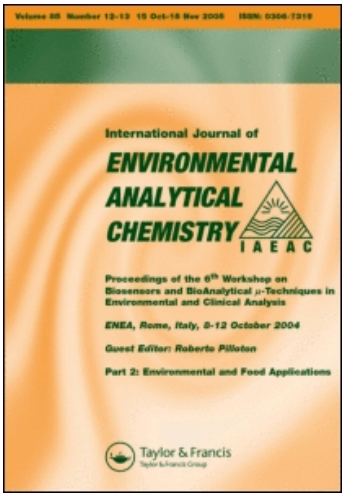

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Gas Chromatographic Trace-Level Determination of Volatile Organic Sulfides and Selenides and of Methyl Iodide in Atlantic Surface Water

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To cite this Article Tanzer, D. and Heumann, K. G.(1992) 'Gas Chromatographic Trace-Level Determination of Volatile Organic Sulfides and Selenides and of Methyl Iodide in Atlantic Surface Water', International Journal of Environmental Analytical Chemistry, 48: 1, 17 — 31
To link to this Article: DOI: 10.1080/03067319208027039
URL: http://dx.doi.org/10.1080/03067319208027039

Intern. J. Environ. Anal. Chem., Vol. 48, pp. 17–31
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GAS CHROMATOGRAPHIC TRACE-LEVEL DETERMINATION OF VOLATILE ORGANIC SULFIDES AND SELENIDES AND OF METHYL IODIDE IN ATLANTIC SURFACE WATER

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(Received 22 March 1991; in final form 25 October 1991)

The concentration of the sulfur compounds dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and carbon disulfide (CS_2) as well as of methyl iodide (CH_3I) was determined in surface sea water of the Atlantic Ocean from 30°S to 45°N during an expedition with the German research vessel 'FS Polarstern' using a purge and trap/gas chromatographic system equipped with a flame photometric and an electron capture detector. The most abundant sulfur compound was DMS with a mean concentration of 55 ng S/l. DMDS and CS_2 could be detected in 14 and 56 out of a total number of 100 sea water samples with concentrations up to 14.7 ng S/l and up to 10.7 ng S/l, respectively. This is the first time that DMDS could be quantified in a number of sea water samples. CH_3I was determined in all samples with a mean of 0.6 ng I/l. In three Atlantic sea water samples dimethyl selenide (DMSe) was detected for the first time (concentration range, 1–5 ng Se/l). Its presence was verified by means of an atomic emission detector. DMSe was the only volatile selenium compound found. Contrary to CS_2, the concentrations of CH_3I and especially of DMS and DMDS are related to the levels of marine primary production. In agreement with this, the DMS concentrations correlated well with those of dimethyl sulfonium propionate (DMSP). However, no clear relationship between CH_3I and DMS could be found, indicating a different pathway of biological production.

KEY WORDS: Dimethyl sulfide, dimethyl disulfide, carbon disulfide, dimethyl selenide, methyl iodide, gas chromatography, Atlantic surface water.

INTRODUCTION

In recent years there has been increasing interest in the role of volatile organic compounds in the global atmospheric chemistry. The interest has developed from concern on acidic precipitation and the influence of these substances on the warming up of the earth and the destruction of the stratospheric ozone layer. It has mainly been focused on anthropogenic substances such as fluorinated and chlorinated hydrocarbons. However, numerous natural, biologically produced compounds contribute significantly to the global geochemistry, too.[1] The biogenesis of organic substances in the oceans provides an important input of several volatile compounds into the atmosphere. For example, a substantial amount of volatile sulfides is emitted from the world's oceans into the atmosphere.[2–4] Their atmospheric oxidation may

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account for a significant portion of sulfur dioxide, sulfate, and methane sulfonate observed in marine air.[5] These substances act as cloud condensation nuclei and thus affect the radiation balance and contribute to the acidity of rain.[6]

It is well known that DMS is the most abundant species among all volatile sulfur compounds in sea water. Other sulfur compounds such as COS, CH_3SH, CS_2, and DMDS have been identified in distinctly lower concentrations. However, most analytical methods concerning the sulfur compounds are either limited to or optimized for the determination of DMS, because these methods suffer from limitations of analytical sensitivity or problems with the chromatographic separation, especially between CS_2 and DMS.[7] Due to the lack of analytical sensitivity, nothing is known about the sulfur-analogous selenium compounds in sea water even though methods for determining volatile selenium species have been published.[8,9] Jiang and Robberecht reported the determination of dimethyl selenide, dimethyl diselenide, and dimethyl selenone in air samples using gas chromatography with atomic absorption detection.[10] Other authors have in fact documented the microbial production of methylated selenium compounds in lake sediments, soil and sewage sludges.[11]

Another natural organic compound, which participates in important atmospheric reactions, is CH_3I. CH_3I was suggested to be involved in ozone-destroying reactions in the tropospheric marine air.[12] Measurements of CH_3I concentrations in the atmosphere and in sea water indicate that this volatile compound plays a key role in the biogeochemical cycling of iodine.[13] It has been found in all ocean waters so far examined, especially in areas of high primary production and seems to be a common product of marine algae.[14] However, the pathway of the biosynthesis and the global distribution of CH_3I are still unknown. The reaction of inorganic iodine with DMSP was suggested to be the source of CH_3I.[15] DMSP, which is produced in different amounts by a variety of unicellular and macrophytic algae, is known to be the direct precursor of DMS. In this case the distribution of CH_3I in sea water might be expected to follow a similar pattern to that of DMS and DMSP.

