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Quantification of volatile sulfur compounds in complex gaseous matrices by solid-phase microextraction

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Abstract

Procedures were assessed for quantifying nine volatile sulfur compounds found in complex gaseous samples collected at a biogas-production plant and a sewage treatment plant. The target compounds were extracted by solid-phase microextraction (using the 75-μm Carboxen–polydimethylsiloxane fiber coating) at 22 °C for 20 min, and analyzed by GC–MS. Detection limits ranged between 1 pptv (v/v) for carbon disulfide and 470 pptv (v/v) for hydrogen sulfide. High amounts of organic compounds were found during full-scan analysis of the samples and standard additions to individual sub-samples revealed that the analysis was subject to matrix effects. However, the functions obtained by standard additions were still linear and quantification was possible for all the compounds tested except hydrogen sulfide. No detectable losses were observed during storage in the sampling containers, made of Tedlar film, over a storage period of 20 h. However, water permeated through the walls and the relative humidity in the bag increased during storage until it reached the ambient level. Finally, it was shown that the drying agent, $CaCl_2$, caused no detectable losses of any of the compounds.

Keywords: Matrix effects; Air analysis; Volatile sulfur compounds; Sulfur compounds

1. Introduction

Volatile sulfur compounds (VSCs) are often the source of malodorous fumes at waste dumping sites and at biogas-production and sewage treatment plants. Due to their highly reactive nature, these compounds also cause operational problems by poisoning catalysts and corroding pumps and pipes. Furthermore, VSCs are toxic and may cause health problems, even when present at low concentrations [1]. The analysis of VSCs is complicated by a number of factors. The compounds are often present in low, but wide-ranging concentrations (often spanning several orders of magnitude). Losses may occur during storage and analysis due to irreversible adsorption onto surfaces, rearrangements catalyzed by different materials, reaction with one other and with substances with which they come into contact. Moreover, VSCs are frequently encountered in complex matrices that can cause interference problems and lead to matrix effects [2].

SPME (solid-phase microextraction) has been used for extraction of VSCs in many different matrices like wine [3–5], beer [6], truffles [7] and butter [8]. It has also been used in analysis of sulfur compounds in air [9,10]. The most effective coating for extracting VSCs is the Carboxen–polydimethylsiloxane (CAR–PDMS) fiber coating [4,6,10]. The detection limits of this material are two to three orders of magnitude lower than those of PDMS fiber coating

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[10]. However, CAR–PDMS is a solid coating to which the analytes are adsorbed, and as adsorption sites are limited competitive adsorption and displacement effects may occur. Consequently, the CAR–PDMS fiber is much more sensitive to interfering compounds present in the matrix compared to PDMS and polyacrylate liquid coatings, where the extraction is governed by absorption and this makes quantification with CAR–PDMS particularly challenging [11].

Only a few studies have considered matrix effects during SPME. For example, fuel-related hydrocarbons have been quantified in surface- and wastewater samples using PDMS fiber coatings. Interfering organic substances in the samples disturbed the extraction and therefore, standard addition or deuterated internal standards were used to quantify the samples [12]. Matrix effects were also encountered during an analysis of organophosphorous pesticides in tap-, sea- and wastewater with polyacrylate fibers [13]. In the wastewater, which had a high content of natural organic matter, matrix effects caused losses in the recoveries for some of the target compounds. However, in the seawater there was an overall tendency for recoveries to increase, which was explained by the presence of salts enhancing the absorption of the analytes by the fiber. In an assessment of sulfur compounds, Murray [14] studied the competitive adsorption of methanethiol, methyl sulfide, carbon disulfide and methyl disulfide in gaseous samples with the CAR–PDMS fiber coating. Severe displacement effects were found to occur, whereby analytes with high affinity to the adsorption sites displaced analytes with lower affinity. However, the study was performed at the mg/l level, at which the compounds can easily be directly analyzed without using SPME as a pre-concentration step.

As well as high contents of organic matter, water vapor present in gaseous samples can significantly decrease the yield of target compounds during SPME [10,15]. Therefore, the samples must be dried prior to analysis and possible losses during the drying step must also be considered. When collecting samples, the losses of analytes in the sample container due to irreversible adsorption, oxidation or diffusion through the walls must be taken into account. Sample bags made of Tedlar film are often chosen for sample collection because of their ease of handling, inertness and comparatively low price [16].

