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Headspace SPME followed by GC/PFPD for the analysis of malodorous sulfur compounds in liquid industrial effluents

François Lestremau · Valérie Desauziers · Jean-Louis Fanlo

Abstract Headspace SPME was used to analyse mal-odorous sulfur compounds in liquid industrial effluents. A pulsed flame photometric detector (PFPD) was selected for a specific and sensitive analysis. Two fibres, PDMS/Dvb and PDMS/Carboxen, which are particularly convenient for extracting small and volatile molecules were tested. To compare these fibres, both sensitivity and artefact formation were considered. The PDMS/Carboxen fibre showed the lower limits of detection and moreover the least artefact formation yields. It was therefore selected and headspace SPME extraction conditions were optimised. Limits of detection of the target compounds evaluated were 12–31 ng L⁻¹ and repeatability was around 7%. Due to the adsorption mechanism involved, extraction is strongly influenced by the sample matrix and the low affinity compounds can suffer displacement effects. To investigate the occurrence of this phenomenon, two sampling times corresponding to non-equilibrium (5 min) and equilibrium conditions (60 min) were investigated. An external calibration was carried out by using standard solutions for both sampling times. The developed procedure was then compared to the standard addition method on a real industrial effluent. The results obtained from the two methods and for the two extraction times were in good agreement, demonstrating that even a long sampling time can be used. Therefore, the simple and timesaving external calibration was defined as relevant for an accurate quantification of sulfur compounds by headspace SPME.

Keywords SPME · Sulfur compounds · Liquid effluent · Headspace

Introduction

Malodorous sulfur compounds are usually low molecular mass compounds (below 150 g mol⁻¹) such as hydrogen sulfide and mercaptans. They originate mainly from the fermentation of amino-acid-containing sulfur and are commonly encountered in liquid industrial effluent such as wastewater, food chemistry, pulp milling etc. The current level of toxicity of these compounds is generally high at about the ppm level. However, the growing concern about health protection should in the near future lead to a better knowledge of the impact of these compounds and will probably result in a decrease of the known toxicity levels. Recent studies [1, 2] emphasised the possible negative effects of trace levels of these compounds on human beings (e.g. inducing nausea and headaches). Moreover they are perceived by human nose at very low levels (sub- $\mu\text{g m}^{-3}$). Their volatilisation into the atmosphere induces terribly unpleasant malodorous nuisance for the neighbouring population of the concerned plant and can lead to complaints. Thus, an effective analytical technique is required to characterise effluents at trace levels for use in determining an appropriate remediation process.

Detection can be carried out by using a non-selective detector such as a mass spectrometer usually in the specific ion monitoring mode or with a more specific detector dedicated to sulfur compounds. The most frequently employed are the flame photometric detector (FPD), the sulfur chemiluminescence detector (SCD) or the atomic emission detector (AED). An improvement of the FPD detector, the pulsed flame photometric detector (PFPD), has been available for a few years [3, 4, 5]. After every ignition of the pulsed flame, light emission is recorded. As sulfur compounds have a delayed emission compared to hydrocarbon compounds, quenching can be avoided and a good selectivity is achieved. Consequently, limits of detection are also improved relative to FPD and despite being less sensitive than SCD and AED, its robustness and low-cost design it is a good tool for the detection of sulfur compounds. However, at trace level concentrations, the direct analysis of effluents is often not possible due to

complex matrices, which can cause interferences, and to the lack of sensitivity of analytical detectors. A preconcentration technique is then necessary.

The purge and trap technique is the most widely used in this case [6]. The liquid sample is purged with an inert gas that takes away the volatile analytes. These are then preconcentrated in a cryogenic trap or onto solid adsorbents and then thermally desorbed to complete the analysis. However, some problems can arise such as clogging of the purge system with a very dense matrix or losses of analytes during the preconcentration step.

The low cost and easy-to-use SPME can constitute a convenient alternative. Owing to the low vapour pressure of malodorous sulfur compounds, a significant proportion of those in the liquid phase will be volatilised into the gas phase. The utilisation of headspace SPME (HS-SPME) rather than direct sampling into the liquid matrix is then preferred because interference from high molecular masses compounds is reduced and it avoids spoiling the fibre. The first publication about sulfur compound analysis by HS-SPME concerned the characterisation of aroma in truffles [7]. In food analysis, wine and beer were also extensively studied [8, 9, 10, 11, 12, 13]. In wastewater, several studies have been related to the investigation of semi-volatile sulfur [14, 15]. Comparison of several fibres showed the PDMS/Carboxen fibre was the best suited to reach the ng L^{-1} level. However, this fibre has been reported to involve competitive adsorption leading to displacement of low affinity analytes [16, 17]. Moreover, with this particular fibre, several papers report formation of artefacts for the sampling of sulfur compounds in the gas phase [18, 19, 20]. Therefore, HS-SPME for quantitative analysis of sulfur compounds in effluents has to be optimised.