The main objective of the present work was to develop gas chromatographic methods which can contribute to a more detailed knowledge of the global distribution of different volatile sulfur and selenium compounds and of methyl iodide as well. In order to check the possible correlation between the occurrence of CH_3I and DMS we analyzed the same sea water samples for both compounds. The results were obtained during an expedition (ANT VII/5) of the German polar research vessel 'FS Polarstern' from 30°S to 45°N using gas chromatography (GC) with different selective detectors.

EXPERIMENTAL

Sampling

Samples of the surface layers of the Atlantic Ocean were collected in March and April, 1989. The cruise track from Cape Town to Bremerhaven is shown in Figure 1. The sea water samples were taken directly from the surface of the ocean (down to

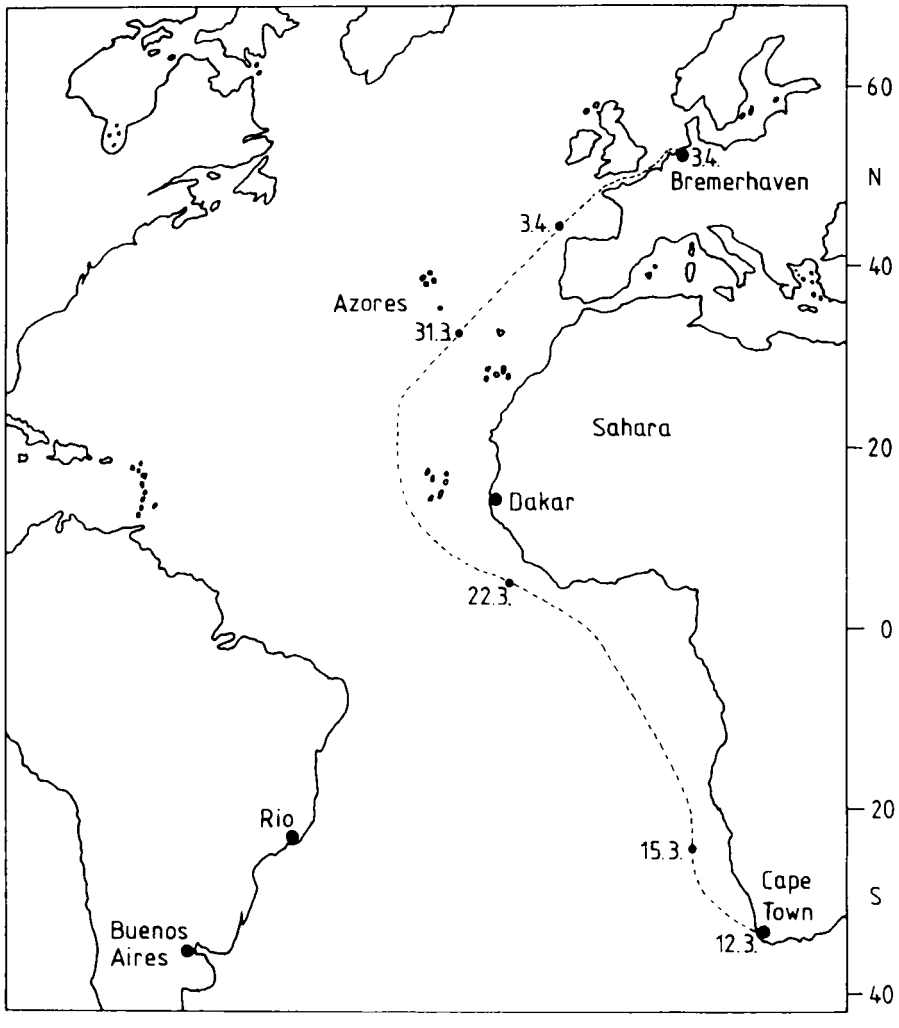

Figure 1 Cruise track with '*FS Polarstern*' from Cape Town to Bremerhaven.

about 30 cm) by dipping a 10 l bucket into the sea; the samples were immediately transferred to a 1 l Teflon vessel (Figure 2). The vessel, which was tightly sealed with a Teflon screw cap, was filled to the brim to minimize headspace. The gas-tight sample vessel was directly connected with the purge and trap system (Figure 2) using special Teflon adaptors. While the analyses of volatile sulfur compounds were performed immediately after sampling, the analyses of CH_3I and of selenium compounds were performed in our laboratory in Regensburg and in the laboratory of Hewlett Packard in Waldbronn, respectively. Samples which were not immediately analyzed, were filled in precleaned glass containers (about 60 ml capacity), which were sealed by melting the open ends of the glass containers with a microflame burner and stored deep-frozen ($-10°C$) until analysis.

