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Determination of Carbon Disulfide in Natural Waters by Adsorbent Preconcentration and Gas Chromatography with Flame Photometric Detection

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Carbon disulfide (CS_2) in natural waters is determined at the picomolar level by a combination of preconcentration on Carbosieve G and gas chromatography with a flame photometric detector. The volatile carbon disulfide is stripped out of up to 1.8 L of sample by a nitrogen gas stream and preconcentrated on a Carbosieve adsorption tube. This tube is then attached to the gas chromatograph/flame photometric detector system and heated to desorb CS_2, which is collected in a liquid-nitrogen-cooled trap, released by heating the cold trap, separated on a Chromosil 330 column, and detected by a flame photometric detector. The CS_2 peak is recorded and integrated electronically. The detection limit is ca. 1 pmol L^{-1} CS_2. The analytical precision is 9%. Results of analyses of natural water samples are presented.

Carbon disulfide (CS_2) was first observed in seawater by Lovelock (*1*). Since then several attempts have been made to evaluate the geochemical cycle of CS_2 and to identify its role in the global sulfur budget by assessing its atmospheric concentration (*2–7*) and oxidation rates (*7–10*).

Although there have been some analytical methods developed for the determination of atmospheric CS_2, they are not directly applicable to the determination of CS_2 in an aqueous matrix due to lack of analytical sensitivity or problems with chromatographic separation, especially between CS_2 and dimethyl sulfide (DMS) (*11*).

Using gas chromatography with an electron capture detector, Lovelock (*1*) reported that the natural background levels of CS_2 in seawater are on the order of 10 pmol L^{-1} CS_2. On the basis of his report, we first investigated the gas chromatography/electron capture detection (GC/ECD) technique. However, with this method, we experienced serious interference problems with organo halogen species depending on the types of columns utilized for separation. Therefore, we developed a new procedure combining gas chromatography/flame photometric detection (GC/FPD) with the Carbosieve preconcentration method which had been introduced for atmospheric measurements of CS_2 by Tucker et al. (*5*). Here we present the first report of an analytical method for the determination of CS_2 in an aqueous matrix at environmental levels.

EXPERIMENTAL SECTION

Preconcentration Apparatus. A schematic diagram of the preconcentration apparatus is shown in Figure 1A. The two stripping vessels with a capacity of up to 2 L are constructed of Pyrex glass with a 40/35 ground glass fitting. A nitrogen gas stream is introduced into the water samples through fritted glass bubblers. This parallel configuration is efficient for testing the precision and accuracy of the analytical system and also allows the simultaneous purging of two samples to reduce analysis time.

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The outlet of the vessel is connected by Teflon tubing to a potassium carbonate filled (K_2CO_3) drying tube (to prevent water vapor from wetting the Carbosieve adsorbent) followed by the Carbosieve adsorption tube. This adsorption tube serves to preconcentrate the volatile CS_2 from the water samples. The adsorption tube consists of a 6 mm o.d., 4 mm i.d., 20 cm long glass tube in which a 1-cm section of 80–100 mesh Carbosieve G adsorbent (Supelco, Inc., Bellefonte, PA) is held by two small glass wool plugs. The breakthrough volume of this adsorption tube is ca. 50 L.

Analytical Apparatus. A Hewlett-Packard Model 5890 gas chromatograph with a flame photometric detector was interfaced with the CS_2 desorption system. A schematic diagram of the instrument is depicted in Figure 1B. Two independently regulated helium carrier gas streams are introduced into the system. The first He carrier gas stream, which supplies the desorption system, passes a 12.7 mm o.d., 80 cm long stainless steel tube scrubber packed with activated charcoal (50–200 mesh, Fisher Scientific, Pittsburgh, PA) and molecular sieve (Union Carbide type 4A, Fluka Chemical Co., Hauppauge, NY).

