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THE CHROMATOGRAPHIC ANALYSIS OF REDUCED SULFUR GASES IN ANTARCTIC WATERS FOLLOWING PRE-CONCENTRATION ONTO TENAX

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A technique was developed using sparging and pre-concentration onto a Tenax trap at ambient temperature allowing field measurements to be made of reduced sulfur gases in Antarctic marine and glacial melt waters. Following thermal desorption, gases were determined by gas chromatography using a flame photometric detector. Detection limits in ng l^{-1} were: H_2S 50, OCS 8, SO_2 160, CH_3SH 6, CH_3SCH_3 20 and CS_2 2. Storage of melt water samples for more than 24 hours resulted in concentration changes of the reduced sulfur gases present. While the Antarctic environment imposed limitations on the analytical method, an investigation of various pond and marine waters was undertaken.

KEY WORDS: Dimethylsulfide, carbon disulfide, Tenax, gas chromatography, Antarctica.

INTRODUCTION

Sulfur gases are ubiquitous in natural waters, but present in extremely low concentrations in pristine environments^{1–3}. As a result, analytical techniques must rely on a pre-concentration step. Typically, this has involved sparging from aqueous samples and collecting the analyte gases downstream by cryogenic trapping^{4,5}. Such low temperature trapping uses liquid nitrogen which can impose severe logistic limitations on its applicability for remote operations. Alternatively, collection onto gold has been utilized for those studies focusing on dimethylsulfide (DMS), of interest owing to its possible role in climate modification^{6,7}. Other methods use accumulation onto porous polymer adsorbents such as Molecular Sieve and Tenax, with the advantage of being able to pre-concentrate the complete suite of volatile sulfur gases at ambient temperature^{8,9}. Adsorption of trace levels of volatile sulfur compounds onto Tenax has been widely used as a pre-concentration technique. Tenax has a low affinity for water and the breakthrough volume is independent of humidity¹⁰. It is well suited for thermal desorption techniques as it exhibits high thermal stability (375°C) and so can be subjected to repeated temperature cycling without deterioration. The

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determination of several sulfur gases can easily be conducted, even though Tenax has a relatively low specific surface area (*ca.* $19 \text{ m}^2 \text{ g}^{-1}$) which as a consequence limits the sampling volume.

Our interests are focused on the geochemical cycling of sulfur in the Antarctic environment. In particular we have examined the glacial melt water ponds on the McMurdo Ice Shelf, a sediment laden ice shelf overlying sea water. These ponds are rich in cyanobacteria and may represent an unusual biogenic source of volatile sulfur¹¹. This paper describes the development of a simple and reliable method for the analysis of reduced sulfur gases suitable for operations at remote sites in Antarctica. The reduced sulfur compounds were pre-concentrated from natural waters onto Tenax-TA and detected by gas chromatography with a flame photometric detector (GC-FPD) following thermal desorption. The breakthrough volume and desorption efficiency of the Tenax-TA traps were determined. A study of the recovery efficiency of sulfur gases from aqueous samples was undertaken. Additionally, sample storage experiments using natural waters were conducted. Techniques were applied in the field in Antarctica examining a range of melt water ponds and sea water.

EXPERIMENTAL

Overview

Technique development requires a description of the standard and innovative techniques employed. In this case, GC-FPD methods were utilized in association with gas sparging from solution and pre-concentration onto Tenax. Routine techniques are outlined in this section and developmental aspects are incorporated into the following section.

Sample collection

Replicate 250 ml water samples were obtained from the edge of ponds at a depth of 10–20 cm using a Millipore plastic 50 ml syringe and a 1 m length of tygon tubing. Sub-surface samples were collected in a 250 ml teflon water bottle, closed via a teflon messenger. In both cases, water was immediately transferred into low density polyethylene bottles, filling them to the top to eliminate any headspace and therefore minimize partitioning into the gas phase. To eliminate storage artifacts, water samples were normally analyzed within 6 hours (but never longer than 12 hours) after sampling. Filtration can affect the speciation of constituents in solution¹² and has been shown to decrease DMS concentrations⁴. Thus, water samples were not filtered prior to analysis as this could have removed volatile constituents or conversely released additional sulfur compounds following cell rupture.

Tenax collectors

The adsorption tubes were constructed from teflon-lined stainless steel tubing in order to minimize surface adsorption effects. They were 0.6×10 cm and packed with

8 cm (0.35 g) 60/80 mesh Tenax-TA (Alltech) which was retained in place with silanized glass wool plugs. All sampling cartridges were pre-conditioned under nitrogen at 110°C for at least one hour. Modified swagelock connections were utilized throughout the sampling system, together with teflon tubing and ferrules, to ensure that the analyte gas sample never contacted the stainless steel surface.