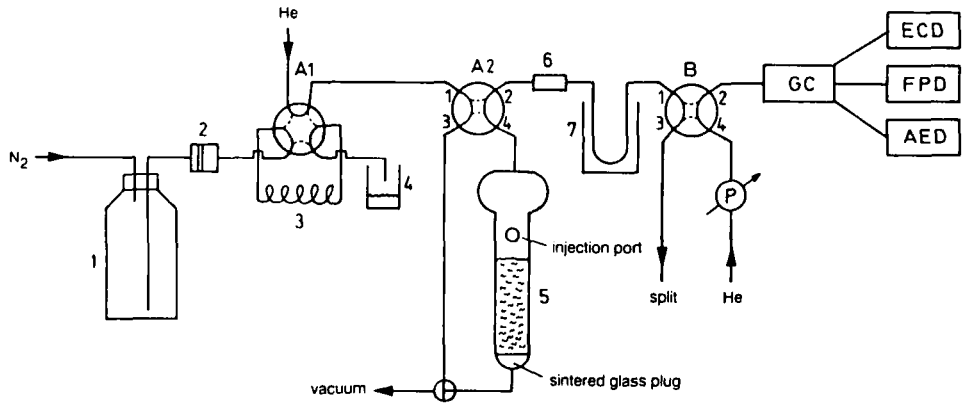

Figure 2 Closed-loop stripping system for the isolation of volatile organic compounds from sea water samples. 1, Sample vessel; 2, filter; 3, sample loop; 4, waste vessel; 5, purging unit; 6, drying tube; 7, capillary cold trap.

Purge and Trap System

Volatile species in the water samples were extracted and concentrated using a purge and trap method. The closed-loop stripping system, which allows to collect volatile organic compounds from sea water in a capillary trap, is schematically shown in Figure 2. For analysis the samples were transferred with precleaned nitrogen from a 1 l Teflon vessel through a membrane filter into a sample loop of known volume (5–35 ml depending on the concentration of the sample) made of Teflon tubing. The filter (0.45 μm pore size) removes algae cells from the water sample. Once loaded, the six-port Teflon valve A1 was switched to the inject position and using precleaned helium the sample was forced out of the sample loop into the glass bubbling chamber, where a continuous purge process begins. Alternatively, the sample can directly be injected with a syringe via the injection port into the evacuated bubbling chamber. This method was applied to samples which could not be analyzed immediately after sampling.

Volatile organic compounds were stripped from the sample and were trapped directly in a capillary cold trap (diameter 0.32 mm, length 250 mm). The sintered glass plug at the bottom of the purging unit distributes the gas flow by very small gas bubbles into the degassing chamber, thus increasing the stripping efficiency. Clogging of the cold trap was prevented by installing a glass tube (2 cm × 6 cm) filled with potassium carbonate or a Nafion drying tube in front of it. Both drying tubes effectively remove moisture from the carrier gas stream without affecting the compounds of interest. The capillary cold trap was coupled with the GC separation column via a 4-way Valco valve. To achieve a sufficient purge gas flow (approx. 60 ml/min) the Valco valve was switched to the split position (1–3; 2–4). After 30 min purging the helium carrier gas was directly passed over the drying tube and capillary trap in the GC separation column by switching the valves A2 and B into the inject position (1–2; 3–4). Then, the liquid nitrogen was removed and the cryogenically trapped compounds were transferred into the GC by heating the cold

trap with a hot air gun. At the same time the temperature program of the GC system was started.

All glassware in contact with sulfides and selenides was thoroughly cleaned and silanized with a solution of dimethyl dichlorosilane in toluene (5% v/v) to avoid possible adsorption of these compounds on the glass walls. For purification the helium carrier gas was pumped through stainless-steel pipes packed with molecular sieve (type 5A) and activated charcoal (50–200 mesh).

Gas chromatography

Depending on the compounds to be analyzed one of two gas chromatographic systems was connected with the purge and trap system. The analyses of volatile sulfur compounds and the CH_3I analyses were carried out with a Shimadzu GC-9A gas chromatograph equipped with a flame photometric detector (FPD) or an electron capture detector (ECD) with a ^{63}Ni source. The determination of volatile selenium compounds was performed using either the same system or a Hewlett Packard HP 5890 gas chromatograph equipped with an atomic emission detector (AED). A capillary column (50 m $\times$ 0.32 mm, I.D.; 5 μm film thickness; SE 54) was used for the separation of the sulfur and selenium compounds. The temperature program was as follows: after 3 min at 70°C the temperature was raised at 3°C/min to 180°C. The GC separation of CH_3I was performed with two coupled capillary columns of different polarity, type OV 1701 (50 m $\times$ 0.32 mm, I.D.; 1 μm) and SE 54 (50 m $\times$ 0.32 mm, I.D.; 5 μm) to achieve sufficient separation of CH_3I from Freon 113 and CH_2Cl_2. In this case the temperature was held for 3 min at 40°C and was then increased at 3°C/min to 180°C.

Calibration

A gaseous diffusion tube with a known, gravimetrically-controlled permeation rate (20 ng/min) was used for the calibration of DMS. The tube was obtained as certified permeation tube from Vici Metronics (Santa Clara, U.S.A.) A temperature-controlled permeation system with precleaned nitrogen for dilution, was used to produce a calibration gas. For calibration the outlet of the permeation system was connected with the Teflon valve A1 of the purge and trap system (Figure 2) instead of the sample vessel. The DMS calibration gas was then treated in the same way as the samples. For the quantitation of CS_2, DMDS, DMSe and CH_3I, standard solutions were prepared from the analytical-grade liquids by a stepwise dilution procedure. Degassed ethylene glycol was used as solvent according to a method of Kim and Andreae.[7] Microliter amounts of these standards with final concentrations of about 100 pg/μl were added to degassed sea water via the injection port and analyzed like a sample. The accuracy of the DMS permeation standards was also checked with liquid DMS standards. The agreement between the two calibration methods was better than 2%. The recovery of the method was investigated by adding known amounts of the standards to degassed sea water samples and found to be quantitative within the precision of the method (6%).