The desorption section is composed of an adsorption tube and a heating device made of about 1 m of 5 Ω m^{-1} Chromel wire wrapped around the tube and connected to a variable transformer. The end of the desorption section is connected to a six-way rotary valve (Altex series 202, Rainin Instrument Co., Woburn, MA). When this six-way valve is in the load position, the carrier gas stream from the desorption section (flow rate 100 mL min^{-1}) passes through a 6 mm o.d., 20 cm long glass U-tube filled with 45–60 mesh Chromosorb W-AW-DMCS, which serves to trap cryogenically the CS_2 desorbed from the adsorption tube. At liquid nitrogen temperatures, no breakthrough has been observed with this trap over trapping times of up to 2 h.

A second He stream serves as chromatographic carrier gas and passes through a 2 m long, 3 mm o.d. FEP Teflon column packed with Chromosil 330, a specially treated silica gel (Supelco, Inc., Bellefonte, PA), which is operated isothermally at 50 °C and separates CS_2 from other sulfur compounds, in particular DMS. After cryogenic trapping, the six-way valve is switched to the inject position and the second carrier gas stream transports the eluted CS_2 into the Chromosil 330 column. The end of the column is connected to a flame photometric detector. This detector consists of a Pyrex burner and a photomultiplier system which are similar to those described by Andreae and Barnard (*12*). The optimal gas flow rates for the burner were found to be as follows: H_2, 110 mL min^{-1}; He, 80 mL min^{-1}; and air, 100 mL min^{-1}.

Standards. Liquid standards were prepared by a stepwise procedure. Primary standards were prepared by injecting a known amount of liquid CS_2 into a known amount of ethylene glycol. The flask was sealed and shaken for about 1 h to ensure complete mixing. The resulting solution was further diluted stepwise until working standards with final concentrations of ca. 0.15 pmol of $CS_2/\mu L$ of glycol were obtained. Microliter amounts of this standard solution were then added to degassed water to obtain the working standards. A CS_2 permeation device with a permeation rate of 6.9 ng min^{-1} $S(CS_2)$ at 24 °C (Vici Metronics, Santa Clara, CA) was used as an alternative standard and cross-checked against liquid CS_2 standards. A similar method was used by Andreae and Barnard (*12*) for the preparation of DMS standards.

Operational Procedures. Water samples (up to 1.8 L) are loaded into the stripping vessels, and the drying and adsorption tubes are attached to the outlets. The nitrogen purging gas stream is then passed through the vessels at a flow rate of 600 mL min^{-1}

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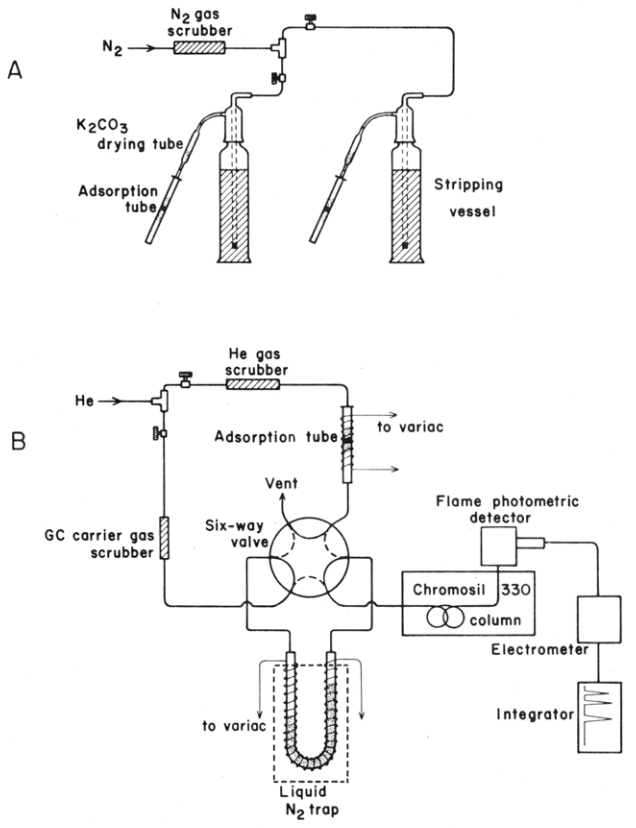

Figure 1. Schematic diagram of (A) the preconcentration apparatus and (B) the analytical apparatus.

