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Field sampling and analysis of volatile reduced sulphur compounds in air, water and wet sediments by cryogenic trapping and gas chromatography☆

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ABSTRACT

A method for the simultaneous analysis of volatile reduced sulphur species such as hydrogen sulphide, carbonyl sulphide, methanethiol, dimethyl sulphide, carbon disulphide and dimethyl disulphide in air, water and wet sediments is described. In the atmosphere these compounds are preconcentrated by pumping air through a U-shaped cryogenic trap cooled with liquid argon. In waters and sediment pore waters they are concentrated by nitrogen purging and cryo-trap condensation. The trap is then connected on-line to a field-portable gas chromatograph provided with a secondary cryofocusing trap and a flame photometric detector. Detection limits less than or equal to 10 pg S/l (air), 1 ng S/l (water) and 10 pg S/g (wet sediment) are achieved for individual compounds. The variation in the quantitative results for water analyses is less than 7%, with the only exception being methanethiol (20%). Examples of application to air, water and wet sediment samples from a stratified karstic lake and a coastal saltern pond are shown.

INTRODUCTION

In the last decade, the number of analytical developments for the determination of volatile reduced sulphur compounds (VSCs) has increased considerably. The methods described are devoted to the study of different natural systems and involve a preconcentration step generally followed by gas chromatographic separation on either capillary [1,2] or packed [3,4] columns. Poor recoveries were obtained with preconcentration by adsorption onto solid surfaces [1,5,6], except when the adsorbent columns were kept at low temperatures [4]. Cryogenic trapping affords better results, being the technique of choice in several studies of air and water samples [2,3]. However, only some of these studies concern the whole set of VSCs (*e.g.* refs. 1, 3 and 5), many of them being only devoted to the analysis of one or two species (*e.g.* ref. 7). Likewise, very few approaches have addressed the determination of VSCs in air, water and sediment pore water [8].

The difficulties in the overall analysis of the VSC mixtures arise from the different properties of their components, such as volatility, polarity and reactivity. Furthermore, the concentrations of the individual species may range over spans as large as 10^{-3}–10^{5} ppt (w/w), involving diverse interference problems between major and minor constituents. The differences in sample matrix represent an additional difficulty which tends to restrict the range of application of the methods and requires dedicated handling procedures. However, these analytical problems are faced with the need for the study of the distribution

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and behaviour of all VSCs in the principal environmental compartments, namely air, water and sediments, for a better understanding of the mechanisms involved in the biogeochemical cycling of sulphur [9].

In order to contribute to a comprehensive description of VSC occurrence in the marine and continental environments we present here an analytical method for the determination of hydrogen sulphide (H_2S), carbonyl sulphide (COS), methanethiol (MeSH), dimethyl sulphide (DMS), carbon disulphide (CS_2) and dimethyl disulphide (DMDS) in air, water and sediment pore water samples, including procedures adapted for field studies. These analyses are performed by cryogenic preconcentration, separation by packed column gas chromatography (GC) and flame photometric detection (FPD). Sampling efficiencies, sensitivity and precision of the measurements are indicated. The procedures have been tested in natural systems as different as a stratified karstic lake and a shallow hypersaline pond. Characteristic GC profiles corresponding to air, water and sediment pore water collected in these environments are described.

EXPERIMENTAL

Cryogenic enrichment samplers

The traps for cryogenic preconcentration were U-shaped borosilicate glass tubes (20 cm × 10 mm O.D. × 6 mm I.D.). The lower portion of the tubes was packed with quartz wool to increase the condensation surface. The inner tube surfaces and quartz wool were silanized periodically. The traps were conditioned before sampling by nitrogen flushing under vacuum at 60–80°C. Series of five U-tubes were connected to two six-way PTFE rotating valves (Rheodyne, Cotati, CA, USA) by means of 0.16-cm PTFE tubing. Each loop was selected by setting both the inlet and the outlet valves to the required position. One position was short-circuited, allowing the loops to be closed without interrupting the gas flow. Further details on this cryogenic system are described elsewhere [10].