RESULTS AND DISCUSSION

Determination of DMS, CS_2 and DMDS

A representative GC-FPD chromatogram of an Atlantic sea water sample is shown in Figure 3. DMS was the major volatile sulfur compound in all analyzed samples. Next to DMS, other sulfur compounds such as carbonyl sulfide (COS), methyl mercaptan (CH_3SH), carbon disulfide (CS_2) and dimethyl disulfide (DMDS) were often detected with distinctly lower concentrations. Because of a lack of suitable calibration gases for COS and CH_3SH we were not able to quantify these compounds. In addition these highly volatile compounds can possibly not be enriched quantitatively in the cryogenic trap as was found in preliminary tests with COS. Figure 4

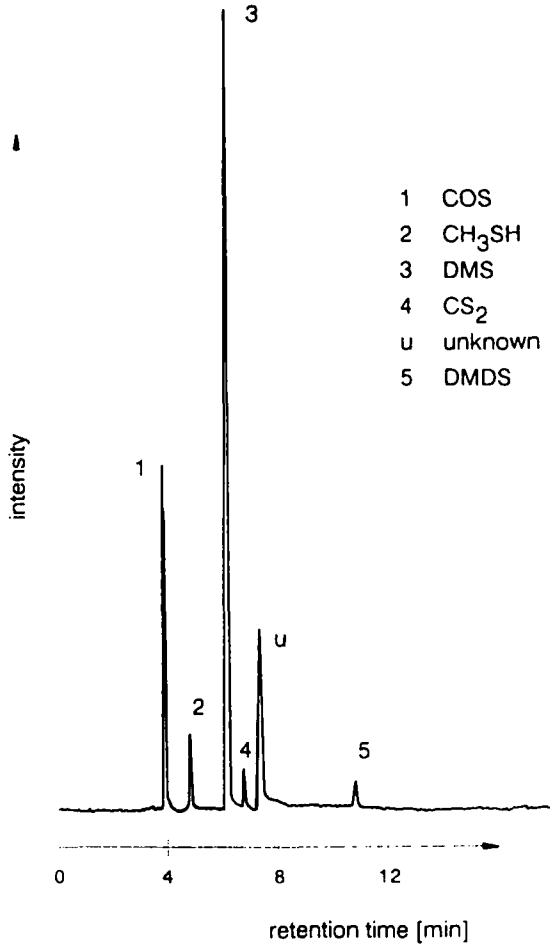

Figure 3 Detection of volatile sulfides in sea water with GC-FPD.

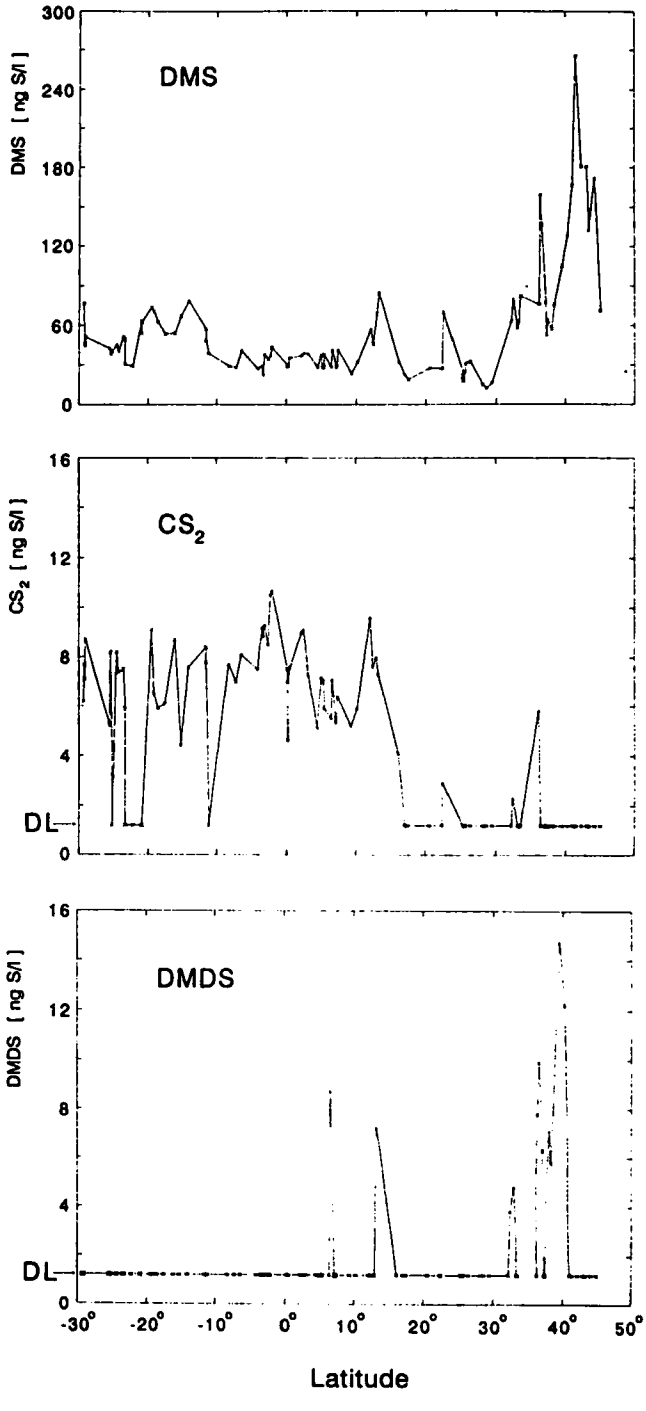

Figure 4 Latitudinal distribution of DMS, CS_2 and DMDS during the cruise (DL, detection limit).

shows the concentrations of DMS, CS_2 and DMDS measured during the cruise from 30°S to 45°N.

