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DETERMINATION OF REDUCED SULFUR GASES IN ANTARCTIC LAKES AND SEAWATER BY GAS CHROMATOGRAPHY AFTER SOLID ADSORBENT PRECONCENTRATION

P. P. DEPREZ, P. D. FRANZMANN and H. R. BURTON*

Department of Science, Antarctic Division, Channel Highway, Kingston, Tasmania 7150 (Australia)

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SUMMARY

A preconcentration method for low levels of reduced sulfur compounds (RSCs), such as dimethyl sulfide (DMS), in aqueous samples was developed and tested in Antarctica. The gases were trapped in a solid adsorbent, Molecular Sieve 5 Å (80–100 mesh). RSCs were backflushed onto a gas chromatographic separation column after thermal desorption from the trap. The RSCs were detected with a sulfur specific dual flame photometric detector. RSCs in fresh samples from two meromictic lakes in the Vesthold Hills (Antarctica) were quantified with this method. A profile of DMS in Antarctic seawater was obtained during a period of phytoplankton bloom in the Antarctic summer. DMS, carbonyl sulfide and hydrogen sulfide were the major RSCs found. A study of recoveries from samples preserved for eight months with mercuric chloride showed that substantial losses of RSCs occurred. Carbon disulfide was detected in preserved samples from the lakes studied. Detection limits of DMS and carbonyl sulfide were 10 ng l^{-1} and 5 ng l^{-1} respectively.

INTRODUCTION

In recent years there has been increasing interest in reduced sulfur compounds (RSCs), such as dimethyl sulfide (DMS), carbonyl sulfide, dimethyl disulfide (DMDS), carbon disulfide and methyl mercaptan as well as others, in relation to sulfur production and influx into the atmosphere from various biological and anthropological sources^{1–3}. Particular emphasis has been focussed on DMS as it is produced in the oceans^{3–7} and salt marshes⁸. Carbonyl sulfide is also considered to be of significance in the earth's environment and is produced in the oceans⁹. Other gaseous sulfur compounds such as sulfur dioxide and hydrogen sulfide play an important role in atmospheric chemistry¹⁰.

The more recent and widely accepted methods for detection and measurement of RSCs in the atmosphere, oceans, coastal ponds and lakes make use of the sulfur specific flame photometric detector and gas chromatography (GC)^{4,11,12}. As the RSC concentrations in natural environments are usually low, a preconcentration step is employed either by cryogenic trapping^{2,13} and/or using an adsorbent^{14,15} followed by thermal desorption and backflushing onto the analytical column.

Andreae and Barnard⁴ found that trapping DMS cryogenically onto a separation column with subsequent rapid heating of the column was a simple and reliable method for collection of trace quantities from seawater. Black *et al.*¹⁵ used a short tube packed with Molecular Sieve 5 Å, as their trap. RSCs are strongly adsorbed on molecular sieve, which allows large breakthrough volumes. This has enabled non-cryogenic trapping of these compounds from atmospheric samples.

A method developed by Steudler and Kijowski¹⁶ for the simultaneous collection of carbonyl sulfide, hydrogen sulfide, methyl mercaptan, carbon disulfide, DMS and DMDS used a combination of Molecular Sieve 5 Å and Tenax GC. Once trapped, the volatile sulfur compounds were thermally released and collected cryogenically in a PTFE loop. These were released with boiling water and injected into a packed column GC system. The RSCs were readily lost to active sites and were subject to chemical changes.

It was our objective to establish a simple and reliable method for the determination of RSCs, particularly DMS, in Antarctic lakes and seawater. In these lakes active cycling of sulfur has been shown to be undertaken by microorganisms^{17,18}. We have developed a purge and trap method that preconcentrated the volatile RSCs on a Molecular Sieve 5 Å trap at laboratory temperatures. These were then thermally desorbed and separated with a packed PTFE column in a gas chromatograph equipped with a dual flame photometric detector.

EXPERIMENTAL

Materials and instruments

A Varian 3700 gas chromatograph equipped with a sulfur specific dual flame photometric detector (Varian, Walnut Creek, CA, U.S.A.) and a Tohshin electronic recorder were used. The gas chromatograph was operated with the flame photometric detector in dual flame mode for optimal response¹⁹. Air was supplied by a JUM burner air supply Model TJ37 and K37 or as otherwise stated (JUM Engineering, München, F.R.G.). Hydrogen was obtained from a General Electric hydrogen generator Model 15EHG4B4 (General Electric, Aircraft Equipment Division, MA, U.S.A.), or from cylinder gases (CIG). The carrier gas was helium (UHP-grade, CIG). The gas flow-rates were checked periodically with a 100-ml soap bubble flow-meter. Flow-rates are shown in Table I.

