

Improvement of HS-SPME for analysis of volatile organic compounds (VOC) in water samples by simultaneous direct fiber cooling and freezing of analyte solution

Elke Fries · Wilhelm Püttmann

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Abstract The sensitivity and precision of headspace solid-phase micro extraction (HS-SPME) at an analyte solution temperature (T_{as}) of +35 °C and a fiber temperature (T_{fiber}) of +5 °C were compared with those for HS-SPME at T_{as} and T_{fiber} of –20 °C for analysis of the volatile organic compounds benzene, 1,1,1-trichloroethane, trichloroethylene, toluene, *o*-xylene, ethylbenzene, *m/p*-xylene, and tetrachloroethylene in water samples. The effect of simultaneous fiber cooling and analyte solution freezing during extraction was studied. The compounds are of different hydrophobicity, with octanol/water partition coefficients (K_{ow}) ranging from 126 and 2511. During a first set of experiments the polydimethylsiloxane (PDMS) SPME fiber was cooled to +5 °C with simultaneous heating of the aqueous analyte solution to +35 °C. During a second set of experiments, both SPME fiber holder and samples were placed in a deep freezer maintained at –20 °C for a total extraction time of 30 min. After approximately 2 min the analyte solution in the vial began to freeze from the side inwards and from the bottom upwards. After approximately 30 min the solution was completely frozen. Analysis of VOC was performed by coupling HS-SPME to gas chromatography-mass spectrometry (GC-MS). In general, i.e. except for tetrachloroethylene, the sensitivity of HS-SPME increased with increasing compound hydrophobicity at both analyte solution and fiber temperatures. At T_{as} of +35 °C and T_{fiber} of +5 °C detection limits of HS-SPME

were 0.5 $\mu\text{g L}^{-1}$ for benzene, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, 0.125 $\mu\text{g L}^{-1}$ for toluene, and 0.025 $\mu\text{g L}^{-1}$ for ethylbenzene, *m/p*-xylene, and *o*-xylene. In the experiments with T_{as} and T_{fiber} of –20 °C, detection limits were reduced for compounds of low hydrophobicity ($K_{\text{ow}} < 501$), for example benzene, toluene, 1,1,1-trichloroethane, and trichloroethylene. In the concentration range 0.5–62.5 $\mu\text{g L}^{-1}$, the sensitivity of HS-SPME was enhanced by a factor of approximately two for all compounds by performing the extraction at –20 °C. A possible explanation is that freezing of the water sample results in higher concentration of the target compounds in the residual liquid phase and gas phase (freezing-out), combined with enhanced adsorption of the compounds by the cooled fiber. The precision of HS-SPME, expressed as the relative standard deviation and the linearity of the regression lines, is increased for more hydrophobic compounds ($K_{\text{ow}} > 501$) by simultaneous direct fiber cooling and freezing of analyte solution. Background contamination during analysis is reduced significantly by avoiding the use of organic solvents.

Keywords HS-SPME · VOC · Freezing-out · Volatile organic compounds · Water samples

E. Fries (✉) · W. Püttmann
Institut für Atmosphäre und Umwelt,
J.W. Goethe-Universität Frankfurt am Main,
Georg-Voigt-Str. 14,
60325 Frankfurt am Main, Germany
e-mail: E.Fries@kristall.uni-frankfurt.de

Introduction

Volatile organic compounds (VOC) such as ethylbenzene, *m/p*-xylene, *o*-xylene and 1,2,4-trimethylbenzene have been detected in rain and snow in a wide range of concentrations

