

Diffusion-based calibration for solid-phase microextraction of benzene, toluene, ethylbenzene, *p*-xylene and chlorobenzenes from aqueous samples

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Abstract

Short-term solid-phase microextraction (SPME) was performed to test a recently proposed semi-empirical model for the prediction of concentrations of analyte in water samples from the fibre-extracted mass without further calibration. The mass uptake rates obtained for benzene, toluene, ethylbenzene and *p*-xylene (BTEX) differ considerably from the before published, showing that interfibre comparability is a serious issue. The relative prediction errors are between –55% for benzene and +82% for *p*-dichlorobenzene under optimal conditions, i.e. they are by an order of magnitude higher than originally published. A sensitivity analysis shows the dominant influence of the estimated thickness of the diffusional boundary layer around the fibre on the concentration predicted. Empirical modification of the model equation for this parameter yields satisfactory results under the conditions tested for both BTEX and the selected chlorobenzenes.

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1. Introduction

In 2000, Koziel et al. proposed an approach for the quantification of volatile organic compounds in air using short-term solid-phase microextraction (SPME) without further calibration [1]. They extended this procedure later to analyse benzene, toluene, ethylbenzene and *p*-xylene (BTEX) in water samples using SPME in immersion mode [2]. The fundamental assumption, and the reason for the denotation of this procedure, is that diffusion of analytes through the stagnant fluid layer established around the SPME fibre under defined hydrodynamic conditions act as the rate-determining step of mass-transfer, at least for short extraction times below 1 min, and thus determines the extraction yield. Such a procedure could be valuable, e.g. for screening purposes to differentiate roughly between heavily and less contaminated water samples in the course of field sampling. Another important application can be the determination of the kinetics of a chemical

reaction or distribution without disturbing the process by withdrawing of samples (“minimal invasive analysis”). On the other hand, some theoretical reservation against the fundamentals of the procedure can be expressed because dissimilarities of heat and mass transfer are insufficiently taken into account in the basic model (c.f. e.g. [3], pp. 642–648, 658–666; [4], pp. 39–53, 57–60, 185–190). Moreover, it is very likely that the diffusion boundary layer model oversimplifies the hydrodynamic situation around the relatively rough fibre surface which can create local turbulent flow with small eddies (instead of a stagnant layer).

All these facts prompted us to perform short-term immersion SPME with the BTEX under similar conditions like in [2], firstly to investigate the reproducibility of the proposed method, and secondly to test the transferability of the procedure to other analytes by additional experiments with chlorobenzene, *o*- and *p*-dichlorobenzene. During our study, we considered also the fibre-to-fibre comparability (of one and the same type of coating) as well as the influence of the different model parameters on the accuracy of prediction of analyte’s concentration in the sample.

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2. Experimental

2.1. Materials

We used three SPME fibres coated with 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) which were purchased together with a manual SPME fibre holder from Supelco (Taufkirchen, Germany). Fibre 1 was an already used one (ca. 40 times for other preconcentrations before the actual experiments). Fibres 2 and 3 were freshly purchased. All fibres were conditioned before use according to instructions of the manufacturer and checked for no carryover during the experiments. The chemicals were obtained as neat substances from Merck (Darmstadt, Germany) and stock solutions of the test analytes were prepared gravimetrically in methanol. Aliquots of these stock solutions were used to spike the water samples (shortly before the start of the SPME experiments) by restricting the upper methanol concentration in the sample to 1% (v/v). The initial aqueous concentration per test substance was adjusted to 500 $\mu\text{g/l}$ to ensure comparability with [2].

Methanol and hexane (both ‘for organic trace analysis’) were obtained from Merck. Double distilled water was prepared freshly before use from tap water by means of an automated laboratory distillation unit GFL 2102 (Gesellschaft für Labortechnik, Burgwedel, Germany).

2.2. SPME procedure

We performed the short-term SPME at room temperature (23–25 $^{\circ}\text{C}$) with water samples of 40 ml in a vial of nearly the same volume so that almost all headspace, which could cause additional volatilisation losses, is eliminated. We placed a special aluminium insert between the hollow plastic cap and the septum. The holes drilled in this insert allow accurate positioning of the fibre, in our experiments 5 mm away from the axis of the vial. The sample was agitated by a teflon-coated stir bar (with a length of 20 mm and a diameter of 8 mm) using a magnetic stirrer M 3000 D (Heidolph, Kehlheim, Germany). By this arrangement, we ensured a tangential flow direction of the sample to the fibre and could use, as in [2], the semi-empirical relationships, given by Pawliszyn [5] for this case, to estimate the linear velocity, u , of sample:

$$u = 1.05\pi N r \left[2 - \left(\frac{r}{0.74R} \right)^2 \right] \quad (1)$$

and the thickness, δ , of the boundary layer

$$\delta = 9.52 \left[\frac{b}{Re^{0.62} Sc^{0.38}} \right] \quad (2)$$

where N is the magnetic stirrer speed (in revolutions per second), r the distance between the fibre and the axis of the vial (in cm), R the radius of the stir bar (in cm), b the

radius of the SPME fibre (in cm), Re the Reynolds number ($Re = 2ub/v$; with v as kinematic viscosity of the matrix medium, here water), and Sc the Schmidt number ($Sc = v/D$; with D as the diffusion coefficient of the analyte molecule in the sample matrix, here in water at “infinite” dilution).