Field sampling and preconcentration

Air. Prior to sampling the U-shaped tubes were immersed in liquid argon. Ambient air samples were collected by connecting the cryogenic trap to a portable pump (Grinyo Rotamix, L'Hospitalet de Llobregat, Catalonia, Spain) and switching the six-way PTFE valves to select the appropriate loop. Air volumes of 1–10 l were drawn through the traps at flow-rates of 150–300 ml/min. After collection, the valves were switched either back to the closed position or to the next loop position for further sampling. The loaded traps were kept closed and under liquid argon until chromatographic analysis, which was performed within the following 2 h.

Water. Water samples were collected in dark, silanized glass bottles that were completely filled and tightly sealed to minimize headspace and air entrance. The samples were stored at 4°C in the dark and analysed within 1–8 h after sampling. The VSCs were determined in 1–50 ml aliquots, which were transferred to a bubbling flask, through a PTFE-coated septum, and purged with a nitrogen stream supplied through a fritted glass diffuser. The stripped volatile compounds were collected in a cryogenic trap as described for the air samples. The bubbling flask was periodically silanized. In the case of small subsample volumes, these were brought to 50 ml by dilution with degassed Milli-Q water. In waters with a high content of suspended particles, the subsamples were filtered through GF/F (Whatman, Maidstone, UK) prior to injection into the flask.

Sediment pore water. Small sediment cores were collected with 10 cm × 2 cm I.D. polyethylene cylinders and frozen immediately under liquid argon. In the laboratory, the cores were carefully sliced in millimetre layers. Each slice was then immersed in a 25-ml spinning tube filled to the brim with degassed water medium that contained a buffered Milli-Q water solution having similar alkalinity and salinity to the values measured in the overlying water. The tube was plugged with a PTFE-coated septum held with a holed screw cap. Homogenization was achieved by shaking for 3 min. Then, the samples were spun down at 4100 rpm for 10 min (2800 *g*). After centrifugation the supernatant solution was

taken by suction with a syringe while nitrogen was simultaneously introduced for restoration of the removed pressure. These water solutions were analysed as described above for water samples.

Blanks. Control blanks were periodically analysed. Volumes of 50 ml of Milli-Q water, previously degassed by flushing with nitrogen, were purged and analysed as an actual sample. Normally, no sulphur compounds were observed above the detection limit. Only small amounts of COS and CS_2 were detected in some cases, when the quality of the purging nitrogen was not adequate.

Gas chromatography

A portable gas chromatograph developed by W. Haunold, University of Frankfurt [10], was used for the *in situ* analysis of volatile reduced sulphur compounds. This instrument was equipped with an FPD (Perkin-Elmer, Norwalk, CT, USA) and a Hewlett-Packard Model 3393A integrator. The optimal detector gas flow-rates were 95 and 170 ml/min for hydrogen (99.999% quality) and synthetic air, respectively. The carrier gas was 99.999% quality nitrogen, additionally purified by passage through molecular sieves, Oxysorb and cryogenic traps. The sulphur components were separated on a 1.4 m × 0.32 cm O.D. Teflon (FEP) column packed with 63–200 μm Carbopack BHT 100 (Supelco, Bellefonte, PA, USA). Column heating and cooling were performed with Peltier elements. The column was conditioned overnight at 100°C with carrier gas at a flow-rate of 20 ml/min. Almost baseline separation of H_2S, COS, CH_3SH, DMS, CS_2 and DMDS was achieved using a temperature programme from −5°C up to 100°C at 30°C/min, with an initial 0.5-min delay and 8 min hold time at the end. Carrier flow-rate was 19 ml/min.

