

Analysis of benzene, toluene, ethylbenzene, xylenes and *n*-aldehydes in melted snow water via solid-phase dynamic extraction combined with gas chromatography/mass spectrometry

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Abstract

The present study describes a method based on headspace-solid-phase dynamic extraction (HS-SPDE) followed by GC/MS for the qualitative and quantitative analysis of benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene (BTEX), and *n*-aldehydes (C₆–C₁₀) in water. To enhance the extraction capability of the HS-SPDE a new cooling device was tested that controls the temperature of the SPDE needle during extraction. Extraction and desorption parameters such as the number of extraction cycles, extraction temperature, desorption volume and desorption flow rate have been optimized. Detection limits for BTEX ranged from 19 ng/L (benzene) to 30 ng/L (*m/p*-xylene), while those for *n*-aldehydes ranged from 21 ng/L (*n*-heptanal) to 63 ng/L (*n*-hexanal). At a concentration level of 2 µg/L, the relative standard deviations (RSDs) for BTEX ranged from 3.9% (benzene) to 15.3% (ethylbenzene), while RSDs for *n*-aldehydes were between 6.1% (*n*-octanal) and 16.5% (*n*-hexanal) (*n* = 7). Best results were obtained when the analyzed water samples were heated to 50 °C. At a water temperature of 70 °C GC responses decreased for all analyzed compounds. At a defined water temperature, a significant improvement of the GC response was achieved by cooling of the SPDE fiber during water extraction in comparison to an extraction keeping the fiber at room temperature. Evaluating the extraction cycles, for BTEX, the sensitivity was almost similar using 20, 40 and 60 extraction cycles. In contrast, the highest GC responses for *n*-aldehydes were achieved by the use of 60 extraction cycles. Optimizing the desorption parameters, best results were achieved using the smallest technical available desorption volume of 500 µL and the highest technical desorption flow rate of 50 µL/s. The method was applied to the analysis of melted snow samples taken from the Jungfrauoch, Switzerland (3580 m asl), revealing the presence of BTEX and aldehydes in snow.

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1. Introduction

Gaseous volatile organic compounds (VOCs) in the atmosphere play an important role in many atmospheric processes, including photochemical reactions, scavenging via precipitation, and sorption on aerosol particles. Various studies have described the potential for snow to scavenge gaseous and particle-bound organic contaminants from the atmosphere [1–5]. Czuczwa et al. [6] detected a large variation in VOC concentrations within snow samples collected from an urban site

in Switzerland. VOCs have also been detected in snow from Antarctica [7] and the Arctic [8]. A number of studies have focused on the presence of VOCs in snow from high-altitude research stations. For example, Fries et al. [9] reported the presence of VOCs in snow at the high-altitude research station Jungfrauoch (3580 m asl) in Switzerland, with median concentrations of benzene and alkylated benzenes between 36 ng/L for *o*-xylene and 260 ng/L for toluene in 2005, and between 34 ng/L for *o*-xylene and 364 ng/L for toluene in 2006. Gröllert and Puxbaum [10] detected aldehyde compounds in snow samples from Mount Sonnblick (3106 m asl) with median concentrations for *n*-decanal of 0.5 ng/L (1996, 1997) and *n*-nonanal of 142 ng/L (1996).

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Among VOCs, benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene (BTEX), and *n*-aldehydes (C₆–C₁₀) were commonly detected as prominent constituents in the atmosphere. BTEX get into the atmosphere mainly via the production and combustion of gasoline, as emissions from motor vehicles and solvents [11]. *n*-Aldehydes (C₅–C₁₁) are ubiquitously present in the atmosphere of urban areas and remote sites in Japan, with *n*-nonanal being the dominant compound [12]. In the atmosphere, combustion residues are the main sources of *n*-aldehydes, whereas *n*-aldehydes in aquatic environments can originate from the photodegradation of dissolved natural organic matter and those in the biosphere can originate from the biological oxidation of lipids [13]. *n*-Aldehydes have also been identified as the major products of gas phase reactions involving the reaction of oleic acid (*n*-nonanal) and linoleic acid (2-nonanal, 4-nonanal, *n*-hexanal) with ozone. Oleic and linoleic acid are the prevalent soluble organic components of marine and urban organic aerosols [14].

Several methods are available to determine BTEX and *n*-aldehyde levels in aqueous matrices. The most commonly used methods are purge and trap [15] and solid-phase micro extraction (SPME). Using SPME, analytes can be sampled via direct immersion in water [8,16,17] or from the headspace of the sample [8,13,16,18]. The sensitivity of the two methods is similar for a wide range of VOCs, whereas shorter equilibration times favour headspace sampling [16]. Liquid-liquid extraction (LLE) techniques are rarely used today due to the high demand of organic solvents and potentially poor recovery of solutes [10]. For a general review of sample preparation for the analysis of VOCs in air and water, see Demeestere et al. [19].

SPME, developed by Arthur and Pawliszyn [20], is an efficient method for analyzing various VOCs in water samples. Attempts to overcome some drawbacks involved in SPME have included the application of an immobilized coating on the inner wall of a needle [21], the use of a capillary as the extraction phase [22], or the packing of sorbent materials for extraction [23]. Solid-phase dynamic extraction (SPDE) is a further development of SPME. The advantage of SPDE over SPME is the increased volume of sorption material. In using SPDE, the sorption material is coated in the steel needle of a syringe. A dynamical extraction is performed from the headspace above an aqueous matrix by the aspiration and release of the syringe volume. Desorption is carried out directly in the GC-injector, similar to SPME.

