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UPTAKE OF CARBONYL SULFIDE BY SILVER NITRATE IMPREGNATED FILTERS: IMPLICATIONS FOR THE MEASUREMENT OF LOW LEVEL ATMOSPHERIC H_2S

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Abstract. Measurements of atmospheric hydrogen sulfide are often made by first collecting H_2S on a paper filter impregnated with silver nitrate. Using this technique on a recent shipboard study, we observed anomalous breakthrough characteristics of sulfide, which caused us to suspect the presence of an artifact. We have investigated the interaction of various sulfur species with these filters as precursors for the artifact sulfide. Laboratory experiments indicate that OCS generates sulfide on the filters with an efficiency of 1-2% under conditions comparable to those used for field sampling in the marine boundary layer. The magnitude of the artifact increases with increasing temperature and is insensitive to humidity and insolation. It appears likely that OCS is responsible for our shipboard results. Since much of the data on H_2S concentrations in marine air have been obtained with this technique, they are most likely in error, producing overestimates of background H_2S concentrations.

Introduction

A balance of the global sulfur cycle requires knowledge of the contribution of both natural and anthropogenic fluxes of sulfur compounds to the atmosphere. Hydrogen sulfide is a major component of biogenic sulfur emissions from both coastal and terrestrial environments, primarily as a result of microbial sulfate reduction in anoxic environments. Measurements of H_2S in marine air (Slatt et al., 1978; Delmas and Servant, 1982; Herrmann and Jaeschke, 1984) yielded concentrations which suggest that there are substantial sources of H_2S in remote oceanic regions, and that these sources may be important in the sulfur budget of the marine boundary layer.

All the reported measurements of low level concentrations of atmospheric hydrogen sulfide have relied on variations of the method of Natusch et al. (1972), which owes its popularity to its high sensitivity and to the purported absence of any known atmospheric interferents. Results of our field work, however, led us to believe that a low level positive interference was present.

Axelrod et al. (1969) had previously reported no interference by Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, $C_2H_3O_2^-$, CHO_2^-, CO_3^{2-}, methyl acetate, ethanol, acetone, acetamide, mercaptoethanol, NH_4OH, Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, K^+, Na^+, slight fluoresence enhancement by I^- and slight quenching by Br^-, SO_3^{2-}, NO_2^-, cysteine and cystine at elevated concentrations. Natusch et al. (1972) found no loss of H_2S from filters exposed to elevated NO_2, and slight loss from

exposure to elevated SO_2 and O_3, but concluded that these losses would not be significant at ambient oxidant concentrations. No interference has been found from the reduced sulfur compounds dimethyl sulfide, methane thiol, and carbon disulfide (Jaeschke et al., 1980). To our knowledge, no one has tested for interference from carbonyl sulfide, despite the fact that OCS is the most abundant sulfur gas in marine air, with concentrations in the marine boundary layer of 500 $\pm$ 50 pptv (Khalil and Rasmussen, 1984).

In this paper we present our anomalous field data and the results of laboratory experiments designed to study the interaction of OCS with silver nitrate impregnated filters. The implications of these results for the analysis of trace concentrations of atmospheric H_2S are discussed.

Methods

Shipboard and laboratory measurements of H_2S were made by a method essentially identical to that of Natusch et al. (1972). An air stream was drawn through a silver nitrate impregnated filter (Whatman 41, 47 mm diameter), held in a Teflon PFA filter holder. The H_2S is fixed on the filter as silver sulfide, which was extracted from the filter using 20 ml of 0.1 M sodium hydroxide/ sodium cyanide solution. The sulfide was determined by the fluorescence quenching of dilute fluorescein mercuric acetate (FMA), using 100 ul of 20 uM FMA in 0.1 M NaOH in each analysis. A Turner Designs model 10-853 fluorometer was used with a blue lamp and 10 nm bandpass filters at 500 nm excitation and 520 nm emission wavelengths.

Routine sampling of background marine air at our maximum flow rate of 8 liter min^{-1} required a sampling time of approximately one hour to give a detection limit of 3 pptv. For the laboratory work, we increased the sampling times to give better precision at low sulfide concentrations. A detection limit of lower than one pptv was achieved by sampling for several hours.

