Journal of Chromatography, 445 (1988) 97–105
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 479

CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS OF LOW-BOILING ORGANIC SULPHUR COMPOUNDS IN ANOXIC LAKE-WATER BY CRYOADSORPTION

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(First received November 5th, 1987; revised manuscript received January 28th, 1988)

SUMMARY

A cryoadsorption method using a stripping system with a cryotrap containing Tenax cooled with solid carbondioxide was developed for the analysis of water samples containing low-boiling organic sulphur compounds of biogenic origin. Heat desorption of the traps onto UCON-coated glass capillary columns was possible without modifying the injection system of the gas chromatograph. The method could be practised unchanged with various kinds of gas chromatographs equipped with either a flame photometric detector, a multi-detection system or a mass selective detector. Methanethiol, carbon disulphide and dimethyl sulphide were found to be the low-boiling organic sulphur compounds present in the anoxic layers of the freshwater lake investigated. Samples where interfering amounts of hydrogen sulphide occurred were treated with ion chloride. Disturbance of the procedure by excessive amounts of the methane also present in the anoxic samples was avoided by using solid carbon dioxide rather than liquid nitrogen to cool the cryotraps.

INTRODUCTION

Various methods concerning pre-concentration, separation and detection have been described that enable the analysis of low-boiling organic sulphur compounds in gaseous and aqueous samples by gas chromatography (GC). Mercaptans present in air or head-space samples have been determined by injection of up to 5 ml of gas onto packed columns equipped with either flame ionization[1], photoionization[2], electron-capture[3] or more commonly flame photometric detectors[4]. Packed columns are still recommended for the analysis of low-boiling sulphur compounds from water samples[5,6]. The use of capillary columns in combination with direct injection of 5 ml of gas has been reported for the analysis of sulphur compounds in tobacco smoke[7]. More complicated procedures involving adsorbent[8] or cryogenic[9] pre-concentration of sulphur gases in air with the use of an intermediate cooling loop for transfer of the compounds onto the column of the gas chromatograph have been described. However, these and other techniques like pre-concentration on metallic foils with subsequent flash desorption[10] result in a strict specialization of the instruments used.

0021-9673/88/$03.50

This paper describes a device that allows the analysis of low-boiling organic sulphur compounds present in water samples by means of unmodified gas chromatographs equipped with capillary columns. The sulphur compounds can easily be recorded by a variety of detectors, including a mass-selective detector. The instrumental requirements of the cryotrapping method described are based on an odour trapping tube packed with Tenax TA, which has been described for the analysis of volatile excretion products from algae[11].

EXPERIMENTAL

Sampling

Water samples containing low-boiling organic sulphur compounds were taken from a stratified lake (Schleinsee). To obtain concentration profiles of the sulphur compounds, water was pumped from various depths through glass tubes into 2-l glass bottles as described[12]. After allowing the water to overflow for a minute so as to remove all the air, the bottles were sealed with 3-mm thick silicone septa and screw caps with a 25-mm aperture. Thus no gas space remained and a volume extension of cold water samples was possible. The samples were analyzed after transport to the laboratory within 5 h of being taken.

Construction of the pre-concentration device

The device used to strip the sulphur compounds from the water samples and sorb them after drying in a cryotrap is presented in Fig. 1. Stainless-steel injection

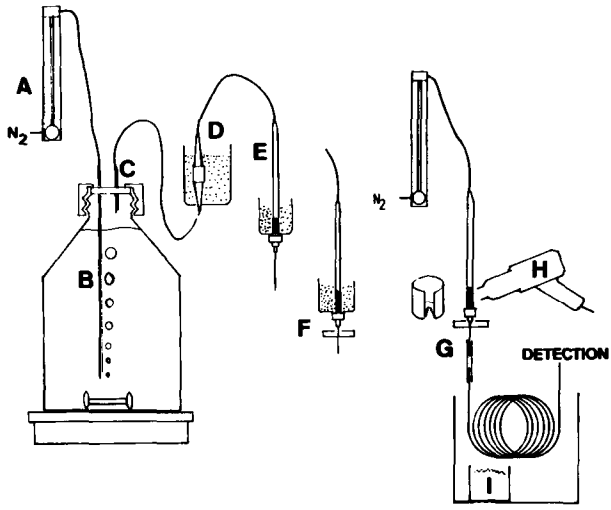

Fig. 1. Cryotrapping system for the pre-concentration of volatile organic sulphur compounds with low boiling points. A = Rotameter for regulation of the nitrogen gas flow (180 ml/min) during purging the water sample and thermal transfer (20 ml/min) of the compounds onto the GC column; B = injection needle; C = exit needle; D = water-trap; E = cryotrap (Tenax TA) both cooled with cold carbon dioxide (packed in flexible polyethylene containers); F = cryotrap in connected to the GC injection system; G = thermal transfer of the compounds onto the capillary column by rapid heating of the cryotrap with a heating gun (H). For the transfer, the oven of the GC was cooled to 0°C. PTFE tubes were fixed to the individual parts of the arrangement with silicone tubing.

