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Development of a quantification method for the analysis of malodorous sulphur compounds in gaseous industrial effluents by solid-phase microextraction and gas chromatography–pulsed flame photometric detection

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Abstract

A quantification method for malodorous sulphur compounds in gaseous industrial effluents using solid-phase microextraction sampling followed by gas chromatography–pulsed flame photometric detection has been developed. A comparative study showed that polydimethylsiloxane–Carboxen fibre led to sufficient sensitivity to achieve the $\mu g\ m^{-3}$ human perception levels of the five analytes studied (hydrogen sulphide, methanethiol, ethanethiol, dimethyl sulphide, dimethyl disulphide). However, this coating is known to suffer from competitive adsorption, which may lead to inaccurate quantification. Therefore, external calibration can only be used under a limited range of concentrations, which were determined from Fick's diffusion law. This approach was tested on a real gaseous sample and compared with the standard addition method. Good correlations were found for ethanethiol, dimethyl sulphide and dimethyl disulphide. However, for more volatile sulphur compounds (i.e., hydrogen sulphide and methanethiol), the easy-to-use external calibration could not be applied and standard additions had to be performed for accurate quantification.
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1. Introduction

Malodorous compounds are usually low-molecular-mass products. They essentially consist of three families: sulphur compounds (H_2S, mercaptans, sulphurs, etc.), oxygen-containing compounds (volatile fatty acids, aldehydes, ketones, etc.) and nitrogen-containing compounds (NH_3, amines, etc.). Two main sources of production can be distinguished: agricultural sources, resulting from fermentation or microbial conversion, for example by farm animals, or industrial sources, such as chemical plants, perfumeries, food companies (e.g., fish processing) or paper manufacturers.

These activities produce high concentrations of odorous compounds (above $mg\ m^{-3}$) that can be analysed directly from gaseous samples. For sulphur compounds, several detectors are commonly used, such as mass spectrometry (MS) or more specific detectors such as sulphur chemiluminescence (SCD) or flame photometric detection (FPD). In the last few years, an improvement of the FPD has been available, a pulsed flame photometric detection (PFPD) system, developed by Amirav and co-workers [1–3].

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This system is based on a flame which is not continuous as for FPD, but pulsed at a rate between 2 and 4 Hz. After ignition of the flame, light emission is recorded. By selecting a suitable range for recording light emission, sulphur compounds, which have delayed emission, can be selectively detected from hydrocarbon compounds, thus avoiding quenching. Consequently, the limits of detection are also improved and despite being less sensitive than SCD and atomic emission detection, its robustness and low cost make it a good tool for the detection of sulphur compounds.

However, when some odorous gas samples are analysed directly, the sensitivity of the PFPD detector is not sufficient to reach the $\mu g\ m^{-3}$ level, which corresponds to the human perception level for sulphur compounds. To reach such a level, a pre-concentration step is required in the analytical procedure.

As an alternative to common pre-concentration methods, solid-phase microextraction (SPME), developed in 1990 [4], is a convenient and attractive solvent-free technique because it combines rapidity and low cost. The SPME device consists of a syringe-like holder containing a fibre mounted in a needle for protection. During sampling, the fibre is directly exposed to the sample. For GC analysis, thermal desorption of the analytes takes place directly in a split/splitless injection port.

With regard to sulphur compounds, SPME has mainly been applied to wastewaters [5], beverages such as wine [6–8] and beer [9,10], and food extracts [11,12]. In these analyses, SPME is mostly carried out in the headspace mode. For gaseous matrices, Wardencki and Namiesnik [13] used polydimethylsiloxane (PDMS) fibre and FPD. They reached a limit of detection of 0.1 mg m^{-3}, which was not low enough to detect volatile sulphur compounds at their olfactory perception levels. Therefore, different coatings were compared in several studies and Carboxen–PDMS fibre was determined to be the most effective for the trace detection of sulphur compounds: limits of detection in the ng m^{-3} range were obtained using mass spectrometry or atomic emission as detection methods [14,15]. However, several limitations were observed with this fibre concerning the decomposition or reaction of analytes in the GC injection port. For example, oxidation of dimethylsulphide to dimethylsulphoxide was observed [14].