In the laboratory experiments, screw cap test tubes (45 ml) sealed with Mininert Teflon valves were filled with an atmosphere of nitrogen, containing approximately 1 ppm OCS from a permeation tube. For these studies, measurements of carbonyl sulfide were made gas chromatographically using a 5' x 1/8" Teflon Tenax GC column (Alltech Associates, Deerfield, IL) held isothermal at 40°C. N_2 was used as the carrier gas at a flow rate of 20 $cm^3 min^{-1}$. Aliquots of gas were injected onto the column through a septum. A sulfur specific flame photometric detector was used, which has a detection limit of approximately 2 picomoles S. Calibration was performed by injecting microliter aliquots of a standard gas mixture (Scott Specialty Gases, Plumsteadville, PA) and using a permeation tube/mass flow controller system.
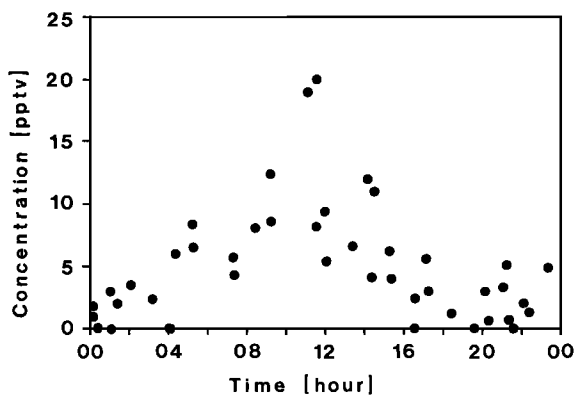
Fig. 1. Diurnal variation of the apparant H₂S measured on back-up (second stage) silver nitrate filters in remote marine air.

Study Sites

The field data discussed in this study were obtained on cruise CI8601 of the R/V Columbus Iselin from Miami to the Cariaco Trench, off the coast of Venezuela, during February and March, 1986. The H₂S data discussed in this paper were obtained from air masses representative of background conditions over the subtropical Atlantic Ocean (E. Saltzman and D. Cooper, manuscript in preparation). The laboratory studies were conducted from a fourth floor rooftop laboratory at the Rosenstiel School of Marine and Atmospheric Science on Virginia Key, FL. Winds were predominantly onshore during these studies. The site has been described in detail by Slatt et al. (1978).

Field Observations

The measurements of H₂S were made in the field using the normal (front) silver nitrate filter with a second (back-up) filter in series as a routine precaution. Previous laboratory and field tests have shown the collection efficiency of a single filter to be greater than 98% (Cooper, 1986). However, on this cruise, which required longer sampling times than previous terrestrial H₂S measurements, a sulfide signal was consistently found on the back-up filter. This signal averaged approximately 30% of that on the front filter, with a calculated mean sulfide (apparent H₂S) concentration of 4.9 pptv (standard deviation = 4.7, n = 44). The concentration on the back-up filter did not correlate with the sulfide concentration on the front filter. In addition, when a third stage was added to the filter train, a signal was measured that was equivalent to that on the second stage filter.

These observations suggested the presence of a previously undiscovered interference to the method. Furthermore, the peculiar "breakthrough" characteristics suggested that the interfering species was not quantitatively collected on the silver nitrate filters, but was present at a concentration significantly higher than H₂S.

An interesting feature of the shipboard measurements is a diurnal cycle in the sulfide content of the second stage filters, shown in Figure 1. While there is considerable scatter in the data (a composite from 12 days of sampling), it is evident that the second stage concentration

is higher for samples collected during the daytime, compared to nighttime samples.

A possible explanation for these results is the uptake of carbonyl sulfide (OCS) by the filters. OCS is known to interact with metal surfaces (Ammons, 1980; Graedel et al., 1981) and to undergo hydrolysis in aqueous solution (Johnson, 1981; and references therein). In both cases sulfide is the most likely product. Consequently, we carried out a series of experiments to determine whether OCS could be responsible for the artifact observed in our field studies.

Laboratory Studies

The first experiment was designed to determine whether OCS has an influence on the collected sulfide and the apparent breakthrough. Two identical samples were collected in parallel, each with five filter stages, at the same flow rates used for the field studies (7.8 liter min⁻¹). An OCS permeation tube was connected in line with one set of filters, adding approximately 1.3 ppbv to the ambient OCS. While we did not determine the ambient OCS, previous studies have shown it to be ubiquitous in the atmosphere, at 500 ± 50 pptv (Khalil and Rasmussen, 1984). Figure 2a shows the results of this experiment. The unspiked set of filters exhibited a concentration of 48 pptv sulfide on the front filter. The back-up filters exhibited sulfide signals equivalent to 1.8-3.3 pptv H₂S, similar in magnitude to the artifact observed at sea. The spiked set of filters exhibited higher sulfide signals on all filter stages, with the difference between the two sample trains ranging from 21 pptv at the front filter to
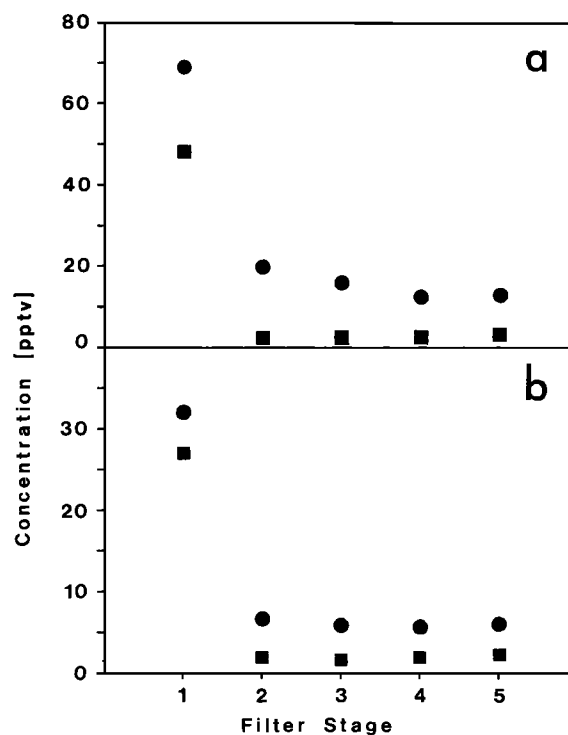