(for a 1.8–L sample) for 40 min.

Following the preconcentration step, the adsorption tube is placed in the analytical apparatus and the trap immersed in liquid nitrogen. The adsorption tube is heated to approximately 300 °C for 3 min in order to desorb CS_2. The heating coil on the adsorption tube is then turned off and the liquid nitrogen removed from the trap. Immediately, the six-way valve is switched to the inject position, and the heating coil on the trap is switched on. The CS_2 peak elutes after about 1.3 min.

RESULTS AND DISCUSSION

Carbosieve Preconcentration. Except for stagnant and polluted waters, CS_2 in natural waters is generally present at picomolar levels. With our detection system, quantification of such trace species requires up to 2 L of sample volume. To efficiently and rapidly strip CS_2 out of this large volume of water, a high degassing flow rate must be employed. However, a purging system with a flow rate of greater than 150 mL min^{-1} cannot be directly combined with the chromatographic column (e.g., in the manner described by Andreae and Barnard (*12*)) due to excessive back pressure. To solve this problem, the Carbosieve preconcentration is performed in an independent purging system. The stripping flow rate is still limited, however, by the density of the adsorption tube packing material and the amount of water captured by the drying tube. In order to maximize stripping efficiency and avoid a safety hazard due to excessive back pressure, the flow rate is kept at or below 650 mL min^{-1}.

Stripping Efficiency. To check the stripping efficiency of the system, glycol standards containing 98.6 pmol of CS_2 were added to 1 L of degassed water, and the amount of CS_2 on the adsorption tubes was measured after 5, 10, 15, 20, 30, 60, and 120 min of stripping at a flow rate of 500 mL min^{-1}. The stripping efficiency for 1.8 L of sample volume was also tested by the same procedure. In this case, a stripping flow rate of 600 mL min^{-1} was used, and the amount of CS_2 adsorbed on the Carbosieve G was measured after 10, 20, 30, 40, 60, 100, and 160 min. The results of both experiments are shown in Table I. From these tests, stripping times of 30 and 40 min appear to result in an essentially quantitative stripping-out of CS_2. Consequently, results reported here are based on stripping times of 30 (1.0 L) and 40 min (1.8 L).

Table I. Results of Stripping Efficiency Test

stripping time, min	cumulative stripping time, min	amt of CS_2 found, pmol of CS_2 mean	amt of CS_2 found, pmol of CS_2 std dev	recovery, cumulative %
(a) 98.6 pmol of CS_2 added to 1 L of degassed water; flow rate, 500 mL min^{-1} (nine replicate samples)				
5	5	72.7	±7.0	73.7
5	10	18.5	±3.2	92.5
5	15	6.2	±2.1	98.8
5	20	2.3	±0.8	101.1
10	30	2.1	±0.8	103.3
30	60	1.9	±0.7	105.2
60	120	<2.0		105.2
(b) 98.6 pmol of CS_2 added to 1.8 L of degassed water; flow rate, 600 mL min^{-1} (four replicate samples)				
10	10	86.5	±7.5	87.7
10	20	10.2	±3.6	98.1
10	30	4.6	±2.0	102.7
10	40	2.6	±0.4	105.4
20	60	<2.0		105.4
40	100	<2.0		105.4
60	160	<2.0		105.4

Table II. Recovery of Standard Additions (39.5 pmol of CS_2) to Seawater Samples (1 L Sample Volume)

sample no.	sample without addition, pmol of CS_2	sample with std added, pmol of CS_2	difference
1	25.7	59.0	33.3
2	18.9	71.4	52.5
3	12.2	55.2	43.0
4	9.8	39.3	29.5
5	11.7	48.3	36.6
6	19.2	51.2	32.0
			37.8 ± 8.6[a]
			95.7 ± 21.8 [b]

[a] Mean and standard deviation. [b] Percent recovery.