In the present work we assessed the quantification procedure for nine volatile sulfur compounds in complex gaseous samples. Factors that could affect the quantification were considered i.e., losses during storage, losses over the drying agent ($CaCl_2$), and matrix effects. The compounds were extracted using SPME in combination with gas chromatography (GC) and mass spectrometry (MS). The target compounds were carbon disulfide (CS_2), carbonyl sulfide (COS), diethyl sulfide (Et_2S), ethylmethyl sulfide (EtSMe), hydrogen sulfide (H_2S), propanethiol (i-PrSH), methanethiol (MeSH), dimethyl disulfide (Me_2S_2) and dimethyl sulfide (Me_2S).

2. Materials and methods

2.1. Chemicals and equipment

H_2S, COS and MeSH were purchased in a gas cylinder containing 100 ppmv (v/v) of each compound in nitrogen (Air Liquide Gas, Sweden). All other compounds were purchased in liquid form: CS_2 (99.9%), Me_2S (99%) and Me_2S_2 (98%) were from Fluka (Sigma–Aldrich, Stockholm, Sweden), while Et_2S (98%), EtSMe (98%) and i-PrSH (98%) were Acros Organics products (Sigma–Aldrich). The pure compounds were stored below 8 °C, except for Me_2S, which was stored at −10 °C and opened in a nitrogen atmosphere to avoid oxidation. The drying agent, granular $CaCl_2$ (0.5–2 mm, >98%), was purchased from Merck Eurolab (Stockholm, Sweden).

To reduce the adsorption of sulfur compounds to interior surfaces, all glass equipment in contact with the sample, e.g., glass bulbs, syringes, liners and glass flasks were silanized using 3.4% dimethyldichlorosilane (Sigma-Aldrich) in toluene according to the manufacturer's instructions. The 75 μm CAR–PDMS fiber coating from Supelco (Sigma-Aldrich) was used for extraction of the target compounds. Relative humidity (RH) in the samples was measured using a digital thermohygrometer.

2.2. Sampling procedure

The samples were collected in 40-l Tedlar sampling bags from SKC (Scantec, Göteborg, Sweden) made of a poly(vinylfluoride) material. The charac-

Table 1
Summary of sample characteristics

Sample name	Sample collected at	Type of sample	Main matrix*	Relative humidity (%)
A	Biogas plant (Linköping Biogas, Linköping, Sweden)	Purified biogas	Methane	2
B	Biogas plant (Linköping Biogas, Linköping, Sweden)	Indoor air sample from the arrival hall	Air	54
C	Sewage treatment plant (Bromma Reningsverk, Stockholm, Sweden)	Outdoor air sample taken during loading of digested sludge	Air	35

*Besides the main matrix, high background levels of volatile organic compounds were present in all samples.

teristics of the samples are presented in Table 1. Three different samples were collected; one of purified biogas and two samples of air from the plants. The RH before drying with $CaCl_2$ was between 2 and 54%. The Tedlar bags were thoroughly flushed three times with nitrogen and before sampling they were flushed twice with the sample. To avoid contamination from earlier samples, a new sampling bag was used for each sample. The air (or biogas) was pumped into the bags using a Capex L2C pump (Charles Austen Pumps, Surrey, UK). During transport and storage, the sampling bags were kept at room temperature and exposure to direct sunlight was avoided. All samples were analyzed within 12 h of sampling.

2.3. Analytical procedure

Extractions were performed in 500-ml glass bulbs Supelco (Sigma-Aldrich) equipped with a half-hole septum. Pre-concentration of the sulfides was accomplished by SPME, in which the target analytes were extracted by inserting the syringe needle through the septum of the sample bulb and then exposing the fiber to the sample. The sample bag was connected to one side of the bulb and the other side was connected to the pump, which had a pumping speed of 114 ml/s. Between the sample bag and the sample bulb, a column filled with the drying agent, granular $CaCl_2$ (138 g, height 28 cm, diameter 2.2 cm), was inserted. PTFE tubing was used for all the connections. The pump was first allowed to create a vacuum in the bulb by keeping the stopcock connected to the sample bag closed. After about 30 s, this stopcock was opened and sample was pumped from the bag and through the sample bulb for 45 s. After filling the sample bulb, the stopcocks were closed and the SPME syringe needle was inserted through the septum and exposed to the sample. The extraction was performed at a temperature of 22 °C and the extraction time was 20 min. The fiber was then withdrawn into the needle and within seconds transferred from the sampling bulb to the injector of the gas chromatograph. The compounds were separated and detected by GC–MS in the selected ion monitoring (SIM) mode. Physical data, retention times and the monitored m/z ratios are summarized in Table 2. The fiber was conditioned for 10 min at 280 °C after each use.

