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A simple method for routine measurement of organosulfur compounds in complex liquid and gaseous matrices

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ABSTRACT

The measurement of VOSCs in complex matrices is challenging due to their volatile and reactive nature. A straightforward method using headspace chromatography was developed for routine analyses of organosulfur compounds in a high saline liquid matrix with a pH of 8.4. Direct sample acidification with a 1M acetate buffer (pH 3.6) showed an increased response for methanethiol, ethanethiol, propanethiol, dimethyl sulfide, dimethyl disulfide and diethyl disulfide. A good quadratic fit (R^2 <0.995) was obtained for each compound over a calibration range of 5 µM-S until 125 µM-S (µmol sulfur/L). Gas standards were measured using the same chromatographic conditions over a calibration range of 0.08 µM-S until 1.85 µM-S (R^2 <0.999). Gas standards could also be used to calibrate the liquid phase with a response ratio of 105.2% for ET, 107% for DMS, 105.7% for PT, 108.9% for DMDS and 106% for DEDS. This alternative calibration strategy reduced the preparation time and does not rely on liquid standards, which were unstable over time. This method was used to determine Henry constants for the organosulfur compounds both in demineralized water and the high saline liquid matrix and to analyze samples from a bio electrochemical experiment that treated methanethiol. This new method allows for routine analysis of samples originating from natural gas desulfurization plants and can potentially also be used to analyze organosulfur compounds in other complex waste streams.

1. Introduction

There is a widespread interest for reliable and simple methods to measure volatile organosulfur compounds (VOSCs) in both gaseous and liquid samples. Low weight organosulfur compounds, such as methanethiol (MT), ethanethiol (ET), propanethiol (PT) and hydrogen sulfide (HS), are formed in industrial processes, including wastewater treatment plants [1–3], manure digestion [4], composting plants [5], paper [6,7] and rayon production [6–8] These organosulfur compounds and hydrogen sulfide are also present in natural gas and crude oil [9–11]. Furthermore, VOSCs play an important role in the global sulfur cycle [6,12–14]. Industrial VOSC emissions are strictly regulated as concentrations as low as 0.14 ppbv can already cause significant olfactory discomfort for the surrounding population and their potential toxicity at higher concentrations [15]. To develop efficient VOSC removal strategies and to comply with environmental safety regulations, reliable and simple measurement methods are required. However, accurate and straightforward measurement of these compounds remains a challenge. These challenges include the highly reactive nature of the VOSCs, the complex matrixes in which they are present and the accurate measurements at low concentrations.

The high volatility and reactivity of VOSCs puts a strain on sampling procedures, sample storage and complicates pretreatment steps [16]. The matrix in which the VOSCs are measured further complicates the measurement of VOSCs. The measurement of gaseous matrices is relatively straightforward as long as the samples are kept anaerobic and sorption to the sampling equipment is avoided. Liquid matrices, however, can also catalyze chemical reactions and may contain particles onto which VOSCs can adsorb [17]. In addition, microorganisms present in liquid samples may convert VOSCs [18]. One particularly difficult matrix containing VOSCs is found in the gas and oil industry, where H_2S and VOSCs are ex-

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tracted using caustic or amine solutions [9,19]. These solutions typically have a high pH (10-12) and salinity (>0.5M Na^+) with a total sulfur content ranging from 0.1 to 4 wt% [20]. High pH values are known to increase reactivity of VOSCs and salt precipitation due to the high salinity in liquid samples may shortens the lifetime of analytical equipment. No straightforward method for routine measurement of VOSCs in this complex liquid matrix has been described so far.

Various techniques, including HPLC [21], spectrophotometry [22], voltammetry [23], have been developed to measure VOSCs in different liquid matrices. Unfortunately, these systems are unable to measure gaseous samples and would require a combination of methods to analyze both gas and liquid samples. Alternatively, gas chromatography (GC) can be used to measure VOSCs in both gas and liquid samples [24,25]. Various detectors can be used to measure sulfur compounds on a gas chromatograph. The Sulfur Chemiluminescence Detector (SCD) and the Flame Photometric Detector (FPD) are two detectors that have a high selectivity and sensitivity towards sulfur compounds [26,27]. High reproducibility and accuracy for gaseous samples can be obtained with both detectors. Even though the SCD has a higher sensitivity, FPD is more widely used due to its lower costs, low maintenance and overall robustness [26].

Another major challenge, in addition to analyze both gas and liquid samples, is measuring VOSCs at low concentrations which often requires preconcentration steps. Usually, concentration methods like purge and trap [28,29] or SPME [30–33]are applied to measure VOSCs at low concentrations. However, these methods obtained results with high standard deviations as the volatile and reactive nature of these compounds becomes an issue during these pre-treatment steps [16]. Furthermore, preconcentration steps are time consuming, require expensive equipment and are sensitive to losses due to dimerization and volatilization [31]. Direct injection of liquid samples in a GC may avoid the need for tedious preparation procedures and is applied in e.g. the analysis of volatile fatty acids [34,35]. A disadvantage of direct injection of liquid samples is that the equipment requires frequent maintenance especially with high saline matrices. Furthermore, the high salt concentrations increase the risk of VOSCs deposition in the injector as a sodium salt.