Cryofocusing and injection

A small second glass loop (25 cm × 1.5 mm I.D.) was located between the injection valve of the gas chromatograph and the column. This secondary loop has been demonstrated to be useful for cryofocusing and separation of the VSC from co-trapped water [2]. Before analysis, the sampling trap was connected to the GC injection valves and the lines were purged with nitrogen for 2–3 min. For injection, the GC valve was switched to the injection position, the valves of the selected sample loop were open and the liquid argon was replaced quickly by hot water (60–70°C). Then, the desorbed gases were brought by the carrier gas into the cryofocusing trap, which was immersed in liquid argon. After 1.5 min, the sample cold trap valves were switched back to the closed position so that the carrier gas flowed directly to the cryofocusing trap without going through the sample loop. This desorption time allowed a complete transfer of the volatile components with a minimal load of water vapour [3]. The VSCs were finally introduced into the GC column by heating the secondary loop with a hot water bath. The GC temperature programme was started at this point.

Calibration

Calibration was performed using certified permeation tubes containing H_2S, COS, CH_3SH, DMS, CS_2 and DMDS (Vici Metronics, Santa Clara, CA, USA). The gaseous standards were obtained in a permeation apparatus, keeping the tubes in glass vessels at a constant temperature of 30.0 ± 0.1°C and under continuous nitrogen flow. Variable volumes of the outcoming nitrogen stream were taken with gas-tight syringes and injected through a septum into a PTFE line connected to the cryofocusing trap of the gas chromatograph.

RESULTS AND DISCUSSION

Cryogenic trapping

Safe sample volumes. Experiments to establish the optimal conditions for cryogenic preconcentration were carried out. The permeation devices were used to generate VSC mixtures with concentrations representative of those found in sulphur-rich atmospheres. These mixtures were produced in a 25-l dilution chamber flowed with nitrogen. The outlet of the chamber was connected to two traps in serial arrangement. The

trapping efficiency was tested twice by collecting volumes of about 1 and 5 l of the outcoming nitrogen at 300 and 340 ml/min, respectively. In both cases no VSC traces were detected in the second trap for a total S of 10 ng. Nevertheless, in order to ensure a complete trapping, flow-rates lower than 300 ml/min were used in the regular field analyses.

Water interferences. Purge stream clogging in the cryo-trap is a common problem in VSC water analyses and results from the freezing of the water vapour carried by the stripping gas. Significant amounts of water are also trapped in the analysis of air samples with a high humidity content. Several methods have been developed to remove water vapour from the sample stream before reaching the cryo-trap, including absorption with hygroscopic salts [6,7] and Nafion driers (ref. 11 and references therein). Both systems have been successfully applied to the determination of DMS in humid air and water samples [6,7,12]. However, their suitability for the whole set of VSCs is still controversial because at low concentrations losses of one or more components are usually observed [1,3,4,11].

Driers were therefore not considered in the development of the analytical procedures of the present study. Clogging was avoided by optimization of both the stripping flow-rate and the depth at which the glass loop was immersed in liquid argon. At a water-saturated nitrogen flow-rate of 150 ml/min, no clogging occurred after 20 min of sampling. Higher flow-rates resulted in ice blocking of the cold trap after 10–15 min. On the other hand, the sample loop was immersed in liquid argon up to one half of its height. In this way, ice was accumulated in the upper portion of the wide loop and not in the narrower, preceding PTFE tube.

Another problem associated with the presence of water in the samples is the gradual deactivation of the chromatographic column after repeated VSC analysis. In the present study water entrance into the GC was minimized by means of the controlled desorption and cryofocusing method described in the Experimental section. The column was, however, periodically reconditioned by heating to 100°C for 1 h.

Stripping efficiency

The stripping efficiency of the purge system for water and sediment pore water samples was determined. Owing to the difficulty in preparing reliable standard solutions with gas components, representative real samples containing all the VSCs of interest were used as test solutions. Volumes of 50 ml of sample were sequentially purged for three periods of 10 min. The stripping gas flow was 150 ml/min. The components released were collected in three different traps corresponding to each period. Recoveries of 100% for most of the components were achieved within 20 min. Only in one case were traces of H_2S detected after 30 min.

