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Analysis of polysulfides in drinking water distribution systems using headspace solid-phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

Sulfide and polysulfides are strong nucleophiles and reducing agents that participate in many environmentally significant processes such as the formation of sulfide minerals and volatile organic sulfur compounds. Their presence in drinking water distribution systems are of particular concern and need to be assessed, since these species consume disinfectants and dissolved oxygen, react with metal ions to produce insoluble metal sulfides, and cause taste and odour problems. The analysis of sulfide and polysulfides in drinking water distribution systems is challenging due to their low concentrations, thermal instability and their susceptibility to undergo oxidation and disproportionation reactions. This paper reports on the development and optimisation of a rapid, simple, and sensitive method for the determination of sulfide and polysulfides in drinking water distribution systems. The method uses methyl iodide to derivatise sulfide and polysulfides into their corresponding dimethyl(poly)sulfides, which are then extracted using solid-phase microextraction in the headspace mode and analysed by gas chromatography–mass spectrometry. Good sensitivity was achieved for the analysis of dimethyl(poly)sulfides, with detection limits ranging from 50 to 240 ng L^{-1}. The method also demonstrated good precision (repeatability: 3–7%) and good linearity over two orders of magnitude. Matrix effects from raw drinking water containing organic carbon (3.8 mg L^{-1}) and from sediment material from a drinking water distribution system were shown to have no interferences in the analysis of dimethyl(poly)sulfides. The method provides a rapid, robust, and reliable mean to analyse trace levels of sulfides and polysulfides in aqueous systems. The new method described here is more accessible and user-friendly than methods based on closed-loop stripping analysis, which have been traditionally used for the analysis of these compounds. The optimised method was used to analyse samples collected from various locations in a drinking water distribution system. Some of the samples were shown to contain inorganic polysulfides, and their presence was associated with high sediment density in the system and the absence of disinfectant residual in the bulk water.

1. Introduction

Sulfide and polysulfides participate in many environmentally significant processes due to their reactivity as strong nucleophiles and reducing agents. Even under mild conditions, sulfur nucleophiles can participate in addition and substitution reactions with organic functionalities such as halides, aldehydes, ketones, and activated double bonds [1]. They have a great affinity for transition metal ions, *e.g.* iron and copper, and thus play a significant role in the formation of sulfide minerals [2]. They are also precursors for the formation of odorous volatile organic sulfur compounds (VOSC) in diverse aquatic systems [3–5]. Among the most abundant VOSC are dimethylsulfide, dimethyldisulfide, and dimethyltrisulfide [6].

Sulfide in aquatic systems arises primarily *via* biogenic dissimilatory sulfate reduction, and partly through organic sulfur compound catabolism by heterotrophic organisms and assimilatory sulfur metabolism, which have been reported to occur in both anoxic [7] and oxic environments [8]. In these systems, sulfide can be progressively re-oxidised to sulfate on contact with oxidants *e.g.* dissolved and atmospheric oxygen, iron oxyhydroxides, manganese dioxide, and nitrate [9,10], through the formation of metastable intermediates, among which the most stable are polysulfides [11]. Anoxygenic phototrophic bacteria can also produce polysulfides as common intermediate products during light-dependent oxidation of sulfide and thiosulfate [12]. In aqueous solutions, polysulfides exist as equilibrium mixtures of dianionic chains of sulfur atoms, S_n^{2-}. The distribution of polysulfide species of different chain length has been reported to be dependent on the concentration of total reduced sulfur, with disul-

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fide being the dominant species at low concentrations of total reduced sulfur (0.05 mg L^{-1}) [6]. Polysulfides have been reported to be present in anoxic and oxic environments [6,13], including in biofilms in drinking water distribution systems [1,4,5,14]. Previous work has shown that pipewall deposits in drinking water distribution systems contain significant concentrations of sulfur (0.03–0.09% by weight) as well as inorganic polysulfide sulfur (up to 79,000 μg kg^{-1}, dry weight, equivalent to 2,000,000 ng L^{-1} wet weight) (*e.g.* [1,4]). The presence of sulfide and polysulfides in drinking water distribution systems is of particular concern because these species consume disinfectants and dissolved oxygen, react with metal ions to produce insoluble metal sulfides, and can cause taste and odour problems. Therefore, there is a need to assess the presence of these compounds in drinking water distribution systems.

