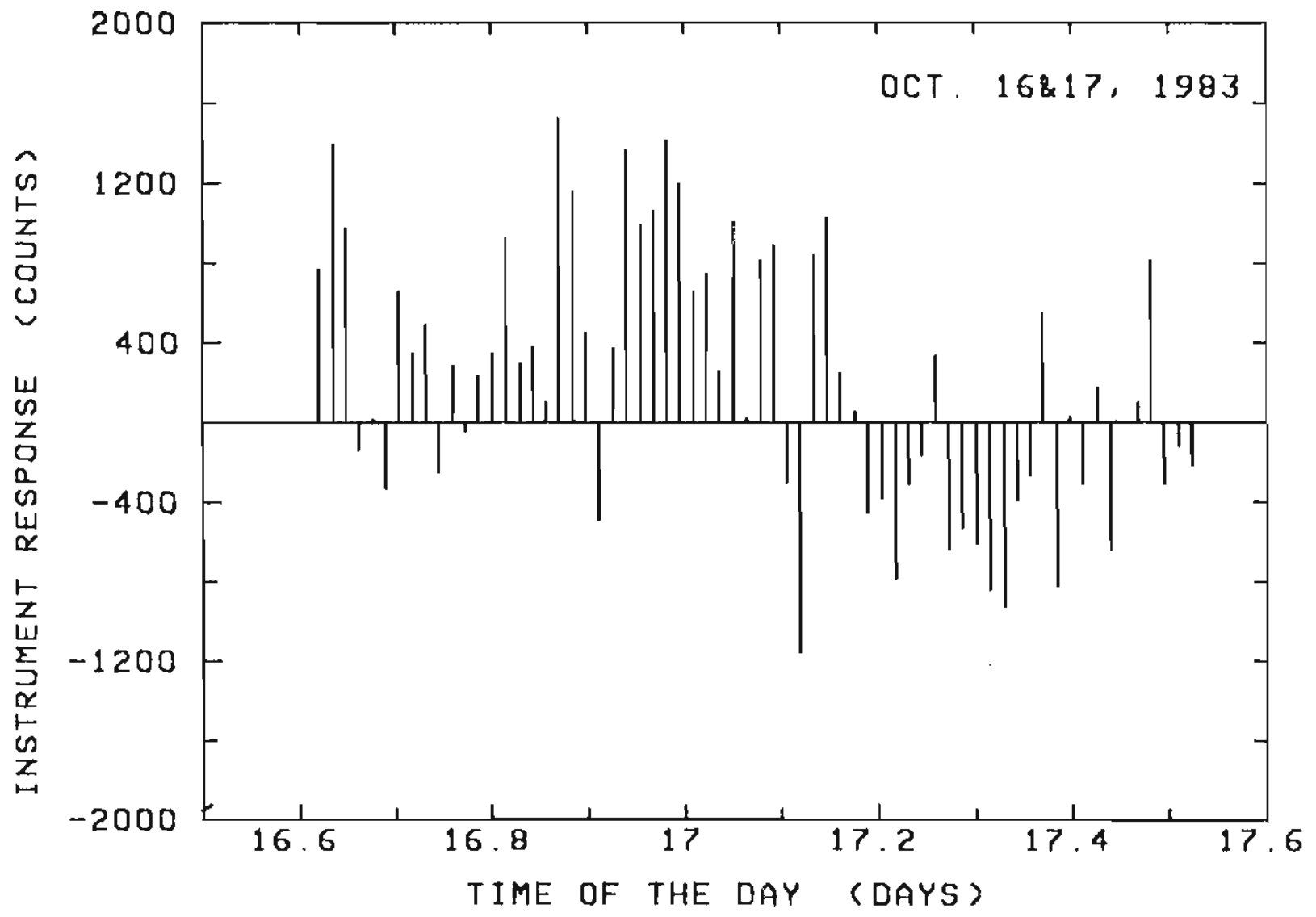


Figure 18. Instrument response to ammonia-free ambient air.

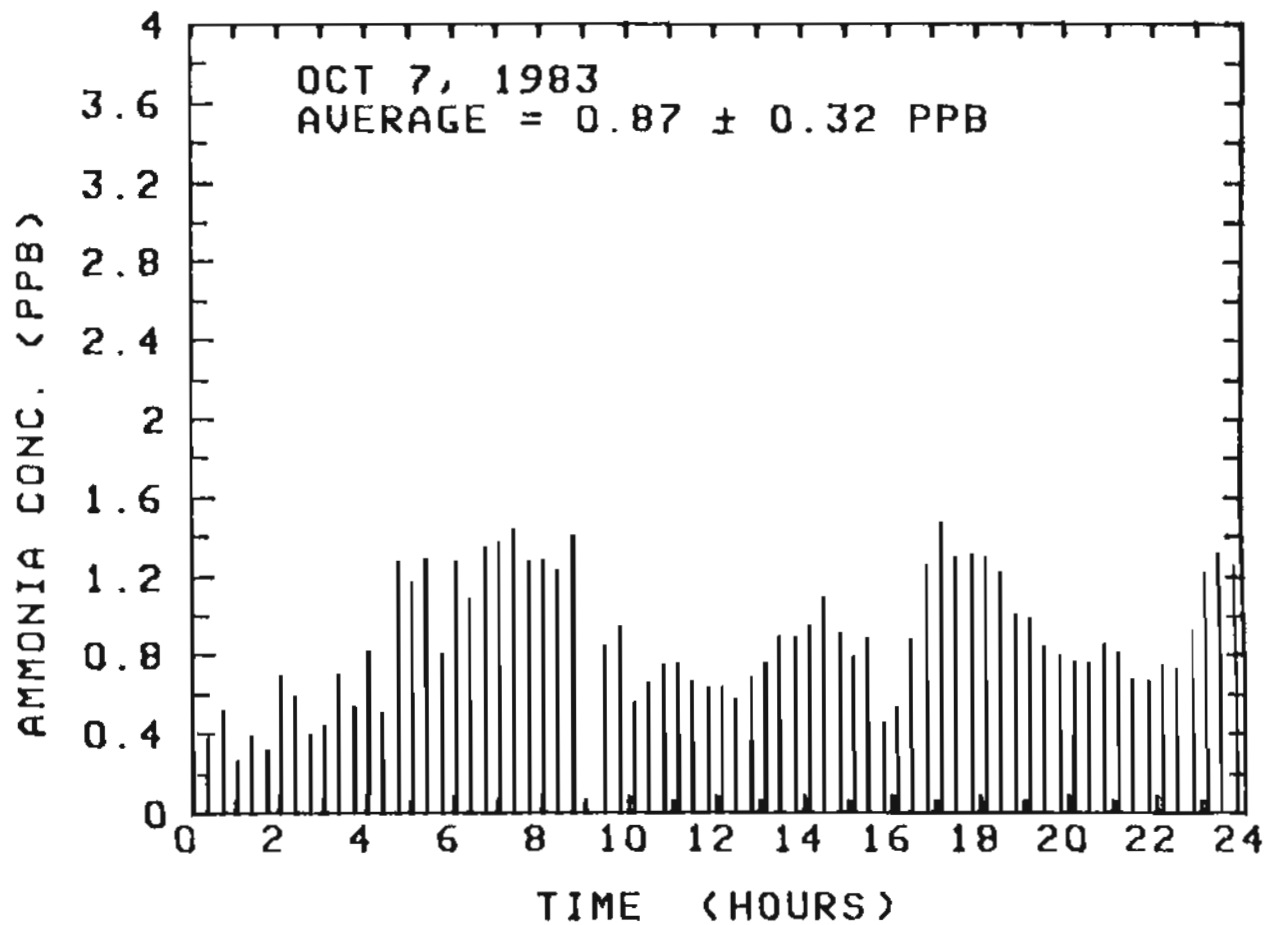


Figure 19. Ambient ammonia measurements for October 7, 1983.