The purge gas used in stripping aqueous samples was helium and was supplied from a separate gas line. Gases to the GC system were connected by copper tubing 0.32 cm O.D. which had been pre-washed in acetone (AR-grade) and flamed²⁰.

The injector and detector temperatures were set at 120°C with the oven temperature at 200°C. When a temperature program was used, the conditions were set as shown in Table II.

The GC column was acetone washed PTFE 50 cm × 0.65 cm O.D. × 0.25 cm I.D., (Microchem, supplied by Varian Techtron, Australia) packed with Porapak QS 80–100 mesh (Waters Assoc., Milford, MA, U.S.A.) which had been pretreated according to De Souza *et al.*²¹. Acetone rinsed PTFE wool plugs were used at the ends of the column (Alltech Assoc., Deerfield, IL, U.S.A.).

The column was preconditioned at 240°C with a 30 ml min⁻¹ helium gas flow for 12 h. This procedure was repeated if the column had not been used for more than three days.

TABLE I
GAS FLOW-RATES FOR GC OPERATION

| Gas | Flow-rate (ml min^{-1}) | Pressure (p.s.i.) |
|-----------|------------------------------------|-------------------|
| Carrier | 30 | 60 |
| Air No. 1 | 92 | 60 |
| Air No. 2 | 184 | 60 |
| Hydrogen | 145 | 42 |

The adsorption tube was PTFE coated stainless-steel 15 cm \times 0.6 cm O.D. \times 0.2 cm I.D. with a PTFE thickness of approximately 0.003 cm (Alltech Assoc.). The packing consisted of 0.39 g Molecular Sieve 5 Å (80–100 mesh) (Supelco, Bellefonte, PA, U.S.A.) packed into a 11.7 cm length of tube. The ends of the trap were plugged with silanised [dimethyldichlorosilane (DMCS)] glass wool and connected by PTFE tubing 0.32 cm O.D. \times 0.16 cm I.D. (Penntube Plastics) to a PTFE lined Valco six-way valve fitted to the GC system (Valco Instruments, TX, U.S.A.; temperature rating of 175°C). All connections were Swagelok with graphite, brass or PTFE ferrules. The gas sampling valve was connected to the flame photometric detector with PTFE tubing and ferrules except for one short glass-lined stainless-steel section prior to the GC column near the detector. PTFE could not be used here as this part was periodically subjected to high temperatures. The trap was activated before use by heating at 240°C for a minimum of 8 h with a helium flow of 30 ml min^{-1} . To desorb trapped compounds, rapid heating was applied with a hot air gun (Ideal Industries, IL, U.S.A.). A uniform distribution of hot air was directed from the centre of an open ended copper tube around the trap (Fig. 1). A final temperature of 180°C was reached in approximately 25 s. The temperature was monitored with a Neslab DR-2 digital readout thermometer ($\pm 200^\circ\text{C}$ range).

Purge and trap assembly

The purge vessel, a drechsel bottle (125 ml) and head with glass frit, was used to sparge RSCs from liquid samples. Initially, experiments were performed with an uncoated drechsel bottle. The bottle was later silanised with DMCS 1.2% (v/v) in dichloromethane (AR-grade). A modified silanisation procedure to that described by Farwell and Gluck²² was used. All glassware including the drying tube was rinsed with water ($>18 \text{ M}\Omega$) and left to soak overnight in concentrated nitric acid–water–glacial acetic acid (1:1:1, v/v). It was then thoroughly rinsed with water, silanised, rinsed again with ethanol (AR-grade), dried, and heated to 110°C for 30 min. The glassware was finally rinsed with water before use.

