

## Atmospheric Measurements of Carbonyl Sulfide, Dimethyl Sulfide, and Carbon Disulfide Using the Electron Capture Sulfur Detector

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Measurements of atmospheric dimethyl sulfide (DMS), carbonyl sulfide (COS), and carbon disulfide (CS<sub>2</sub>) were conducted over the Atlantic Ocean on board the NASA Electra aircraft during the Chemical Instrumentation Test and Evaluation (CITE 3) project using the electron capture sulfur detector (ECD-S). The system employed cryogenic preconcentration of air samples, gas chromatographic separation, catalytic fluorination, and electron capture detection. Samples collected for DMS analysis were scrubbed of oxidants with NaOH impregnated glass fiber filters prior to preconcentration. The detection limits (DL) of the system for COS, DMS, and CS<sub>2</sub> were 5, 5, and 2 ppt, respectively. COS concentrations ranged from 404 to 603 ppt with a mean of 489 ppt for measurements over the North Atlantic Ocean (31°N to 41°N), and from 395 to 437 ppt with a mean of 419 ppt for measurements over the Tropical Atlantic Ocean (11°S to 2°N). DMS concentrations in the lower marine boundary layer, below 600-m altitude, ranged from below DL to 150 ppt from flights over the North Atlantic, and from 9 to 104 ppt over the Tropical Atlantic. CS<sub>2</sub> concentrations ranged from below DL to 29 ppt over the North Atlantic. Almost all CS<sub>2</sub> measurements over the Tropical Atlantic were below DL.

### INTRODUCTION

Sulfur gases are emitted into the atmosphere by anthropogenic and biogenic processes, where they are photochemically oxidized via SO<sub>2</sub> to sulfate particles. These particles can affect climate and the environment by their modification of the optical properties of clouds [Charlson *et al.*, 1987], direct reflection of sunlight back to space [Shaw, 1983; Charlson *et al.*, 1991], and acidification of precipitation [Charlson and Rodhe, 1982].

Anthropogenic sulfur gases, primarily in the form of SO<sub>2</sub>, are emitted in localized regions of industrial activity. Biogenic sulfur gases are emitted in the form of reduced sulfur gases such as dimethyl sulfide (DMS) and carbonyl sulfide (COS). These biogenic sulfur emissions have a low flux density but occur over a large area, so that their total flux is significant [Andreae, 1986].

Measurements of atmospheric sulfur gases are critical to understanding their atmosphere cycles. In order to evaluate present analytical methods for sulfur gas measurements, NASA conducted the third Chemical Instrumentation Test and Evaluation (CITE 3) experiment, which occurred in August and September of 1989. The primary objectives of CITE 3 were to (1) test and evaluate via airborne field intercomparisons the capability to make reliable concentration measurements of the sulfur species SO<sub>2</sub>, DMS, COS, CS<sub>2</sub>, and H<sub>2</sub>S, and (2) determine in a predominantly marine environment the abundance and distribution of major sulfur species over a wide range of atmospheric conditions. The measurements were performed from the NASA Electra aircraft, over the North Atlantic (31°N to 41°N) on flights based out of Wallops Island, Virginia, and over the Tropical Atlantic (11°S to 2°N) on flights based out of Natal, Brazil.

A number of techniques based on different principles of detection have been developed for the measurement of ambient sulfur gases. Gas chromatography (GC) with flame photometric

detection (FPD) is the most widely used method for sulfur gas measurements [Farwell and Barinaga, 1986]. The FPD uses as its principle of detection the emission of blue light from excited S<sub>2</sub> molecules in a hydrogen rich flame. The FPD is a relatively simple and inexpensive detector, but its signal output is proportional to the square of the sulfur concentration, so that it is limited in its ability to measure extremely low amounts of sulfur. Most FPD-based systems require preconcentration of 1 to 10 L of sample air for analysis of ambient sulfur gases. GC methods with mass selective detection (MSD) have also been employed in the measurement of atmospheric sulfur compounds [Thornton, 1990]. The MSD relies on the detection of molecular fragments of preselected mass in a sensitive mass spectrometer. This method offers the advantages of high sensitivity and the possibility of using isotopically labeled standards. The disadvantages of GC-MSD are its size, complexity, and expense.

We have developed a method that detects three of the five sulfur species chosen for the CITE 3 project. This method uses an automated cryotrap for preconcentration, followed by gas chromatographic separation of sulfur compounds, catalytic fluorination, and a conventional electron capture detector (ECD). The ECD detects the change in conductivity in a radioactively induced plasma from oxygenated and halogenated molecules of high electron affinity.

The ECD-S system without sample preconcentration (i.e., with direct injection of 2 to 5 mL of air) has a minimum detection level (MDL) of approximately 50–100 ppt for DMS (defined as sample size at signal-to-noise ratio of 2). It has been used in this mode on oceanographic cruises to measure DMS in air equilibrated with seawater [Johnson *et al.*, 1987]. A seawater equilibrator sprays seawater through a closed volume of air, in which trace gases accumulate and approach their seawater partial pressures. Because the partial pressure of DMS in most surface seawater is 500 to 5000 pico atmospheres (patm), the concentration of DMS in the equilibrated air is 500 to 5000 ppt. These concentrations, which are 5 to 50 times our MDL, allow the ECD-S to obtain useful measurements of seawater DMS without preconcentration. However, atmospheric DMS and CS<sub>2</sub> cannot be measured without preconcentration,

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as their atmospheric concentrations typically range from 1 to 200 ppt and 1 to 30 ppt, respectively. In order to make atmospheric measurements, a cryogenic concentrator was designed, constructed, and added to the system. The system was installed and used on the NASA Electra aircraft for the CITE 3 project during August and September of 1989. In this paper we describe the ECD-S system used onboard the Electra for CITE 3 and present some of the data collected as an illustration of the instrument performance.

#### METHOD

The ECD is an extremely sensitive detector of halogenated and oxygenated species. This ability, combined with simplicity and relatively low cost, has resulted in its widespread use. Unfortunately,  $\text{SF}_6$  is the only common sulfur compound that gives a substantial signal in the ECD. To make the ECD sensitive to reduced sulfur compounds, we have added a fluorination step between the separation column and the ECD,

in which sulfur compounds are catalytically fluorinated to an electron capturing species, presumably  $\text{SF}_6$ . The original ECD sulfur detector has been described in detail elsewhere [Johnson and Lovelock, 1988]. The modified system used for CITE 3 (Figure 1) is described below.

Sulfur compounds were separated using nitrogen carrier gas flowing at 40 mL/min through a 2-m-long,  $\frac{1}{8}$ -inch OD, Teflon column packed with 60/80 Carboxack B/1% XE-60/1.5%  $\text{H}_3\text{PO}_4$ , held at  $68^\circ\text{C}$ . The effluent from the separation column was transferred through a  $\frac{1}{16}$ -inch OD Teflon line connected to a short  $\frac{1}{16}$ -inch stainless line that was inserted through a tee and then several centimeters into a 10-cm-long  $\frac{1}{8}$ -inch OD stainless steel tube packed with Ag wool. A 20 mL/min flow of 200 ppm  $\text{F}_2$  in  $\text{N}_2$  entered through the third inlet to the tee. The  $\text{F}_2/\text{N}_2$  mixture maintained the surface of the silver as  $\text{AgF}_2$ , which served as the fluorinating catalyst. The  $\text{F}_2/\text{N}_2$  mixture was generated in a permeation source made from a sealed nickel vessel (volume 3 L), which contained 1%  $\text{F}_2$  in  $\text{N}_2$  at room temperature and pressure.  $\text{N}_2$  flowed through

