SIMPLIFIED ANALYTICAL METHOD FOR TRACE LEVELS OF DIMETHYL SULFIDE IN FRESHWATER.

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MANAGEMENT PERSPECTIVE

Our stable sulfur isotope data suggest that the release of volatile organosulfur compounds from lakes, marshes, bogs, and other wetlands may be a major contributor to the atmospheric sulfur burden, and hence to the acidity of rainfall at rural and remote areas of Canada. To confirm this suggestion, we need to actually determine the distribution of such compounds in freshwater ecosystems of the country. No reliable and convenient method, however, was available for measuring the low levels of dimethyl sulfide (believed to be the predominant organosulfur species) expected in freshwater environments. We were therefore forced to develop an appropriate analytical methodolgy for trace levels of dimethyl sulfide (DMS).

The report describes a purge and trap method for extracting trace levels (ng/l) of DMS in freshwater samples. The DMS extracted was analyzed in a gas chromatograph equipped with a flame photometric detector and Chromosil 330 teflon colum . The detection limit achievable is less than 0.8 ng/l DMS, and is about an order of magnitude lower than the detection limits of some of the oceanographic techniques. With this highly sensitive technique, we have been able to detect DMS in all the water samples we have so far analyzed. For example, the DMS concentrations in surface waters of Hamilton Harbor varied from 40 to 70 ng/l between April and July, 1986. The concentrations in selected freshwater marshes and bogs are comparable to, and at times even exceed, the levels gnerally found in the oceans. Future studies will be aimed at determining the contribution of biogenic sources to the atmospheric sulfur burnden at selected areas of Canada.

ABSTRACT.

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 analyzed in a gas chromatograph equipped with a dual-flame photometric detector and a 2 m Chromosil 330 teflon column. Excellent recoveries (93-105%) are achieved when diethyl sulfide is used as an internal standard. The standard error for replicates is about ± 5% at low (8-10 $ng.l^{-1}$) DMS concentrations and about ± 3% in the higher (90-130 $ng.l^{-1}$) concentration range. The detection limit for the method is about 0.8 $ng.l^{-1}$ DMS. Water samples containing DMS can only be stored at low temperature for less 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 70 $ng.l^{-1}$, and were much lower than the levels generally observed in the oceans.

INTRODUCTION.

It is now well documented that dimethyl sulfide (DMS) is not only the prevalent form among the volatile sulfur compounds in seawater but also is an important natural source of sulfur in the atmosphere (1-5). It has been implicated as an major contributor to the acidity of rainfall at remote locations (6-7). In contrast to the marine environment, little is known about DMS production in, and release from, freshwater ecosystems. Research in the later 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 freshwaters (see 2; 8-9). The lack of 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 analytical methodology that uses a standard gas chromatograph equipped with a flame photometric detector and a direct on-column injector. The extraction device is simple, robust and can be operated under field conditions. Since the DMS concentrations are generally low, 2.0 l 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 degradation or accentuation, and hence can be stored for several weeks.

EXPERIMENTAL SECTION.

Apparatus. The device used to extract the DMS from the 2 l water sample is shown schematically in Figure 1. The trap consists of 8 mm I.D. glass tubing wound into 55 mm diameter coils approximately 80 mm high. The entire system, excluding the 2 l Erlenmeyer flask, was silanized using 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 usually in the square root mode. 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 by 3.2 mm O.D. teflon column packed with chromosil 330. All chromatography was run isothermally and involved the injection of 10 ml gas sample drawn from the sample vial using a Dynatech precision gas syringe. Gas flow rates used were 80 and 170 $ml.min^{-1}$ for Air 1 and Air 2; 180 $ml.min^{-1}$ for hydrogen and 30 $ml.min^{-1}$ for the helium carrier gas. The zero air was delivered at 60 psi while the hydrogen and helium were ultra-high 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 closing the two valves, the trap is emersed in liquid nitrogen. The sample in a 2 l Erlenmeyer flask with a side arm sealed by a clamp (V4) is attached to the system after adding 40 ul of 50 ppm

(v/v) of DES as the internal standard. A short pulse of He is applied through the glass frit to the sample by quickly opening and closing the needle valve (V1). As the sample is brought to a slow boil by means of a Bunsen burner, V2 is opened and short pulses of He are applied periodically. When the sample is brought to a slow boil (usually 22-26 minutes of heating depending on initial sample temperature), the heating is stopped and V1 slowly opened to allow for a vigorous sparging of the sample with He. The purging is continued until bubbling stops (the system having reached 7 psi). V2 is closed and the freeze-out of any DMS and DES into the trap continued for 15 more minutes.

