



**HAL**  
open science

## **Evaluation of Solid-Phase Microextraction for Time-Weighted Average Sampling of Volatile Sulfur Compounds at ppb Concentrations**

François Lestremau, Fräs Annika T. Andersson, Valérie Desauziers, Jean-Louis Fanlo

### **► To cite this version:**

François Lestremau, Fräs Annika T. Andersson, Valérie Desauziers, Jean-Louis Fanlo. Evaluation of Solid-Phase Microextraction for Time-Weighted Average Sampling of Volatile Sulfur Compounds at ppb Concentrations. *Analytical Chemistry*, 2003, 75 (11), pp.2626-2632. <10.1021/ac034124g>. <hal-04664982>

**HAL Id: hal-04664982**

**<https://imt-mines-ales.hal.science/hal-04664982v1>**

Submitted on 4 Feb 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Evaluation of Solid-Phase Microextraction for Time-Weighted Average Sampling of Volatile Sulfur Compounds at ppb Concentrations

François Lestremau,<sup>\*,†</sup> Fräs Annika T. Andersson,<sup>\*,‡,§</sup> Valérie Desauziers,<sup>†</sup> and Jean-Louis Fanlo<sup>†</sup>

Laboratoire Génie de l'Environnement Industriel, Ecole des Mines d'Alès, 6, Avenue de Clavières, 30319 Alès Cedex, France, and Department of Water and Environmental Studies, Linköping University, S-581 83 Linköping, Sweden

**The potential of solid-phase microextraction (SPME) for time-weighted average (TWA) sampling of volatile sulfur compounds in air at ppb concentrations was investigated. The target compounds (hydrogen sulfide, methanethiol (MeSH), ethanethiol (EtSH), dimethyl sulfide (Me<sub>2</sub>S), and dimethyl disulfide (Me<sub>2</sub>S<sub>2</sub>)) were extracted using SPME with a Carboxen–poly(dimethylsiloxane) fiber coating, and diffusion was controlled by keeping the fiber retracted within the needle of the sampling device. The effects of several important experimental variables (air velocity, direction of air flow, analyte concentration, humidity, temperature, extraction time) were studied. The uptake by the fiber was not affected by the direction of the air flow or the air velocity. The effects of concentration, humidity, temperature, and extraction time were examined in experiments with a central composite face design. The results showed that all or most of the investigated parameters had a significant impact on the uptake rates of H<sub>2</sub>S, MeSH, EtSH, and Me<sub>2</sub>S, which invalidated time-weighted average sampling of these compounds by SPME under the tested conditions. Moreover, reverse diffusion of H<sub>2</sub>S, MeSH, and EtSH occurred at 40% relative humidity. For Me<sub>2</sub>S<sub>2</sub>, the uptake rate had a variation of only 8% within the whole experimental domain, and the experimental value derived for the uptake rate was consistent with the theoretical value. This result was confirmed by comparative analyses of industrial samples by the standard addition method. Therefore, SPME appears to be a suitable technique for TWA sampling of Me<sub>2</sub>S<sub>2</sub> using the Carboxen–poly(dimethylsiloxane) fiber coating. Finally, in an investigation of potential losses during storage of the fiber, no significant losses of the target compounds were detected after 3 days at –80 °C.**

Volatile sulfur compounds (VSCs) are commonly emitted during industrial processes involving the handling or degradation of organic material, e.g., biogas production, sewage treatment, landfilling, pulp milling, and slaughtering. Exposure to high levels

of VSCs, e.g., hydrogen sulfide, can cause unconsciousness and death. In addition, previous studies have concluded that prolonged exposure to ppb levels of these compounds can cause symptoms such as headaches and nausea along with adverse eye, respiratory and neuropsychological symptoms.<sup>1,2</sup> Moreover, VSCs give rise to very unpleasant odors even at the low-ppb level, which affect not only workers at plants emitting VSCs but also people living nearby. Thus, there are important reasons for determining the average levels of VSCs emitted from the above-mentioned industries.

There are generally two ways to determine the average concentration of a compound over a certain period of time, e.g., a working day (8 h). In the first approach, a large number of grab samples reflecting changes in analyte concentration over time can be analyzed, after which the average concentration can be calculated. The other approach, which is less expensive and less time-consuming, is to collect just one sample over the time period of interest that provides an average concentration. This can be done using either active or diffusive (passive) sampling methods. Diffusive sampling is more advantageous, since it does not require the use of a pump, which can be very inconvenient, especially for field sampling. The theory of diffusive sampling is based on Fick's first law of diffusion (eq 1), where  $m$  is the mass of the compound

$$m = D_g(A/Z)(C_a - C_{\text{sorb}})t \quad (1)$$

fixed on the sorbent ( $\mu\text{g}$ ),  $D_g$  is the diffusion coefficient of the analyte ( $\text{m}^2 \text{min}^{-1}$ ),  $A$  is the diffusion surface area ( $\text{m}^2$ ),  $Z$  is the length of the diffusion zone ( $\text{m}$ ),  $C_a$  is the analyte concentration in the sample ( $\mu\text{g m}^{-3}$ ),  $C_{\text{sorb}}$  is the analyte concentration above the sorbent surface ( $\mu\text{g m}^{-3}$ ), and  $t$  is exposure time ( $\text{min}$ ).

The uptake rate (UR) is a function of  $D_g$ ,  $A$ , and  $Z$ , according to eq 2.

$$\text{UR} = (D_g A)/Z \quad (2)$$

$D_g$  is a constant for each compound at a given temperature. If the sorbent acts as an infinite sink,  $C_{\text{sorb}}$  is negligible and eq 1 can be simplified to eq 3.