The analysis of polysulfides in aqueous systems is often challenging due to their low concentrations and their thermal instability, and their susceptibility to oxidation and transformation. Several analytical methods are available to determine the concentrations of polysulfides in aqueous systems. These include UV absorbance [15,16], liquid chromatography-based techniques [17,18], and electrochemical methods [9,19,20]. Each method has its limitations and advantages, and the choice of analytical method depends on the specific application and requirements. Recently, a liquid chromatography-based method using methyl trifluoromethanesulfonate (methyl triflate) as a derivatisation agent for the analysis of polysulfides in aqueous solutions was reported [21]. Derivatisation of polysulfides using methyl triflate ($CF_3SO_3CH_3$) in the presence of excess methanol converts labile inorganic polysulfides into a stable set of dimethylpolysulfides ($(CH_3)_2S_n$) that can be analysed using liquid chromatography with diode array detection. Using this method, the speciation of polysulfides (S_3^{2-}–S_7^{2-}) in aqueous solutions can be determined. The method is relatively sensitive, with detection limits in the nM range, however, it was not validated for S_2^{2-} and it is labour intensive. The method involves multiple liquid–liquid extraction and harsh sample preparation conditions associated with total solvent drying and subsequent dissolution [21].

A technique based on methylation of polysulfides using methyl iodide (Eq. (1)), followed by analysis of the dimethylpolysulfides using gas chromatography-based methods has been reported previously [1,4–6,22]. Inorganic polysulfides can react rapidly and quantitatively with alkyl halides in aqueous solution to form dialkylpolysulfides [23], which are volatile and can be analysed by gas chromatography (GC). Methylated polysulfides are more stable to oxidation than inorganic polysulfides and hence quantitative recovery of polysulfides, collectively as methylated polysulfides (*e.g.* dimethyldisulfide, dimethyltrisulfide) can be achieved [5].

$$S_n^{2-} + 2CH_3I \rightarrow (CH_3)_2S_n + 2I^- \quad (1)$$

Although, it is likely that methylation of the inorganic polysulfides does not preserve their original distribution, this method can still provide a quantitative assessment of total sulfides and polysulfides. The technique was developed to provide the required sensitivity to measure the concentrations of polysulfides in drinking water distribution systems and other environmental systems [5,6,20–22]. An analytical technique based on this reaction was used in semi-quantitative assessment of polysulfide sulfur in groundwater and biological samples [24]; as well as in quantitative determination of microgram-per-litre (nanomolar) concentrations of polysulfide sulfur in anoxic groundwater and in biofilm samples [5]; and in quantitative analysis of inorganic polysulfides in an oxygen rich freshwater lake [6,22].

Closed-loop stripping analysis (CLSA) was used as the preconcentration method in the studies mentioned above [5,6,21,22], and also in a study investigating the role of dimethyltrisulfide in the generation of swampy odours in potable waters [14]. CLSA allows pre-concentration of volatile organic compounds from large volumes and is therefore very sensitive and suitable for odorous compounds with very low sensory thresholds such as dimethylpolysulfides. However, it is time-consuming, laborious and requires large sample sizes [1]. Solid-phase microextraction (SPME) has been used in the analysis of trace levels of volatile organic sulfur compounds (VOSC) in various matrices, such as wine, beer, and spirits [25,26]; air/atmosphere [27]; and cheese [28]; and offers an attractive alternative method to pre-concentrate dimethylpolysulfides. It is rapid, relatively inexpensive, easily automated, and solvent-free, and it also allows for minimal sample handling, which is highly desirable in the analysis of volatile sulfur compounds due to their low chemical stability.

The aim of this study was to develop and optimise a rapid, simple, and sensitive analytical method for the analysis of trace levels of total sulfides and polysulfides in drinking water distribution systems, including both in the water phase and in the biofilm. This method used methyl iodide derivatisation followed by headspace SPME/gas chromatography–mass spectrometry (HS SPME/GC–MS) for the analyses total sulfide and polysulfides as dimethylsulfide and dimethylpolysulfides. This derivatisation reaction has been reported to overestimate the concentration of polysulfides in aqueous solutions and as unsuitable for determination of speciation of polysulfides [21]. However, in another study it has been demonstrated that the reaction between methyl iodide and polysulfides is quantitative [5]. The alternative derivatisation method using methyl triflate is laborious and uses harsh conditions [21] and therefore derivatisation using methyl iodide was the preferred method for this study. It is acknowledged that methyl iodide derivatisation shows predominant dimethyldisulfide and dimethyltrisulfide production, which suggests redistribution of polysulfides species during derivatisaion, and this method is thus not suitable for determination of individual polysulfide species. However, since the speciation of polysulfides was not the focus of this study, the chosen method using methyl iodide was sufficient and appropriate for this application.

The major novel aspect of this paper is that there currently exists no published method for analysis of methylated polysulfides using SPME in aqueous systems. Even though our SPME method does not have sufficient sensitivity to determine dimethyltrisulfide at its odour threshold concentration (10 ng L^{-1}), the objective of the study was to show that the method can be used for analysis of methylated polysulfides at higher concentrations, such as when they are formed from methyl iodide derivatisation in the analysis of inorganic polysulfides. Information on the presence of these compounds in aquatic systems is important for water supply operators and managers, since reduced sulfur consumes disinfectant and is linked to the production of off-flavours and other water quality problems. Our new method demonstrates a relatively simple and easily available (*e.g.* in commercial laboratories) way to screen for these compounds which have been poorly studied to-date, partly because of the lack of a practicable analytical method.