Another drawback of Carboxen–PDMS fibre is its limited number of adsorption sites due to the small volume of the Carboxen coating. The fibre thus rapidly becomes saturated, leading to competitive adsorption between low-molecular-mass sulphur compounds and compounds with high affinity for the sorbent [16]. Under these conditions, accurate quantification is difficult, particularly when complex matrices are studied [16]. To prevent this phenomenon, the amount of adsorbed molecules needs to be decreased. This can be achieved by decreasing the exposure time. For volatile organic compounds (VOCs), a non-equilibrium extraction method was developed to find co-adsorption conditions for analytes, i.e. when the fibre is not yet saturated and where matrix effects can be considered to have no influence on compound adsorption, thus allowing their quantification by external calibration [17].

Several commercially available SPME fibres in combination with pulsed flame photometric detection were compared with respect to their ability to detect sulphur compounds at their human perception levels and also with regard to artefact formation. To our knowledge, SPME has not been used combined with PFPD before.

According to the selected fibre, the extraction time was defined from adsorption kinetics, to avoid coating saturation. To be more accurate in the determination of the co-adsorption conditions, a methodology based on Fick's diffusion law and commonly applied to passive samplers was used [18,19]. The aim was to determine the concentration range for which an accurate quantification can be achieved by external calibration, whatever the extraction time chosen by the analyst. This new methodological approach was then tested on a real sample and compared with the standard addition method. Sampling and storage conditions were also examined.

2. Experimental

2.1. Chromatography

A Varian 3800 gas chromatograph equipped with a

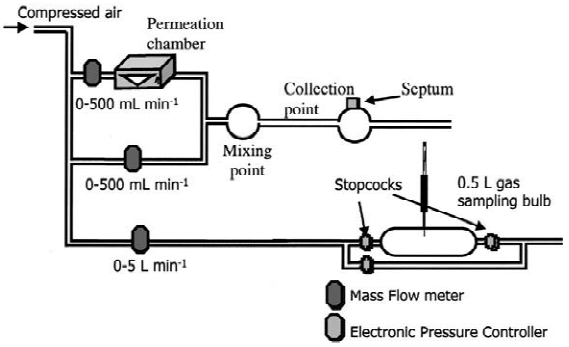

Fig. 1. Apparatus for the generation of gas test atmosphere.

1079 split/splitless injector and a pulsed flame photometric detector was used for analysis. The injector had a 0.8 mm I.D. liner. The detector temperature was set at 200 °C, the detector voltage at 600 V, the detector gate delay at 6 ms, the gate width at 20 ms, and the detector trigger at 200 mV. The gas flow-rates of the detector were 14 mL min^{-1} for hydrogen, 18 mL min^{-1} for air1 and 11 mL min^{-1} for air2. Star software (Varian, Les Ulis, France) was used to record the signal and integrate peaks. The carrier gas was helium at a flow-rate of 2 mL min^{-1}. The column was a SPB1-sulphur 30 m×0.32 mm I.D., 4 μm (Supelco, Bellefonte, PA, USA). The oven temperature was held for 3 min at 30 °C, then ramped at 20 °C min^{-1} to 150 °C for 2 min.

2.2. Generation of gas test atmosphere

Gas test atmospheres were produced using a permeation tube system. It has been successfully tested on sulphur compounds [20] and has shown itself to be a reliable technique for generating analytes at trace level. The setup can be viewed in Fig. 1. The permeation apparatus was made up of a permeation chamber which contained five certified permeation tubes (Calibrage, St. Chamas, France) filled with hydrogen sulphide (H_2S), methanethiol (MeSH), ethanethiol (EtSH), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS). The permeation chamber was thermostated at 40 °C and a constant flow of dry, hydrocarbon-free air was passed through at a flow-rate of 200 mL min^{-1}. According to the tube, the permeation rates ranged from 138 to 270 ng min^{-1}. All fittings were made of Teflon PFA to minimise adsorption or reaction of sulphur compounds. The analyte flow could be further diluted to generate a concentration range from 0.2 to 8 mg m^{-3}.

