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AIRBORNE *IN-SITU* MEASUREMENT OF PARTICULATE SULFUR AND SULFURIC ACID WITH FLAME PHOTOMETRY AND THERMAL ANALYSIS

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Abstract—An airborne *in-situ* particulate sulfur monitor based on the FPD principle has been developed and tested. The lower detection limit for particulate sulfur is about 1 ppb ($4 \mu\text{g SO}_4 \text{ m}^{-3}$). Time response to 90% of signal is about 5 s. The characteristic FPD zero drift caused by changes in pressure, humidity and other environmental factors has been compensated for by including an automatic zeroing cycle so that the zero signal can be monitored along with the sulfur signal. Preliminary results indicate that data collected during altitude descents or ascents is of good quality. With the addition of a preheater system, simultaneous measurement of sulfuric acid and total particulate sulfur profiles in plumes and haze palls is possible with a single monitor.

1. INTRODUCTION

Airborne measurements of particulate sulfur, along with other relevant pollutant parameters, have been carried out by a number of investigators (e.g. Hegg and Hobbs, 1980; Husar *et al.*, 1978; Newman *et al.*, 1975a, 1975b; Gartrell *et al.*, 1963), mostly for the purpose of determining oxidation rates in plumes. The measurement techniques (Tanner and Newman, 1976) for these studies have mainly been based upon filter sampling and subsequent chemical analysis for total sulfur or sulfate. The time resolution of filter based techniques has been at best about 10 min.

Recently, the principle of *in-situ* flame photometric detection (FPD) of particulate sulfur compounds (Huntzicker *et al.*, 1975) has been applied to continuous monitoring in the atmosphere (Cobourn *et al.*, 1978; 1980). Ambient particulate sulfur measurements with the FPD can be obtained with a time resolution of several seconds. It is therefore possible with FPD to make detailed airborne measurements of the structure of particulate sulfur and sulfuric acid in plumes and regional air masses. Such information should be useful for answering questions concerning the physical and chemical evolution of plumes and the formation and structure of regional haze palls.

An airborne *in-situ* FPD monitor has been recently developed and tested which provides a semi-continuous signal indicating particulate sulfur concentration. In addition, an add-on preheater system has been developed which measures the sulfuric acid concentration from the change in FPD signal during heating. This measurement system was successfully used during EPA's recent 1980 PEPE-NEEROS field project. A somewhat similar system, but without automatic zeroing, was used during EPA's 1978 STATE field project.

2. MEASUREMENT SYSTEM DESCRIPTION

The measurement system is designed specifically for use in aircraft sampling, where pressure sensitivity, zero drift, time response and detection limit are critical factors. The basic principle of the design is to provide adjacent free streams of aerosol and filtered air from which the FPD analyzer alternately samples by means of a movable tube. Thus, a continuous cycle of ambient and zero air is fed into the analyzer, but without introducing any pressure pulses or fluctuations which could upset the crucially important flame conditions.

2.1 Particulate sulfur analysis system

The Continuous Airborne Particulate Sulfur (CAPS) system consists of a simple flow processor, an FPD sulfur analyzer, and a linear pico-amp electrometer (Fig. 1). Air enters the instrument through a 6.4 mm dia. tube which is connected to the ram air supply. The inlet tube is vented so as to give about 50 mm Hg supply pressure, which delivers about $60 \text{ cm}^3 \text{ s}^{-1}$ of flow through the system. The flow then divides, half going through a glass fiber particulate filter (Gelman Products, Inc.), and half going through a nozzle to balance the flow between the two lines. These lines feed either side of a divided rectangular duct which is open at the other end. Thus, two adjacent free streams with rectangular cross-sections emerge from the duct.