\* Corresponding authors. F. Lestremau and A. T. Andersson contributed equally to this study. E-mail: francois.lestremau@ema.fr; annni@tema.liu.se.

<sup>†</sup> Ecole des Mines d'Alès.

<sup>‡</sup> Formerly Annika T. Nielsen.

<sup>§</sup> Linköping University.

(1) Kilburn, K. H.; Warshaw, R. H. *Toxicol. Ind. Health* **1995**, *11*, 185–197.

(2) Marttila, O. Ph.D. Thesis, Helsinki University, Helsinki, Finland, 1995.

$$UR = m / (C_a t) \quad (3)$$

Consequently, the uptake rate can be calculated experimentally by determining the amount of the compound trapped on the sorbent ( $m$ ) at given concentrations ( $C_a$ ) and a given extraction time ( $t$ ). Once the uptake rate has been determined for a certain compound, it can be used to determine unknown concentrations. In the case of an ideal passive sampler, the uptake rate remains constant as time and concentration change, and the uptake rate must not be influenced by external parameters such as humidity, temperature, air velocity, and direction of the air flow.

There have been few publications concerning time-weighted average (TWA) sampling of sulfur compounds. Passive TWA sampling of  $H_2S$  at ppb levels has previously been performed using acrylic tubes or filter paper and then the  $H_2S$  was detected fluorometrically.<sup>3</sup> Passive card monitors can also be used to indicate the presence of  $H_2S$  or to quantify it at ppm levels by optical or visual detection of color changes.<sup>4</sup> Several active sampling methods have also been described. For  $H_2S$ , the U.S. Occupational Safety and Health Administration (OSHA) Technical Center has validated a method using filters impregnated with silver nitrate,<sup>5</sup> and the U.S. National Institute for Occupational Safety and Health (NIOSH) has validated a method using charcoal tubes.<sup>6</sup> For methanethiol (MeSH), OSHA validated a method using a filter impregnated with mercuric acetate,<sup>7</sup> which was then modified by NIOSH for the determination of several mercaptans (methyl butyl and *n*-butyl).<sup>8</sup> For dimethyl sulfide ( $Me_2S$ ) and dimethyl disulfide ( $Me_2S_2$ ), OSHA has partially validated a method involving the use of charcoal tubes.<sup>9,10</sup> All the methods validated by the NIOSH and OSHA require a pump for sampling and the use of organic solvents to desorb the analytes, as well as various other poisonous reagents (e.g., cadmium sulfate, mercuric acetate, methylene chloride, and toluene). Moreover, they have high detection limits that exceed the odor thresholds. Thus, there is a need to develop more sensitive and convenient analytical techniques for TWA sampling of VSCs in air.

As an alternative to more common methods, solid-phase microextraction (SPME) can be used for TWA sampling in a technique where the fiber is kept retracted within the needle so extraction is governed by diffusion.<sup>11–17</sup> SPME is solvent-free, the

equipment is reusable, and compared to commonly used passive samplers such as sorbent tubes or passive card monitors, it is easy to use. It also offers the possibility to use the same sampling device for both TWA and grab sampling. The fiber is protected during sampling since it is housed in stainless steel tubing. Moreover, by changing the distance from the opening of the needle to the sorbent face, the concentration range to be sampled can be adjusted, as appropriate.<sup>11</sup>

The potential of SPME has already been successfully demonstrated for the analysis of sulfur compounds in many different matrixes, such as wine,<sup>18–20</sup> beer,<sup>21</sup> butter,<sup>22</sup> water,<sup>23–25</sup> and air.<sup>25–29</sup> The difficulties encountered, e.g., artifact formation and competitive adsorption, have been addressed in previous publications.<sup>26–30</sup> However, to our knowledge, SPME has not been used for TWA sampling of VSCs before.

In the present work, the potential of SPME for TWA sampling of five volatile sulfur compounds was investigated. The target compounds were  $Me_2S_2$ ,  $Me_2S$ , ethanethiol (EtSH),  $H_2S$ , and MeSH. Carboxen–poly(dimethylsiloxane) (CAR–PDMS) fiber coating was used since it has the highest adsorption capacity of currently available coatings for VSCs<sup>21,23,26,27</sup> and also induces the least artifact formation.<sup>31</sup> The influence of flow rate and the direction of the air flow on the amount adsorbed was investigated, and an experimental design was used to determine whether the variables' concentration, humidity, temperature, extraction time, and their interactions had a significant influence on the uptake rates. We also investigated the stability of the adsorbed compounds in storage between sampling and analysis. Finally, the developed method was applied to an industrial air sample, and the results were compared with those obtained by analyzing samples with the standard addition method.

## EXPERIMENTAL SECTION

**Chemicals and Equipment.** EtSH,  $H_2S$ , MeSH,  $Me_2S$ , and  $Me_2S_2$  were purchased in certified permeation tubes (Calibrage, St Chamas, France) with permeation rates ranging from 138 to 270  $ng\ min^{-1}$  at 40 °C (Table 1).

CAR–PDMS fibers (75  $\mu m$ ) were used with a manual SPME device, all from Supelco (Bellefonte, PA).