Aqueous samples (100 ml aliquots) were placed in a 125 ml glass Dreschel bottles. No attempt was made to adjust the pH. Samples were sparged with oxygen-free nitrogen for 10 minutes at a flow rate of 60 ml min⁻¹. The sulfur gases were trapped in a Tenax-loaded tube at ambient temperature, 12–23°C. The Tenax-loaded trap was ballistically heated to 110°C and the trapped sulfur gases flushed with oxygen-free nitrogen carrier gas directly onto the analytical column.

Gas chromatography

The gas chromatograph consisted of a Perkin Elmer 8500 GC equipped with a Flame Photometric Detector. Signal processing was carried out on an IBM-clone PC using Delta Junior Chromatographic Delta Handling software. The sulfur compounds were separated in a teflon column (3 m × 0.25 cm) packed with Carbopack B/1.5% × XE60/1% H₃PO₄ (Supelco Inc.) using temperature programming (40–140°C). This column resolved in order of retention time: H₂S, OCS, SO₂, CH₃SH, CH₃SCH₃ and CS₂. The column was pre-conditioned overnight with the carrier gas, oxygen-free nitrogen, at 100°C using a flow rate of 20 ml min⁻¹. The detector was maintained at 190°C. The carrier gas, hydrogen and air flow rates were 18, 65 and 90 ml min⁻¹, respectively. Permeation tubes individually containing one sulfur compound were maintained at constant temperature of 25°C in an aluminium block heater and the permeation rate determined by repeated weighing over a prolonged period. Calibration was achieved by using a variable speed peristaltic pump to draw ambient air over the porous plug of the permeation tube and into the sample loop of the gas chromatograph. Controlling the pump speed allowed different, known amounts of sulfur gases to be loaded. Finally, it is worth noting that in Antarctica power for the gas chromatograph, computers and all ancillary equipment was supplied using a 2.5 kW portable generator.

RESULTS AND DISCUSSION

TECHNIQUE DEVELOPMENT

Tenax sampling efficiency

The sample recovery characteristics of the Tenax loaded tubes as used here were examined. Breakthrough volumes were determined by temperature extrapolation¹³ (i.e. to ambient conditions), whereby the log of the retention volume determined at various temperatures was plotted against the reciprocal temperature in K. The desorption efficiency of the Tenax traps was determined by measuring the recovery

Table 1 Breakthrough volumes and desorption efficiencies for various sulfur gases from Tenax traps.

Sulfur gas	H ₂ S	OCS	CH ₃ SH	CS ₂	CH ₃ SCH ₃	SO ₂
Breakthrough volume (l)	0.08	0.24	0.54	4.60	3.80	8.00
Desorption efficiency (%)	27	62	87	88	99	51

of known additions of gaseous sulfur components loaded onto the traps from permeation tubes. The breakthrough volumes and desorption efficiencies at 110°C for the various sulfur compounds are presented in Table 1. Although the 0.6 l sparge volume used here exceeded the breakthrough volume for H₂S and OCS, the results confirm the suitability of Tenax as an appropriate adsorbent for sulfur compounds, especially DMS, at ambient temperatures. It should be noted that SO₂ can be quantitatively removed at about 300°C, too high for use of teflon traps as described here.

Stripping efficiency

For sparging techniques, the extraction efficiency varies with respect to the gas considered and the extraction facilities employed, such as the dimensions of the sample vessel, bubble size distribution, sample volume and temperature, purge gas flow rate and sparge time^{4,5,14,15}. In this study, the breakthrough volume of the downstream gas trap imposed an upper limit on the sparge time that could be used. Practical considerations for analysis in the field may also limit the time available per analysis.

The extraction efficiency of our system was tested using natural waters, known to contain sulfur gases, from three ponds of markedly different characteristics as exemplified in Table 2. In each case, a 100 ml aliquot was sparged repeatedly for 10 minutes as described above, and the sulfur gases determined following each pre-concentration stage. Only CS₂ and DMS were observed in these waters. However, as H₂S and CH₃SH are deprotonated at the pH of these waters, not adjusting the pH to 5 might have adversely affected the stripping efficiency of these gases¹⁴. As observed by Leck and Bågander¹⁴, the CS₂ was quantitatively removed during the first sparge, whereas the DMS concentration in successive sparges decreased exponentially. This allowed the calculation of the total mass present initially through

Table 2 The characteristics of three natural waters used in sparging efficiency experiments.