Accuracy. The accuracy of this analytical method cannot be directly assessed due to the lack of certified standards in an aqueous matrix. In order to reduce any possible systematic errors, we base our calibrations on the standard addition method. Taking advantage of our parallel purging systems, we made simultaneous determinations with and without the addition of known amounts of CS_2 standards (39.5 pmol of CS_2) to aliquots of samples which contained natural levels of CS_2. Quantitative recoveries of the added amounts of CS_2 were obtained within the uncertainty of the analytical method (Table II).

The accuracy of our method was further assessed by comparing the results obtained from stripping 1-L water samples as described above with the direct analysis of glycol standards, thereby eliminating the effects of matrix composition and stripping efficiency. For this purpose, the concentrated glycol standards were injected directly into a heating device attached to the analytical apparatus. CS_2 is thus volatilized and then detected via the same procedure as described above. Also, known amounts of CS_2 from a permeation standard device were injected through the desorption section and determined in the same manner. The results of this test were compared with those of the Carbosieve preconcentration method applied

Table III. Results of Duplicate Determinations of CS_2 from North Atlantic Seawater Samples Collected on a Cruise of the R/V *Columbus Iselin* (22 April–2 May 1986)

date	time	concn, pmol L^{-1} CS_2 1st	2nd
22 April	1900	18.9	22.3
23 April	1000	14.5	16.7
23 April	1300	46.2	44.5
23 April	1900	11.2	13.7
24 April	1500	7.3	7.3
25 April	0700	63.0	56.8
25 April	0900	31.5	39.2
25 April	1300	8.6	9.5
27 April	0900	9.1	7.6
28 April	1100	46.8	42.0

to aqueous standards and were found to be in good agreement.

Precision. Variability in the determination of CS_2 is estimated based on determinations of 10 duplicate samples shown in Table III. The precision of the analytical system is calculated as 9% by averaging the percent standard deviations (the ratio of the standard deviation to the mean).

Linearity, Detection Limit, and Sensitivity. Typical FPD response relationships, in which the log of the peak area (response) is a linear function of the log of the amount of $S(CS_2)$ detected, have been observed (*13*, *14*). Slopes slightly lower than the theoretical value of 2.0 for the S_2 emission have been calculated. A log–log plot of calibration graphs for CS_2 is linear from the detection limits to about 150 pmol of CS_2 (10 ng of $S(CS_2)$). This range covers most water samples except those from extremely polluted sources.

The detection limit for CS_2 in aqueous samples, defined as twice the level of the instrument noise, varies somewhat from day to day. It is typically ca. 2 pmol of CS_2, corresponding to a concentration of about 1 pmol L^{-1} CS_2 in a 1.8-L sample.

The relationships between detector response and gas flow rates were similar to those found in previous investigations on the determination of DMS by Andreae and Barnard (*12*), who used the same detection system (e.g., variation of the air flow rate affects the sensitivity more than variation of the H_2 flow rate).

Separation and Peak Characteristics. The major separation problem in the determination of CS_2 is due to DMS, which has similar retention characteristics and is present at much higher concentrations than CS_2 in most natural waters, especially seawater. The following columns were found to be capable of separating CS_2 from DMS: Carbopack B/1.5% XE-60/1.0% H_3PO_4; Carbopack B HT 100; Supelpak-S; Chromosil 330; and Silicone DC 550 (all manufactured by Supelco, Inc., Bellefonte, PA). Chromosil 330, a silica gel treated by a proprietary process, was chosen for this study because the CS_2 peak preceded the DMS peak by approximately 0.4 min, which made the separation of CS_2 from large amounts of DMS possible. With the other columns, CS_2 eluted on the tail of the DMS peak.