TABLE II
TEMPERATURE PROGRAM CONDITIONS

| | |
|----------------------|------------------------|
| Post injection delay | 1 min |
| Initial temperature | 40°C |
| Final temperature | 210°C |
| Temperature ramp | 40°C min^{-1} |

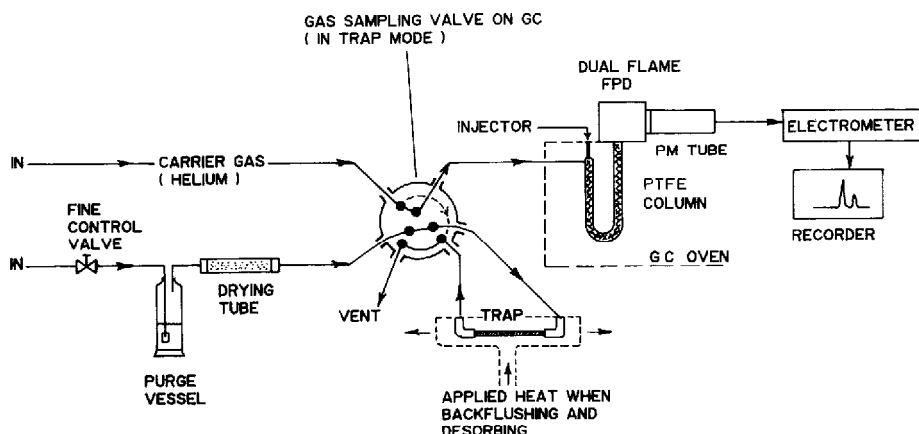


Fig. 1. A schematic diagram of a purge and trap system for RSC determinations. FDP = Flame photometric detector; PM = photomultiplier.

The drechsel bottle was modified with a glass side arm and a Mininert screw top valve. This enabled direct injection of standards into liquid samples or blanks without loss which occurred if the head of the bottle was opened. The purge and trap system is shown in Fig. 1.

The drying tube (Pyrex, 19 cm \times 0.85 cm O.D. \times 0.65 cm I.D.) was packed with anhydrous potassium carborate (AR-grade) and connected to the purge vessel with a short length of Tygon tubing and to the gas sampling valve with PTFE tubing. The tube was plugged with DMCS treated glass wool. The packing was renewed as required.

Calibration

Two types of standards were used in the identification and quantitation of RSCs; first, certified permeation tubes with known gas diffusion rates (GC Industries, CA, U.S.A.) and secondly, liquid DMS, carbon disulfide (Ajax Chemicals) and DMDS (Sigma). Liquid standards dissolved in *n*-hexane (AR-grade) or ethanol (AR-grade) were used for initial experimentation. The concentrations of stock solutions were typically 1.5 $\mu\text{g } \mu\text{l}^{-1}$. Stock and working solutions were stored at 4°C. Working solutions were prepared by a further dilution of stock solutions with solvent in 10-ml volumetric flasks (15–30 ng μl^{-1}). These were stable for at least three months.

Ultra-high-purity helium was used as the diluent gas for generating known concentrations of standards using the gas permeation tubes. Gas flow-rates were measured with the soap bubble flow-meter and regulated by a fine needle valve (Nu-pro, OH, U.S.A.). Short lengths of Tygon and PTFE tubing carried the diluent gas to a stainless-steel T-piece on the permeation tube. The gas mixture was stored in a PTFE coated 250-ml glass sample flask (J. Young, U.K.). The flask contained six small PTFE pieces of tubing to assist in mixing gases when shaken. The permeation tubes were kept at constant temperature by immersion in a Dewar flask filled with water. It was left to equilibrate for a minimum of 2 h. Samples of the diluted standard gas were withdrawn from the glass tube with a gas tight syringe (SGE, Australia) and injected either directly on column or into a liquid sample blank [*i.e.*, water

(> 18 M Ω), lake water or seawater which had been presparged with helium]. Liquid standards were injected with a 10- μ l Hamilton syringe. Calibration curves (log of peak height *versus* log concentration) had a slope of 1.9 for DMS in the 0.4–10 ng range and a slope of 1.6 for carbonyl sulfide in the 0.5–10 ng range.

Sample collection

Water samples from the Antarctic lakes and sea were obtained with a Kammerer bottle and immediately dispensed into 500-ml Duranol bottles (polyethylene). The bottles were filled to the top with no remaining headspace. Duplicate sets were obtained at each depth sampled and preserved with mercuric chloride (1.0 g l⁻¹). One set was analysed within hours of sample collection and the other frozen at -18°C to allow later evaluation of this storage technique. The fresh, unfrozen samples were kept at 4°C between determinations. Excess mercuric chloride was used in samples that contained high concentrations of hydrogen sulfide (as occurred in waters collected from the anoxic hypolimnion of one lake) which would otherwise have interfered with the determination of other RSCs. These samples were then gravity filtered through a Whatman filter No. 1 to remove the mercuric sulfide precipitate prior to sparging. Hydrogen sulfide was in such high concentrations that an ion selective electrode was used for its quantitation instead of the GC method. The ion selective electrode method used is described elsewhere²³.

