



Headspace solid-phase microextraction for the determination of volatile sulfur compounds in odorous hyper-eutrophic freshwater lakes using gas chromatography with flame photometric detection

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ABSTRACT

A simple and efficient method based on headspace solid-phase microextraction (HS-SPME) followed by gas chromatography coupled to flame photometric detection was developed for the simultaneous determination of five volatile sulfur compounds (VSCs; hydrogen sulfide (H₂S), methanethiol (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)) in hyper-eutrophic freshwater lakes suffering from black water agglomerate. Carboxen/polydimethylsiloxane (CAR/PDMS) fiber was selected for the extraction of VSCs, and various parameters, such as the stirring rate, sample volume, ionic strength, duration and temperature of extraction and the duration and temperature of desorption, were optimized for extraction efficiency. The linearity spanned approximately three orders of magnitude for all of the studied compounds. The method detection limits (MDLs) and method quantification limits (MQLs) ranged from 1.6 to 93.5 ng L⁻¹ and 10 to 500 ng L⁻¹, respectively, depending on the analyzed compound. The reproducibility of the method was between 3.7 and 11.9%, and the recovery was approximately 100%. The developed analytical method was successfully applied to the determination of VSCs in odorous freshwater lakes, and the concentrations of the five target compounds were detected in the 0.33 to 166.60 µg L⁻¹ range.

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1. Introduction

Volatile sulfur compounds (VSCs) have caused great concern due to their offensive odor, low sensory threshold, important role in atmospheric chemistry and their resulting potential to influence the global climate [1–3]. VSCs, such as hydrogen sulfide (H₂S), dimethyl sulfide (DMS), methanethiol (MeSH), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), carbonyl sulfide (OCS), and carbon disulfide (CS₂), are released from natural sources, including oceans, marshes, soils, vegetation, and geothermal and volcanic activity, as well as from anthropogenic activities that involve biogas production, sewage treatment, landfilling, pulp milling, and slaughtering [4–6]. In modern society, eutrophication is a serious problem in freshwater lakes that are extensively used for not only agricultural, fishery and industrial purposes but also as sources of drinking water. The odorous drinking water crisis that occurred in Lake Taihu, Wuxi, China during the summer of 2007 drew public attention for its severe impact on the water supply. The black color and foul smell, known as “black water agglomerate” during the crisis, may have originated from the decomposition of a massive algal bloom triggered by illegal industrial discharge and

inadequately regulated domestic pollution. Black water agglomerate was typically observed in the near-shore area of the lake with massive algal accumulation that lasted for several days during the late spring to the summer of each year. Studies of the Lake Taihu odor episode indicated that H₂S, DMTS, and related alkyl sulfide compounds were the most common VSC species [7,8]. In these previous works, however, the presence of H₂S was only qualitatively confirmed, and only certain VSC species were considered in each study due to the lack of suitable detection methods. Therefore, the task at hand was to develop an economical and operationally feasible method to detect odorous compounds.

Before gas chromatography was widely used in quantitative analysis, chemical method such as titration was mainly employed in the determinations of volatile sulfur compounds [9]. In recent years, with the rapid development of chromatography, VSCs were generally analyzed by gas chromatography (GC) with different detectors. GC coupled to flame ionization (FID) has been the most economical method for detecting volatile organic sulfur compounds such as MeSH, DMS, and DMDS [10,11]. However, this method has seldom been employed in the determination of environmental samples because of its low sensitivity and poor response to VSCs such as H₂S, OCS, and CS₂. For the analysis of a variety of VSCs at trace levels, a wide range of sulfur-selective detectors, including flame photometric detector (FPD) [12], pulsed flame photometric detector (PFPD)

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[13,14], sulfur chemoluminescence detector (SCD)[15], and atomic emission detector (AED)[16], together with a universal mass spectrometry mass selective detector (MSD)[17,18] have been widely applied in VSC analysis. However, in most cases, these instruments are impractical due to technical problems (PFPD and SCD) or high costs (AED and MSD). An FPD, however, is a stable and relatively economical sulfur-selective detector that has been employed in the trace analysis of VSCs in different matrices [19,20]. At very low concentrations (i.e., less than 0.03 nM L^{-1}), FPD has been successfully used in conjunction with a preconcentration step [21].