Pond	Conductivity (mS cm ⁻¹)	pH	DMS in initial sparge (ng l ⁻¹)	Total DMS (ng l ⁻¹)	Sparging efficiency (%)
Fogghorne	0.8	10.5	20.1	148	13.6
P-70	5.5	9.5	69.6	374	18.6
Brak	10.8	10.3	19.4	136	14.3

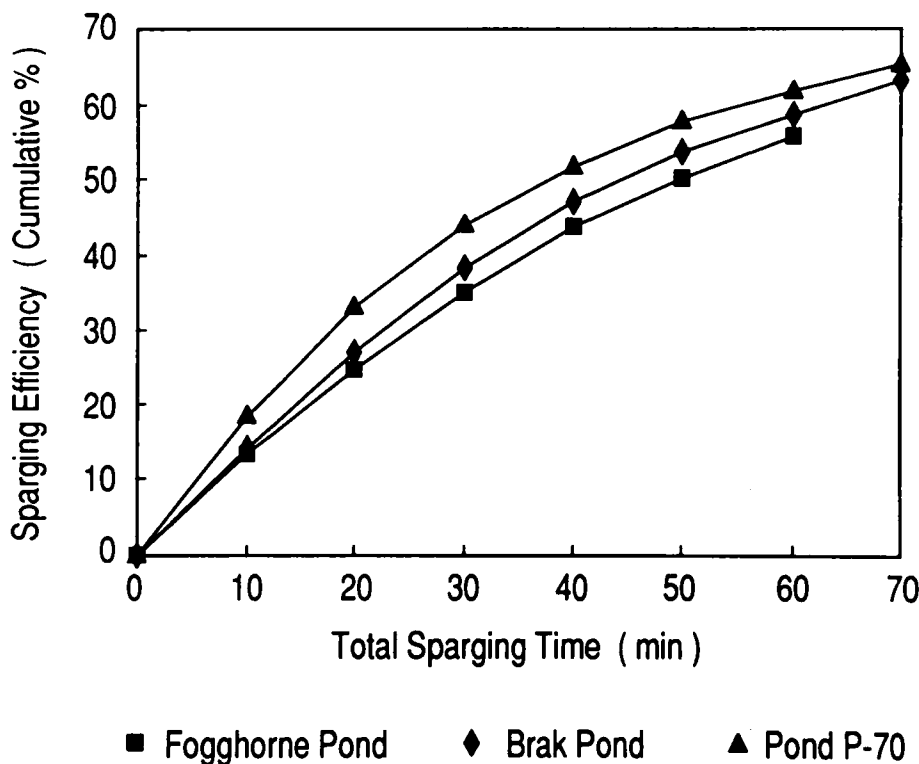


Figure 1 DMS data for the three ponds, normalized to show the extraction efficiency (expressed as a cumulative percent) as a function of the purge time.

summation to infinite sparge time. As illustrated in Figure 1, the DMS data for the three ponds were normalized to show the extraction efficiency (expressed as a cumulative percent) as a function of purge time. In agreement with other studies¹⁴, the extraction efficiency was invariant with solution characteristics and initial DMS concentrations. The extraction efficiency of the first 10 minutes purge was 15% for DMS which was subsequently used for quantitation of all samples. This contrasts with the complete extraction observed elsewhere^{2,4,5}, but can be explained in terms of the low solution temperature during sparging and the low sparge gas flux necessitated by the breakthrough volume of the Tenax trap.

Detection limits

In our method, the detection limits for individual sulfur gases was dependent on the sample volume sparged, sparging efficiency, breakthrough volume, desorption efficiency and instrumental response. Using the procedure as outlined above and taking all of these factors into account, the following detection limits (normalized to ng l^{-1}) were observed: H_2S , 50; OCS , 8; CH_3SH , 6; CH_3SCH_3 , 20; SO_2 , 160; and CS_2 , 2.

FIELD APPLICATIONS IN ANTARCTICA

Sample storage

The degradation of biological material is known to cause the formation of volatile sulfur species, especially DMS, OCS and CS₂^{16,17}, consequently a time delay between the sampling and analysis of natural water samples is likely to lead to analytical artifacts. Typical preservation techniques similarly alter the concentration of dissolved sulfur gases¹⁸. Thus, it was necessary to examine to what extent unfiltered samples could be stored after collection.