The vacuum pump is then turned on for a few seconds to remove any unfrozen gases from the system. The liquid nitrogen flask is transfered from the trap to the gas sample container (15 ml dark glass vial capped with a Mininert valve) and another Dewar flask containing ice water is place over the trap to retain the moisture. V2 is opened and He used to flush the sulfur compounds from the trap to the sample container. When the bubbling of He through the frit stops (has reached 7 psi), the sample collection vial may be completely immersed in liquid nitrogen. Bubbling at the frit can usually be observed if the sample inlet needle is not blocked by solid deposits, thus providing a sort of check that the system functions 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 now evacuated by

turning the pump on for 2-3 seconds. The sample container is removed from the extraction line, the Mininert valve quickly closed and then stored in a refridgerator to await the GC analysis.

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

Chemical Standards. Standard solutions of dimethyl sulfide and diethyl sulfide (DES) were made up from the analytical grade liquids (Polyscience Corp., Niles, Illinois) using de-gassed ethylene glycol as the solvent (10). The stock solutions were kept in a refridgerator and when required, small aliqouts 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 in the method described was the heating of the water sample to boiling. At ambient temperature, little or no recovery of the DMS or DES spike was achieved. As the temperature of the sample was increased to boiling, 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 degredation of the DMS.

The importance of elevated temperatures in facilitating the

stripping of volatile compounds from freshwater samples is well documented (see 11). In a related development, Richardson and Mocek (12) also noted that heating led to enhanced stripping of DMS from beer samples. In spite of these reports, hot sparging of samples had not been used in previous measurements 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.

Standard curves for DMS and DES were established daily relating known concentrations of the standard solutions to their respective peak areas using log-log regression (10). The experimental data invariably fit equations of the type:

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

where Y is $\log_{10}$(DMS or DES peak area), and X is $\log_{10}$(DMS or DES concentration in $ng.l^{-1}$). For the experimental conditions used, the constant, k_1, typically had a value of 4.86 for DES and 3.44 for DMS while the values for k_2 were about 1.13 for DES and 1.45 for DMS. The standard curve for determining the extraction efficiency for DMS from the internal standard was generated by running a series of extractions using water samples spiked with both DMS and DES. The extraction efficiencies for the two compounds were then related by the equation:

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

where X and Y were the percentage DMS and DES extraction efficiencies respectively and, for the experimental conditions

used, k_3 and k_4 were generally found to be close to 3.46 and 17.2 respectively.

Diethyl sulfide was found to be a good choice as internal standard because (a) it is a readily available compound and is 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 column retention time (about 7 minutes) is such that it 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 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 $\pm$ 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 $\pm$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 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 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 hrs) if the bottles were not completely filled to eliminate any headspace. By comparison, samples stored at $4^{o}C$ retained most 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 l 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 minute presumably represent combined air, H_2S, carbonyl sulfide (COS) and methyl marcaptans (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 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 n $.l^{-1}$ 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 ranges, are likely to be more representative of the DMS concen-

trations in many other lakes. The method is now being used in the study of DMS distribution in the Great Lakes, and the results will be forthcoming

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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 of raw surface water from Hasmilton Harbour. Multiple spikes with 10 ul solutions containing 86 ng/l DMS were used to obtain the concentrations listed.

Amount of DMS added (ng)	DMS recovered (ng)	% Recovery*
0	89	--
86.3	80	93
173	180	105
259	247	96
345	321	93

* Percentage recovery shown is based on diethyl sulfide as the internal standard.

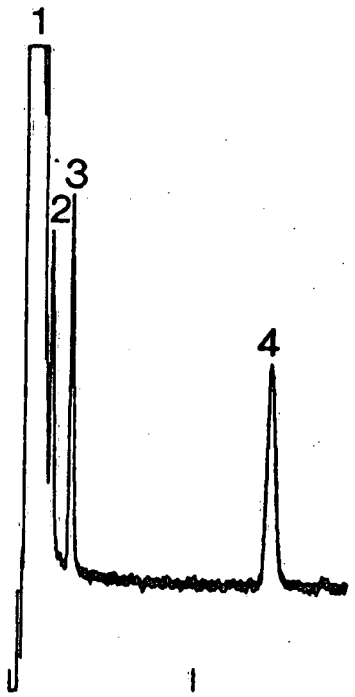
Table 4. Stability of DMS as function of storage time and temperature.