Fig. 2. Sulfide concentrations measured in ambient air on Virginia Key, using silver nitrate filters (a) in the presence (●) and absence (■) of added carbonyl sulfide, and (b) in holders covered by aluminum foil (■) and uncovered (●).
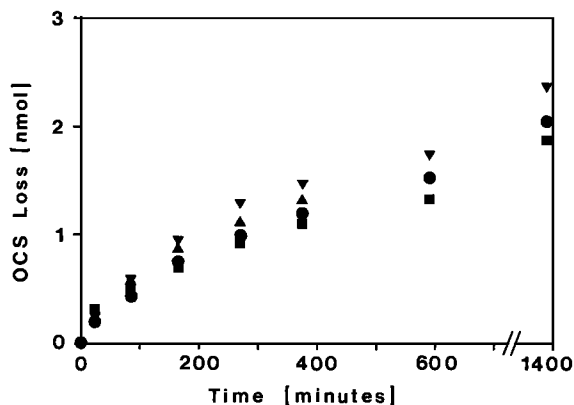
Fig. 3. Effect of light intensity and moisture on the loss of OCS to silver nitrate filters. Irradiated/dry (■); irradiated/humidified (●); dark/dry (▲); dark/humidified (▼).

10 pptv at the last stage. These differences suggest that the efficiency of the process generating the artifact is of the order of 1-2% of the added OCS.

Initially we suspected that the diurnal changes in the magnitude of the artifact were related to the effect of sunlight irradiation on the filters. It was noted that filters collected during the daylight hours acquired a grey coloration, indicating the formation of metallic silver via the photoreduction of silver ion. While the reaction between OCS and silver has not been studied, the interaction of OCS with other metals such as gold, copper and iron is well known (Ammons, 1980; Graedel et al., 1981; and references therein).

An experiment was therefore designed to study the effect of insolation on artifact generation. As in the previous experiment, two parallel sets of samples were collected; this time one set was covered with aluminum foil, preventing light from penetrating the translucent filter holders. The results, presented in Figure 2b, show a significant difference between the two sets of filters, with the uncovered filters exhibiting a substantially greater artifact. However, this experiment does not conclusively show that the irradiation of the silver nitrate filter is the primary factor governing artifact generation. Absorption of sunlight by the Teflon PFA filter holders also has the effect of increasing the temperature of the filters during sample collection.

A series of laboratory experiments was conducted in an attempt to distinguish more specifically between the environmental factors which may affect the uptake of OCS by the $AgNO_3$ filters. The filters were placed in test tubes containing an atmosphere of approximately 1 ppm OCS in nitrogen, and exposed to various light intensities, humidities and temperatures. The concentration of OCS in the test tube was measured by periodically sampling small aliquots of the headspace which were analysed by gas chromatography.

Control experiments, using a moist unimpregnated filter paper, showed negligible loss of OCS from the gas phase, indicating that losses of OCS to the glass walls or filter material were not important. Both light intensity and moisture content of the air were shown to have a negligible effect on the loss of OCS to the filter (Figure
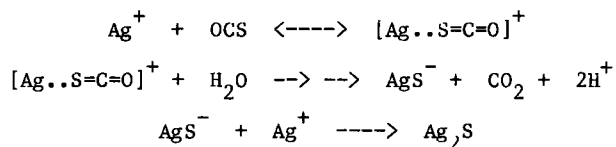
3). Temperature, on the other hand, had a significant effect. Figure 4 shows the loss of OCS to silver nitrate filters in test tubes maintained at 0, 25 and 50°C.

The magnitude of the temperature effect alone is sufficient to explain the differences observed between the foil covered and the uncovered filters in the earlier experiment, and to explain the diurnal variations in the artifact observed in the shipboard data.