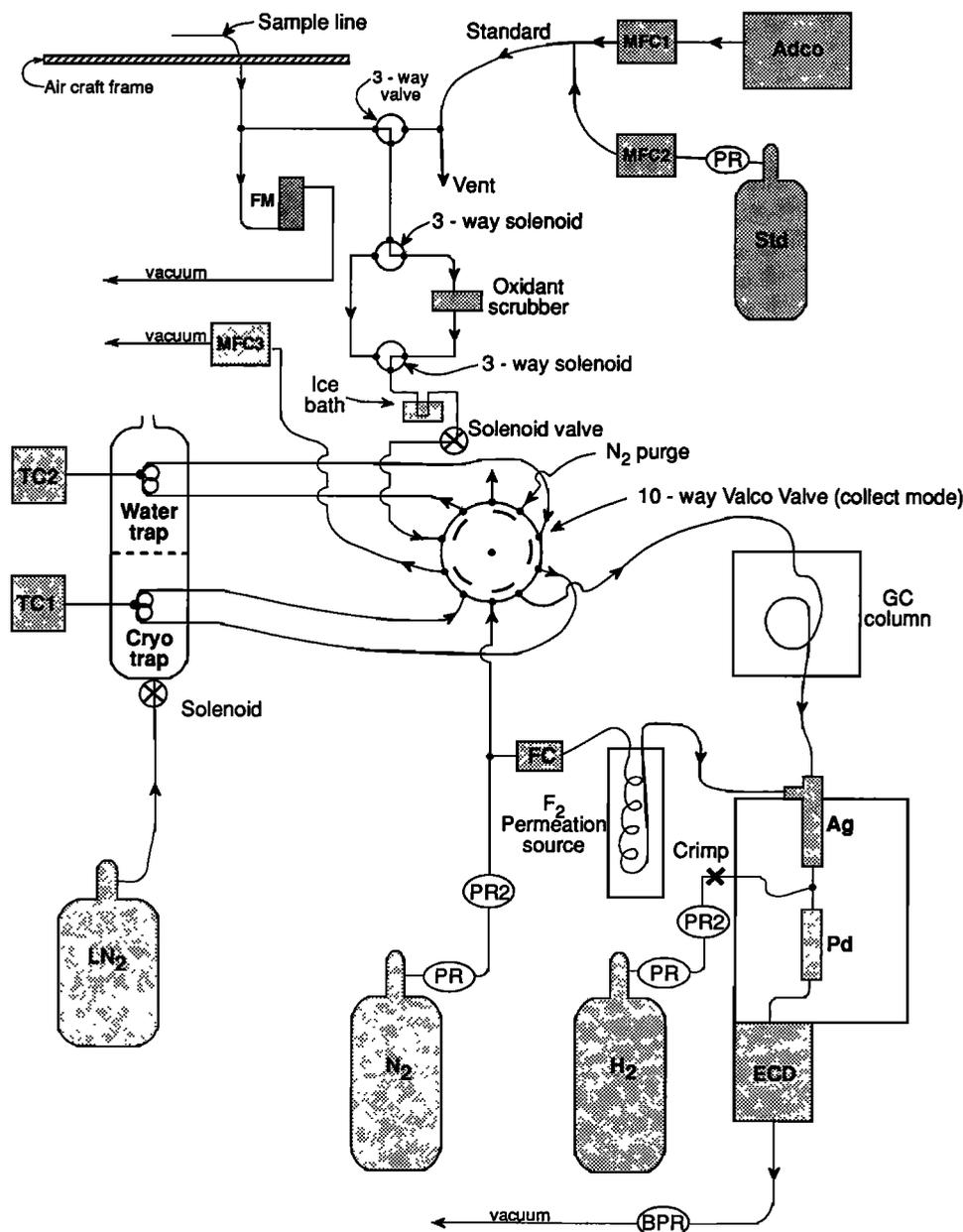


Fig. 1. A schematic of the ECD-S system.

30 m of polytetrafluoroethylene tubing coiled inside this vessel, and the permeation of  $F_2$  through the wall of the tubing generated the desired  $F_2$  concentration.

Following fluorination, the excess fluorine was removed by the addition of 1 mL/min of  $H_2$  to the flow stream prior to its entry into 10-cm-long palladium on alumina column, where excess  $F_2$  was converted to HF, which produces a minimal response in an ECD. We have demonstrated that  $SF_6$  is not reduced in the column, but chlorofluorocarbons are, thus eliminating interferences from these halocarbons [Johnson and Lovelock, 1988]. The Ag and Pd catalyst columns were held at 150°C in the "column oven" of the Shimadzu GC. The carrier flow stream then entered the conventional ECD of a Shimadzu Mini-2 GC.  $SO_2$  is not detected in this system, possibly because it may be fluorinated to  $SO_2F_2$ , which is reduced in the Pd/ $H_2$  reduction column.

Modifications of this system for aircraft use in the CITE 3 project included rack mounting the system and special pressure regulation to compensate for changing cabin pressure in the aircraft. Pressure regulators with their reference side connected to a vacuum ( $\approx 1$  torr) were placed on the  $N_2$  and  $H_2$  inlet lines, so that a constant absolute pressure was maintained. The exhaust flow out of the ECD was also maintained at a constant absolute pressure by a similarly referenced backpressure regulator. During field operations, overnight electric heat and flowing  $H_2$  were not allowed on the Electra aircraft. Because the system takes many hours to stabilize after a "cold start," the module containing the ECD, catalysts, and  $F_2$  source was removed from the aircraft each evening and placed in a laboratory in the aircraft hanger, where it was connected to  $N_2$ ,  $H_2$ , and electrical power.

#### Sample Inlet

Air samples were collected from an aft-facing probe which contained a 1/4-inch OD Teflon tube that extended 3 m to the ECD-S equipment rack. The sampling probe protruded beyond the boundary layer of the aircraft body. The sample line was pumped by a Venturi pump, located outside the airframe, and a flow of 5 L/min was controlled with a rotameter/needle valve ("FM" in Figure 1). Air samples were drawn into the sampling system through a tee located upstream of the rotameter. Air from the sampling system, or from a standard system described below, was selected by a manually operated three-way Teflon valve to the cryogenic sampling system.

The sample flow stream then entered a 10-port Valco valve, which had two states, collect and inject. During the collect state, the flow was directed through a cold trap to remove water, and then through a cryo trapping loop to collect and concentrate the sulfur compounds. During the inject state, the cryo trapping loop was switched into the carrier gas stream and simultaneously warmed, so that sulfur compounds were injected on the isothermal (68°C) chromatographic column.

#### Cryogenic Trap

The cryogenic trapping chamber (cryotrap) was constructed out of a 30-cm-long, 5.5-cm ID aluminum tube. A trapping loop consisting of 45 cm of 1/8-inch OD Teflon-lined stainless steel tubing (Altech part number 3154) was coiled inside the cryotrap. A temperature controller, using the input temperature signal from a thermocouple glued onto the outside of the tubing with silicone compound, maintained the cryogenic temperature by throttling a flow of liquid  $N_2$  into the cryogenic chamber through a solenoid valve. During the warm-up mode

the temperature controller switched off the flow of liquid  $N_2$  and switched on 50 A at 2.4 VAC to the stainless steel portion of the trapping loop tubing, providing 120 W of heat directly inside the tubing. During the warm-up phase, the thermocouple sensor temperature changed from  $-175^\circ C$  to  $+50^\circ C$  in 20 s. As the thermocouple was held in silicone compound with somewhat insulating properties, the rate of temperature change inside the tubing was likely more rapid.

A baffle separated the first half of the cryotrap, containing the cryo trapping loop, from the second half, containing the water trapping loop. The baffle was a perforated metal disk that limited the flow of cold gas phase  $N_2$  from the first half of the tube. The water trapping loop consisted of coiled, Teflon-lined stainless steel tube, similar to the cryo trapping loop. During the collection phase the water trapping loop was set at a temperature 10°C warmer than the temperature that would begin to trap DMS.

#### Oxidant Scrubbing

Some of the early measurements of atmospheric DMS were compromised by reactions with oxidants during cryogenic or gold wire collection [Ammons, 1980; Andreae et al., 1985]. Our laboratory measurements have shown that more than 90% of a 70 ppt DMS air sample will be lost in a Teflon cryogenic trapping loop by the addition of 40 ppb of ozone to the air. We assume the loss of DMS occurs because ozone and other oxidants are concentrated along with the sulfur compounds, allowing subsequent oxidation reactions to occur during the warm-up phase due to the greatly increased concentration of the reactants.