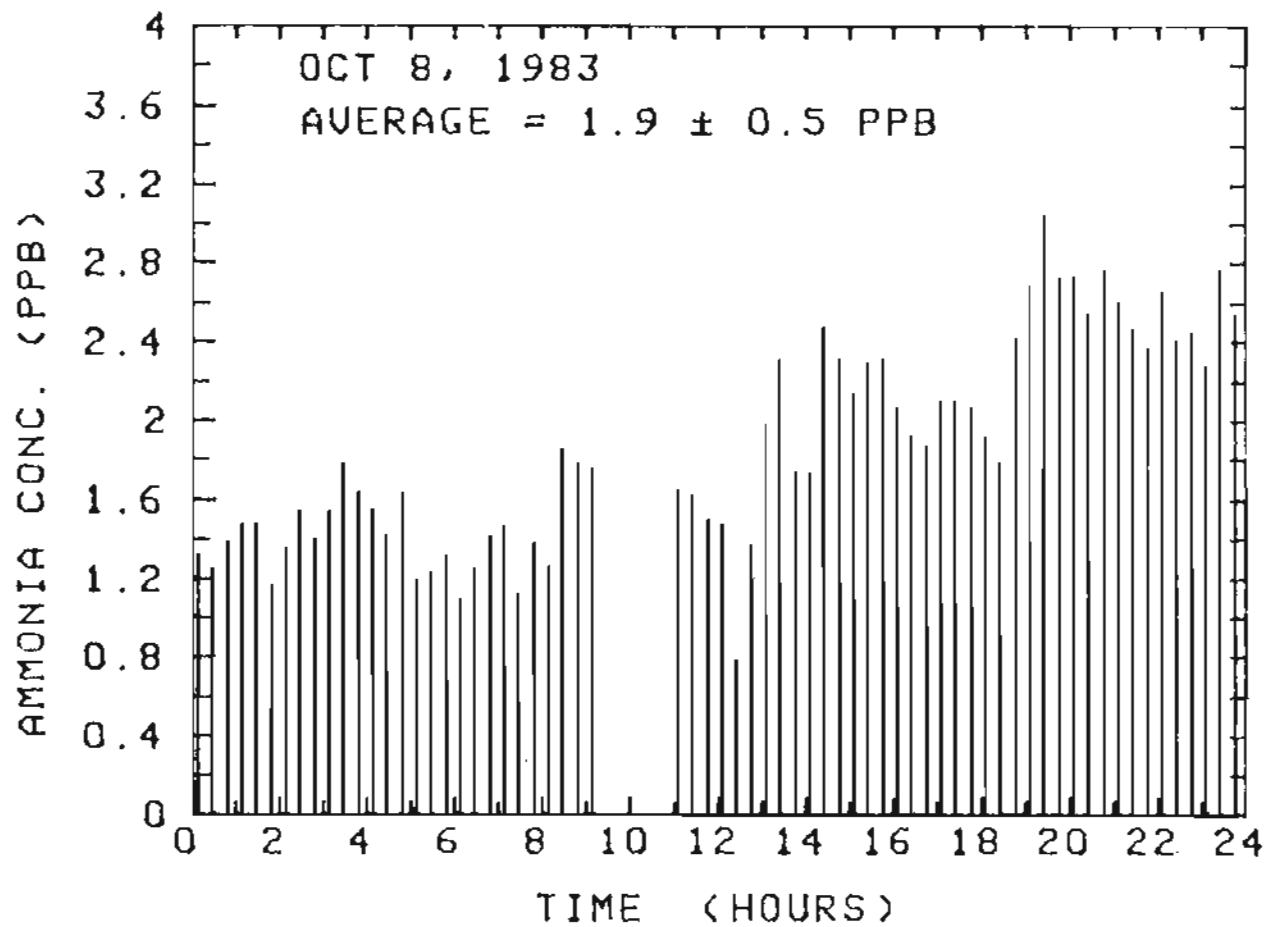


Figure 20. Ambient ammonia measurements for October 8, 1983.

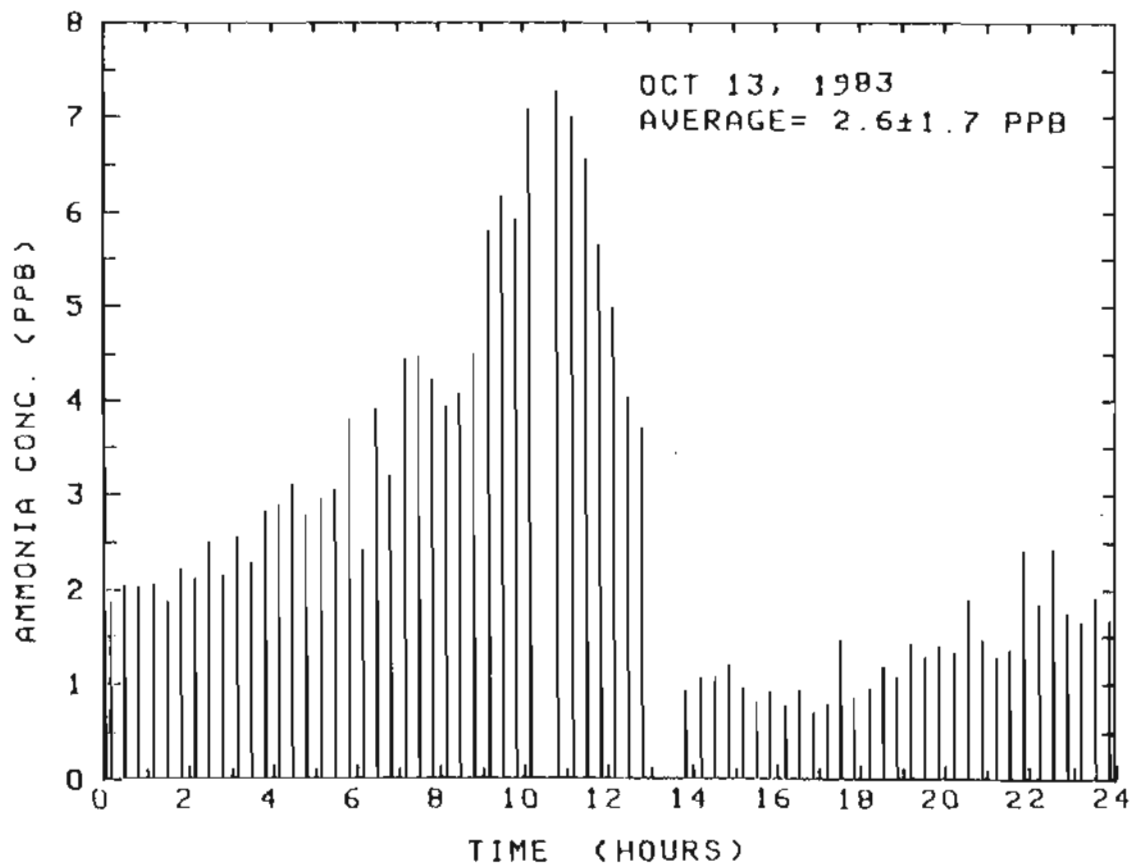


Figure 21. Ambient ammonia measurements for October 13, 1983.

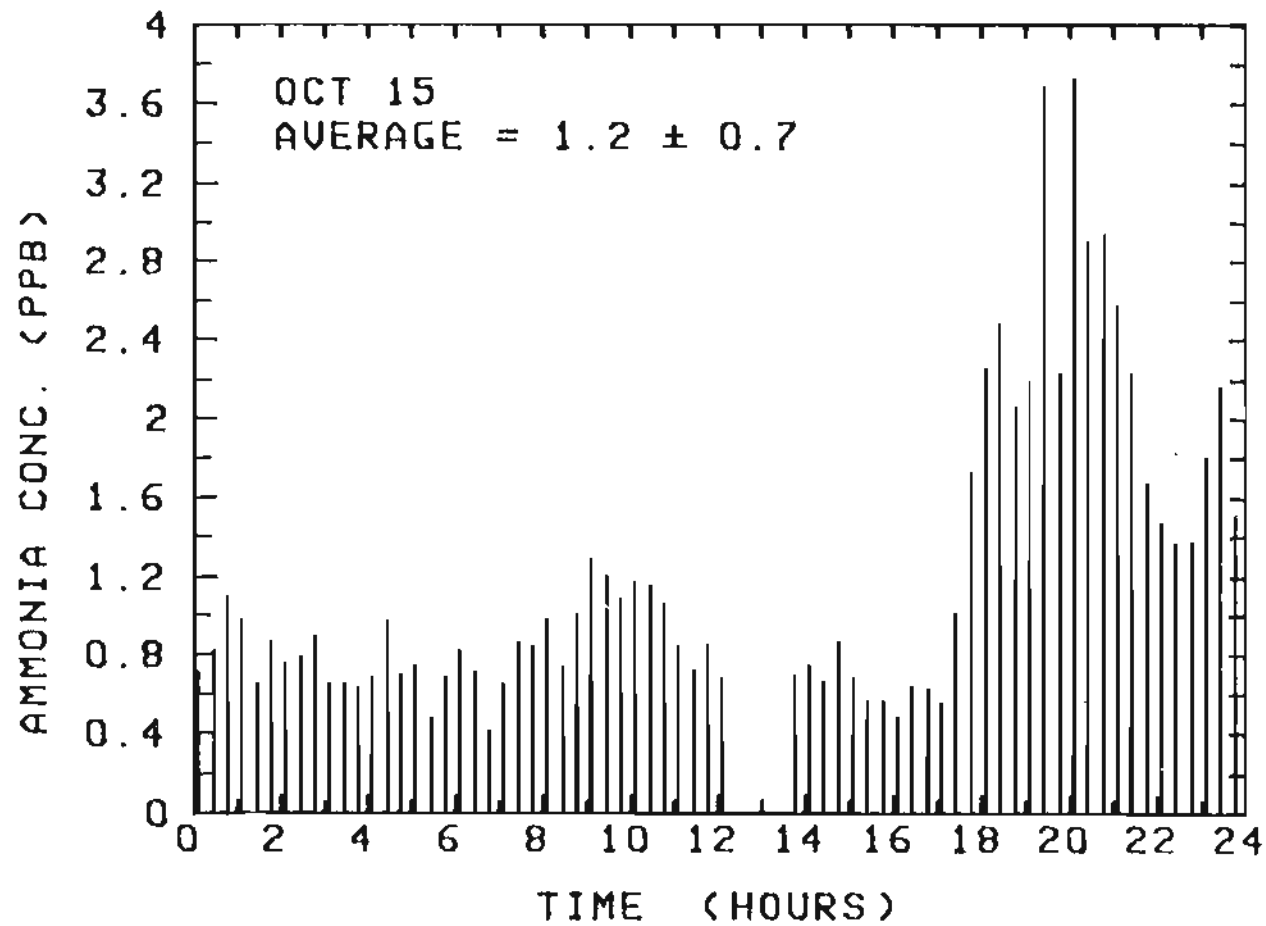


Figure 22. Ambient ammonia measurements for October 15, 1983.