A sample line leading to the FPD burner block moves back and forth between the two streams, the movement being actuated by a timer-switch-solenoid mechanism. The FPD sample flow (about $3.3 \text{ cm}^3 \text{ s}^{-1}$) then goes through a diffusion tube denuder coated with PbO (Tanner *et al.*, 1980) to remove gaseous SO_2 and H_2S . The denuder is constructed of four parallel

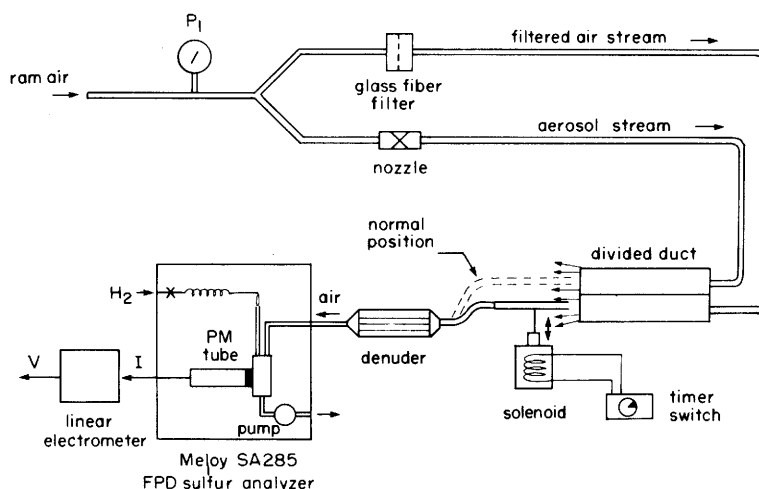


Fig. 1. Diagram of the continuous airborne particulate sulfur (CAPS) monitor. The FPD analyzer samples alternately from two adjacent free streams of aerosol and filtered air.

tubes, each 10 cm long. According to theory (Durham *et al.*, 1978) the denuder removes $> 99.99\%$ of SO_2 , but less than 1% of the $0.1\text{--}1.0\mu\text{m}$ particles passing through. The FPD analyzer is a standard Mejoy SA-285 sulfur analyzer.

The current signal from the analyzer photomultiplier tube is measured by an analog linear amplifier which has a gain of about 1×10^8 volts/amp and a resolution better than 1×10^{-11} amps. The amplifier voltage output is recorded on a data acquisition system, and subsequently processed by a computer.

The raw signal is in the form of a modulated current, stepping between zero current and total current. The zero current generally exhibits significant drift, especially with changes in ambient pressure. The zero cycling is timed to deliver 10 s of zero air every minute, so that the zero current can be adequately monitored.

Because of the requirements of accuracy and high time resolution, especially for plume measurements, it is a practical necessity to record the data on a high resolution ($> 10,000$ counts) fast scanning (< 2 s.) data acquisition system. The sulfur concentration is then

calculated during the data processing stage using an equation which relates net current to sulfur concentration (Section 2.3). The constants in the equation are determined by calibration of the FPD sulfur analyzer with a sulfur dioxide permeation tube system.

2.2 Sulfuric acid analysis system

Sulfuric acid can be distinguished from the ammonium sulfate salts by incorporating the principle of *in-situ* thermal analysis (Huntzicker *et al.*, 1975; 1978; Cobourn *et al.*, 1978) into the basic measurement system described above. This involves the placement of a heater upstream of the CAPS monitor. Sulfuric acid volatilizes at a lower temperature than ammonium sulfate or ammonium bisulfate (Kiyoura *et al.*, 1970), so for certain heater temperatures it will exhibit a larger degree of volatilization. This principle is incorporated into the CAPS monitoring system by setting the heater at a fixed temperature and cycling it on and off during sampling (Fig. 2). In the present system, the heater is timed to go on during zeroing, and

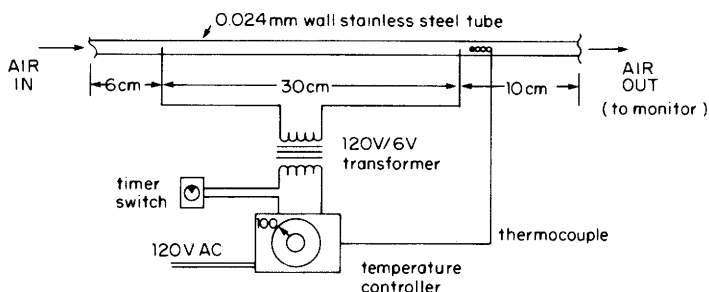


Fig. 2. Diagram of the preheater system. The heater is cycled between ambient temperature and 100°C exit temperature, using direct resistance heating.

remain on for 20 s after zeroing. The heater is a thin-walled (0.15 mm) stainless steel tube, which works by direct resistance heating. The heater is regulated near a fixed temperature during the heating cycle by a set point temperature controller (Omega Engineering Company), which powers the heater through a step-down transformer.