Preconcentration is essential prior to chromatographic analysis because sulfur compounds are usually found at trace levels, and more importantly, water samples cannot be directly injected into a GC system. The liquid–liquid extraction (LLE) [22], static headspace (HS) [15], and dynamic HS (purge and trap) preconcentration methods had been the most widely used techniques for the determination of sulfur compounds [23,24]. Each of these methods has significant disadvantages, which can include excessive solvent use, low efficiency, or expensive equipment, as well as being tedious. SPME is a recently developed solvent-free enrichment method that combines the sampling and preconcentration of analytes in a single step using a liquid polymeric coating fiber to extract analytes from a variety of both liquid and solid matrices. SPME has also been applied to the analysis of air samples via the extraction of sulfur compounds from air collected in containers or sampling bags [25,26] or extraction in the field [27–29]. The fiber is then directly transferred into the injector of a GC system for thermal desorption and analysis. Conventional SPME is performed by exposing the fiber to a sample matrix [30], although SPME is now mainly applied to the headspace above solid and liquid samples (HS-SPME) because the fiber is susceptible to matrix interference [18,31]. Fiber selection is important to the SPME extraction process, as the varied behavior of different coatings in the analysis of volatile sulfides has been previously demonstrated [32–34].

The objective of this work was to develop a simple and efficient methodology based on HS-SPME-GC/FPD for the simultaneous determination of the five VSCs (H_2S , MeSH, DMS, DMDS, and DMTS) that are mainly responsible for foul odors in eutrophic lakes. Despite that SPME has been previously used for the analysis of volatile alkyl sulfides (VASSs) in wastewater and contaminated groundwater [18,32], a comprehensive study of all parameters that may affect to the analysis of volatile organic sulfur compounds and inorganic species H_2S by HS-SPME-GC/FPD has not yet been carried out. In the present study, a comprehensive study was conducted to optimize the extraction and analytical performance. The optimized method was then applied to samples from Lake Taihu collected during the occurrence of a black water agglomerate in the summer.

2. Experimental

2.1. Reagents and solutions

Standard solutions were obtained for the proper identification of chromatographic peaks. Methanethiol, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide were purchased from Sigma-Aldrich with a purity greater than 98%. Hydrogen sulfide was purchased in a cylinder from Dalian Date Gas Co. Ltd. (Dalian, China). Chromatographically pure methanol was supplied by Merck (Darmstadt, Germany). Other chemicals for routine use were purchased from Sinopharm Chemical Reagent Co. and were of analytical-grade purity.

Individual standard solutions of 2000 mg L^{-1} of each sulfur compound were prepared in methanol and protected from light at -10°C with the exception of hydrogen sulfide, which was prepared by bubbling into methanol immediately prior to use. A global standard solution containing all of the analytes was prepared using each individual stock solution and diluted with methanol. Working solutions used in further studies were freshly prepared by diluting the

global standard solution with doubly distilled water to the required concentrations and stored at 4°C before analysis.

2.2. HS-SPME procedure

The SPME device for manual sampling consisted of a holder assembly and a replaceable fiber, both of which were obtained from Supelco (Bellefonte, PA, USA). SPME fibers coated with StableFlex bonded carboxen/polydimethylsiloxane (CAR/PDMS) of $75 \mu\text{m}$ film thickness were obtained from Supelco. The fibers were conditioned prior to use by heating in the injection port of the chromatographic system under the conditions recommended by the manufacturer. All analyses were performed in 40 mL SPME glass vials sealed with PTFE/silicone septa and stirred with a magnetic stirrer (Guohua HJ-3, China) using PTFE-coated magnetic stir bars ($15 \text{ mm} \times 5 \text{ mm}$ O.D.). Preconcentration of the analytes was performed by exposing the $75 \mu\text{m}$ CAR/PDMS fiber to the sample solution headspace. The parameters that influenced the HS-SPME analysis were studied in this present work, including the stirring rate, sample volume, ionic strength, and duration and temperature of extraction.

