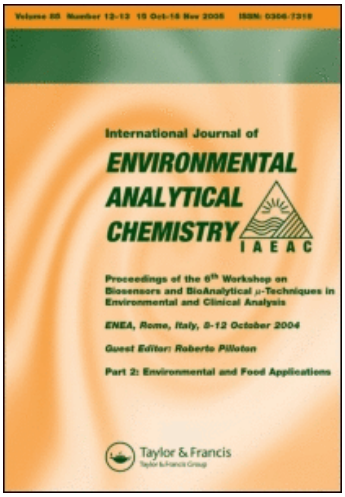

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Purge and Trap Gas Chromatographic Method for Dimethyl Sulfide in Freshwater

Douglas A. Holdway[ab]; Jerome O. Nriagu[a]
[a] National Water Research Institute, Burlington, Ontario, Canada [b] Office of the Supervising Scientist, Alligator Rivers Region Research Institute, Jabiru, Australia

To cite this Article Holdway, Douglas A. and Nriagu, Jerome O.(1988) 'A Purge and Trap Gas Chromatographic Method for Dimethyl Sulfide in Freshwater', International Journal of Environmental Analytical Chemistry, 32: 3, 177 — 186
To link to this Article: DOI: 10.1080/03067318808079112
URL: http://dx.doi.org/10.1080/03067318808079112

Intern. J. Environ. Anal. Chem., Vol. 32, pp. 177–186
Reprints available directly from the publisher
Photocopying permitted by licence only

Printed in Great Britain

A Purge and Trap Gas Chromatographic Method for Dimethyl Sulfide in Freshwater

DOUGLAS A. HOLDWAY* and JEROME O. NRIAGU†
National Water Research Institute, Box 5050, Burlington, Ontario L7R 4A6, Canada

(*Received 19 June 1987; in final form 30 July 1987*)

A simple purge and trap method is described for extracting trace levels ($ng.l^{-1}$) of dimethyl sulfide (DMS) in freshwater samples. The DMS extracted is determined in a gas chromatograph equipped with a dual-flame photometric detector and a 2-m Chromosil 330 Teflon column. Good recoveries (93–105%) are achieved when diethyl sulfide is used as an internal standard. The standard error of the mean (for replicates) is about 5% at low (8–10 $ng.l^{-1}$) DMS concentrations and about 3% at higher (90–130 $ng.l^{-1}$) concentrations. The detection limit for the method is about 0.8 $ng.l^{-1}$ DMS. Water samples containing DMS should not be stored even at low temperature for more than 6 hours, but once extracted, the DMS may be preserved in the gas sample vials for weeks. The method has been used in determining the natural levels of DMS in surface waters from Hamilton Harbour (Lake Ontario). The values found between April and July, 1986 typically varied from 40 to 770 $ng.l^{-1}$, and were much lower then the levels generally observed in the oceans.

INTRODUCTION

It is well documented that dimethyl sulfide (DMS) is the prevalent form among the volatile sulfur compounds in seawater and also is an important natural source of sulfur in the atmosphere.[1–5] It has been implicated as a contributor to the acidity of rainfall at remote locations.[6–7] In contrast to the marine environment, little is known

*Present Address: Office of the Supervising Scientist, Alligator Rivers Region Research Institute, Jabiru, Northern Territory 5796, Australia.
†Author to whom all correspondence and reprint requests should be addressed.

about DMS production in, and release from, freshwater ecosystems. Research on the latter environment has been hampered, at least partially, by the fact most of the methods that have been used in seawater studies lack the necessary sensitivity for detecting the trace concentrations of DMS in freshwater (see refs. 2, 8, 9). The lack of a simple and reliable analytical technique has even led to the erroneous supposition that DMS is not produced in freshwater environments.

We present here a simple method that uses a standard gas chromatograph equipped with a flame photometric detector and a direct on-column injector. The extraction device is simple and robust, and can be operated under field conditions. Since the DMS concentrations are generally low, a 2-liter of water sample is stripped to obtain measurable quantities of the gas. Once removed from the water, the DMS becomes less subject to chemical and biological modifications, and if necessary can be stored for several weeks before determination.