During the recent 1980 PEPE-NEROS project, this heater was set and calibrated so that sulfuric acid aerosol exhibited a modulated signal with about 50% attenuation during heating, while ammonium sulfate exhibited only about 5% attenuation during heating (Section 3.5). Previous work by Cobourn *et al.* (1978) and Huntzicker *et al.* (1978) indicates that this particular heater configuration did not provide the optimum separation between H_2SO_4 and the ammonium salts, but nevertheless, the response difference was adequate for sulfuric acid measurement.

2.3 Flame photometric detector

The principle of operation of FPD sulfur analyzers is described by Crider (1965) and Sugiyama *et al.* (1973). Basically, sulfur molecules introduced into a hydrogen flame produce an activated S_2^* species which emits a broad band of radiation centered at 394 nm. The radiation is detected by a photomultiplier tube, after passing through a 5 nm band pass filter. The net photomultiplier tube current follows a power law response

$$\Delta I = kS^n \quad (1)$$

wherein the exponent is slightly less than two. The net current is the difference between the total current and the "zero current" arising mainly from the hydrogen flame itself.

$$\Delta I = I - I_0. \quad (2)$$

The zero current is typically about 10–20 nA, whereas the net current typically ranges 0.1–10.0 nA for sulfur concentrations in the 2–20 ppb range.

The zero current is dependent on the sample flow rate and fuel-to-air mixing ratio, and on several environmental variables, such as humidity, barometric pressure and CO_2 concentration. As a result, the zero current is subject to drift, which is particularly significant when measuring ambient sulfur in ppb levels. The drift problem is compounded when making measurements in aircraft, because ambient pressure changes produce drastic changes in the airflow and in the fuel-to-air mixing ratio. The net sensitivity, expressed by the factor 'k' in (1), is also sensitive to pressure changes. The power law exponent 'n' is practically insensitive to pressure (Sugiyama *et al.*, 1973). The net sensitivity is also weakly dependent on water vapor pressure and carbon dioxide concentration (Tanner *et al.*, 1980). In general, it has been found that environmental factors such as temperature, barometric pressure, H_2O concentration and CO_2 concentration mainly affect the zero current. The change in net sensitivity produced by these environ-

mental factors is moderate, and easily corrected. Therefore, a workable approach to compensate for the interference effects is to frequently monitor the zero signal, so as to have an accurate measurement of the net current.

3. LABORATORY PERFORMANCE TESTS AND SAMPLE DATA

3.1 FPD calibration

Since the FPD sensitivity is so dependent on the air and hydrogen flows, it is necessary to keep the flow settings constant between calibrations. The sensitivity normally remains constant for a fixed flow setting; this is demonstrated by results from one test in which an FPD instrument was calibrated on several successive days (Fig. 3).

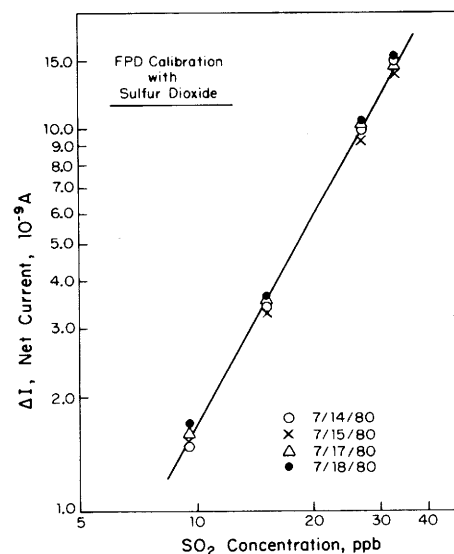


Fig. 3. Calibrations of one FPD instrument on successive days produced close results. A permeation tube calibration system was used, and the FPD hydrogen and air flows were held constant.