Pairs of samples were collected from seven ponds. One replicate was analyzed immediately and the second was analyzed following storage in the dark at about 4°C for 24 h. The data are presented in Table 3. Only CS₂ and DMS were detected in all cases. Although concentration generally did not change during storage, the CS₂ concentration in one instance and the DMS concentration in another nearly doubled, in marked contrast to previous observations of DMS decline during storage¹⁵. A second storage experiment was undertaken whereby a set of eight samples from Fresh Pond were collected and stored for varying lengths of time before analysis. One pair of samples were determined immediately and gave good agreement for both CS₂ and DMS concentrations. As indicated in Figure 2, the CS₂ content changed little with time. However, the DMS level rose dramatically after the first 24 h and moreover CH₃SH was detected in all samples stored longer than 24 h. Accordingly, samples could not be stored prior to the pre-concentration step onto Tenax. As the sulfur gases cannot be stored on the Tenax for longer than a week, this necessitated conducting analyses in the field, despite the associated difficulties, hence samples should be analyzed within 12 h of collection.

Glacial melt waters

A profile of sulfur gases was obtained in Duet Pond on the McMurdo Ice Shelf. This is an oval shaped pond, approximately 30 by 50 m, about 3.5 m deep and 95%

Table 3 Changes in sulfur gas concentrations as a result of storage in the dark for 24 hours.

<i>Pond</i>	<i>S-1</i>	<i>S-2</i>	<i>S-3</i>	<i>S-4</i>	<i>S-5</i>	<i>P-70</i>	<i>Fresh</i>
Conductivity (mS cm ⁻¹)	2.13	12.11	2.35	1.66	1.10	5.43	0.67
DMS 1 (ng l ⁻¹)							
Day 1	87.7	245	90.0	279	181	87.7	156
Day 2	81.6	406	80.9	263	183	77.9	153
% Change	-7	66	-10	-6	1	-11	-2
CS ₂ (ng l ⁻¹)							
Day 1	12.8	35.4	13.5	10.5	8.4	8.8	5.5
Day 2	15.8	39.0	12.4	10.2	9.6	7.7	9.8
% Change	23	10	-8	-3	14	-12	80

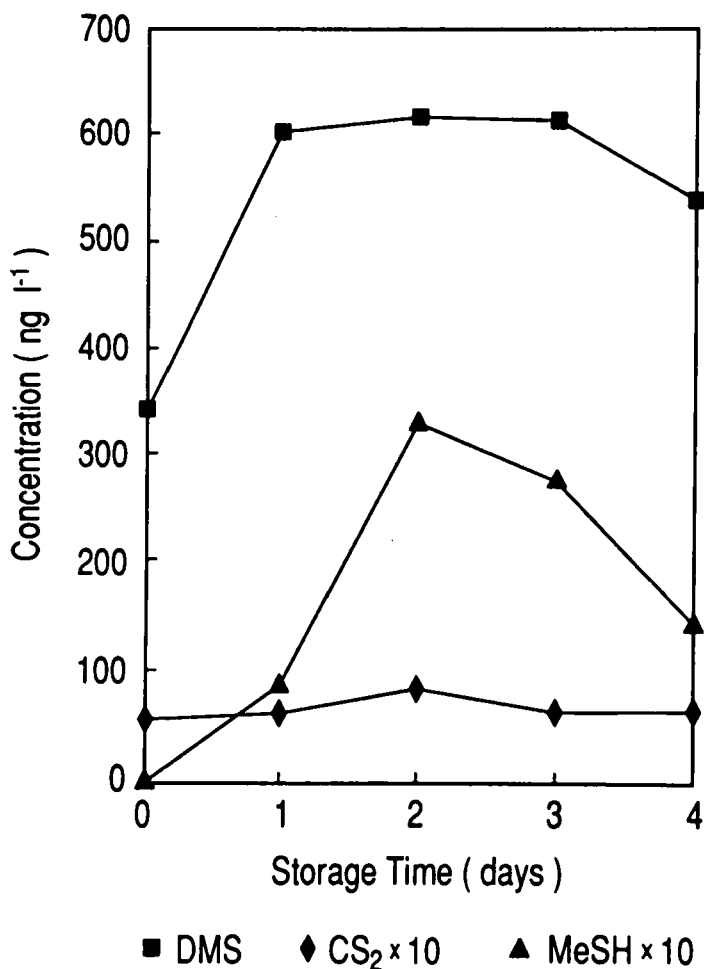


Figure 2 The dependence of sulfur gas concentrations in a natural water sample as a function of storage time in the dark.

covered with a layer of ice about 50 cm thick. A cyanobacterial mat was visible on the bottom beneath the unfrozen moat around the perimeter of the pond. The water is relatively fresh in the upper 3 m (0.16 to 0.41 mS cm⁻¹), rising to 2.84 mS cm⁻¹ at a depth of 3.5 m.