This paper presents the comparison of two SPME fibres considering performance attained with each coating but also artefact formation. Then, the possible occurrence of competitive adsorption between analytes and matrix was investigated. Two sampling times were studied and quantification based on external calibration was developed. The methodology was applied to industrial effluents and compared to a second quantification method assessed as reference and based on standard additions.

Experimental

Chromatography

A Varian 3800 gas chromatograph (Varian, Les Ulis, France) equipped with a 1079 split/splitless injector and a Varian pulsed flame photometric detector was used. The injector had a 0.8-mm-ID liner. The detector temperature was set at 200°C, detector voltage at 600 V, detector gate delay at 6 ms, gate width at 20 ms, and detector trigger at 200 mV. The gas flows to the detector were at 14 mL min^{-1} of hydrogen, 18 mL min^{-1} of air1 and 11 mL min^{-1} of air2. Star software (Varian, Les Ulis, France) was used to record signal and integrate peaks. Carrier gas for the column was helium at a flow rate of 2.0 mL min^{-1} . An SPB1-sulfur 30 $\text{m} \times 0.32\text{-mm-ID}$, 4- μm column from Supelco (Bellefonte, PA, USA) was used. The oven program was: 3 min at 30°C then ramped at 20°C min^{-1} to 150°C for 5 min.

Table 1 Physical characteristics of standard sulfur compounds

Compounds	Molecular mass (g mol^{-1})	Boiling point ($^{\circ}\text{C}$)	Henry coefficient (M atm^{-1})
Ethanethiol	62	36	0.28
DMS	62	38	0.56
CS_2	76	46	0.076
DMDS	94	110	0.96

Chemical and materials

Ethanethiol, dimethylsulfide (DMS), carbon disulfide (CS_2) and dimethyldisulfide (DMDS) were obtained from Acros (Noisy Le Grand, France) and were all over 99% purity. Physical characteristics of standard compounds are given in Table 1. Primary standard solutions were prepared by weighing respective sulfur compounds and diluting them in methanol Purge & Trap grade (Fluka, Saint-Quentin Fallavier, France) to obtain 50 g L^{-1} solutions. Individual and mixture solutions were prepared from the primary solutions by dilution with 18 M Ω water (MilliQ water, Waters, Saint-Quentin-en-Yvelines, France). All solutions were stored in the dark at 4°C.

Preparation of sample solutions

The solutions were prepared by using micropipettes (Gilson, Roissy, France) of 20, 200, 1,000 and 5,000 μL . In 15-mL vials, 4 mL of sample was prepared by addition of a known volume (between 5 and 1,280 μL) of diluted solution and completed by MQwater. Solutions ranging between 62.5 and 2,000 ng L^{-1} were then obtained. The vials were capped with PTFE-faced silicone septa. The samples were constantly stirred with a Teflon magnetic stirrer bar by using a magnetic stirrer (Bioblock, Illkirch, France). No salt was added, since Abalos et al. [15] demonstrated that changing this factor had no influence on the uptake. These authors also investigated the influence of temperature during extraction and concluded that although temperature enhanced volatilisation of compounds into headspace when increased, the adsorption was also significantly decreased, since it is an exothermic phenomenon. The lowest temperature tested (25°C) was determined to provide the best extraction [15]. It can therefore be supposed that extractions could be efficiently achieved at ambient temperature. Our experiments were thus performed in a thermostated room at 20°C.

Standard addition method

As a comparison method to the result obtained by external calibration, the standard addition method was applied to real samples. For each calibration point, a new 4-mL sample solution was used and spiked with a known volume of standard solution. The spiked volume did not exceed 50 μL to keep the sample volume constant. HS-SPME was then applied under the experimental conditions defined in the following paragraphs.