Some reports have described systematic investigations of extraction parameters and applications of SPDE. SPDE has been applied in the analysis of chlorinated pesticides in water [24], ethers and alcohols in water [25], volatile flavors in plants and food [26], and cannabinoids, amphetamines and synthetic designer drugs in hair samples [27–29]. Ridgway et al. [30] reported the SPDE analysis of furans, benzene and toluene in water with a polydimethylsiloxane (PDMS) needle coating as a method comparison between HS-SPDE-GC/MS and liquid-SPDE-GC/MS (direct sampling mode).

Recently, HS-SPDE-GC/MS has been developed for the analysis of chlorinated solvents, bromoform and benzene in ground water, with detection limits ranging from 13 ng/L (benzene) to

176 ng/L (chloroform) [31]. This earlier study did not use a cooling device for the extraction needle. In the present paper, the analysis of BTEX and aldehydes (C₆–C₁₀) in melted snow water based on HS-SPDE-GC/MS and using a cooling device for the needle during extraction is reported. Extraction and desorption parameters were optimized. The method was applied to melted snow samples collected from the Jungfrauoch (3580 m asl) in Switzerland during the field campaign CLACE 5 (CLOUD and Aerosol Characterization Experiment) in spring 2006.

2. Experimental

2.1. Chemicals and reagents

The three following stock solutions (100 mg/L) were prepared by dissolving the standards in methanol: benzene, toluene, ethylbenzene, and xylenes (standard solution 1); *n*-hexanal, *n*-heptanal, *n*-octanal, *n*-nonanal and *n*-decanal (standard solution 2); and fluorobenzene and 1-bromo-2-chloroethane (standard solution 3). The latter was used as an internal standard (IS). All of the standards were purchased from Neochema (Bodenheim, Germany). Working standards were produced as follows. Stock solutions were diluted with ultra pure water from a “Seralpur Pro 90c” water purification system (Elga, Germany) to concentration levels of 0.1–2 mg/L. These standard solutions were then stored in a refrigerator at +4 °C and renewed monthly. From these working standards, lower-concentration standard solutions of 0.1, 0.5, 1.0, 1.5 and 2.0 µg/L were prepared directly in screw-sealed vials with PTFE/silicon septa for calibration and determination of the detection limit (DL). Vials and septa were purchased from Gerstel (Mülheim an der Ruhr, Germany). Table 1 lists selected physical and chemical properties of BTEX and *n*-aldehydes.

2.2. Standard operation procedure (SOP) and blank samples

The following standard operation procedure (SOP) was employed to minimize background contamination. All glass devices and septa were cleaned for 15 min in an ultrasonic bath filled with deionized water, rinsed with deionized ultra pure water and finally dried in an oven at 105 °C. Septa and vials were not reused. Laboratory blank samples were prepared by spiking 4 mL of deionized water with the internal standard solution no. 3. One blank sample was analyzed after every eight water samples. Additional field blanks were collected during the sampling of real snow samples. Ultra pure water (Merck) was purchased and transported to the sampling location. After snow sampling one blank sample was prepared and stored with the snow samples until analysis. The maximum time span between sampling and analysis was 2 months.

2.3. Instrumentation

Samples were analyzed using a CTC-CombiPAL autosampler (Bender and Hobein, Zurich, Switzerland) mounted on top of a GC/MS system. The autosampler was equipped with a heatable CTC agitator for incubation and shaking, an extraction

Table 1
Physical and chemical properties, selected ion masses for quantification and retention times of BTEX and *n*-aldehydes analyzed in the present study

	Boiling point ^a (°C)	Water solubility ^a (at 25 °C) (g/L)	Vapor pressure ^a (at 25 °C) (kPa)	H (at 25 °C) ^a (kPa m ³ /mol)	Selected ion masses (<i>m/z</i>)	retention time (min)
Benzene	80	1.79	12.64	0.557	78	10.6
Toluene	110.6	0.53	3.79	0.673	91	13.0
<i>o</i> -Xylene	144.5	0.18	0.88	0.525	91	15.7
<i>m</i> -Xylene	139.1	0.16	1.11	0.728	91	15.1
<i>p</i> -Xylene	138.3	0.16	1.18	0.699	91	15.1
Ethylbenzene	136.1	0.17	1.28	0.798	91	15.0
<i>n</i> -Hexanal	131	5.64	1.51	0.021	57	13.9
<i>n</i> -Heptanal	152.8	1.25	0.47	0.027	70	15.9
<i>n</i> -Octanal	171	0.56	0.16	0.052	84	18.1
<i>n</i> -Nonanal	191	0.10	0.05	0.074	98	20.5
<i>n</i> -Decanal	208.5	0.06	0.01	0.182	112	23.7
Fluorobenzene	84.7	1.54	8.10	0.638	96	10.9
1-Bromo-2-chloroethane	107	6.90	0.40	0.092	63	12.4

^a Data from SRC Phys Prop Database (<http://esc.syrrees.com>).

cooler (Chromtech, Idstein, Germany) to cool the SPDE needle during extraction to -15°C , and an additional gas station (Chromtech, Idstein, Germany) to aspire desorption gas. To prevent the carry over of analytes, we used a heated flushing station for conditioning of the SPDE needle and reconditioning after each analysis. Both the gas station and the heated flushing station were flushed with helium. The syringe body was held at a temperature of $+35^{\circ}\text{C}$ in the syringe adapter heater. All of the SPDE steps were fully controlled by the autosampler.