At a carrier gas flow rate of 100 mL min^{-1} and an oven temperature of 50 °C, the retention times of the sulfur compounds were as follows: 0.7 min for H_2S, 0.8 min for COS, 1.3 min for CS_2, and 1.7 min for DMS. A typical chromatogram obtained from a seawater sample is shown along with that of a standard in Figure 2.

Interferences. Using our separation and detection system, we have not observed any other sulfur compounds interfering with the CS_2 peak. However, we further investigated the recovery rate of the desorption procedures and the possibility of the adsorption of $S(CS_2)$ onto the reaction vessels or tubing surfaces as potential causes of positive and/or negative interferences.

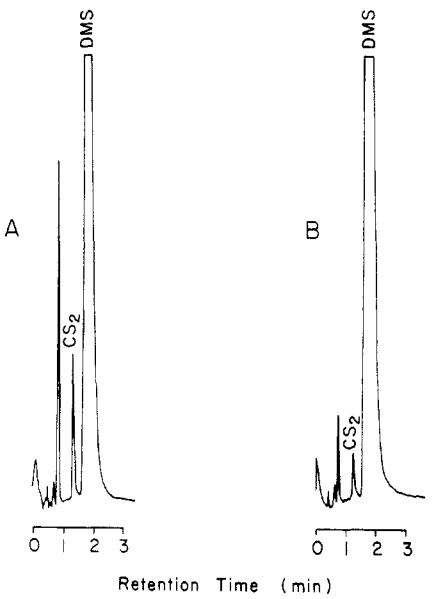

Figure 2. (A) Chromatogram from a standard containing 19.7 pmol L^{-1} CS_2. (B) Chromatogram from North Atlantic surface seawater with concentration of 3.6 pmol L^{-1} CS_2 (sampling time: 2 May 1986, 2100 EDT; position: 27°03.4′N, 79°35.8′W).

Table IV. Effect of Storage on the Concentration of CS_2 in Seawater Samples

storage time, h	no. of samples	concn, pmol L^{-1} CS_2 av	std dev
0	2	55.8	
24	8	49.4	7.0
48	10	54.6	6.5

Table V. CS_2 Concentrations in Some Environmental Samples

sampling location and time	no. of samples	concn, pmol L^{-1} CS_2 (range)
open ocean surface seawater of the North Atlantic and the Sargasso Sea (22–26 April 1986)	65	5.2 ± 3.1 (1.2–14.2)
continental shelf waters along the eastern coast of the United States (25–45°N; 27 April–2 May 1986)	47	16.8 ± 11.5 (2.8–60.0)
St. Marks Estuary, Florida (8–9 April 1986)	6	103.0 ± 20.0 (73.3–117)
Ochlockonee Bay Estuary, FL (23 Feb 1986)	7	31.8 ± 7.8 (20.6–42.1)
Lake Bradford, Tallahassee, FL (22 May 1986)	4	43.0 ± 7.4 (35.2–50.5)

By use of a permeation device, the recovery rate of CS_2 was checked via three different procedures: (1) injection of known amounts of CS_2 onto a Carbosieve adsorption tube through a glass T injection port placed in front of the tube, desorbing CS_2 by heat, collecting CS_2 by a liquid-nitrogen-cooled trap, and detection by GC/FPD; (2) injection directly into the desorption section in the absence of an adsorption tube, followed by the same detecting procedure; (3) direct injection to the GC/FPD through the injection port of the GC without using the cold trap. We observed the same result in each case, demonstrating that no losses occurred in the desorption and trapping system.

The possibility of adsorption loss of $S(CS_2)$ by the glass or tubing surfaces in the stripping system was also tested by

injecting known amounts of gaseous standards into the purging gas upstream of the stripping flask. The recovery rate in this test was also quantitative.