Solid-phase microextraction (SPME)

A manual SPME device was used. Two different coatings were tested: PDMS/Dvb (polydimethylsiloxane/divinylbenzene) (65- μm coating thickness) and PDMS/Carboxen (75- μm coating thickness), all from Supelco (Bellefonte, PA, USA). The fibre was inserted in the vial through the septum and exposed to the headspace for sampling. At the end of the sampling, the fibre was retracted in the housing, removed from the vial and thermodesorption was performed in the injection port of the GC. Desorption was held at 250°C for 2 min, since no carry over was noticed at these settings.

Real samples

Two different samples were used to evaluate the potential of the SPME for quantitative analysis. The first sample was wastewater from a wastewater treatment plant (Saint Christol les Alès, France). The second samples were from a poultry factory (in the area of Nîmes, France), which suffer from severe odour problems. By-products (hearts, livers etc.) are processed into a cooker under high temperature and pressure to produce animal proteins. This activity produces gases with high concentrations of odorous compounds and high water content, which is collected in a condenser. But the aqueous fraction collected also contains solubilised odorous compounds. Analysis of these samples was carried out by using the method developed.

Result and discussion

Influence of agitation

Magnetic stirring of sample (about 700 rpm) before sampling was studied to get the most reliable analysis in terms

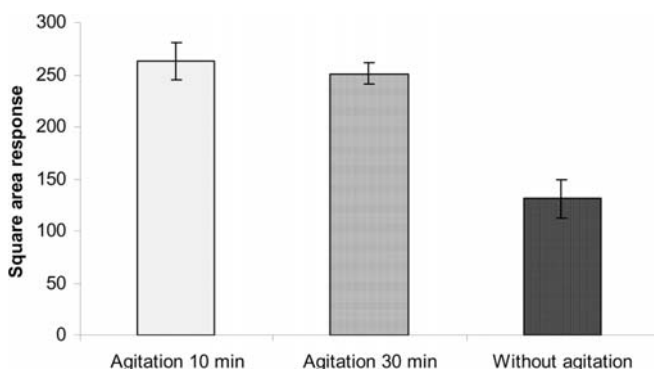
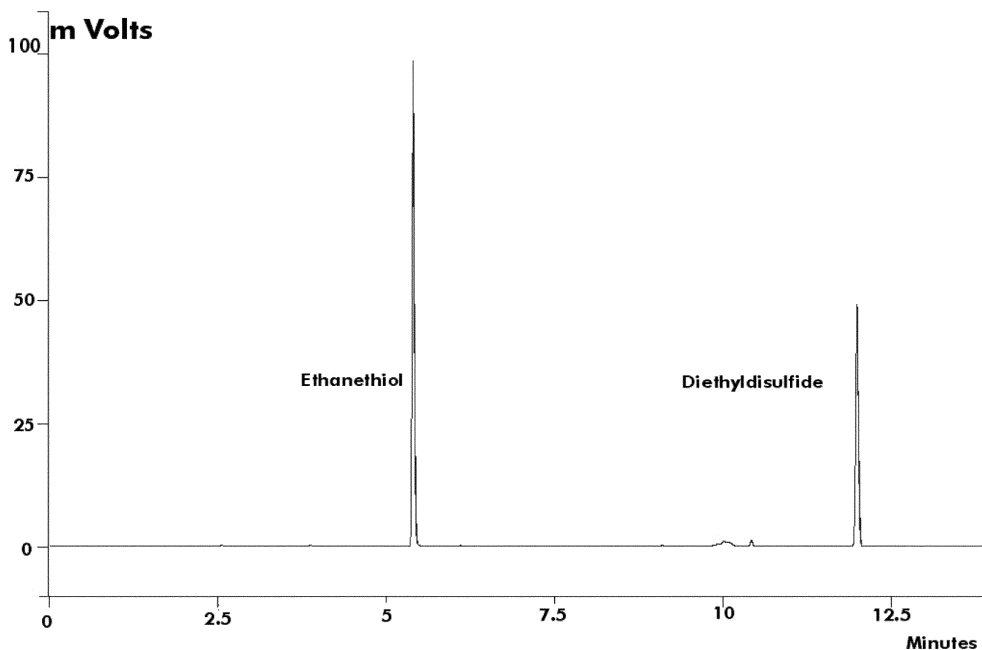


Fig. 1 Influence of agitation on extraction of DMS for a 5-min sampling time (calculated with 3 replicates)

Fig. 2 Chromatogram of ethanethiol using the PDMS/Dvb fibre for a 5-min sampling and $1,000 \text{ ng L}^{-1}$



of repeatability and sensitivity. DMS extraction was studied without agitation (for 30 min) and with agitation for 10 and 30 min. Without stirring, results in terms of repeatability and sensitivity were poor compared to stirred samples (Fig. 1). The results obtained for 10-min and 30-min stirring times were similar in terms of sensitivity; however, the repeatability was better for the latter (4% versus 7% relative standard deviation). As a compromise between time of analysis and repeatability, a 20-min stirring time was applied in the further experiments.