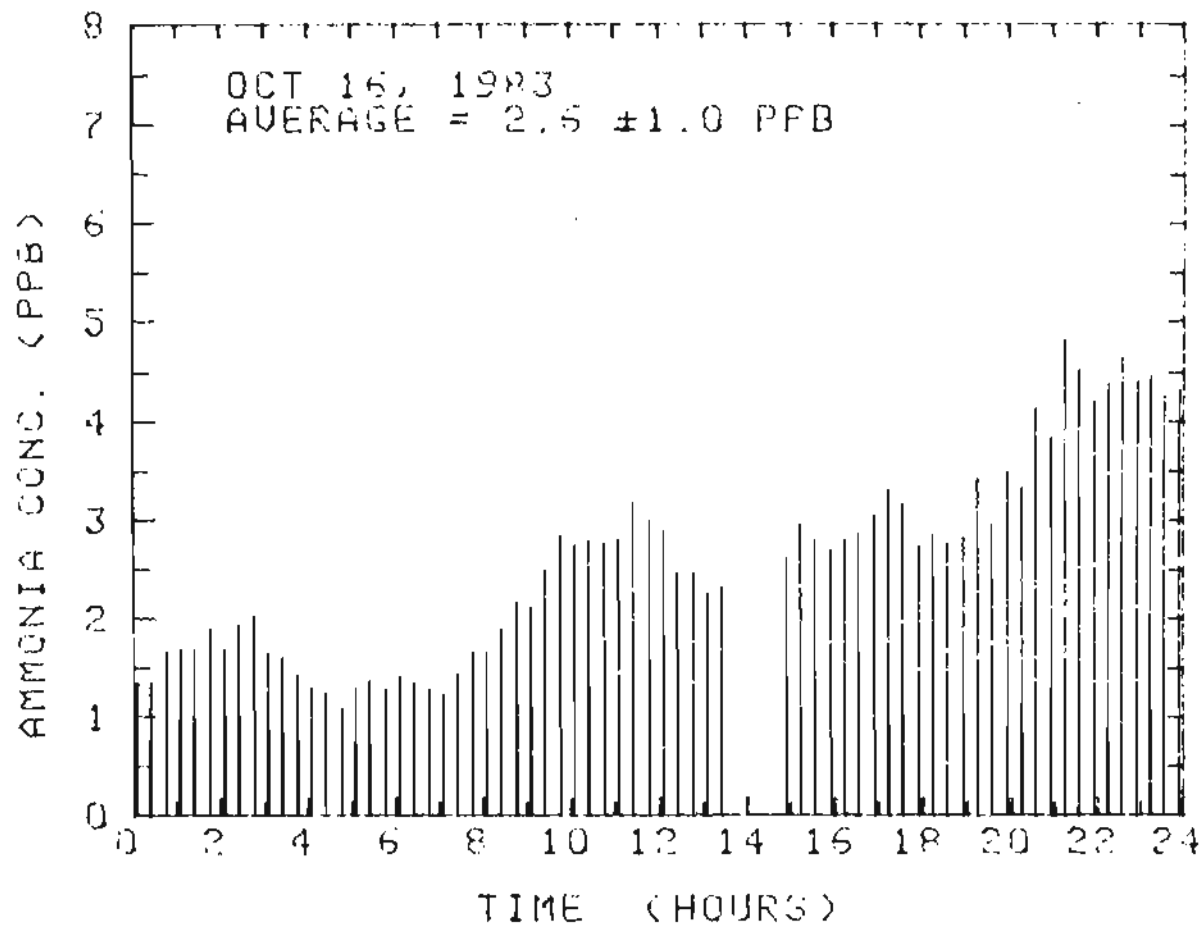


Figure 23. Ambient ammonia measurements for October 16, 1983.

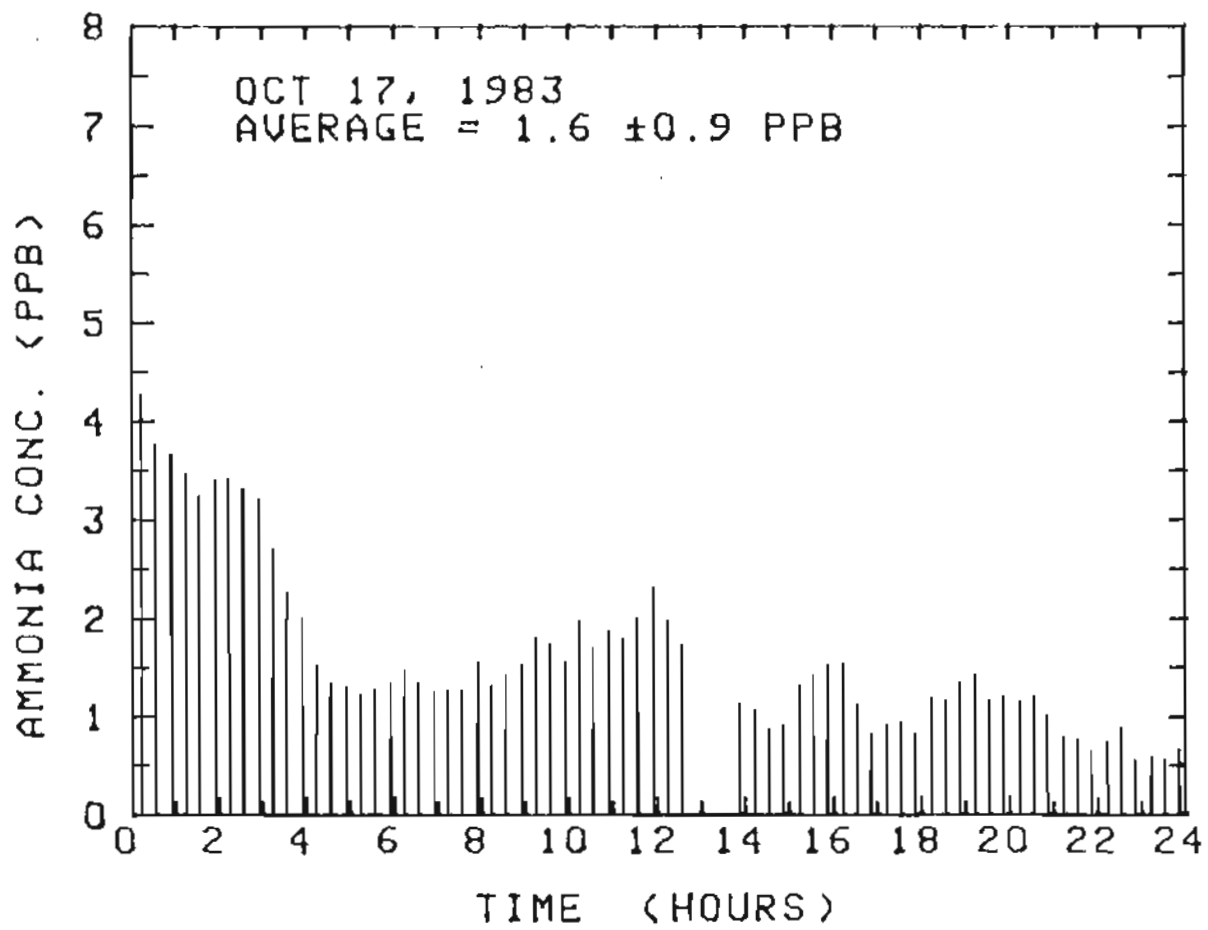


Figure 24. Ambient ammonia measurements for October 17, 1983.