Sensitivity and precision of the method

The detection limits of the chromatographic system, defined as signal-to-noise ratios of 2 for the different compounds of interest, are displayed in Table I. The values are similar to those reported previously for methods based on FPD [3,5,7]. The precision of the chromatographic method was determined by repeated injection of standards (four replicates) at the whole range of the response curve. The resulting mean standard deviations and the variation ranges are shown in Table I. Minimal standard deviations were obtained within the 0.5–100 ng S range. As expected, the highest variations were observed near the detection limit. The precision of the entire water sample procedure was determined by analysis of five replicates of a representative sample. Standard deviations are also included in Table I.

Identification and quantitation

Peak identifications were performed by retention time comparison between the GC traces of samples and standard mixtures. The quantitative composition of the reference mixtures was set by adequate operation of the permeation device. These mixtures were repeatedly injected between samples. Calibration curves for each VSC of interest were obtained prior to sample analysis.

The non-linearity of the FPD signal is illus-

TABLE I

DETECTION LIMITS AND PRECISION IN THE ANALYSIS OF AIR, WATER AND SEDIMENT PORE WATER

n.d. = Not determined.

	Detection limits				Precision (% of standard deviation)		
	Absolute (pg S)	5 l air sample (pg S/l)	50 ml water sample (ng S/l)	5 g wet sediment sample (pg S/g)	Gaseous standard mixtures		Water sample replicates
					Mean	Range	
H_2S	40	8	0.8	8	7	1–18	7
COS	25	5	0.5	5	7	0.1–13	5
MeSH	50	10	1.0	10	7	1–15	20
DMS	25	5	0.5	5	6	1–17	6
CS_2	15	3	0.3	3	6	1–16	2
DMDS	10	2	0.2	2	7	4–13	n.d.

trated in Fig. 1, where peak areas *versus* injected masses of sulphur are represented for COS and DMS. The chemiluminescence is generally proportional to $[S]^n$, where S is the amount of sulphur reaching the detector and n ideally equals 2 [13]. Accordingly, linearized plots of log (area) *vs.* log[S] have commonly been used for quantitation (Fig. 1). These plots flatten in the upper portion of the linearized response, which is probably due to analyte autoquenching when large amounts of a sulphur species reach the flame [13]. Obviously, quantitation was only performed within the linearity range.

Application to environmental samples

Field measurements were conducted in a variety of natural environments. Representative chromatograms of VSC in air and water column (from the surface to the deep layer) of a karstic monomictic lake (Cisó, Catalonia, Spain) are shown in Fig. 2. The highest concentrations were found in the anoxic sulphide-rich hypolimnion (3 m depth), where the predominant organic VSCs were MeSH (40 μg S/l) and COS (15 μg S/l) occurring together with very high H_2S amounts generated by sulphate reduction in the bottom part of the lake. Large amounts of CS_2 (34 μg S/l) were occasionally observed. These concentrations decreased sharply in the metalimnion (1.6 m), where MeSH and COS occurred in the 50 ng S/l level. In the oxic epilimnion (0.5 m), the only VSC observed, in addition to H_2S, was COS, which was found at concentration levels of 18 ng S/l. Consistently, COS was the only organic VSC detected in the air over the lake, at a concentration of 0.8 ng S/l, which is one-half of the mean value in the lower troposphere [14]. In brief, in the stratified Ciso Lake system VSC concentrations in the hypolimnion are extremely high, but an elevated bacterial sulphur consumption seems to occur in the metalimnion, considerably decreasing the VSC output to the atmosphere.

One representative gas chromatogram of a water sample from a shallow coastal salt marsh is displayed in Fig. 3A. The VSC composition was clearly dominated by DMS (124 ng S/l). This concentration is in good agreement with values reported for marine coastal areas [15] but somewhat lower than levels found in other salt ponds [16].