- (3) Shooter, D.; Watts, S. F.; Hayes, A. J. *Environ. Monit. Assess.* **1995**, *38*, 11–23.
- (4) Saunders, F.; Larson, L.; Tatum, V. *Am. Ind. Hyg. Assoc. J.* **2002**, *63*, 317–325.
- (5) Occupational Safety and Health Administration Technical Center, Method ID-141, U.S. Department of Labor, 1989.
- (6) *NIOSH Manual of Analytical Methods*, 4th ed.; Method 6013; National Institute for Occupational Safety and Health: Washington, DC, 1994.
- (7) Occupational Safety and Health Administration Technical Center, Method 26, U.S. Department of Labor, 1981.
- (8) *NIOSH Manual of Analytical Methods*, 4th ed.; Method 2542; National Institute for Occupational Safety and Health: Washington, DC, 1994.
- (9) Occupational Safety and Health Administration Technical Center, electronic version of partially validated method, U.S. Department of Labor, 1992.
- (10) Occupational Safety and Health Administration Technical Center, electronic version of partially validated method, U.S. Department of Labor, 1992.
- (11) Martos, P. A.; Pawliszyn, J. *Anal. Chem.* **1999**, *71*, 1513–1520.
- (12) Khaled, A.; Pawliszyn, J. *J. Chromatogr., A* **2000**, *892*, 455–467.
- (13) Koziel, J. A.; Pawliszyn, J. *Air Waste Manage. Assoc.* **1995**, *51*, 173–184.
- (14) Koziel, J. A.; Mingyu, J. A.; Khaled, A.; Noah, J.; Pawliszyn, J. *Anal. Chim. Acta* **1999**, *400*, 153–162.
- (15) Koziel, J. A.; Noah, J.; Pawliszyn, J. *Environ. Sci. Technol.* **2001**, *35*, 1481–1486.

- (16) Battle, R.; Kolmsjö, A.; Nilsson, U. *Fresenius' J. Anal. Chem.* **2001**, *371*, 514–518.
- (17) Battle, R.; Kolmsjö, A.; Nilsson, U. *Fresenius' J. Anal. Chem.* **2001**, *369*, 524–529.
- (18) Mestres, M.; Busto, O.; Guasch, J. *J. Chromatogr., A* **1998**, *808*, 211–218.
- (19) Mestres, M.; Sala, C.; Marti, M. P.; Busto, O.; Guasch, J. *J. Chromatogr., A* **1999**, *835*, 137–144.
- (20) Mestres, M.; Marti, M. P.; Busto, O.; Guasch, J. *J. Chromatogr., A* **1999**, *849*, 293–297.
- (21) Hill, P. G.; Smith, R. M. *J. Chromatogr.* **2000**, *872*, 203–213.
- (22) Shooter, D.; Jayatissa, N.; Renner, N. *J. Dairy Res.* **1999**, *66*, 115–123.
- (23) Popp, P.; Möder, M.; McCann, I. In *Applications of solid-phase microextraction*; Pawliszyn, J., Ed.; Royal Society of Cambridge: Cambridge, 1999; pp 227–237.
- (24) Abalos, M.; Prieto, X.; Bayona, J. M. *J. Chromatogr., A* **2002**, *963*, 249–257.
- (25) Wardencki, W.; Namiesnik, J. *Chem. Anal.* **1999**, *44*, 485–493.
- (26) Lestremou, F.; Desauziers, V.; Fanlo, J. L. Accepted for publication in *J. Chromatogr., A*.
- (27) Haberhauer-Troyer, C.; Rosenberg, E.; Grassbauer, M. *J. Chromatogr., A* **1999**, *848*, 305–315.
- (28) Nielsen, A. T.; Jonsson, S. *J. Chromatogr., A* **2002**, *963*, 57–64.
- (29) Nielsen, A. T.; Jonsson, S. *Analyst* **2002**, *127*, 1045–1049.
- (30) Murray, R. A. *Anal. Chem.* **2001**, *73*, 1646–1649.
- (31) Andersson, A. T. (formerly Nielsen, A. T.), submitted.

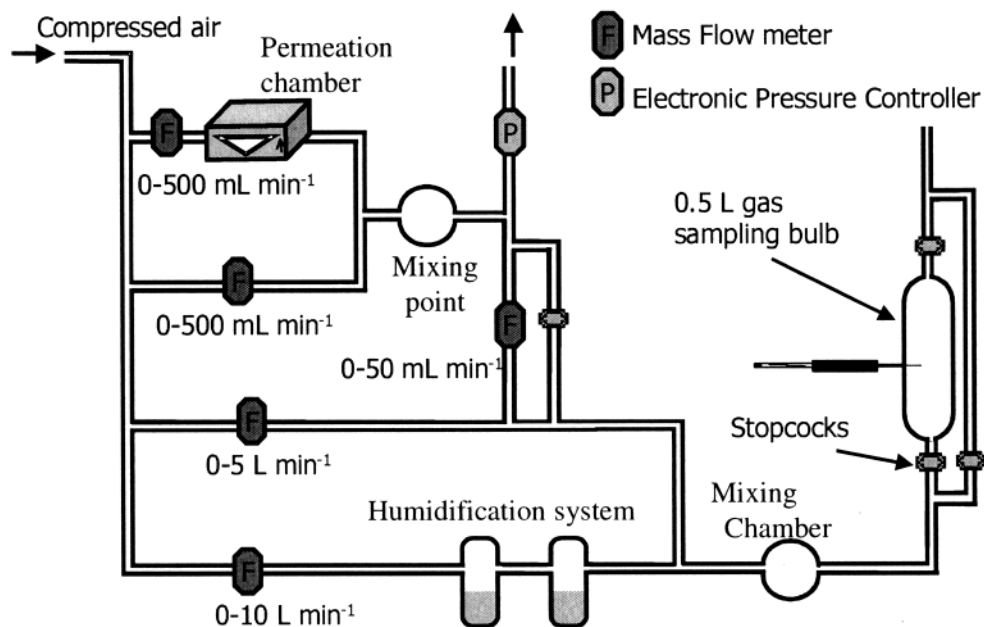


Figure 1. Apparatus for the generation of gaseous standard mixtures of sulfur compounds.