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

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

Sampling date*	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

* All the sampling was done in 1986



Chromatogram of raw Hamilton Harbour water containing 89 ng of natural DMS plus a double 86.3 ng spike of 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.

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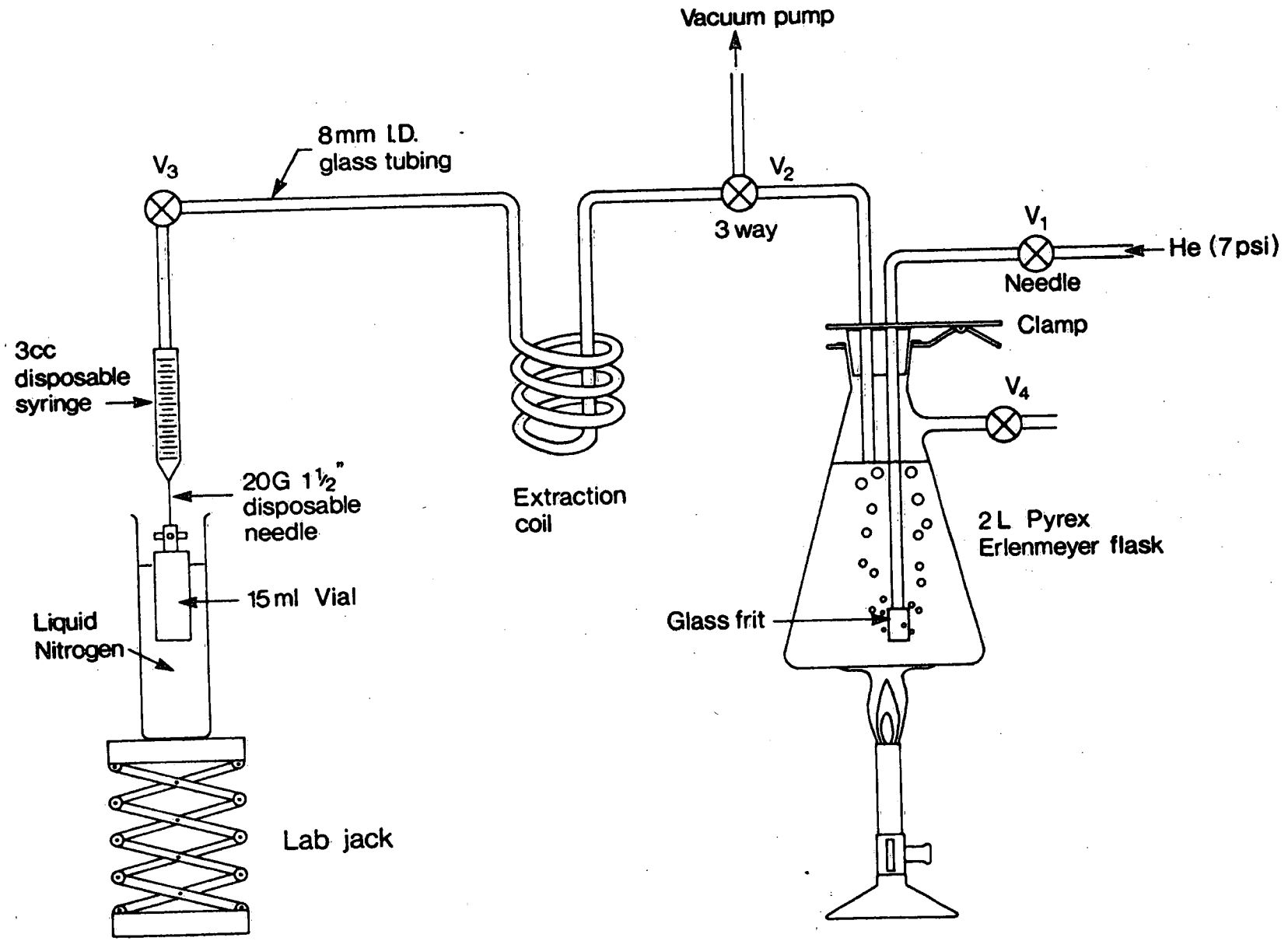

Figure 1 Organic sulphur extraction apparatus.