We eliminated interference from oxidants by pulling air samples through NaOH-coated, 47-mm glass fiber filters that were held in a Teflon filter holder. These filters were prepared by immersion in a 0.1 M NaOH aqueous solution, followed by drying at 80°C in a nitrogen-purged oven. These filters are able to reduce ambient amounts of ozone (20 to 80 ppb) to undetectable (<2 ppb) levels. At least 10 L of ozone containing air can pass through one of these filters before its ozone-destroying ability is exhausted. It has been shown that DMS is the only sulfur gas affected by the co-trapping of oxidants during a cryogenic concentrations step (P. Goldan, personal communication, 1991). Because  $CS_2$  is not affected by co-trapping of oxidants, and because COS undergoes base-catalyzed hydrolysis, we divided our sample collection into two modes. In the first mode, samples for DMS analysis were directed through the oxidant scrubber; in the second mode, the oxidant scrubber was bypassed to collect samples for analysis of  $CS_2$  and COS.

#### Sample Cycle

During the CITE 3 mission, a 10-min sampling cycle composed of two 5-min segments was used. Air samples were collected during the first 40 s of each 5-min segment. A timing diagram of the relevant valve switches, sample collection flows, and cryotrap temperature is shown in Figure 2. One minute prior to the start of collection, the cryotrap cooled to  $-175^\circ C$  (shown in Figure 2d). At this time, MFC3 opened and began controlling a sample flow of 200 mL/min (Figure 2b) to a vacuum pump. At zero minutes the sample collection was started when the 10-port Valco valve was switched from inject to collect mode (Figure 2c), forcing the sample flow through the water trap and the cryotrap. Fifty seconds into the sample collection a Teflon solenoid valve, positioned on the sample

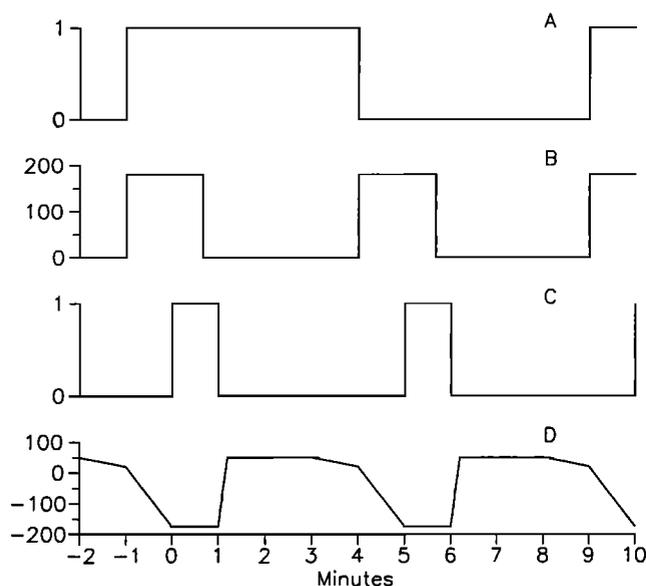


Fig. 2. Timing diagram for operation of the automated cryotrap. (a) State of the valve controlling flow through the NaOH oxidant scrubbing filter; 0, flow bypassing NaOH filter; 1, flow through NaOH filter. (b) Flow of sample air in mL/min as controlled by MFC3 (in Figure 1). (c) State of the Valco 10 port GC sampling valve; 0, Inject mode; 1, Collect mode. (d) Temperature of the cryotrap in degrees Celsius.

inlet to the Valco valve, was closed, stopping the sample flow and allowing the vacuum pump to evacuate the cryotrap loop, removing most of the oxygen. At 1 min into the sample segment the Valco valve was switched from collect to inject mode, heat was applied to the cryotrap loop, and the sulfur gases were rapidly evaporated into the carrier gas stream and swept onto the head of the separation column. The next 5-min segment, starting with the cryotrap cooldown 4 min into the first segment, was identical to the first, except that the valve controlling the sample flow through the oxidant scrubber (Figure 2a) was switched so that the sample flow bypassed the NaOH filter. The three sulfur compounds eluted in less than 3 min, allowing the chromatograph column to accept samples on a 5-min collection cycle.

A manually operated three-way Teflon valve was used to select either ambient air from the sample inlet probe of the aircraft or calibration air from a standard system described below. During the CITE 3 flights, air samples were collected and analyzed for typical periods of 40 to 60 min, followed by 10 to 20 min of calibration standards.

#### Calibration Standards

The working sulfur standards used during the CITE 3 mission were based on two high-pressure sulfur standards mixed in nitrogen. The first standard was purchased from Scott Specialty Gases (Plumsteadville, Pennsylvania) in an AcuLife™-treated aluminum cylinder and contained the following concentrations: H<sub>2</sub>S, 79 ppb; COS, 509 ppb; DMS, 116 ppb, and CS<sub>2</sub>, 106 ppb. The second cylinder was prepared in our laboratory by introducing the pure sulfur gases to a Spectra-Seal™ aluminum cylinder and then pressurizing with 100 atm of ultrapure nitrogen. This second cylinder contained COS, 639 ppb; DMS, 173 ppb; and CS<sub>2</sub>, 15.7 ppb. This second standard was used as the working standard during the CITE 3 data flights. The sulfur gas concentrations in the bottled standards were approximately 1000 times ambient atmospheric

values. A dynamic dilution system reduced the sulfur gas concentrations to ambient levels. This dynamic dilution system used a 0 to 10 mL/min range mass flow controller (MFC2 in Figure 1, Sierra 840) to mix a constant flow of the bottled standard, typically 3 mL/min, into a flow of dilution air, typically 3 L/min that was controlled with a 0 to 10 L/min mass flow controller (MFC1 in Figure 1, Sierra 840). The dilution air was generated in an Adco pure air generator. With the exception of the stainless steel regulator on the gas standard cylinder and the stainless steel mass flow controller, the entire flow stream was made of Teflon. All of the plumbing parts containing the diluted ambient level standard were made of Teflon. By altering the flows with the mass flow controllers, dilution ratios of 100 to 10,000 could be obtained. Blank standards were created by setting the flow of the bottled standard (MFC2) to zero.

At Wallops Island, the flow controllers were calibrated against National Institute of Standards and Technology (NIST) flowmeters, and appropriate linear transformations of the Sierra flow controller outputs were calculated and used in the calculation of the dilution ratios.

The working standard cylinder also contained some SF<sub>6</sub>, which was cryotrapped and analyzed along with the reduced sulfur compounds. Because SF<sub>6</sub> eluted just before COS and was unaltered on the fluorination and reduction catalysts, its ratio to the COS peak served as a useful check on the stability of the fluorination efficiency. The two bottled standards were compared on three occasions during the CITE 3 field project, and those comparisons were used to fix the sulfur gas concentrations in the working bottled standard.

The concentrations of sulfur gases in our primary bottled standard were determined using standards generated from gravimetrically calibrated permeation tubes. These permeation tubes are our primary standards and are stored in our laboratory under flowing nitrogen in glass tubes immersed in a temperature-controlled water bath. The purpose of the nitrogen environment is to eliminate any chemical reactions in the permeation tubes with atmospheric oxygen. The weight-loss history of each primary standard permeation tube has been tracked for at least 1 year.

During the CITE 3 flights, only a span and blank were used for standardization to minimize the time spent analyzing standards. Thus, the ECD-S was assumed to produce a linear response. Although the ECD-S detector is not perfectly linear, it is very nearly so. DMS was the compound with the largest dynamic range in concentration and, consequently, the one most prone to nonlinearity-induced errors. We have previously demonstrated [Johnson and Lovelock, 1988] that these errors would be 5% at most over the concentration range encountered (5 to 200 ppt, 1.2 to 47 pg S for 167-mL sample size). For COS, samples and standards were much closer in concentration, so that nonlinearity errors were less than 1%. For CS<sub>2</sub> measurements the nonlinearity errors were less than 2%.