Table 1. Physical Characteristics of the Target Compounds

	molecular mass (g mol <sup>-1</sup> )	boiling point (°C)	vapor pressure (kPa, 20 °C)	permeation rates (ng min <sup>-1</sup> )	theoretical diffusion coefficients (cm <sup>2</sup> s <sup>-1</sup> ) <sup>a</sup>
H <sub>2</sub> S	34.08	-60	1786	210	0.137
MeSH	48.11	6	158	270	0.106
EtSH	62.13	35	59	138	0.089
Me <sub>2</sub> S	62.13	37	53	200	0.089
Me <sub>2</sub> S <sub>2</sub>	94.19	109	29	176	0.076

<sup>a</sup> Calculated from ref 35.

**Experimental Setup.** A standard gas generating device (Figure 1) was used to provide known concentrations of the target sulfur compounds by passing clean dry air at a constant flow rate over the five certified permeation tubes containing the target compounds. The analytes could then be further diluted using mass flow meters (Brooks, Lyon, France) to generate final concentrations ranging between 0.01 and 1000  $\mu\text{g m}^{-3}$ . To ensure constant diffusion of the sulfur compounds from the vials, the permeation chamber was thermostatically set at 40 °C. All tubing and fittings used were made of Teflon PFA (Swagelock, Solon, OH) to minimize possible adsorption or reaction of sulfur compounds. Solid-phase microextractions were performed using two different glass units equipped with a Teflon septum: a 500-mL glass tube (i.d. 5.0 cm) with stopcocks at each end, and a specially designed glass tube (i.d. 2.1 cm) with an opening in the side, 5 cm from the septum (Figure 2). Air with different relative humidities (RH) was generated by mixing dry and water-saturated air (generated by flushing dry air through two glass bottles filled with water, Figure 1). Tubes with different diameters were used in order to broaden the range of the air velocity. At flow rates of 2.5 and 10 L min<sup>-1</sup>, the air velocity was 2 and 8 cm s<sup>-1</sup>, respectively, in the 5-cm-i.d. tube, while the velocity was 48 cm s<sup>-1</sup> in the 2.1-cm-i.d. tube at 10 L min<sup>-1</sup>. All these flows were laminar.

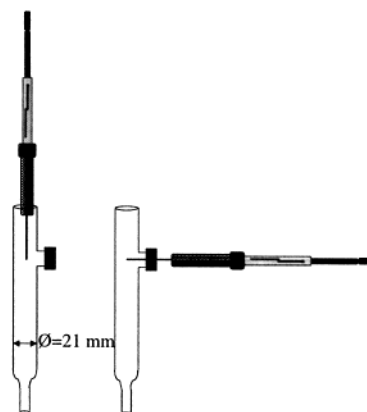


Figure 2. Different fiber positions used to investigate the influence of the direction of the air flow.

To vary the temperature in the bulb, the setup was adjusted in different ways depending on whether a temperature above or below ambient was desired. To lower the temperature, the air was passed through a spiral condenser before entering the glass tube. Cooled water was pumped over the condenser using a type D pump (Dosapro Milton Roy) and then through poly(divinyl) tubing wound around the glass tube housing the SPME fiber to cool the sampling environment. The cooled water was held at a temperature of 7 °C using an immersion cooler (TC40E, Huber, Offenburg, Germany), giving a temperature of 12 °C in the tube. For experiments at temperatures higher than room temperature, the humidification system also needed to be heated in order to combine high temperatures and high humidity levels. To do this, the humidification system and the sampling tube were placed in a heated unit (Infor HT), in which the temperature could be constantly controlled at levels above room temperature, which was set at 22 °C. Temperature and humidity in the tube were carefully measured at the point where the SPME needle was inserted using a humidimeter (P570, Dostmann Electronic GmbH, Wertheim, Germany). For these measurements, we used the tube, described above, that was open at one side.

**Sampling.** Field samples were collected at a poultry factory located in the south of France that suffered from severe odor problems. The samples were pumped into homemade 100-L Tedlar sampling bags using a KNF pump (Midisciences) since previous studies had shown these bags to be suitable for storage of sulfur compounds for at least 20 h.<sup>28,32</sup>

**Analytical Procedure.** For TWA sampling, the SPME syringe needle was inserted through the septum of the sampling tube; the fiber was left retracted (0.3 cm from the exit of the stainless steel needle) and exposed to the sample, by diffusion, throughout the extraction period. The fiber was then withdrawn and within seconds transferred to the injector of the gas chromatograph. To perform SPME in static mode, the stopcocks of the sampling tube were closed. In standard addition experiments, ~10 L of the sample was pumped (using the same pump as for the field sampling) from the Tedlar bag through the 500-mL sample tube to ensure that the air in the tube was completely replaced by the sample. After that, the stopcocks were closed and the extraction was performed in static mode. For each standard addition, a suitable amount of the analytes of interest were injected into the sampling tube with a gastight syringe prior to extraction.