2.3. GC-FPD analysis

After preconcentration, the fiber was retracted into the needle and immediately transferred to the inert injection port of an Agilent 7890A gas chromatograph equipped with a flame photometric detection (FPD) system operated in sulfur mode. The optimum SPME desorption temperature and duration were studied to achieve complete desorption of the analytes from the fiber in splitless mode without thermal decomposition of the analytes. The temperature of the detector was set to 250°C , and it was supplied with 50 mL min^{-1} of hydrogen, 65 mL min^{-1} of synthetic air and 30 mL min^{-1} of helium as the auxiliary gas. Separation was performed using a GS-GasPro capillary PLOT column ($60 \text{ m} \times 0.32 \text{ mm}$ I.D., film thickness not specified). Helium was used as the carrier gas at a constant flow rate of 3.0 mL min^{-1} . The column oven temperature was controlled as follows: initial hold at 50°C for 5 min, increase at $25^\circ\text{C min}^{-1}$ to 250°C and hold for 7 min.

2.4. Field sampling

Water samples were taken from Bafang Bay, Lake Taihu in Wuxi, China. The sampling site was located near the western shore of Lake Taihu where algal blooms and black water agglomerate have often appeared during the late spring and summer in recent years. Water samples were collected when the black color and foul smell were observed on July 29, 2011. A PTFE tube was used to pump the water from different depths at 30 cm intervals from the surface to a depth of 150 cm. All samples were stored in 1 L dark glass bottles without headspace, tightly capped with PTFE/silicone septa, and transported in an icebox to a refrigerator. The analyses were completed in duplicate as quickly as possible, and the average values are reported.

3. Results and discussion

3.1. Method development

SPME fibers composed of carboxen and polydimethylsiloxane (CAR/PDMS) with a $75 \mu\text{m}$ coating thickness were selected for the extraction of VSCs based on previous studies [35–37]. The CAR/PDMS fiber extraction process consists of the adsorption of small molecules into micro-pores of the carboxen phase and the PDMS coating, thereby leading to a high capacity for extracting extremely volatile, low-molecular-weight molecules, which includes most VSCs. Therefore, a CAR/PDMS fiber was used for further optimization of VSC extraction.

To optimize the headspace microextraction procedure, the relevant parameters influencing the performance of SPME were considered (i.e., the magnetic stirring rate, sample volume, ionic strength, extraction time, extraction temperature, and desorption conditions including the desorption temperature and desorption duration). All optimization experiments were performed in duplicate, and the average values are reported. Because the FPD response is derived from the emission of two excited sulfur atoms (S_2^*), which corresponds to a second-order response, the FPD response (chromatographic peak area or height) is nearly quadratic with respect to the concentration for all volatile sulfur compounds. Therefore, the square roots of the peak areas obtained by SPME are reported.

3.1.1. Magnetic stirring

To investigate the influence of magnetic stirring on the extraction efficiency, the stirring rate was varied from 0 to 1000 rpm. The results showed that the passage of less-volatile sulfur compounds (DMS, DMDS, and DMTS) to the headspace, and therefore to the fiber, could be accelerated by stirring the liquid sample. This behavior was exemplified by increases in the relative peak areas as the stirring rate was increased from 0 to 750 rpm (Fig. 1). However, the extraction efficiency did not show an appreciable increase for stirring rates greater than 750 rpm. For the more-volatile species (H_2S and MeSH), the extraction efficiencies were independent of the magnetic stirring rate. Therefore, all subsequent experiments were performed using a stirring rate of 750 rpm.

3.1.2. Sample volume

The influence of the sample volume on the SPME was also taken into account. Sample volumes of 5, 10, 15, and 20 mL were placed into 40 mL SPME vials, and the effect of the sample volume on the signal intensity was investigated. A maximum sample volume of 20 mL was used because larger volumes could lead to partial immersion of the fiber in the sample solution, thereby resulting in poor reproducibility and a shorter fiber lifetime. The experimental results showed that the extraction efficiency increased as the sample volume increased (Fig. 2). Thus, a sample volume of 20 mL in 40 mL SPME vials was used in the remaining optimization experiments.