The vertical VSC distribution in microbial mats from several solar saltern ponds has also been studied. Enhanced VSC emission due to the osmotic shock of the living organisms was prevented by sediment suspension in water solutions of alkalinity and salinity values similar to

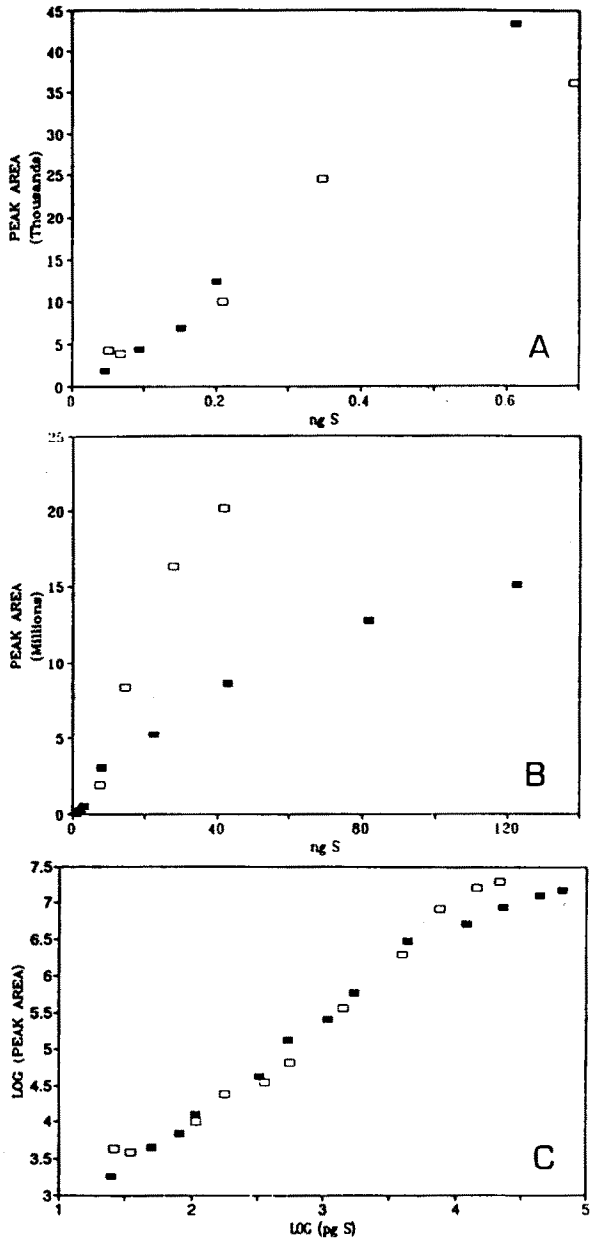

Fig. 1. Characteristic non-linear (A and B) and linearized (C) plots of FPD response *vs.* injected amount of sulphur as (■) COS and (□) DMS. (A) Peak area *vs.* weight of S in the 0.05–0.7 ng range. (B) Peak area *vs.* weight of S in the 1–120 ng range. (C) Log(peak area) *vs.* log(pgS) in the 0.05–120 ng range.