(low ppt to low ppb) [1–3]. For analysis of these compounds in small volumes of airborne droplets and ice crystals a highly sensitive analytical method is required. High vapor pressures of VOC and their ubiquitous occurrence in ambient air increase the risk of background contamination during analysis, and a highly precise analytical method is required [4, 5]. At the beginning of the last decade Arthur and Pawliszyn [6] introduced a new solvent-free method termed solid-phase micro extraction (SPME) to enrich VOC from low-volume water samples. With the SPME method, analytes are directly adsorbed from the water phase or, after transport of the analytes through the air barrier, from the headspace (HS-SPME) on to a fused-silica fiber coated with a polymer [7]. The processes responsible for analyte adsorption depend on the fiber coatings. The fiber distribution coefficients (K_f) can be estimated from octanol/water partition coefficients (K_{ow}) for compounds of medium and high hydrophobicity [8, 9]. Extraction times in HS-SPME are lower than for other extraction methods, for example solid-phase extraction (SPE) or liquid-liquid extraction (LLE); the method also prevents a substantial amount of moisture from reaching the GC column [10]. Heating the sample matrix while simultaneously cooling the fiber facilitates mass transfer and release of analytes into the headspace and creates a temperature gap between the cold fiber coating and the hot analyte solution; this significantly increases the partition coefficients of analytes to the cold fiber coating [11, 12]. SPME has been coupled successfully with gas chromatography (GC) with flame-ionization detection (FID) or electron-capture detection (ECD) for analysis of VOC [6, 8]. The detection limits of these techniques vary between approximately 0.1 and 1.0 $\mu\text{g L}^{-1}$. By coupling SPME with gas chromatography-mass spectrometry (GC-MS), detection limits are reduced substantially to the lower ppt range, depending on the type of analyte [4, 12, 13].

In this study, the effect on HS-SPME of simultaneous direct fiber cooling and freezing of the analyte solution was studied. First, the analyte solution temperature was kept at +35 °C and the polydimethylsiloxane (PDMS) fiber was cooled simultaneously to +5 °C as reported by Achten et al. [5]. Second, analyte solution and fiber temperature were maintained at -20 °C. Special attention was paid to the effect of freezing-out on method sensitivity and precision for the analysis of VOC of different hydrophobicity in aqueous samples. The compounds investigated were 1,1,1-trichloroethane, benzene, trichloroethylene, toluene, ethylbenzene, xylenes, and tetrachloroethylene. The octanol/water partition coefficients (K_{ow}) of those compounds varied from 126 to 2511. Extraction yields obtained with both methods were compared for different concentrations of the analytes.

Experimental

Chemicals and sample preparation

1-Bromo-2-chloroethane, benzene, toluene, ethylbenzene, *m/p*-xylene, *o*-xylene, 1,1,1-trichloroethane, tetrachloroethylene, and trichloroethylene were purchased from Sigma-Aldrich at 99% purity and used as received. All standards were dissolved in deionized ultra pure water (Seralpur Pro90CS). Stock solutions (200 mg L^{-1}) of 1-bromo-2-chloroethane, used as internal standard (IS), were prepared in methanol and deionized water. Working standard solutions of a mixture of all the compounds were prepared at concentrations of 200, 100, 50, 20, 2, 0.4, 0.2, 0.02, and 0.01 mg L^{-1} . All standard solutions were stirred in an ultrasonic bath for 15 min and stored at +4 °C for a maximum of four weeks. To keep the background contamination to a minimum, 10-mL vials were thoroughly rinsed twice with ethanol and purified water and heated for 12 h at 200 °C. Subsequently, vials were rinsed and refilled with argon gas (4.6) to purge laboratory air. Vials were sealed with polystyrene caps provided with small holes matching the external diameter of the syringe needle of the fiber holder. The caps were equipped with 20 mm, 1-inch-thick silicone rubber bonded to aluminium barrier septa (Supelco). Septa and vials were not reused. Purified water (4 mL) was spiked with 5 μL of IS solution and with 5 μL of each working standard solution. The resulting concentrations of the test solutions were 250, 125, 62.5, 25, 2.5, 0.5, 0.25, 0.025, and 0.0125 $\mu\text{g L}^{-1}$. RSD values were determined by analyzing the same solution six times during a single day. Twelve samples of deionized water were prepared for measuring background contamination from solvent use. Six blank samples were spiked with IS dissolved in methanol and six additional blank samples were spiked with IS dissolved in water. Six empty vials were prepared using the SOP to study background contamination from laboratory air.