Comparison of SPME fibres

Previous studies [9, 14, 15] on HS-SPME of sulfur compounds showed that only two fibres (PDMS/Dvb and PDMS/Carboxen) were suited to reach low concentration levels. However, the use of these fibres can lead to the formation of artefacts during the thermodesorption step. This phenomenon is dependent of the nature of the fibre. For example, with amines, the PDMS/Carboxen fibre caused extended decomposition of tested compounds, whereas artefact formation was negligible with PDMS or PDMS/Dvb coatings [21]. Therefore, the studied fibres were also compared not only in term of sensitivity but also in regards to artefact formation. With the four compounds tested (ethanethiol, DMS, CS_2 and DMDS), the same reaction, dimerisation of ethylsulfide into diethyldisulfide, occurred with both fibres (Fig. 2). A similar reaction was found in the air analysis with methanethiol to form DMDS [18, 19, 20]. With a PDMS/Dvb fibre, ethanethiol was partly decomposed. However, none of the other tested compounds were affected by the thermal oxidation phenomenon, thereby allowing their qualitative and quantitative analysis. The PDMS/Carboxen fibre led to the total dimerisation of ethanethiol into diethyldisulfide; thus, quantification of

ethanethiol was not possible by SPME using these fibres. However, no other compounds were affected by the ethanethiol reaction and could be analysed without interference. Analysis was carried out in further experiments only for DMS, CS₂ and DMDS. Limits of detection were also evaluated. The PDMS/Carboxen fibre allows one to reach a better level of sensitivity than the PDMS/Dvb fibre. Limits of detection of 12–31 ng L⁻¹ were achieved with this fibre. They were about 4 times lower than those obtained with the PDMS/Dvb fibre (Table 2). Repeatability was notably the same for both fibres, around 7%. The PDMS/Carboxen fibre was chosen for the further studies.

Adsorption kinetics/ determination of extraction time

Adsorption kinetics were determined for a mixture of analytes at a concentration of 250 ng L⁻¹ up to 2 h (Fig. 3). The three compounds displayed significantly different adsorption profiles. For CS₂, equilibrium is reached rapidly, after about 5 min, whereas for DMS, this occurs only after 60 min. After 2 h of sampling, for DMDS, the equilibrium had not been reached. CS₂ possesses the lowest Henry coefficient, so its diffusion from the condensed phase to the gas phase is faster than for the other compounds. Then, the adsorption equilibrium can be reached rapidly. DMDS, which has the highest Henry coefficient, diffuses more slowly but as its affinity for the coating is better than that of CS₂, adsorption proceeds for a long time before reaching equilibrium.

For determining the optimum SPME sampling time, two main theories can be considered. The first one is based on the establishment of adsorption equilibrium of the considered analyte between the sample and the fibre coating. This can be advantageous, since at this stage the uptake does not depend on sampling time, and reproducibility and sensitivity are improved. However, this methodology can involve some limitations, especially when using solid microporous adsorbents such as Carboxen. In this case, as a result of the limited number of adsorption sites, saturation

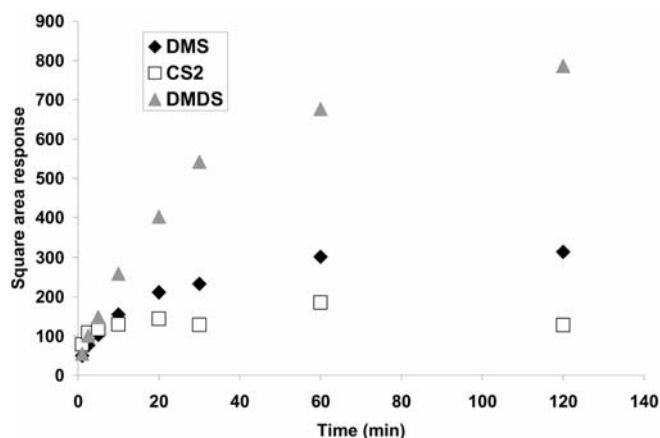


Fig. 3 Kinetics of a mixture of sulfur compounds at a concentration of 250 ng L⁻¹ each