**GC and Detector Parameters.** GC analysis was performed with a Varian 3800 GC equipped with a 1079 split/splitless injector and a pulsed flame photometric detector (Varian, Les Ullis, France). Analytes were separated on a 30-m SPB-1 sulfur column (fused silica, 0.32-mm i.d., 4- $\mu$ m film thickness; Supelco, Bellefonte, PA). The samples were injected in splitless (2 min) mode, and the column temperature was held at 30 °C for 3 min and then increased by 20 °C min<sup>-1</sup> to 150 °C, where it was held for 5 min. The carrier gas was helium at a constant flow rate of 2 mL min<sup>-1</sup>. The injector temperature was held at 250 °C. The operating conditions of the detector were as follows: temperature, 200 °C; voltage, 600 V; gate delay, 6 ms; gate width, 20 ms; detector trigger, 200 mV; hydrogen flow rate, 14 mL min<sup>-1</sup>; air flow rate, air 1, 18 mL min<sup>-1</sup>, and air 2, 11 mL min<sup>-1</sup>. The injector was equipped with a 0.8-mm-i.d. liner.

## RESULTS AND DISCUSSION

### Effects of Air Velocity and Direction of the Air Flow.

Previous studies have shown that air velocity strongly influences uptake onto the SPME fiber when it is fully exposed to the sample.<sup>33</sup> Under these conditions, an increase in the flow reduces the diffusion layer around the fiber, which enhances the extraction of analytes.<sup>34</sup> To investigate the influence of the air velocity when the fiber is retracted within the needle, the amounts adsorbed at four different air velocities (0, 2, 8, and 48 cm s<sup>-1</sup>) were compared. For this, three samples in which each analyte was present at a concentration of 20  $\mu$ g m<sup>-3</sup> were extracted at each of the four flow rates for 2 h at 0% humidity. Since 0 cm s<sup>-1</sup> was included, the investigation also compared the difference between sampling in static and dynamic modes. The results from these experiments showed that the air velocity did not influence the uptake by the fiber. Furthermore, there was no difference between sampling in static (0 cm s<sup>-1</sup>) and dynamic modes. The influence of the

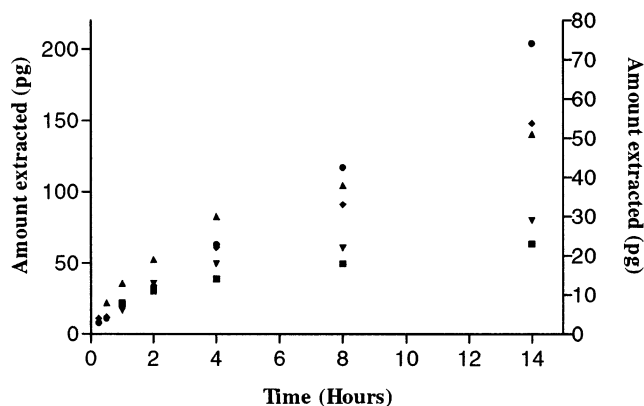


Figure 3. Uptake kinetics for the five investigated compounds (concentration, 20  $\mu$ g m<sup>-3</sup>; RH, 40%; air velocity, 2.1 cm s<sup>-1</sup>): left axis for Me<sub>2</sub>S (◆) and Me<sub>2</sub>S<sub>2</sub> (●); right axis for H<sub>2</sub>S (■), MeSH (▲), and EtSH (▼).

direction of the air flow was also investigated, by comparing results obtained when the fiber was placed parallel to the direction of the air flow with those obtained when it was facing the air flow (Figure 2). In these experiments, three samples were extracted for 2 h at a flow rate of 48 cm s<sup>-1</sup> for each position. There were no significant differences in the responses observed at the different positions, perhaps because the stainless steel needle acts as a windshield, breaking the flow before the air reaches the sorbent, in a way similar to the stainless steel grids used in passive samplers.

**Investigation of the Influence of Time and Concentration on the Uptake Rates.** To investigate the influence of the time and concentration parameters on the uptake rates (see eq 3), we initially studied kinetics at a constant concentration and the influence of concentration at constant extraction time. The aim was to evaluate the inherent potential of the SPME fiber for TWA sampling without interference from external factors. Thus, these experiments were conducted at room temperature (22 °C) and 0% RH. The kinetics were evaluated at extraction times of 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, and 14.0 h at concentrations of 20 and 100  $\mu$ g m<sup>-3</sup>. Linearity of uptake with time was observed for extraction periods up to 14 h for Me<sub>2</sub>S and Me<sub>2</sub>S<sub>2</sub>. However, for the compounds of lower molecular weight (H<sub>2</sub>S, MeSH, EtSH) the net uptake started to decline after 2 h of sampling for H<sub>2</sub>S and MeSH and after 4 h for EtSH (Figure 3). For each given time and each compound, the uptake rates were similar for the two concentrations. To gain further information about the potential of the sorbent for TWA sampling, the influence of concentration was studied at 0% RH, where samples with concentrations of 5, 10, 20, 40, 80, 200, 400, 667, 800, and 1000  $\mu$ g m<sup>-3</sup> were extracted for a fixed time of 2 h. The relationship between concentration of the analyte and the amount adsorbed on the fiber was linear up to 1000  $\mu$ g m<sup>-3</sup> for all compounds until saturation of the detector was reached. Higher concentrations than 1000  $\mu$ g m<sup>-3</sup> were not analyzed, since this was the upper limit of the gas-generating device. In conclusion, considering only the variables time and concentration, TWA sampling using the CAR-PDMS fiber coating seemed to be possible at sampling times up to 2 h for H<sub>2</sub>S and MeSH, 4 h for EtSH, and 14 h for Me<sub>2</sub>S and Me<sub>2</sub>S<sub>2</sub>.