Sub-surface water samples were collected from the centre of the pond and the sample from a depth of 20 cm was obtained from the moat. While qualitative analyses have demonstrated the presence of several reduced sulfur gases beneath the cyanobacterial mats in these glacial melt water ponds¹¹, only DMS and CS₂ were detected in the water column. Results, shown in Figure 3, indicated that the CS₂ concentration was relatively uniform with depth and in the range 5.4 to 8.8 ng l⁻¹. DMS levels increased from 21.7 ng l⁻¹ near the surface to a maximum of 54.6 ng l⁻¹ at 3 m.

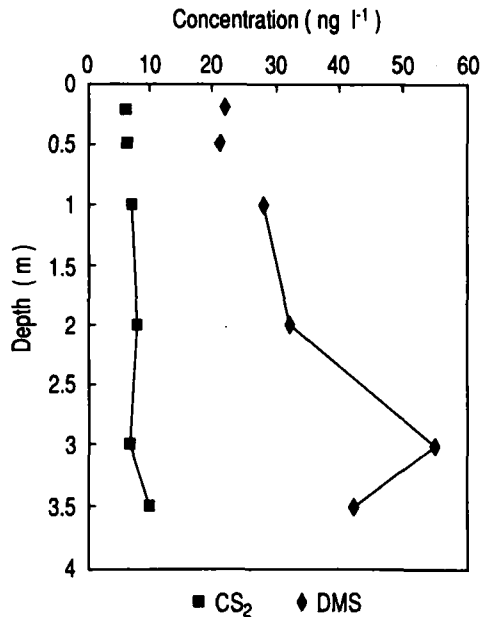


Figure 3 Depth profiles of CS₂ and DMS in Duet Pond, a fresh water pond on the McMurdo Ice Shelf.

These results are in marked contrast with those of Deprez *et al.*¹⁸ who investigated reduced sulfur compounds in two Antarctic lakes, namely Burton Lake (16 m depth) and Organic Lake (5.5 m depth). These lakes are similar to Duet Pond in that they were ice-covered when the measurements were made in the austral summer, but differed in that they were larger, deeper and stratified. The upper two thirds of Burton Lake appeared to contain only DMS, whereas H₂S and OCS were the only sulfur volatiles found in the bottom third. Organic Lake apparently only contained DMS. DMS levels in Burton Lake (50–1400 ng l⁻¹) and Organic Lake were much higher than those observed in Duet Pond (22–55 ng l⁻¹), which is attributed to the different biological content and much greater activity in these lakes. It was recognized by Deprez *et al.*¹⁸ that the chromatographic technique did not allow the detection of CS₂ in the presence of DMS. However, our results now confirm CS₂ as a significant reduced sulfur species in the aquatic Antarctic environment.

Marine waters

The ubiquitous nature of reduced sulfur gases was clearly demonstrated in a depth profile (0–30 m) obtained for DMS and CS₂ in McMurdo Sound. The profile was obtained at a 5 m wide ice rift in the McMurdo Ice Shelf some 2 km west of Bratina Island. The thickness of the sea ice in the vicinity of the rift was estimated to be about 10 m, and the water depth exceeded 30 m. Figure 4A shows the changes with depth of temperature and conductivity. The water temperature decreased with depth and the conductivity indicated a sharp halocline between 10 and 15 m depth. The