needles (150 or and 40 mm in length, 1 mm I.D., 2 mm O.D.) were used to introduce (B) and release (C) the purge gas (nitrogen) through the silicone seeptum. PTFE lines (2 mm O.D., 1.5 mm I.D.) connected by short silicone tubes were used to guide the purge gas from a rotameter (A) to the sample bottle and subsequently via a water-trap (D) to the cryotrap (E). The water-trap was constructed using two 1-ml pipette tips (Gilson, pipetman) connected end-to-end by silicone tubing. The cryotrap consisted of a glass tube packed with 150 mg of Tenax TA (60–80 mesh, Chrompack). A Luer lock was attached to one side as described in detail[11]. Polyethylene containers (100 ml) filled with pulverized solid carbon dioxide were used to cool both the water-trap and the cryotrap. The polyethylene container belonging to the cryotrap was laterally sliced through down to the bottom hole. When the sorption of the sulphur compounds was terminated, the container could rapidly be removed sideways to permit thermal transfer (F,G) of the trapped compounds onto the glass capillary column. Transfer through the injection port was mediated by an injection needle (Henke & Saas, Tuttlingen, F.R.G.) which was fixed to the cryotrap with the Luer lock.

Procedure

The nitrogen purge gas was first used to generate an oxygen-free headspace inside the sealed bottles. Therefore, the exit needle was initially plunged in far enough for a volume of 20 ml of water to be displaced by purge gas. Then the exit needle was withdrawn to a position so that its tip was just below the septum. After loading the containers of both traps with pulverized solid carbon dioxide, stripping was performed for 10 min at a flow-rate of 180 ml/min. To allow the sample bottle and the water-trap to be withdrawn from the gas stream, the cryotrap was directly attached to the nitrogen gas line coming from the rotameter by quickly changing the tube connections. The gas flow was then reduced to 20 ml/min and the cryotrap with its solid carbon dioxide for cooling still in place was connected to the gas chromatograph by introducing the injection needle through the septum of the injection port. The carrier gas of the gas chromatograph was now replaced by the purge gas entering through the cryotrap. After removing the cooling container with the solid carbon dioxide, the cryotrap was immediately heated with an air gun (200°C) for 2 min. When the transfer was finished, the carrier gas valve was opened and the cryotrap lifted off from the injector port. When anaerobic samples with high concentrations of sulphide had to be analyzed, 1.5 g of iron trichloride hexahydrate together with a magnetic stirring bar were added to the bottle with the water sample. The bottle was closed, leaving no gas space below the septum. The iron salt was stirred when the nitrogen headspace was generated, and the sample was treated as described above.

Gas chromatography

Separation. Wall-coated open-tubular (WCOT) glass capillary columns (25 and 50 m) coated with UCON 50 HB 5100 (WGA, Darmstadt, F.R.G.) and mounted in different gas chromatographs (Models Fractovap 2150 and 4200, Carlo Erba, Milan, Italy) were used to separate the volatile sulphur compounds. The entrance splitting ratio was 1:10 during transfer. The initial temperature of the separation (which is also the temperature at the beginning of the transfer) was 0°C. The heating rate was 3°C/min. The separation was terminated after 15 min at 45°C. Nitrogen (25-m col-

umn) and hydrogen (50-m column) with a flow-rate of 2 ml/min were used as the carrier gasses.

Detection. The volatile organic sulphur compounds were detected with sulphur-selective detection (SSD) (Model 250, 394-nm filter, Carlo Erba) after separation on a 25-m column. The SSD was supplied with nitrogen as the make-up gas (30 ml/min). Hydrogen (70 ml/min) and air (100 ml/min) were used as the combustion gases. The photomultiplier was set at 700 V. When signals from a flame ionization detector required for multidetection, the exit of a 50-m column was split in a ratio of 1:1 (with an all-glass exit-splitter) and the branches guided to flame ionization and sulphur-selective detectors maintained at 250 and 200°C, respectively. The temperature of the injection port was 225°C.

Since the dynamics of the SSD were not sufficient to cover the whole range of methanethiol concentrations occurring in amoxic samples, two calibration curves were established. At high concentrations of methanethiol (up to 3 μg/l) the water sample was stripped for 5 min with a purge gas flow of 70 ml/min. At lower concentrations of methanethiol (up to 1.4 μg/l) the stripping time was 10 min at a flow-rate of 180 ml/min.

