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Evaluation of solid-phase microextraction for sampling of volatile organic sulfur compounds in air for subsequent gas chromatographic analysis with atomic emission detection

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Abstract

The use of solid-phase microextraction (SPME) followed by GC–AED (atomic emission detection) for the analysis of volatile organic sulfur compounds (methanethiol, dimethyl sulfide, isopropanethiol and isobutanethiol) in spiked air samples was investigated. Gaseous standard mixtures were generated by means of a permeation apparatus with stopped flow facilities to permit sampling of the analytes with the SPME fiber. Detection limits between 4 ppt for dimethyl sulfide and isobutanethiol and 50 ppt (v/v) for methanethiol were achieved for extraction with the Carboxen–PDMS (polydimethylsiloxane) fiber followed by GC–AED analysis. The comparison of the performance of the 100 μm PDMS and the 75 μm Carboxen–PDMS fiber coating demonstrates the superiority of the latter in terms of sensitivity and repeatability. Despite the principal applicability of SPME to sampling of organosulfur compounds, artifacts are observed during analysis. Furthermore, the low storage stability, the dependence of the extraction efficiency on the relative humidity and the pronounced differences in sensitivity between fibers limit the usefulness of the method for quantitative on-site analysis.

Keywords: Air analysis; Extraction methods; Volatile organic compounds; Volatile sulfur compounds; Organosulfur compounds

1. Introduction

The determination of organic pollutants in air and water has become a major task in environmental monitoring. Isolation and preconcentration of trace analytes are usually essential steps of the analytical procedure. Solid-phase microextraction (SPME) is a new method for the extraction of organic analytes from different matrices, e.g. air and water, and a solventless, rapid, inexpensive and portable alternative to traditional extraction methods such as liquid–liquid extraction, headspace, purge-and-trap procedures or solid-phase extraction for water samples and adsorptive sampling for air samples. Belardi and Pawliszyn [1] first described the basic concept of SPME. By placing the fiber in a microsyringe the technique was made practical [2] and commercialized in 1993. Typical applications of SPME for water analysis are reviewed by Eisert and Levsen [3] whereas new trends in SPME are described by Eisert and Pawliszyn [4].

SPME integrates sampling and preconcentration in one step. A chemically modified fused-silica fiber is

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exposed to the aqueous or gaseous samples and the organic compounds are extracted into the organic coating of the fiber. The extraction process is governed by the kinetics of diffusion in the surrounding medium and/or the polymer fiber coating. When SPME is combined with gas chromatographic analysis, the fiber is transferred to the injection port of the gas chromatograph, where thermal desorption and transfer of the analytes onto the GC column take place. Meanwhile a variety of coated fibers of different polarity and film thickness are commercially available. As the coating/air partition coefficients for the most volatile organic compounds are relatively small with the fiber coating materials commercially available previously, the detection limits of this range of compounds were not satisfactory. To improve the enrichment of the volatile organic compounds fused-silica fibers coated with the graphitized carbon black Carbograph I [5] and porous layer activated charcoal-coated fused-silica fibers [6] were developed. Chai and Pawliszyn [7] compared the performance of two carbon-based coatings (Carboxen and Carbopack B) with a 100 μm PDMS fiber for the analysis of aromatic compounds in air. Carboxen–PDMS fibers have been made commercially available and seem to be particularly suited for the analysis of volatile organic compounds [8]. They have been used e.g. for the analysis of BTEX (benzene, toluene, ethylbenzene, xylenes) and volatile halogenated compounds in water and air [9].

Quantitative analysis for air samples can either be carried out with standard gas mixtures of known concentration and temperature [10] or by calibration strategies based on physicochemical properties of the coating or retention indexes obtained from linear temperature-programmed capillary gas chromatography [11,12].

Volatile organosulfur compounds are of interest due to their adverse organoleptic characteristics even at very low concentrations. Some authors have already applied SPME to the analysis of these compounds in diverse matrices. Rivasseau and Caude [13] have compared on-line solid-phase extraction (SPE)–HPLC and SPME–GC with the 100 μm PDMS fiber for the analysis of tetrahydrothiophene, tert-butylmercaptan and *n*-butylmercaptan in water. Polydimethylsiloxane and polyacrylate coated fused-silica fibers have been used for the analysis of volatile sulfides and disulfides in wine aroma [14]. Volatile organic sulfur compounds in black and white truffle aroma [15], aromatic sulfur containing substances in aqueous samples [16,17] and both aliphatic and aromatic sulfur compounds in waste water deposits [18] have also been analyzed by SPME. None of these publications considers the possible formation of artifacts. This is remarkable since organic sulfur compounds are known for their highly reactive nature [19], and irreversible losses, elimination and oxidation reactions catalyzed by heated metal surfaces easily take place during sampling and transfer of the compounds. Even oxidants in ambient air are known to oxidize analytes sampled cryogenically or on solid adsorbents [19and references therein]. In addition, dryers which are necessary for cryogenic and adsorptive sampling of low molecular-mass compounds can cause severe losses of sulfur compounds [20,21].