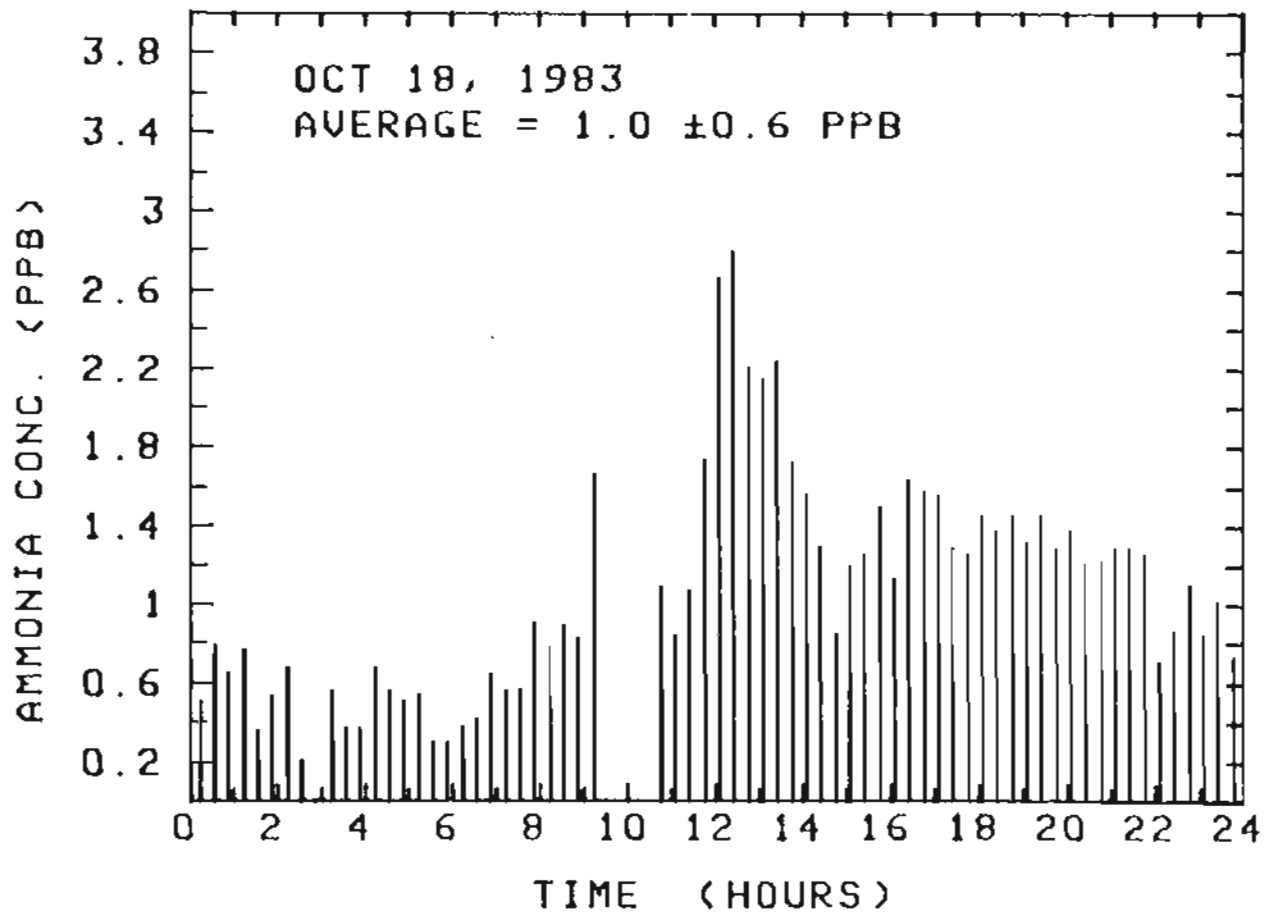


Figure 25. Ambient ammonia measurements for October 18, 1983.

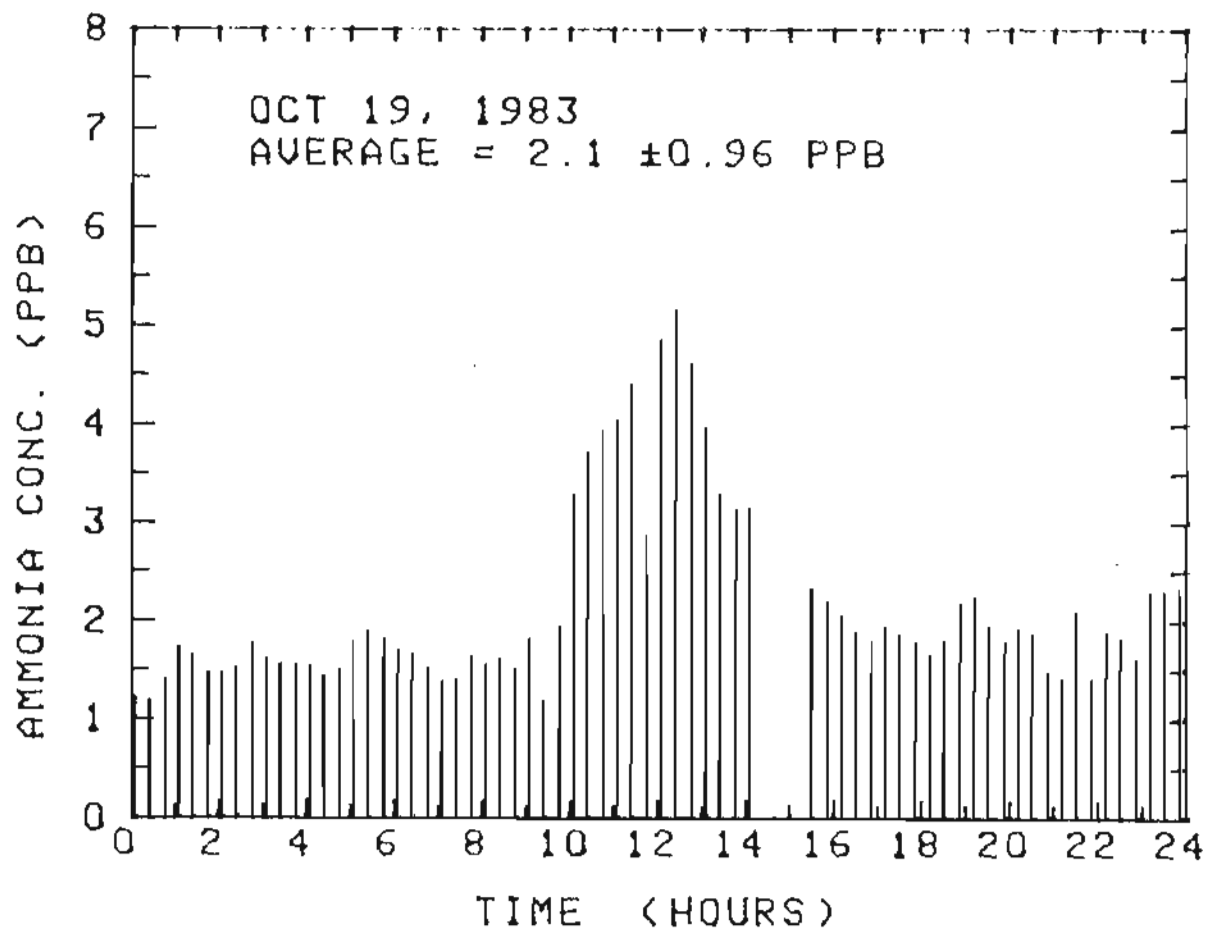


Figure 26. Ambient ammonia measurements for October 19, 1983.

the rise in the atmospheric temperature. This results in a warming of the ground surface and evaporation of its water. The dissolved ammonia is consequently released (Dawson, 1977). At mid-day and afternoon, the atmospheric ammonia concentration is lower than the morning high due to the following: (1) depletion of available ammonia from surface water evaporation, (2) ammonia reaction with hydroxyl radical and photochemically generated aerosols (McClenny et al., 1982), and (3) the increase in the atmospheric mixing as the atmosphere is heated and the inversion layer is lifted. Possible explanations for the evening maximum include: first, an increase in local ammonia emission due to the evening rush hour traffic on the nearby highways and roads (Pierson & Brachaczek, 1983; Harkins & Nicksic, 1967) and to the heating of homes by woodstoves and fireplaces (Miner, 1969); and second, the lowering of the inversion layer after sunset.

Real-time temperature data were collected between October 15 and October 19 (Figures 27 to 31). They show that the morning rise in ammonia concentration correlated with atmospheric warming. The morning ammonia maximum occurs when the temperature reaches 10 to 11 degrees centigrade. Figures 32 to 36 show a plot of the daily ammonia concentration vs. temperature. They show that the ammonia morning maximum occurred when temperatures were between ten and eleven degrees centigrade.

The advantage of our real-time ammonia instrument over the methods that give only averaged ammonia concentrations as the impregnated filter