**Experimental Design.** Since TWA sampling is done in situ, not only the parameters time and concentration that are included

(32) Sulyok, M.; Haberhauer-Troyer, C.; Rosenberg, E.; Grassbauer, M. *J. Chromatogr., A* **2001**, *917*, 367–374.

(33) Tuduri, L.; Desauziers, V.; Fanlo, J. L. *J. Chromatogr., A* **2002**, *963*, 49–56.

(34) Koziel, J.; Jia, M.; Pawliszyn, J. *Anal. Chem.* **2000**, *72*, 5178–5186.

Table 2. Results Obtained from the Central Composite Face Experimental Design: Predictive Capacities Expressed as  $Q^2$ , the Average Uptake Rates ( $\mu\text{L min}^{-1}$ ), RSDs (%), and Theoretical Uptake Rates ( $\mu\text{L min}^{-1}$ )

	H <sub>2</sub> S	MeSH	EtSH	Me <sub>2</sub> S	Me <sub>2</sub> S <sub>2</sub>
$Q^2$	0.939	0.850	0.869	0.813	0.432
average uptake rate	2.2	4.2	2.0	12.3	13.3
RSD	86.9	73.9	86.8	24.0	7.5
theoretical uptake rate	23.6	18.3	15.4	15.4	13.0

in the calculation of the uptake rates but also external factors such as humidity and temperature can affect the extraction. Previous studies have shown that when the fiber is exposed to the sample, both temperature and humidity have a negative effect on adsorption. For solid sorbents such as Carboxen, water molecules can compete with the analytes, since the surface available for adsorption is limited. Molecules with the lowest affinity for the coating (usually low molecular weight compounds) are most affected. Temperature also affects the extraction rate, because of the exothermic nature of adsorption: increasing the temperature should theoretically decrease the extraction rate. Therefore, the influence of humidity and temperature on the uptake rates in TWA sampling must be investigated; i.e., robust testing is required. For this reason, we applied experimental design to simultaneous investigations of the influence of concentration, humidity, temperature, and time on the response (the uptake rate of each sulfur compound). Experimental design is also very valuable for detecting interactions among factors, which are not detectable with classical experimental methods in which each factor is studied separately. To facilitate the design process, we employed Modde 6.0 software (Umetrics, Umeå, Sweden) to create a central composite face (CCF) design with 3 levels of each variable and 27 independent samples, including 3 center points. We used a concentration range between 20 and 80  $\mu\text{g m}^{-3}$ , to obtain a sufficiently strong response but avoid saturating the detector. The humidity was varied between 20 and 80%, since the humidity encountered both indoors and outdoors is normally within this range. The temperature range was between 10 and 30 °C. The shortest sampling time used was 2 h in order to ensure there was a measurable response, and the longest extraction time used was 12 h, since we wanted to investigate the possibility of using the technique for prolonged sampling times.

It was not possible to randomize the runs fully since the setup had to be adjusted in order to test the effects of varying the temperature. Therefore, all runs at a certain temperature were performed together. For each compound, the response (UR) was modeled and multiple linear regression (MLR) was used to calculate the coefficients of the polynomial functions with linear, quadratic and interaction terms. The predictive capacity expressed as  $Q^2$  was also evaluated, which is a measure of how well the model will predict the responses under new experimental conditions. A large  $Q^2$  value, 0.7 or more, indicates that the model has good predictive ability and will give small predictive errors. Some variables were kept in the model despite nonsignificance (i.e., less than 95% confidence), since the  $Q^2$  value decreased if they were deleted. Linear terms were also kept in the model if a quadratic or interaction term containing this variable was significant.

However, in the following equations, the variables that had larger errors than the coefficients have been eliminated.

$$\text{UR}_{\text{H}_2\text{S}} = 0.85 - 1.36\text{Time} - 1.05\text{Hum} - 0.72\text{Temp} - 0.57\text{Conc} + 1.39\text{Time}^2 + 0.32\text{TempConc} + 0.36\text{TimeHum} + 0.38\text{TimeConc}$$

$$\text{UR}_{\text{MeSH}} = 2.11 - 2.34\text{Time} - 1.34\text{Hum} - 1.33\text{Temp} - 1.12\text{Conc} + 1.46\text{Time}^2 + 1.44\text{Conc}^2 + 0.54\text{TempTime} + 0.78\text{TimeConc}$$

$$\text{UR}_{\text{EtSH}} = 1.00 - 1.09\text{Time} - 1.30\text{Hum} - 0.85\text{Temp} + 0.72\text{Time}^2 + 0.63\text{Conc}^2 + 0.32\text{TempTime} + 0.41\text{TempConc} + 0.46\text{TimeHum}$$

$$\text{UR}_{\text{Me}_2\text{S}} = 11.27 - 2.05\text{Time} - 2.02\text{Hum} - 2.05\text{Temp} + 1.48\text{Time}^2 + 0.59\text{TempConc}$$

$$\text{UR}_{\text{Me}_2\text{S}_2} = 13.05 - 0.74\text{Time} - 0.56\text{Temp} + 0.42\text{TempConc}$$

The regression coefficient ( $R^2$ ), which indicates how well the model fits the data, was larger than 0.92 for all compounds except Me<sub>2</sub>S<sub>2</sub>.  $Q^2$  varied between 0.813 for Me<sub>2</sub>S and 0.939 for H<sub>2</sub>S (Table 2), which implies that if the sampling parameters could be kept constant, the model would predict a value for the uptake rate close to the real value. However, this is not possible since all parameters except the extraction time normally vary during sampling. For Me<sub>2</sub>S<sub>2</sub>,  $Q^2$  and  $R^2$  were considerably lower, with values of 0.432 and 0.68, respectively. This is probably because the differences in the values of the uptake rate were small compared to the experimental error (3.6%).