Table 1. Effects of heating on the efficiency of extraction of DMS from 2 l doubly distilled water spiked with 86.3 ng of the compound dissolved in degassed ethylene glycol.

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

* Temperature was measured at end of each extraction.

MÉTHODE SIMPLIFIÉE D'ANALYSE DU SULFURE DIMÉTHYLIQUE À L'ÉTAT DE TRACE DANS L'EAU DOUCE

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PERSPECTIVE GESTION

Nos données sur l'isotope sulfure stable suggèrent que certains des principaux agents reponsables de la pollution atmosphérique par le sulfure, et donc de l'acidité des pluies dans des régions rurales et éloignées du Canada, pourraient être des composés volatils de sulfure organique qui se libèrent des lacs, marais, tourbières et autres marécages. Afin de confirmer cette hypothèse, il nous a fallu déterminer la distribution exacte de ces composés dans les écosystèmes d'eau douce au Canada. Cependant, il n'existait pas de méthode fiable et pratique pour mesurer les niveaux faibles de sulfure dyméthylique (qui est, croit-on, le sulfure organique prédominant) que l'on s'attendait à trouver dans les écosystèmes d'eau douce. Nous avons donc dû mettre au point une méthode d'analyse appropriée pour déterminer les niveaux de sulfure diméthylique à l'état de trace.

Ce rapport décrit une méthode de purification et d'extraction de quantités infinitésimales (ng/L) de sulfure diméthylique dans des échantillons d'eau douce. On a analysé le produit extrait dans un appareil de chromatographie en phase gazeuse équipé d'un photomètre à flamme et d'une colonne Chromosil 330 en teflon. La limite inférieure de détection de cet appareil est inférieure à 0,8 ng/L pour le sulfure diméthylique, et est d'environ un ordre de grandeur inférieure aux limites de détection de certaines techniques utilisées en océanographie. Avec cet appareil hautement sensible, nous avons pu détecter du sulfure diméthylique dans tous les échantillons d'eau analysés jusqu'à maintenant. Par exemple, les concentrations de ce composé dans les eaux de surface du port d'Hamilton variaient de 40 à 70 ng/L entre avril et juillet 1986. Les concentrations contenues dans des échantillons extraits de marais et de tourbières d'eau douce sélectionnés étaient comparables aux niveaux trouvés en général dans les océans, et pouvaient être plus élevées à l'occasion. Des études ultérieures auront pour but de déterminer la contribution de sources biogéniques à la pollution atmosphérique par le sulfure à certains endroits au Canada.

SOMMAIRE

On décrit ici une méthode simple de purification et d'extraction du sulfure diméthylique à l'état de trace (ng/L) dans des échantillons d'eau douce. Le sulfure diméthylique extrait est analysé par un appareil de chromatographie en phase gazeuse équipé d'un photomètre à deux flammes et d'une colonne Chromosil 330 de teflon de 2 m. Le taux de récupération du sulfure diméthylique est excellent (93 à 105 p. 100) lorsque l'on utilise du sulfure diéthylique comme étalon interne. L'erreur-type pour les échantillons subdivisés était d'environ ±5 p. 100 lorsque les concentrations de sulfure diméthylique étaient faibles (8-10 ng/L), et d'environ ±3 p. 100 lorsque les concentrations étaient élevées (90-130 ng/L). La limite inférieure de détection de cette méthode est d'environ 0,8 ng/L pour le sulfure diméthylique. Les échantillons d'eau contenant ce composé peuvent être entreposés à faible température seulement pendant moins de 6 heures, mais une fois le sulfure diméthylique extrait, celui-ci peut être conservé pendant des semaines dans des flacons en verre. On a utilisé cette méthode pour déterminer les niveaux naturels de sulfure diméthylique dans les eaux de surface du port d'Hamilton (lac Ontario). Pour la période d'avril à juillet 1986, les valeurs types variaient entre 40 et 70 ng/L, et étaient de beaucoup inférieures aux niveaux observés en général dans les océans.