The GC-MS (Thermoquest CE Instruments Trace GC 2000 Series combined with Voyager MS) was equipped with a 60 m DB-624 capillary column (Agilent Technologies) with an I.D. of 0.32 mm and a film thickness of 1.8 μm . Helium (purity 5.0) served as carrier gas. The desorption of the analytes from the SPDE needle was carried out in the injector of the GC by adjusting the injector temperature to 230°C . Measurements were carried out in the splitless mode. The column was operated in the constant pressure mode at 70 kPa. The GC oven temperature program was as follows: held at 32°C for 2 min, then heating at $12^{\circ}\text{C}/\text{min}$ to 190°C , and finally held at 190°C for 20 min. Data acquisition, processing, and instrument control were performed using Excalibur software (Thermoquest). Detection of the analytes was performed by a Thermoquest Finnigan Voyager MS in the electron ionization positive ion (EI+) and full scan mode (scan range 35–300).

2.4. SPDE configuration

A commercially available SPDE needle (74×0.8 mm, Chromtech, Idstein, Germany) was used in this analysis. The sorption material consisted of PDMS with 10% embedded activated carbon (PDMS/AC) phase with 50 μm film thickness. The needle was preconditioned in the flushing station for 1 h at 250°C . Extraction was performed from the headspace of the sample.

To increase sensitivity for the compounds of interest, several parameters, i.e. the number of extraction cycles (*n*), extraction temperature (T_{ex} in $^{\circ}\text{C}$), extraction volume (V_{ex} in μL), extrac-

tion flow rate (\bar{V}_{ex} in $\mu\text{L}/\text{s}$), desorption temperature (T_{des} in $^{\circ}\text{C}$), desorption volume (V_{des} in μL), desorption flow rate (\bar{V}_{des} in $\mu\text{L}/\text{s}$), and the pre-desorption time (t_{predes} in s) were optimized. The influence of the time before the first extraction cycle in terms of attaining equilibrium between the water and headspace (t_{preex} in s) was also investigated. An extraction scheme is presented in Fig. 1. The time taken for the entire extraction procedure is referred to as extraction time (t_{ex} in s).

2.5. Experimental setup

Several extraction and desorption parameters were optimized during development of the method. Sample vials were filled with 4 mL deionized ultra pure water and closed with magnetic screw caps with PTFE/silicon septa. Working standards were then added to each vial through the septum using a microliter syringe to obtain concentration levels in the samples of 0.1–2.0 $\mu\text{g}/\text{L}$. The internal standards (fluorobenzene and 1-bromo-2-chlorethane) were added at an end concentration of 1 $\mu\text{g}/\text{L}$ in the sample. Experiments for the extraction and desorption parameters were carried out as triplicate measurements.

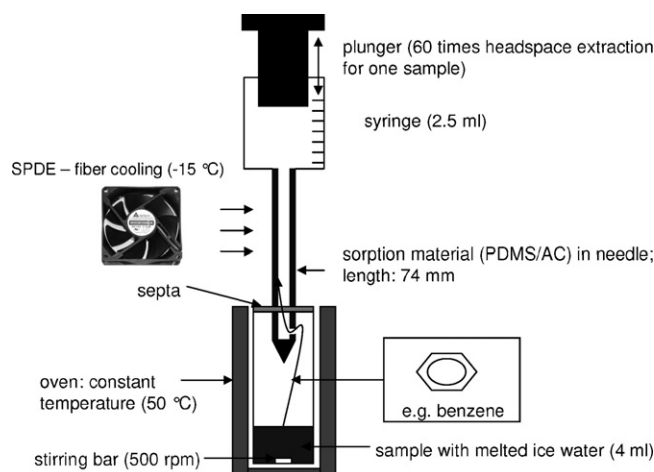


Fig. 1. Scheme of SPDE extraction.

Experiments for the calculation of detection limits, precision, and calibration curves were performed seven times for each concentration level. Detection and quantification limits were determined according to DIN 32645 [32]. Calibration curves were obtained by dividing the peak area of the compounds by the peak area of IS and relating this to the concentration of the solution. Identification of the analytes was achieved from retention times and mass spectra (NIST spectral match). The ions used for quantification are shown in Table 1.

3. Results and discussion

Various SPDE parameters were evaluated during the method development, and the results were compared with those of previous studies. A general survey of different SPDE applications and the reported optimal method parameters is provided in Table 2. In the present study, the evaluation of individual parameters was carried out while all other method parameters were kept constant (see Table 2).