3.1.3. Ionic strength

The influence of the ionic strength of the matrix was studied by adding 0 to 40% NaCl to the samples. The peak areas of DMS, DMDS, and DMTS were found to increase considerably with increasing NaCl content from 0 to 20%, although the peak areas remained approximately constant with a NaCl content of greater than 20% (Fig. 3). In contrast, NaCl did not significantly enhance the signal responses of

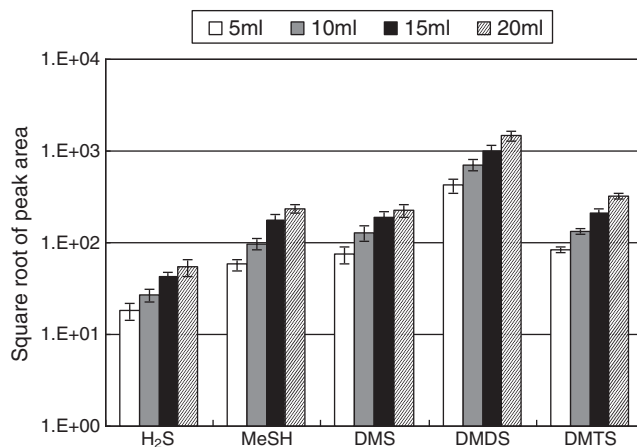


Fig. 2. Effect of the sample volume on the SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

H_2S and MeSH. Therefore, 20% NaCl was subsequently added to all the HS-SPME samples.

3.1.4. Extraction duration and temperature

For the extraction durations trials, a fixed temperature was chosen (40 °C), and the time of extraction was varied. Extraction times of 10, 20, 30, 40, 50, 90, and 120 min were tested for the optimization. As shown in Fig. 4, a significant increase in peak area was observed from 10 to 30 min, and then a smaller increase was observed from 30 to 90 min. At 90 min, the analytes were assumed to have reached equilibrium between the water, gas and fiber phases. With longer extraction times, the peak areas decreased slightly for most compounds. Because the composition of the real samples is more complex than that of standard samples, numerous volatile compounds can compete for adsorption sites on the fiber. Although the FPD is selective for volatile sulfur compounds, the SPME fiber is not similarly selective and will extract a wide range of volatile compounds. When a CAR/PDMS fiber is used to extract analytes from a complex matrix, the porous structure of the fiber can readily become saturated upon prolonged extraction [33]. Once saturation occurs, compounds with a higher affinity for the fiber will essentially displace those compounds with a lower affinity. This phenomenon is well known and is often referred to as competitive adsorption [38,39]. This competition can be minimized with the use of shorter extraction times [33,38]. Moreover, although equilibrium was not reached in 30 min, the obtained response was sufficient for the sulfur compounds studied here. In addition,

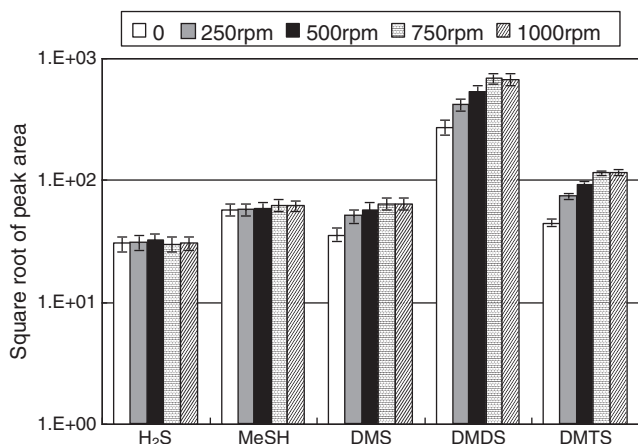


Fig. 1. Effect of the magnetic stirring rate (rpm) on the SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