Surface DMS concentrations ranged from 12.1 to 265.4 ng S/l with an average of 55 ng S/l. These concentrations are comparable to values observed in oligotrophic areas of the oceans and are much lower than concentrations generally observed.[16] Maximum levels were measured toward the end of the cruise between 35°N and 45°N. These findings were consistent with the increased primary production rate in this region, recognizable by parallel measured ATP and chlorophyll concentrations, the most important indicators of algae biomass. The ATP and chlorophyll measurements were carried out by a group of the Alfred-Wegener-Institut.[17] Based on a great number of investigations the biogenic origin of DMS in the oceans is commonly accepted.[2–5] Its biogenic precursor in sea water is DMSP, which is produced by various species of marine phytoplankton and macroalgae. The formation of DMS is due to the enzymatic cleavage of DMSP.[14] A clear relationship (correlation coefficient, 0.7) was indeed, observed between our DMS data and DMSP concentrations determined at the University of Bremen.[18] In addition the vertical distribution of DMS and DMSP in the water column, which was measured at four different locations down to 250–1200 m (12°S 3°E; 0°S 6°W; 12°N 28°W; 25°N 28°W), correlated well.

While many DMS measurements were performed in sea water samples because of the great significance of DMS as the most important biogenic sulfur source for the atmosphere,[6] analytical data on the concentration of CS_2 are scarce and, up to now, no published data on DMDS is available.[16] This may partly be due to the lack of analytical sensitivity for measuring the low concentrations. On the other hand, it may also be due to chromatographic separation problems, especially between CS_2 and DMS.[7] Contrary to former investigations with packed columns we used a capillary column which allowed a suitable separation of CS_2 from DMS even at high DMS levels (see Figure 3 and Figure 5 below). A survey of published CS_2 results in sea water including our measurements is listed in Table I. The first measurements of CS_2 in surface samples of the ocean were reported by Lovelock.[19] Using a GC-ECD system he analyzed a mean of 0.44 ng S/l in the Atlantic Ocean. Remarkably higher concentrations were found in coastal sea water samples. For example, Holligan *et al.*[20] reported CS_2 concentrations in the order of 4 ng S/l in the English Channel. Because CS_2 was not always resolved from large DMS peaks they could not present more exact quantitative information. Similar concentrations (4.7 to 7.5 ng S/l) were found by Kim and Andreae[7] in an estuary in Florida (U.S.A.) using an adsorbent preconcentration method which was especially developed for CS_2 analyses. High concentrations (up to 64 ng S/l) were found in the low-salinity region of another estuary.[16] In the open ocean of the North Atlantic Ocean and the Sargasso Sea, however, remarkably lower concentrations in the range of 80–910 pg S/l were determined. As a result of these findings the presence of CS_2 in sea water was explained by its diffusion from the porewater of the underlying sediments, where it can be formed, for example, by fermentation reactions of organosulfur compounds.[16] Our CS_2 results are in reasonable agreement with previous investigations. We detected CS_2 in 56 out of 100 analyzed samples (detection limit, about 1 ng S/l) mainly in the first part of our cruise. The highest concentrations (up to 10.7 ng S/l) were

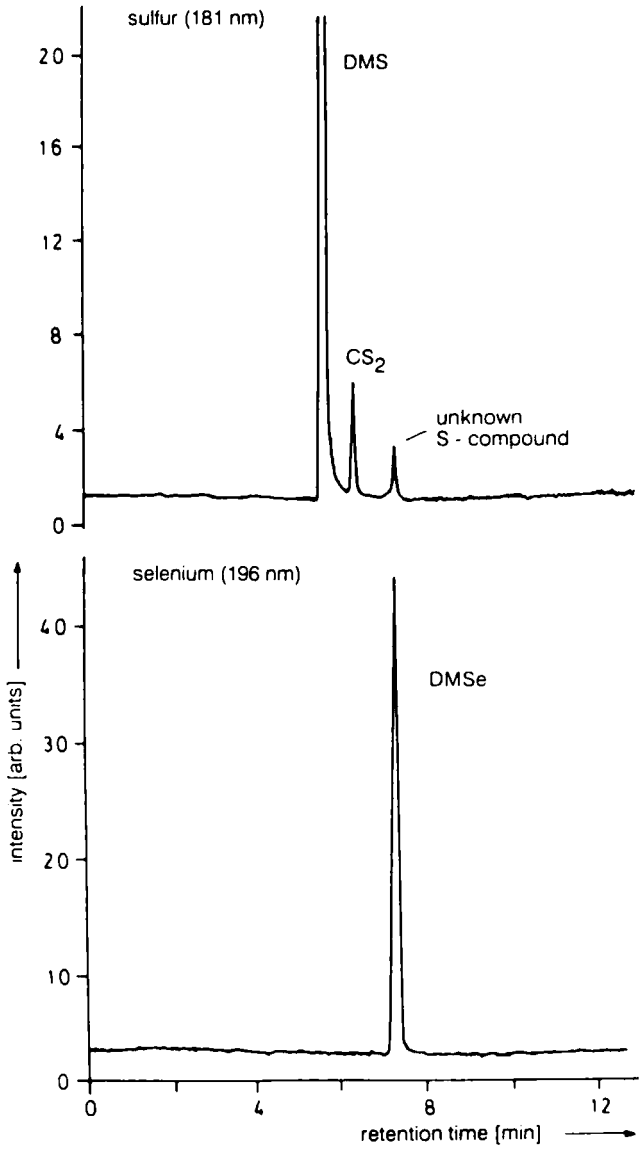

Figure 5 Detection of volatile sulfides and selenides in sea water with GC-AED.

found near the equator, when the ship was close to the continent. There is no correlation between on the one hand, CS_2, and on the other hand, DMS and DMDS (see Figure 4). This demonstrates the different biological sources of these two groups of sulfur compounds.