HS-SPME

The HS-SPME apparatus consisted of a 100- μm PDMS coating on a 1-cm fiber mounted on the syringe needle of the fiber holder (Supelco). Before starting the extraction the fiber was withdrawn into the needle of the syringe and the needle was used to penetrate the septum of the sealed vials. The fiber was then introduced into the headspace of the analyzed sample by depressing the plunger. In a first series of experiments the temperature of the analyte solution was kept constant at +35 °C by placing the vial in a water bath filled with 3 cm water. The sample holder was connected to a cryostat maintained at +5 °C as reported by Achten et al. [5]. Samples were stirred at 890–900 rev min^{-1} during

analysis. In a second series of experiments extraction was performed by placing the SPME holder and the samples in a freezer maintained at $-20\text{ }^{\circ}\text{C}$. After approximately 2 min ice formed from the sides inwards and from the bottom upwards. After approximately 30 min the solution was completely frozen. All background contamination studies were performed by the latter extraction method.

GC-MS

Once adsorbed, VOCs were thermally desorbed from the fiber coating by inserting the fiber immediately into the GC injector kept at $260\text{ }^{\circ}\text{C}$. Splitless injection was used and the fiber remained in the injector for 10 min. After this reconditioning time all compounds had been removed from the fiber. The GC (Thermoquest CE Instruments Trace GC2000 Series) was equipped with a 60-m DB-624 capillary column (Agilent Technologies) with an ID of 0.32 mm and a film thickness of $1.8\text{ }\mu\text{m}$. Helium served as the carrier gas. The column flow was set at 1 mL min^{-1} . The GC oven temperature was maintained at $50\text{ }^{\circ}\text{C}$ for 2 min then programmed at $10^{\circ}\text{ min}^{-1}$ to $190\text{ }^{\circ}\text{C}$ which was held for 20 min. Data acquisition, processing, and instrument control were performed by using Excalibur software (Thermoquest). Detection of the analytes was accomplished by use of a Thermoquest Finnigan Voyager MS in the electron-impact ionization, positive-ion, full-scan mode (scan range 50–600). To reduce the number of simultaneously monitored m/z ratios, we used different m/z windows of the compound-specific ions given in Table 1: 1,1,1-trichloroethane, $m/z=97$; benzene, $m/z=78$, trichloroethylene, $m/z=166$; toluene, tetrachloroethylene, $m/z=95$; ethylbenzene, m/p -xylene, o -xylene, $m/z=91$. To relate the peak intensity of the compound-specific ions (A_{SIC}) to the total ion intensity (A_{TIC}), a correction factor C must be introduced, where:

$$C = A_{\text{TIC}}/A_{\text{SIC}}$$

Values of C for all the compounds (listed in Table 1) were: 5.3 for 1,1,1-trichloroethane, 2.0 for benzene, 5.3 for 1,1,1-trichloroethane, 5.5 for trichloroethylene, 2.0 for toluene, 2.0 for o -xylene, 3.0 for ethylbenzene, 3.0 for m/p -xylene, and 6.0 for tetrachloroethylene. Detection limits were defined at a signal-to-noise ratio of 10:1. Calibration plots were obtained by dividing the peak areas of the compounds by the peak area of the IS and plotting this ratio against the concentration of the solution.