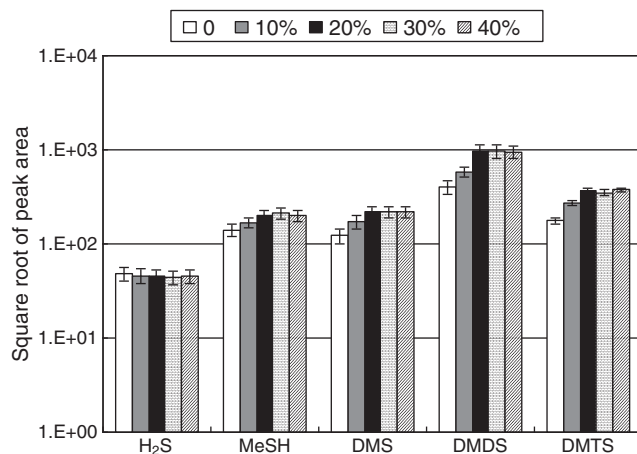


Fig. 3. Influence of the ionic strength (% NaCl addition) on the efficiency of SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

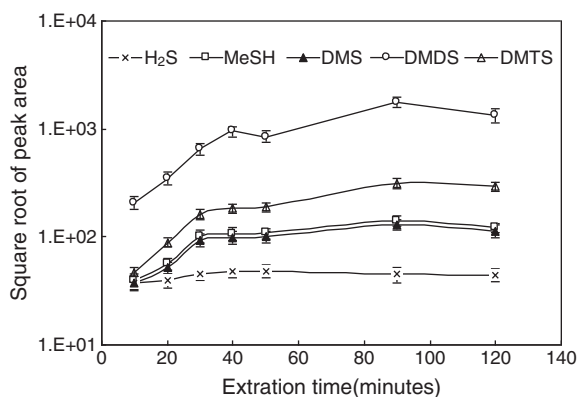


Fig. 4. Effect of the extraction time on the SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

SPME quantification prior to equilibrium has been demonstrated to be feasible provided constant extraction conditions are maintained [40,41]. In addition, the chromatographic run duration was 30 min, and because the shortest successful extraction time is desired, 30 min was chosen as a good compromise between the overall sensitivity and the runtime efficiency. Therefore, a 30 min duration was used for all subsequent extraction experiments.

Extractions were performed at temperatures of 25, 35, 45, and 60 °C at a consistent extraction time of 30 min. Fig. 5 shows that the peak areas increased for DMDS and DMTS, but remained nearly constant for DMS and slightly decreased for H_2S and MeSH, as the temperature increased from 25 to 60 °C. When performing HS-SPME, two opposing factors must be considered to evaluate the effect of temperature in the extraction. Higher temperatures typically increase the volatility of compounds, thus increasing their concentrations in the headspace. However, the distribution of the sample within the fiber ($K_{\text{fiber-headspace}}$) decreases with higher temperatures [42]. For certain highly volatile compounds, such as H_2S and MeSH, the volatility remained nearly constant for all temperatures that were tested. Therefore, elevated temperatures were expected to negatively impact the extraction by the fiber. Conversely, higher temperatures allow less-volatile compounds, such as the larger-molecular-weight compounds DMDS and DMTS, to be more readily released into the headspace. The distribution between the headspace and the fiber was expected to be positively affected, and this effect should increase the extraction efficiency for these less-volatile compounds. Although the relationship between temperature and adsorption rate was different for each of the tested sulfur compounds, the best overall extraction of the target analytes by HS-SPME was achieved at 45 °C.

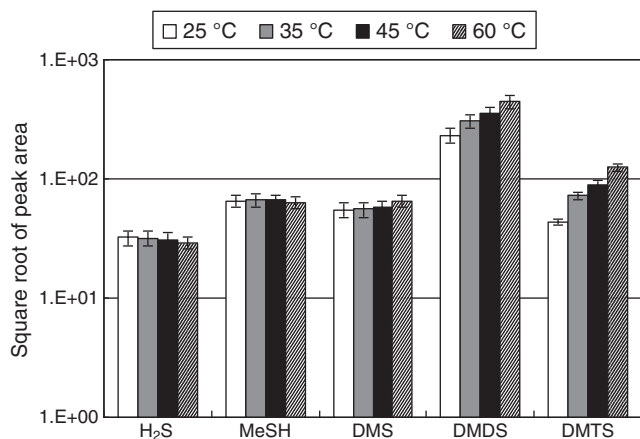


Fig. 5. Effect of the extraction temperature on the SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