Although the sulfur compound DMDS was detected in sea water samples before, no concentration levels were published so far. However, Caron and Kramer[21] have

Table I CS_2 data measured in sea water

Region	*Concentration (ng S/l)*	*Literature*
St. Marks Estuary, Florida	4.68–7.50	Kim and Andreae[7]
Eastern Coast of the United States	0.18–2.36	
North Atlantic and Sargasso Sea	0.08–0.91	
English Channel	≈4.0*	Holligan *et al.*[20]
Atlantic Ocean	0.44	Lovelock[19]
Atlantic Ocean	<1.2–10.7	This work

* Separation problems between DMS and CS_2.

recently quantified DMDS in a highly bioactive fresh water sample from Canada. Its concentration of 7.1 ng S/l was even higher than that of DMS (3.3 ng S/l). This relatively high DMDS concentration could be attributed to the extremely high CH_3SH concentration of 35 ng S/l, because DMDS is known to be an oxidation product of CH_3SH.[2] We detected DMDS in 14 out of 100 samples, mainly in the region with increasing primary production rate, where also the highest DMS levels were measured (see Figure 4). The maximum concentration was 14.7 ng S/l. The results demonstrate that DMS and DMDS have the same biological source.

Determination of DMSe

Besides the well-known sulfur species COS, CH_3SH, CS_2, DMS and DMDS we detected an 'unknown' peak (see Figure 3) in a few cases, which could not be identified by means of the flame photometric detector. The existence of sulfur species in sea water other than those listed above was already reported in the literature. During GC-FPD measurements of sulfur-containing gases in coastal water samples of the North Sea by Turner and Liss[22] various peaks were detected which could not be identified. They suggested that small amounts of propyl sulfide, amongst others, do occur in the samples. Unknown peaks were also detected during the GC determination of volatile sulfides in fresh water samples by means of a Hall electrolytic conductivity detector. Caron and Kramer[21] postulated the unknown peaks to be a 2-propanethiol or methyl ethyl sulfide. In model experiments we could not associate our unknown peak with one of the discussed compounds. However, the substance showed the same retention time in GC as we found for DMSe. Like sulfur, selenium compounds can be detected with a flame photometric detector due to Se_2 emissions. Because the spectral emissions of Se_2 and S_2 overlap extensively it is, however, not possible to differentiate between sulfur or selenium compounds when using an FPD.

The best choice of distinguishing sulfur and selenium compounds with a single-channel FPD is the greater quenching of sulfur peaks by methane doping.[23] In order to identify the unknown peak unequivocally we coupled the purge and trap system with a GC-AED. This allows the simultaneous measurement of sulfur and selenium compounds. The photodiode array technology of the AED yields high selectivity for these two elements and a low detection limit.[24] Figure 5 shows a typical gas chromatogram of an Atlantic sea water sample (collected at 4°N 14°W) using the AED. As can be seen, the unknown peak (see Figure 3) was identified to be a mixture of two different compounds, an unknown sulfur compound and DMSe, which were not resolved under the applied conditions. To our knowledge this is the first time that a volatile selenium compound is detected in a natural water sample. DMSe was the only selenium compound in three samples from the Atlantic Ocean (taken near the equator) in the concentration range of 1–5 ng Se/l.

Methods to determine volatile selenium compounds in sea water have been published but these methods lack the necessary sensitivity for detecting low trace concentrations or they were combined with non-specific detectors.[8,25] The detection of methylated selenium species in air, however, has been documented. Reamer[26] identified alkylselenium compounds in the vicinity of sewage digestion tanks (0.2–5.4 ng Se/m^3) and Jiang and Robberecht[10] in air samples of various aquatic environments in Belgium at concentrations of up to 2.4 ng Se/m^3. The detected selenium compounds include dimethyl selenide, dimethyl diselenide and dimethyl selenone. At the present time, however, measurements of vapour-phase selenium speciation are not available for marine areas.

From the investigations known, up to now, it is evident that selenium is susceptible to natural biomethylation under certain environmental conditions.[10,11]. Therefore methylation of inorganic selenium by micro-organisms may be the most probable mechanism for the production of DMSe in sea water. This mechanism is supported by the findings of Cutter and Bruland[27] who have shown the importance of marine biota in the cycling of selenium. On an equatorial transect from 4°N to 8°S at 160°W they found elevated nitrate and selenate concentrations in surface waters, while selenite concentrations were very low. Selenite is known to be preferentially removed by biological activity.[28] Because sulfur and selenium follow similar biochemical pathways a similar way of formation for DMS and DMSe can be assumed. As already discussed, DMSP is known to be the precursor of DMS. The possible existence of a selenium analogue of DMSP has already been taken into consideration by Lovelock[1] because marine algae are known to produce an arsenic analogue of the phosphor compound cholin.