2.3. Solid-phase microextraction

A manual SPME device was used. Three different coatings were tested: PDMS 100 μm, divinylbenzene–PDMS (DVB–PDMS) 65 μm and Carboxen–PDMS 75 μm, all from Supelco. The characteristics of these fibres are presented in Table 1. Extraction was performed at 20±3 °C in a 500 mL glass bulb (Fig. 1). After the bulb was flushed with the sample, the stopcocks were closed to perform SPME in static mode. Desorption was achieved in splitless mode at 250 °C for 2 min, since no carryover was observed at these settings. Desorption was not complete for temperatures lower than 250 °C, and artefact formation (dimethyldisulphide from methanethiol, dimethyl sulphoxide from dimethyl sulphide, diethyl disulphide from ethanethiol) increased with higher temperatures.

Table 1
Characteristics of SPME external coatings (only pure materials of Carboxen 1006 and DVB are considered in this table for the fibers Carboxen–PDMS and DVB–PDMS, respectively)

	Nature of coating	Density (g mL^{-1})	BET surface area (m^2 g^{-1})	Porosity (mL g^{-1})		
				Micro 2–20 Å	Meso 20–500 Å	Macro >500 Å
Carboxen 1006	Solid	0.47	720	0.29	0.26	0.23
DVB	Solid	0.36	750	0.11	0.85	0.58
PDMS	Liquid	0.97	–	–	–	–

2.4. Sampling and SPME of the real sample

The real sample was collected in laboratory-made 100 L Tedlar bags which were filled on site using a KNF N86KN pump (Midisciences, Rousset, France). (The system was tested with a mixture of sulphur compounds at 10 μg m^{-3} each and no contamination or loss was observed.) The sampling rate was about 3 L min^{-1}, and the temperature and relative humidity (RH) of the sampled air were 26 °C and 56%, respectively. Temperature and humidity were measured using a humidimeter (P570, Dostmann Electronic, Wertheim, Germany).

SPME was carried out under the same conditions as described in Section 2.3. Before each extraction, the glass bulb was flushed with about 15 L of sample to avoid cross-contamination.

2.5. Calibration methods

2.5.1. Standard additions

For each calibration point, the glass bulb was flushed with 15 L of the real sample before closing the stopcocks. Then, up to 5 mL of standard gas containing different concentrations of the five model sulphur compounds was added using a gas-tight syringe. The same volume was taken out of the sampling bulb in order to prevent overpressure.

2.5.2. External calibration

The same procedure (addition of 5 mL standard gas using a gas-tight syringe) was applied, except that the glass bulb was previously flushed with about 15 L of clean dry air.

3. Results and discussion

3.1. Comparison of different fibres

Three widely used SPME fibres, Carboxen–PDMS (75 μm), PDMS (100 μm) and DVB–PDMS (65 μm), were tested. Extractions were performed for 5 min and at various concentrations. Detection limits were then determined for a signal-to-noise ratio of 3. The PDMS fibre was found to be the least efficient, leading to an average detection limit of 300 μg m^{-3}. This fibre had already been shown to extract sulphur compounds poorly [13,14], and even with a specific and sensitive detection method such as PFPD, it is not particularly suitable for the analysis of sulphur compounds at their perception level. As had been demonstrated in previous studies [7,9], the utilisation of the Carboxen–PDMS fibre achieved better sensitivity than the DVB–PDMS fibre. The detection limits obtained with the DVB–PDMS fibre were in the range between 0.4 and 7 μg m^{-3}, while extraction with the Carboxen–PDMS fibre achieved a range between 0.05 and 1 μg m^{-3} for the compounds tested (Table 2). This performance can be explained by the micro-porosity of Carboxen, which is particularly adapted to extract small molecules (Table 1). In terms of sensitivity, analyses with both the Carboxen–PDMS and DVB–PDMS fibres are able to attain the odour threshold for sulphur compounds. A possible limitation for the use of SPME fibres could be the formation of artefacts from the decomposition (or reactions) of the target compounds. For example, the DVB–PDMS and Carboxen–PDMS fibres were found to be unsuitable for volatile amine sampling due to significant compound decomposition in the GC injection port [24]. With