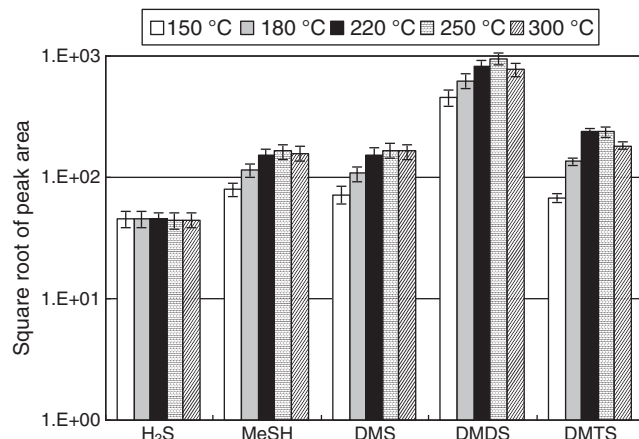


Fig. 6. Effect of the desorption temperature on the SPME of H_2S , MeSH, DMS, DMDS, and DMTS using 75 μm CAR/PDMS fiber.

3.1.5. Desorption conditions

The optimum SPME desorption temperature (injector temperature) was studied to achieve the total desorption of analytes from the fiber during the injection in splitless mode and to prevent the thermal decomposition of the analytes. For this purpose, desorption temperatures of 150, 180, 220, 250, and 300 °C were tested. Duplicate analyses at each temperature revealed increasing peak areas with temperature ranging from 150 to 250 °C for MeSH, DMS, DMDS, and DMTS (Fig. 6). However, higher temperatures led to decreased responses due to the thermal decomposition of the analytes [43]. For H_2S , the increase in peak area with temperature was not statistically significant because of its lower affinity for the fiber and its higher thermal stability. Therefore, 250 °C was chosen as the optimum desorption temperature.

The duration of the desorption process is also an important factor and must be taken into account during SPME method development to increase the desorption efficiency and avoid carryover. In this work, desorption times of 1, 2, 3, and 5 min were evaluated. The results indicated that for all of the studied VSC species, the peak areas directly increased with the desorption time, particularly for the heavier molecules (data not shown). However, extended desorption times may result in carryover. With a fixed desorption temperature of 250 °C, a desorption time of 3 min resulted in carryover of less than 0.7%, which is comparable to previously reported results [17,32]. Therefore, the optimum desorption temperature and duration were 250 °C and 3 min, respectively.

3.2. Analytical performance of the method

3.2.1. Linearity

The optimized SPME conditions used were as follows: a 20 mL water sample was placed into a 40 mL headspace vial with 20% NaCl and magnetically stirred at 750 rpm at a temperature of 45 °C for 30 min for extraction. Then, the fiber was desorbed in the injector port at 250 °C for 3 min. For the calibration, global standard solutions

Table 1

Analytical performance parameters for the determination of VSCs using HS-SPME-GC/FPD.

VSC	Linear range (ng L^{-1})	R^2	MDLs (ng L^{-1})	MQs (ng L^{-1})	Method reproducibility (R.S.D. %, $n=3$)
H_2S	500–100,000	0.9951	93.5	500	11.9
MeSH	50–10,000	0.9902	18.6	50	8.6
DMS	50–10,000	0.9989	21.4	50	10.3
DMDS	10–5,000	0.9998	1.6	10	10.2
DMTS	20–10,000	0.9994	3.6	20	3.7