#### Data System

The output signal from the Shimadzu ECD/electrometer was directed to an HP 3393 integrator. The integrator also controlled the timing sequence of the valves and started the temperature program on the cryotrap temperature controller. The integrator provided printouts of the chromatograms, which were also stored in digital form on an HP 9122 floppy disk drive. Sample peaks that had obvious integration problems were reintegrated after each flight. Better reproducibility of

duplicate standards was obtained using peak heights rather than peak areas, so our results are based on the integrator calculated peak heights.

## RESULTS AND DISCUSSION

### Lower Limit of Detection

Analytical systems, especially those employing preconcentration methods, generally have their lower limit of detection determined by some constraint on the total amount of sample that can be processed. In the ECD-S cryogenic system, interference from water limits the total amount of sample which can be injected through the ECD-S system. During early work with direct injection of 5 mL of moist sample air every 10 min, it was found that after approximately 2 hours the fluorination ability of the silver catalyst would cease. We found that the addition of a water trap consisting of a Teflon loop held at a temperature of  $-40^{\circ}\text{C}$  would eliminate the problem. We assume that the problem resulted from water eluting from the chromatographic column and reacting with the  $\text{AgF}^2$  coated silver catalyst, stripping off the fluorine. We did not see a similar effect from running standards made with dry air from the Adco air generator.

To alleviate the water problem in our cryotrapping system, we designed a cold water trap as an integral part of our cryotrap. However, we found that 170 mL of moist sample, collected and injected at 5-min intervals, was the upper limit on the sample through-put before degradation of the fluorination catalyst. This upper limit was obtained while first predrying the sample in a  $\frac{1}{4}$ -inch OD Teflon loop held in an ice-water bath. Thus, during the CITE 3 mission, samples were collected for 40 s at 200 mL/min for a total of sample size of 167 mL.

It may be possible that ice crystals, created in the cold water trap, did not collect on the inside of the Teflon-lined tube and were swept into the cryotrap, making the water trap less efficient. In this case, a more efficient water trap may result in a lower limit of detection.

This sample size limitation, approximately 50–100 times less than some of the other techniques used on CITE 3 [Cooper and Saltzman, this issue; Ferek and Hegg, this issue] was a fundamental constraint on our lower limit of detection. However, the smaller sample size is compensated for by the greater sensitivity of the ECD-S.

### Uncertainty Estimates

We have chosen to represent our uncertainties as

$$\pm (AC + B) \quad (1)$$

Where  $C$  is the reported concentration,  $A$  is fractional uncertainty, and  $B$  is the lower limit of detection.

The  $A$  term results from uncertainties that vary linearly with the sample size, such as uncertainties in the standards arising from errors in the mass flow controllers used to generate the standards. The  $A$  term can be represented as the Pythagorean sum of its individual components, provided that those components are random and uncorrelated with each other.

Thus

$$A = (F_1^2 + F_2^2 + S^2 + L^2 + P^2 + R_1^2 + R_2^2 + T^2 + U^2)^{1/2} \quad (2)$$

Where  $F_1$  and  $F_2$  are the fractional uncertainties in the flow

rates in the dynamic dilution system that creates the working standard;  $F_1 = F_2 = 0.03$  at the  $\frac{1}{2}$  full scale that they were typically operated.  $S$  is the uncertainty in the determination of the bottled standard from our primary permeation standard; we conservatively estimate that  $S = 0.05$ .  $L$  is the uncertainty that arises from assuming linearity in the detector; as previously mentioned,  $L = 0.01, 0.05,$  and  $0.02$  for COS, DMS, and  $\text{CS}_2$ , respectively.  $P$  is the uncertainty in our primary permeation standard; we estimate that  $P = 0.05$ .  $R_1$  is the uncertainty in the determination of the peak height of the sample; we assume this is the same as the sigma from our response to replicate standards, so that  $R_1 = 0.01$ .  $R_2$  is the uncertainty in the determination of standard; as with  $R_1$ ,  $R_2 = 0.01$ .  $T$  is an uncertainty that arises from temporal variation of the response of the standards over the 1- to 2-hour period between analyzing standards. This appeared to be more serious during flight conditions than during the NIST calibration period while the aircraft was stationary in the hanger. We assign  $T$  its upper limit value of 0.05. Finally, we have allowed all other unlisted uncertainties to be represented by  $U$  and have given this the value of 0.05. Thus,  $A = 0.11, 0.12,$  and  $0.11$  for COS, DMS, and  $\text{CS}_2$ , respectively.

The above uncertainty represents the accuracy. The precision, the degree to which replicate analysis agrees, is not affected by uncertainties in knowing the absolute value of the concentration of the standard. Therefore, the fraction precision,  $A_p$ , can be calculated similar to (2), but with the  $S$  and  $P$  terms deleted.

The  $B$  term in (1) is the lower detectable level (LDL) and is either the concentration where the  $S/N$  becomes 2, or the sigma in the reproducibility of the blank. At very low concentrations, we were limited by sample blanks for  $\text{CS}_2$  and COS but not for DMS. Although the noise varied somewhat, the concentration at which the  $S/N$  for DMS became 2 (the LDL) was 5 ppt.

$\text{CS}_2$ , having twice as much sulfur per mole and a greater fluorination efficiency in the ECD-S, has a response about 3 times that of DMS. However, there was a significant  $\text{CS}_2$  signal in our blanks which were made both from the Adco generated "zero air" and from ultrahigh purity (UHP) nitrogen. For data reduction, we subtracted the  $\text{CS}_2$  blank, in peak height units, from the sample and standard peak heights. This blank amounted to approximately 10 ppt, the reproducibility of which determined the lower limit of detection of 2 ppt.

For COS the blank from the Adco air was greater than the blank from the UHP nitrogen. We assumed that the Adco air generator did not remove all of the COS. For our data reduction, we subtracted the Adco blank from the peak height of the standards and we subtracted the UHP nitrogen blank from the peak height of the air samples. As with  $\text{CS}_2$ , we assume that the reproducibility of the blank of 5 ppt was the limiting factor for the lower limit of detection, although atmospheric values less than 395 ppt were not encountered during the CITE 3 mission.

The values for  $A$ ,  $A_p$ , and  $B$  for each of the three gasses are listed in Table 1.

TABLE 1. The  $A$ ,  $A_p$ , and  $B$  Terms for the Uncertainty in the Sulfur Gas Measurements

Gas	$A$	$A_p$	$B$ ppt
COS	0.11	0.08	5
DMS	0.12	0.10	5
$\text{CS}_2$	0.11	0.09	2

### Flight Measurements

The distribution and variability of a trace gas in the atmosphere depend on its source function, atmospheric lifetime, and the prevailing meteorological mixing. The three sulfur gases we measured had a wide range in lifetimes and source functions. In addition, the CITE 3 flights encountered a variety of air masses that contained very different histories of trace gas source functions. Although almost all flights occurred over ocean water, many of the flights, especially over the North Atlantic, were influenced by anthropogenic sources from industrial regions.

The dominant ocean-to-atmosphere flux of biogenic sulfur occurs as DMS. Once in the atmosphere, DMS is rapidly oxidized to sulfate particles. Its short lifetime of less than 1 day [Thompson *et al.*, 1990], however, regulates it to relatively low concentrations, generally less than 200 ppt. The relatively high flux and short lifetime make DMS the largest contributor of sulfur to sulfate particle production in remote marine locations. DMS is not believed to have any significant anthropogenic sources.

CS<sub>2</sub> has an atmospheric lifetime of approximately 6 days [Toon *et al.*, 1987] and a rather small flux into the atmosphere. Near industrial regions, anthropogenic emissions of CS<sub>2</sub> dominate, but a widespread, weak flux from the ocean apparently exists [Kim and Andreae, 1987]. CS<sub>2</sub> does not significantly affect the rapid cycling of sulfur into particles in the atmosphere; however, one product of the atmospheric oxidation of CS<sub>2</sub> is COS. This process could be a major source of atmospheric COS [Barns *et al.*, 1983].

Although COS has a small flux through the atmosphere, it is the dominant sulfur gas in terms of concentration (500 ppt) due to its long lifetime (greater than 1 year). Although COS is photochemically inert in the troposphere, it is a major source of sulfur to the stratosphere, where it is photochemically oxidized to sulfate particles that have a small but demonstrable effect on climate [Turco *et al.*, 1980].