Another question concerning the calibration concerns the FPD response to different sulfur compounds. Tanner *et al.* (1980) reported that the responses of SO_2 and aerosols of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 are essentially the same, while H_2SO_4 aerosol gives a 20% reduced response. Cobourn *et al.* (1978) and Huntzicker *et al.* (1978) reported an inverse relation between burner block temperature and H_2SO_4 response, suggesting that volatilization of H_2SO_4 and partial scavenging upstream of the flame had occurred. Apparently, the reduced H_2SO_4 response can be compensated for by converting the acid to sulfate salt by ammonia addition (Huntzicker *et al.*, 1978). However, a general understanding of the $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ response difference is lacking. Because of these uncertainties, the accuracy of parti-

culate sulfur measurements made with this system is probably no better than $\pm 30\%$.

3.2 Pressure sensitivity

The FPD zero signal increases with atmospheric pressure and thus decreases with altitude. The amount of change is peculiar for each instrument, and depends on the initial flows, photomultiplier voltage, etc. Pressure chamber tests on 6 FPD analyzers revealed that the zero current of each analyzer was reduced by a factor of two to three as the chamber pressure was reduced from ambient to 550 mm Hg (Fig. 4). In these

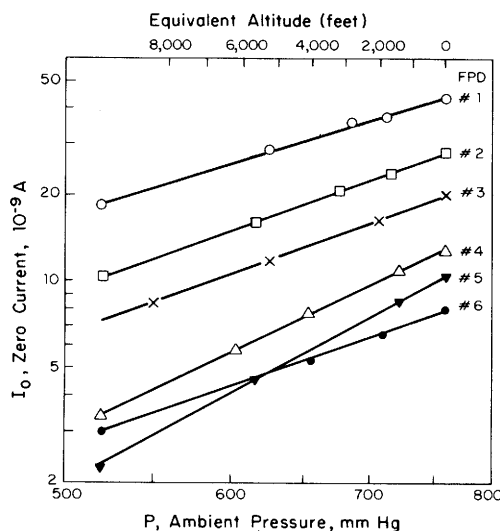


Fig. 4. Results of pressure chamber tests on six different FPD analyzers all showed decreasing zero current with decreasing ambient pressure.

tests, the instruments with lower initial zero currents exhibited less absolute change in current with pressure.

The change in net sensitivity with pressure can be expressed by modifying (1) to include a non-dimensional, pressure dependent correction factor $k(p)/k_0$

$$I = \frac{k(p)}{k_0} \cdot k_0 \cdot S^n$$

where k_0 is the sensitivity at ground level.

The change in sensitivity of 6 FPD analyzers with pressure was also tested using a pressure chamber. The results, in terms of the pressure correction factor in Fig. 5, show that the pressure sensitivity is different for each machine. However, it may be noted that the curves are sufficiently in agreement so that an average of these curves could be used to estimate the pressure sensitivity of untested machines, with a maximum expected error in calculated sulfur concentration ($S = (I/k(p))^{1/n}$) of $\pm 7\%$.

3.3 Time response

The time response of the FPD analyzers to a step change in concentration generally exhibits both a lag and an exponential type relaxation. The lag time can be reduced to < 1 s by using short sampling tubes. The relaxation function arises from absorption or desorption processes in the lines and in the region of the burner tip. The time response for particulate sulfur is generally faster than that for sulfur dioxide (Fig. 6). Several tested burners responded with varying quickness, depending on the burner tip material, age and condition, but all showed the same trend between gaseous and particulate sulfur. For the relatively new burner tips, the signal reached 90% of the final value only five seconds after zeroing. The repeatability of this test makes it possible to perform a time response