Table 2
Detection limits of sulphur compounds for three different fibres, human perception levels for these compounds (expressed in μg m^{-3}) and repeatability (expressed as RSD) for the Carboxen–PDMS fibre at a concentration of 10 μg mol^{-3} and 5 min exposure time

	PDMS (μg m^{-3})	DVB–PDMS (μg m^{-3})	Carboxen–PDMS (μg m^{-3})	Repeatability (RSD, %)	Human perception level [21] (μg m^{-3})
H_2S	1000	7	1	15.4	26
MeSH	340	1	0.7	7.8	2
EtSH	200	2	0.3	5.4	3
DMS	220	0.09	0.09	9.2	6
DMDS	20	0.4	0.05	4.5	48

regard to sulphur compounds, one paper has reported possible oxidation occurring during desorption, catalysed by the stainless steel part of the SPME device [14]. In our experiments, we observed dimerisation of methanethiol to dimethyl disulphide. As this phenomenon was greater with the DVB–PDMS fibre, the use of Carboxen–PDMS fibre appeared to be the best compromise between sensitivity and artefact formation. Moreover, the dimerisation ratio was constant (methanethiol/DMDS=1.66), independent of compound concentration or matrix. It was therefore taken into account when calculating the concentrations. Consequently, the Carboxen–PDMS fibre was chosen for further experiments.

Repeatability was then evaluated for one Carboxen–PDMS fibre through five independent extractions (5 min) of a model compound mixture (10 μg m^{-3} each). Relative standard deviations (RSDs) were measured at between 4.5 and 9.2% for almost all compounds (Table 3). These results are in good agreement with other values reported in several papers dealing with this coating [7,22,23]. However, H_2S displayed low repeatability (about 15%), probably due to its high volatility.

3.2. Experimental approaches for quantification by external calibration

Two different methods are commonly used for quantification: standard addition and external calibration. Standard addition is the most accurate method because it takes into account interferences caused by matrix effects [15]. However, this method is tedious and time-consuming, especially for gas analysis. A considerable volume of sample is also needed. Therefore, given these drawbacks, external calibration appears to be more convenient for simple and time-saving quantification (the sample just has to be analysed once). However, due to the possible occurrence of competitive adsorption, it is necessary to determine the SPME conditions in a range which must be independent of matrix effects. In this context, extraction time is a key parameter because an arbitrary choice can dramatically influence result quality. For porous solid phases such as Carboxen, extraction involves adsorption onto the coating surface. As adsorption sites are limited, competitive adsorption can occur and molecules having a high affinity for the adsorbent can displace and desorb molecules with lower affinity. As this phenomenon strongly depends on the sample matrix (nature and concentration of analytes), quantitative analysis with such fibres is not easy to perform. To try to solve this problem, recent studies on Carboxen–PDMS fibres dealt with extraction under non-equilibrium conditions to avoid analyte discrimination [23,25]. This implies that the extraction time must be set within a time range where saturation of the coating has not yet been reached, which corresponds to short exposure times.