Results and discussion

Table 1 shows molecular weights (MW), octanol/water partition coefficients (K_{ow}), water solubility (S), vapor pressures (P), and Henry's Law constants (H). Such physical and chemical properties determine compound distribution between the gas phase, water phase, and the fiber coating. In Table 2, detection limits obtained for HS-SPME at an analyte solution temperature (T_{as}) of $+35\text{ }^{\circ}\text{C}$ and a fiber temperature (T_{fiber}) of $+5\text{ }^{\circ}\text{C}$ are compared with detection limits for HS-SPME at T_{as} and T_{fiber} of $-20\text{ }^{\circ}\text{C}$. HS-SPME-GC-MS detection limits for both HS-SPME methods varied from $0.025\text{--}0.5\text{ }\mu\text{g L}^{-1}$ for all compounds. Detection limits of HS-SPME decreased for both methods with increasing hydrophobicity of the compounds, except for tetrachloroethylene. Detection limits for HS-SPME at T_{as} of $+35\text{ }^{\circ}\text{C}$ and T_{fiber} of $+5\text{ }^{\circ}\text{C}$ were $0.5\text{ }\mu\text{g L}^{-1}$ for benzene, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene, $0.125\text{ }\mu\text{g L}^{-1}$ for toluene, and $0.025\text{ }\mu\text{g L}^{-1}$ for ethylbenzene and xylenes. Detection limits were reduced for compounds of low hydrophobicity ($K_{\text{ow}} < 501$), e.g. benzene, toluene, 1,1,1-trichloroethane, trichloroethylene, by keeping T_{as} and T_{fiber} at $-20\text{ }^{\circ}\text{C}$. Lower detection limits are indicative of better sensitivity of HS-SPME if the analyte solution and fiber temperatures are $-20\text{ }^{\circ}\text{C}$. One possible explanation is the effect of direct fiber cooling, because of better adsorption of the compounds on the fiber coating. The positive effect of a fiber cooling on sensitivity has already

Table 1 Quantification ions (m/z) used in GC-MS analysis, correction factors (C), molecular weights (MW), octanol/water partitioning coefficients (K_{ow}), water solubility (S), vapor pressures (P), and Henry's Law constants (H) of selected volatile organic compounds

	m/z	C	MW (g mol^{-1})	K_{ow}	S (mg L^{-1})	P (kPa)	H (at $25\text{ }^{\circ}\text{C}$)
Benzene	78	2.0	78	126	1780	12.6	0.22
1,1,1-Trichloroethane	97	5.3	167	158	2870	1.8	0.04
Trichloroethylene	95	5.5	131	251	1280	9.2	0.40
Toluene	91	2.0	92	501	526	3.8	0.27
o -Xylene	91	2.0	106	1259	178	0.9	0.21
Ethylbenzene	91	3.0	106	1585	169	1.3	0.32
m/p -Xylene	91	3.0	106	1585	161	1.1	0.29
Tetrachloroethylene	166	6.0	166	2511	206	2.5	0.72

been reported by Zhang and Pawliszyn [11] and Achten et al. [12]. Cooling the fiber increased the partition coefficient of the analytes to the cold fiber coating. Improvement of the sensitivity of HS-SPME by heating the sample, because of greater mass transfer and better release of the analytes into the headspace, has also been described [11, 12]. Heating the sample to an elevated temperature provides energy for analyte molecules to overcome the energy barriers which bind them to the matrix [14], enhances the mass-transfer process, and increases the vapor pressure of the analytes [15]. At temperatures between 3 and 25 °C the air-water partition coefficient (Henry's law constant, H) for methyl *tert*-butyl ether (MTBE) increases with increasing temperature [16]. H decreases by a factor of approximately two for every decrease in temperature of 10° [1]. The results of our study reveal that the sensitivity of HS-SPME for VOC is also enhanced by performing the extraction at T_{as} and T_{fiber} of -20 °C. The concentration of a compound in the headspace should be lower at -20 °C than at $+35$ °C, however, according to Henry's law. A possible explanation of the higher extraction yield of HS-SPME at T_{as} and T_{fiber} of -20 °C is transfer of the analytes from the solution to the gas phase during freezing. This process has been described previously as a "freezing-out effect" [17]. As the ice formed from the sides inwards and from the bottom upwards, the author observed concentration of the solutes in the central liquid. Freezing-out is widely used industrially to separate impurities from aqueous solutions or organic liquids [18, 19]. Pfann [20] observed inhomogeneous solute distribution after freezing. This effect has not yet been discussed in the context of HS-SPME analysis of traces of organic compounds in aqueous solutions, however. Our results could be explained by concentration of analytes during freezing in the residual unfrozen solution followed by enhanced evaporation of the compounds into the gas phase. Exclusion of a solute from the ice sets up a concentration gradient in the remaining solution which drives solute transfer away from the