3.1. Extraction parameters

Previous studies using SPME have shown that higher transfer rates of the analytes from the water to the headspace are observed upon a continuing increase of the temperature of the analyzed water. However, this advantage is compensated by a concomitant increase in fiber temperature which increases the desorption of the analytes from the fiber. As a consequence of these two processes, an optimal extraction temperature has to be found for every compound [18,33,34]. SPME methods can be improved by cooling the fiber in the headspace and thereby minimizing the unwanted desorption of analytes from the fiber during extraction at higher water temperatures [35]. To overcome this disadvantage for SPDE methods, a cooling device for SPDE was used in the present study. First of all, the general usability of the cooling device was tested by analyzing 4 mL of water with a concentration of 1 µg/L of BTEX and *n*-aldehydes with and without cooling of the SPDE needle to -15°C during extraction at a defined water temperature of 50°C . The results of the GC response of BTEX and *n*-aldehydes are shown in Figs. 2 and 3,

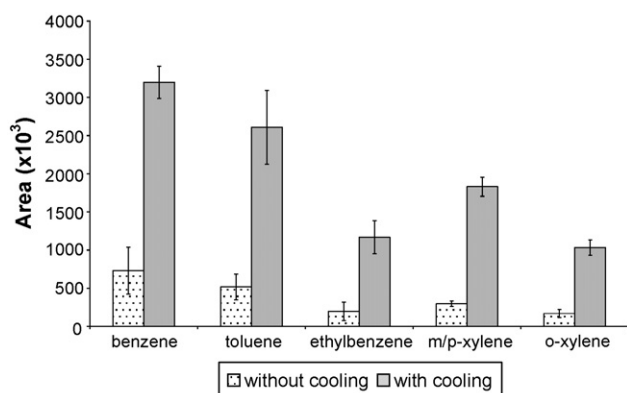


Fig. 2. Recovery of BTEX during extraction with and without cooling the SPDE needle to -15°C . Detailed SPDE parameters are listed in Table 2.

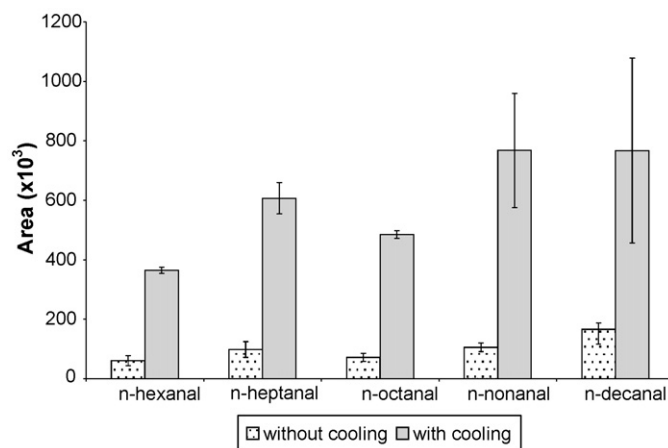


Fig. 3. Recovery of *n*-aldehydes during extraction with and without cooling the SPDE needle to -15°C . Detailed SPDE parameters are listed in Table 2.

respectively. The error bars in the figures represent the RSDs of triplicates.

The GC responses for all BTEX and *n*-aldehydes were higher by cooling the needle during extraction at -15°C in comparison to an extraction keeping the needle at room temperature. The ratio between the GC response with a cooled needle to a non-cooled needle ranged from 3.0 (benzene) to 4.7 (*o*-xylene) for BTEX and from 3.8 (*n*-decanal) to 5.8 (*n*-nonanal) for *n*-aldehydes. The GC response for all analyzed compounds profits significantly from using the cooling device during extraction and therefore increases the sensitivity of the method. The enhanced adsorption of analytes by cooling of the needle is due to the exothermic process of sorbent-air partitioning.

Due to positive impact on extraction quantity by cooling the SPDE needle to -15°C the cooling device was used in all further experiments. Extractions were carried out at 30, 50 and 70°C to evaluate the extraction temperature of the water phase. The results are shown in Figs. 4 and 5, respectively. Considering the RSDs there was no significant difference in responses for all BTEX compounds for the extraction at 30°C and 50°C , respectively. For all BTEX compounds the GC response decreased at 70°C . For aldehydes, the highest GC response was observed at 50°C , followed by 70°C . According to the temperature depen-

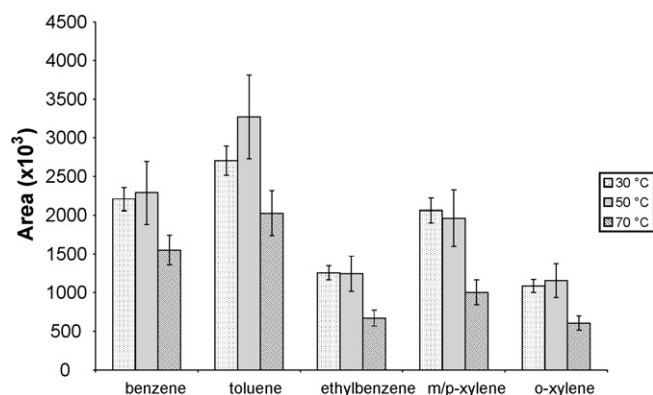


Fig. 4. Influence of the extraction temperature on the recovery of BTEX. Detailed SPDE parameters are listed in Table 2.

