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Determination of volatile alkyl sulfides in wastewater by headspace solid-phase microextraction followed by gas chromatography–mass spectrometry

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Abstract

An analytical procedure based on headspace solid-phase microextraction (SPME) followed by gas chromatography coupled to mass spectrometry in the electron impact mode has been developed for the determination of low-molecular-mass sulfides and disulfides in wastewater. Parameters affecting to the extraction of these volatile alkyl sulfides (VASs) with the SPME, such as the extraction temperature, sample volume, pH and the NaCl addition to the matrix, have been optimised using a polydimethylsiloxane–Carboxen fibre. The linear dynamic range was close to three orders of magnitude for all the studied compounds. Detection limits of 4 ng l^{-1} for dimethyl sulfide, 0.7 ng l^{-1} for ethylmethyl sulfide, 5 ng l^{-1} for diethyl sulfide and 1 ng l^{-1} for dimethyl disulfide were achieved, with a relative standard deviation between 4 and 6%. The developed analytical methodology was applied to determine those VASs in different wastewaters.

Keywords: Water analysis; Headspace analysis; Volatile sulfur compounds; Alkyl sulfides; Sulfides; Organosulfur compounds

1. Introduction

Urban and industrial wastewater contains a great variety of substances, which can generate a wide range of unpleasant odours. Of all these substances, sulfur compounds are the ones with the greatest effect, followed by nitrogen compounds and organic oxygenated compounds [1]. Volatile sulfur compounds (VSCs) are commonly associated with anaerobic decomposition of organic matter. They are well known for their characteristic bad odours, even at very low concentrations, due to their low sensory threshold values. They also contribute significantly to the flavour or odour of many foods and drinks, such as truffle [2], fish [3], garlic [4], coffee [5], and wine [6] or beer [5].

In wastewaters, VSCs can originate from the fermentation of organic sulfur compounds (i.e., sulfonates from surfactants) and proteinaceous material, which contains the sulfur-containing amino acids cysteine, cystine and methionine. Sulfate-reducing bacteria are also responsible mainly for the generation of H_2S at a lower redox potential than fermentation processes [7]. In addition, VSCs are by products of some industries such as tannery [8], paper and wood [9,10] in which inorganic sulfur compounds are used for dehairing and bleaching, respectively. The harmful effects of VSCs have been known for a long time: acid rain, corrosion of steel and concrete conductions in wastewater treatment

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plants (WWTPs) and malodorous emissions into the atmosphere are the main consequences of the presence of these compounds in wastewater effluents [7]. The toxicity of some volatile sulfur species, especially in the case of hydrogen sulfide, has also to be taken into account, although the common levels of these compounds in wastewater are not dangerous to human health.

Whereas efforts have been focused to reduce the chemical oxygen demand (COD) and to remove nitrogen and phosphorus from waters, less attention has been paid to substances like VSCs. Only the increase in complaints referring to odour problems has led governments to change their prevention policies in recent years [11]. Dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are two of the most commonly found VSCs in wastewater. This work focused on volatile alkyl sulfides (VASs) since they are stable at room temperature. This allows an easy preparation of standard solutions in water required for quantitation in headspace solid-phase microextraction (HS-SPME).

Most of the techniques for the analysis of VASs in aqueous matrices use purge and trap with cryogenic trapping of the analytes in glass tubes [12,13] or different adsorbents [14,15]. Other authors have described trapping of VASs on solid adsorbents at room temperature [16,17], although loss of the more volatile compounds can occur. HS-SPME seems to be a good alternative to purge and trap for the analysis of VASs, especially when wastewaters have to be analysed due to the high content of suspended particulate matter that could clog the system frit. The most widely used detection methods for VASs are flame photometric detection (FPD) [13–16], atomic emission detection (AED) [5], both because their high selectivity, and mass spectrometry (MS) [18].