Table 2 Limits of detection (LOD) of sulfur compounds for the PDMS/Dvb and PDMS/Carboxen fibres, and repeatability (expressed as RSD on 3 replicates) for the PDMS/Carboxen fibre for 5-min and 60-min exposure times

Compounds	PDMS/Dvb 5 min LOD (ng L ⁻¹)	PDMS/Carboxen			
		5 min		60 min	
		LOD (ng L ⁻¹)	RSD (%)	LOD (ng L ⁻¹)	RSD (%)
DMS	63	31	7	11	3
CS ₂	462	19	10	15	2
DMDS	84	12	5	3	2

tion may occur rapidly. Compounds with the lowest affinity for the adsorbent can be displaced, thus leading to inaccurate quantification by external calibration. This phenomenon has already been observed for gaseous analysis using SPME [16, 17]. To prevent this phenomenon, a short sampling time in non-equilibrium conditions was investigated [22]. Tuduri et al. [23] demonstrated that with a short exposure time, amount extracted on the fibre is reduced; therefore, the range of concentration that can be sampled is increased, since saturation of the coating occurs at a later stage. On the other hand, limits of detection are also increased.

Two extraction times were then considered for evaluating the possibility of quantification by external calibration. The first one was set at 60 min for sampling under equilibrium conditions. An extraction time of 5 min (i.e. non-equilibrium conditions) was also evaluated to shorten the analysis time and possibly to avoid displacement effects.

Limits of detection and repeatability

With a 60-min sampling time, detection down to 3 ng L⁻¹ could be achieved, whereas for 5 min and for DMDS, detection limit was evaluated at 12 ng L⁻¹ (Table 2). In general, a 60-min sampling time increased the sensitivity by an order of magnitude between 1.5 and 4 compared to a 5-min sampling. The gain of sensitivity is not linear with time as shown in adsorption kinetics and a higher uptake rate occurs at the beginning of the sampling. Repeatability was determined between 2 and 3% for 60 min and between 5 and 10% for 5 min. As previously stated, a better precision was obtained for a longer sampling time; however, an acceptable 10% precision could be achieved with a 5-min sampling time.

Quantitative analysis

As already mentioned earlier, quantitative analysis using a PDMS/Carboxen fibre must be carefully controlled because it can lead to inaccurate results due to competitive adsorption. For headspace extraction, the phenomenon could be increased due to the presence of water. Although Car-

boxen is rather a non-polar coating, the humidity is known to produce interference [18] and can constitute a severe competitor for analytes. The limits of use must therefore be carefully defined in order to sample in a range not influenced by competitive adsorption. The test of two different sampling times (short and long) demonstrates if displacement could be observed especially for long exposure time and if external calibration could be applied by using the two different sampling periods.