This paper discusses the applicability of the Carboxen–polydimethylsiloxane (PDMS) SPME fiber to the determination of volatile organic sulfur compounds in spiked air samples as an alternative to conventional sampling on solid adsorbents and its advantage over other SPME fiber coating materials. The influence of the relative humidity and the storage stability of the analytes were investigated as well as artifact formation. Oxidation products were identified by GC–MS, while element selective sulfur detection was carried out with atomic emission detection (AED). The limitations of the method are discussed in detail.

2. Experimental

2.1. Preparation of standards

A schematic of the apparatus used for the dynamic generation of gaseous standard mixtures is given in Fig. 1. Certified permeation tubes (VICI Metronics, Santa Clara, Ca, USA) filled with methanethiol (MeSH), dimethyl sulfide (DMS), isopropanethiol (i-PrSH) and isobutanethiol (i-BuSH) (compound data in Table 1) were placed in the thermostated oven (30±0.1°C) of the permeation apparatus (VICI). The standards were prepared in ambient air, which was supplied by an oil-free compressor and

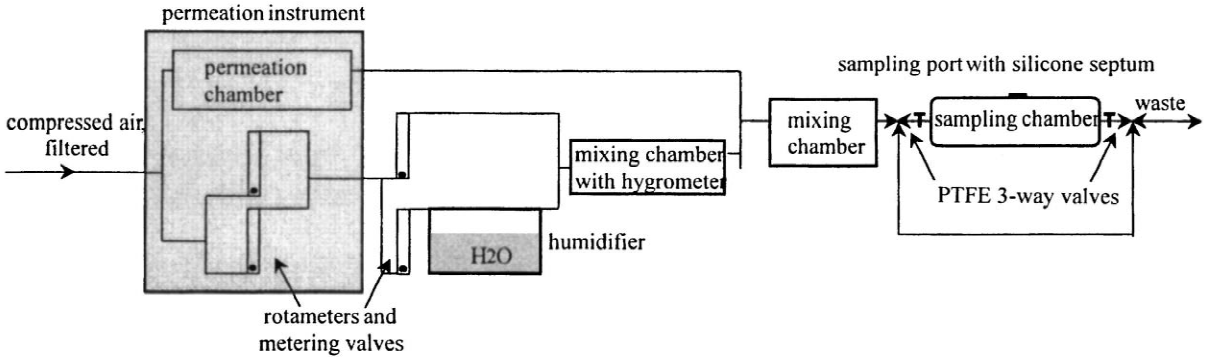

Fig. 1. Apparatus for the generation of gaseous standard mixtures.

further purified from water and organic compounds by the use of silica gel and activated charcoal traps. The standard compounds were released at a constant permeation rate into the chamber flow of the permeation apparatus, which could further be diluted by a dilution gas flow of variable relative humidity. The concentration ranges of the compounds of interest are given in Table 1. After having passed through a mixing chamber the stream of the gaseous standard was directed into a glass mixing chamber with a volume of approximately 500 ml (sampling chamber), which could be bypassed by switching two PTFE 3-way valves. By bypassing the sampling chamber the flow in the mixing chamber was stopped during the exposition of the fiber. The needle of the SPME device can be inserted into the sampling chamber through a PTFE-coated septum.

2.2. SPME procedure and gas chromatographic conditions

SPME was carried out manually with the appropriate SPME holder and 100 μm PDMS- and 75 μm Carboxen–PDMS-coated fused-silica fibers (all obtained from Supelco, Bellefonte, PA, USA).

The analytes were extracted by piercing the septum of the mixing chamber port with the protecting needle and exposing the fiber to the standard mixture for a given time. Before retracting the SPME fiber holder the fiber was withdrawn into the protecting needle. Immediately after extraction the needle was introduced into the split/splitless injector of the gas chromatograph, which was equipped with a dedicated SPME liner (0.75 mm I.D., Supelco). By exposing the fiber to the carrier gas stream the analytes were thermally desorbed and transferred onto the GC column. The needle with the exposed fiber was left in the heated split/splitless injector (250°C) for at least 4 min. Applying this procedure no memory effects could be observed, which was confirmed by desorbing the same fiber a second time after the initial desorption. All experiments were carried out at a temperature of 21°C.