2.4. Losses of sulfur compounds over the drying agent $CaCl_2$

To investigate losses of the target compounds due to passage over the drying agent, the sample bag was filled with nitrogen, and sulfur compounds were added, each to a final concentration of 100 ppbv. The study was performed with samples at two different relative humidities: 0% and 40%. Since SPME can be affected by humidity, gas samples were withdrawn before and after the $CaCl_2$ column and injected directly into the GC system. To enable sampling before the drying agent, a three-way valve was connected to the bag, allowing samples to be withdrawn through a septum in one of the ports. After sampling, the valve was closed, preventing leakage of the compounds from the Tedlar bag. Samples were also withdrawn, after passing over the drying agent, through the septum on top of the 500-ml sample bulb.

Table 2
Physical data, retention times (t_R) and characteristic mass/charge (m/z) ratios of fragments used in the GC–MS-SIM analysis of the investigated compounds

Compound	Molecular formula	Molecular mass	Boiling point (°C)	t_R (min)	m/z
Hydrogen sulfide	H_2S	34.1	−60	4.1	33, **34**, 36
Carbonyl sulfide	COS	60.1	−50	5.2	32, 44, **60**, 62
Methanethiol	CH_3SH	48.1	6	9.4	45, **47**, 48, 50
Dimethyl sulfide	$(CH_3)_2S$	62.1	38	13.4	45, **47**, 62, 64
Carbon disulfide	CS_2	76.1	46	14.2	44, **76**, 78
Propanethiol	$(CH_3)_2CHSH$	76.2	57–60	14.8	27, **43**, 76, 78
Ethylmethyl sulfide	$C_2H_5SCH_3$	76.2	66–67	16.9	48, **61**, 76, 78
Diethyl sulfide	$(C_2H_5)_2S$	90.2	90–92	19.6	47, 75, **90**, 92
Dimethyl disulfide	$(CH_3)_2S_2$	94.2	108–110	20.9	47, **94**, 96

Mass fragments used for quantification are shown in bold.

2.5. Effects of storing sulfur compounds in Tedlar sampling bags

The procedure described for investigating the losses over the drying agent was also used during a stability test of the compounds in the Tedlar bags, whereby five samples were withdrawn through the septum in the three-way valve and analyzed over a storage period of 20 h. Changes in the RH in the sampling bags were monitored by filling the bags with pure nitrogen with a RH of less than 3%. The bags were then stored at the laboratory and the RH inside the bags was measured over time by pumping nitrogen from the sampling bag into a plastic bag where the digital thermohygrometer was inserted.

2.6. GC parameters and mass spectrometric conditions

GC–MS-SIM analyses were performed with a Hewlett-Packard 6890 GC system coupled to a HP 5973 mass spectrometer. Analytes were separated with a 50-m CP-SIL 5 CB column (fused-silica, 0.32 mm I.D., 5 μm film thickness, Chrompack, Sweden). Cryogenic focusing with liquid nitrogen was required to achieve a separation of the compounds with low boiling points. The samples were injected in splitless (1 min) mode and the column temperature program was held at −10 °C for 1 min, then increased by 8 °C/min to 100 °C and, finally, increased by 10 °C/min to 160 °C. The injector temperature was held at 200 °C. For the direct injections, 1 ml was injected splitless (1 min). The carrier gas was helium at a constant flow-rate of 1.3 ml/min. When operated in the full-scan mode, masses between 30 and 300 u were monitored and ionization was carried out in the electron impact (EI) mode. The transfer line temperature was maintained at 280 °C and the ion source temperature was 200 °C. The injector was equipped with a silanized 0.75 mm I.D. liner with deactivated glass wool.

2.7. Quantification

Calibration parameters were established by analyzing a total of ten 500-ml samples with concentrations of 0, 0.5, 5, 20 and 100 ppbv of H_2S, COS and MeSH and 0, 0.1, 1, 10 and 100 ppbv for the remaining compounds. All concentrations were based on volume/volume ratios. Standards were prepared according to Nielsen and Jonsson [17]. Standard addition was performed by three additions of suitable amounts of sulfur compounds (corresponding to 0.1–100 ppbv) to individually prepared sub-samples from the 40-l sample bag. An alternative method was also tested in which standard additions were successively added to the same sample.

2.8. Reproducibility and detection limits

The RSDs were based on repetitive analyses of five individually prepared samples at concentrations of 20 ppbv. The detection limit was defined as a signal-to-noise ratio of 3:1.