Direct measurement using a static headspace chromatography forms a potential solution for measuring VOSCs in high saline liquid matrices. This method requires minimal sample treatment and small sample volumes and was applied to analyze samples from a municipal wastewater treatment plants [25]. With this method a recovery of 83% for methanethiol, 103% for dimethyl sulfide (DMS) and 102 for to 103% dimethyl disulfide (DMDS) was achieved in wastewater samples. However, the method included various pretreatment steps including acidification for sample storage and neutralization before analysis. Furthermore, the method was not specialized for highly saline samples with high pH values, and its applicability for ethanethiol, propanethiol, diethyl disulfide (DEDS) and hydrogen disulfide, was not evaluated.

In this work, a fast and straightforward method to measure VOSCs in the gas and the liquid phase using static headspace chromatography on a GC-FPD was developed. All samples were analyzed without preconcentration steps to minimize the risk of VOSCs losses and conversions during sample preparation. Different acidification strategies were evaluated to improve the chromatographic response for the liquid samples. The influence of different (bio) gas compositions in gas samples was evaluated. The calibration range, intermediate precision, quantification, and detection limits were evaluated. Additionally, the method was used to determine Henry coefficients in a high saline liquid matrix and in demineralized water

2. Material and methods

2.1. Equipment

Gas chromatography was used to analyze gas and liquid samples. The gas chromatograph (Shimadzu Nexis GC-2030, Shimadzu, Germany) was equipped with a headspace autosampler (Shimadzu H20 plus, Shimadzu, Germany) increasing injection precision and minimizing physical presence. The incubation temperature of the autosampler was set at 60°C with an equilibration time of 7 min. Additional mechanical shaking was applied for liquid samples during the incubation period. Following the incubation period, nitrogen gas was used to obtain an overpressure in the sample vials before sample injection (35 kPa for gas samples and 60 kPa for liquid samples). The split/splitless injector with a 250 µL loop was operated in spitless mode at 150°C. A total volume of 250 µL was injected. The sulfur compounds were separated on an intermediate polar capillary column (ZB-624PLUS, 30 m length, 0.530 mm diameter, 3.0 µm film thickness, Phenomenex, UK) using nitrogen as a carrier gas with a flow of 2.54 mL/min. The oven temperature was programmed at 35°C and maintained for 3 min after injection. Thereafter a temperature ramp of 40°C/min until 180°C was applied. The temperature was maintained at 180°C for 4 min. The gas chromatograph was equipped with a flame photometric detector (FPD) using an optical sulfur filter (Optical filter ASSY (S) for FPD-2030 Shimadzu, Germany) and operated at 250°C with a 40 mL/min hydrogen and 60 mL/min air flow. Labsolutions 5.93 (Shimadzu, Germany) was used to operate the system and analyze the data.

2.2. Gas calibration standards

Amber glass vials (1.5 mL) were filled with liquid organosulfur compounds (purity >99.6%) and were used to prepare mixed gas standards. The vials were closed with PTFE lined caps (Septa N11 rubber/PTFE red hardness 45, shore A, MACHEREY-NAGEL, Germany). The equivalent of 1 mmol-S of ET, PT, DMS, DMDS and DEDS was transferred from the amber glass vials with a glass syringe (Hamilton, USA) to a 2.28 L glass bottle that was closed with a butyl rubber stopper (Bromobutyl rubber Stopper for GL 45, DWK Life Sciences GmbH, Germany) to prepare a mixed gas standard. Following preparation, the mixed gas standard was heated for 30 min at 50°C to fully vaporize the organosulfur compounds before further gas dilutions were made. To obtain the final working stock, 5 mL of the mixed gas standard was transferred to a 120 mL serum flask resulting in a final concentration of 20 µM-S (µmol sulfur/L) for each compound. These working stocks were used for 2 weeks without changes in the gas composition and signal intensity. The calibration curve was obtained by diluting the working stock into 10 mL vials over a concentration range of 0.08–1.85 µM-S for each compound. All standard preparations were performed in an anaerobic chamber that was continuously flushed with nitrogen gas. Serum flasks and 10 mL vials were closed with 3 mm PTFE lined butyl rubber crimp seal caps in a 100% nitrogen atmosphere (Septa butyl/PTFE Gray hardness 50, shore A, MACHEREY-NAGEL, Germany). H_2S and MT standards were prepared from a gas standard containing 207 ppmv H_2S and 206 ppmv MT in 100 $\%N_2$ (Linde Gas Benelux B.V, The Netherlands)

The accuracy of the calibration is strongly influenced by the evaporation of the pure compounds used to prepare the mixed gas standard. Full vaporization of pure compounds was therefore evaluated by comparing the chromatographic response for mixed gas standards that were prepared at room temperature and subsequently heated for 30 min at 40, 50 and 60° before working stocks with a final concentration of 0.223 µM and 0.372 µM were prepared.