From the derived equations, it was concluded that all the investigated parameters had a significant effect on the uptake rates of H<sub>2</sub>S and MeSH, and all the variables were negatively correlated with uptake; i.e., increasing the concentration, humidity, temperature, or time decreased the uptake rate. For both compounds, time was the most significant parameter. Humidity and temperature had approximately the same strength of influence, while concentration was the least influential of the four factors. For EtSH and Me<sub>2</sub>S, concentration was not a significant parameter, which may be due to the higher molecular masses of these compounds reducing the effects of competitive adsorption. For EtSH, humidity replaced time as the most important parameter, followed by time and temperature. For Me<sub>2</sub>S, all parameters had similar degrees of influence. Finally, for Me<sub>2</sub>S<sub>2</sub>, only time and temperature were found to be significant. For Me<sub>2</sub>S and Me<sub>2</sub>S<sub>2</sub>, the values of the uptake rates were considerably higher than for the other compounds. Hence, the influence of the significant parameters was relatively weak. Generally, as the molecular weight increased, fewer parameters were significant.

Interaction terms were included in all the functions, and significant interactions were detected between several parameters. For example, a commonly observed interaction was between concentration and temperature, which had a positive effect on the uptake rate. For H<sub>2</sub>S and MeSH, there was a significant interaction between time and concentration, and for H<sub>2</sub>S and EtSH, there was a significant interaction between time and humidity, both of which had a positive effect on the uptake rate. In a previous study where

the fiber was exposed to the sample, the relationship between temperature and adsorbed amount was investigated and found to be practically linear between 22 and 25 °C.<sup>34</sup> However, in the cited study, all the other parameters that may affect the extraction (extraction time, humidity, concentration) were kept constant. Our study shows that when all these experimental parameters are simultaneously altered, nonlinear relationships may occur, due to interactions between the factors.

According to the models, within the experimental domain the uptake rates varied between 0 and 6.3  $\mu\text{L min}^{-1}$  for  $\text{H}_2\text{S}$ , 0 and 11.0  $\mu\text{L min}^{-1}$  for MeSH, 0 and 5.6  $\mu\text{L min}^{-1}$  for EtSH, 5.5 and 18.6  $\mu\text{L min}^{-1}$  for  $\text{Me}_2\text{S}$ , and finally, 11.6 and 15.6  $\mu\text{L min}^{-1}$  for  $\text{Me}_2\text{S}_2$ . The uptake rates had RSDs of 86, 74, 79, 24, and 8% for  $\text{H}_2\text{S}$ , MeSH, EtSH,  $\text{Me}_2\text{S}$ , and  $\text{Me}_2\text{S}_2$ , respectively (Table 2), corroborating the finding that the influence of the tested variables on the uptake rate decreased as the molecular weight increased. The average uptake rate is given for each compound in Table 2, and the resulting figures were compared with theoretical values for the uptake rates obtained by calculating respective diffusion coefficients.<sup>35</sup> For  $\text{Me}_2\text{S}_2$ , there was very good agreement between the theoretical and experimental values, while for the other compounds, there were large differences between them, especially for  $\text{H}_2\text{S}$ , MeSH, and EtSH. From these results, we conclude that the only investigated compound for which TWA sampling using SPME is suitable under the tested experimental conditions is  $\text{Me}_2\text{S}_2$ .

**Investigation of Reverse Diffusion.** If the adsorbent is not strong enough, the extracted analytes can be released back into the bulk air when the concentrations vary from a high to a low level. To investigate the occurrence of reverse diffusion, the fiber was exposed both continuously and intermittently to the gas mixture at a flow rate of 2  $\text{cm s}^{-1}$  at both 0 and 40% RH, and the results were compared. For continuous exposure, the fiber was continuously exposed to the gas mixture at a concentration of 20  $\mu\text{g m}^{-3}$  for 120 min. For intermittent exposure, two different experiments were conducted. In experiment 1, the fiber was exposed to gaseous analytes at a concentration of 20  $\mu\text{g m}^{-3}$  for 30 min and then to analyte-free gas for 15 min. This sequence was repeated three times, giving a total exposure time of 120 min. In experiment 2, the fiber was exposed to gaseous analytes with a concentration of 40  $\mu\text{g m}^{-3}$  for 30 min and then to analyte-free gas for 30 min. This sequence was then repeated, giving a total exposure time of 60 min at 40  $\mu\text{g m}^{-3}$ , equivalent to 120 min at 20  $\mu\text{g m}^{-3}$ . At 0% RH, there were no differences in the amount adsorbed between the experiments with intermittent and continuous exposure (Table 3). Thus, no reverse diffusion occurred when the fiber was exposed to clean, dry air. However, at 40% humidity, significant losses of 23–27, 19–20, and 11–16% occurred for  $\text{H}_2\text{S}$ , MeSH, and EtSH, respectively, while there were no significant losses of  $\text{Me}_2\text{S}$ , and  $\text{Me}_2\text{S}_2$ . This is most likely due to displacement by water molecules of the compounds with the lowest affinities for the sorbent.