### Flight Data

We show in detail data from flights 5, 6, and 8 from the North Atlantic and flights 14 and 15 over the Tropical Atlantic

(the flight tracks are shown in Figure 3). For each flight, a detailed meteorological analysis is given by Shipham *et al.* [this issue], which includes back trajectories of the wind field. Using these back trajectories along with supporting measurements of ozone and NO<sub>x</sub> that were provided on each flight, we rate the air that was sampled as "clean marine," "continental and polluted," or some mixture of both. Clean marine air, in the Atlantic boundary layer, has low ozone levels, generally below 40 ppb [Winkler, 1988]. NO<sub>x</sub>, due to its short lifetime and lack of strong marine sources, is also a key indicator of continental and anthropogenic influence. Boundary layer air with NO<sub>x</sub> levels greater than 100 ppt is obviously polluted, while air with NO<sub>x</sub> levels below this value is generally considered "clean."

Flight 5 (Figure 4) occurred off the North Carolina coast on August 23 and experienced relatively clean marine air, as seen by the relatively low ozone levels. Back trajectory analysis showed that the air masses reaching the flight track traveled across the Atlantic as easterlies before turning north and arriving at the flight track as southwesterlies. The back trajectories indicate that the air may have brushed the Carolina coast before moving eastward back over the ocean. There were two flight segments below 600 m of altitude; the first, between 16 and 17.5 hours, had ozone levels near 25 ppb, and the second segment, between 19 and 20 hours, had ozone levels near 40 ppb, indicating the air was of more continental character. In the first segment our DMS concentration averaged 115 ppt, while in the second our DMS concentration averaged 23 ppt. Our DMS measurements at 1500 m were all below our detection limit of 5 ppt. In all cases the CS<sub>2</sub> concentrations were below our detection limit of 2 ppt. Our COS measurements show a slight increase with time over the flight, no correlation with altitude, and a mean value of 552 ppt.

Flight 6 (Figure 5), occurring off the coast of New Jersey on August 25, sampled continental air that had originated in northern Canada and passed over the industrial northeastern United States before moving out over the Atlantic. The flight track consisted of three loops at 50, 150, and 270 km from the coast at 15–16, 17–18, and 18.5–19.3 hours, respectively. The high ozone (>50 ppb) and NO<sub>x</sub> (>200 ppt) concentrations

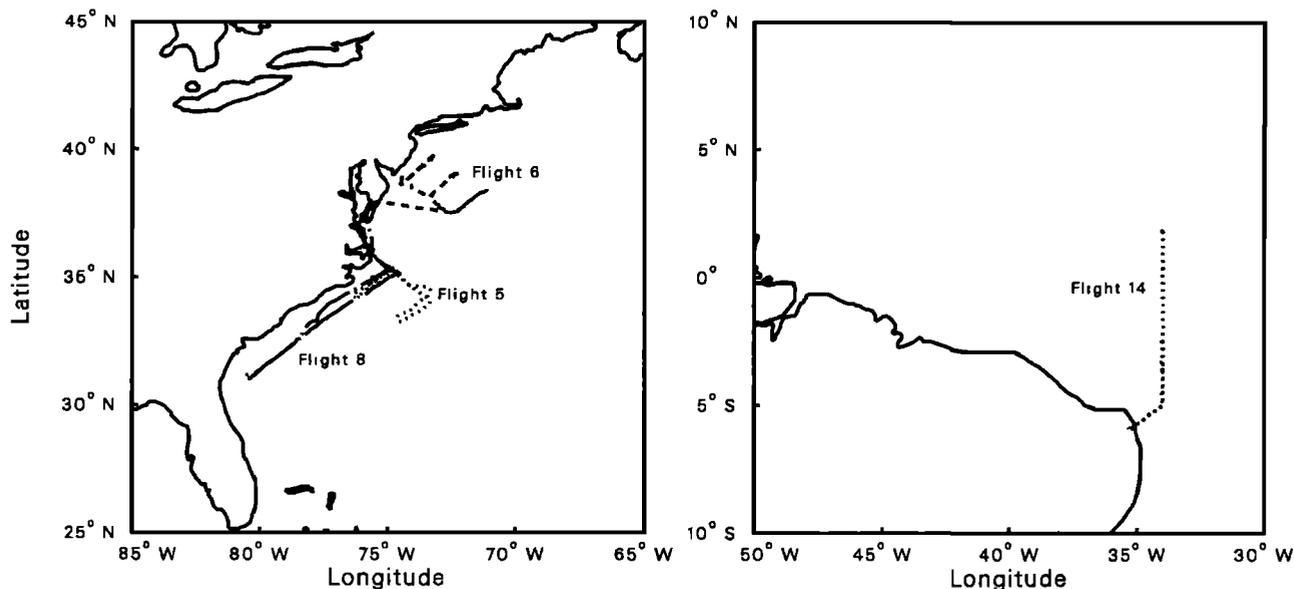


Fig. 3. A map of flight tracks for (left) flights 5, 6, and 8 and (right) flight 15. Flight track 15 repeated track 14, so only track 14 is shown.

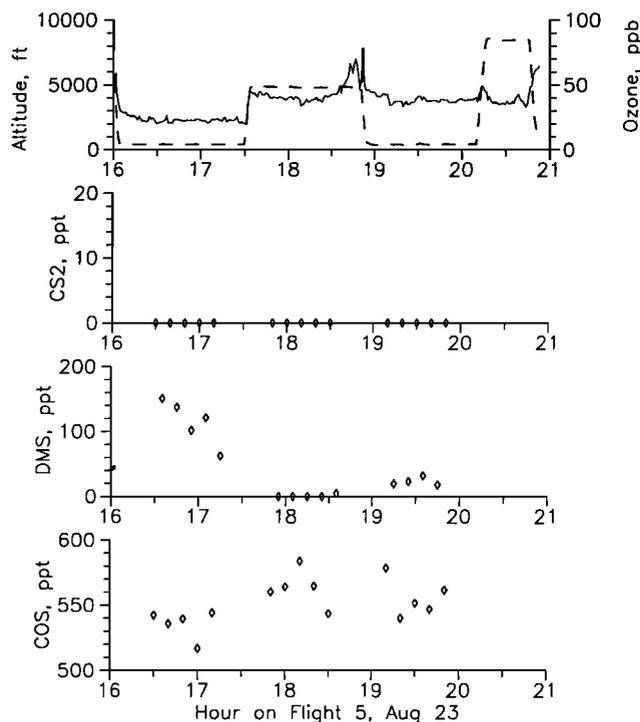


Fig. 4. A time series of altitude, ozone, and our measurements of COS, CS<sub>2</sub>, and DMS on flight 5 on August 23, 1989. The time coordinate is in UT.

indicated air which had been modified by urban emissions, consistent with the calculated back trajectories. The boundary layer segment nearest the coast contained the highest DMS concentrations with a mean value of 58 ppt, about half that measured in the first boundary layer segment during flight 5. The two flight segments further from the coast had average DMS concentrations of 14 ppt. DMS concentrations from the flight segments above 1500 m were below the detection limit of 5 ppt. CS<sub>2</sub> levels averaged 9.2 ppt in the boundary layer segment nearest the coast and 2.2 ppt in the boundary layer segments further from the coast. CS<sub>2</sub> was below the detection limit of 2 ppt at altitudes above 1500 m. COS averaged 426 ppt, about 28% lower than on flight 5.

Flight 8 (Figure 6) occurred on August 30 off the coast of South Carolina and Georgia. The air near the surface had originated over the Great Lakes, passed over the industrial northeastern United States, and then traveled over the Atlantic for as long as 4 days before arriving on the flight track. The back trajectories for the air that was sampled at 1500 m showed that it came directly from the Carolina region. In the 150-m altitude segments, we detected a mean value of 18 ppt DMS. In the 1500-m altitude segments, the DMS concentrations were again below our detection limit. During the 1500-m altitude segments, we recorded a mean value 12.4 ppt of CS<sub>2</sub>, and during the lower boundary layer segments, CS<sub>2</sub> was below our detection limit. This is the exact opposite of flight 6, where CS<sub>2</sub> was found at 150 m and not at 1500 m. The COS concentration for this flight averaged 483 ppt and was higher at 1500-m altitude, than at 150 m (mean concentrations of 496 and 469, respectively, a difference significant at the 99.5% level).