GC–AED analysis was carried out with an HP 5890 gas chromatograph coupled to an HP 5921A atomic emission detector or an HP 5989A MS Engine, respectively, for the identification of artifacts

Table 1
Concentrations of sulfur compounds investigated compound data

Compound analyzed	Molecular mass (g mol^{-1})	Boiling point (°C)	Range of analyte concentrations	
			ppb (v/v)	ng S l^{-1}
Methanethiol	48.11	6	0.89–48.04	1.17–63.23
Dimethyl sulfide	62.13	38	1.16–62.99	1.53–82.91
Isopropanethiol	76.16	57–60	0.33–17.94	0.44–23.61
Isobutanethiol	90.19	87–89	0.38–20.32	0.50–27.02

Table 2
Separation and detection parameters of the GC–AED system

Injection port	split/splitless, SPME-liner 0.75 mm I.D. (Supelco)
Injector temperature	250°C for the Carboxen–PDMS fiber 150°C for the PDMS fiber
Location of the fiber	4.4 cm from the top of the injector
Desorption time (=purge delay time)	100 s
Analytical column	HP 1, 60 m×0.32 mm I.D., 1 μm film thickness
Column flow	2.5 ml/min He, purity>99.9996%
Temperature program	−20°C for 2 min, with 15°C min^{-1} to 120°C, with 25°C min^{-1} to 180°C, with 40°C min^{-1} to 280°C, 2 min hold
AED total He flow	20 ml min^{-1}
AED reagent gases	O_2: 2.1 bar H_2: 0.7 bar
Wavelengths	181 nm (sulfur), 193 nm (carbon)
Data rate	5 Hz
Cavity temperature	300°C
Transfer line temperature	290°C

(Hewlett-Packard, Palo Alto, CA, USA). The parameters of the GC–AED system are given in Table 2.

3. Results and discussion

3.1. Optimization of sampling, desorption and GC analysis

The determination of the equilibrium time is an important step in the development of an SPME method. Additional factors which have been shown to affect the precision and sensitivity of the SPME technique are the location of the fiber in the injector of the GC system, the desorption temperature and the time delay between the end of sampling and injection.

In order to determine the equilibration time the Carboxen–PDMS fiber was exposed to the gaseous standard for different periods of time (5–90 min). In Fig. 2 a plot of the peak areas versus exposition time is given. The equilibration process is — despite enrichment from the gaseous phase is usually said to occur fast — relatively slow. Equilibration times exceed 1.5 h and hence by far the GC run time. Experiments under continuous flow conditions showed that the extraction speed is limited by the speed of gas phase diffusion. A flow of 100 ml/min through a 300 ml sampling chamber increases the extracted amount by up to 40% at a sampling time of 20 min. Since sampling under controlled flow conditions needs more elaborate equipment than sampling under stopped flow conditions — which is of special importance for field sampling — all further experiments were carried out under stopped flow non-equilibrium conditions using a 20 min extraction time.

The influence of the injector temperature on the desorption efficiency of the analytes was investigated for both fiber materials in the range of 100–250°C. For the PDMS and the Carboxen–PDMS fiber injector temperatures of at least 150°C and 200°C, respectively, are needed for complete desorption. For the Carboxen–PDMS fiber no significant difference was found for desorption times between 60 and 120 s. Provided that the injector temperature is high enough no significant influence of the fiber location in the injector in the range of 2.0 to 4.4 cm (measured from the top of the injector) was found, which supports the assumption that no analyte losses over the septum purge vent occur even when the fiber is positioned close to the upper end of the injector. All subsequent analyses were carried out according to the conditions given in Table 2.

Due to the high volatility of methanethiol the refocusing of this compound at the column head is insufficient and distorted peak shapes are observed even with a column film thickness of 1 μm and a narrow bore SPME insert. Oven temperatures as low as −40°C were investigated but did not significantly