Table 3
Uptake rate U and $C_a t$ range

	U (10^{-6} m^{-3} min)	$C_a t$ range (μg m^{-3} min)
H_2S	–	–
MeSH	–	–
EtSH	1.02	1.5–15
DMS	2.11	0.5–15
DMDS	2.59	0.3–50

3.2.1. Study of adsorption kinetics

In order to define a convenient extraction time in good agreement with the previous statements, the adsorption kinetics of the model compounds were determined from a gaseous mixture containing model compounds at a concentration of about 10 μg m^{-3} each (Fig. 2). DMDS displayed linear adsorption until 15 min, whereas for all the other compounds, adsorption was linear up to 8 min. Within this time

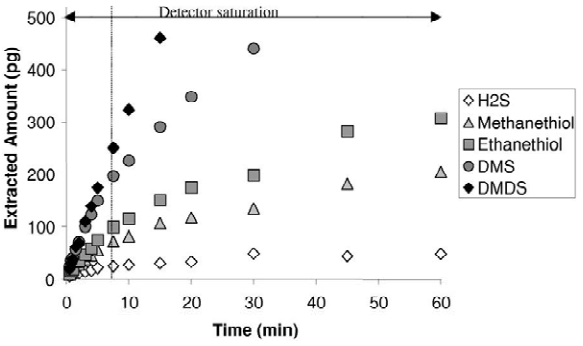

Fig. 2. Variation of time (min) vs. amount extracted for a mixture of sulphur compounds: about 10 μg m^{-3} for each component (desorption temperature, 250 °C; desorption time, 2 min).

range, co-adsorption of the sulphur compounds occurred. After this limit, the adsorption rates decreased progressively, tending towards equilibrium. For example, at the longer extraction time tested, i.e. 60 min, H_2S was nearly at equilibrium. For MeSH, EtSH and DMS, equilibrium was estimated to be reached after 90 min. DMDS was assumed to reach adsorption equilibrium after a longer fibre exposure time. Under these experimental conditions, no competitive adsorption, leading to displacement and desorption of low-affinity compounds, was observed. Therefore, according to this methodology, sulphur quantification by external calibration could be envisaged if the extraction time is chosen within the co-adsorption range of all the analytes studied (i.e., <8 min).

However, this experimental approach was only carried out for one compound concentration (10 μg m^{-3}) and for a standard gas mixture. To ascertain that the extraction time previously defined was suitably determined, other tests at different concentrations and matrix compositions would need to be performed, leading to numerous and tedious experiments. Therefore, a new, more rapid and practical method was developed.

3.2.2. Fick's law-based method

When external parameters which can affect extraction such as temperature and air velocity are controlled, only time, analyte concentration and analyte diffusion can influence the uptake on the fibre. Therefore, SPME can be considered as a passive sampler [18,19,26] and the concentrations in the gas sample can be determined from Fick's first law of diffusion:

$$m = D \cdot \frac{A}{l} \cdot (C_a - C_{sorb})t \quad (1)$$

where m is the mass of the compound fixed on the sorbent (μg), D is the diffusion coefficient of the analyte (cm^2 min^{-1}), A is the diffusion surface (cm^2), l is the length of the diffusion zone (cm), C_a is the analyte concentration in the sample (μg m^{-3}), C_{sorb} is the analyte concentration above the sorbent surface (μg m^{-3}) and t is the exposure time (min).

Assuming that, for a short sampling time, the adsorbent acts as a perfect sink, C_{sorb} can be considered as negligible compared to C_a. Therefore, the equation is assumed to be

$$m = D \cdot \frac{A}{l} \cdot C_a t \quad (2)$$

The ratio $D\,A/l$ is called the uptake rate (U). It is constant for a given temperature and is compound-dependent. Under our conditions, the length of the diffusion zone (l) is not determined because the fibre is entirely exposed to the sample and not retracted in the needle as in other studies where SPME was used as a passive sampler [27,28]. It is fixed by the air velocity conditions around the fibre. The diffusion surface (A) can be estimated by considering the SPME fibre as cylindrical (1 cm long and 0.260 mm in diameter) [29].