Table 2
General survey on different SPDE applications and reported optimal method parameters

Compounds of interest	Unit	[27,28] Cannabinoids	[26,28] Amphetamine and synthetic designer drugs	[29] Furan, benzene, toluene	[30] Benzene, 11 chlorinated and brominated HC	[24] PVOC (3 ethers and 12 alcohols)	[25] Beta-pinene, isoamyl acetate, linalool	This study BTEX, aldehydes
Extraction								
Equilibrium time before extraction	s	300	300	600	300	300	900	30
Extraction temperature	°C	90	50	30	60	70	50	50
Stiring bare	rpm	200	600	500	700	500	n.s.	500
Number of extraction cycles	–	30	50	25	15	50	50	60
Extraction flow rate	μL/s	50	200	50	50	125	50	100
Extraction volume	μL	1000	1000	1000	1000	2500	1000	1000
Extraction time	min	25.0	13.3	26.7	15.0	38.3	48.3	20.5
Desorption								
Equilibrium time before desorption	s	15	15	n.s.	0	0	30	15
Desorption volume	μL	1000	2500	2000	1000	1000	1000	500
Desorption flow rate	μL/s	10	10	200	10	50	15	50
Desorption temperature	°C	260	250	150	300	200	230	230
Desorption time	s	115	265	10	100	20	96.7	25
Miscellaneous								
Sorption material	–	PDMS/AC	PDMS/AC	PDMS	PDMS/AC	PDMS/AC	PDMS/AC	PDMS/AC
Sample matrix	–	Water	Water	Water	Water	Water/alcoholic beverage	Water/aromatic plants and food matrices	Water/snow
Heating of the needle between samples	–	n.s.	n.s.	10 min/260 °C	2 min/280 °C	5 min/200 °C	n.s.	30 min/200 °C

n.s.: not specified.

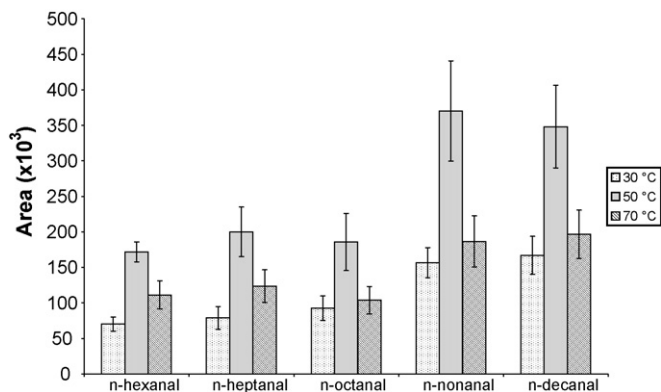


Fig. 5. Influence of the extraction temperature on the recovery of *n*-aldehydes. Detailed SPDE parameters are listed in Table 2.

dence of the Henry constant, one should expect higher transfer rates of the analytes from the water phase to the gas phase with increasing temperatures leading in turn to a higher analytical response.

The analytical results demonstrate that the increase in water temperature has only a minor influence on the yield of BTEX adsorbed at the needle. Only for *n*-aldehydes, the increase in water temperature from 30 to 50 °C led to an increase in the analytical response. However, for both, BTEX and *n*-aldehydes, extraction yields were lowest at a water temperature of 70 °C.

A possible explanation for the decrease in GC response at 70 °C is the transfer of heat to the needle which therefore cannot be expected to remain at a temperature of –15 °C because, during pulling and pushing the plunger, heated air from the vial is transferred into the adsorption channel of the needle. This explanation for the decrease in GC-response at 70 °C water temperature needs certainly further detailed examination.

An extraction temperature of 50 °C was chosen for further analysis as a compromise in consideration of the different physical and chemical properties of the compounds of interest.

For evaluating the optimal number of extraction cycles, the cycles were set to 5, 20, 40 and 60 extraction strokes. The results of the GC responses of BTEX and *n*-aldehydes are shown in Figs. 6 and 7, respectively. Analyses were carried out as triplicate measurements. The error bars in the figures represent the RSDs of the three measurements.

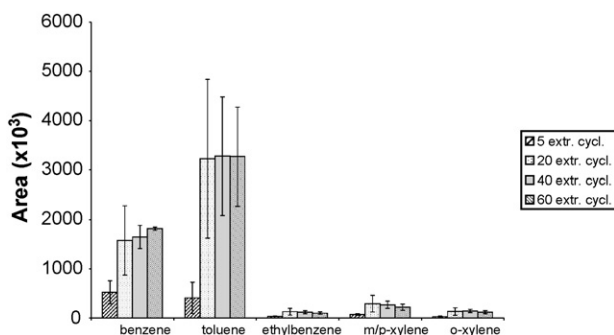


Fig. 6. Influence of the number of extraction cycles on the recovery of BTEX. Detailed SPDE parameters are listed in Table 2.

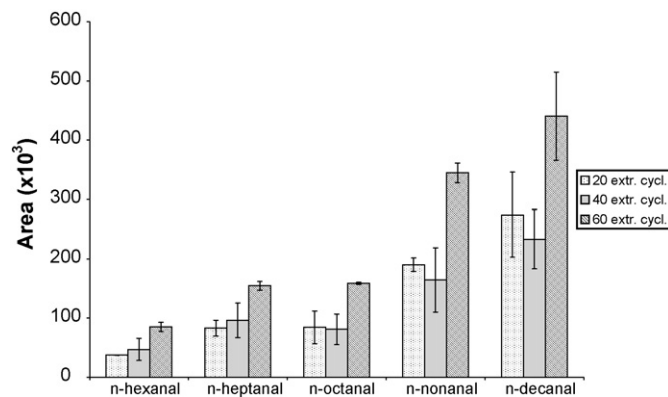


Fig. 7. Influence of the number of extraction cycles on the recovery of *n*-aldehydes. Detailed SPDE parameters are listed in Table 2.