Fig. 1 Calibration plots for HS-SPME-GC-MS at analyte solution temperature (T_{as}) of $+35$ °C and fiber temperature (T_{fiber}) of $+5$ °C (*open squares*) and at T_{as} and T_{fiber} of -20 °C (*filled squares*) for selected volatile organic compounds (deionized water with concentrations between 0.5 and 250 $\mu\text{g L}^{-1}$ for each analyte, three replicates)

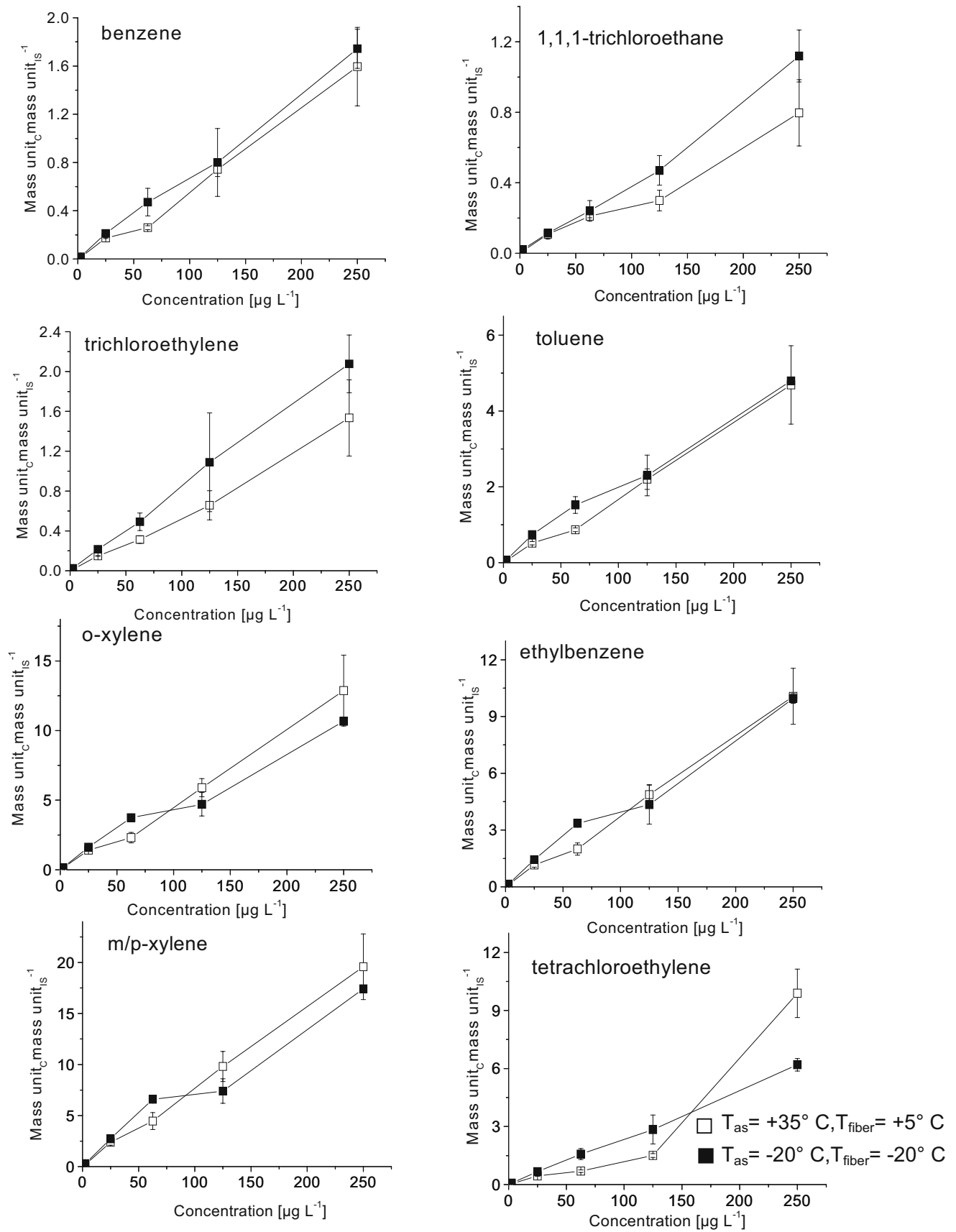
solid-liquid interface into the gas phase [21]. Sato [22] observed that acetate evaporated to the gas phase when an aqueous solution was frozen starting from the bottom of the solution. Jayne et al. [23] observed a negative dependence of the surface accommodation coefficients of C_1 to C_4 alcohols on the temperature of supercooled liquid water droplets.