The relationship can be simplified as follows:

$$m = UC_a t \quad (3)$$

This means that, at the beginning of adsorption, as long as C_{sorb} is negligible, the relationship $m = f(C_a t)$ is linear and the uptake rate U is constant. This range thus corresponds to the co-adsorption range. Therefore, it can be assumed that, if such a linear relationship [Eq. (3)] can be obtained for sulphur compounds, it will allow concentration ranges and extraction times to be determined simultaneously for which quantification by external calibration could be assumed to be accurate. For example, for a simple matrix with few analytes at low concentrations, a long sampling time would be preferred to increase sensitivity. With a complex matrix, a short sampling time would be used in order to avoid competitive adsorption of analytes. This methodology has already been successfully applied to the quantitative analysis of VOCs [30].

For the experimental plot of Eq. (3), three sampling times were tested, 1, 2.5 and 5 min, with $C_a t$ up to 50 μg m^{-3} min. Standard gas mixtures of the model compounds were used. For the higher-molecular-mass compound (DMDS), linearity was observed within the whole range tested (Fig. 3e). For DMS and EtSH (Fig. 3c and d), only a narrow range was linear, between the detection limit and 15 μg m^{-3} min. The lightest compounds, H_2S and MeSH (Fig. 3a and b), did not display any linearity. However, linearity was observed for each sampling time. The slopes decreased with shorter sampling time, clearly