The aim of this work was to develop a fast methodology, based on HS-SPME, for the analysis of volatile sulfides and disulfides in wastewater. Despite that SPME has been previously used for the analysis of VASs in contaminated groundwater [18], a comprehensive study of all variables that may affect to the extraction has not yet carried out. In the present work, parameters such as extraction temperature, sample volume, pH and salt addition have been evaluated in Milli-Q water and the latter two variables in urban wastewater effluents in order to reach detection limits close or below the olfactory threshold level. Finally, the methodology has been applied to the determination of sulfides and disulfides in urban and industrial wastewater.

2. Experimental

2.1. Chemicals and materials

Dimethyl sulfide (DMS) (98%), ethylmethyl sulfide (EMS) (99%), diethyl sulfide (DES) (98%), dimethyl disulfide (DMDS) (98%) and thiophene (99+%) were obtained from Aldrich (Steinheim, Germany). Analytical-grade HCl (25%) was from Merck (Darmstadt, Germany) and NaOH and NaCl were from Carlo Erba (Milan, Italy). The SPME holder and polydimethylsiloxane–Carboxen fibres (PDMS–CAR, 75 μm) were obtained from Supelco (Bellefonte, PA, USA). Stock individual standard solutions of each analyte (2500 mg l^{-1}) were prepared in SupraSolv MeOH from Merck and mixed standard solutions for the preparation of spiked samples were obtained diluting the individual solutions with MeOH. All standard solutions were stored at −20 °C in the dark.

2.2. SPME procedure

Samples were prepared by adding a certain volume of Milli-Q water to a 40-ml vial, sealed with a PTFE septum and then spiked with a known amount of VAS mixture by injection through the septum. An approximate concentration of 400 ng l^{-1} for each compound in the aqueous solution was considered. For those cases in which pH was adjusted to 3 and 11, 30 μl of 0.2 *M* HCl or 2 *M* NaOH, respectively, were also injected through the septum. Extraction was performed in the headspace mode under magnetic stirring (1000 rpm). Taking into account the volatile character of the analytes, headspace extraction was preferred over direct extraction to avoid matrix effects.

2.3. Instrumental analysis

SPME was carried out using an electronically-controlled magnetic stirrer IKAMAG RCT Basic

Table 1
Diagnostic and quantitation ions used for DMS, EMS, thiophene, DES and DMDS. The % of abundance of the ions is indicated in brackets

Compound	Quantitation ion m/z	Other ions m/z (rel. abund.)
Dimethylsulphide	62 (100%)	61 (31%)
Ethylmethylsulphide	76 (100%)	61 (100%), 48 (35%)
Thiophene	84 (100%)	58 (38%)
Diethylsulphide	90 (100%)	75 (94%), 62 (40%), 61 (40%)
Dimethyldisulphide	94 (100%)	79 (43%), 64 (7%), 61 (8%), 48 (5%)

with heating and an electronic contact thermometer IKATRON ETS-D4 fuzzy. Chromatographic analysis was carried out using a Thermo-Finnigan Trace GC–MS system (Manchester, UK) equipped with electronic pressure control in the GC injector. A GS-GasPro capillary column for volatile sulfur compounds analysis from J&W Scientific (Folsom, CA, USA) of 60 m×0.32 mm I.D. coated with a polymeric phase (film thickness not specified) was used. Helium at 35 cm s^{-1} was used as carrier gas. The oven temperature was programmed at 80 °C for 3 min, then a 15 °C min^{-1} rate until 260 °C, holding the final temperature for 10 min. Ion source and transfer line temperatures were held at 200 and 240 °C, respectively.

Capillary gas chromatography (cGC) coupled to electron impact (70 eV) mass spectrometry (EI-MS) operated in the selected ion monitoring mode (SIM) was used. Quantitation was carried out according to internal standard using diethyl sulfide. Molecular ions were used as quantitation ions, besides other secondary ions were considered for confirmation (Table 1).

3. Optimisation of the SPME procedure

Relevant parameters affecting to the performance of SPME were evaluated for the extraction of DMS, EMS and DMDS. All experiments were performed in duplicate and the average values are reported.