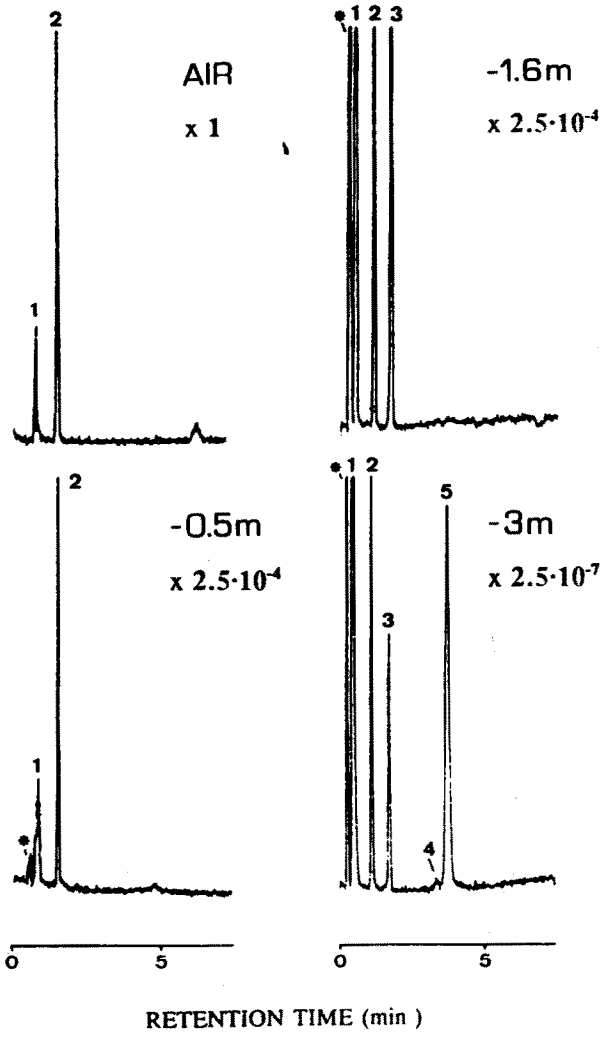

Fig. 2. Gas chromatograms of volatile sulphur compounds in the water column (0.5, 1.6 and 3 m depth) and adjacent air layer of Lake Ciso. Sample dilution is indicated as multiplying factors referred to the air sample. Peak assignments as follows: 1 = H_2S; 2 = COS; 3 = MeSH; 4 = DMS; 5 = CS_2; * = CO_2.

those in the overlying waters. The GC trace resulting from the 3–6 mm depth layer of a cyanobacterial mat essentially composed of *Aphanotece halophytica* is shown in Fig. 3B. This benthic community exhibits a VSC composition very distinct from that observed in the overlying water. In particular, the DMS content is very low, which may be due to either a poor capacity to produce the precursor, dimethylsulphonium propionate, or a strong DMS consumption within the mat system [17]. The difference between the water column and the underlying

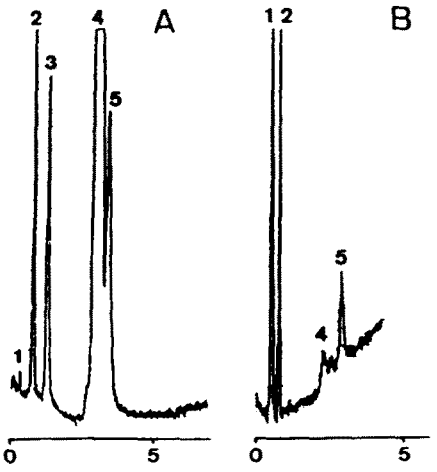

Fig. 3. Gas chromatograms of water (A) and sediment pore water (B) samples from an hypersaline pond containing an *Aphanotece halophytica* mat. Peak assignments as in Fig. 2.

sedimentary benthic community prompts the need for measurements in the diverse compartments of the same natural environment and the development of suitable technology to achieve this goal.

CONCLUSIONS

The methodology presented here enables the collection and simultaneous analysis of trace amounts of H_2S, COS, MeSH, DMS, CS_2 and DMDS in diverse types of environmental samples. Reliable determinations of VSCs in air, waters, and sediment pore waters are achieved with procedures derived from minor modifications of a basic analytical method. The use of cryogenic enrichment traps followed by gas chromatography in a portable apparatus enables the analysis close to the field site, thus minimizing storage times. The VSCs are efficiently separated from bulk co-trapped water by means of cryofocusing in a second cold trap, avoiding possible losses associated with the use of drying devices. This technique has been successfully applied to field studies of VSCs in salt ponds and stratified freshwater lakes.

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