In Fig. 1, HS-SPME calibration plots obtained at T_{as} of $+35$ °C and T_{fiber} of $+5$ °C are compared with plots obtained at T_{as} and T_{fiber} of -20 °C. For all compounds, the sensitivity of HS-SPME at T_{as} and T_{fiber} of -20 °C is greater than the respective values at T_{as} of $+35$ °C and T_{fiber} of $+5$ °C, as is apparent from the greater slopes of the calibration plots for concentrations between 0.5 and 62.5 $\mu\text{g L}^{-1}$. At higher concentrations, 100–250 $\mu\text{g L}^{-1}$, sensitivity of HS-SPME at T_{as} and T_{fiber} of -20 °C was higher for benzene, 1,1,1-trichloroethane, and trichloroethylene. Again, the greater extraction yields can be explained by the positive effect of simultaneous direct fiber cooling and solution freezing at -20 °C on HS-SPME sensitivity.

Correlation coefficients, R , for the calibration plots obtained for HS-SPME at T_{as} of $+35$ °C and T_{fiber} of $+5$ °C and for HS-SPME at T_{as} and T_{fiber} of -20 °C are shown in Table 2. Calibration plots were linear for all compounds. Higher R values were obtained for HS-SPME at T_{as} and T_{fiber} of -20 °C for toluene, ethylbenzene, *m/p*-xylene, and tetrachloroethylene. For those compounds, quantification by external-standard calibration is improved by simulta-

Table 2 Detection limits (DL), correlation coefficients (R), relative standard deviations (RSD) at 0.5 $\mu\text{g L}^{-1}$, and blank values for HS-SPME at an analyte solution temperature (T_{as}) of $+35$ °C and a fiber temperature (T_{fiber}) of $+5$ °C, and for T_{as} and T_{fiber} of -20 °C

	DL ($\mu\text{g/L}^{-1}$)		R		RSD at 0.5 $\mu\text{g L}^{-1}$ (%)		Blank IS _{methanol} / IS _{water} ($\mu\text{g L}^{-1}$)
	T_{as} $+35$ °C, T_{fiber} $+5$ °C	T_{as} -20 °C, T_{fiber} -20 °C	T_{as} $+35$ °C, T_{fiber} $+5$ °C	T_{as} -20 °C, T_{fiber} -20 °C	T_{as} $+35$ °C, T_{fiber} $+5$ °C	T_{as} -20 °C, T_{fiber} -20 °C	
Benzene	0.500	0.125	0.995	0.977	12	15	0.5/0.5
1,1,1-Trichloroethane	0.500	0.125	0.998	0.991	18	22	-/-
Trichloroethylene	0.500	0.125	0.999	0.997	15	18	0.7/-
Toluene	0.125	0.025	0.983	0.984	6	6	2.7/0.3
<i>o</i> -Xylene	0.025	0.025	0.992	0.982	9	5	0.4/0.1
Ethylbenzene	0.025	0.025	0.989	0.993	4	1	1.3/0.5
<i>m/p</i> -Xylene	0.025	0.025	0.994	0.996	7	1	0.1/0.1
Tetrachloroethylene	0.500	0.500	0.973	0.999	4	2	1.4/-



neous direct fiber cooling and solution freezing at $-20\text{ }^{\circ}\text{C}$, because of more constant equilibrium conditions in a very cold environment.