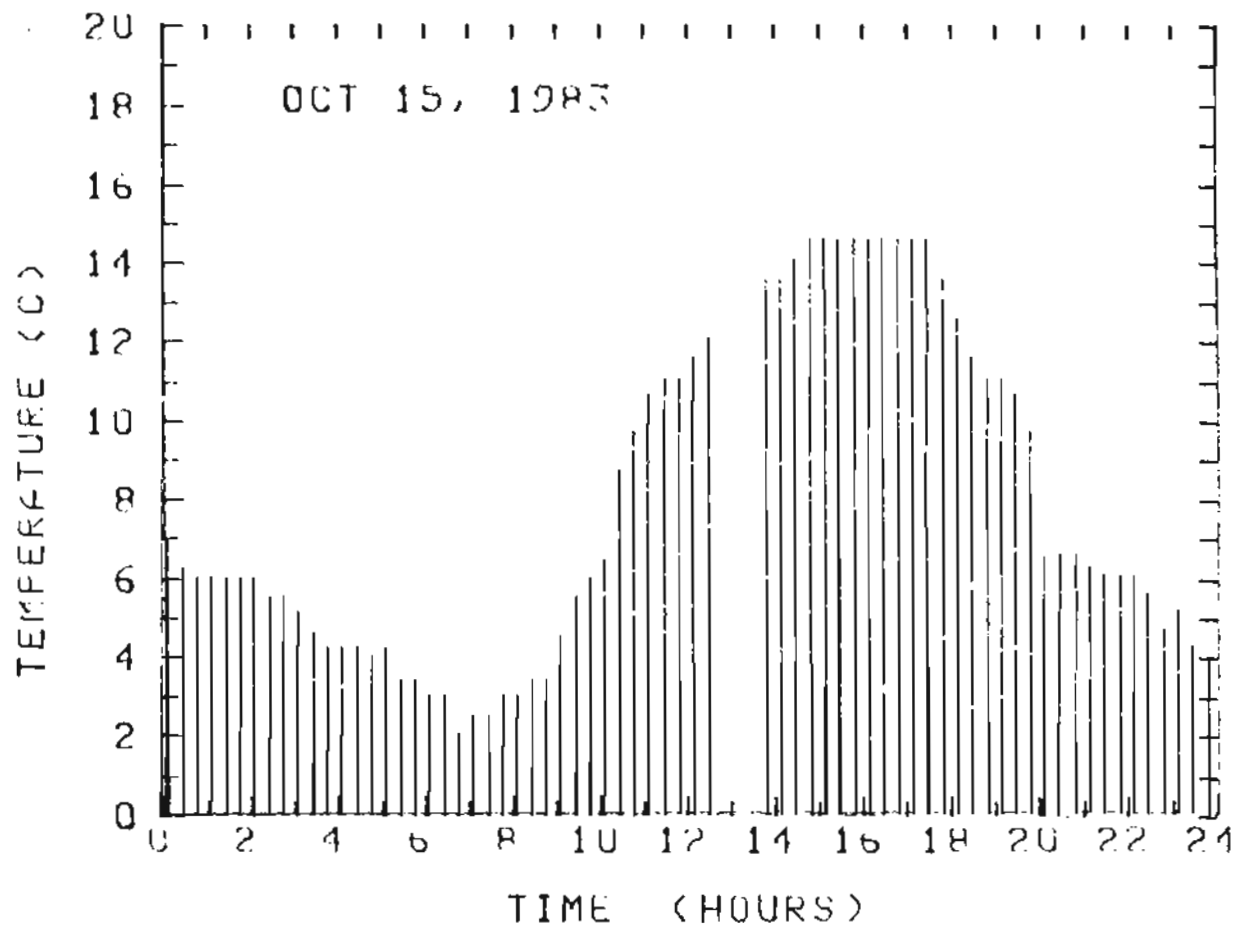


Figure 27. Ambient temperature data for October 15, 1983.

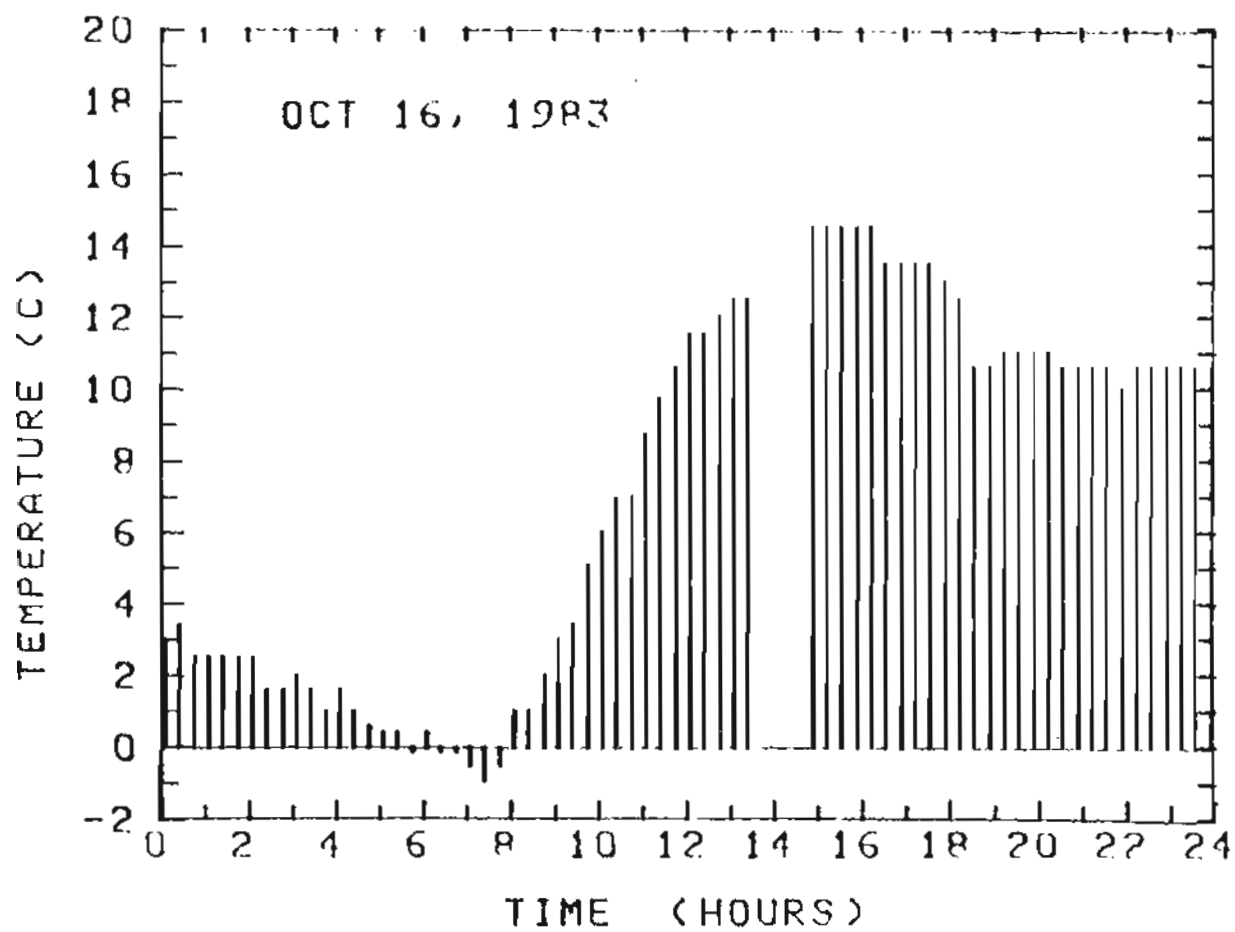


Figure 28. Ambient temperature data for October 16, 1983.

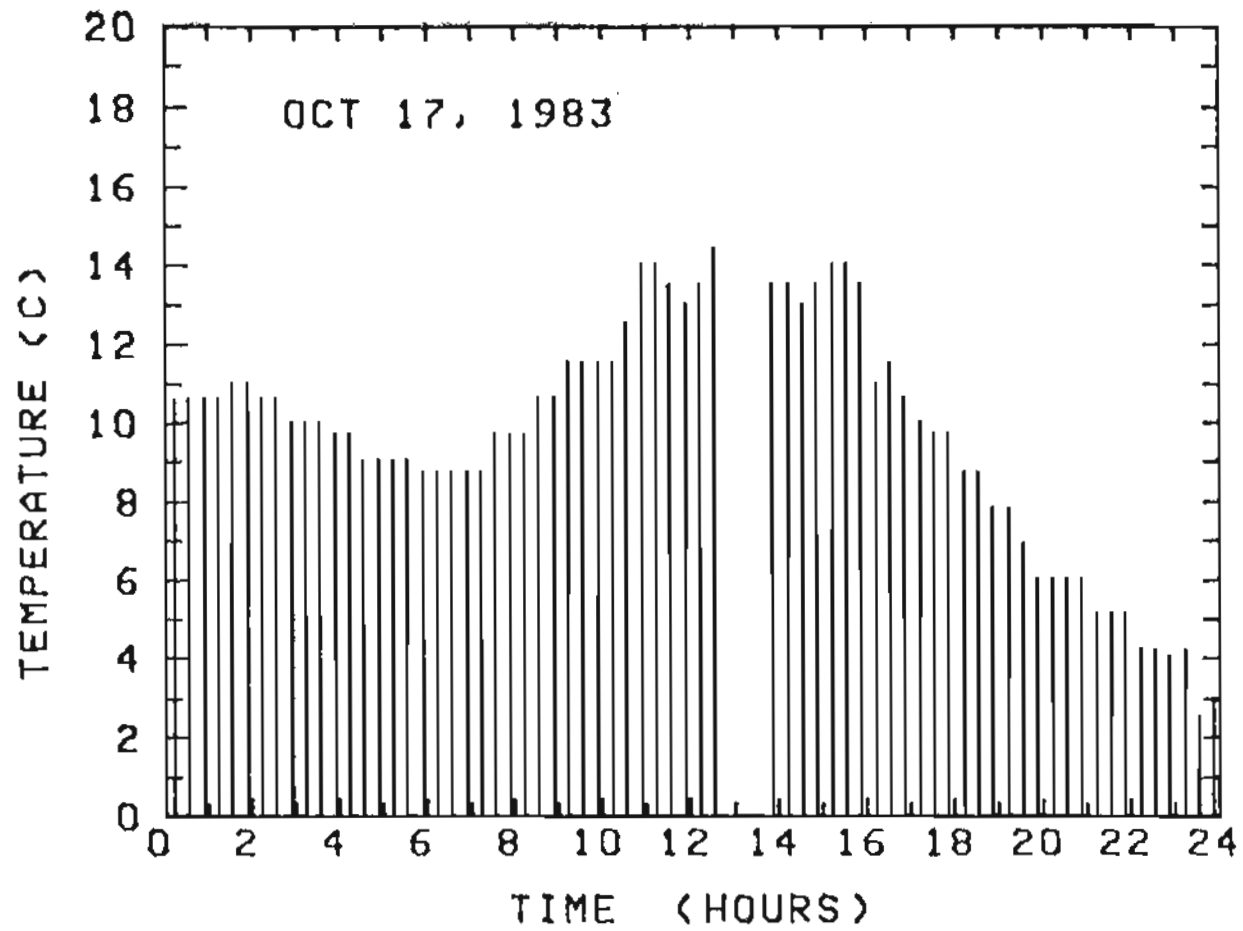


Figure 29. Ambient temperature data for October 17, 1983.