2. Material and methods

2.1. Chemicals and materials

Commercially available inorganic reagents, organic solvents, and organic compounds were of analytical grade purity or better, and were used without further purification. Dimethylsulfide (DMS) and dimethyldisulfide (DMDS) were obtained from Aldrich. Dimethyltrisulfide (DMTS) was synthesised according to the method of Milligan et al. [29]. A mixture of deuterated analogues of DMDS (DMDS-d_6) and DMTS (DMTS-d_6) was obtained using

a similar method, but omitting the addition of sodium chloride and formaldehyde. Two types of SPME fibres were used: 100 μm polydimethylsiloxane (PDMS) and 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS).

2.2. Standard solutions

Stock standard solutions (mixture of native DMS, DMDS, and DMTS; mixture of deuterated DMDS and DMTS) were prepared in hexane, while the corresponding working standard solutions were prepared in dichloromethane or methanol. Deuterated DMDS (DMDS-d_6) and DMTS (DMTS-d_6) were used as internal standards.

2.3. HS SPME/GC–MS procedure

Methylated (poly)sulfides (DMS, DMDS, and DMTS) were analysed by headspace SPME using a 100 μm PDMS fibre, followed by GC–MS analysis. SPME was performed using a Gerstel MPS2 Autosampler interfaced with a Hewlett Packard 6890N GC and a Hewlett Packard 5973Network Mass Selective Detector. The sample volume used for SPME was 15 mL, in a 20 mL vial. Anhydrous sodium sulfate (2.5 g) and an aliquot of the internal standard solution (75 μL of 7.2 ng mL^{-1} of a mixture of deuterated standards solution) were added to the sample. The SPME fibre was introduced to the headspace of the vial and extraction was carried out for 5 min at 30 °C. The fibre was then desorbed at 200 °C for 2 min in the injector port of the GC, while the analytes were simultaneously cryofocused on the GC column at 10 °C. GC separation of the dimethyl(poly)sulfides was carried out using helium as the carrier gas, and a 30 m × 0.25 mm ID ZB-5 (Phenomenex®) column with a film thickness of 1 μm. Details of the GC temperature program and the MS settings are given in the supporting document.

2.4. Analytical method validation

Following the optimisation of the HS SPME/GC–MS procedure for the analysis of dimethyl(poly)sulfides, validation of the analytical method was carried out. The linearity of the method was evaluated by calibration over two orders of magnitude. Precision and sensitivity of the method were determined, and the matrix effects in the analysis were also evaluated.

2.5. Sample collection and preparation

Samples of biofilm and sediment material adhering to the internal walls of potable water pipes were collected from selected sampling locations in a drinking water distribution system east of Perth, Western Australia. The samples were collected by scraping the material from the inside wall of the pipe and filling the sample container with water from the same pipe, to exclude headspace. Methyl iodide (0.05% v/v) was added directly into each sample, immediately upon sampling. The mixture was allowed to react in darkness for 24 h prior to analysis of dimethyl(poly)sulfides by HS SPME/GC–MS.

3. Results and discussion

3.1. Optimisation of GC–MS conditions

GC–MS conditions for the analysis of dimethyl(poly)sulfides were optimised, in order to achieve maximum sensitivity, good baseline separation of analytes and Gaussian peak shapes. In order to optimise the sensitivity of the method and to minimise interferences from other compounds, the MS was operated in selected ion monitoring (SIM) mode. For each dimethyl(poly)sulfide, the most abundant and characteristic m/z ions were selected (Table 1).

Table 1
Characteristic mass ions of dimethyl(poly)sulfides selected for MS analysis.

Compound	Characteristic m/z ions
Dimethylsulfide (DMS)	m/z 47 and 62
Dimethyldisulfide (DMDS)	m/z 79 and 94
Dimethyldisulfide-d_6 (DMDS-d_6)	m/z 82 and 100
Dimethyltrisulfide (DMTS)	m/z 79 and 126
Dimethyltrisulfide-d_6 (DMDS-d_6)	m/z 82 and 132

Other key characteristics m/z ions were also included in the GC–MS analysis:

- m/z 64 (characteristic of elemental sulfur),
- m/z 97 (characteristic of mixture of DMDS and DMDS-d_6),
- m/z 129 (characteristic of mixture of DMTS and DMDS-d_6),
- m/z 158 (characteristic of dimethyltetrasulfide (DMTeS), for qualitative purpose only, since DMTeS has been reported as a minor component in dimethyl(poly)sulfides found in biofilms and pipewall sediments in drinking water distribution systems [5]).