EXPERIMENTAL

Apparatus

The device used to extract the DMS is shown schematically in Figure 1. The coil consists of 8-mm bore glass tubing wound into a 55-mm diameter spiral approximately 80 mm high. The entire system, except the 2-liter Erlenmeyer flask, was silanized by means of a 10% dichlorodimethylsilane solution in *n*-hexane.

The gas chromatograph used was a Varian 3400 equipped with a dual-flame photometric detector and interfaced with a Varian 4270 integrator. An optical filter was used to select the emission spectrum to be measured. The photomultiplier voltage was set at 600 volts. The oven temperature was 50 °C, injector temperature 160 °C, and detector temperature was 220 °C. The column was a Supelco 1.83 m × 3.2 mm O.D. Teflon column packed with Chromosil 330. All the chromatography was done isothermally, with injection of 10 ml of gas sample drawn from the sample vial with a Dynatech precision gas syringe. The gas flow rates used were 80 and 170 $ml.min^{-1}$ for "Air 1" and "Air 2" respectively, 180 $ml.min^{-1}$ for hydrogen and 30 $ml.min^{-1}$ for the helium carrier gas. The air was delivered at

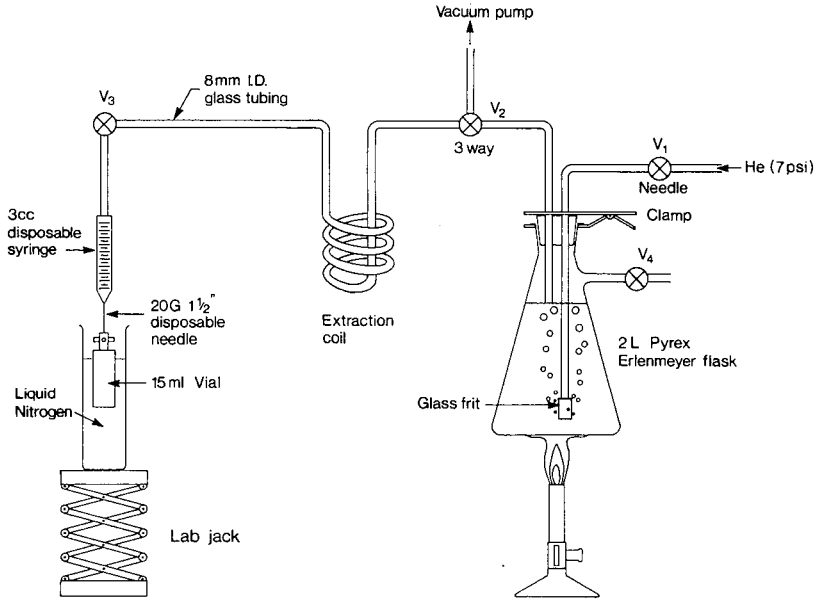

Figure 1 Organic sulfur extraction apparatus.

60 psi and the hydrogen and helium were ultrahigh purity, carrier-grade delivered at 40 and 80 psi respectively.

Analytical procedure

The system is first evacuated by opening valves 2 (V2) and 3 (V3) and turning on the vacuum pump. After the evacuation, these two valves are closed and the trap (extraction coil) is immersed in liquid nitrogen. The sample, in a 2-liter Erlenmeyer flask with a side-arm sealed by a valve (V4) is clamped to the system after addition of 40 μl of 50 ppm (v/v) of diethyl sulfide (DES) solution in ethylene glycol as the internal standard. A short pulse of helium is passed through the glass frit into the sample by quickly opening and closing the needle valve (V1). While the sample is being heated to a slow boil with a non-luminous flame of a Bunsen burner, V2 is opened and short (10-sec) bursts of helium are applied every 3–4 minutes; continuous sparging with helium leads to excessive water in the coil. When the sample has just come to the boil (usually 22–26 minutes of

heating, depending on the initial sample temperature), the heating is stopped and V1 is slowly opened to allow vigorous sparging of the sample with He. The purging is continued until bubbling of helium stops (the pressure in the system having reached 7 psi). V2 is closed and the system left for 15 minutes to ensure complete condensation of DMS and DES in the coil.