Our few measurements are not sufficient to calculate a selenium flux, but they support the theory of a natural vapour-phase selenium flux from the ocean to the atmosphere. Based on determinations of particulate selenium in the atmosphere in the North Pacific, Mosher and Duce[28] estimated the marine biosphere flux to be $(5–8) \times 10^9$ g Se/yr. The evidence of DMSe in sea water is a significant contribution to a better knowledge of the natural selenium cycle in the environment. This also contributes to the cycling of selenium in the atmosphere, because gas-to-particle conversion of the DMSe compound may explain the remarkably uniform distribution

of selenium in the atmosphere and its anomalous enrichment in the particulate phase observed in remote marine areas.[28–30]

Determination of CH_3I and Comparison with DMS Data

The determination of CH_3I in sea water is not easy because of the low concentrations and the problematic separation from other halocarbons, especially from Freon 113 ($C_2F_3Cl_3$) and CH_2Cl_2. Therefore, analytical data on the concentration of CH_3I in sea water are also scarce. Figure 6 shows a representative gas chromatogram of an Atlantic sea water sample under the described conditions by means of electron capture detection. CH_3I could be detected in all sea water samples (n = 48) with concentrations ranging from 0.22 to 1.16 ng I/l with a mean of (0.6 ± 0.3) ng I/l. A compilation of published CH_3I results in the literature is given for comparison in Table II. The mean concentration we observed in the Atlantic Ocean is in excellent

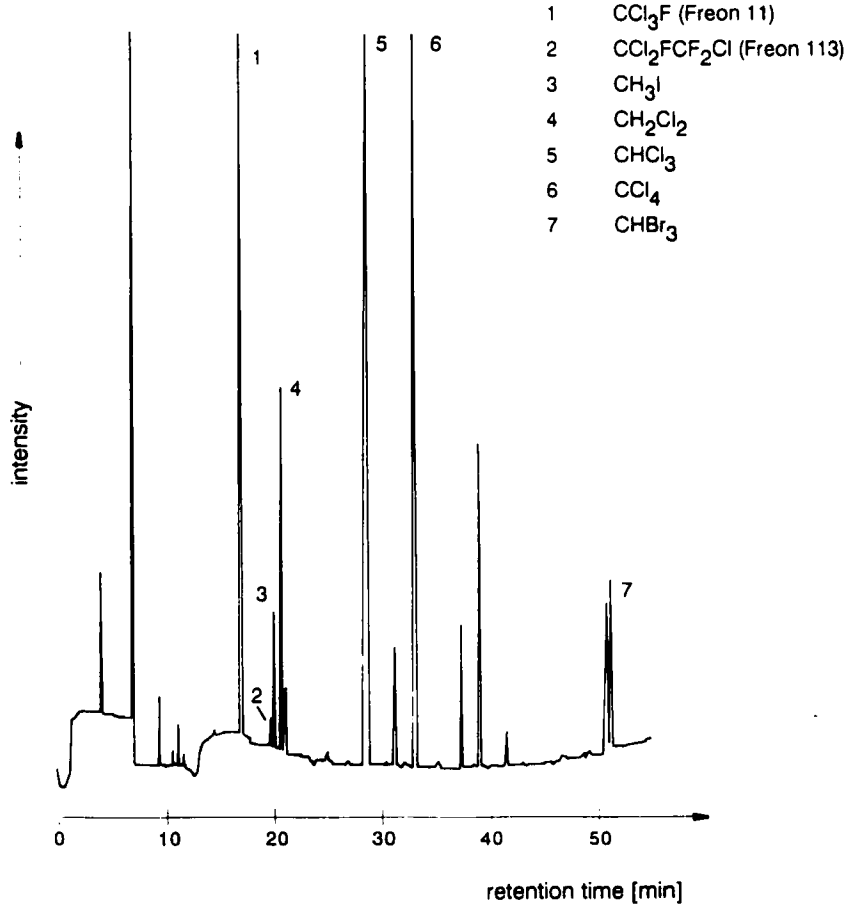

Figure 6 Detection of CH_3I and other halocarbons in sea water with GC-ECD.

Table II CH_3I data measured in sea water

Region	*Concentration (ng I/l)*	*Literature*
Antarctic Peninsula	2.4 ± 1.9	Reifenhäuser[31]
Eastern Pacific	1.5 ± 1.3	Singh *et al.*[32]
Pacific Ocean:		
Oregon (42°–45°N)	0.5 ± 0.1	Rasmussen *et al.*[13]
Morro Bay (35°N)	1.1 ± 0.4	
Atlantic Ocean	0.7	Lovelock[19]
Atlantic Ocean	0.6 ± 0.3	This work

agreement with the CH_3I concentration of 0.7 ng I/l in the open ocean reported by Lovelock.[19] The relatively low CH_3I levels are consistent with other investigations of comparable regions and are due to the moderate bioactivity in the sea water during our cruise. Similar concentrations were observed in the Pacific Ocean near Oregon, a region with equally low to moderate bioactivity.[13] Remarkably higher concentrations were found in sea water samples with high primary production rate, e.g. the Antarctic Peninsula.[31]