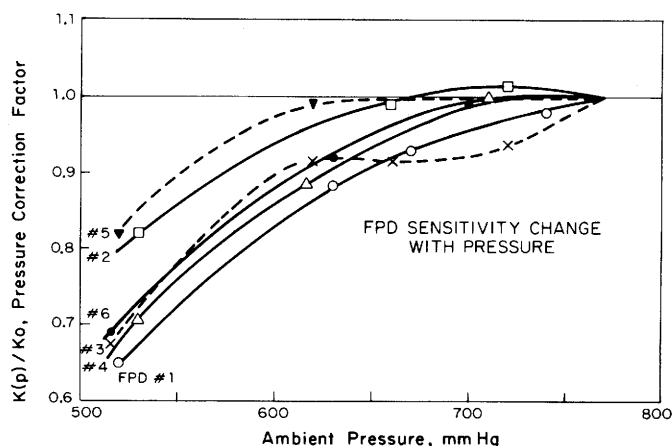


Fig. 5. The changes in net sensitivity with pressure for the six FPD sulfur analyzers were similar, but not identical. The correction factor appears to be rather large, because it is based on net current rather than calculated sulfur concentration.

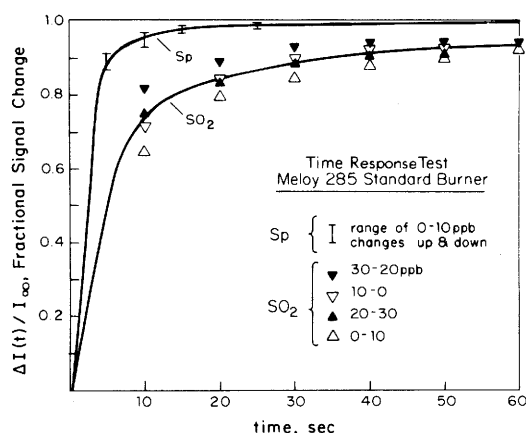


Fig. 6. Time response tests on a standard (stainless steel burner tip) burner block indicate a faster response for particulate sulfur compared to gaseous sulfur dioxide.

correction for field data taken from five seconds after zeroing and onward.

3.4 Signal to noise ratio

The noise of the FPD signal arises from the photomultiplier tube and the flame, but the flame noise predominates (Pescar and Hartman, 1973). Two of the CAPS monitors were tested for noise and found to exhibit noise levels of 6×10^{-11} A and 4×10^{-11} A. The instrument with higher noise also had a higher sensitivity, so that the signal to noise ratios were comparable (Fig. 7). Increasing the PMT voltage

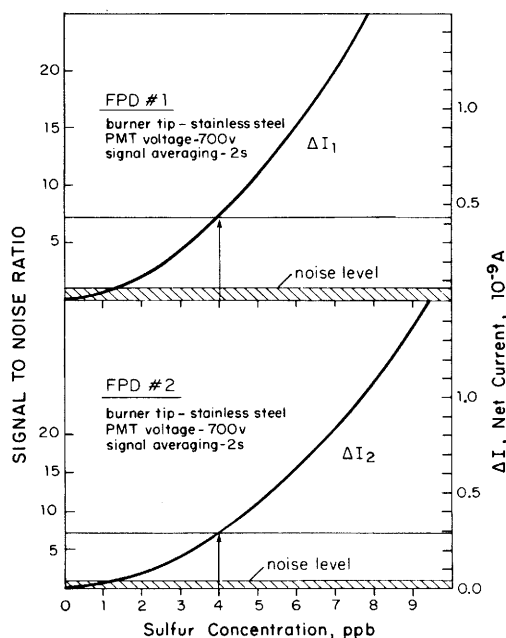


Fig. 7. The signal-to-noise ratios of two tested FPD instruments were comparable, though the absolute responses were different by about 50%.

enhances the sensitivity, but noise levels rise correspondingly, so little improvement in signal to noise ratio can be gained this way. Also, increasing the PMT voltage increases the zero current, which is generally undesirable because the zero drift problems are then compounded. A substantial improvement in signal to noise ratio can be gained by adding a constant amount of sulfur concentration to the sample air (Tanner *et al.*, 1980). For most applications without sulfur addition, the limit of detection as determined by the noise level is roughly 1 ppb.