The vacuum pump is then turned on for a few seconds (with V2 appropriately switched) to remove any uncondensed gases from the system. The liquid nitrogen flask is transferred from the coil to the gas sample container (a 15-ml dark glass vial capped with a Mininert valve) and the coil is surrounded with ice-water in another Dewar flask to minimize volatilization of water. V2 is opened and helium is used to flush the sulfur compounds from the coil into the sample container. When the bubbling of He through the frit stops (i.e., the gauge pressure has reached 7 psi), the sample collection vial may be completely immersed in liquid nitrogen. Bubbling at the frit can usually be observed unless the sample inlet needle is blocked by solid deposits, and thus provides a check that the system is functioning properly. The system is allowed to remain at 7 psi for at least 15 minutes to ensure complete transfer of sulfur compounds to the sample collector. Any residual gases in the system are then evacuated by turning the pump on for 2–3 seconds with V2 appropriately switched. The sample container is removed from the extraction line, the Mininert valve quickly closed and the container is stored in a refrigerator to await the GC analysis.

At any time during the transfer of gases from the tap to the sample container, V4 may be opened to release the pressure and another sample can be attached to the extraction line.

Chemical standards

Standard solutions of DMS and DES were made up from the analytical grade liquids (Polyscience Corp., Niles, Illinois) in degassed ethylene glycol as solvent.[10] The stock solutions were kept in a refrigerator and when required, appropriate volumes were transferred into vials sealed with Mininert valves (Chromatographic Specialties, Brockville, Ontario) for further dilution.

RESULTS AND DISCUSSION

One of the critical factors and a novel feature of the method was the heating of the water sample to boiling. At room temperature, little or no recovery of DMS or the DES spike was achieved. As the temperature of the sample was raised, the efficiency of DMS recovery increased from almost zero to over 95% (Table 1). There is no evidence to suggest that the heating resulted in any significant degradation of the DMS.

The importance of elevated temperatures for stripping volatile compounds from freshwater samples is well documented (see ref. 11). Richardson and Mocek[12] have reported that heating leads to enhanced stripping of DMS from beer samples. In spite of these reports, hot sparging of samples has not previously been used in the measurement of volatile sulfur compounds in natural waters. This may explain the low recovery efficiencies and other discrepancies that have generally been reported especially at low DMS levels.

Calibration curves for DMS and DES were established daily relating known concentrations in the standard solutions to their respective peak areas (integrator counts). The experimental data invariably fitted equations of the type (see ref. 10):

$$X=(Y-k_1)/k_2; \quad n=10,\ r=0.995$$

where Y is log(peak area) and X is log(concentration). For the

Table 1 Effects of heating on the efficiency of extraction of DMS from 21 doubly distilled water samples spiked with 86.3 ng of the compound dissolved in the degassed ethylene glycol.

Duration of (mns)	*Final water temp. (°C)*[a]	*DMS recovery (%)*
0	22	0
5	35	0
10	56	0
15	80	20
20	93	59
22 (boiling)	97	93

[a]Temperature was measured at end of each extraction.

experimental conditions used, the constant, k_1, was typically 4.86 for DES and 3.44 for DMS and k_2 was about 1.13 for DES and 1.45 for DMS (10 replicates, correlation coefficient of 0.95). The recovery efficiencies for DMS and DES (the internal standard) were established by running a series of extractions with water spiked with both compounds. The extraction efficiencies (%) for DMS (X) and DES (Y) were found to be related by the equation:

$$X = k_3 . Y + k_4; \quad (n = 20, r = 0.88)$$

where k_3 and k_4 constants.

Diethyl sulfide was chosen as internal standard because (a) it is readily available and relatively stable in water; (b) its air-water partition coefficient is close to that of DMS and it can be extracted by the purge and trap technique; (c) its GC peak (column retention time about 7 minutes) does not interfere with the DMS peak; (d) compositionally, it is closer to DMS than the only other internal standard (thiophene) whose use has been reported in the literature (see ref. 13).