Sample Storage. Seawater samples collected from coastal locations were stored in 1-L glass bottles. The bottles had been previously rinsed with double-deionized water and baked overnight in a drying oven at about 180 °C. In order to eliminate partitioning of CS_2 into the head space, the bottles were filled to the top. Storage experiments in the laboratory showed that there was no significant change in CS_2 content over a 24–48-h period (Table IV). Aboard an oceanographic research vessel, samples were analyzed within 8–10 h.

Analysis of Environmental Samples. This method of analysis has been primarily applied to seawater samples; however, it has also been extended to various other natural water samples. The results are shown in Table V. We have found that CS_2 is ubiquitous in natural waters. The average concentration of CS_2 in the open ocean is slightly lower than the value of 6.9 pmol L^{-1} CS_2 found by Lovelock (*1*).

Registry No. CS_2, 75-15-0; H_2O, 7732-18-5.

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Influence of Sorption Processes on Aluminum Determinations in Acidic Waters

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Progressive removal of particles from freshwater samples by filtration using various pore diameter polycarbonate capillary membranes (0.4, 0.1, 0.05, and 0.015 μm) caused a reduction in the levels of labile aluminum (0–23%), as detected with pyrocatechol violet (PCV), in the filtrates. Removal of aluminum adsorbed onto suspended solids and aluminum losses through adsorption onto the membranes are thought to be responsible for these observations. Losses of aluminum during filtration of freshwater samples were evaluated by filtration of particle-free synthetic solutions and found to be <10%. Experiments with a sample of Na-illite showed that aluminum adsorbed thereon is partially labile and detectable with PCV in synthetic and natural solutions. It appears that for freshwater samples with high solid surface to aluminum ratios, a significant fraction of the experimentally determined monomeric or inorganic monomeric aluminum may actually be adsorbed aluminum.

The continuing acidification of soils with low buffering capacity has led to an increase in the mobilization of aluminum from soils into freshwater systems (*1*, *2*). A detailed knowledge of aluminum speciation in acidified waters is required for the elucidation of aluminum transport mechanisms (*3*, *4*) and interpretation of aluminum toxicological data (*5*). However, the complexity of the aqueous chemistry of aluminum renders this difficult (*6*, *7*).

The direct detection of specific forms of aluminum is not possible at present, this makes the use of equilibrium computational models attractive as a means of describing aluminum speciation (*6*, *8*, *9*). Their application to this end with respect to natural water systems is, however, presently restricted by the limited availability of stability constants for sorption equilibria and complexes of aluminum and other metals with humic acids (HA). It is also doubtful as to whether certain bodies of natural water are in chemical equilibrium with respect to dissolution and precipitation reactions, particularly during storm surges and snow melt (*3*, *4*, *10*). These problems render an experimental approach to the determination of various aluminum species more appropriate, despite the fact that storage may affect the chemistry of samples that were not in equilibrium at the time of collection. Furthermore, such an approach relies on operational definitions which are only appropriate for particular conditions and which may give little or no resolution between chemical species of a similar kind (*11*).

The simplest analytical classification of aluminum consists of separating "dissolved" and "particulate" forms of aluminum by filtration of a sample aliquot through a membrane of some suitable pore diameter (typically 0.1 and 0.45 μm), both sample and filtrate can subsequently be acidified prior to total aluminum analysis or be directly reacted with a strong aluminum complexing agent for a prescribed period of time (*12*, *13*). A more widely used scheme (*14*) involves the passage of a water sample through a column packed with an ion exchange resin capable of retaining labile aluminum species. The difference in concentration of aluminum present in the sample, determined colorimetrically, prior and subsequent to ion exchange was defined (*5*) as being the inorganic monomeric aluminum fraction, Al_i, which herein will be referred to as exchangeable aluminum.

Ion exchange resins employed in aluminum speciation schemes require careful preconditioning with respect to pH and ionic strength so that modification of solution equilibria

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