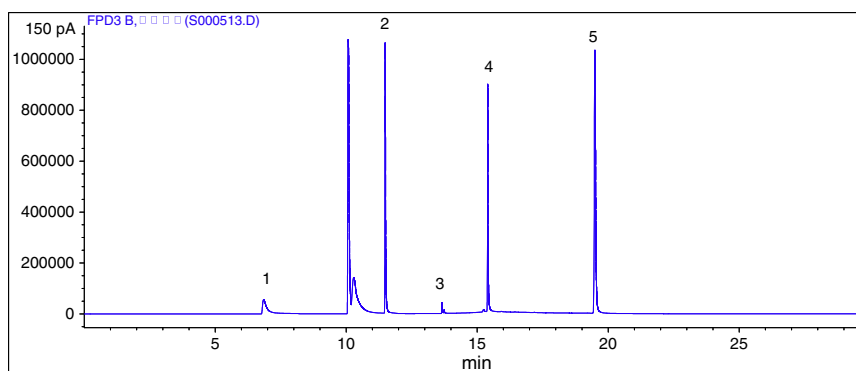


Fig. 7. Chromatogram of an odorous water sample of Lake Taihu after microextraction using CAR/PDMS fiber. 1 = H_2S , 2 = MeSH, 3 = DMS, 4 = DMDS, 5 = DMTS.

at concentrations ranging between 1.0 and 100,000 ng L^{-1} were analyzed. To construct the calibration graphs, the square roots of the peak areas were subjected to a linear least-squares regression. Good linearity was obtained for all target analytes using this method with correlation coefficients greater than 0.99 (Table 1).

3.2.2. Detection and quantification limits of the method

The method detection limits (MDLs) for each compound were defined as the concentration corresponding to three times the noise ($S/N = 3$) in the analysis. Although the calibration of VSCs showed good linearity (Table 1), it was more prone to analytical bias for the lighter molecular weight (MW) VSCs (especially H_2S) due to distinctively reduced sensitivity relative to the heavier MW compounds. As such, the method detection limits (MDLs) vary by approximately dozens of times for the lighter and heavier MW VSCs (MDLs = 93.5 ng L^{-1} for H_2S and 1.6 ng L^{-1} for DMDS). The previous research also showed that the MDLs values of SPME varied greatly across different sulfur compounds, as large as an order of magnitude across DMS (1.46) to H_2S (16.9 ng) in the analysis of reduced sulfur compounds in the gas phase [44]. The lowest calibration levels were selected as the method quantification limits (MQLs). The MQLs and MDLs of the five target compounds are shown in Table 1.

3.2.3. Precision

The method reproducibility was obtained through triplicate analysis of standard solutions at the following concentrations: 10,000 ng L^{-1} H_2S , 500 ng L^{-1} MeSH, 200 ng L^{-1} DMS, 200 ng L^{-1} DMDS, and 500 ng L^{-1} DMTS. The reproducibility for all compounds, expressed as the relative standard deviation (R.S.D. %), was between 3.7 and 11.9% (Table 1).

3.3. Sample analysis

The developed methodology was applied to the analysis of several real samples collected from freshwater suffering from black water agglomerates in Lake Taihu. Fig. 7 shows a typical chromatogram for these samples after HS-SPME. All of the studied VSCs showed similar vertical distribution patterns, with the maximum peak concentrations appearing at the intermediate layer of the water column (Fig. 8). At the surface, the most-volatile VSC species, H_2S and MeSH, were found at levels as low as 0.52 and 0.33 $\mu\text{g L}^{-1}$, respectively, whereas DMS, DMDS, and DMTS were present at concentrations of 2.51, 4.29, and 8.73 $\mu\text{g L}^{-1}$, respectively. The concentrations of all VSCs increased to a certain depth and decreased thereafter. The maximum VSC concentrations of 166.60, 35.57, 16.27, and 14.66 $\mu\text{g L}^{-1}$ for H_2S , MeSH, DMDS, and DMTS, respectively, were observed at a depth of 90 cm, whereas the maximum DMS concentration of 49.72 $\mu\text{g L}^{-1}$ occurred at a 60 cm depth. The concentrations of H_2S , MeSH, and DMS showed larger fluctuations with depth than did DMDS and DMTS, which were relatively constant with depth.