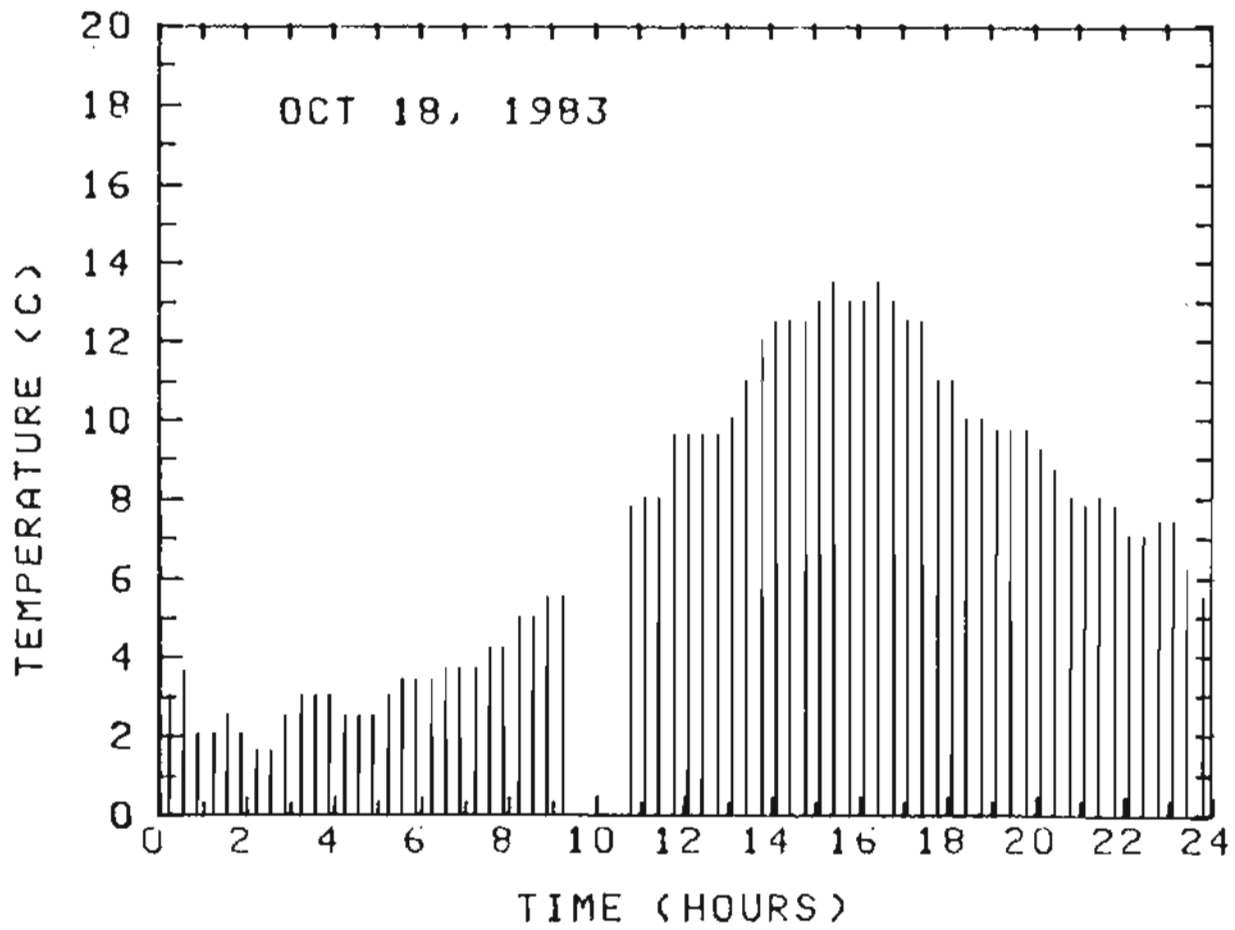


Figure 30. Ambient temperature data for October 18, 1983.

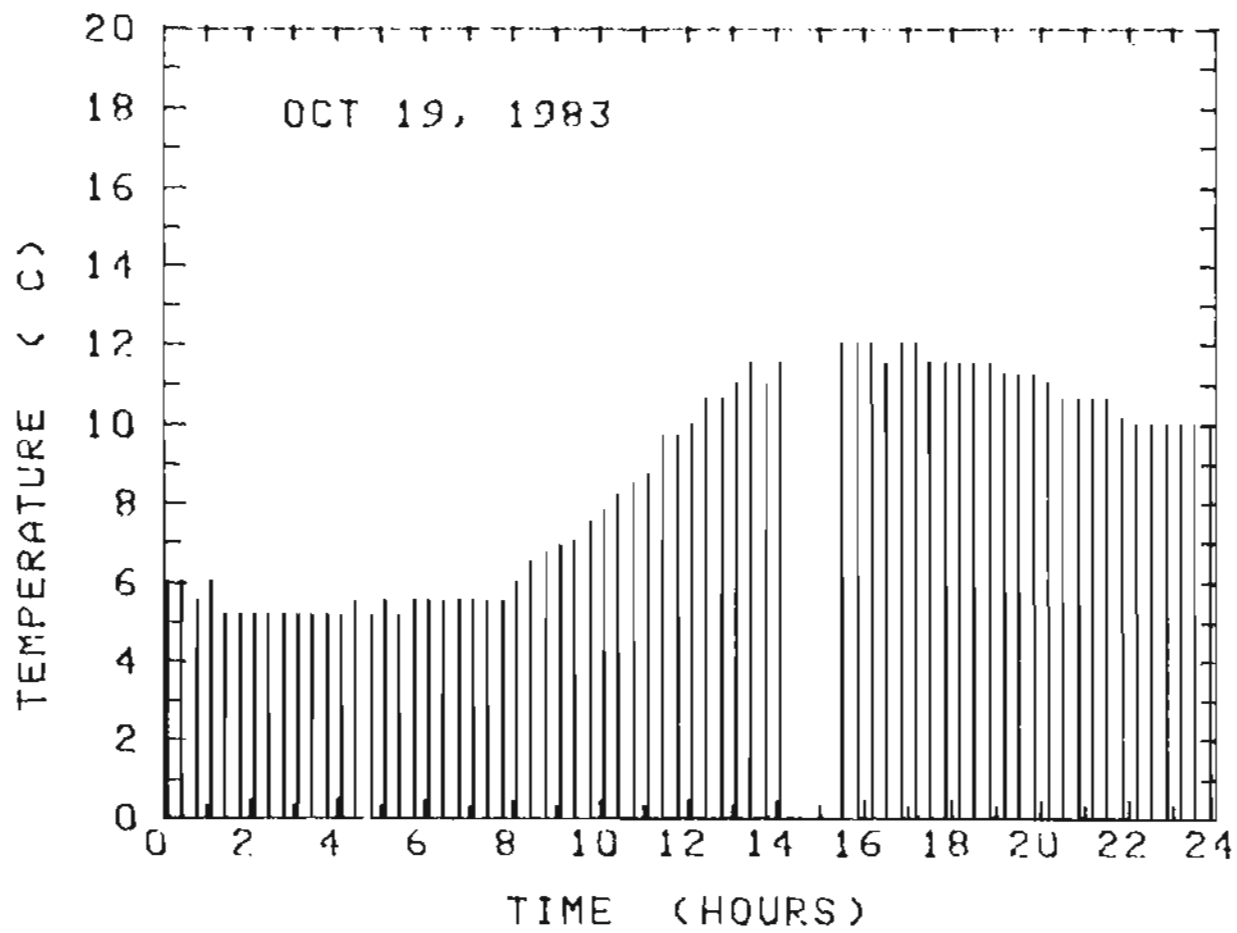


Figure 31. Ambient temperature data for October 19, 1983.