An internal standard was found to be extremely important in assessing the extraction efficiency for DMS (Table 2); in fact, it is surprising that its use in the determination of volatile sulfur compounds in natural waters has not been more widespread. For raw water samples containing only 9.2 ng.l^{-1} of DMS, a standard error of ± 0.5 ng.l^{-1} (or about 5% of mean) was obtained. At higher DMS concentration of 108 ng.l^{-1}, the reproducibility was even better, the standard error being only ± 3.7 ng.l^{-1} (Table 2).

The extraction efficiency itself was independent of DMS concentration in raw water. In a multiple spike experiment using raw water with background DMS concentration of 89 ng.l^{-1}, the extraction efficiency remained fairly constant (93–105%) even after the addition of 345 ng.l^{-1} DMS, equivalent to 434 ng.l^{-1} total concentration (Table 3). It should be noted that the extraction efficiencies reported were based on the DES internal standard.

Detection limit

The detection limit for the method was found to be about 0.8 ng.l^{-1} DMS. Below this concentration, the ratio of sample peak

Table 2 Reproducibility of DMS extraction from raw water samples containing different amounts of this compound

Sample	*DMS conc.* ($ng.l^{-1}$)
Surface water, Hamilton Harbour, June 18, 1986	8, 10, 8, 8, 11, 10 *Mean* = 9.2; *S.E.* = 0.5
Surface water, Luther Bog, A. 5, 1986	102, 117, 95, 107 98, 114, 108, 127 *Mean* = 108; *S.E.* = 3.7

Table 3 Effect of DMS concentration on its recovery from 2 l raw surface water samples from Hamilton Harbour. Multiple spikes with 10 μl solutions containing 86 ng/l DMS were used to obtain the concentrations listed

Amount of DMS	*DMS recovered (ng)*	*% Recovery*[a]
0	89	–
86.3	80	93
173	180	105
259	247	96
345	321	93

[a]Percentage recovery shown is based on diethyl sulfide as the internal standard.

to instrumental noise was generally less than 2. Our detection limit is higher than the 0.06 $ng.l^{-1}$ attained by the method of Andreae and Barnard[10] but is well below the 5–10 $ng.l^{-1}$ achieved by many other workers (see refs. 2, 8, 9).

Sample stability

The stability of the water sample was strongly affected by the temperature at which it was stored (Table 4). Samples stored at room temperature lost about 7% of their DMS content after just one hour and the concentration had declined by over 40% after 6 hours. The decomposition rate was much faster (over 50% in less than 6 hours) if the bottles were not completely filled to eliminate any headspace. By comparison, samples stored at 4 °C retained most

Table 4 Stability of DMS as function of storage time and temperature

Time after collection (hr)	*Storage temp. (°C)*	*DMS conc. (ng/l)*	*% Change*
0	24	41	—
1	24	38	−7.3
6	24	24	−42
24	24	25	−39
0	4	71	—
1	4	70	−1.4
6	4	72	+1.4
24	4	40	−44
72	4	38	−47

of their DMS for up to 6 hours; the DMS concentration however declined by about 40% after 24 hours (see Table 4). The stability of DMS in freshwater samples thus appears to be shorter than the 48 hours reported for seawater.[10]

Once extracted from the water samples, the DMS can be stored in the dark-colored, gas container (vial) for over 7 days even at room temperature.

Field tests

The new method was used to measure the concentrations of DMS in water samples from Hamilton Harbour, a contaminated body of water at the western end of Lake Ontario. Surface water samples were collected by hand either from a pier or a boat. Deeper waters were obtained using a peristaltic pump. The 2 liter Erlenmeyer flasks were quickly filled to the top, corked immediately and stored in an ice bucket or in a cold room until the samples were analyzed, always within 6 hours from time of collection. Just before the extraction began, the excess water was gently poured off and the DES spike was added.