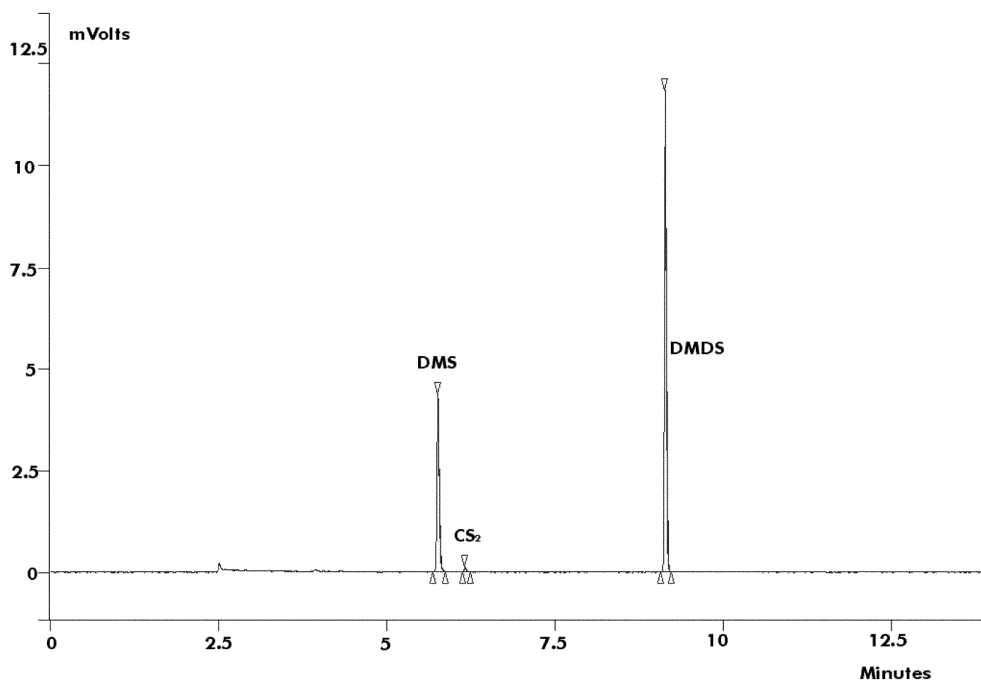
Determination of calibration curves

Compounds were sampled individually up to 2,000 ng L⁻¹ for both sampling times. This concentration constituted the maximum that can be detected before reaching the saturation of the PFPD detector. This feature is also particularly convenient to prevent extracting too much onto the fibre, which could cause competitive adsorption. As predicted by theory [24], a linear relationship between the amount extracted and the concentration was found if the sampling time is held constant. For all compounds and for

Table 3 Slopes ((square area (ng L⁻¹))⁻¹) for extracted compounds sampled individually and in mixture for exposure time of 5 and 60 min

Com- pounds	Sampling time			
	5 min		60 min	
	Individual compounds	Compounds in mixture	Individual compounds	Compounds in mixture
DMS	0.36±0.04	0.38±0.02	1.01±0.04	1.03±0.03
CS ₂	0.61±0.08	0.61±0.04	0.89±0.10	0.93±0.08
DMDS	0.76±0.05	0.76±0.03	2.63±0.26	2.51±0.03

Fig. 4 Chromatogram of wastewater sample using the PDMS/Carboxen fibre for a 5-min sampling time



both sampling times, R^2 values greater than 0.99 were determined within the tested range.

Experiments with a mixture of standard compounds

To check the influence of a simple matrix on the analytes extraction, the target compounds were sampled in a mixture up to 2,000 ng L⁻¹ for both sampling times. Linear calibration curves were achieved in all cases. The slopes determined were compared to the slopes obtained when compounds were sampled individually (Table 3). Identical results were noticed demonstrating that no competitive adsorption due to other analytes or moisture occurred. Indeed, although affinity of water for the coating is low, its high concentration (up to g m⁻³) compared to analytes present in the headspace (µg m⁻³) could cause it to act as a major competitor. However, as headspace SPME extractions are performed in repeatable conditions, moisture can be considered to remain constant at a level corresponding to the saturation of the headspace. Thus, it can be assumed that moisture plays an equivalent influence for each analysis performed in the headspace and consequently can be considered as relatively insignificant. Then, only high concentrations of analytes and eventually a really complex matrix could induce competitive adsorption for remaining sites available for adsorption. As confirmed experimentally, the simple mixture tested does not constitute a significant complex matrix to disrupt the linear uptake with concentration even for long sampling time.

Test on real samples

Analyses of real samples were carried out to confirm the potential of the SPME for quantitative analysis by exter-

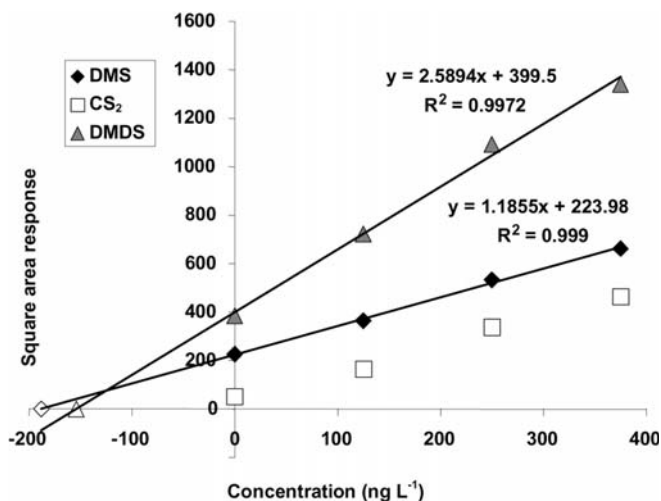


Fig. 5 Linear regression of standard addition on real sample with exposure time of 60 min

nal calibration. The method was first tested with a wastewater sample. An example of chromatogram of a real sample is shown in Fig. 4. To compare with the calibration previously determined, standard addition methodology was also carried out on the sample. The standard addition method has the advantage of taking into account the influence of the matrix during sampling. It can be considered that this method leads to reliable results. However, it is time consuming and more sample is needed to complete the analysis; hence, it is tedious for routine analysis. This method was assessed as reference and the results were compared with those obtained by external calibration. An example of calibration curves obtained by standard additions are given in Fig. 5.