When mass spectra or single ions were recorded, a mass-selective detector (Model 5970 B, Hewlett-Packard) was used. It was connected to a gas chromatograph (Model 5790 A, Hewlett-Packard) equipped with a 50-m column. Helium was used as the carrier gas and served also as the purge gas as described above.

Calibration. For the quantitation of methanethiol, carbon disulphide and dimethyl sulphide, different amounts of reference compounds were added to distilled water, which was then treated in the same way as the natural samples. To avoid any loss of compounds by evaporation, it was absolutely necessary to handle methanethiol and its dilution in diethyl ether at solid carbon dioxide temperature. Dilution steps were performed with pipetman pipettes which proved to be preferable to glass pipettes, since the latter were immediately dimmed by ice caused by air moisture when handled at solid carbon dioxide temperature.

In order to remove oxygen from the reference water, sodium dithionite was added. A Clarke-type oxygen electrode served to minimize the addition of dithionite. Hydrogen sulphide and ion(III) chloride were added in amounts similar to those present in natural samples.

High concentrations of methanethiol were determined by flame ionization detection.

RESULTS AND DISCUSSION

Trapping efficiency

The procedure for trace analysis of low-boiling organic sulphur compounds was developed with samples from the sediment-near water layers of Lake Schleinsee. During summer stratification, the water samples from the anoxic water layers are rich in methane and hydrogen sulphide. Usually methane bubbles appeared at the inner surface of the sample bottles only a few minutes after filling. At ambient temperature the trapping efficiency of Tenax TA was not sufficient to retain the low-boiling organic sulphur compounds present in the samples. When the Tenax trap was cooled to the temperature of liquid nitrogen as recommended by Tangerman[13], meth-

ane was trapped in such high amounts that explosive evaporations occurred when the trap was heated by hot air for the transfer of the volatile compounds onto the capillary column. Methane did not condense in the Tenax trap when solid carbon dioxide instead of liquid nitrogen was used for cooling. The trapping efficiency of the Tenax tubes cooled with pulverized solid carbon dioxide was enough completely to retain the stripped sulphur compounds, including hydrogen sulphide. This was controlled on one occasion by arranging two identical cryotraps in tandem. No sulphur compounds could be observed in the second trap.

Drying the purging gas

A serious problem with this method of cryotrapping was the elimination of water vapour in the purging gas stream. Chemical drying with inorganic salts had already occasioned negative reports[13] and the results are still controversial. Tangerman[13] recommended calcium chloride as a drying agent for pre-trapping water rather than other salts, such as magnesium sulphate sodium sulphate and sodium carbonate. Andreae and Barnard[5] and Deprez[6] used potassium carbonate as a drying agent. During this study a number of different salts were tested, but all were found to be unsuitable, because traces of water vapour rapidly led to the clogging of the drying agents.

To overcome this problem, we constructed a simple cryogenic water-trap consisting of two plasic pipette tips connected end-to-end by silicone tubing. This water-trap was introduced into the purge gas line and cooled with solid carbon dioxide. It was able to retain up to 100 μl of water from the purging gas. When reference sulphur compounds were added before and after the water-trap, it was shown that the compounds were not retained. This supported observations by Graydon and Grob[14] that only a large surface area in combination with a low temperature results in an efficient retention of low-boiling compounds. Low-boiling compounds were not trapped when only one of the two criteria was fulfilled.

Interference by hydrogen sulphide

The biogenic production of organic sulphur compounds in the anoxic water layers was accompanied by the formation of high concentrations of sulphide. The maximum concentrations observed were as high as 2.5 mg/l[12]. At these high concentrations but also at much lower ones in the μg/l range, sulphide interfered with the SSD signals of the low-boiling organic sulphur compounds (Fig. 4). To reduce the amount of hydrogen sulphide, Deprez *et al.*[6] recommended the addition of mercury chloride and subsequent gravity filtration of the precipitate prior to sparging. However, the addition of iron(III)chloride proved to be superior because the additional step of filtration was then unnecessary and no problems of decontamination arose. Methanethiol was the compound most sensitive to the treatment with iron chloride. A substantial loss of this compound was observed only after incubation for 24 h. A peak of dimethyl disulphide with a retention time of 16 min could then be observed. The concentrations of carbon disulphide and dimethyl sulphide remained almost unchanged. This corresponds with observations on methanethiol concerning its capacity easily to undergo various reactions[15]. The loss of methanethiol with the iron salt is, however, low enough to be tolerated in the incubation time allowed.