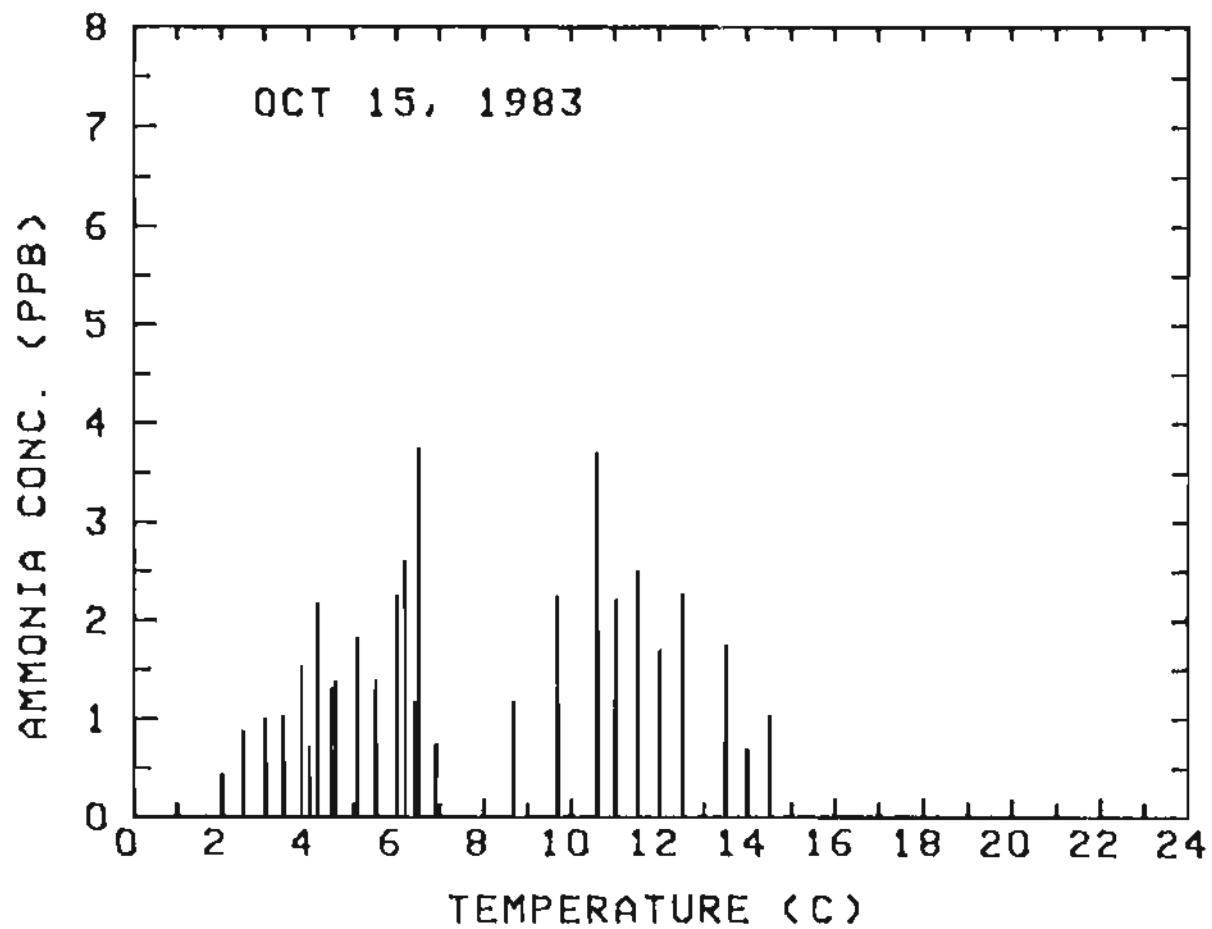


Figure 32. Ammonia vs. temperature plot for October 15, 1983, data.

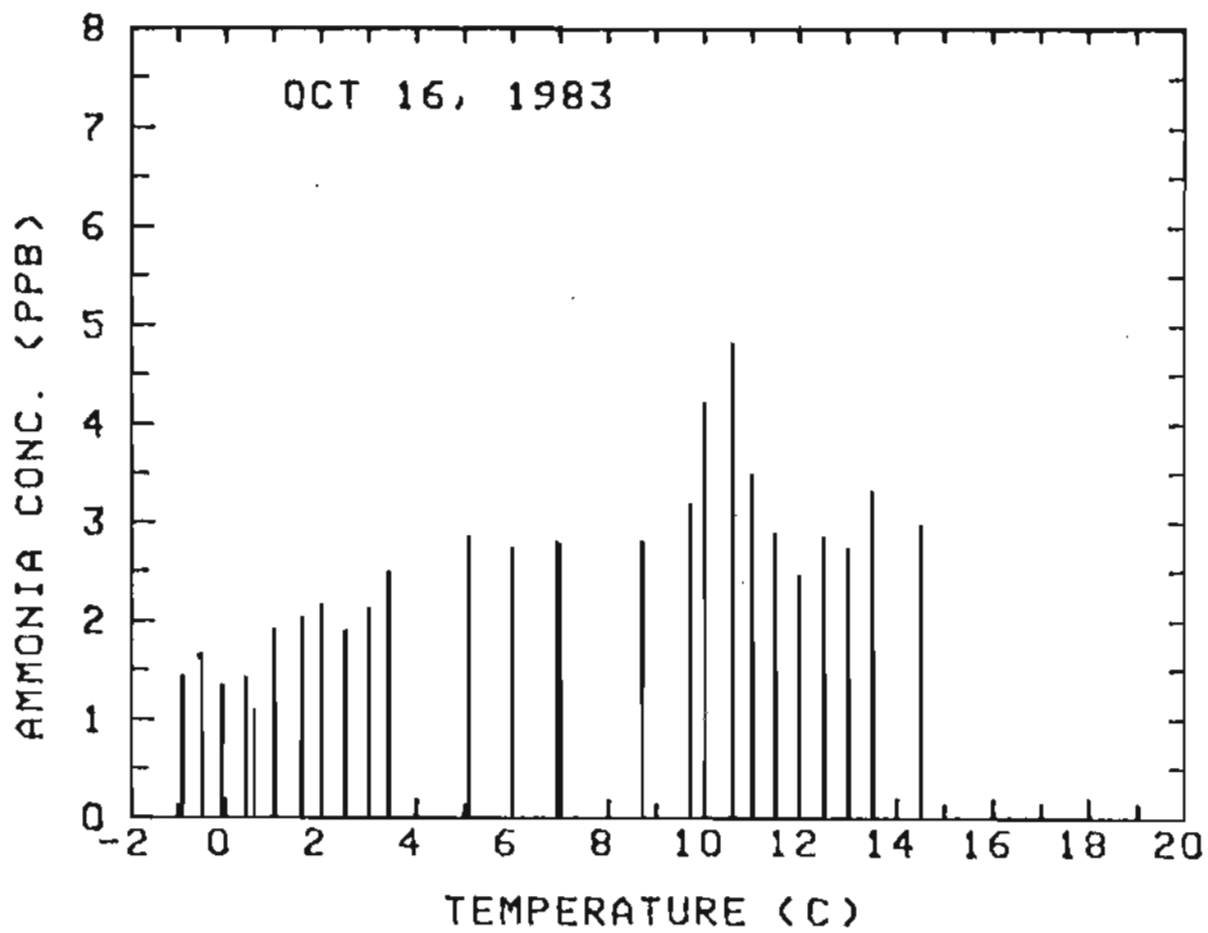


Figure 33. Ammonia vs. temperature plot for October 16, 1983, data.

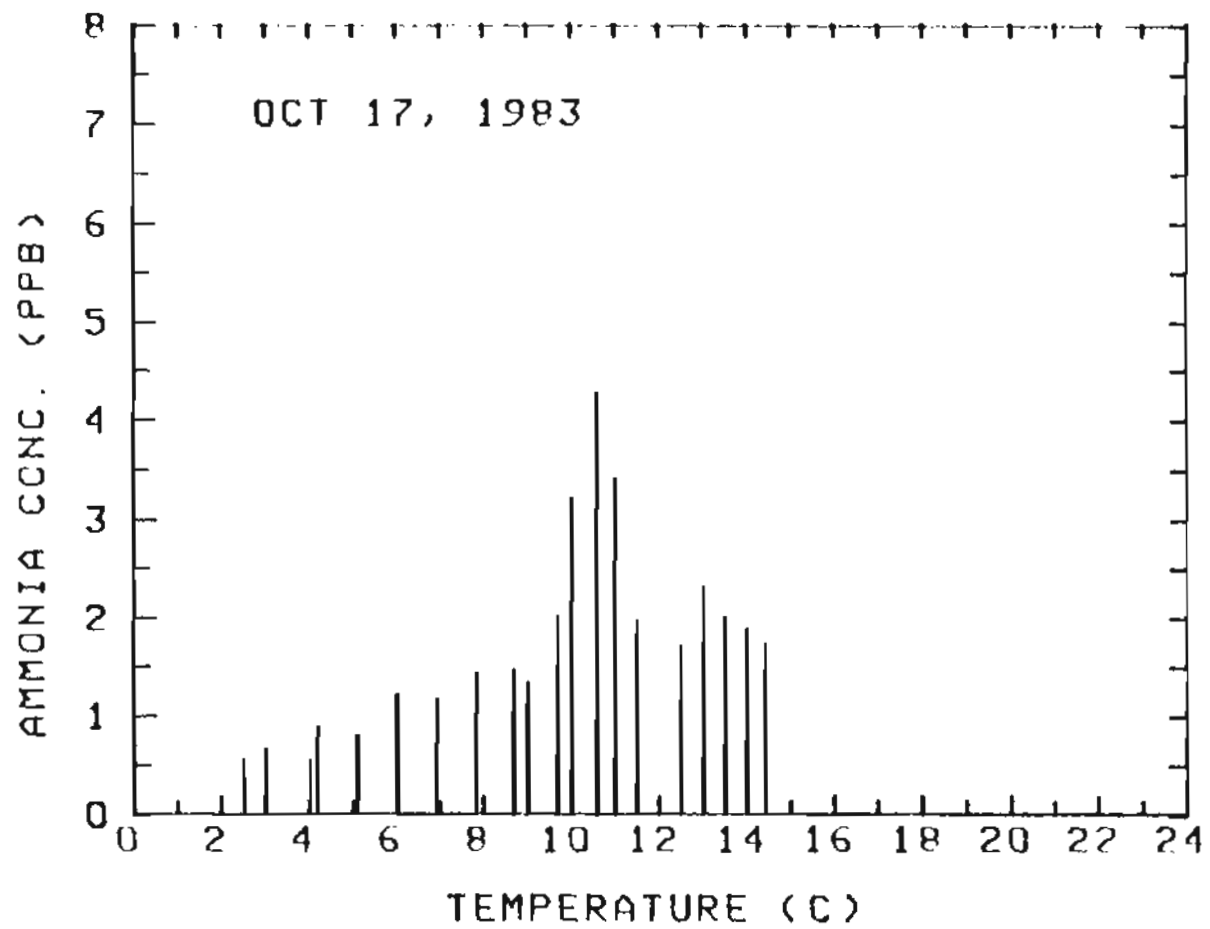


Figure 34. Ammonia vs. temperature plot for October 17, 1983, data.