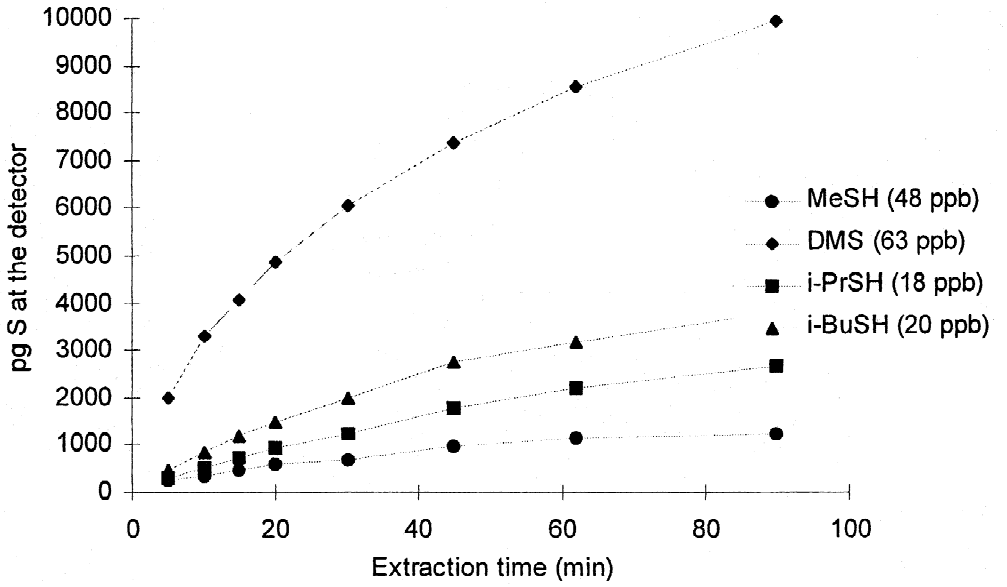

Fig. 2. Time profile of the quantity adsorbed by the Carboxen–PDMS fiber from a standard at the highest concentration level (18–48 ppb).

improve the peak shape of methanethiol. An initial oven temperature of −20°C was chosen as a compromise between peak shape, liquid nitrogen consumption and GC run time.

3.2. Figures of merit

The linearity of the calibration graphs was tested with four calibration points over the concentration range accessible with the permeation apparatus (Table 1). For each concentration level at least three independent measurements were made. The relationship between SPME–GC–AED response (expressed as peak area) and analyte concentration in the gaseous mixture can be assumed to be linear within the examined concentration range for MeSH, i-PrSH and i-BuSH. Non-linearity is only observed for the highest concentration of DMS. This non-linearity seems not to be caused by non-linearity of the detector response, which is linear up to an absolute amount of 6 ng of sulfur. Correlation coefficients for MeSH, i-PrSH and i-BuSH range from 0.9997 to 0.99999, standard deviations of the method from 0.4 to 1.7 ppb. Sensitivity decreases with volatility and ranges from 132 to 1050 peak area units/ppb.

In Table 3 detection limits of the volatile sulfur compounds for the 100 μm PDMS and the 75 μm Carboxen–PDMS fiber are given (measured on the peak heights and defined as three times the standard deviation of the baseline noise). The detection limits had to be estimated, since no analyses could be carried out near the detection limits due to the restricted concentration range of the standard mixtures generated with the permeation apparatus. They clearly demonstrate that the sensitivity which can be achieved with the Carboxen–PDMS fiber exceeds

Table 3
Detection limits for the 100 μm PDMS and the 75 μm Carboxen–PDMS fiber. Detection limits were estimated based on the peak heights and three times the standard deviation of the noise since no analyses could be carried out near the detection limits due to the restricted concentration range of the standard mixtures.

Detection limit (ppb)	MeSH	DMS	i-PrSH	i-BuSH
100 μm PDMS	4	2	2	0.7
75 μm Carboxen–PDMS	0.04–0.06	0.003–0.004	0.005–0.007	0.003–0.004

the 100 μm PDMS fiber by at least a factor of 100 for all of the compounds under investigation. Standard deviations of consecutive measurements of samples of the highest investigated concentration range from typically 2 to 5% for the Carboxen–PDMS fiber and from 3 to 15% for the PDMS fiber. Day-to-day repeatability ranges from 4 to 11% for the Carboxen–PDMS fiber. Due to the high sensitivity and the good repeatability which can be achieved with the Carboxen–PDMS coating this fiber is better suited than the 100 μm PDMS fiber for the analysis of low-boiling sulfur compounds, which generally occur in very low concentrations.

To assess the reproducibility of the measurement with different SPME fibers, five new Carboxen–PDMS fibers were compared. The results for the enrichment of the tests substances are shown in Fig. 3. The performance of the fibers varies significantly (relative standard deviations between fibers range from 10% for i-BuSH to 22% for MeSH). This effect cannot be explained by the observed differences in fiber lengths (10.16±0.07 mm). It can neither be attributed to decomposition reactions, since the extent of decomposition due to oxidation does not differ significantly between fibers as will be discussed in more detail later. Consequently, calibrations have to be performed for each fiber separately in order to achieve accurate quantitative results. This has especially to be taken into account when different fibers are used for field sampling and makes quantitative analysis time consuming, thus annulling the claimed speed of analysis which is one of the main advantages of SPME.