A 50-ml sub-sample was transferred from each sample to the purge vessel and sparged with helium for 30 min at a flow-rate of 50 ml min⁻¹. A magnetic stirring bead was used to ensure mixing. The helium gas stream which contained water vapour and volatile compounds was dried by passage through the Pyrex drying tube prior to adsorption on the molecular sieve trap. The sample was desorbed by rapid heating with the heat gun with the gas sampling valve switched to backflush. This resulted in complete desorption of the RSCs which were then separated on the analytical column. To check for the complete recovery of RSCs, the trap was again reheated and backflushed. Each sample was analysed in duplicate.

Recovery experiments with known concentrations of DMS injected into seawater or lakewater that had been prefiltered (0.22 μ m) and kept at 4°C in the dark were performed with the purge and trap method. Blanks were checked for residual RSCs before standard additions.

RESULTS AND DISCUSSION

The chromatographic technique previously described was able to separate the RSCs, listed with their retention times in Table III. It was experimentally determined (after return to Australia) that carbon disulfide and DMS were not resolved if both were present in a sample. This problem has been observed by others^{3,4}. The temperature programme was similar to one published by De Souza *et al.*²¹. A more recent publication by De Souza¹² showed that up to fourteen commonly encountered sulfur compounds could be separated, these included carbon disulfide and DMS with respective retention times of 4.55 and 4.50 min. The difference in retention times for these two compounds is too small (0.05 min) for adequate resolution.

Experiments by Davies²⁴ showed that carbon disulfide and DMS could be separated by as much as a minute using the same chromatographic system but with

TABLE III

CHROMATOGRAPHIC DATA FOR VOLATILE SULFUR COMPOUNDS

Temperature program: initial temperature 40°C to a final temperature of 210°C with 40°C min⁻¹ ramp and post injection delay of 1 min, carrier gas flow-rate was 30 ml min⁻¹.

| Compound | Retention times |
|--|-----------------|
| Hydrogen sulfide | 2 min 40 s |
| Carbonyl sulfide | 3 min |
| Sulfur dioxide | 4 min |
| Methyl mercaptan | 4 min 34 s |
| Ethyl mercaptan | 5 min 26 s |
| Dimethyl sulfide (and carbon disulfide) | 5 min 40 s |
| Dimethyl disulfide | 8 min |

a different temperature programme. The initial temperature was kept at 40°C for 3 min post injection then increased via a 7°C min⁻¹ ramp to a final temperature of 150°C²⁴. Carbon disulfide eluted at 16.4 min and DMS at 17.4 min. With this program, carbon disulfide and DMS eluted in a reverse order to that reported by De Souza¹². It was also observed that methyl mercaptan eluted prior to ethyl mercaptan which is contrary to the order reported by De Souza. The temperature program²⁴ should be used on samples which are suspected to contain both DMS and carbon disulfide. The trap design was based on that used by Black *et al.*¹⁵ who preconcentrated hydrogen sulfide and sulfur dioxide on Molecular Sieve 5 Å 60–70 mesh. The method of preconcentration on a solid adsorbent trap had special advantage in a remote environment where cryotrapping was difficult to provide. Black *et al.*¹⁵ and Steudler and Kijowski¹⁶ packed their adsorbent material in Pyrex glass tubing. We minimised selective adsorption on glass surfaces by using a PTFE lined stainless-steel tube and PTFE and Tygon lines to the purge and trap system.

It was desirable to use a packing material which provided high breakthrough volumes for sulfur gases. Molecular Sieve 5 Å 60–70 mesh was reported to have breakthrough volumes (defined by Black *et al.*¹⁵ as the volume of gas needed to elute 50% of the adsorbed compounds at 25°C) of 25 l g⁻¹ for sulfur dioxide and 22.5 l g⁻¹ for hydrogen sulfide¹⁵. We chose to test and use Molecular Sieve 5 Å 80–100 mesh. Experiments showed that the breakthrough volume for nanogram quantities of DMS was 7.7 l, which was within limits as a maximum volume of 1.5 l of helium was used to sparge samples.