The two sampling times were tested especially to evaluate the potential of a long sampling time on the sample with a complex matrix. Good agreement was achieved between concentrations calculated by standard addition and the concentration found by using the calibration curved determined for both sampling times (Table 4). The discrepancy noticed for DMDS and CS₂ could be due to the possible evolution of the sample between the two different modes of analysis. As the 5-min experiments were performed before the 60-min experiments, DMDS could have decomposed while CS₂ was formed.

Table 4 Calculation of concentrations (ng L⁻¹) in a real sample using external calibration and standard addition method for exposure times of 5 and 60 min

Compounds	Sampling time			
	5 min		60 min	
	External calibration	Standard additions	External calibration	Standard additions
DMS	251±21	197±6	218±4	191±7
CS ₂	10± 1	8±1	44±6	37±2
DMDS	182±11	179±5	159±4	154±9

Table 5 Calculation of concentrations in a real sample from a poultry factory using external calibration and standard addition method for exposures time of 5 min

Compounds	Concentration (µg L ⁻¹)	
	External calibration	Standard additions
DMS	N.D.	N.D.
CS ₂	1.39±0.04	1.37±0.04
DMDS	0.69±0.02	0.63±0.05

N.D. not determined

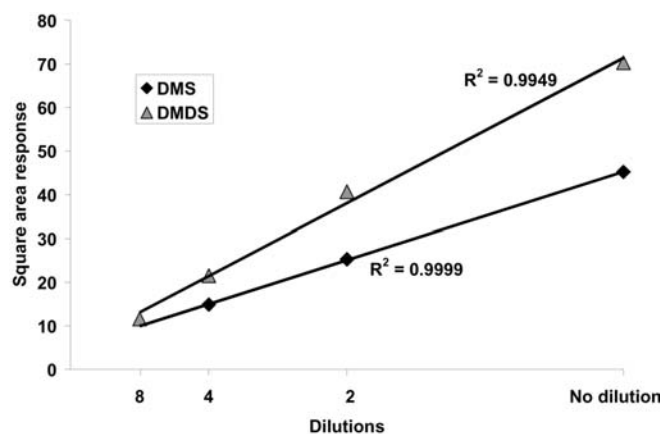


Fig. 6 Dilution of a wastewater sample for an exposure time of 5 min using the PDMS/Carboxen fibre

The method was also tested with a 5-min sampling time on condensates from a poultry factory and good agreements were also determined (Table 5).

Indeed, it should be pointed out that a long sampling time should be used only if sensitivity or precision is required. For high concentrations of analytes, a short sampling time is sufficient and/or the effluent can be diluted if necessary. A wastewater sample was analysed without dilution and was then further diluted several times (Fig. 6). Good linearity was achieved showing that no competitive adsorption occurred. Supposedly, it could be assumed that if no linearity occurs for concentrated sample, then the sample would have to be diluted until a linear range was reached. With the PFPD, some samples from the poultry factory had to be diluted due to the saturation of the detector. But within the working range of the PFPD, it could however be noticed that no displacement effect occurred thereby validating the method even for the longest sampling time tested. Considering the length of the chromatographic analysis which can be evaluated to 20 min including the time for cooling the oven, short sampling times should be better for routine analysis and to prevent inaccurate quantification due to competitive adsorption, since repeatability and limits of detection were in an acceptable range.

Conclusion

The use of headspace SPME for quantification of volatile sulfur compounds can be applied to aqueous industrial effluents. The PDMS/Carboxen fibre was determined as the most suited but care should be taken as artefact formation can arise during analysis. The two sampling times tested (5 and 60 min) were suitable to fulfil the analysis in the samples tested. A long sampling time can be used for accurate and sensitive results, whereas a short sampling time could be preferred for a rapid analysis. However, for the analysis of a really complex matrix, special care should be taken when dealing with long sampling time in order to prevent the possible occurrence of displacement effects. For unknown matrices, a short sampling time should be preferred, since sample can be analysed directly or diluted for really complex matrices.

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