3.3. Factors influencing precision and accuracy

3.3.1. Conditioning effects, losses and artifacts

Conditioning effects occurred every day at the beginning of a new series of measurements. In general 2–3 injections of the standard with the highest concentration were necessary to achieve a stable response, even when freshly silanized liners were used. When the injector was opened in order to change or clean the liner 4–5 injections were necessary to recondition the system. In addition to the four analytes the following oxidation products could be detected in the chromatograms and were identified by GC–MS: dimethyl disulfide (DMDS), dimethylsulfoxide (DMSO), methyl isopropyl disulfide, methyl isobutyl disulfide, diisopropyl disulfide, diisobutyldisulfide and isopropyl isobutyl disulfide. A GC–AED chromatogram of these and the parent compounds as detected on the sulfur channel of the AED system is given in Fig. 6 (see discussion of

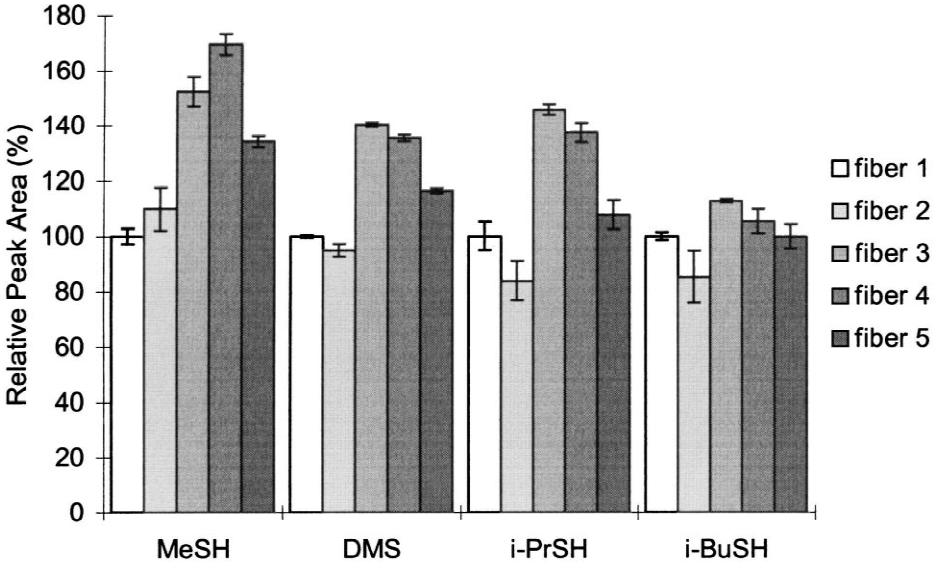

Fig. 3. Comparison of the performance of five new Carboxen–PDMS fibers (peak areas of fiber 1 are set at 100%).

storage stability). The peak area of dimethyl disulfide was found to be between 20 and 24% of the peak area of MeSH. Unlike MeSH, i-PrSH and i-BuSH do not seem to be readily oxidized to the corresponding disulfides. The peak areas of the disulfides consisting of isobutyl and isopropyl-chains are negligible in comparison with the corresponding mercaptans (1 to 4%). The peak area of DMSO is less than 0.5% of the peak area of DMS when the gas standard is prepared in N_2 with a purity of >99.999% and between 1.5 and 11% when the standard is prepared in compressed air, while no differences are noted for the formation of disulfides. Therefore it was concluded that further purification of the carrier gas would not lower the extent of oxidation, since oxygen is also introduced in the injector with the SPME needle and seems to cause the oxidation of DMS into DMSO. The extent of the oxidation reactions does not differ significantly between fibers unless they have been extensively used (more than 150 injections) but does differ significantly between days thereby reflecting the condition of the liner. It has to be pointed out that the percentages given are the percentages of the peak areas and do not necessarily reflect the ratio of the amounts because underestimation of the higher boiling compounds could occur due to incomplete desorption.

The extent of the losses due to decomposition, oxidation reactions and irreversible adsorption can be estimated from the comparison of the results of successive analyses of the same sample with the apparent extraction efficiency obtained by repetitive analysis of fresh standard samples. This apparent extraction efficiency (EE_{app}) can be calculated by the following equation:

$$EE_{app} = \text{peak area}/(\text{sensitivity} \cdot cV)$$

where EE_{app} is apparent extraction efficiency, sensitivity is expressed as (peak area/ng S), c is concentration (ng S/l) and V is volume of the sampling chamber (l).

This apparent extraction efficiency can be easily calculated due to the fact that the AED response can be assumed to be substance independent within 2–3%. It is called ''apparent'' since it is only based on the amount of sulfur actually reaching the detector and therefore does not take into account possible losses on the fiber and in the GC system during sampling and analysis.

The experimental extraction efficiency (EE_{exp}) assumes larger numeric values than the apparent extraction efficiency since it takes into consideration that a larger amount of sulfur compounds is removed from the atmosphere in the sampling chamber than is finally detected by AED due to irreversible adsorption or decomposition of the analytes.