Limitations of the purge and trap system

The optimal flow-rate of purge gas was 45–50 ml min⁻¹. Higher flow-rates (60–100 ml min⁻¹) resulted in system leaks. Backpressures were due to gas flow restriction in the trap, not the drying tube.

As anhydrous potassium carbonate is inert for DMS and other RSCs it was chosen for its efficient removal of moisture in the drying tube. Sulfur dioxide, being acidic, would be lost due to its reaction with potassium carbonate. Braman *et al.*²⁵ removed interfering sulfur dioxide from air samples with sodium carbonate treated

TABLE IV

MEAN RECOVERIES OF DMS AT ROOM TEMPERATURE* USING THE PURGE AND TRAP SYSTEM

| Matrix | Purge vessel/drying tube | Amount added (ng) | Recovery \pm R.S.D. (%) |
|--------------|--------------------------|-------------------|---------------------------|
| Lake water** | Non-silanised | 26*** | 85 \pm 1 (n = 2) |
| Sea water | Non-silanised | 1 [§] | 64 \pm 2.9 (n = 3) |
| | | 10 [§] | 76 \pm 7.0 (n = 2) |
| Sea water | Silanised | 1 [§] | 72.6 \pm 3.2 (n = 7) |
| | | 10 [§] | 100 \pm 5.6 (n = 5) |

* Room temperature was $21 \pm 1^\circ\text{C}$.

** Burton lake water collected from a depth of 7 m, salinity (‰) = 37.7.

*** DMS in *n*-hexane.

§ DMS in helium (UHP-grade).

glass beads and this did not affect hydrogen sulfide, DMS, methyl mercaptan and DMDS.

The optimal temperature for the desorption of trapped compounds was 180°C . A second desorption of the trap detected no trace of sulfur compounds.

Recoveries

Sulfur compounds are very reactive and losses can occur on glass, steel and other active surfaces. A series of recovery experiments was performed at room temperature (typically $21 \pm 1^\circ\text{C}$) to establish the combined effects of adsorption losses and the effectiveness of the purge and trap procedure (see Table IV). Similar experiments were repeated using silanised glassware for comparison.

The results in Table IV indicate a high recovery for DMS (85%) from a lake water matrix. Losses to active sites on untreated glassware were high with a recovery of 76% DMS. Recovery of 1 ng DMS added to 50 ml of seawater showed an improvement with the use of silanised (72%) over untreated glassware (64%). When using silanised glassware, the recoveries of 10 ng DMS amounts from seawater were found to be extremely good (100%).

Standards

Preliminary work was performed with the liquid standards DMS, DMDS and carbon disulfide dissolved in the solvents *n*-hexane or ethanol. Although the solvents did interfere to some extent with the signal of the sulfur compounds they were of value in recovery experiments.

Other solvents such as methanol, *n*-propanol, propan-2-ol, ethylene glycol and *n*-hexane also produced interferences. Quenching due to hydrocarbons has been previously documented^{11,19,26,27}. Ethylene glycol had been successfully used elsewhere⁴ but this solvent produced a very large and broad peak that masked the sulfur response. Andreae and Barnard⁴ used ethylene glycol with a different column and packing material.

The major restrictions with the use of hydrocarbon solvents are that low concentrations of DMS (1 ng) co-elute with large solvent peaks which can cause temporary flameouts¹⁹. Nonetheless the chromatogram in Fig. 2 shows separation of