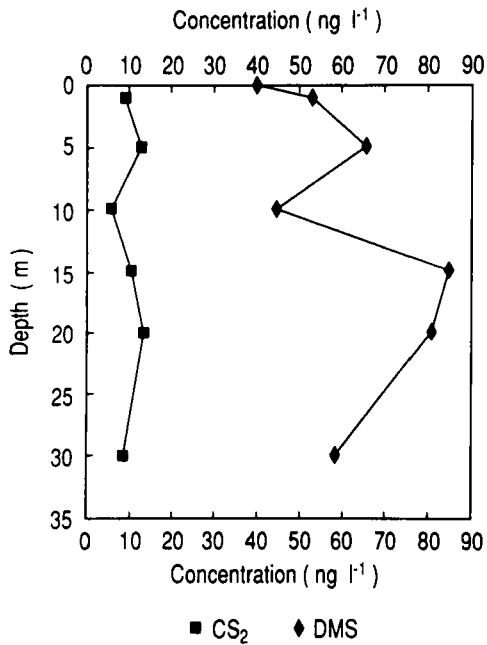
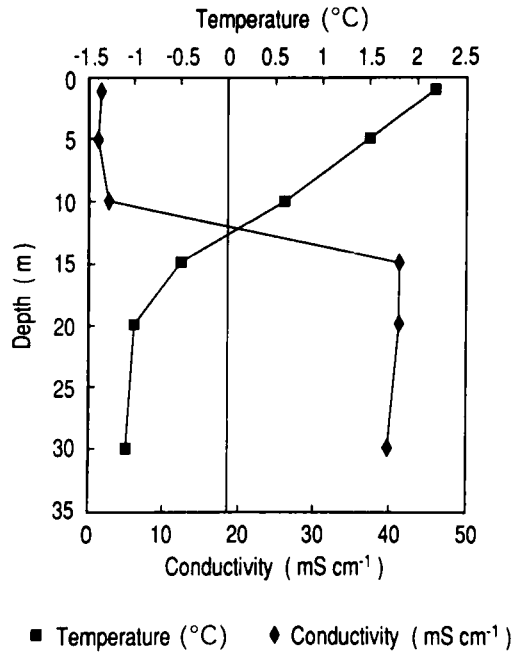


Figure 4 Depth profiles of temperature and conductivity (A) CS₂ and DMS (B) in a 10 m ice rift overlying sea water.

conductivity profile indicated that a buoyant fresh water layer was trapped within the ice rift and it overlaid sea water.

Concentration profiles for DMS and CS₂ are given in Figure 4B. Considering firstly the DMS, concentrations varied in the range 44.2 to 83.8 ng l⁻¹. While there was no distinct trend attributable to the observed water structure, it was noticeable that the greatest concentration was found immediately below the ice. The CS₂ profile was similar to that of DMS, but concentrations varied between 5.3 and 11.9 ng l⁻¹.

Both gases exhibit similar profiles, indicative of comparable sources and sink processes. In both cases the sulfur gases are derived from biological activity. DMS is released by the breakdown of dimethylsulfonium propionate (DMSP), an algal exudate¹. CS₂ is produced from the photodegradation of organic material. The maximum concentrations immediately beneath the sea ice are indicative of a sea water source, with the ice cover effectively preventing ventilation to the atmosphere. Similarly, the sharp halocline ensures little transfer into the buoyant fresh water and so sulfur gases in this layer are likely to have been produced *in situ*.

Few other measurements for reduced sulfur gases in Antarctic sea water have been made. Deprez *et al.*¹⁸ found an average DMS concentration of 3500 ng l⁻¹ in Davis Bay, but this elevated value was the result of an ongoing phytoplankton bloom. Considering other marine waters, Andreae¹⁹ stated that the mean DMS concentration for the upper regions of the world's oceans was 186 ng l⁻¹. DMS levels in coastal waters around Great Britain have been reported²⁰ to average about 8 ng l⁻¹ in the winter and 425 ng l⁻¹ during the summer. These summer DMS concentrations exhibit considerable variation, in the range 27 to 2130 ng l⁻¹, depending upon taxonomic composition of the phytoplankton present. Thus, the DMS results reported here are somewhat lower than expected for typical oceanic waters but fall within the range reported for coastal waters in the absence of bloom conditions.

With respect to CS₂ content, Kim and Andreae²¹ obtained a concentration of 1.2 ng l⁻¹ in the open ocean and 2.5 ng l⁻¹ for coastal sea water. Alternatively, Turner and Liss²² reported values in the vicinity of 25 ng l⁻¹ for English coastal waters. The CS₂ concentration reported here lies within the range of values that have been observed.

CONCLUSIONS

Successful sampling and subsequent analysis of reduced sulfur compounds in glacial melt waters and sea water was conducted in Antarctica. The limitations imposed by the environment such as sample storage, lack of cryogenic traps and limited analysis time were circumvented by the appropriate choice of analysis conditions and technique, specifically using GC-FPD determination following preconcentration onto Tenax at ambient temperatures. While several sulfur gases could be detected, the technique was particularly well suited for the concurrent measurement of DMS and CS₂. DMS and CS₂ were detected under the sea ice in McMurdo Sound and in glacial melt water ponds overlying the McMurdo Ice Shelf.

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