**Storage of Fibers.** Several studies of the storage stability of VSCs have shown that the stability can be improved by keeping the samples at subambient temperature (see ref 36 and references therein). A previous study by Haberhauer-Troyer et al.<sup>27</sup> suggested

Table 3. Investigation of Reversible Diffusion of the Target Compounds at 0 and 40% RH<sup>a</sup>

RH, %		$\text{H}_2\text{S}$	MeSH	EtSH	$\text{Me}_2\text{S}$	$\text{Me}_2\text{S}_2$
0	exp 1	105 ± 16	94 ± 8	125 ± 16	112 ± 12	109 ± 6
	exp 2	102 ± 8	96 ± 16	120 ± 9	118 ± 13	105 ± 3
40	exp 1	73 ± 3	80 ± 6	88 ± 12	102 ± 22	98 ± 7
	exp 2	77 ± 13	81 ± 18	93 ± 5	110 ± 9	107 ± 6

<sup>a</sup> The results are expressed as percentages of the reference value (obtained following continuous exposure for a sampling time of 120 min at 20  $\mu\text{g m}^{-3}$ ).

that the stability in storage of isopropanethiol (i-PrSH), isobutanethiol (i-BuSH), and  $\text{Me}_2\text{S}$  is only acceptable at low temperatures. Even at the lowest investigated temperature (−23 °C), significant losses of i-PrSH and i-BuSH were observed. We therefore chose to investigate storage stability at −80 °C, which is a convenient temperature for field sampling since it can be maintained using dry ice. In this experiment, three fibers were exposed to 100  $\mu\text{g m}^{-3}$  of the compounds for 2 h at an air velocity of 2  $\text{cm s}^{-1}$  and 40% RH and were then stored for 1, 3, and 7 days in a freezer at −80 °C. The results showed that the fibers could be stored for 7 days at −80 °C without incurring significant losses of  $\text{H}_2\text{S}$ , MeSH, and  $\text{Me}_2\text{S}_2$ . For EtSH and  $\text{Me}_2\text{S}$ , the fibers could be stored without losses for 3 days, while significant losses of 25 and 19%, respectively, occurred after 7 days of storage.

**Comparison with Real Samples Using the Method of Standard Addition.** To validate the method developed for TWA sampling of  $\text{Me}_2\text{S}_2$ , we initially intended to compare the results with data collected using a partially validated method developed by OSHA.<sup>10</sup> In the cited method,  $\text{Me}_2\text{S}_2$  is extracted by pumping the sample through sorbent tubes of coconut shell charcoal for 100 min at a flow rate of 0.1  $\text{L min}^{-1}$ . However, during initial tests, we found that severe artifact formation occurred through the oxidation of MeSH to  $\text{Me}_2\text{S}_2$ . For this reason, we found the OSHA method to be unsuitable for the validation of real samples, which often contain high amounts of MeSH. To use the OSHA method for validating analyses of real samples, further investigations must first be undertaken in order to determine the extent of this oxidation. Therefore, we instead chose to use a standard addition for comparison of the results, in which two additions of suitable amounts of  $\text{Me}_2\text{S}_2$  (corresponding to 20 and 60  $\mu\text{g m}^{-3}$ ) were made to the sample prior to extraction for 2 h under static conditions. The concentration derived from the uptake rate obtained from the experimental design described above was  $56 \pm 5 \mu\text{g m}^{-3}$ . Good agreement was found when this value was compared with the value obtained from standard additions ( $55 \pm 10 \mu\text{g m}^{-3}$ ). The agreement also showed that the complex matrix (consisting mainly of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and oxygenated compounds, e.g., butanal-2-methyl and 2-butanol) present in the sample did not affect the uptake rate of  $\text{Me}_2\text{S}_2$ .

## CONCLUSIONS

Neither the air velocity nor the direction of the air flow had a significant influence on the uptake of the investigated sulfur compounds by the fiber. No reverse diffusion occurred at 0% RH; however, at 40% RH, significant losses occurred for  $\text{H}_2\text{S}$ , MeSH, and EtSH. SPME using the CAR–PDMS fiber coating is not

(35) Perry, J. H. *Chemical engineers' handbook*; McGraw-Hill Book Co.: Tokyo, 1963.

(36) Wardencki, W. *J. Chromatogr., A* **1998**, *793*, 1–19.

suitable for TWA sampling of H<sub>2</sub>S, MeSH, EtSH, and Me<sub>2</sub>S at the investigated concentrations since the uptake rates of these compounds vary greatly with humidity, temperature, and time, and for H<sub>2</sub>S and MeSH, concentration also has significant effects. Nevertheless, SPME could still be a successful technique, if a coating with higher affinity for compounds with low molecular weights can be developed. For Me<sub>2</sub>S<sub>2</sub>, the uptake rate had a variation of only 8% within the whole experimental domain, and the value experimentally derived for the uptake rate correlated well with the theoretical value. Comparison of values derived from standard additions showed good agreement with the results obtained using the calculated uptake rates. Therefore, it was concluded that SPME is a suitable technique for TWA sampling of Me<sub>2</sub>S<sub>2</sub>. However, since artifact formation occurs via oxidation of MeSH, the extent of this oxidation must be carefully investigated for each fiber used. Furthermore, the fibers can be stored

for 3 days at -80 °C without incurring significant losses of the target compounds.

#### ACKNOWLEDGMENT

The authors are grateful to Michael Sjöström of Umeå University, Sweden, for help with the experimental design. The authors thank the Association for Research With Industrial and Educational Links from the French *Conférence des Grandes Ecoles*, the Swedish Natural Science Research Council, and the National Swedish Board for Industrial and Technical Development for funding.