2.3. Liquid headspace calibration standards for liquid samples

Liquid headspace calibration standards were prepared in a similar matrix (high salinity, high pH) that can be found in biodesulfurization plants [20] and contained 4.42 g/L Na_2CO_3, 49 g/L $NaHCO_3$, 0.2 g/L $MgCl_2$ x 6 H_2O, 1 g/L KH_2PO_4, 0.01 g/L $CaCl_2$ 2 H_2O, 0.6 g/L CH_4N_2O, 1 g/L NaCl, with a final pH of 8.4.

Pure solutions (>99.6%) of ET, DMS, PT, DMDS and DEDS were used to prepare individual 10 mM stock solutions in methanol. A MT stock solution (10 mM) was prepared from its sodium salt in Milli-Q. Mixed working stock solutions were prepared in the high pH and highly saline matrix from the 10 mM standards obtaining a concentration of 125 µM-S for each compound. The working stock was further diluted with same matrix into the 10 mL vials creating the calibration standards over a range of 5 µM-S until 125 µM-S. The volume of the liquid standards in the 10 mL vials was 200 µL.

The influence of different acids on the exclusion of organosulfur compounds from the liquid phase was evaluated. The acids used to lower the pH of liquid samples were a glycine buffer (0.2 M glycine and 0.2 M HCl, pH 3), a HCl solution (0.5 M, pH 0.3) and an acetate buffer (1M, pH 3.6). Working solutions with a concentration of 50 µM-S following the procedure described in this manuscript were prepared. The 10 mL vials were filled with 200 µL of working solution and 200 µL of acid. The blank was prepared by adding 200 µL of working solution without VOSCs.

The use of gas standards to calibrate liquid samples was evaluated to shorten and ease the liquid calibration procedure. The 10 mL vials were filled with 200 µL of saline matrix and 200 µL of acetate buffer. Organosulfur compounds from the mixed gas standard were added with an air-tight syringe (Hamilton, USA). The response was compared with results obtained with liquid standards.

All standard preparations were, like gas standard preparations, performed in an anaerobic chamber that was continuously flushed with nitrogen and dilutions were made with gas tight glass syringes. Water, high pH saline matrix and buffer solutions were sparged with nitrogen for 20 min to ensure anaerobic conditions, before the addition of organosulfur compounds.

2.4. Assessment of chromatographic response

The chromatographic method was evaluated by comparing the results of 6 (MT and H_2S) and 10 (ET, PT, DMS, DMDS and DEDS) replicates of the calibration curve of gas and liquid standards. The peak separation was observed to assess the selectivity. The determination coefficient was used to evaluate linearity and the precision was evaluated by comparing the RSD values at the lowest calibration point. The limit of quantification (LOQ) and limit of detection (LOD) were calculated by using the calibration approach [36,37].

The chromatographic method was further evaluated by assessing the influence of incubation time and different (bio)gas compositions. The influence of incubation time was evaluated by injecting the headspace of a 10 µM-S ethanethiol liquid standard (gas standard for liquid calibration procedure) after an incubation time of 5, 7 min and with a gas standard containing 10 µM-S propanethiol and dimethyl disulfide after an incubation time of 5, 7, 10, 12 and 15 min. Additionally, the influence of (bio)gas composition was evaluated by preparing working stocks in 120 mL serum flasks with different gas compositions (Table 1). Working stocks containing ethanethiol, dimethyl sulfide, propanethiol and dimethyl disulfide were diluted into the 10 mL vials to obtain a final concentration of 1 µM-S. The relative response at different conditions was calculated by dividing the natural logarithm of the response area (µV·min) by the natural logarithm of the response area obtained under a 100% nitrogen atmosphere.

Table 1
Evaluated gas compositions for signal quenching

Mixture	N2	CO2	CH4
1	100	0	0
2	25	50	25
3	50	25	25
4	50	50	0
5	90	0	10
6	85	10	5
7	80	10	10

2.5. Method application

2.5.1. Henry coefficient determination

Henry coefficients were defined for MT, ET, PT, DMS, DMDS, and DEDS. The standard solutions, with a concentration of 3.8 mM-S for DEDS and 10 mM-S for all other evaluated compounds, were prepared in demineralized water under anaerobic conditions. The experiments were performed in 120 mL serum flasks that were sealed with PTFE lined butyl rubber crimp seal caps. The flasks were filled with 50 mL saline matrix or demineralized water and sparged with nitrogen gas for 20 min. The organosulfur compounds were injected from the standard solution into these vials resulting in the addition of 100 µmol-S. Flasks were stored at 25°C during 24 h before samples were taken from the gas phase. Henry coefficients were defined in triplicate for each compound in both saline matrix and demineralized water.

The henry coefficient was calculated by the following equation:

$$Hc = \frac{c_L}{c_g} = \frac{\frac{V_L c_{in} - V_g c_g}{V_L}}{c_g}$$

With Hc (-) as the water-air partitioning coefficient, C_L (µM) as the concentration in the liquid phase, C_g (µM) concentration in the gas phase, C_{in} (µM) initial concentration of organosulfur, V_L (L) volume of the liquid phase in the serum flask and V_g (L) volume of the gas phase in the serum flask.