Table 3
Limits of detection (LODs) and RSDs, based on repeated analyses of five individually prepared samples at concentrations of 20 ppbv of each compound

Compound	Molecular formula	LOD (pptv)	RSD (%)
Hydrogen sulfide	H_2S	470	9
Carbonyl sulfide	COS	21	6
Methanethiol	CH_3SH	24	5
Dimethyl sulfide	$(CH_3)_2S$	8	2
Carbon disulfide	CS_2	1	2
Propanethiol	$(CH_3)_2CHSH$	15	3
Ethylmethyl sulfide	$C_2H_5SCH_3$	7	6
Diethyl sulfide	$(C_2H_5)_2S$	6	12
Dimethyl disulfide	$(CH_3)_2S_2$	5	8

The compounds were extracted by the 75-μm CAR–PDMS fiber at 22 °C for 20 min.

3. Results and discussion

3.1. RSDs, linearity and detection limits

Table 3 summarizes detection limits and RSDs for the target compounds extracted at 22 °C for 20 min. The detection limits were between 1 pptv for CS_2 and 470 pptv for H_2S and the RSDs ranged between 2 and 12%. The detection limit for H_2S was improved by reducing the extraction temperature. However, a low extraction temperature resulted in poor RSDs for the compounds with higher boiling points (the compounds purchased as liquids) [17]. By increasing the extraction temperature to 22 °C in the present study, the RSDs were improved from 8 to 2, 9 to 2, 10 to 3, 13 to 6, 16 to 12 and 18 to 8% for Me_2S, CS_2, i-PrSH, EtSMe, Et_2S and Me_2S_2, respectively. For all the target compounds, the equilibration is slow and the equilibration times exceeded an hour [17]. Therefore, to achieve low detection limits, a long extraction time was preferred. Moreover, the repeatability is better with longer extraction times, as the relative error is reduced [18]. A shorter extraction time, however, will decrease the amount of analyte trapped on the fiber and thus minimize the effects of competitive adsorption. As a compromise between these conflicting factors, the experiments were carried out at non-equilibrium conditions using a 20 min extraction time.

The response was found to be linear (R^2=0.995–1.000) over three orders of magnitude (0.1–100 ppbv) for all compounds investigated except H_2S during extractions at 22 °C. A comparison of the amounts of H_2S extracted at −15 and 22 °C showed that linearity was obtained for H_2S at an extraction temperature of −15 °C. Consequently, lowering the extraction temperature from 22 to −15 °C improved the conditions for analysis of H_2S by decreasing the detection limit and achieving linearity within a concentration range of 0.1–100 ppbv. However, there was no difference in the RSD, which was 9% at both temperatures. In the present study, all extractions were performed at 22 °C to improve the RSD for the majority of the analytes and H_2S could not therefore be quantified.

3.2. Stability of the compounds over the drying agent $CaCl_2$

At a sample flow-rate of 114 ml/s, the $CaCl_2$ column dried the sample to a RH of less than 3% when filled with 138 g of granular $CaCl_2$. It is possible that a lower amount of $CaCl_2$ is sufficient to dry the sample at these conditions, but this was not tested in the present study. Table 4 shows a comparison of the amount of the target compounds present before and after the drying agent where the areas before have been normalized to 100 and the areas after are expressed as a percentage of these values. Three individual samples were taken before and after the $CaCl_2$, respectively. These are too few observations to perform any statistical analysis to test if there are significant losses. However, taking the standard deviations into account, there are no deviations from the initial value, except for one compound, i-PrSH at 0% RH, which assumes a higher value after the $CaCl_2$. Tangermann [19] stated that powdery $CaCl_2 \cdot 2H_2O$ does not adsorb any sulfur volatiles, but did not mention the affects of humidity. In this study, the comparison was performed at two different relative humidities, 0 and 40%.