In contrast to the apparent extraction efficiency the experimental extraction efficiency (EE_{exp}) is independent of the losses during transfer and analysis. Its calculation is based on the decrease of the concentration in the sampling chamber and can be calculated from the peak areas of successive analyses. Peak areas decrease exponentially with the number of extractions. The logarithm of the peak areas and hence also the amount of sulfur at the detector (peak area divided by sensitivity) show a linear relationship with the number of extractions, which was calculated by linear regression and can be described by the following equation:

$$ng\ S_n = (1 - EE_{exp})^{(n-1)} \cdot ng\ S_1$$

and, after logarithmic transformation of the equation:

$$\log(ng\ S_n) = (n-1) \cdot \log(1 - EE_{exp}) + \log(ng\ S_1)$$

where EE_{exp} is the experimental extraction efficiency, $ng\ S_n$ is the amount of sulfur at the detector from the nth extraction (ng) and n is the number of the extraction

The experimental extraction efficiency can be calculated from the slope of the linear regression. By comparing the experimental and the apparent extraction efficiency the extent of the losses can be calculated:

$$\text{losses}(\%) = 100 \cdot (EE_{exp} - EE_{app})/EE_{exp}$$

These percentages reflect the fraction of the analyte, which is adsorbed onto the fiber but not transferred to the detector.

The losses were determined in two series with two different SPME fibers (results in Table 4). After having conditioned the analytical system six repetitive extractions of fresh samples were carried out for the calculation of the apparent extraction efficiencies followed by nine successive extractions of the same

Table 4
Losses of MeSH, DMS, i-PrSH and i-BuSH during the transfer of the analytes from the sampling chamber into the detector (uncertainties were estimated from the confidence intervals of the slopes only)

Losses (%)	MeSH	DMS	i-PrSH	i-BuSH
Series 1	65±15	−6±3	25±5	49±2
Series 2	89±1	4±3	47±3	61±2

sample. For series 1 a 500 ml sampling chamber was used. Due to the small decrease in concentration in comparison to the original concentration uncertainty of the calculated losses is high. This is especially the case for methanethiol, which has the smallest extraction efficiency of the compounds investigated. Therefore a smaller volume sampling chamber (300 ml) was used for the second series. The differences in the losses between the two series reflect the condition of the fiber and the system.

Oxidation of MeSH into dimethyl disulfide accounts for 8–20% of the losses of MeSH, oxidation of isopropanethiol and isobutanethiol into the corresponding disulfides for only up to 2.3 and 1.5%, respectively, of the losses (percentages were calculated based on the absolute amount of sulfur converted into disulfides divided by the absolute loss of sulfur calculated from the results of successive analyses). Other decomposition reactions or irreversible adsorption on the fiber seem to account for the biggest part of the losses. In thermodesorption studies carried out by GC–MS, i-BuSH was shown to undergo surface catalyzed elimination of H_2S. The extent to which this decomposition reaction takes place cannot be determined with the GC–AED set up due to coelution of H_2S with the air peak.

Decomposition products of volatile sulfides and disulfides analyzed from the headspace of wines were also observed by Mestres et al. [14] if the extraction temperature is increased to more than 30°C. Recoveries of >94% were found by the standard additions method. However, it has to be considered that the method of standard additions only corrects for proportional systematic errors caused by the matrix, whereas it does not necessarily reveal the occurrence of other errors. Pelusio et al. [15] lowered the extraction temperature of white and black truffles from 80 to 30°C in order to avoid the possible formation of artifacts. Rivasseau and Caude [13] compared on-line SPE–HPLC and SPME–GC with the 100 μm PDMS fiber for the analysis of tetrahydrothiophene, tert-butylmercaptan and *n*-butylmercaptan in water. They consider both techniques well suited to trace analysis of these compounds in water and did not report any artifacts. This is in accordance with the low extent of oxidation of higher mercaptans into disulfides which was observed in our studies. Additionally their work was carried out with a flame ionization detector which is incapable of detecting eventually formed H_2S. None of these papers investigated losses by irreversible adsorption, decomposition and oxidation reactions in more detail or provided identification of the decomposition products.

3.3.2. Influence of humidity

Humidity was shown to cause a significant decrease of the adsorbed amount of MeSH, DMS, i-PrSH and i-BuSH (Fig. 4). Due to the coelution of water interferences in the detection of MeSH are observed at 80% relative humidity (RH), which leads to an increase of the response and drastically reduced repeatability at high relative humidity. The strong dependence of the adsorption behavior of the SPME fiber on the relative humidity of the spiked air sample does not only demand for calibration at the same temperature but also at the same relative humidity for accurate quantitative results or alternatively a correction of the extraction efficiency as a function of the relative humidity has to be applied.