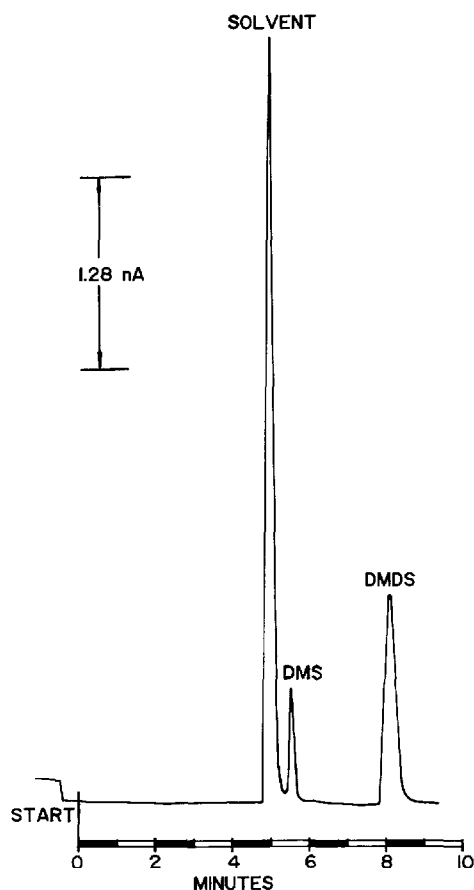


Fig. 2. Chromatographic separations of DMS and DMDS, both dissolved in *n*-hexane. Temperature program: initial temperature 40°C, final temperature 210°C, post injection delay 1 min, temperature ramp 40°C min⁻¹.

DMS (16 ng) and DMDS (22 ng). The solvent peak from *n*-hexane overlaps the DMS peak slightly. A linear calibration curve was obtained in the range of 20–100 ng DMS in *n*-hexane with a slope of 2.26 from log peak height *versus* log concentration plot.

Calibration curves for DMS and carbonyl sulfide were obtained with permeation tubes.

Sample analysis

Samples were obtained and analysed from two lakes in the Vestfold Hills, Antarctica. The lakes were both covered with ice (up to 1.5 m thick) for about ten months of the year. Burton Lake and Organic Lake were meromictic (stratified) but differed in many physicochemical parameters *e.g.* salinity, size, depth^{28,29}. Both lakes were sampled in summer and profiles of the RSCs in each lake are given in Figs. 3 and 4.

Hydrogen sulfide was found only in the anoxic hypolimnion (11–16 m) of Burton Lake. High concentrations of hydrogen sulfide interfered with the determi-

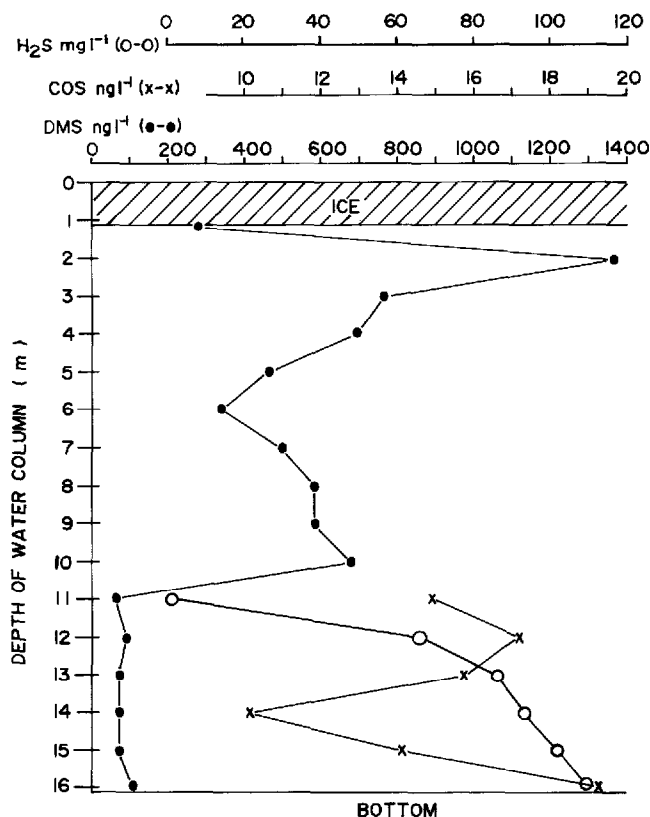


Fig. 3. A profile of Burton Lake (December 1984) which shows concentrations of RSCs.

nation of other reduced sulfur compounds by supersaturation of the trap; a problem noted by Wakeham *et al.*³⁰ who used mercuric chloride to precipitate out hydrogen sulfide.

Excess mercuric chloride was added to water samples which contained hydrogen sulfide. Burton Lake showed a sharp DMS increase below the ice layer which coincided with the presence of a large population of the alga *Rhodomonas* sp. DMS has been reported to be an excretion and breakdown product of many marine algae³¹. The DMS peak above the oxic-anoxic boundary has also been observed in a study of DMS throughout a stratified coastal salt pond³⁰ and is thought to correspond to high rates of bacterial activity.