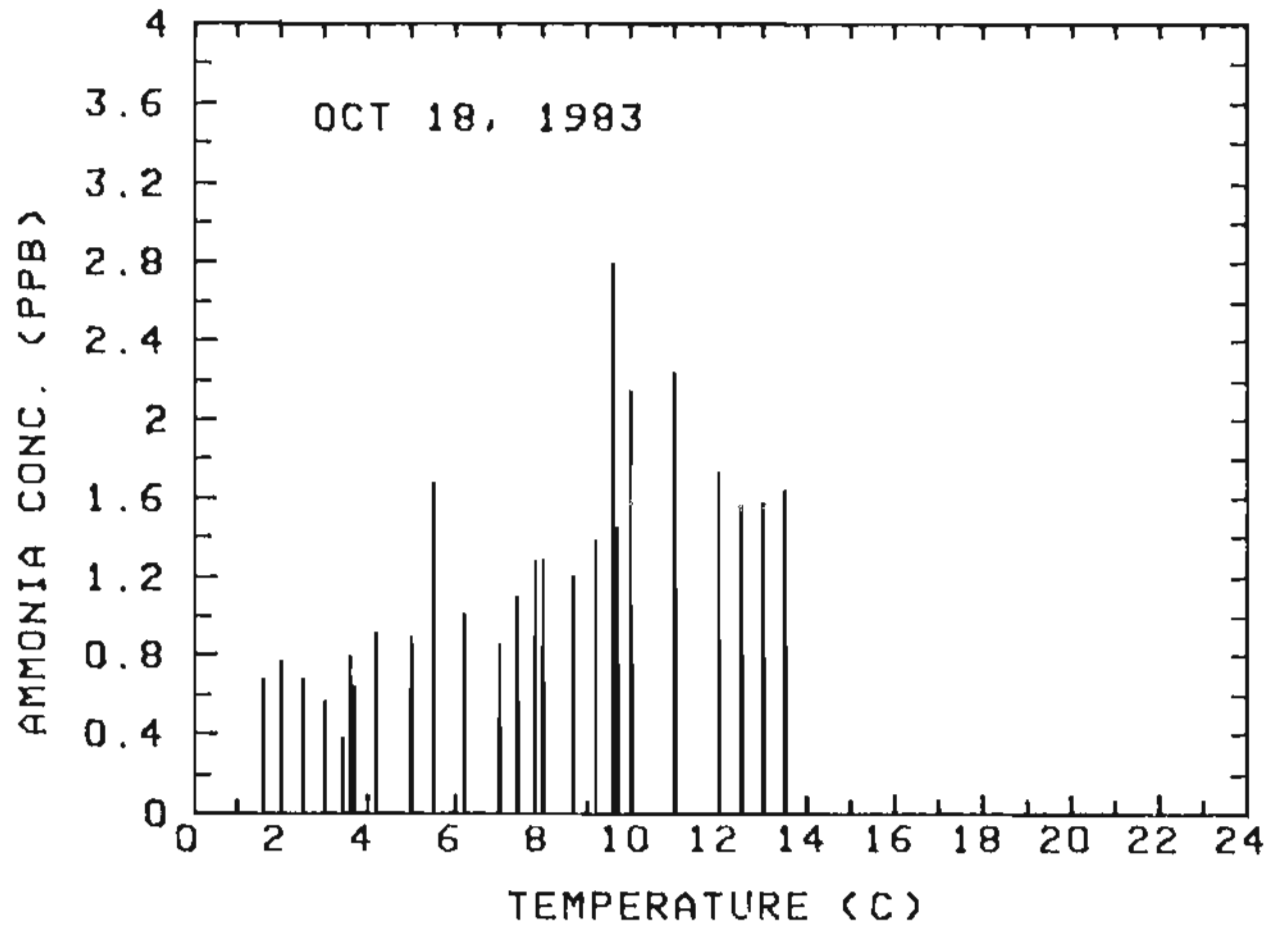


Figure 35. Ammonia vs. temperature plot for October 18, 1983, data.

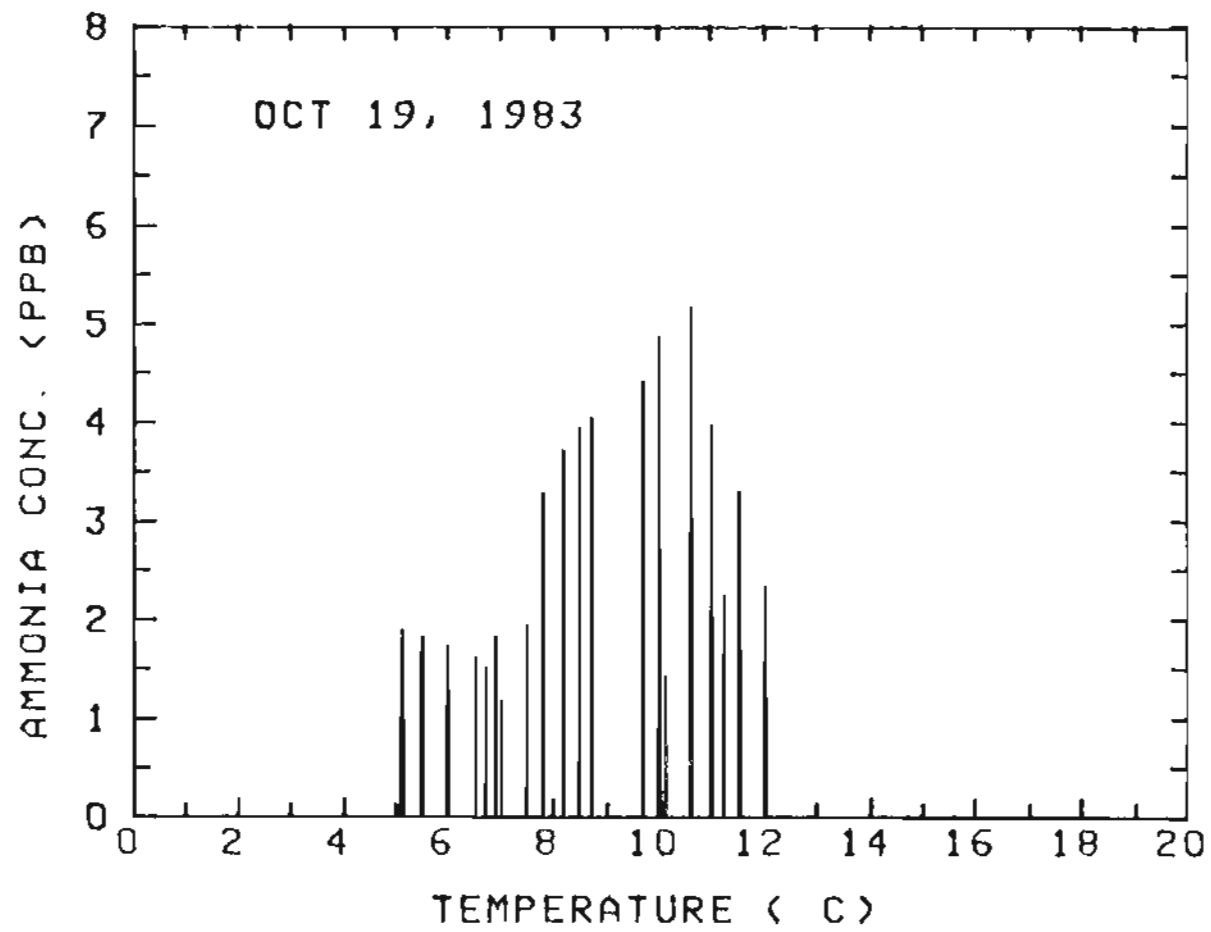


Figure 36. Ammonia vs. temperature plot for October 19, 1983, data.

method and the diffusion absorption method is evident from the analysis of the ammonia concentration figures and from Table 11. The real-time instrument shows the fluctuation of ammonia concentration that the 8- or 24-hour averaging methods mask. For example, on October 13 the ammonia concentration was higher than the 24-hour average of 2.7 ppb all morning, with a maximum of 7.3 ppb about 11 A.M., and a standard deviation of 1.7 ppb for the day.

IV. CONCLUSION

An automated in-situ real-time ammonia monitor has been developed and field tested. It is the first instrument that uses the flame photometric detector to measure gaseous ammonia. This study also reports the first use of carbon disulfide to improve the sensitivity of the FPD.

The instrument gives reproducible NH_3 measurements. It does not need daily calibrations and zeroing, which is an advantage over the automated fluorescence derivatization technique. The instrument is free of poisoning during ambient sampling, which is a problem with the automated tungstic acid technique.

Finally, the automated in-situ real-time ammonia monitor can be an important contribution to the study of the role ammonia plays in atmospheric chemistry.

TABLE 11. Ambient Ammonia Data

Date	Ammonia Concentration (ppb)		
	Maximum	Minimum	Average
October 7, 1983	1.5	0.4	0.87 ± 0.3
October 8, 1983	3.1	0.8	1.9 ± 0.5
October 13, 1983	7.3	0.7	2.6 ± 1.7
October 15, 1983	3.8	0.4	1.2 ± 0.7
October 16, 1983	4.8	1.1	2.6 ± 1.0
October 17, 1983	4.3	0.6	1.6 ± 0.9
October 18, 1983	2.8	0.2	1.0 ± 0.6
October 19, 1983	5.2	1.2	2.1 ± 1.0

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