2.5.2. Samples of lab scale bioelectrochemical reactor treating MT

The conversion of VOSCs in lab scale bioelectrochemical systems treating methanethiol was analyzed using the developed method for gas phase measurements and the obtained henry coefficients in the saline matrix. A bioelectrochemical systems was constructed as described by Elzinga et al., and the biocathode potential was controlled at – 800 mV vs Ag/AgCl [18]. The reactors were inoculated with biomass obtained from a papermill wastewater treatment plant (Eerbeek, the Netherlands) and at the start of the experiment 75 µmol MT was added to the reactor. Gas samples (1 mL) were taken during the first 9 days and analyzed directly. The Henry coefficients that were defined in this manuscript were used to estimate the concentration in the liquid phase.

3. Results and discussion

3.1. Method development

The method parameters were varied to obtain a good chromatographic response. The chromatograms show a good peak separation and resolution (Fig. 1) under the conditions described in the materials and methods. Each compound has a different response area, which is typical for FPD systems were the response is influenced by the molecular structure [38,39]. The background noise of the blank sample was small indicating a high sensitivity for the

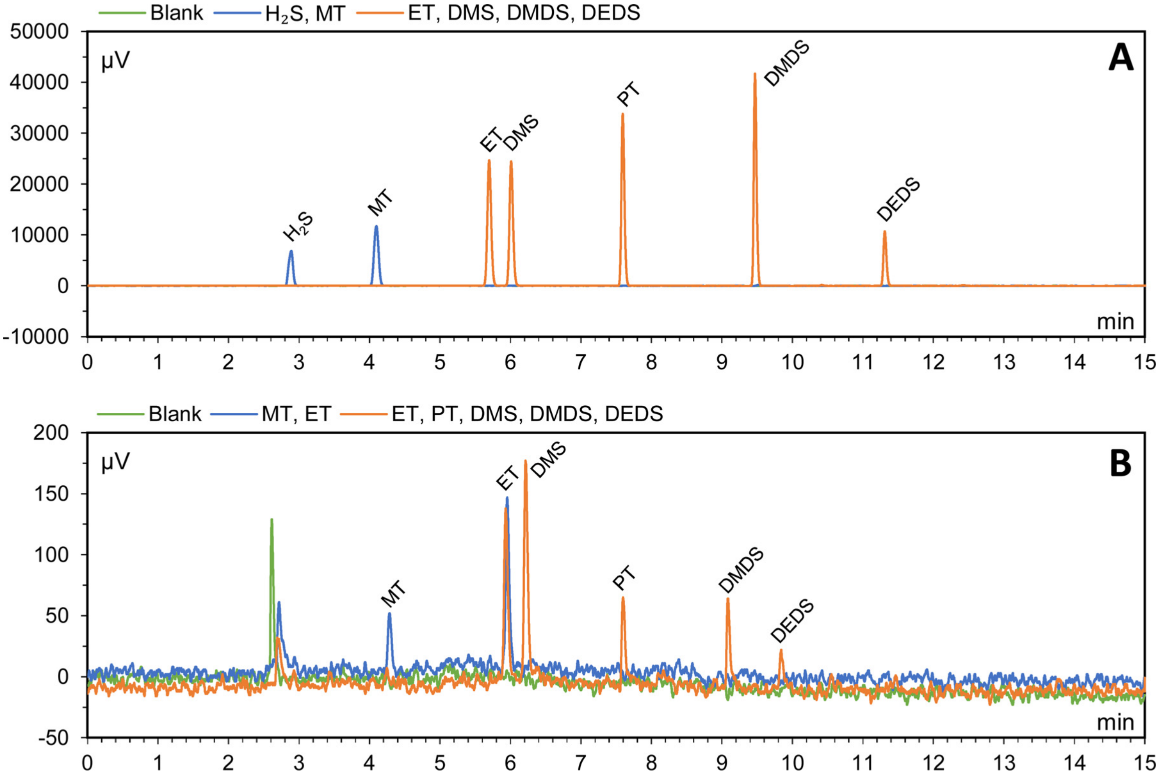

Figure 1. Chromatogram showing a good peak separation of H_2S, MT, ET, DMS, PT, DMDS and DEDS in the gas phase (A) and liquid phase (B) at the lowest gas calibration point.

sulfur compounds typical for FPD detectors [39]. The method had a high selectivity as no detectible interference was observed in the blank chromatograms in both gas and liquid phase.

3.1.1. Equilibration time

The influence of the equilibration time in both the gas and liquid phase was evaluated by analyzing the response area after different equilibration times. The test showed a similar response area (SI-1) with RSD values of 0.29 % for ethanethiol in the liquid phase, and 0.35% for propanethiol and 0.46% for DMDS in the gas phase. The low variation between the different equilibration times shows sorption/desorption processes in the glass vials were finalized within 7 min for both propanethiol and DMDS and that a gas-liquid equilibrium was obtained for ethanethiol within the same period. Similar behavior for the other organosulfur compounds was assumed. Therefore, a equilibration time of 7 min was considered sufficient to measure all compounds accurately.