3.1. Coating selection

The behaviour of different coatings for the analysis of volatile sulfides and disulfides has been previously evaluated by Popp et al. [18]. In this study, it has been proved that extraction yields of VASs were 100–1000-times higher for the 75 μm PDMS–CAR fibre than for the rest of the commercially available fibres. Consequently, PDMS–CAR fibre was used for further optimisation of VAS extraction.

3.2. Desorption conditions

Injector temperature and desorption time are important factors to take into account during the SPME method development in order to avoid the carryover effect. In this work, desorption temperature was fixed to 280 °C and the fibre was left 3 min at the injector port. In these conditions carryover effect in all the cases was less than 0.5%, which is comparable to those results reported previously [18]. The low carryover effect observed can be explained according to PDMS–CAR pore characteristics. Small analytes, like VASs can be rapidly desorbed with relatively low temperatures (280 °C), whereas bigger molecules, trapped in the mesopores, require higher temperatures (300–320 °C) to be desorbed [19]. This fact has been already observed in the SPME analysis of volatile fatty acids (VFAs) [20].

3.3. Extraction time

Extractions were performed at 5, 10, 15, 20, 30, 45 and 60 min. As shown in Fig. 1, 45 min was enough to reach the equilibrium for all the analytes. Taking into account that working in the equilibrium conditions slight differences in the extraction time produce less relative error in the determination and, considering that chromatographic runs were 25 min long, 45 min was selected as a suitable extraction time for further studies.

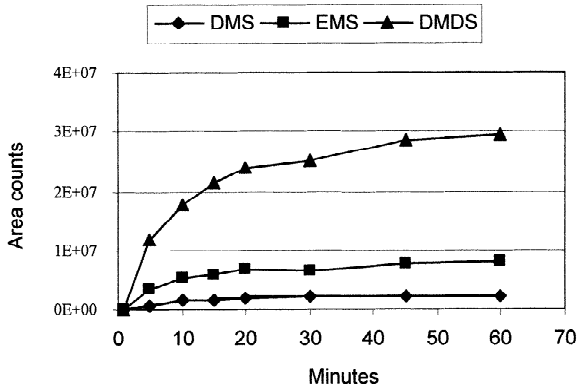

Fig. 1. Extraction time profiles of dimethyl sulfide (DMS), ethylmethyl sulfide (EMS) and dimethyl disulfide (DMDS) using a 75 μm PDMS–CAR fibre.

3.4. Extraction temperature

Extractions were performed at different temperatures in the equilibrium (45 min). Three temperatures were checked: 25, 35 and 45 °C. Fig. 2 shows that the peak areas obtained slightly decrease as the temperature increases. In HS-SPME, two opposite factors have to be considered in order to evaluate the effect of the temperature in the extraction when working in equilibrium conditions. At higher temperatures, the concentration in the headspace increases, however there is also a decrease in the distribution constant between the headspace and the fibre. Depending on the relative variation of these two distribution constants, the extraction yield will increase or not. The last situation is the most common in case of volatile compounds [21]. Therefore, the observed experimental behaviour of VASs with the extraction temperature confirms theoretical considerations.

3.5. Sample volume

Sample volume was optimised in this step of method development. Thus, 5, 10 and 20 ml of a spiked sample were placed in 40-ml vials. Sample volumes higher than 20 ml were not tested due to the difficulty in avoiding a direct contact between the fibre and the aqueous phase during the headspace extraction. As shown in Fig. 3, higher areas were obtained when extraction was performed using higher sample volumes. Very volatile compounds, such as VASs, prefer to accumulate in the headspace, resulting in a substantial loss of sensitivity when the headspace is large [21]. However, this seems to be applicable only in the equilibrium conditions. Low headspace/sample volume ratio can significantly affect extraction kinetics [22], giving rise to a response decrease [20].