For BTEX, a large increase in GC response was observed by increasing the number of extraction cycles from 5 to 20. However, from 20 extraction cycles on, GC responses were relatively similar. *n*-Aldehydes were not detected using five extraction cycles. An increase of responses was observed for *n*-hexanal and *n*-heptanal from 20 to 40 extraction cycles. For *n*-octanal, *n*-nonanal and *n*-decanal a slight decrease in GC-responses between 20 and 40 extraction cycles was found. However, the decrease was in the range of RSDs and therefore without statistic significance. For all *n*-aldehydes, the highest GC responses were obtained by use of 60 extraction cycles. Therefore, in subsequent analyses 60 extraction cycles were used because of the overall advantages provided by this number of cycles.

Comparing the GC response of individual BTEX and *n*-aldehydes the different volatilization behavior of the compounds has to be considered. The differences between BTEX and *n*-aldehydes in terms of GC-response can be explained by their different values of Henry constant (H , defined as the vapor pressure divided by the solubility in water). Higher H values of BTEX compared to aldehydes leads to higher GC responses for BTEX. For *n*-aldehydes, a slight increase in GC response was detected from *n*-hexanal to *n*-decanal. Apparently, in case of *n*-aldehydes an increase in GC response is linked to a decrease in water solubility and an increase in the Henry constant (see Table 1).

Lee et al. [36] noted that the volatilization rates of compounds with high H ($H > 0.47 \text{ kPa m}^3 \text{ mol}^{-1}$) and especially for BTEX, are proportional to solubility in water and inversely proportional to the molecular weight of the compound. Comparing the solubility and molecular weight of BTEX (see Table 1), the results from the present study are in good agreement with those of Lee et al. [36].

In agreement with Jochmann et al. [25], no significant variations in the obtained GC responses were observed with different pre-extraction times (30, 150, 300 and 450 s). Therefore, a pre-extraction time of 30 s was used for the following experiments.

Bicchi et al. [26] reported that the extraction flow rate has only minor influence on the overall extraction performance during the analysis of volatiles. In the present study, the extraction flow rate was held constant at 100 $\mu\text{L/s}$.

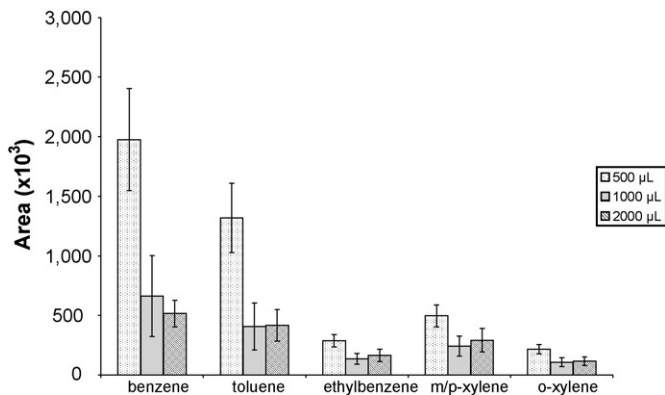


Fig. 8. Influence of the variation of desorption volumes on the recovery of BTEX. Detailed SPDE parameters are listed in Table 2.

3.2. Desorption parameters

Before desorption of compounds from the SPDE adsorbent in the GC injector a variable volume (desorption volume) of helium as a carrier gas was acquired in a separate flush station. The carrier gas promotes the transport of the desorbed compounds through the SPDE-needle into the GC injector. The desorption temperature (equivalent to the injector temperature) was set to 230 °C.

Different desorption volumes (500, 1000, and 2000 µL) were tested at a concentration of 1 µg/L of BTEX and *n*-aldehydes. Other SPDE parameters such as desorption flow rate (50 µL/s), desorption temperature, pre-desorption time, and all extraction parameters, were kept constant (see Table 2). Figs. 8 and 9 show the results for three different desorption volumes for BTEX and *n*-aldehydes, respectively. The error bars in the figures represent the RSDs ($n=3$). For all compounds, the highest GC response was observed using a desorption volume of 500 µL. The RSDs of the GC responses of the analyzed compounds are largely independent of the desorption volume. Variation of the desorption flow rate (10, 30, and 50 µL/s) in combination with a higher desorption volume (2000 µL), was also tested. Resulting GC responses were all lower than those achieved with a desorption flow rate of 50 µL/s in combination with a desorption volume of 500 µL.

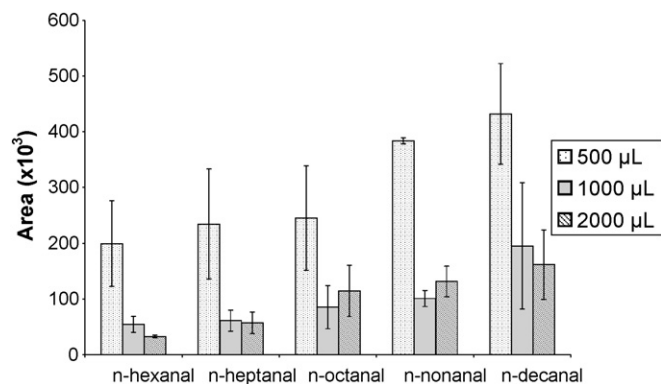


Fig. 9. Influence of the variation of desorption volumes on the recovery of *n*-aldehydes. Detailed SPDE parameters are listed in Table 2.