3.3.3. Storage stability

For the application of the method in the field the storage stability of the samples preconcentrated on the fiber is of crucial importance. To investigate the storage stability fibers were sealed with silicone septa immediately after sampling and stored at temperatures between 4 and −23°C. Analyses were carried out after approximately 0.5, 24 and 48 h. The results in Fig. 5 indicate that acceptable storage

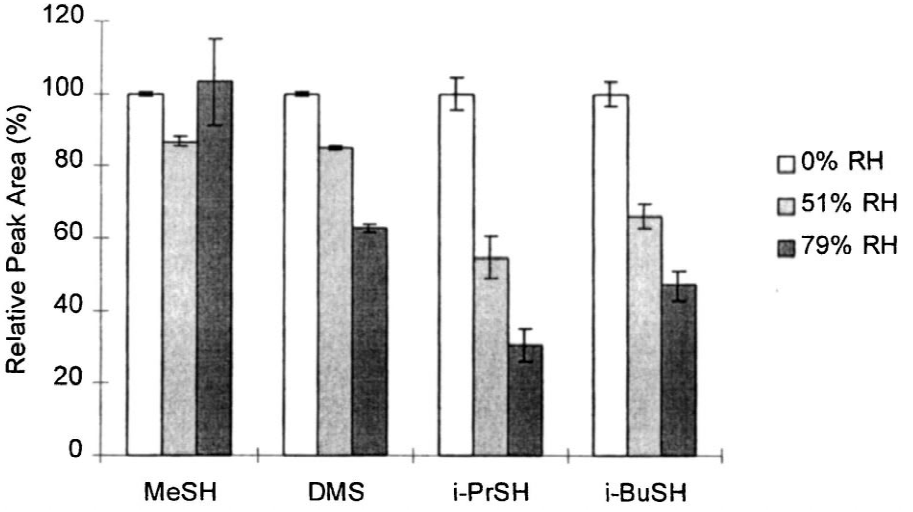

Fig. 4. Influence of the relative humidity on the extraction efficiency (peak areas at 0% RH are set at 100%).

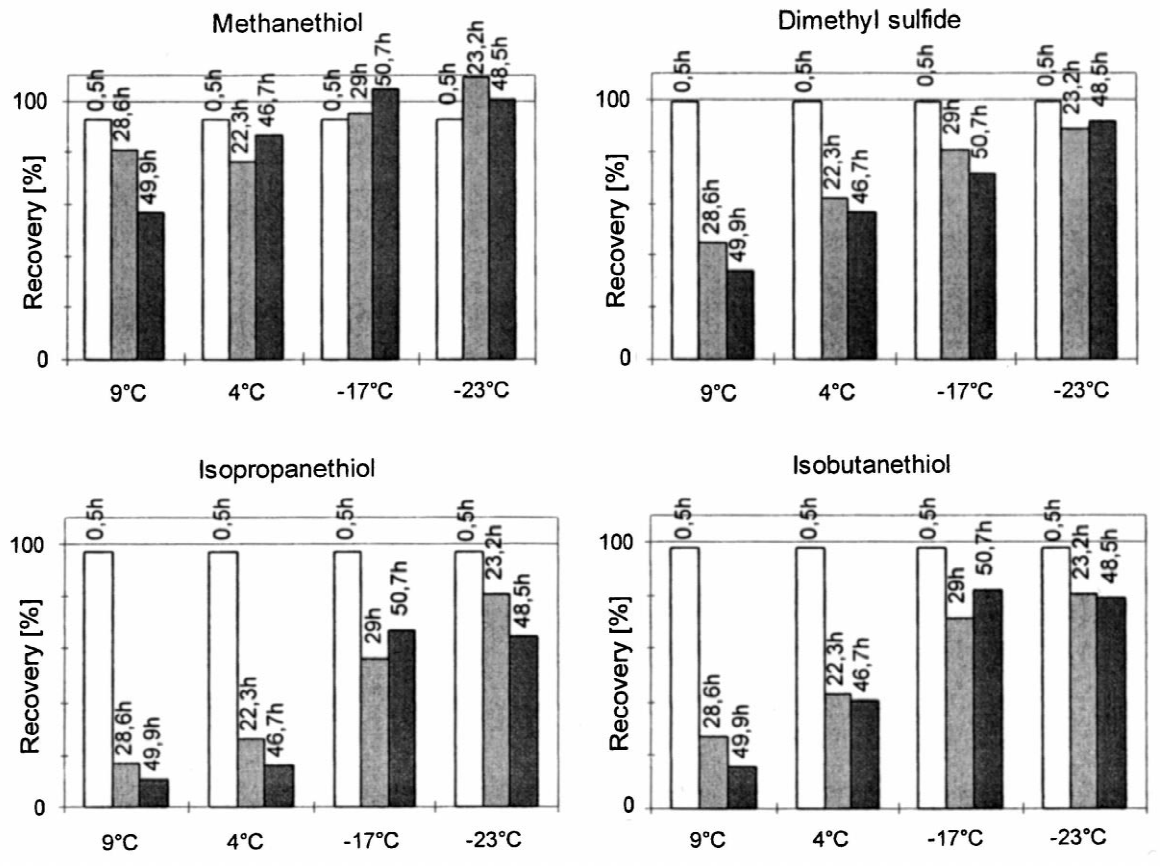

Fig. 5. Influence of the storage time (0.5 h, 1 and 2 days) and temperature on the recovery of the investigated compounds.