3.6. Effect of pH modification and salt addition

Experiments at pH 3, 7 and 11 were performed in order to evaluate the pH effect in the extraction of VASs in a pure aqueous matrix. Also VAS extraction in water containing NaCl (50% of the saturation

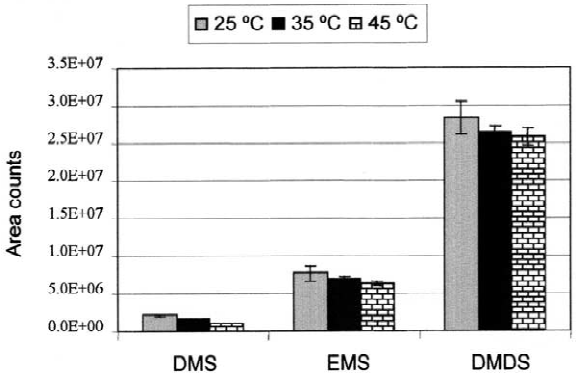

Fig. 2. Effect of extraction temperature on the SPME of dimethyl sulfide (DMS), ethylmethyl sulfide (EMS) and dimethyl disulfide (DMDS) using a 75 μm PDMS–CAR fibre.

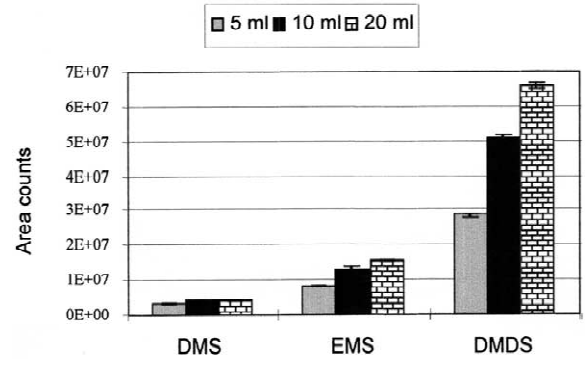

Fig. 3. Effect of sample volume on the SPME of dimethyl sulfide (DMS), ethylmethyl sulfide (EMS) and dimethyl disulfide (DMDS) using a 75 μm PDMS–CAR fibre.

concentration) was examined. As expected, the pH does not affect to the extraction as the VASs have no acid/basic properties. In addition, the presence of salt does not affect significantly the analyte response, the increase factors are between 1.05 and 1.18 (Fig. 4a). This could be explained in terms of the lower Henry constants (mol l^{-1} atm^{-1}) of VASs ($\cong 10^{-1}$) compared to other compounds, such as VFAs ($\cong 10^{3}$), for which salting out effect is very marked [23] (1 atm=101 325 Pa). In real matrices, however, pH and salt addition can affect to the solubility of other compounds, such as humic acids, affecting to the extraction yields of analytes. In order to discard these possible effects, the same experiments explained above were made in real samples. No significant changes were observed according to pH variations. Conversely, when 50% of the salt saturation concentration was added to the samples, the increase factors were between 2.44 and 4.03, probably due to the release of VASs associated with the colloidal phase to the dissolved phase, which can be transferred to the headspace (Fig. 4b). Therefore, the addition of salt in a real sample allows us to estimate the total concentration of the analytes. However, the aim of this work was to evaluate the feasibility of the transfer of odorous compounds from the dissolved phase to the atmosphere, therefore no salt addition was performed in further studies.

3.7. Precision

The method reproducibility was determined by performing extractions of five water samples spiked at the same concentration (500 ng l^{-1}) in 3 consecutive days. The relative standard deviations (RSDs) obtained for the studied compounds were between 4.08 and 6.12%.

3.8. Linearity

The linearity of the HS-SPME–GC–MS procedure was evaluated in the SIM mode over a range of three orders of magnitude considering the concentration of the studied compounds in the aqueous phase. Firstly, thiophene was used as internal standard, but, later on, since it was detected in some real samples, it was substituted for diethyl sulfide. Although extraction time profile for thiophene was not studied in Section 3.3, previous studies have shown that after 45 min, the equilibrium is reached for thiophene using the 75 μm PDMS–CAR fibre. Moreover, the same authors demonstrated that linear dynamic range for thiophene is similar to the rest of VASs [18]. Therefore, as thiophene properties are similar to those of the VASs studied, a similar behaviour regarding the extraction parameters previously optimised was assumed. The