A typical chromatogram of a water sample from Hamilton Harbour is shown in Figure 2. The first two unresolved peaks with retention times of less than 1.0 minutes presumably represent combined air, H_2S, carbonyl sulfide (COS) and methyl marcaptans

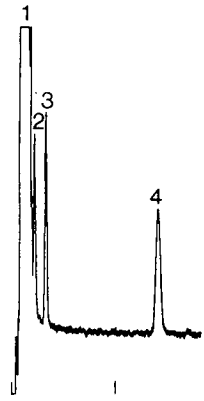

Figure 2 Chromatogram of raw Hamilton Harbour water containing 89 ng of natural DMS plus a double 86.3 ng spike DMS [262 ng of DMS total] and a 1726 ng spike of the internal standard DES. Peak number 1 is the air peak plus H_2S, peak number 2 is unknown (likely methyl mercaptan), peak number 3 is the DMS peak and peak number 4 is the DES peak.

(CH_3SH) peaks. The third peak at 1.47 min is the DMS peak of interest, and the very large peak at 7.08 min is from DES spike.

The concentrations of DMS in the harbor waters at different times and various depths are shown in Table 5. The levels in surface waters ranged from 39 to 71 $ng.l^{-1}$ and are somewhat higher than

Table 5 DMS concentrations in Hamilton Harbour water at various depths and time

Sampling date[a]	*Location*	*Water depth (m)*	*DMS conc. (ng/l)*
April 23	CCIW Pier	1.0	41
April 29	Central Harbour	1.0	71
		20	45
April 29	Cootes Paradise	1.0	39
		12	21
July 21	CCIW Pier	1.0	44

[a]All the sampling was done in 1986.

the concentrations observed in the deeper waters. The average surface water concentration of 49 ng.l^{-1} DMS is much less than the mean value for surface seawater of about 200 ng.l^{-1}.[4] Comparable information on DMS distribution in freshwater ecosystems is very limited. Bechard and Rayburn[14] showed that the DMS concentrations in an hypereutrophic pond near Pullman, Washington varied from trace amounts in spring and fall to over 70,000 ng.l^{-1} in summer, the DMS concentration being closely related to algal composition and productivity. A previous study of the same pond[8] had reported DMS concentrations of 20–3800 ng.l^{-1}. Our data, which fall in the lower end of the reported concentrations, are likely to be more representative of the DMS concentrations in many other lakes. The method has been used in the study of DMS distribution in the Great Lakes.[15]

References

1. J. E. Lovelock, R. J. Maggs and R. A. Rasmussen, *Nature* **237,** 452 (1972).
2. B. C. Nguyen, B. Bonsang and A. Gaudry, *J. Geophys. Res.* **88,** 10903 (1978).
3. W. R. Barnard, M. O. Andreae, W. E. Watkins, H. Bingemer and H. W. Georgiu, *J. Geophys. Res.* **87,** 8787 (1982).
4. M. O. Andrewe and H. Raemdonck, *Science* **221,** 744 (1983).
5. J. W. H. Dacey and S. G. Wakeham, *Science* **233,** 1314 (1986).
6. J. O. Nriagu and R. D. Coker, *Tellus* **30,** 365 (1978).
7. R. J. Charlson and H. Rodhe, *Nature* **295,** 683 (1982).
8. R. A. Rasmussen, *Tellus* **26,** 254 (1974).
9. S. D. Hoyt and R. A. Rasmussen, *Adv. Chem.* **209,** 31 (1985).
10. M. O. Andreae and W. R. Barnard, *Anal. Chem.* **55,** 608 (1983).
11. M. E. Comba and K. L. E. Kaiser, *Intern. J. Environ. Anal. Chem.* **16,** 17 (1983).
12. P. J. Richardson and M. Mocek, *J. Inst. Brew.* **79,** 26 (1973).
13. S. G. Wakeham, B. L. Howes and J. W. H. Dacey, *Nature* **310,** 770 (1984).
14. M. J. Bechard and W. R. Rayburn, *J. Phycol.* **15,** 379 (1979).
15. J. O. Nriagu and D. A. Holdway, *Tellus*, in press (1987).