To explain these results, it is necessary to consider also additional parameters such as desorption temperature, desorption flow rate, column flow rate, injection mode and injector design. A perfect combination of these parameters should lead to the optimum transfer of the analytes to the GC column. Bicchi et al. [26] and Musshoff et al. [28] reported that a desorption flow rate above 50 µL/s is not compatible with pressure control in their injector.

Musshoff et al. [27] reported that the GC response for amphetamine and synthetic designer drugs increased with increasing desorption volume, achieving a maximum at the full syringe volume of 2.5 mL and a low desorption flow rate of 10 µL/s. For more volatile compounds (beta-pinene, isoamyl acetate, linalool), Bicchi et al. [26] reported that the highest GC response was obtained using a desorption volume of 1.0 mL and a desorption flow rate of 15 µL/s. Jochmann et al. [25] used a desorption volume of 1.0 mL and a desorption flow rate of 50 µL/s to analyze ethers and alcohols in water samples. In the present study, the best results were achieved using the smallest technical available desorption volume of 500 µL and the highest technical desorption flow rate of 50 µL/s. Compared to the studies mentioned above the higher volatility of the compounds analyzed in this study is the reason for an optimum desorption of the analytes at a lower desorption volume and a higher desorption flow rate.

The above findings lead to the conclusion that for the analysis of higher volatile compounds the ideal desorption volume is lower and the ideal desorption flow rate is higher than for less volatile compounds.

Jochmann et al. [31] reported peak tailing or even peak splitting at desorption volumes above 1000 µL (desorption flow rate: 10 µL/s), and concluded that the slow transfer of the analytes to the capillary column at high desorption volumes is responsible for this effect. In the present study, we observed similar effects for benzene at desorption volumes of 1000 and 2000 µL, but an optimal peak form at 500 µL.

3.3. Precision and detection limits

Following DIN 32645 [32], detection and quantification limits were determined as follows.

Seven calibration curves and linear fits were produced for BTEX and *n*-aldehydes (C₆–C₁₀) with a concentration range from 0.1 to 2.0 µg/L. The y-axis intercept represents the blank values of compounds. Detection limits (DL) of the SPDE-GC/MS method for individual compounds were calculated according to the following equation:

$$DL = \frac{3s_{\text{Blank}}}{b_{\text{Blank}}}$$

where s_{Blank} is the standard deviation of the seven blank values and b_{Blank} is the mean of the slopes of the seven linear fits for individual compounds. Table 3 lists the fitting parameters of the calibration curves, detection limits, quantification limits and the relative standard deviation (RSD) for the studied compounds. The quantification limits of the method were set to three times the detection limits [32]. Detection limits for BTEX

Table 3
Fitting parameters for the calibration curves, detection limits, quantification limits and relative standard deviations

	Slope mean (<i>n</i> = 7)	Intercept mean (<i>n</i> = 7)	<i>r</i> ²	Detection limit (μg/L)	Quantification limit (μg/L)	Relative standard deviation for 0.1 μg/L (%) (<i>n</i> = 3)	Relative standard deviation for 2 μg/L (%) (<i>n</i> = 3)
Benzene	1.386	0.044	0.997	0.019	0.058	8.8	3.9
Toluene	1.605	0.033	0.916	0.024	0.071	12.4	4.2
Ethylbenzene	0.958	−0.014	0.999	0.018	0.053	16.1	15.3
<i>m/p</i> -Xylene	2.169	−0.020	0.999	0.030	0.089	14.1	13.9
<i>o</i> -Xylene	1.103	−0.048	0.998	0.021	0.063	13.5	12.9
<i>n</i> -Hexanal	0.592	0.081	0.997	0.063	0.188	21.7	16.5
<i>n</i> -Heptanal	0.779	−0.061	0.987	0.021	0.062	15.8	10.5
<i>n</i> -Octanal	1.132	−0.024	0.992	0.043	0.130	23.5	6.1
<i>n</i> -Nonanal	1.304	0.081	0.999	0.023	0.069	26.1	11.9
<i>n</i> -Decanal	1.637	0.091	0.998	0.026	0.079	21.4	11.7

were between 0.018 μg/L (ethylbenzene) and 0.030 μg/L (*m/p*-xylene) and for *n*-aldehydes between 0.021 μg/L (*n*-heptanal) and 0.063 μg/L (*n*-hexanal). The RSDs were calculated for BTEX and *n*-aldehydes at 0.1 and 2.0 μg/L (*n* = 7) to evaluate the overall precision of this method. At 0.1 μg/L, the RSDs for BTEX were between 8.8% (benzene) and 16.1% (ethylbenzene) and for aldehydes between 15.8% (*n*-heptanal) and 26.1% (*n*-nonanal). For a concentration level of 2.0 μg/L, RSD values for BTEX were between 3.9% (benzene) and 15.3% (ethylbenzene) and for aldehydes between 6.1% (*n*-octanal) and 16.5% (*n*-hexanal). Higher RSD values at 0.1 μg/L, especially for aldehydes, can be explained by the low concentration level.