3.5 Sulfuric acid heater calibration

The heater must be calibrated to determine the heater exit temperature which best separates sulfuric acid from the ammonium salt compounds. For the particular heater used during the 1980 PEPE field project (Fig. 2), a temperature of 100°C was selected. At this setting, sulfuric acid aerosols were about 50% volatilized, and ammonium sulfate aerosols were about 5% volatilized (Fig. 8). Both signals fluctuated

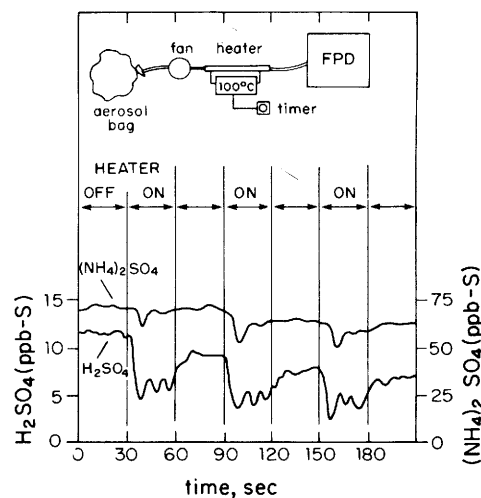


Fig. 8. Aerosols of sulfuric acid and ammonium sulfate elicited different responses in the heated FPD system. The short initial dip in the ammonium sulfate trace is due to overshoot of the heater.

somewhat during heating, because the temperature controller overshoot the setpoint by about 10°C each time power was applied. This heater was much shorter than those that we have previously used for ground monitoring systems. The shorter heater length undoubtedly created steeper radial temperature gradients in the heater (Cobourn *et al.*, 1978) and therefore poorer thermal separation between the compounds. Nevertheless, the uniqueness of the sulfuric acid response made it possible to estimate sulfuric acid concentrations when this system was operated in the field.

4. FIELD PERFORMANCE TESTS AND SAMPLE DATA

The raw data from the CAPS monitor appears as a modulated signal with a period of one minute. The maximum values correspond to the total current, and the minimums correspond to the zero current (Fig. 9).

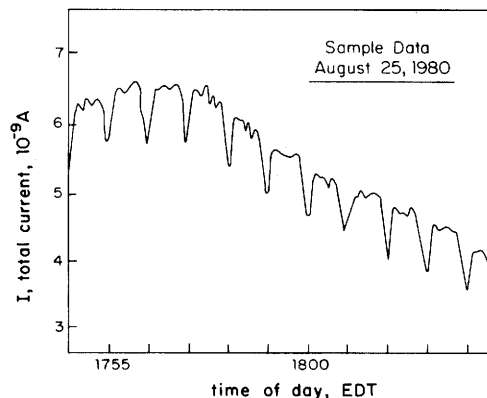


Fig. 9. The raw data from the CAPS monitor is a modulated signal going between zero and total current. This data was collected during an ascent, and as a result the zero current decreased.

The zero drift apparent in this figure is due to the pressure change which occurred during the ascent. The net current is calculated during the data processing stage, by taking interpolated values of the zero current and subtracting them from the total current. A small time response correction is also done at this stage. Particulate sulfur concentration is calculated from the net current using (1). The processed particulate sulfur signal is then an intermittent signal which delineates the concentration profile along a given flight path.

Such detailed measurements are useful for characterizing the dynamics of sulfur conversion in plumes and haze palls. For example, the particulate sulfur concentration profile measured in a twin plume of fresh and aged power plant emissions is compared with other pollutant profiles in Fig. 10. The fresh plume is characterized by relatively high values of SO_2 , NO_x , charge (Husar *et al.*, 1976) and condensation nuclei, and by an ozone deficit. The aged plume is characterized by relatively high particulate sulfur and light scattering coefficient and by an ozone excess. The light scattering and particulate sulfur profiles track well, indicating that most of the particulate sulfur material has been formed in the light scattering size range. There is some suggestion from these data that the formation rate on the edges of the plume was higher, because of the sharp increase in particulate sulfur at the edges compared to that of sulfur dioxide.