Although CH_3I is known to be formed biologically in sea water, its mechanism of formation is not exactly understood. Lovelock suggested that CH_3I is a kelp product, because he measured a 1000-fold higher CH_3I concentration in the surrounding sea water of an Irish Laminaria digitata kelp bed as compared to the open ocean.[19] He proposed biological methylation of iodine as a potential source of oceanic CH_3I. Subsequent studies have shown that many marine macroalgae are able to release numerous volatile halocarbons, e.g. $CHBr_3$ and CH_2Br_2.[14] These bromomethanes are known to be formed via an enzymatic bromination of ketones in marine macroalgae. For CH_3I, however, another mechanism must be assumed, because of the lack of a correlation between CH_3I and the brominated methanes in sea water.[31] On the other hand, Gschwend *et al.* argued a direct release of CH_3I from marine algae.[33] CH_3I may possibly result from a reaction between dimethyl sulfonium ions and iodide, both present in marine algae.[15] This mechanism is supported by the ability of some algae to concentrate large amounts of iodide and the nucleophilic reactivity of the iodide ion.[15] Because dimethyl sulfonium ions are an important intermediate for the biological production of DMS, a similar distribution of CH_3I and DMS in sea water might be expected in this case.

Figure 7 shows the results of our parallel analyses of CH_3I and DMS during the cruise. As can be seen, elevated concentrations of both CH_3I and DMS were obtained towards the end of the cruise between 30°N and 45°N, consistent with the increasing primary production rate in this region. The lowest CH_3I concentrations measured between 20°N and 30°N coincided with the minimum DMS values, too. However, no correlation could be established near the equator. While CH_3I concentrations increased in this region from 0.5 ng I/l up to 1.2 ng I/l, the DMS concentrations remained comparably low at 30–35 ng S/l. Comparison of all data shows no distinct correlation (correlation coefficient, 0.34) between CH_3I and DMS. We have, therefore, to doubt the proposed mechanism of CH_3I formation. However, the relatively low

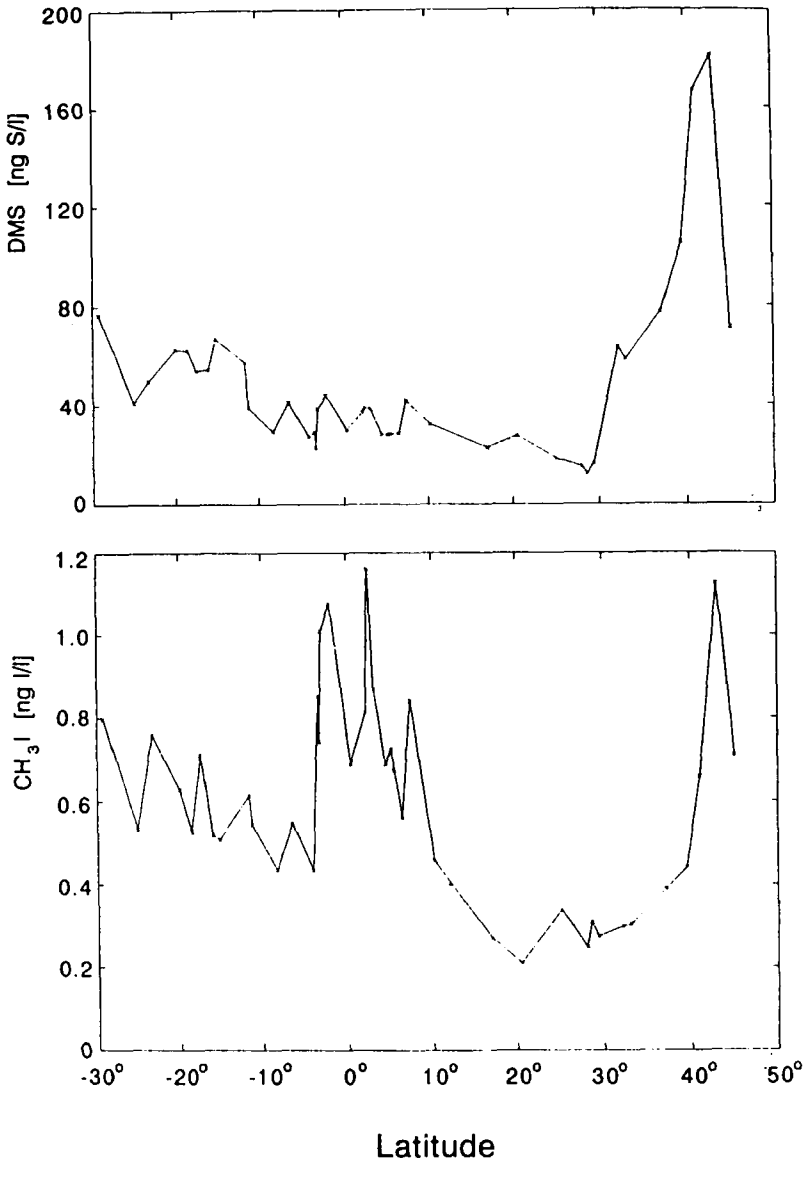

Figure 7 Latitudinal distribution of DMS and CH_3I during the cruise.

and only slightly varying concentrations of both compounds in the sea water samples of the Atlantic Ocean do not allow us to exclude completely this mechanism. Similar investigations in biological productive regions of the world's oceans like the Antarctica, where up to now the highest DMS as well as CH_3I concentrations have been found,[3,31] may provide more detailed information.

Acknowledgements

We are grateful to the '*Alfred-Wegener-Institut für Polar- und Meeresforschung*', Bremerhaven, and to the crew of the polar research vessel '*FS Polarstern*' for all support during the expedition. We further thank Hewlett Packard, Waldbronn, for putting a GC-AED system at our disposal to measure dimethyl selenide, and Mr. R. Weber for his assistance.

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