3.3. Effect of storing sulfur compounds in Tedlar sampling bags

The RH in the sampling bags was monitored over time and it was found that water permeated through the Tedlar film and into the bags. The RH in the bag increased during storage until it reached the ambient

Table 4
A comparison of the target sulfur compounds before and after passage over the drying agent, $CaCl_2$, at two different initial relative humidities (RHs), 0% and 40%

Compound	Molecular formula	Before $CaCl_2$	After $CaCl_2$ (0% RH)	After $CaCl_2$ (40% RH)
Hydrogen sulfide	H_2S	100±38	88±35	120±19
Carbonyl sulfide	COS	100±12	99±5	87±10
Methanethiol	CH_3SH	100±31	111±10	90±23
Dimethyl sulfide	$(CH_3)_2S$	100±18	105±12	95±21
Carbon disulfide	CS_2	100±11	96±8	88±13
Propanethiol	$(CH_3)_2CHSH$	100±24	122±7	98±33
Ethylmethyl sulfide	$C_2H_5SCH_3$	100±14	104±15	98±24
Diethyl sulfide	$(C_2H_5)_2S$	100±14	109±29	99±20
Dimethyl disulfide	$(CH_3)_2S_2$	100±21	127±47	96±32

Samples of 1 ml were withdrawn before and after the $CaCl_2$ and directly injected into the GC system. The areas obtained before $CaCl_2$ have been normalized to 100.

level (which at the time of the experiment was 30%), after about 8 h. This experiment was repeated several times, both with pure nitrogen and with real samples, with the same results. The RH in the sampling bag reached ambient levels within a few hours of storage. A test of the storage stability of the target compounds in the sampling bags was also performed. No detectable losses were observed over the test period of 20 h (data not shown). This illustrates that water permeates through the poly(vinylfluoride) material, but the target compounds do not seem to be affected.

3.4. Sample characteristics

The selected target compounds were chosen since several analyses of samples collected at biogas-production and sewage-treatment plants have shown that these sulfur compounds were the most commonly encountered. Fig. 1 (left) shows a chromatogram of a full-scan analysis of sample C extracted with the 75-μm CAR–PDMS fiber coating and illustrates the complexity of the sample matrix. Besides sulfur compounds present at various concentrations, the samples contained high amounts of other volatile organic compounds. Fig. 1 (right) shows the SIM chromatogram of the same sample used for quantification of the target sulfur compounds.

3.5. Investigation of matrix effects

The three samples (A, B and C; Table 1) were investigated for matrix effects by standard additions

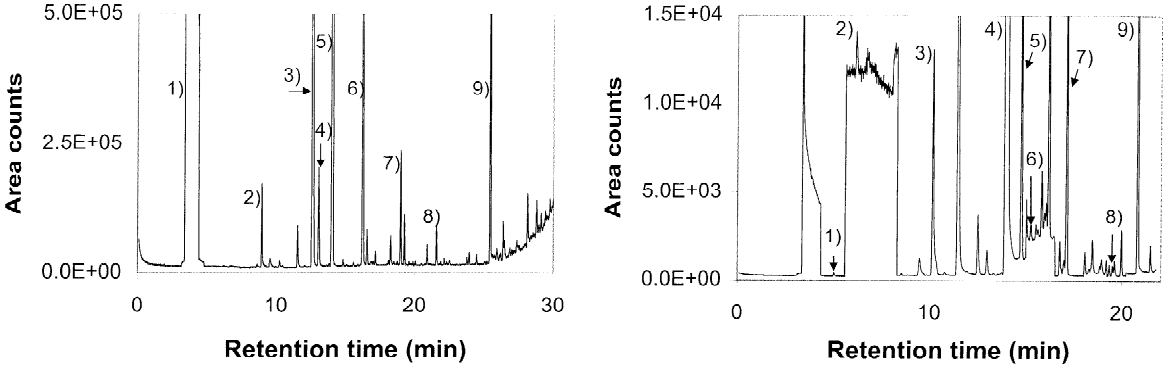

Fig. 1. Left: Illustration of a total ion current full-scan chromatogram from a fiber extraction of sample C. The largest peaks are: (1) oxygen and carbon dioxide, (2) unknown, (3) ethanol, (4) acetone, (5) 2-propanol, (6) dimethyl sulfide, (7) 2-butanone, (8) 2-pentanone and (9) phenol. Right: Illustration of an SIM chromatogram from a fiber extraction of sample C used for quantification. Sulfur compounds present in the sample are: (1) H_2S, (2) COS, (3) MeSH, (4) Me_2S, (5) CS_2, (6) i-PrSH, (7) EtSMe, (8) Et_2S and (9) Me_2S_2.