With the addition of the thermal volatilization cycle, it is possible to analyze for sulfuric acid also. In this case, the raw signal appears as a three-step modulated signal (Fig. 11). Particulate sulfur as sulfuric acid (S_a)

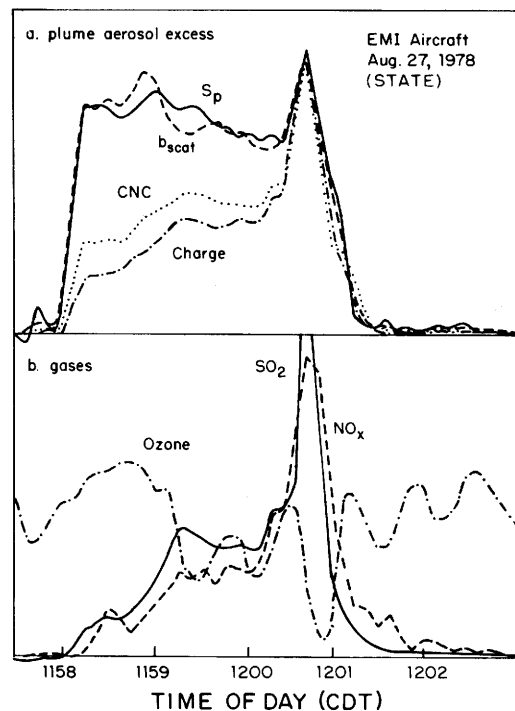


Fig. 10. Traverse data of a twin plume of fresh and aged power plant emissions. Particulate sulfur correlated well with light scattering coefficient, but not with charge or CNC.

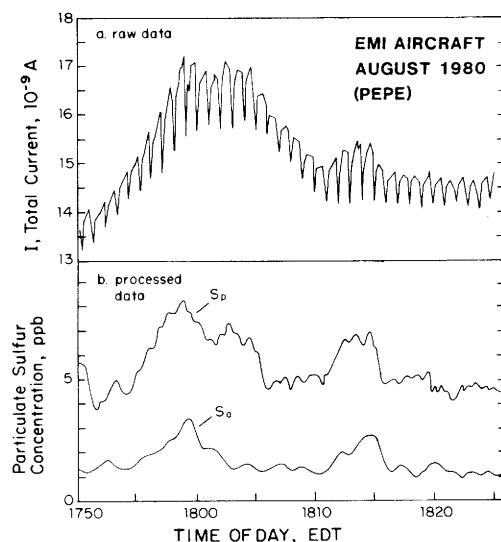


Fig. 11. (a) The raw data from the heated CAPS system is a three step modulated signal with a period of one minute. The first ten seconds is the zero signal and the next twenty seconds is the total signal. (b) In the processed data, total particulate sulfur (S_p) and particulate sulfur as sulfuric acid (S_a) have been calculated from the raw data. In these plots, some interpolation has been done to form continuous signals.

is calculated during the data processing stage by the difference between the unheated and heated sulfur signal, using interpolated values, and multiplying by a factor to account for the efficiency of the particular heater in volatilizing the sulfuric acid (Section 3.5).

An example of the processed signals (Fig. 11) shows a wide sulfate plume in which nearly half of the particulate sulfur was present as sulfuric acid. In the background air, the fraction as sulfuric acid was lower. Measurements taken thus far over the eastern U.S. indicate that the proportion of particulate sulfur present as sulfuric acid varied substantially, depending on time and location. These kind of measurements can be useful in providing crucial information concerning the distribution of acid sulfates and ammonium sulfates over regions affected by sulfur oxide emissions.

5. SUMMARY

The present *in-situ* FPD technique for airborne particulate sulfur measurement provides a high time resolution (2 s) semi-continuous signal. The FPD pressure sensitivity and zero drift have been compensated for by a zero air cycle. A preheater cycled on and off makes it possible to periodically measure sulfuric acid concentration. The FPD time response for particulate sulfur is fast enough that both heating and zeroing can be done in a one minute cycle. The detection limit of the present system is about 1 ppb. An accuracy of $\pm 30\%$ is claimed for the present system, but this can probably be improved in the near future. Examination of field data indicates that plume profiles of particulate sulfur and sulfuric acid can be measured with good detail. Vertical profiles measured using the zero cycling system also appear to be of good quality.

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