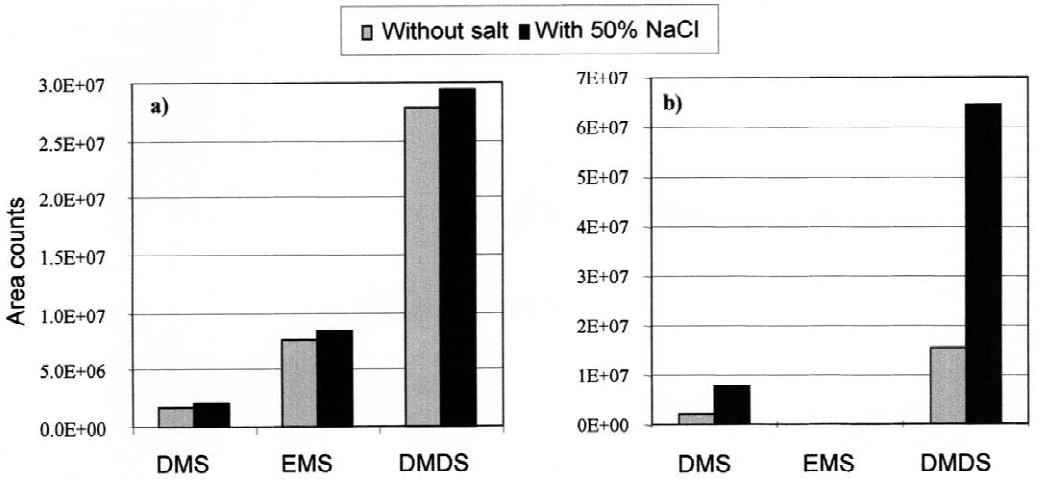

Fig. 4. Salting out effect in the SPME of dimethyl sulfide (DMS), ethylmethyl sulfide (EMS) and dimethyl disulfide (DMDS) using a 75 μm PDMS–CAR fibre, (a) in Milli-Q water and (b) wastewater.

Table 2
Linear dynamic ranges, with their corresponding equations, R^2 values and calculated limits of detection (LOD) and quantitation (LOQ) for the studied sulphides and disulphides

Compound	Linear dynamic range (ng l^{-1})	Equation	R^2	LOD (ng l^{-1})	LOQ (ng l^{-1})
Dimethylsulphide	4–10200	$y = 0.1849x - 0.0042$	0.995	3.6	13
Ethylmethylsulphide	3–10600	$y = 0.4622x + 0.0188$	0.994	0.6	3
Thiophene	30–8700	$y = 3.6785x - 0.2355$	0.997	35	146
Diethylsulphide	4–8900	$y = 0.2876x + 0.0502$	0.997	4.6	22
Dimethyldisulphide	1–8700	$y = 1.9464x - 0.1486$	0.997	1	4

linear dynamic range obtained for the studied VASs is shown in Table 2.

3.9. Limits of detection and quantitation

Limits of detection (LODs) and quantitation (LOQs) were calculated from the calibration plots by considering the peak area corresponding to three and ten times the signal-to-noise ratio of a procedural blank, respectively. Standards with concentrations close to the calculated detection limits were also analysed to confirm them. Results are shown in Table 2. The LODs obtained with this methodology are approximately five times higher than those obtained with purge and trap techniques coupled to FPD [13–15], but lower to those reported by Popp et al. [18] using HS-SPME. Therefore, the developed method provides enough sensitivity to reach the odour threshold of the VASs occurring in wastewaters.

4. Analysis of real samples

The developed methodology was applied to the analysis of several real samples, (1) urban wastewater treated in constructed wetlands (influent and effluent) and (2) wastewater from the effluent of a paper recycling industry. Despite the presence of additional peaks that were coextracted with the SPME fibre not related to the VASs studied, the analytes were well separated and determined. Fig. 5 shows the ion chromatograms corresponding to an urban wastewater spiked with approximately 500 ng l^{-1} of a standard mixture.