A small number of studies investigated the odorants of black water agglomerate during the Wuxi water crisis. Yang et al. [6] identified DMTS at concentrations up to 11.4 $\mu\text{g L}^{-1}$ as a major contributor to the odor of the Wuxi tap water. In addition, Zhang et al. [7] indicated that MeSH (204 $\mu\text{g L}^{-1}$) and DMS (93.9 $\mu\text{g L}^{-1}$) were the dominant VSCs in the early stages of black water agglomerate formation. The major VSCs then occurred as the more oxidized compounds DMDS (46.1 $\mu\text{g L}^{-1}$) and DMTS (17.2 $\mu\text{g L}^{-1}$) at the later stages. This discrepancy was probably due to the different time of sampling by the two groups. However, the depth of sampling was not considered in these studies. Our research, however, indicated that the composition and level of VSCs was strongly dependent on

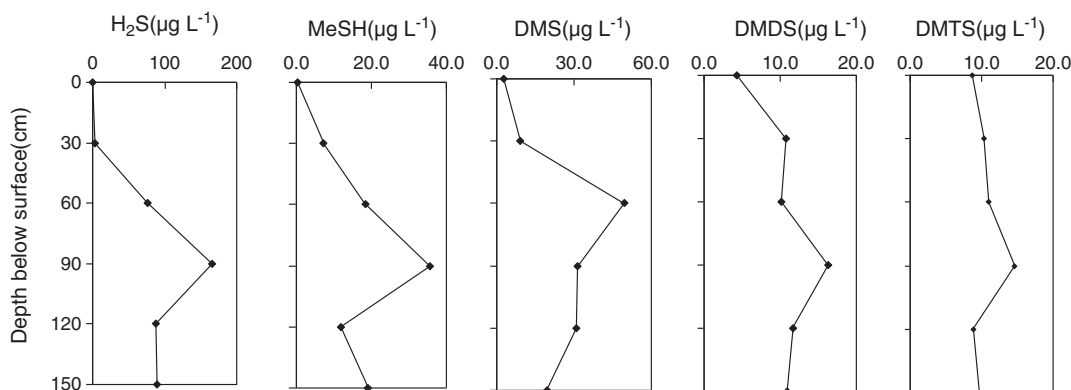


Fig. 8. Vertical distribution of VSCs in the water column of the sampling site suffering from black water agglomerate in Lake Taihu.

Table 2

Average recoveries and RSD values (in parentheses).

VSC	H ₂ S	MeSH	DMS	DMDS	DMTS
Known concentration (ng L ⁻¹)	1000	1000	1000	1000	5000
Measured concentration (ng L ⁻¹)	872.1	902.7	901.2	1118.1	5067.2
Recovery (%)	87.2 (11.4)	90.3 (10.2)	90.1 (9.8)	111.8 (8.9)	101.3 (4.7)

the sampling depth, with less-volatile VSCs being predominant at the surface of the water column; H₂S, MeSH, and DMS steadily increased with depth and became the dominant species. In addition, H₂S was not previously determined due to its high volatility in aqueous samples and difficult determination. However, this compound was present at relatively high levels in black water agglomerate regions of the lake and especially in the intermediate region of the water column (Fig. 8).

Recovery was defined as the ratio between the measured concentrations of target compounds and the known concentrations of the analytes. The surface samples were spiked with the compounds of interest at concentrations of 1000 ng L⁻¹, 1000 ng L⁻¹, 1000 ng L⁻¹, 1000 ng L⁻¹, and 5000 ng L⁻¹ for H₂S, MeSH, DMS, DMDS, and DMTS, respectively. Each sample was analyzed in triplicate, and the recoveries were calculated. As shown in Table 2, the recoveries were approximately 100% for the spiked samples using the optimized method.

4. Conclusions

In this study, a simple and sensitive method was developed for the determination of five volatile sulfur compounds, which are responsible for the foul smell induced by algal blooms in freshwater lakes, using CAR/PDMS SPME combined with GC-FPD detection. Parameters that affected the method performance were optimized, thereby leading to ideal extractions conditions of 20 mL of a water sample in a 40 mL headspace vial with 20% NaCl addition and magnetic stirring at 750 rpm at a temperature of 45 °C for 30 min. The fiber was then desorbed in the injector port at 250 °C for 3 min. The method showed satisfactory detection and quantification limits as well as good precision and recovery values for all the studied volatile compounds. The detection of VSCs was linear over approximately three orders of magnitude for all of the studied compounds. The optimized method was successfully applied to the measurement of VSCs in a freshwater lake suffering from black water agglomerate and can also be used to determine VSCs in other aquatic systems suffering from similar odorous problems.

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