Ridgway et al. [30] reported an estimated DL of 0.40 μg/L for benzene and 0.48 μg/L for toluene using a HS-SPDE-GC/MS in single ion monitoring (SIM) mode and with PDMS as the SPDE material. The main difference between this previous study and the present study is the choice of SPDE material (Table 2). One reason for the lower DLs in the presented study could be that the employed PDMS/AC fiber is more efficient in extracting volatiles than the PDMS fiber used by Ridgway et al. [30]. In analyzing volatiles such as methyl-*tert*-butyl ether (0.07 μg/L) and 1-hexanol (0.004 μg/L) using a PDMS/AC fiber, the DLs reported by Jochmann et al. [25] are in the same range as those obtained in the present study. A more recent study by Jochmann et al. [31] reported a DL for benzene at 0.013 μg/L with HS-SPDE-GC/MS and a SPDE needle with a PDMS/AC

coating. Precision for benzene was reported to be 3.7% at a “low” concentration level (approximately 5 times higher than the DL; *n* = 9) and 3.2% at a “high” concentration level (100 μg/L; *n* = 9).

3.4. Application to real samples

The described SPDE-GC/MS method has been applied to freshly fallen snow samples collected during the CLACE 5 campaign (CLOUD and Aerosol Characterization Experiment) at Jungfraujoch, Swiss Alps (46.55°N; 7.98°E), in February and March of 2006. Twenty-seven snow samples were collected in 20 mL vials using a self-developed snow sampling device, as reported by Fries et al. [9]. Volumes of the melted snow samples were between 1.7 and 6.7 mL. Four field blank samples were also collected, as mentioned above. The concentrations of BTEX and *n*-aldehydes in the snow samples were corrected by the concentration of contemporary field blanks.

Table 4 lists the results obtained from three selected snow samples. BTEX ranges from <DL (*m/p*-xylene) to 0.236 μg/L (toluene) and *n*-aldehydes ranges from 0.253 μg/L (*n*-heptanal) to 1.891 μg/L (*n*-nonanal). Among the BTEX compounds, toluene is present with the highest concentrations, while *n*-hexanal and *n*-nonanal are the dominant aldehydes. Further results for VOCs in snow obtained during the CLACE 5 campaign are discussed in detail elsewhere [9].

Table 4
Concentrations of BTEX and aldehydes in selected snow samples from Jungfraujoch (Switzerland) in February and March 2006 (DL: detection limit; QL: quantification limit)

	Snow sample 1; sampling time: 24.02.06/12.45	Snow sample 2; sampling time: 25.02.06/21.30	Snow sample 3; sampling time: 01.03.06/14.50
Benzene (μg/l)	<QL	<QL	<QL
Toluene (μg/l)	0.236	<QL	0.206
Ethylbenzene (μg/l)	0.112	<QL	0.086
<i>m/p</i> -Xylene (μg/l)	0.105	<DL	<QL
<i>o</i> -Xylene (μg/l)	0.124	<QL	<QL
<i>n</i> -Hexanal (μg/l)	1.538	0.681	1.577
<i>n</i> -Heptanal (μg/l)	0.371	0.253	0.281
<i>n</i> -Octanal (μg/l)	0.594	0.355	0.324
<i>n</i> -Nonanal (μg/l)	1.891	0.837	0.932
<i>n</i> -Decanal (μg/l)	1.053	0.635	0.574

The concentrations of BTEX in snow samples from Jungfrau-joch are comparable to the concentrations found in the “Gaspe-Low” sample analyzed by Kos and Arya [8], who assumed that the low concentrations reflected the large contribution of freshly fallen snow. In comparison, other analyzed samples [8] were significantly enriched in BTEX (e.g. toluene at $316 \pm 46.8 \mu\text{g/L}$; sample “Gaspe-High”) and originated from altered snowpacks indicating that airborne organic compounds accumulate on snow surfaces after deposition.

4. Conclusions

In the present study, Headspace-SPDE-GC/MS was optimized to analyze BTEX and *n*-aldehydes in snow after melting. A significant increase in GC response was obtained due to cooling the SPDE needle during extraction. Due to positive impact on extraction quantity by cooling the SPDE needle to -15°C the cooling device was used in all further experiments. Evaluating the extraction cycles, for BTEX, the sensitivity was almost similar using 20, 40 and 60 extraction cycles. In contrast, the highest GC responses for *n*-aldehydes were achieved by the use of 60 extraction cycles. An extraction temperature of 50°C was chosen for further analysis as a compromise in consideration of the different physical and chemical properties of the compounds of interest. Different desorption volumes (500, 1000, and 2000 μL) were tested at an analyte concentration of 1 $\mu\text{g/L}$. For all compounds, the highest GC responses were observed using a desorption volume of 500 μL in combination with a desorption flow rate of 50 $\mu\text{L/s}$. Detection and quantification limits were in the lower ng/L range. In general, higher Henry constants for BTEX compared to *n*-aldehydes lead to higher GC responses for BTEX. BTEX and aldehydes were detected in snow samples collected from the Jungfrau-joch, Switzerland (3580 m asl).

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