Optimisation of the GC conditions involved optimisation of the initial temperature and heating rate of the GC oven. A heating rate of 5 °C/min was sufficient to separate DMS, DMDS, and DMDS-d_6. However, good baseline separation of DMTS and DMTS-d_6 required a slower heating rate of 3 °C/min. The initial temperature of the GC oven was found to affect the peak shape of the analytes. At initial GC oven temperature of 40 °C, tailing of chromatography peaks that corresponded to DMDS and DMTS was observed. Decreasing the initial GC oven temperature was found to improve the peak shape of these analytes. Good Gaussian peak shape for each analyte was obtained with an initial GC oven temperature of 10 °C. Fig. 1 shows a chromatogram of the analysis of standard solutions of dimethyl(poly)sulfides using the optimised GC–MS conditions.

Fig. 1 shows that for the same concentration of native dimethyl(poly)sulfides in the sample, the magnitude of the response for each compound was different. Direct injection of a mixture containing the same concentrations of native dimethyl(poly)sulfides into GC–MS resulted in similar chromatographic responses for the dimethyl(poly)sulfides (results not shown). This suggests there may have been preferential absorption of these compounds by the SPME fibre (PDMS) during HS SPME. This phenomenon of fibre selectivity has been observed in other studies as well *e.g.* in SPME of VOSC in gas samples using CAR-PDMS fibre [27]; in HS SPME of 28 volatile organic carbon compounds and HS SPME of a series of *n*-alkanes (C_5–C_{12}) using PDMS fibre [30]; and in HS SPME of six species of haloacetonitriles using DVB-CAR-PDMS fibre [31].

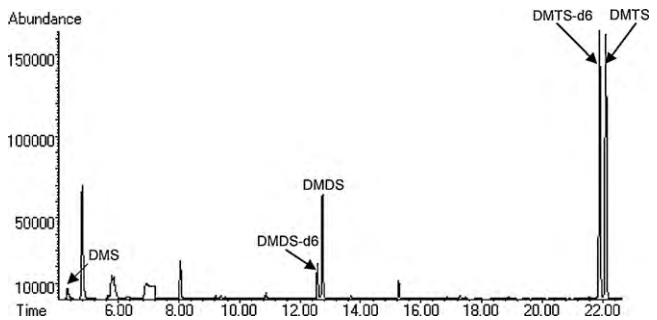

Fig. 1. Chromatogram of the HS SPME/GC–MS analysis of dimethyl(poly)sulfides standards (native standards at 20 μg L^{-1} each).

3.2. Optimisation of HS SPME procedure

In order to develop an HS SPME method for the analysis of dimethyl(poly)sulfides, the following factors needed to be considered and optimised: fibre type, salt addition, sample and headspace volume, extraction temperature and time, and desorption conditions. These factors were optimised using Teflon-lined screw cap vials (20 mL) containing aqueous solutions of the dimethyl(poly)sulfides (20 $\mu g\,L^{-1}$).

3.2.1. Fibre choice

Two different types of SPME fibres were evaluated, in order to achieve the best sensitivity and selectivity in the analysis of dimethyl(poly)sulfides. Initially, DVB-CAR-PDMS fibre was tested for its suitability in HS SPME of these compounds. Preliminary results showed that dimethyl(poly)sulfides were strongly adsorbed onto the DVB-CAR-PDMS fibre but were not completely desorbed within the GC injector, irrespective of injector temperature, resulting in carry-over of analytes in subsequent analyses. These results showed that this fibre was not suitable for the analysis of dimethyl(poly)sulfides.

However, when the PDMS fibre was used, carry-over was not observed, irrespective of GC injector temperature, demonstrating that the analytes were not as strongly adsorbed onto the fibre and were readily desorbed. Therefore, the PDMS fibre was used in subsequent method optimisation processes.

3.2.2. Salt addition

SPME can be carried out in the direct extraction or headspace (HS) extraction mode. Since dimethyl(poly)sulfides are volatile compounds, and HS extraction usually results in a longer fibre lifetime, the HS extraction mode was chosen for the analysis of these compounds. The addition of salt to aqueous samples has been shown to increase the amount of analyte extracted by SPME in HS mode [32]. The effect of salt addition was thus investigated, using sodium sulfate (10–30% w/v). The addition of salt increased the extraction efficiency of all analytes up to 5-fold. For DMDS, DMTS, and DMTS-d_6, the extraction efficiency increased with increasing salt amount, with only slight improvements in extraction efficiencies resulting from an increase in the salt concentration from 25 to 30% w/v. For DMS and DMDS-d_6, increasing the salt concentration from 25 to 30% w/v did not result in significant changes in their extraction efficiencies (within experimental errors). Based on these results, salt concentration of 25% w/v was used in subsequent experiments.

3.2.3. Sample volume

The choice of sample and headspace volume needs to be considered in HS SPME. When the volume of the sample (V_s) is much greater than the volume of the fibre (V_f) *i.e.* $V_f \ll V_s$, there is a linear relationship between the concentration of the analytes in the sample and the amount absorbed or adsorbed by the fibre at equilibrium [32]. Furthermore, the volume of the gaseous phase should be minimised to achieve high sensitivity [32].