Carbonyl sulfide was only found in the hypolimnion as shown in Fig. 3. The carbonyl sulfide levels ($14\text{--}19\ ng\ l^{-1}$) were very much less than DMS and showed a slight increase near the bottom. The likely source of carbonyl sulfide was breakdown of organic debris. Carbonyl sulfide and hydrogen sulfide were not found in Organic Lake. Instead, large quantities of DMS were measured with a range of $200\text{--}97\ 000\ ng\ l^{-1}$ (Fig. 4). Concentrations in the range of $70\ 000\ ng\ l^{-1}$ in a freshwater pond have been reported elsewhere³¹. The salinity of Organic Lake is about five times the salinity of seawater.

Seawater from Davis bay (Antarctica) was also analysed for RSCs during De-

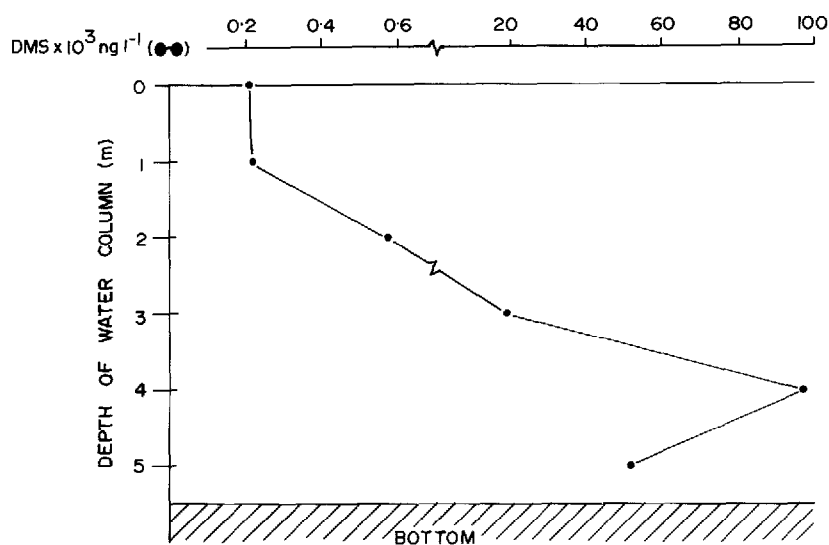


Fig. 4. A profile of Organic Lake (January 1985) where DMS was the only RSC detected.

cember, a period in which a phytoplankton bloom developed. Bladders of *Phaeocystis pouchetii*, a unicellular alga $< 5 \mu\text{m}$ in length were observed throughout the sampling depths down to 20 m. DMS was the only RSC detected (see Table V). The concentrations are high in comparison to other seawater concentrations reported, e.g. 100 ng l^{-1} (ref. 6). The DMS was attributed to the presence of the *Phaeocystis* bloom. Similar correlations between DMS production and *Phaeocystis pouchetii* have been recently reported by Barnard *et al.*³² in the south eastern Bering sea.

Upon return to Australia further experiments were performed on preserved lake samples (eight months old) using the temperature program of Davis²⁴. The samples showed the presence of carbon disulfide, although in lower concentration than DMS (see Fig. 5). Unlike DMS, carbon disulfide has not been considered to be a major reduced sulfur compound in aquatic environments^{3,8,30}. The remoteness of these Antarctic lakes has prevented the collection of fresh samples to quantitate and confirm the presence of carbon disulfide.

Preservation of samples

A comparative study was made of RSCs in freshly obtained samples of Burton

TABLE V

DMS CONCENTRATION IN SEAWATER FROM DAVIS BAY DURING A PHYTOPLANKTON BLOOM

| Depth (m) | DMS (ng l ⁻¹) |
|-----------|---------------------------|
| Surface | 2950 |
| 1 | 3100 |
| 2 | 3250 |
| 5 | 3350 |
| 10 | 4250 |