3.1.2. Temperature gas standard preparation

The preparation of the mixed gas standard from pure liquids requires complete vaporization of these compounds towards the gas phase before further dilutions can be made to obtain the calibration line. Therefore, vaporization of the VOSCs was evaluated after heating the mixed gas standard to different temperatures. Full vaporization of thiols occurred at room temperature, whereas 30 min of heating at 50°C was required for the full vaporization of disulfides (SI-2). This temperature was therefore used to prepare standards for further evaluation of the method.

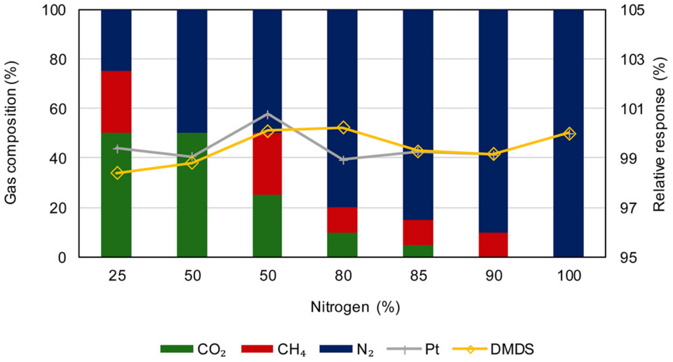

Figure 2. The relative response of propanethiol (PT) and dimethyl disulfide (DMDS) at different gas compositions compared to the response under a 100% nitrogen atmosphere

3.1.3. Signal quenching

Signal quenching due to the coelution of hydrocarbon compounds is a well-known problem for flame photometric detectors [38–41]. The (bio)gas composition in industrial processes can vary substantially at different sites with varying concentrations of methane and carbon dioxide and may therefore influence the FPD response. Propanethiol and DMDS were used as model compounds to represent thiols and disulfides to evaluate the influence signal quenching (chromatograms can be found in SI-3). The response of PT and DMDS was close to 100% with increased carbon dioxide or methane concentrations (Fig. 2). The results show a maximum response variation of 1.1% for propanethiol and 1.6% for DMDS compared to the 100% nitrogen reference. Therefore, the matrix effects and signal quenching due to the presence of methane and carbon dioxide were minimal under the evaluated conditions.

Signal quenching in liquid samples due to the coelution of organic solvents e.g. methanol is another known phenomenon that can be limited by operating the injector in split mode [42]. However, the developed method was specified for a highly saline water

Table 2
Influence of acidification on pH and response area measured at an organosulfur concentration of 0.05 mM-S.

		Response Area (μV*min)					
	pH	MT	ET	DMS	PT	DMDS	DEDS
No buffer	8.5	15	0	68	9	42	n.d
0.2 M Glycine + 0.2 M HCl	4.7	30	24	79	22	0	0
0.5 M HCl	3.4	2.881	1.743	12.050	6.217	3.035	2.855
1 M Acetic acid	6.4	140.654	107.457	657.432	179.327	535.185	571.821

* n.d = not detected.

solvent. VOSCs are more volatile compared to water and presence of water vapor was expected to have limited influence on the signal intensity and therefore not further evaluated.

3.1.4. Sample acidification and salting out effects

In general, organosulfur compounds oxidize faster at a high pH values [43] and acidification can be used as a strategy to minimize the oxidation and maintain sample integrity. Acidification of municipal wastewater samples with HCl in anaerobic vials was previously shown to suppress oxidation of methanethiol and samples remained stable for 24 h [29]. Alternative strategies to avoid oxidation include the addition of Na_2SO_3 to a sample vial. Na_2SO_3 consumes the available oxygen and can limit oxidation. However, when added in excess, sodium sulfate can reduce DMDS to methanethiol, altering the concentrations of both components [29]. To maintain sample integrity, acidification was therefore preferred in this study.

The obtained response areas for acidified samples are presented in Table 2. The largest response area for each VOSCs was found when an acetate buffer was added to the samples. The response when HCl was used for acidification was 28 to 200 smaller compared to the acetate buffer and samples acidified with a glycine and HCl showed almost no response for each of the organosulfur compounds. Interestingly, the solution with the highest pH after acidification showed the largest response area. A pH of 6.4 is sufficient to convert over 99% of thiols to their conjugate acid (i.e. pKa thiols >10 see SI-4), allowing them to transfer to the gas phase. Therefore, the acid formation did not form the main contribution for the increased exclusion of VOSCs from the liquid phase and the higher response areas that were found. This is also confirmed by the increased exclusion of disulfides which do not dissociate. The salting out effect on the other hand may have played a dominating role in the increased exclusion. The acetic acid buffer had the highest salinity and therefore might have the largest salting out effect. Which would also explain the increased exclusion of DMDS and DEDS.

3.1.5. Simplification of liquid calibration procedure

Gas working standards were stable for 2 weeks after preparation when stored at 4°C(See SI-5). Liquid working standards, however, did not remain stable and dimerization and oxidation reactions in the liquid resulted in various peaks in the chromatograms within 2 days after standard preparation (See SI-6). These peaks were not further identified, and liquid standards could thus only be used directly after preparation.