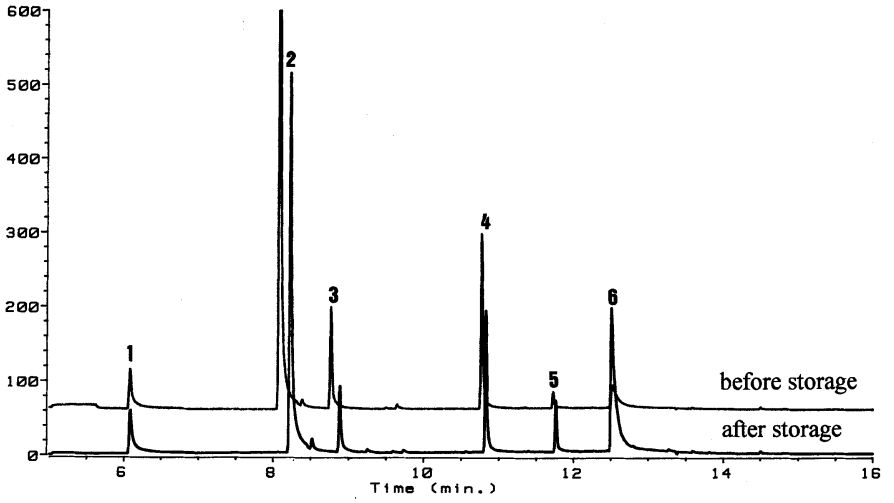

Fig. 6. Chromatograms corresponding to 13 ppb MeSH (1), 17 ppb DMS (2), 5 ppb i-PrSH (3) and 5 ppb i-BuSH (4) obtained (a) by immediate analysis and (b) after a storage time of 50 h at −17°C (additional peaks of decomposition products: DMDS (5), DMSO (6)).

stability is only achieved at low storage temperatures. However even at the lowest temperature investigated (−23°C) significant losses of i-PrSH and i-BuSH were observed. While the peak areas of dimethyl disulfide and dimethylsulfoxide increased with storage time and temperature, the peak areas of the other disulfides were unaffected. The overall increase of the artifacts' peak areas accounts only partially for the overall loss of the analytes. The rest may be attributed to irreversible adsorption, adsorption onto the silicone septa, decomposition or oxidation into highly polar compounds of low volatility which cannot be detected by SPME–GC–AED.

Fig. 6 shows the sulfur selective chromatograms corresponding to 13 ppb MeSH, 17 ppb DMS, 5 ppb i-PrSH and 5 ppb i-BuSH analyzed immediately after sampling and after a storage time of 50 h at −17°C.

4. Conclusion

SPME is considered to be a quick and simple extraction procedure for volatile organic compounds in air. Since the SPME fiber itself acts as a passive sampler no elaborate equipment like for active sampling is needed (e. g. pumps, flow meters, flow controllers...), which makes the technique particularly attractive for field and emergency case sampling. Additionally, drying of the sample is said to be unnecessary due to the hydrophobic nature and the small sample capacity of the fiber coatings. Therefore SPME is propagated for field sampling. According to the presented study, SPME with Carboxen–PDMS fibers is suitable for determining a range of sulfur compounds in spiked air samples, if certain limitations of the method are respected. Being principally well suited for the analysis of volatile sulfur compounds, SPME with Carboxen–PDMS fibers and subsequent analysis by GC–AED leads to severe artifacts for some of the investigated compounds. Methanethiol is readily oxidized to DMDS to a considerable extent, while oxidation of isopropanethiol and isobutanethiol into disulfides and oxidation of dimethyl sulfide into dimethyl sulfoxide is negligible. Therefore the detection of dimethyl disulfide cannot be taken as a proof for its presence in the sample if methanethiol is also observed. Proportional systematic losses of the compounds of up to 89% were observed due to the fibers´ lack of inertness. The use of Carboxen–PDMS fibers for field sampling is complicated by the pronounced dependence of the extraction efficiency on the relative humidity and the low storage stability of the reduced volatile sulfur compounds on the fiber, which leads to the occurrence of decomposition products. Additionally, sensitivity differs significant-

ly between fibers. Therefore calibration has to be carried out not only under the same conditions as sampling (temperature, relative humidity) but also for each fiber separately. This makes quantitative analysis time consuming, thus annulling speed of analysis which is one of the main advantages of SPME in comparison to classical sampling. Nevertheless SPME is well suited for qualitative analysis and enables quick screening for the identification of organosulfur compounds with adverse organoleptic characteristics and for their source apportionment.

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