Flights 14 (daytime, Figure 7) and 15 (nighttime, Figure 8) occurred on September 15 and 16 out of Natal, Brazil as a pair of flights that repeated the same flight track 12 hours apart to

investigate the diurnal pattern in DMS concentrations. Back trajectory analysis indicated that the air traveled westward in the trade winds over the Atlantic Ocean, so that it was presumed free of any recent continental influence. On each flight the first 1500-m altitude segment had several measurable DMS values (daytime 8 ppt, nighttime 18 ppt), while the remaining measurements at altitudes of 1500 m or greater were below the detection limit. The 150-m altitude segments showed a diurnal cycle with a mean value of 20 ppt during daytime flight 14, and a mean DMS concentration of 39 ppt during nighttime flight 15, 13 hours later. Only two CS<sub>2</sub> measurements of 3 and 2 ppt were above the detection limit on flight 14, and none were above detection limit on flight 15. The COS measurements showed very little variation, with an average of 424 ppt on flight 14 and 414 ppt on flight 15.

For a statistical representation of the entire data set, we have divided the measurements into categories by location (North Atlantic and Tropical Atlantic) and by altitude (>600 m and <600 m). Statistics for these four categories for each of the three sulfur gases are given in Table 2, and histograms for each gas in each category are shown in Figure 9. Data from the ferry flight from Wallops Island to Natal are not shown because only mid-tropospheric measurements were made. The COS measurements from the ferry flight are the subject of another paper [Johnson *et al.*, this issue].

There was considerable variability in meteorological conditions over the North Atlantic Ocean and North American continent during the flights based in Wallops Island. Back trajectory analysis showed very different origins of the air masses encountered on the flights. The geographical positions

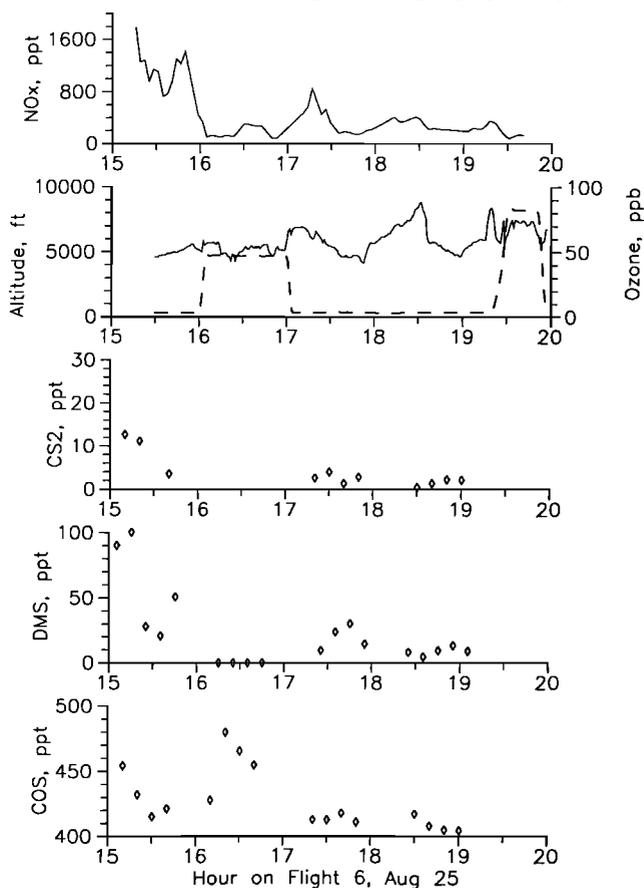


Fig. 5. A time series of altitude, ozone, NO<sub>x</sub>, and our measurements of COS, CS<sub>2</sub> and DMS on flight 6 on August 25, 1989. The time coordinate is in UT.

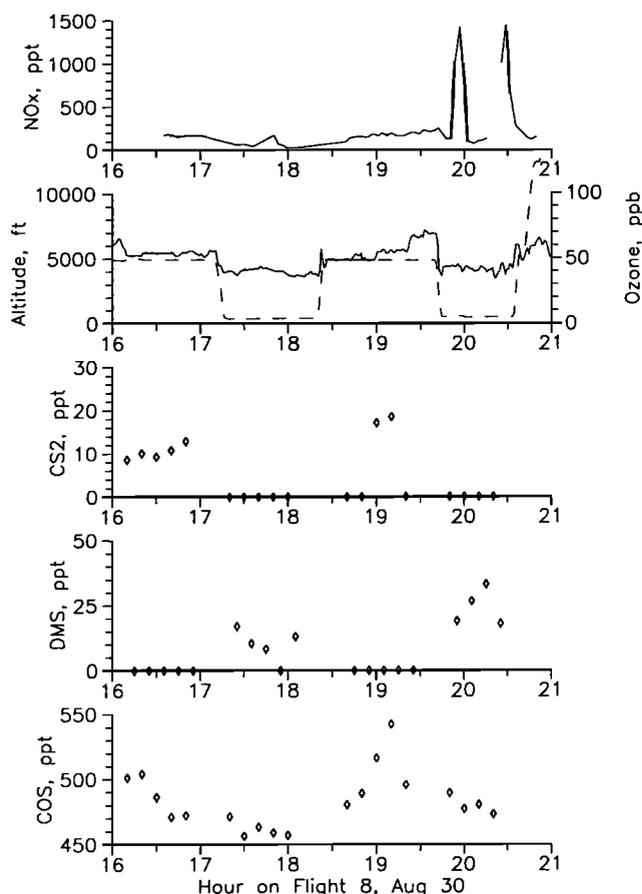


Fig. 6. A time series of altitude, ozone,  $\text{NO}_x$ , and our measurements of COS,  $\text{CS}_2$ , and DMS on flight 8 on August 30. The time coordinate is in UT.

of air parcels 5 days before they intersected the boundary layer flight tracts included the north Tropical Atlantic on flights 4 and 5, the north Canadian Arctic on flight 6, the Great Lakes region on flight 7, and the northeastern United States on flight 8. Thus flights 4 and 5 sampled relatively clean marine air, and flights 6 and 7 sampled air of urban/continental or "polluted" character. Flight 8 sampled air near the surface that 5 days previous had been over the northeastern United States, but had spent at least four of the intervening days over the Atlantic Ocean, so that it contained both marine and polluted characteristics.

Because the air masses sampled over the North Atlantic had originated from different regions, each with very different sulfur gas emissions, most of the variations in sulfur gas concentrations during these flights can be attributed to the atmospheric chemistry and sulfur gas sources of the various regions. This is in contrast to the conditions encountered over the Tropical Atlantic, where the meteorological conditions were much more homogeneous. During the tropical flights, based in Natal, the trade winds blew consistently from the east, and back trajectory analysis showed that all of the air masses which intersected the boundary layer flight tracts had been over the central Tropical Atlantic for the previous 5 days. Because of the homogeneous meteorological conditions, diurnal variations in short-lived species such as DMS and ozone, caused by the diurnally varying photochemistry, were much more apparent.

The DMS measurements over the North Atlantic generally showed that DMS concentrations were higher in "clean

marine" air. The highest DMS concentrations (150 ppt) were found in the lower boundary layer on flight 5. Since ozone was generally higher in "dirty" air, DMS concentrations below 600-m altitude and ozone were anticorrelated, with a correlation coefficient of  $-0.70$ . The lower values of DMS in continental air are consistent with DMS sulfur fluxes to the atmosphere and shorter DMS lifetimes due to higher hydroxyl and nitrate radical concentrations.