The effect of sample and HS volume in the analysis of dimethyl(poly)sulfides was examined by varying the sample volume (10, 12, 15, and 17 mL) in the 20 mL vial. Other parameters were kept constant. For the analysis of dimethyl(poly)sulfides, a sample volume of 15 mL, which corresponded to a HS volume of approximately 5 mL, gave the highest response for all analytes.

The condition of $V_f \ll V_s$ is shown to be fulfilled when there is no analyte depletion after several extractions from the same sample [32]. Verification of $V_f \ll V_s$ in the extraction system was done by testing for analyte depletion after three extractions from the same vial. There was no significant difference between responses from each extraction (% RSD = 0.9–3.4), indicating that there was no analyte depletion. Therefore, with a sample volume of 15 mL, the condition of $V_f \ll V_s$ was fulfilled. Hence, a sample volume of 15 mL, was used in subsequent experiments.

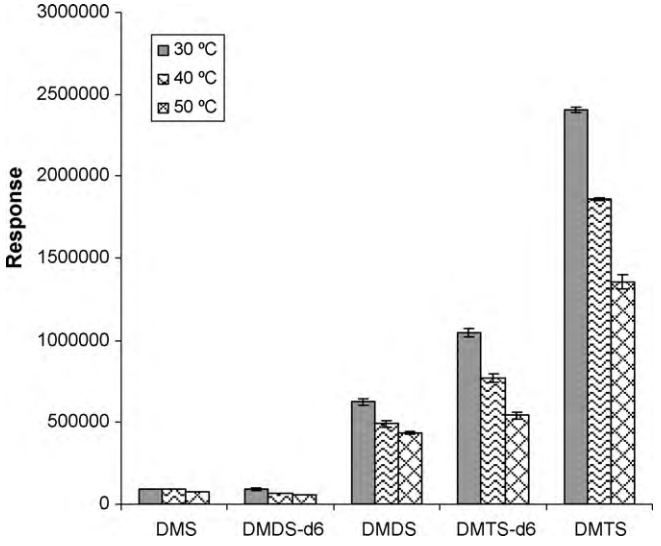

Fig. 2. The effect of extraction temperature on the extraction of dimethyl(poly)sulfides by HS SPME.

3.2.4. Extraction temperature

In SPME, extraction temperature affects both sensitivity and extraction kinetics, with an increase in extraction temperature resulting in an increase in extraction rate, and a simultaneous decrease in the amount of analyte extracted by the fibre, *i.e.* decrease in sensitivity [32]. Therefore, the optimum extraction temperature for SPME is selected as a compromise between these factors. The optimum extraction temperature for the analysis of dimethyl(poly)sulfides was determined by observing the variation in the responses of each analyte when only the extraction temperature was varied (30, 40, and 50 °C). The lowest extraction temperature that could be evaluated (30 °C) was limited by the capability of the Gerstel MPS2 Autosampler; while higher extraction temperatures were not studied due to their detrimental effects on the extraction of dimethyl(poly)sulfides. Fig. 2 displays the effect of extraction temperature on the amount of dimethyl(poly)sulfides extracted by the fibre. There was a clear trend of decreasing response of each homologue with increasing temperature. Although carrying out the extraction at a temperature higher than 30 °C may have decreased the extraction time, the associated decrease in sensitivity was significant and undesirable. Hence, a compromise was made and an extraction temperature of 30 °C was chosen for this method.

3.2.5. Extraction time

Unlike most extraction methods, SPME is an equilibrium extraction method, rather than an exhaustive one, therefore, the optimal approach is to allow the analyte to reach equilibrium between the sample and the fibre coating [32,33]. The equilibrium time refers to the time after which the amount of extracted analyte remains constant and corresponds to the amount extracted after infinite time, within the limits of experimental error [32]. In order to determine the equilibration time, and hence the extraction time, for each dimethyl(poly)sulfide homologue, analyses were conducted after different extraction times, and the GC–MS response was plotted against extraction time. It was shown (Fig. 3) that the response of each dimethyl(poly)sulfide was constant, within experimental error, after an extraction time of 5 min, which corresponded to the

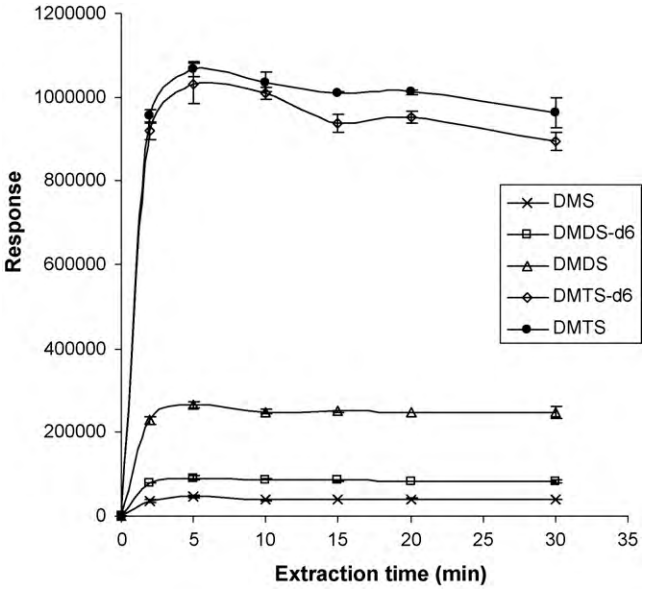

Fig. 3. Extraction time profile for the extraction of dimethyl(poly)sulfides by HS SPME.

equilibration time. Therefore, the optimum extraction time for this analysis was 5 min.