Gas standards were more stable compared to liquid standards and were therefore used to simplify the calibration procedure of the liquid phase. An average response ratio of 105.2% for ET, 107.0% for DMS, 105.7% for PT, 108.9% for DMDS and 106.0% for DEDS was found (SI-7) when the use of gas standards to calibrate the liquid phase were compared to liquid standards. Therefore, the use of gas standards for liquid calibration under the applied conditions results in a slight under-estimation of the actual concentration. However, we recommend the use of gas standards for liquid calibration for routine analyses, as it simplifies the calibration procedures and obtains good results to follow system dynamics and long-term trends.

3.2. Method validation

3.2.1. Linearity

Calibration lines for H_2S, MT, ET, PT, DMS, DMDS and DEDS for gas analyses were constructed over a concentration range of 0.074–1.85 μM. The calibration curves are presented in Fig. 3a and 3b and the corresponding line equations can be found in Table 3. These calibration lines had exponential characteristics typical for FPD detectors. A linear relationship with determination coefficients $R^2 > 0.999$ for all compounds was obtained when analyzing the natural logarithm of the peak area and the natural logarithm of the sulfur concentration. Preliminary results showed that the concentration range could be extended to 10 μM without compromising the determination coefficients of the calibration line (results not shown). The extension of the calibration line was not further evaluated as gaseous samples can be diluted within the calibration range by adjusting the sample volume added to the 10 mL vials.

The calibration lines for MT, ET, PT, DMS, DMDS and DEDS for liquid analyses were constructed over a calibration range of 5–125 μM (Fig. 3c and 3d). Liquid samples with higher concentrations can be measured by decreasing the sample injection volume and addition of saline matrix reaching a total volume of 200 μL. The determination coefficient for liquid standards is slightly lower ($R^2 > 0.996$) than the determination coefficient for the gaseous standards and could be the result of the observed increased reactivity of organosulfur compounds in the liquid phase. Even though an increased reactivity in liquid standards was observed, the determination coefficients were still good. We observed an increased reactivity of the VOSCs standards when H_2S was added to the liquid standard (results not shown). When a calibration for H_2S in the liquid phase is required we recommend constructing separate calibration curves for H_2S and for VOSCs. For analyses of environmental samples containing both organosulfur compounds and H_2S in the liquid phase we recommend fast analyses to maintain sample integrity.

3.2.2. Reproducibility and detection limits

Multiple gas calibration lines, produced over various days, indicated a high reproducibility with RSD values below 3.5% at the lowest calibration point (0.074 μM) (Table 3). The liquid phase calibration lines showed lower RSD values ranging from 0.4% to 0.9% at the lowest calibration point (5μM). The increased reproducibility in liquid samples is likely related to the higher concentration at which the calibration of the liquid phase started. Cheng et al. measured organosulfur compounds in the liquid phase on a GC-MS and found RSD values in the same range with values varying between 0 and 8%. However, their method required a 25-min purge and trap pretreatment procedure [29], whereas the method described