Desorption and separation

In order to analyse the cryosorbed low-boiling sulphur compounds by separation on a capillary column they had to be transferred rapidly into the gas chromatography. This was accomplished by heating the cryo-trap with hot air at 200°C, which increased the temperature measured in the centre of the Tenax bed from −76 to +50°C within 10 s. This measurement was performed with a rapidly responding thermoresistance introduced into the Tenax bed. A further 10 s were required in order to obtain the final temperature of 200°C. However, the actual desorption of the compounds occurred in the initial phase of the heating process. In combination with chromatography on a glass capillary column coated with UCON 50 HB 5100, reproducible separations of low-boiling sulphur compounds (carbonyl sulphide, hydrogen sulphide, methanethiol, carbon disulphide, ethanethiol, dimethyl sulphide) were achieved (Fig. 2). Glass capillary columns coated with a polar phase (UCON) were preferred because these made possible separation of low-boiling sulphur compounds at an oven temperature of 0°C. When capillary columns of lower polarity were used, extremely low oven temperatures around −70°C[16] became necessary for narrow peak widths to be obtained. The sulphur compounds were completely separated without tailing on a 50-m glass capillary column coated with UCON 50 HB 5100.

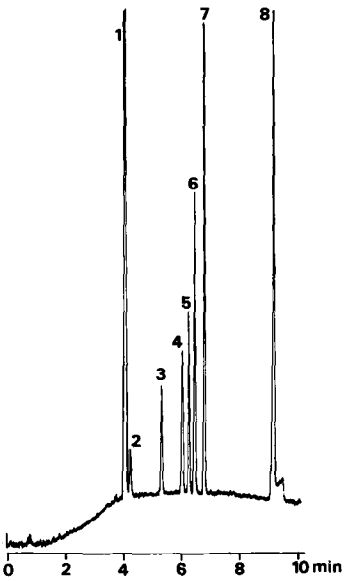

Fig. 2. Gas chromatographic separation of low-boiling organic sulphur compounds. Signals were recorded by sulphur-selective detection (SSD). A 1-μl volume of a reference mixture in *n*-octane was injected into a stream of helium leading to the cryotrap cooled with solid carbon dioxide. Transfer to the gas chromatograph was performed by desorption with hot air at 200°C. A 50-m glass capillary column coated with UCON 50 HB 5100 was used with helium (60 kPa) as the carrier gas. The initial temperature was 0°C, the heating rate of the temperature program 5°C/min. Peaks: 1 = carbonyl sulphide; 2 = hydrogen sulphide; 3 = methanethiol; 4 = carbon disulphide; 5 = ethanethiol; 6 = dimethyl sulphide; 7 = isopropanethiol; 8 = 2-propenethiol.

Identification of the sulphur compounds detected

The SSD signals obtained from samples of the anoxic hypolimnion were identified by retention time analysis and by mass spectrometry. Complete mass spectra were obtained from methanethiol and dimethyl sulphide. Carbon disulphide was identified by retention time analysis and selective detection of the fragment ion at *m/z* 76. Carbonyl sulphide was eluted before sulphide (Fig. 3). Mass spectrometric single-ion detection of the ions at *m/z* 60 and 62 also indicated the presence of this compound in trace concentrations in the sediment-near water layer. Quantitation of carbonyl sulphide was difficult, because of its high rate of hydrolysis, reported to be 4 ng/s[17].

Recovery and sensitivity of the method

The recoveries of the low-boiling sulphur compounds present in the water samples were about 20%. Both the large volume of the sample and the low flow-rate of the purging gas may be responsible for the partial recovery. The large sample volume of 2 l was necessary to reduce the danger of oxidation of the low-boiling sulphur compounds during sampling, transport and work-up. Due to the sensitivity differences of the flame photometric detector to the individual sulphur compounds, carbon disulphide was detectable with the lowest limit (5 ng/l). The detection limit of methanethiol and dimethylsulphide was around 50 ng/l when the stripping was performed for 10 min at a flow-rate of 180 ml/min.