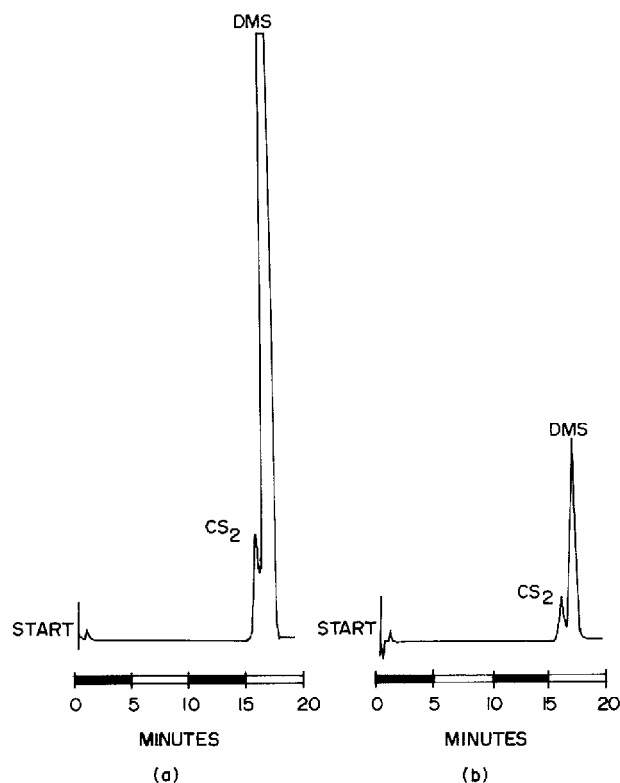


Fig. 5. Chromatograms of preserved water (eight months old) from; (a) Burton Lake 4 m, (b) Organic Lake 2 m which show the separation of carbon disulfide (16.4 min) from DMS (17.4 min) which is in greater concentrations. Temperature program; initial temperature 40°C, final temperature 150°C, post injection delay 3 min, temperature ramp 7°C min⁻¹.

Lake (mercuric chloride only) and preserved samples (mercuric chloride and kept frozen at -18°C). The aim of the study was to find a suitable preservation method for difficult to obtain samples, such as those collected in remote areas. The addition of 1.0 g l⁻¹ mercuric chloride and freezing of the sample was used to minimize biological activity. Mercuric chloride was used to stabilise DMS, precipitate hydrogen sulfide and act as a biocide. This chemical has been used for similar purposes by Rasmussen *et al.*⁹ and Wakeham *et al.*³⁰, but concentrations were not specified. A 5% solution of mercuric chloride has been used to form stable mercury-DMS and mercury-mercaptan complexes by Gaudry *et al.*³³. DMS was released with concentrated hydrochloric acid. Their work indicated that DMS was stable up to 40 weeks if kept in the dark at 2°C. Wakeham *et al.*³⁰ measured low levels of DMS by sparging coastal pond samples treated with mercuric chloride without acidification and reported the occasional presence of carbonyl sulfide, carbon disulfide, methyl mercaptan and DMDS.

The concentration of mercuric chloride is likely to be critical in complexing and in releasing DMS as well as being an efficient biocide. Excessive mercuric chloride may result in an incomplete release of DMS from solution. We made a comparison between acidified (concentrated hydrochloric acid) and unacidified sub-samples (50

TABLE VI

COMPARATIVE STUDY OF PRESERVED BURTON LAKE WATER KEPT IN REFRIGERATION FOR EIGHT MONTHS AT -18°C

| Depth (m) | DMS concentration (ng l ⁻¹) | | |
|-----------|---|------------------------------|---------------|
| | Fresh sample | Preserved and stored sample* | Remaining (%) |
| 1 | 282 | 84 | 30 |
| 2 | 1369 | 788 | 58 |
| 3 | 764 | 628 | 82 |
| 4 | 690 | 248 | 36 |
| 5 | 465 | 132 | 28 |

* Mercuric chloride (1.0 g l^{-1}) was used as preservative and samples were stored at -18°C for eight months. They were analysed in duplicate.

ml) from a preserved sample and found no increase in DMS. This indicates the DMS was completely released without acidification.

Results in Table VI show that after a period of 8 months preservation, as little as 28–82% of the original DMS concentration remained. A study on sample storage by Andreae and Barnard⁴, concluded that to maintain sample integrity for at least 48 h was to refrigerate them at 4°C . They compared DMS concentrations in acidified, unacidified, filtered, unfiltered and refrigerated samples. Filtration was found to decrease DMS concentrations.

The method we have developed can be used with small water samples (50 ml) for the determination of sulfur compounds such as DMS, carbonyl sulfide, hydrogen sulfide, methyl mercaptan, carbon disulfide and DMDS. The profiles obtained from two Antarctic lakes and the Antarctic sea, indicated measureable levels of RSCs present. DMS was found in both lakes studied and in seawater. Carbonyl sulfide and hydrogen sulfide were also measured in Burton Lake.

Preservation of the samples with 1.0 g l^{-1} mercuric chloride at -18°C was found to be inadequate for long term storage.

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