3.2.6. Desorption conditions

In SPME/GC–MS, the analytes adsorbed or absorbed by the fibre are released by way of thermal desorption in the vapourising injector port and are transferred into the GC column [32]. Temperature and time affect desorption of analytes from the fibre. The maximum desorption temperature is limited by the stability of the fibre as well as the analytes. The recommended operating temperature for the 100 μm PDMS fibre, as specified by the manufacturer, is 200–280 °C. In this experiment, desorption temperatures of 200, 220, and 240 °C were evaluated. The highest responses for dimethyl(poly)sulfides were obtained at desorption temperature of 240 °C. At this temperature, a more efficient desorption of the analytes from the fibre was achieved. However, further examination of the chromatograms from these analyses showed thermal degradation of DMTS at the higher desorption temperatures. This was indicated by the presence of a new peak in between peaks of DMTS-d_6 and DMTS, containing ions from both DMTS-d_6 and DMTS. This is evidence of the reaction between DMTS-d_6 and DMTS in the hot injector, causing thermal cleavage of C–S bonds and rearrangement to form the 'scrambled' compound DMTS-d_3. The higher dimethyl(poly)sulfides are known to be thermally unstable [14]: the size of this peak was found to decrease with decreasing desorption temperature, confirming that the effect was caused by thermal decomposition. At 240 °C, the peak area was 20% of that of DMTS, while at 200 °C, the peak area was only 4% of that of DMTS. Considering the thermal degradation of DMTS, a lower desorption temperature, 200 °C, was selected for the analysis of dimethyl(poly)sulfides. Although lower desorption efficiency is achieved at this temperature, as signified by the lower responses for dimethyl(poly)sulfides compared to those obtained at 240 °C, thermal degradation of the analytes and interactions between DMTS-d_6 and DMTS are minimised at this temperature. A desorption time of 2 min was initially used in this optimisation process. With desorption temperature of 200 °C, no carry-over of analytes was observed, thus a desorption time of 2 min was used in subsequent experiments.

In summary, the optimum HS SPME conditions for the extraction of dimethyl(poly)sulfides using a 100 μm PDMS fibre and a 20 mL sample vial were extraction for 5 min at 30 °C, with 15 mL sample volume and addition of 2.5 g of salt. The optimum fibre desorption conditions were 2 min at 200 °C.

3.3. Method validation

3.3.1. Thermal degradation of analytes

As mentioned above, dimethylpolysulfides are susceptible to disproportionation and thermal degradation, with thermally induced disproportionation resulting in the formation of lower dimethylpolysulfide homologues and elemental sulfur. Wajon et al. [14] reported that GC column heating rates and the presence of active sites within the GC injector liner are crucial factors in the analysis of dimethylpolysulfides. In order to further examine the potential for thermal degradation of these compounds in the GC injector port during SPME, the presence of elemental sulfur was investigated. Elemental sulfur may appear as S_6 or S_8 in the chromatogram and is not usually well resolved on conventional chromatography phases so appears as an unresolved non-Gaussian peak, as well as any additional chromatographic peaks. In order to minimise the probability of thermal degradation and disproportionation, the GC injector liner was deactivated prior to use. As described in Section 3.2.6, thermal degradation of DMTS was observed, especially at high injector temperature (240 °C). However, at 200 °C, thermal degradation of DMTS was minimal and negligible. Thermal degradation of DMDS was not observed at any of the injector temperatures investigated. A characteristic lump in the chromatogram, indicating the presence of elemental sulfur and thus disproportionation, was also not detected. In this study, the use of a deactivated liner and a relatively low injector temperature (200 °C) in the analysis of dimethylpolysulfides using HS SPME/GC–MS was shown to minimise thermal degradation of the analytes of interest to negligible levels, and disproportionation of dimethylpolysulfides was not observed under these conditions.

3.3.2. Blank analyses

Analysis of blank samples was carried out to check for interfering peaks. A blank sample contained MQ water, internal standards, and salt. No interfering peaks with the same retention time as the target analytes were observed in the chromatograms of the blank samples, indicating that the analytical method was free from interferences.