The dominant variation in DMS concentrations over the Tropical Atlantic appeared to be diurnal (E. S. Saltzman et al., Diurnal variations in atmospheric sulfur gases over the western equatorial Atlantic Ocean, submitted to *Journal of Geophysical Research*, 1992). Figure 10 displays a plot of all ECD-S DMS concentrations at altitudes below 600 m from flights 13 through 19 as a function of hour of the day. The following least squares sinusoidal fit, which explains 52% of the variance in the DMS concentrations, is also shown:

$$\text{DMS (ppt)} = 44.8 + 17.9 \cos [2\pi(H - 2.9)/24]$$

where  $H$  is the local time in hours. Unlike the North Atlantic, where ozone and DMS were anticorrelated, DMS and ozone concentrations below 600-m altitude had a positive correlation with a correlation coefficient of  $+0.74$ . This was likely due to a similar photochemical cycle in both DMS and ozone with concentration maxima late at night and minima in the afternoon. As seen in the histograms in Figure 9, the low-altitude DMS concentration over the North Atlantic had much greater variability than the low-altitude DMS concentrations over the Tropical Atlantic.

The isolated cases of measurable DMS at the 1500-m altitude occurred in the vicinity of cumulus clouds and are consistent with the hypothesis of "cloud pumping" as described by Ferek et al. [1986].

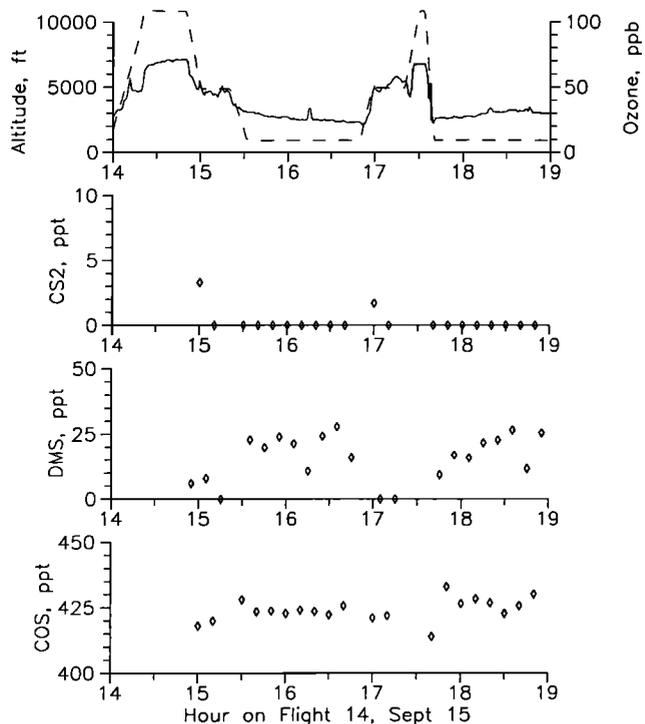


Fig. 7. A time series of altitude, ozone, and our measurements of COS,  $\text{CS}_2$ , and DMS on flight 14 on September 15, 1989. The time coordinate is in UT.

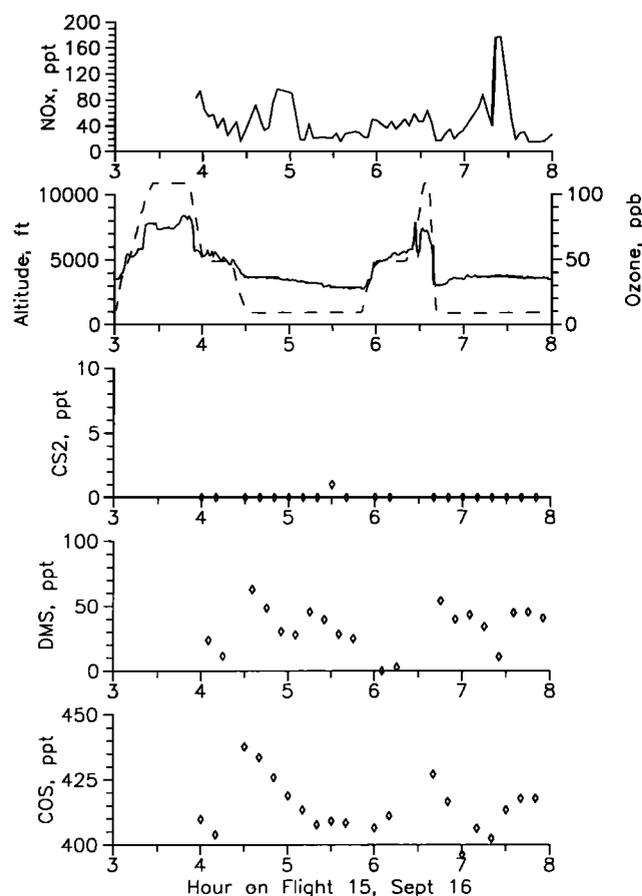


Fig. 8. A time series of altitude, ozone,  $\text{NO}_x$ , and our measurements of COS,  $\text{CS}_2$ , and DMS on flight 15 on September 16, 1989. The time coordinate is in UT.

COS concentrations had a higher mean value over the North Atlantic (North, 489 ppt; Tropical, 419) and much lower variability over the Tropical Atlantic. Both of these features can be clearly seen in the histograms in Figure 9. Although the North Atlantic atmosphere contained the highest concentrations of COS, flight 6, which encountered air that had originated the

TABLE 2. Number of Samples, Mean, and Standard Deviation for Each of the Histograms Displayed in Figure 9

	North Atlantic		Tropical Atlantic	
	Low	High	Low	High
DMS				
<i>n</i>	41	5	125	21
Mean	44.1	14.2	45.0	24.5
Sigma	43.9	8.5	20.2	18.9
Sigma/mean	1.00	0.60	0.45	0.77
COS				
<i>n</i>	43	38	39	23
Mean	470	508	420	415
Sigma	48.9	43.8	8.8	8.9
Sigma/mean	0.10	0.09	0.02	0.02
$\text{CS}_2$				
<i>n</i>	14	13	4	6
Mean	3.8	12.8	0.8	1.8
Sigma	3.5	6.0	0.2	1.1
Sigma/mean	0.93	0.47	0.31	0.64

The measurements that were below detection limit were deleted from these statistics.

furthest north of any of the flights, had very low COS concentrations. One possible explanation for these low values is that the air mass had traversed the boreal forests of Canada and may have lost COS to the land plants [Goldan *et al.*, 1988]. The large variability in the North Atlantic measurements is consistent with closer proximity to both anthropogenic COS sources and a land plant COS sink.

The mean COS concentration from samples collected below 600-m altitude was 38 ppt less than in samples collected above 600 m over the North Atlantic. Over the Tropical Atlantic the vertical gradient was reversed, so that the mean COS concentration below 600 m was 5 ppt higher than that above 600 m. One possible explanation may be that for the North Atlantic samples, a sink to land plants over the North American continent had depleted COS in the lower atmosphere, while over the Tropical Atlantic a weak ocean source [Johnson and Harrison, 1986; Ferek and Andreae, 1983; Rasmussen *et al.*, 1982] may have elevated the COS concentrations in the lower boundary layer.

High values of  $\text{CS}_2$ , i.e., greater than 10 ppt, were only found in the North Atlantic flights in air which had recently passed over the eastern United States. From this it can be inferred that the only major  $\text{CS}_2$  sources are associated with continental and/or industrial activity. The reversal of the vertical gradients between flights 6 and 8 can be explained by the differences in the isentropic back trajectories at the surface (300 K) and at the 1500-m altitude (307 K). For flight 8 the 300 K trajectories had passed over the northeastern United States 4 days earlier, then traveled over the Atlantic Ocean, while the 307 K trajectories came directly from the southeastern United States. If the southeastern United States had a higher flux density of  $\text{CS}_2$  to the atmosphere than did the Atlantic Ocean, then the 1500-m altitude air could have had greater concentrations of  $\text{CS}_2$ , provided that the lifetime of  $\text{CS}_2$  was shorter than 4 days.