to individual sub-samples from the 40-l sampling bag. Matrix effects were determined by comparing the slopes of the calibration functions in nitrogen with the slopes obtained by addition of standards within the same concentration range. If the slopes from standard additions were lower, matrix effects had occurred. Comparison of the slopes presented in Table 5 reveals that the CAR–PDMS fiber was affected by matrix effects for all the compounds in samples A and C, probably due to saturation of the coating followed by competitive adsorption by interfering compounds present in the matrix [11]. In sample B, most of the compounds were virtually unaffected and the slopes for COS and MeSH are even steeper than the slopes of the calibration functions. In spite of the complex matrix in the samples, the calibration functions obtained by standard additions corresponding to 0.1–100 ppbv were linear (R^2=0.992–1.000) for all compounds except for H_2S, which could not therefore be quantified due to reasons described earlier. In sample C, the fiber was saturated with Me_2S since even the highest addition (corresponding to 100 ppbv of Me_2S) did not induce an increased response. Quantification of Me_2S was then performed by diluting the sample in nitrogen (1:5000). The dilution suppressed all matrix effects and Me_2S could then be quantified by external calibration. However, all the other sulfur compounds in the sample were present at the sub-ppbv and ppbv levels, for which the pre-concentration step was necessary for analysis. The occurrence of matrix effects in the investigated samples invalidated quantification by external calibration. Furthermore, there are also uncertainties if single (one-point) standard additions are performed, since non-linearities that may be present will not be revealed. A possible way to minimize the matrix effects may be to further shorten the extraction time. This would, however, also increase the detection limits and the relative error of determination.

Successive standard additions to the same sample were tested as an alternative quantification method to avoid the preparation of individual sub-samples. When analyzing real samples, the target compounds are often present in a wide range of concentrations. Additions of individual analytes were not possible in this study and, therefore, when small amounts of the analytes were added, the removal of compounds already present at high concentrations in the sample exceeded the amounts added, leading to nonlinear results. This was due to the high affinity for the target compounds of the CAR–PDMS fiber coating. Therefore, during the experimental conditions described in this study, individual sub-samples had to be prepared to obtain accurate quantifications of the investigated sulfur compounds using standard additions. However, successive standard additions to the same sample might be possible if the sample volume is increased or if the extraction time is decreased, thereby decreasing the relative amount of analytes

Table 5
Comparisons between slopes derived from the calibration functions and standard additions (n=4) to the A, B and C samples (see Table 1)

Compound	Calibration function (N_2)	Sample A		Sample B		Sample C	
		Slope	Concentration (ppbv)	Slope	Concentration (ppbv)	Slope	Concentration (ppbv)
H_2S	1.000±0.043*	0.586*	*	1.096±0.031*	*	0.625±0.084*	*
COS	1.000±0.003	0.421	1.4	1.284±0.012	793	0.813±0.010	8.6
MeSH	1.000±0.028	0.677	n.d.	1.301±0.062	6.4	0.670±0.028	16.3
Me_2S	1.000±0.006	0.573±0.003	0.5	1.024±0.020	16.8	*	820
CS_2	1.000±0.004	0.601±0	0.2	1.010±0.001	4.7	0.578±0.004	2.0
i-PrSH	1.000±0.012	0.535±0.006	n.d.	0.895±0.001	n.d.	0.544±0.005	0.7
EtSMe	1.000±0.002	0.614±0.003	n.d.	0.950±0.003	n.d.	0.548±0.003	2.9
Et_2S	1.000±0.007	0.729±0.003	n.d.	0.940±0.006	n.d.	0.522±0.004	0.1
Me_2S_2	1.000±0.011	0.707±0.006	n.d.	0.882±0.006	42.6	0.490±0.015	5.9

The slopes of the calibration functions in nitrogen have been normalized to 1. The concentrations of the target compounds in the samples are also presented.

* The calibration function was not linear within the investigated concentration range.

n.d.=Non detectable.

removed. Choosing a fiber coating to which the target compounds have a lower affinity would give the same effect, though the detection limits would then be increased.

The concentrations of the target compounds in the three different samples determined by the standard additions to individual sub-samples are presented in Table 5. The compounds were present at a wide concentration range, from non-detectable to 820 ppbv.

4. Conclusions

This study addresses issues involved in the quantification of VSCs in complex gaseous samples collected at a biogas-production facility and a sewage treatment plant. The drying agent $CaCl_2$ was successfully used to dry samples down to an RH of less than 3% without any detectable loss of the sulfur compounds. Moreover, the samples were stable in the Tedlar sampling bags over the storage period, which did not exceed 12 h. However, water permeated through the Tedlar film and into the bags, and within a few hours of storage the RH in the sampling bag reached the ambient level. Matrix effects occurred during the SPME analysis using the 75-μm CAR–PDMS fiber coating. However, quantification was still possible by using the standard addition procedure and the obtained functions were linear over three orders of magnitude.

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