4.1. Urban wastewater treated in constructed wetlands

Samples were collected from pilot plants in Can Suquet (Catalonia, Spain) where urban wastewater from a small community ($\cong 200$ inhabitants) is treated in constructed wetlands (CWs). Several studies have shown the efficiency of constructed wetlands in removing a wide range of pollutants from wastewater [24] but no information is available on the mechanisms of organic matter degradation. Analysis of VASs from the wetland influent and its effluent during the first operational month since its construction are reported here. The concentrations of VASs found are listed in Table 3. The evolution of the effluent–influent concentration ratio for the most abundant VAS compounds is shown in Fig. 6. From these results, the efficiency of CWs in removing DMDS is evident, whereas the removal of DMS in the effluent improves according to the CW operational time.

4.2. Wastewater from a paper recycling industry

Samples were collected at different stages of a closed circuit treatment of wastewater generated in a paper recycling industry. In addition, two more samples were obtained at the well from which water is supplied to the industry and a nearby river. The VASs concentrations found are listed in Table 3. High levels of DMS (μg l^{-1}) were observed along the treatment process, together with significant amounts of other VASs, such as DMDS and EMS. They may originate from sodium hydrosulfite and sodium metabisulfite used as bleaching reagents in the paper paste processing. On the contrary, VAS concentrations found in the well and the river are