3.3.3. Matrix effects

In SPME, various components of a sample can alter the partitioning between the phases involved [34], and hence matrix effects need to be investigated and controlled for quantitation purposes. Standard addition experiments were carried out to simulate any matrix effects in the analysis of dimethyl(poly)sulfides in aqueous samples and biofilms. Raw water sample (DOC 3.80 mg L^{-1}) and a sediment sample that contained no dimethyl(poly)sulfides were spiked with a standard solution of dimethyl(poly)sulfides, at low (2 μg L^{-1}) and high (100 μg L^{-1}) concentrations, and analysed using the optimised conditions. The recovery of the standard compounds in these samples was then evaluated to determine the extent of matrix effects in the analysis.

Table 2 gives the recoveries of the standard compounds in raw water and sediment samples at low and high concentrations. Good recoveries (94–112%) were obtained for all standard compounds, at both concentration levels, indicating that matrix effects were negligible in the analysis of dimethyl(poly)sulfides in aqueous samples and biofilms using HS SPME/GC–MS.

3.3.4. Calibration

The linearity of the responses obtained from the analysis of dimethyl(poly)sulfides was evaluated by constructing calibration

Table 2
Recoveries of dimethyl(poly)sulfides standards in raw water and sediment samples.

Sample	% Recovery		
	DMS	DMDS	DMTS
2 μg L^{-1}			
Raw water	110	101	94
Sediment sample	97	112	100
100 μg L^{-1}			
Raw water	112	96	98
Sediment sample	122	104	96

Table 3
Precision, sensitivity, and linearity of the method for the analysis of dimethyl(poly)sulfides by HS SPME/GC–MS.

	DMS	DMDS	DMTS
Repeatability (% RSD)			
2 μg L^{-1}	6%	6%	7%
100 μg L^{-1}	3%	5%	4%
Reproducibility (% RSD)			
2 μg L^{-1}	20%	21%	20%
100 μg L^{-1}	12%	4%	10%
Detection limit (μg L^{-1})	0.23	0.37(0.0005[a])	0.13(0.0018[a])
Determination limit (μg L^{-1})	0.39	0.62(0.0014[a])	0.28(0.0054[a])
Typical r^2 values	0.988–0.994	0.991–0.998	0.995–0.999

[a] Values reported by Heitz [1] for the analysis of DMDS and DMTS using CLSA/GC–MS.

curves for each analyte over the concentration range of interest. A calibration curve for each analyte was obtained by plotting the ratios of the peak areas of the analyte and the internal standard *vs.* the concentration of the analyte. Each analyte was analysed in duplicate. Linear calibration curves with high correlation coefficients were achieved for all dimethyl(poly)sulfides. Typical correlation coefficients (r^2) values obtained for the calibration of dimethyl(poly)sulfides are given in Table 3.

3.3.5. Method precision

The precision of the method was evaluated by determination of the repeatability and the reproducibility of the method. Repeatability refers to 'run-to-run' precision, while reproducibility refers to 'day-to-day' precision [35]. The repeatability and reproducibility were assessed at low (2 μg L^{-1}) and high (100 μg L^{-1}) concentrations, by analysis of six samples in a day and a total of six samples on three different days, respectively, with calculations of the associated % RSD. The results are summarised in Table 3. The repeatability of this method compares well to that reported by Heitz [1], who reported repeatability of 10.4% in the analysis of synthetic solutions of DMDS and DMTS. Higher % RSDs were obtained for the reproducibility of the method, which is consistent with the higher variability experienced over the course of several days compared to variations within the same day. Higher % RSDs were also obtained for the precision of the method at low concentration, indicating that the method is more sensitive towards systematic errors at low concentrations.

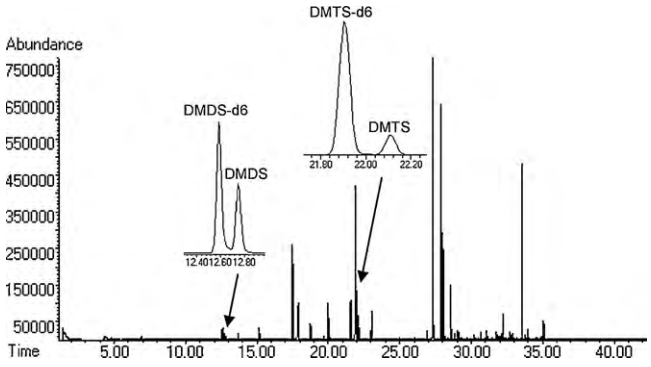

Fig. 4. Total ion chromatogram from analysis of dimethyl(poly)sulfides in a sediment sample.

3.3.6. Method sensitivity

The sensitivity of the method was determined from a series of six 'blank' (sediment samples containing internal standards only) analyses. Detection and determination limits were calculated from a signal to noise ratio of 3 and 10, respectively. The calculated detection and determination limits are given in Table 3. Detection and determination limits in sub parts per billion range were obtained, indicating good method sensitivity.