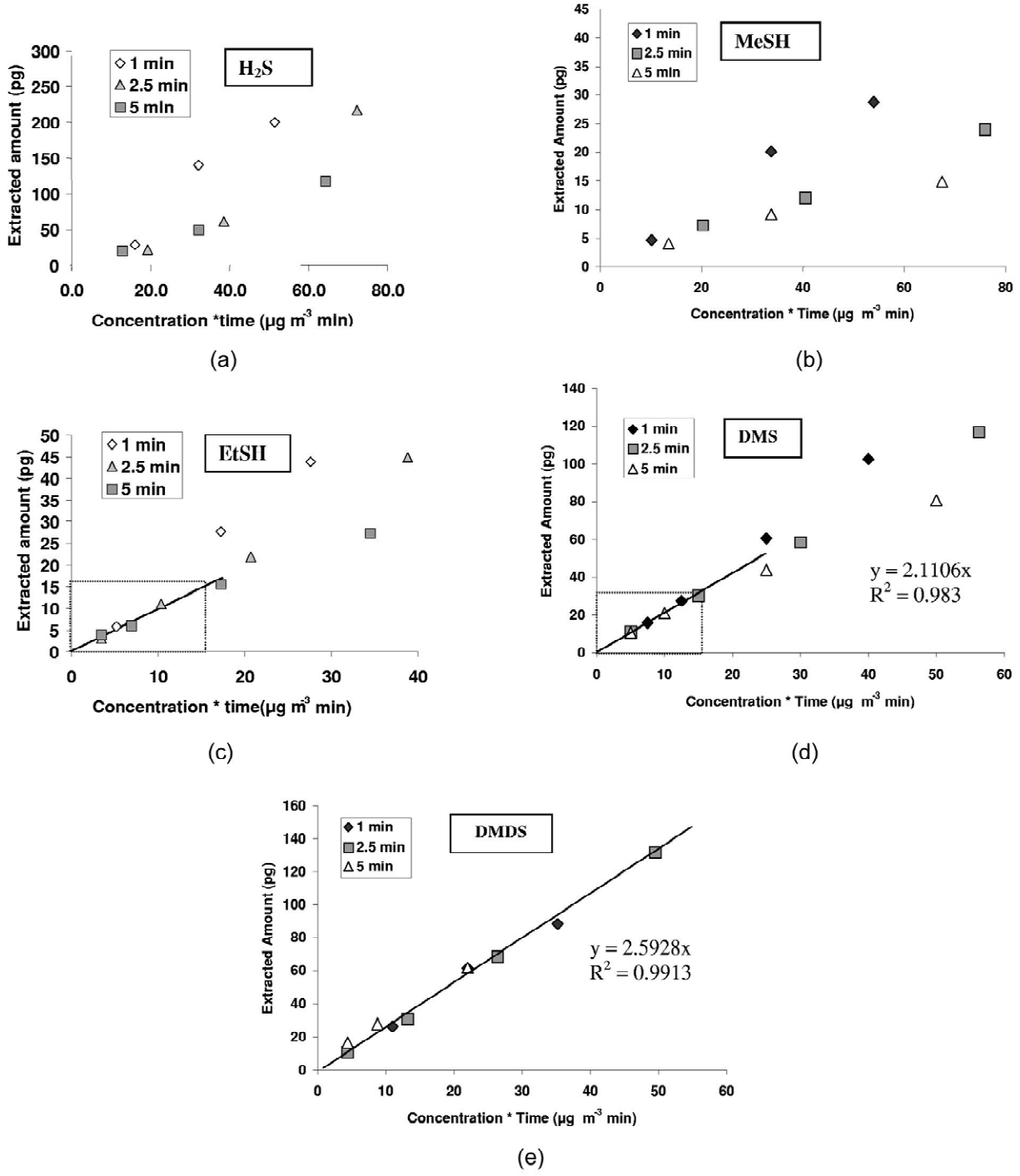

Fig. 3. Calibration curves obtained by the Fick's law-based method for sulphur compounds: (a) H_2S; (b) MeSH; (c) EtSH; (d) DMS; (e) DMDS.

demonstrating the influence of the matrix, especially for long extractions. In this case, it can be assumed that the sorbent does not behave as a perfect sink, thus leading to an increase in concentration at the surface. Therefore, for these compounds, external calibration cannot be used and standard addition will be the only way to achieve an accurate quantification. For the other model compounds, Table 3 shows the linear ranges obtained for the relationship $m = f(C_a t)$. These ranges are very narrow, confirming that the Carboxen extraction of small and highly volatile molecules is influenced dramatically by competitive adsorption.

3.3. Test of the Fick's law-based method on real samples

To take into account the influence of matrix effects, an external calibration performed according to the Fick's law-based method was tested on real samples and the results compared with a second method of quantification: the standard addition method.

3.3.1. Description of samples

The industrial site was a poultry factory. By-products, essentially giblets, are cooked in a furnace under pressure. The resulting products are further treated to produce animal flour destined to be included in pet food. During the cooking step, hydrolysis of sulphur amino acids and keratin produces effluents containing high amounts of sulphur compounds and ammonia, which cause an odour nuisance even after dilution in ambient air. Therefore, ambient air from the workplace (about 10 m from the furnace) was sampled as described in Section 2.4.

3.3.2. Discussion concerning sampling conditions

SPME samplings of air matrices can be performed on site. However, in this case, temperature and air velocity around the fibre, which have a significant influence on analyte adsorption, are not controlled. Therefore, it is very difficult to perform calibrations in the laboratory under the same operating conditions. Hence, it was decided first to sample the air in Tedlar bags and then to carry out SPME in the laboratory under controlled conditions (Section 2.3). Indeed, when the temperature (20 °C) was raised by 5 °C, the extraction of the most volatile compounds, such as H_2S, was reduced by 20%. Care was then taken to perform SPME at a temperature set constant at 20±3 °C. Moreover, the static mode was chosen because it reduces the analyte uptake rate (U) and thus leads to wider $C_a t$ ranges than those obtained in dynamic mode [17]. For low concentration sampling in static mode, depletion of the sample after successive extractions is also a cause for concern. Several extractions were performed for 5 min on the same sample (standard gas containing 20 μg m^{-3} of each model compound). The first two extractions gave the same results and a decrease in response was only observed after the third extraction. Depletion occurring during the first extraction was considered not to have a significant influence on the uptake. Therefore, it was decided to refresh the sample for each solid-phase microextraction.