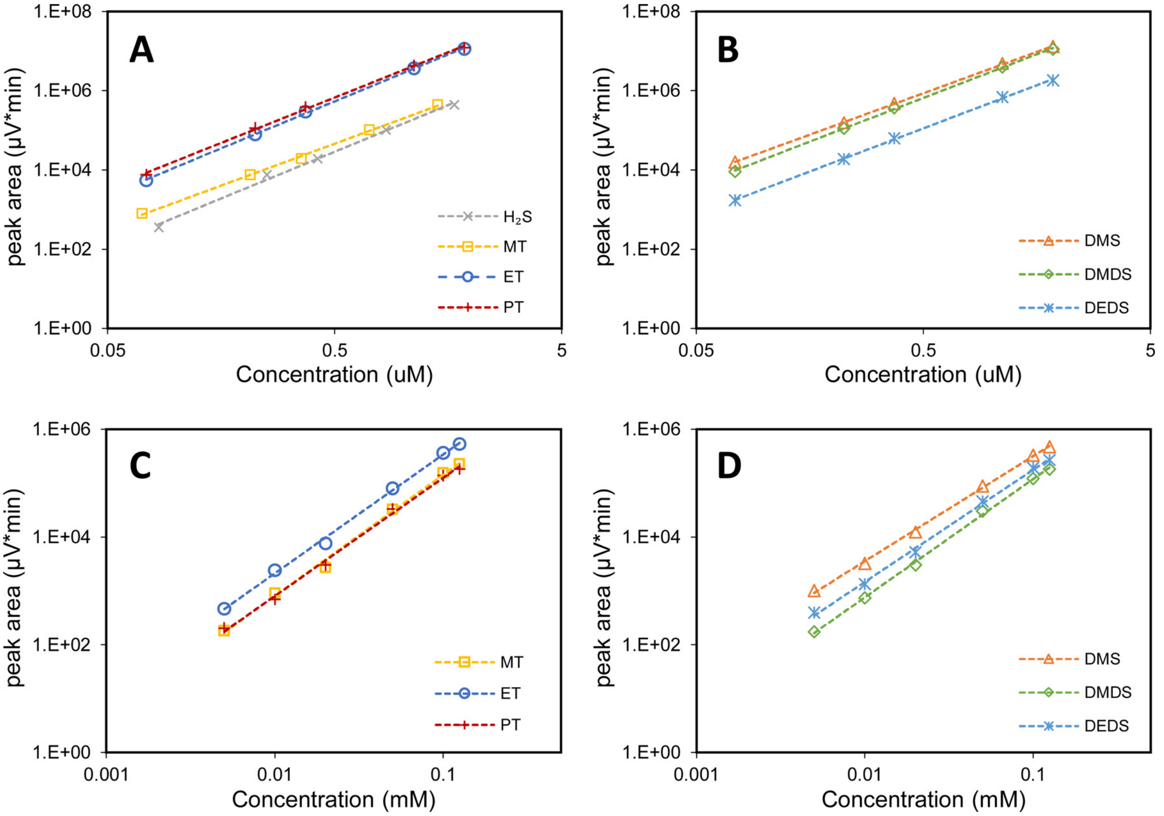

Figure 3. Calibration curve and linearity of tested VOSCs in the gas phase (A and B) and liquid phase (C and D) using gas standards showing good linearity.

Table 3
Overview of gas and liquid calibration parameters.

VOSCS	Calibration Range (µM)	LOQ nM	LOD nM	Slope	Intercept	R^2	RSD %*
Gas							
H2S	0.084-1.68	10.05	4.22	2.114	12.200	0.999	1.85 (n=6)
MT	0.071-1.42	16.2	7.07	2.114	12.200	0.999	1.35 (n=6)
ET	0.074-1.85	5.76	3.72	2.372	14.838	0.999	3.08 (n=10)
DMS	0.074-1.85	2.17	1.30	2.089	7.875	0.999	1.51 (n=10)
PT	0.074-1.85	4.85	3.09	0.964	0.691	0.999	2.48 (n=10)
DMDS	0.074-1.85	2.83	1.72	1.056	-1.034	0.999	2.70 (n=10)
DEDS	0.074-1.85	4.83	2.90	0.951	-1.128	0.999	3.48 (n=10)
Liquid**							
MT	5-125	7.22	4.43	0.646	3.451	0.996	0.6 (n=10)
ET	5-125	2.59	1.55	0.982	1.080	0.998	0.4 (n=10)
DMS	5-125	2.01	1.18	1.126	-2.521	0.999	0.5 (n=10)
PT	5-125	2.63	1.57	0.882	1.422	0.997	0.6 (n=10)
DMDS	5-125	2.06	1.23	1.000	-0.053	0.999	0.5 (n=10)
DEDS	5-125	14.02	7.66	0.948	1.004	0.998	0.9 (n=10)

* RSD at for the lowest calibration point; 0.074 µM for gas and 5 µM for liquid standards.
** Liquid calibration with gas standards

in this manuscript shows not only a higher reproducibility but is also based on direct measurement. Direct headspace analyses in wastewater samples was also performed by Sun et al., and showed a spiked sample recovery between 83 and 103% for MT, DMS and DMDS using a GC-SCD [25].

The limit of quantification for gas standards was between 2.17nM and 16.2 nM and for liquid standards between 2.01 and 14.2. Within the gas standards, the quantification limits were higher for the smaller molecules, i.e. hydrogen disulfide and methanethiol, whereas the limit of quantification in the liquid phase was especially high for DEDS. Indicative experiments (results not shown) demonstrated that the limit of quantification can be further increased by increasing the injection volume to the column for both gaseous and liquid analyses. The signal to noise ratio should be studied to further evaluate the limit of quantification when using larger injection volumes. Furthermore, the use of different split ratios may assist in avoiding loss of efficiency by overloading the column. Another strategy to increase the limit of quantification for liquid samples is to further explore the influence of acidification and salting out as these resulted in a higher VOSCs concentration in the headspace and an increased response area on the chromatograms. However, changes in matrix effect should be considered and further evaluated. Direct liquid injection is not preferred as the expansion volume of the water and the resulting pressure changes will limit the methods precision. Furthermore, the deposition of salts reduce

Table 4
Overview of the henry coefficients for the five studied organosulfur compounds: ethanethiol, propanethiol, dimethyl sulfide, dimethyl disulfide, and diethyl disulfide, in demineralized water and saline matrix and their relative standard deviations.

OSC	Demineralized water	Saline matrix	Demineralized water		
	This study	*This study*	[30]	[32]	[33]
MT	11.93 ± 5.0	7.48 ± 1.0	9.88		
ET	5.90 ± 3.4	4.69 ± 0.4	6.88	5.45	
PT	5.03 ± 4.3	3.32 ± 1.0	5.99		
DMS	13.93 ± 5.2	9.46 ± 2.4	13.72	15.12	11.52
DMDS	13.53 ± 1.8	9.31 ± 2.7	22.22	20.58	14.38
DEDS	9.67 ± 2.6	6.24 ± 2.5	16.06	11.65	9.17

the lifetime and efficiency of the column and requires frequent maintenance.