These detection and determination limits are significantly higher than those previously reported for the analysis of dimethyl(poly)sulfides using CLSA/GC–MS [1,4]. The CLSA/GC–MS method was developed primarily to analyse for DMTS which caused unpleasant swampy odours in drinking water at very low concentrations (odour threshold concentration of 10 ng L^{-1}). The aim of the current study was to develop a rapid and simple method suitable for automated analysis of large numbers of samples. This was to be applied to the determination of inorganic (poly)sulfides (after derivatisation using methyl iodide) in biofilm and sediment samples taken from drinking water distribution systems. The expected concentrations of these compounds were in the parts per billion range, an order of magnitude higher than those of the dimethylpolysulfides in earlier studies.

3.4. Analysis of samples

The optimised HS SPME/GC–MS method was applied to determine the concentrations of (poly)sulfides in eight sediment samples collected from selected locations in an extensive drinking water distribution system. Prior to the analysis by HS SPME/GC–MS, methyl iodide was added to each sample for *in situ* derivatisation of inorganic (poly)sulfides to the dimethyl(poly)sulfides. Fig. 4 shows a typical total ion chromatogram obtained from the analysis of these compounds in a pipewall sediment sample using HS

Table 4
Polysulfides concentrations and water quality characteristics in drinking water distribution system samples.

Sample	DMDS (μg L^{-1})	DMTS (μg L^{-1})	Total suspended solid (mg L^{-1})	Cl_2 residual (mg L^{-1})	pH	Sulfate (mg L^{-1})	Total S (mg L^{-1})	Alkalinity as $CaCO_3$ (mg L^{-1})
Sample A	<0.37	<0.13	140	0.15	7.3	29	9.8	62
Sample B	35	25	2700	<0.05	7.2	89	30	81
Sample C	5	30	960	<0.05	6.7	41	14	91
Sample D	<0.37	<0.13	120	0.17	8	34	11	88
Sample E	130	15	610	<0.05	7.6	36	12	91
Sample F	30	10	530	<0.05	7.7	33	11	290
Sample G	<0.37	<0.13	160	0.21	7.4	27	8.7	74
Sample H	<0.37	<0.13	110	0.19	7.2	38	10	85

SPME/GC–MS. DMS was not observed in any of the collected samples, while DMDS and DMTS were detected in four samples. The concentrations of DMDS and DMTS in these samples, together with the water quality characteristics of these samples, are shown in Table 4. The four samples that contained DMDS and DMTS had higher sediment content compared to the other samples. Moreover, disinfectant residual was not detected in the bulk water in these sediment samples, while low-level residuals were detected in the other samples. This observation indicates that inorganic polysulfides are more likely to be found in distribution systems that contain thicker layers of sediments and biofilms. These layers can provide a barrier to oxygen and disinfectants, allowing the formation of anoxic microenvironments and conditions conducive for sulfate reducing bacteria. This observation is consistent with previous studies that reported the occurrence of high concentrations of methylated and inorganic polysulfides in pipewall biofilms and sediments in distribution systems; and the role of chlorine in the oxidation of polysulfides [1,5].

4. Conclusions

An analytical method for the determination of trace levels of polysulfides in drinking water distribution systems, in both the water phase and in the biofilms, was developed and optimised. The method used HS SPME for the extraction of the analytes of interest and GC–MS for the analysis of these analytes. The reliability and the performance of the method were evaluated by considering matrix effects, linearity, precision, and limits of detection and quantification. HS SPME/GC–MS method for the analysis of methylated polysulfides in aqueous systems and biofilms proved to be a rapid and simple method with good sensitivity, linearity, and precision, free from interferences. The method provides a more accessible and user-friendly mean to analyse trace levels of sulfides and polysulfides in aqueous systems, than methods based on closed-loop stripping analysis, which have been traditionally used for the analysis of these compounds. Using this method, some samples from an extensive drinking water distribution system were shown to contain inorganic polysulfides, and their presence was associated with high sediment density and the absence of disinfectant residual in the bulk water. The presence of sulfide and polysulfides in drinking water distribution systems is of particular concern as they consume disinfectants, react with metal ions to produce insoluble metal sulfides that contribute to the build up of sediments in the system, and can indirectly lead to taste and odour problems. These compounds are associated with sulfate reduction, and indeed are an indication of the likely presence of sulfate reducing bacteria, which also has implications for corrosion. Therefore, evaluation of their presence in distribution system is needed, especially in parts of distribution systems where disinfectant residual is difficult to maintain, and where a build up of biofilm and sediment materials is expected as a result of difficulty in cleaning and maintenance of pipes and infrastructure. This information is currently not available, and the impact of sulfate reduction in drinking water distribution systems is not widely recognised and studied. The rapid, reliable, and user-friendly HS SPME/GC–MS method developed for the analysis of dimethyl(poly)sulfides in aqueous systems and biofilms will assist in the assessment of the occurrence and production of these compounds in drinking water distribution systems and other aqueous environments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.07.051.

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