One remaining question concerns the storage conditions of the sample in Tedlar bags. A laboratory study performed using a standard gas containing 20 μg m^{-3} of each model compound showed that Tedlar was suitable for the storage of sulphur compounds over a 24 h period, with 15% maximum loss for H_2S. Hence, analyses were carried out after a maximum time lapse of 1 day. The bags had a capacity of 100 L in order to be able to perform the required number of analyses with the same sample. The RH of the sample was measured at 56%. However, this parameter is highly dependent on the ambient RH, since Tedlar is porous to water. After 8 h storage, equilibrium between ambient air and the sample was reached [15]. Experiments were carried out at a RH of 52%.

3.3.3. Comparative study between external calibration and standard addition

The real sample was analysed as described in Section 2.4. Four sulphur compounds were identified: H_2S, MeSH, DMS and DMDS. Standard additions between 2 and 50 μg m^{-3} were then performed using a 5 min exposure time. Linearity of the calibration curves was achieved for all the compounds. The slopes obtained were compared with those deduced from the Fick's law-based method, i.e. uptake rate (U)·exposure time (t) ($t = 5$ min in this case) (Table 4). As EtSH was not detected,

Table 4
Slopes of calibration curves determined by two different methods: Fick's law for external calibration ($t = 5$ min) and standard addition. For H_2S and MeSH, slopes were determined through a classic external calibration ($t = 5$ min)

	Slopes for external calibration (10^{-6} m^{-3})	Slopes for standard addition (10^{-6} m^{-3})
H_2S	0.97±0.15	0.31±0.02
MeSH	2.54±0.36	1.41±0.09
EtSH	5.12±0.80	5.01±0.11
DMS	10.55±0.85	10.30±0.19
DMDS	12.95±0.40	13.02±0.42

the sample matrix was spiked with different concentrations of this compound. Good correlations were observed between the two methods for DMS, DMDS and EtSH (Table 4). For these compounds, quantification by external calibration can be carried out under the conditions defined in Section 3.2.2 and described in Table 3. As no uptake rate could be determined for H_2S and MeSH (see Section 3.2.2), external calibration using a 5 min exposure time was increased from 10 to 50 μg m^{-3}. Comparison with standard addition shows that external calibration overestimates the results (Table 4), confirming that this method is not accurate for the quantification of these sulphur compounds. Table 5 summarises the concentrations of sulphur compounds in the real sample and the quantification methods used.

4. Conclusion

Although sulphur compounds are generally considered as being non-toxic at low concentrations, they may induce an odour nuisance at these concentrations. It is therefore necessary to quantify them at their odor perception levels, which are in the μg m^{-3} range. SPME was therefore evaluated according to sensitivity and quantitative analysis at concentrations close to human perception levels. Of the three fibre materials tested, Carboxen–PDMS fibre proved to be the most appropriate for volatile sulphur compound analysis, leading to the best compromise between sensitivity and artefact formation. To avoid competitive adsorption mainly due to matrix effects and allow accurate quantification through external calibration, an experimental approach based on Fick's diffusion law was applied. The results showed that external calibration can be applied for the higher-molecular-mass compounds (EtSH, DMS and DMDS), whereas only standard addition can be used for H_2S and MeSH.

To conclude, quantitative analysis of highly volatile compounds by SPME is possible, but the operating conditions (external calibration or standard addition) should be carefully examined.

Table 5
Concentrations of the sulphur compounds identified in the real sample and calibration methods used for their determination

	Concentrations in the real sample (μg m^{-3})	Calibration method
H_2S	68±10	Standard addition
MeSH	25±3	Standard addition
EtSH	<0.3	External calibration (Fick's law)
DMS	1.0±0.1	External calibration (Fick's law)
DMDS	1.5±0.1	External calibration (Fick's law)

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