3.3. Method application

3.3.1. Henry coefficient determination

The Henry coefficient of ET, PT and DMS in demineralized water with our measurement method are similar to the Henry coefficients found in the literature (Table 4). However, the obtained Henry coefficients for DMDS and DEDS in this work are, in the same order of magnitude, but lower than previously reported Henry coefficients for reasons not well understood. Henry coefficients in the saline matrix are lower than coefficients obtained in demineralized water for each compound. This means that a larger fraction of the compounds was present in the gas phase. The salting out effect that drives thiols to the gas phase due to the high salinity and influences the henry coefficient. The effect of increasing ionic strength resulting in lower Henry coefficients was also observed when comparing Henry coefficients obtained in demineralized water and sea water [44]. Another parameter that can influence the measured Henry coefficient is the acid base dissociation constant. The pKa of MT, ET and PT at 25°C is 10.33, 10.39, 10.44 respectively (SI-4) [45]. With a pH of 8.4 in the liquid matrix, only a small fraction <0.99% of the organosulfur is present as its conjugate base. Therefore, the pKa has a limited influence on the Henry coefficient and was not further considered.

3.3.2. Samples of lab scale bioelectrochemical reactor treating MT

The results of the lab scale bioelectrochemical system treating methanethiol are presented in Fig. 4. MT and DMDS were successfully measured with the developed method. No other organosulfur compounds nor H_2S were observed in the chromatograms (See SI-8 for an example chromatogram). The concentration of methanethiol decreased from 0.95 µM-S towards zero during the first 3 days of the experiment, while DMDS increased from 0 to 1.33 µM-S during the first two days. DMDS can be formed from methanethiol under microaerobic conditions in an autocatalytic or biocatalytic reaction. Not all MT was recovered in the form as DMDS which may be the results of microbial degradation, volatilization from the system or the formation of other, unknown, sulfur compounds. DMDS may also adsorb to the graphite felt electrode material, another reason why not al MT was recovered as DMDS. The applied chromatographic method can be used to further study the degradation kinetics and interaction of the organosulfur compounds with the electrode fur further development of this new technology. Furthermore, the method may also be used for the measurement of VOSCs in a full-scale bio-desulfurization plant that operates with a similar matrix.

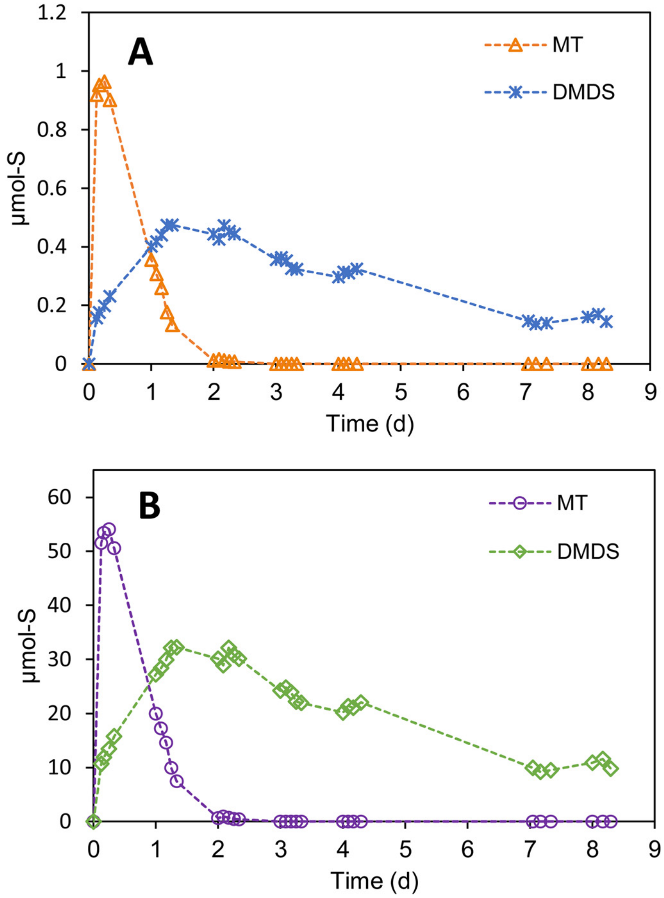

Figure 4. Detected VOSCs in the gas (A) and liquid (B) phase of a bio electrochemical lab reactor treating methanethiol.

4. Conclusion and outlook

A new method using GC-FPD was developed for routine analyses of VOSCs in complex liquid and gaseous samples. We demonstrated that apart from the more commonly measured compounds H2S, DMS and DMDS also PT, ET and DEDS could be measured accurately. VOSCs could be measured in a range from 5 µM-S to 125 µM-S for liquid and 0.08–1.85 µM-S for gaseous samples. Gas standards can be used to calibrate the liquid phase with response ratios between 105.2 and 108.9 % for the different VOSCs. Samples with higher concentrations could be easily diluted to fall within the calibration range. High reproducibility values with a relative standard deviation below 3.5% were found for both gas and liquid standards. The results show that signal quenching due to coelution with carbon compounds in the gaseous phase was minimal under the tested concentrations. Henry coefficients were defined in both demineralized water and saline matrix and can be used to obtain a rapid indication of the concentrations in the liquid phase while only analyzing the static gas phase above the liquid. The method is suitable for routine analyses of highly saline samples with a high pH and can potentially be extended to other complex matrices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2022.463276.

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