#### SUMMARY AND CONCLUSIONS

We have described a working airborne system for measurements of COS, DMS, and  $\text{CS}_2$ , which has minimum detection limits of 5, 5, and 2 ppt, respectively. This system has several specific advantages. It is not sensitive to  $\text{SO}_2$ , thus improving the chromatography in environments with high  $\text{SO}_2$  concentrations. This situation occurred on flights 6 and 7 off the New Jersey coast. The ECD-S detector is 10 to 100 times more sensitive than the FPD detector, therefore requiring smaller sample volumes. The smaller sample volume enables shorter collection times and longer oxidant scrubber lifetimes. Another advantage of the ECD-S over the conventional FPD is that no hydrogen flame is utilized. Although hydrogen is still required for the reduction catalyst, the lower flow rate (1 mL/min) allows much smaller amounts of hydrogen to be carried on research platforms, where safety concerns about hydrogen exist.

Measurements of atmospheric sulfur gases showed much greater variability of DMS and COS concentrations in the Wallops Island flights compared with the Natal flights. For DMS this was likely due to the very different origin of the air masses, from the Tropical North Atlantic Ocean (flight 5) to the Canadian Arctic (flight 6). Air trajectories that passed over the industrial northeastern United States likely had much greater photochemical oxidizing potential, as indicated by the measurements of ozone and  $\text{NO}_x$ . In this oxidizing atmosphere, DMS had a shorter lifetime, resulting in lower DMS concen-

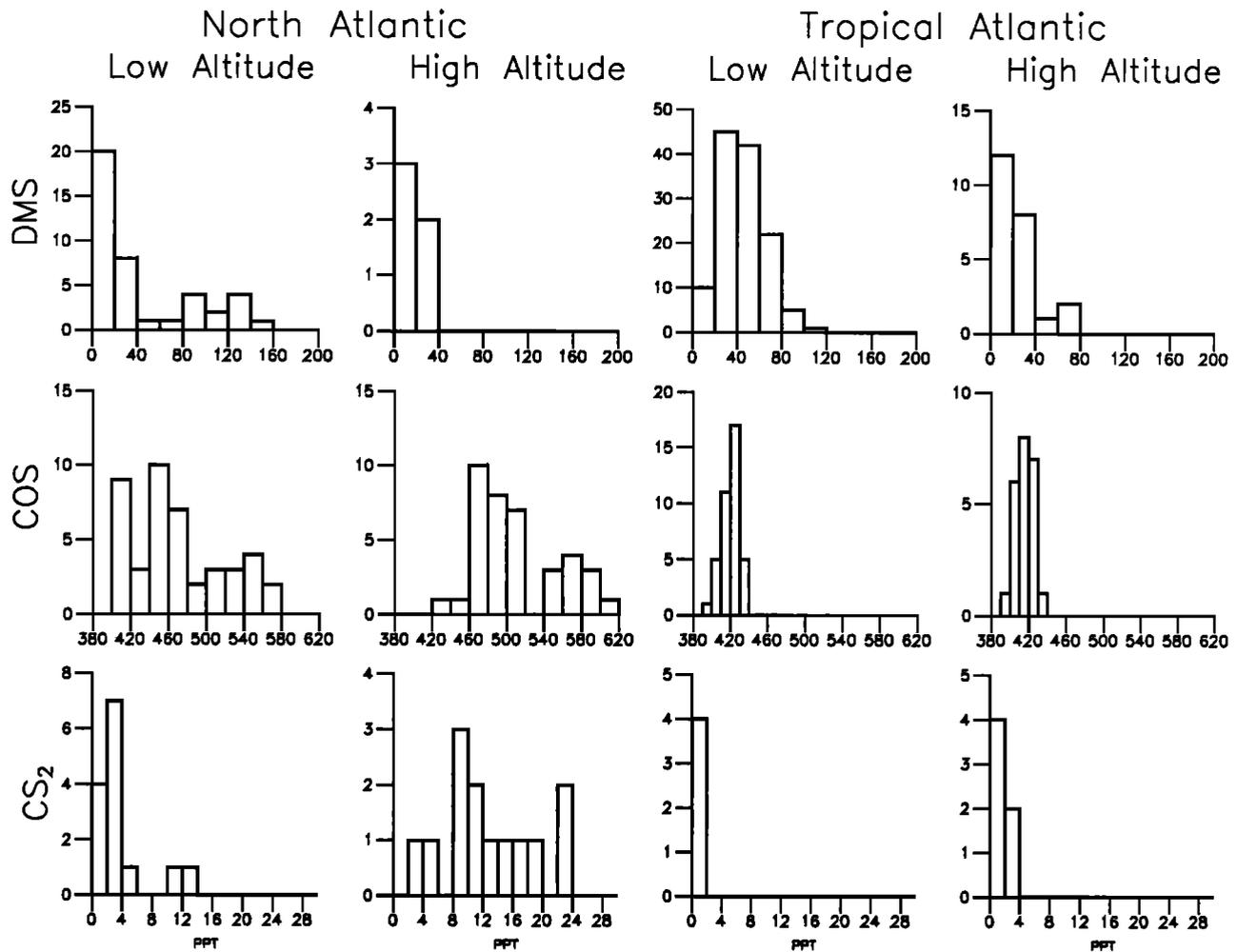


Fig. 9. Histograms of the sulfur gas measurements. Each of the three measured gases are broken down into four categories: measurements from below 600 m from the North Atlantic (Wallops Island) flights, measurements from above 600 m from the North Atlantic flights, measurements from below 600 m from the Tropical Atlantic (Natal) flights, and measurements above 600 m from the Tropical Atlantic (Natal) flights. The DMS histograms show the number of samples in each 20 ppt wide concentration bin between 0 and 200 ppt. Samples in which the DMS concentration was below the detection limit of 5 ppt are not counted in the bins. The North Atlantic COS histograms show the number of samples in each 20 ppt wide concentration bin between 380 and 600 ppt. Because of the lowered variability of COS in the Tropical Atlantic measurements, the Tropical Atlantic COS histograms show the number of samples in each 10 ppt wide bin between 380 and 600 ppt. The  $CS_2$  histograms show the number of samples in each 2 ppt wide concentration bin between 0 and 30 ppt. Samples in which the  $CS_2$  concentration was below the detection limit of 2 ppt are not counted in the bins.

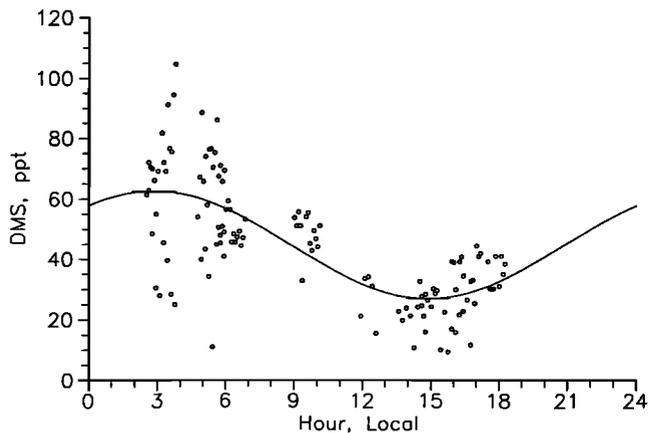


Fig. 10. The diurnal cycle in the DMS concentration from the lower boundary layer of the Tropical Atlantic. All of the DMS samples that were collected below 600 m in altitude during the Natal flights are plotted as a function of local time of day (UT - 2 hours). The line is the best least squares fit of a sinusoidal function with a period of exactly 24 hours.

trations. For the Natal flights, the steady advection of air masses westward in the trade winds resulted in a more steady state environment with lower DMS variability. Much of the variability that was present was diurnal, resulting from the daytime oxidation of DMS.

COS exhibited a north-south gradient with mean concentration of 489 ppt over the North Atlantic and 419 ppt over the Tropical Atlantic. COS concentrations had a dramatic difference in variability with  $\sigma/\text{mean} = 0.10$  over the North Atlantic and 0.02 over the Tropical Atlantic. One possible explanation for this difference is that both the major sources and sinks for COS are located in the northern hemisphere [Johnson *et al.*, this issue].

$CS_2$  apparently has a major source associated with continental and/or industrial activity.  $CS_2$  concentrations were generally less than 2 ppt everywhere except over the North Atlantic in air which had recently passed over the eastern United States.

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