Relative standard deviations (RSD) for HS-SPME-GC-MS at $0.5\text{ }\mu\text{g L}^{-1}$ are shown in Table 2. Values of RSD varied between 1 and 22% for all compounds and decreased with increasing compound hydrophobicity. Reproducibility of HS-SPME improves with increasing compound hydrophobicity. RSD values for ethylbenzene, xylenes, and tetrachloroethylene ($K_{ow}>1259$) varied between 4 and 9% for HS-SPME at T_{as} of $+35\text{ }^{\circ}\text{C}$ and T_{fiber} of $+5\text{ }^{\circ}\text{C}$. For HS-SPME at T_{as} and T_{fiber} of $-20\text{ }^{\circ}\text{C}$, RSD values for those compounds decreased to 1–5%. For toluene ($K_{ow}=501$), a similar RSD value of 6% was obtained for both HS-SPME methods. RSD values for benzene, 1,1,1-trichloroethane, and trichloroethylene ($K_{ow}<251$) were lower for HS-SPME at T_{as} of $+35\text{ }^{\circ}\text{C}$ and T_{fiber} of $+5\text{ }^{\circ}\text{C}$ (12–18%) and higher at T_{as} and T_{fiber} of $-20\text{ }^{\circ}\text{C}$ (15–22%). Our results reveal that simultaneous direct fiber cooling and freezing of the analyte solution improves precision of HS-SPME for more hydrophobic VOC with $K_{ow}>1259$. For compounds with lower values of K_{ow} , however, precision deteriorates slightly when the fiber is cooled and the aqueous analyte solution is frozen.

Background concentrations of all the analytes in the blank samples are also listed in Table 2. Because highly volatile compounds are ubiquitous in laboratory air, background contamination of VOC must be carefully checked. Use of an internal standard dissolved in methanol is an additional source of contamination. When the fiber was desorbed in the GC injector after a reconditioning time of 10 min no background concentration is detected. Background contamination during HS-SPME was determined by extracting empty vials and deionized water samples spiked with IS dissolved in methanol and in deionized water. All the compounds were detected above their detection limits in vials without water samples with the exception of 1,1,1-trichloroethane reflecting background contamination from laboratory air. Blank values in water samples spiked with IS dissolved in methanol varied between 0.1 and $2.7\text{ }\mu\text{g L}^{-1}$. The highest concentration was detected for toluene, which is frequently used as an organic solvent. Dissolving the IS in deionized water reduced background contamination for all compounds. For trichloroethylene and tetrachloroethylene, background contamination is completely removed when the internal standard solution is prepared without methanol as solvent. These results indicate that avoiding the use of organic solvents when preparing internal standard solutions which are to be added to the analyte solutions leads to reduction of the risk of background contamination by a factor of approximately 10. RSD values for background concentrations were 4–30% when the IS was dissolved in methanol. These values are

slightly higher than those reported by Schimming et al. [4] for benzene, toluene, ethylbenzene, and xylenes. Achten et al. [5] reported an RSD of 9% for MTBE.

Conclusions

The effect of cooling the PDMS fiber concomitant with freezing of the analyte solution at a temperature of $-20\text{ }^{\circ}\text{C}$ on the sensitivity and precision of HS-SPME for determination of different VOC in aqueous samples was studied. The analytical approach was to perform HS-SPME in a deep freezer using an extraction time of 30 min. For a wide concentration range the sensitivity of the method was improved for all the compounds tested by performing the extraction at $-20\text{ }^{\circ}\text{C}$, because of better adsorption by the cooled fiber and enhanced evaporation of the analytes during freezing of the water phase (freezing out-effect). This effect is shown to be more important for compounds of lower hydrophobicity. The concentrations of the analytes must increase in the gas phase and in the residual liquid phase, assuming they are not incorporated into the ice phase generated during freezing of the solution. The application of HS-SPME based on the freezing-out effect will be used in future work to determine chemical retention coefficients of a variety of VOC during freezing of hydrometeors to provide data for atmospheric chemical transport models.

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