Distribution of the sulphur compounds in the vertical profile

The vertical profile of low-boiling organic sulphur compounds determined in Lake Schleinsee during stratification showed that the occurrence of methanethiol,

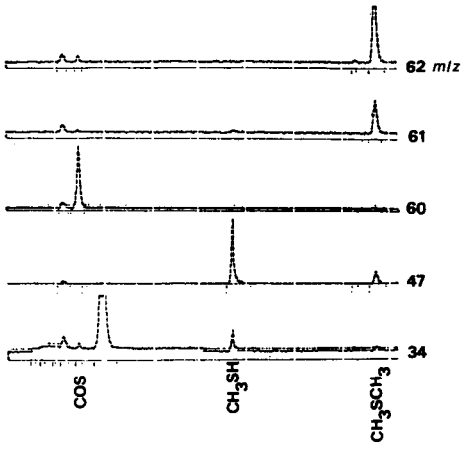

Fig. 3. Gas chromatographic analysis of low-boiling organic sulphur compounds by mass spectrometric detection (single-ion monitoring). The masses (*m/z* 34, 47, 60, 61, 62) were selected to monitor carbonyl sulphide, methanethiol and dimethyl sulphide. The fragment ions *m/z* 47 and 60 were recorded with an attenuation of 11 and 2 respectively. The compounds were separated on a 50-m glass capillary column (UCON 50 HB 5100) using helium as the carrier gas. The sample was taken from the same anoxic layer as in Fig. 5. For other details see Figs. 2 and 4.

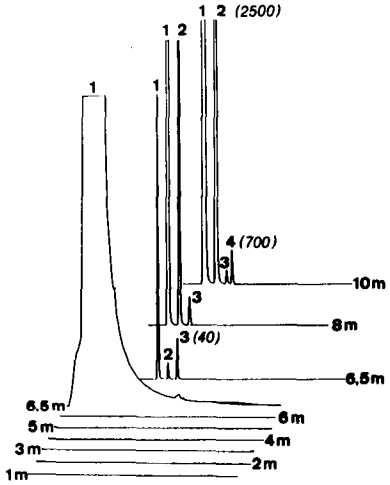

Fig. 4. Gas chromatographic analysis of low-boiling sulphur compounds in a vertical profile of lake Schleinsee after pre-concentration by cryoadsorption. Sulphur-selective detection (SSD) was used for recording the compounds (1 = hydrogen sulphide; 2 = methanethiol; 3 = carbon disulphide, 4 = dimethyl sulphide) which were separated on a 25-m glass capillary column (UCON 50 HB 5100). The traces of the SSD signals obtained are staggered according to the depth from which the water samples were taken. The 6.5-m sample contained high amounts of hydrogen sulphide. The lower trace of the 6.5-m sample presented was analyzed without the addition of iron chloride, the upper trace as those of the 8- and 10-m samples after addition of iron chloride. The numbers in brackets give the maximum concentrations of each compound in ng/l.

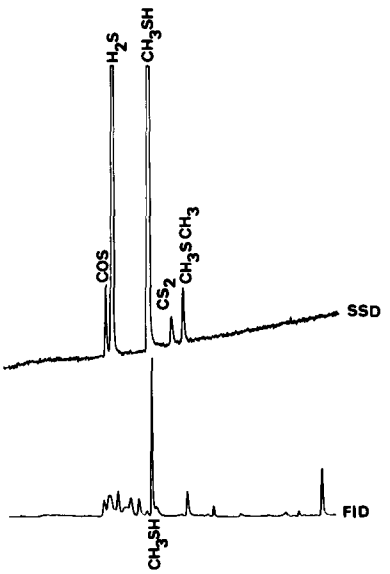

Fig. 5. Gas chromatographic analysis of low-boiling sulphur compounds by multidetection (FID and SSD). The compounds were separated on a 50-m glass capillary column (UCON 50 HB 5100) using hydrogen as the carrier gas. The sample volume, pre-concentration and the transfer onto the column were as in Figs. 2 and 4.

carbon disulphide and dimethyl sulphide was restricted to the anoxic hypolimnion (Fig. 4). Methanethiol was dominant, reaching maximum concentrations of 2–3 μg/l in the deepest water layers. The maximum concentrations of dimethyl sulphide were around 700 ng/l and these were also found in the deepest layer of the vertical profile. The concentrations of carbon disulphide were highest in the upper layers of the anoxic hypolimnion, but never exceeded 50 ng/l. Carbonyl sulphide (Fig. 5) was present in the deepest layers only in trace amounts and does not seem to be of the same order or importance as in the marine environment[18].

CONCLUSIONS

The method described enabled the quantitative trace analysis of methanethiol, carbon disulphide and dimethyl sulphide in anoxic water samples. A cryotrap of Tenax TA cooled with solid carbon dioxide was found to be suitable for efficient trapping of the low-boiling sulphur compounds. Cooling with solid carbon dioxide solved the problem of excessive amounts of methane present in the samples. The method can be practised without modifying the injection system of various gas chromatographs. Capillary columns coated with UCON 50 HB 5100 gave tailing-free separations of the low-boiling sulphur compounds.

ACKNOWLEDGEMENT

This work was supported by the Deutsche Forschungsgemeinschaft.

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