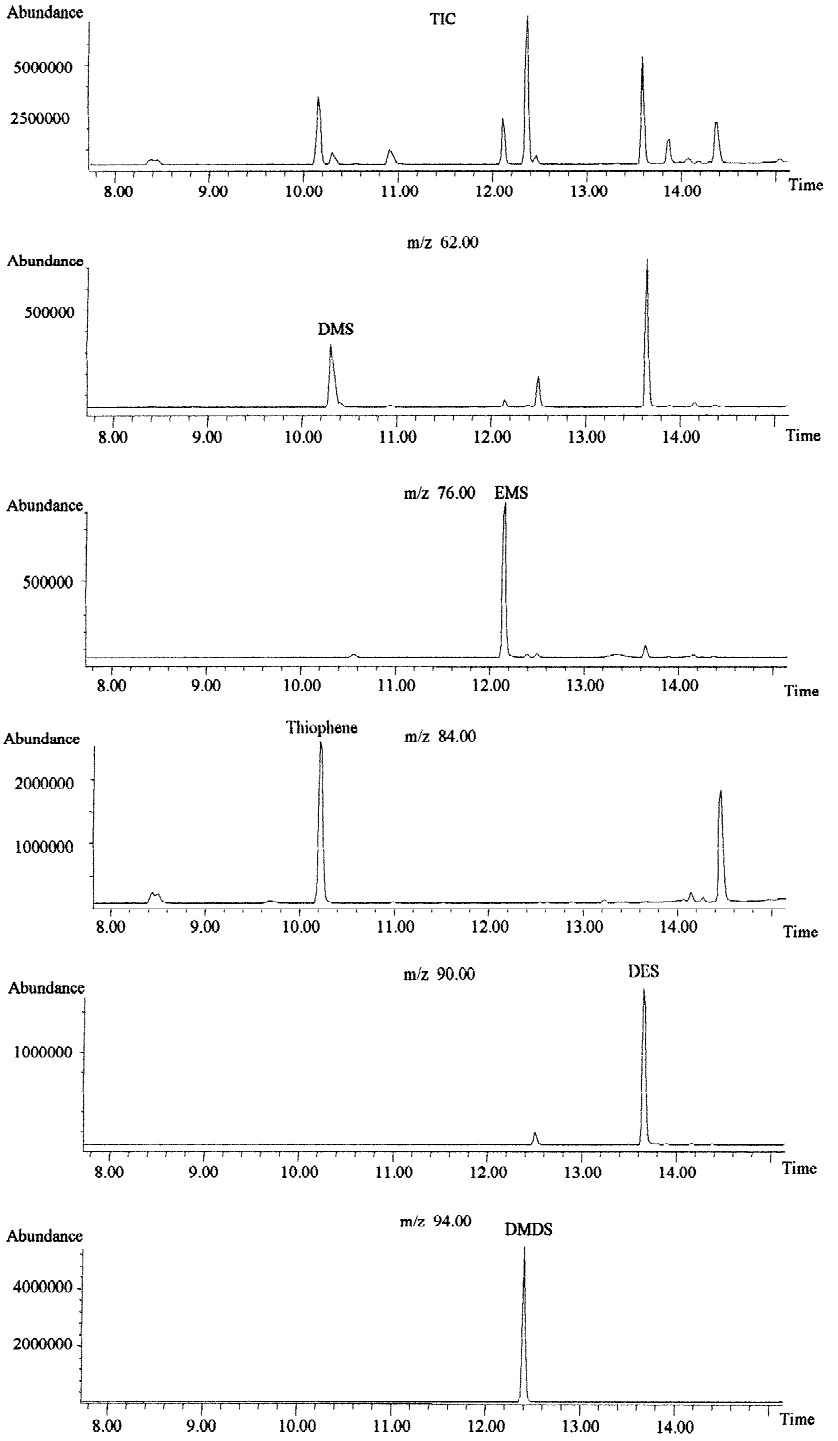

Fig. 5. Total ion current and selected ion chromatograms at m/z 62, 76, 84, 90 and 94 characteristic of DMS, EMS, thiophene, DES and DMDS, respectively.

Table 3
Concentration (ng l^{-1}) of sulphides and disulphides found is urban and industrial wastewater

Sample	DMS	EMS	DMDS	Tiophene
Urban wastewater treated in constructed wetlands				
Can Suquet influent (28/May)	1118	n.d.	551	n.q.
Can Suquet effluent (28/May)	4041	n.d.	146	n.q.
Can Suquet influent (5/June)	1853	n.d.	893	n.q.
Can Suquet effluent (5/June)	3548	n.d.	117	n.q.
Can Suquet influent (18/June)	3927	n.d.	763	n.q.
Can Suquet effluent (18/June)	3408	n.d.	142	n.q.
Can Suquet influent (22/June)	2879	n.d.	946	n.d.
Can Suquet effluent (22/June)	2430	n.d.	100	n.d.
Wastewater from a paper recycling industry				
Untreated wastewater	8022	97	734	n.q.
Wastewater (floculant applied)	24 436	299	952	n.q.
Recycled wastewater	7201	45	359	n.q.
Well water	74	15	98	n.d.
River water	70	n.q.	96	n.d.

quite low and comparable to those reported for unpolluted waters [5].

5. Conclusions

A simple, fast and solvent-free methodology for the determination of volatile sulfides and disulfides in wastewater samples has been developed and optimised. The SPME procedure is based on the use of a PDMS–CAR fibre combined with GC–MS detection. Parameters that might affect to the method performance have been optimised. Thus, extraction was finally carried out in 45 min at 25 °C, neutral pH and without addition of salt to the aqueous phase in order to determine the truly dissolved VASs. Desorption in the injector port was at 280 °C for 3 min, observing less than 0.5% of carryover effect. The optimised SPME procedure has been successfully applied to the monitoring of VASs occurring in wastewaters and in the treatment plant effluents.

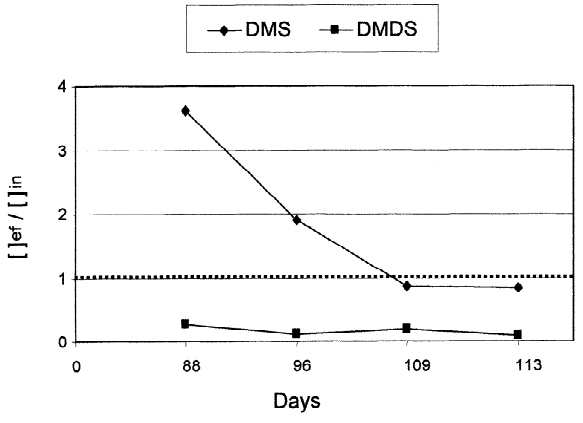

Fig. 6. Effluent–influent concentration ratio ($[]_{ef}/[]_{in}$) of the sulfides and disulfides found in wastewaters from Can Suquet according to the lapsed time in days following the wetland operation.

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