The Mechanism of Artifact Formation

While the experiments conducted in this study have demonstrated that OCS interacts with silver nitrate impregnated filters to increase the apparent hydrogen sulfide concentration, the mechanism of the low efficiency process is not known. The first step must be the adsorption of gaseous OCS onto the filter surface. The subsequent hydrolysis step could occur in either of two ways. In the first case, OCS may remain stable on the filter until extraction of the filter for analysis. Any OCS on the filter would hydrolyse within seconds in the strongly basic NaOH/NaCN solution used to extract the sulfide. The experimental evidence argues against this mechanism; if adsorption was the rate controlling step, the artifact formation would most likely exhibit a negative temperature dependence, in contrast to the positive dependence observed.

The other, more probable, mechanism is that OCS undergoes both adsorption and hydrolysis on the filter, with the latter being the rate determining step. We speculate that the process involves the following steps:

$$Ag^+ + OCS \longleftrightarrow [Ag..S{=}C{=}O]^+$$

$$[Ag..S{=}C{=}O]^+ + H_2O \longrightarrow \longrightarrow AgS^- + CO_2 + 2H^+$$

$$AgS^- + Ag^+ \longrightarrow Ag_2S$$

Water is readily available to form an intermediate hydrated adduct, required in the second step, as it constitutes a significant proportion of the paper filter matrix (13% at 60% relative humidity; Natusch et al., 1974). This speculative mechanism is analogous to those
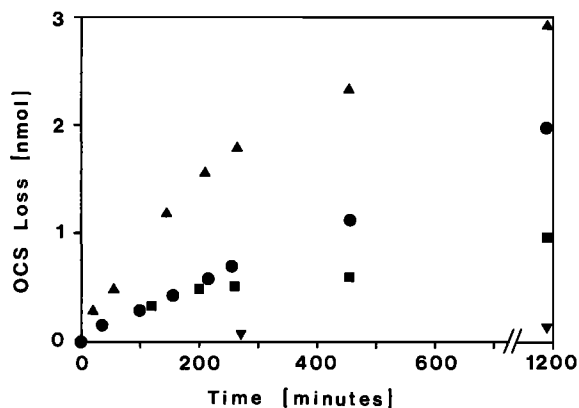

Fig. 4. Effect of temperature on the loss of OCS to silver nitrate filters. 0°C (■); 25°C (●); 50°C (▲); control with no silver nitrate at 50°C (▼).

discussed by Johnson (1981) for the hydrolysis of OCS in aqueous media, with the silver ion acting as a catalyst in the reaction. At higher pH, the rate of the reaction can be expected to increase as the mechanism shifts to the nucleophilic addition of OH⁻ in place of water.

Implications for the Analysis of H_2S in Air

The low efficiency trapping of OCS on silver nitrate filters observed in our experiments generates a sulfide concentration of the correct magnitude to explain the artifact found in hydrogen sulfide measurements made both at sea and at Virginia Key. The temperature dependance found in the laboratory experiments is the probable cause of the diurnal variations found in the magnitude of the artifact. We next considered the possibility of correcting the field data for this interference in an effort to obtain a real background concentration measurement of H_2S.

The consistency of the artifact sulfide on sequential back-up filters suggests that it is reasonable to assume that the efficiency of OCS conversion is the same at all stages, including the front filter. If this is the case, then a simple subtraction of the sulfide concentration on the back-up filter from that on the front filter should give the true ambient H_2S concentration. As examples, the data presented in Figures 2a and 2b can be used to calculate two pairs of replicate analyses. As an extreme case, the spiked sample in Figure 2a had a signal of 69 pptv on the front filter and 20 pptv on the back-up, yielding a calculated concentration of 50 pptv, slightly higher than the 46 pptv calculated from the unspiked pair. Contaminant H_2S from the OCS permeation tube could explain this difference. A more realistic case, the two samples collected with and without foil covering (Figure 3b) give two identical concentrations of 25 pptv (32-7 and 27-2 pptv).

The magnitude of this correction is clearly of significance in remote marine air, where H2S levels are low. The magnitude of carbonyl sulfide interference in previous studies is impossible to assess, but applying this correction to our own shipboard data resulted in a substantial lowering of the H2S levels. Hence, the importance of H2S as a flux of sulfur to the marine atmosphere is considerably reduced.

The artifact may also explain the apparent lack of diurnal variation in H2S noted by Herrmann and Jaeschke (1984) or the reversed cycle noted by Delmas and Servant (1982). A species as reactive as H2S should be removed during the daytime by photochemically generated OH radicals, but should accumulate at night. This behaviour was noted in our own measurements of H2S in remote marine air (E. Saltzman and D. Cooper, manuscript in preparation) only after correcting the H2S data for OCS interference.

While this correction is necessary for H2S data from remote regions, many of the previous studies of atmospheric H2S have been conducted in polluted air, over exposed mudflats, or in coastal wetlands, where the high concentrations make the magnitude of these corrections insignificant.

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