The exposure times of the SPME fibres were between 15 and 120 s and we stirred the samples between 150 and 1270 min^{-1} . For 60 s exposure time we repeated the extraction several times to calculate the reproducibility of the method.

2.3. Instrumental analysis

All analyses were performed with an HP 5890 II gas chromatograph equipped with a split/splitless injector, a 7673 autosampler and a flame ionization detector. The analytes desorbed from the SPME fibres and those injected directly afterward as standard solutions in hexane (1 μl) for calibration of the GC response were separated on a 30 m \times 0.32 mm i.d. HP1 column coated with 4 μm film. The injector was programmed to return to split mode 2 min after insertion of the SPME fibre and 1 min after liquid injection. Nitrogen was used as carrier gas with a constant column flow rate of 1.0 ml/min. The injector temperature was held constant at 250 $^{\circ}\text{C}$. The GC oven temperature program was: 40 $^{\circ}\text{C}$ for 3 min, 8 $^{\circ}\text{C}/\text{min}$ to 180 $^{\circ}\text{C}$, then 40 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$, held for 6 min. The detector temperature was 300 $^{\circ}\text{C}$.

The calibration of GC response was carried out by triplicate injections of six to seven different standard solutions (in hexane). The peak area-to-mass relationships are linear within the checked range (from a few to several hundreds of nanograms) with correlation coefficients better than 0.9995 for all analytes under investigation and standard deviations of residuals only between 0.8 and 3.8%.

3. Results and discussion

3.1. Short-term SPME of BTEX from water

With fibre 2, we conducted preliminary experiments to see the velocity dependence of the extracted amounts. The extraction time was fixed here to 60 s and the experiment was repeated at least once with every stirrer speed. Fig. 1 shows that perhaps a plateau region exists above 40 cm/s where a further increase of sample velocity has no effect on the extracted mass. This is a well-known fact from other investigations [4,6] showing that mass transfer from the bulk liquid to the interface is no longer the rate-limiting step. Sukola et al. [2] suggested that diffusion of analytes into the pores of the fibre coating becomes the limiting factor in this specific case.

The following experiments for comparing the three different PDMS–DVB fibres were carried out with a stirrer speed

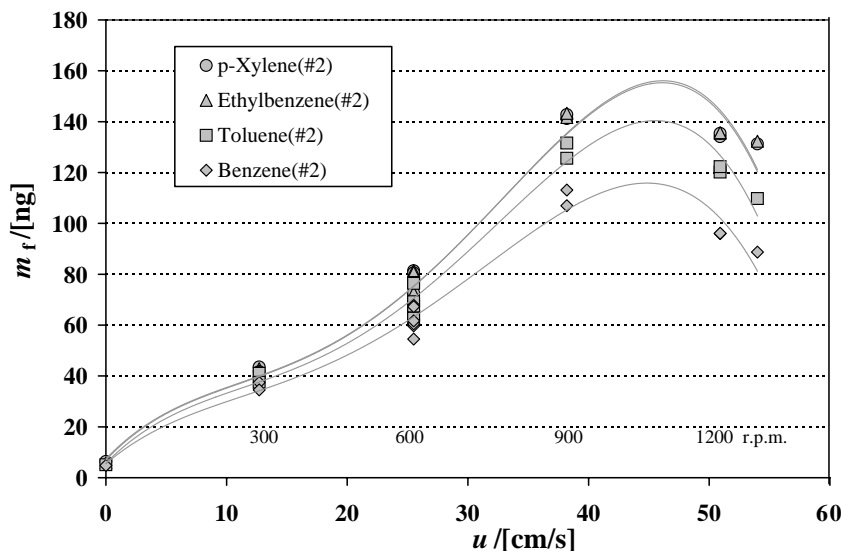


Fig. 1. Extracted amount of BTEX with PDMS–DVB fibre 2 vs. tangential sample velocity ($c_{W(0)} = 500 \mu\text{g/l}$; $t = 60 \text{ s}$).

of 600 min^{-1} (“optimal” with respect to the findings in [2]). This speed is equivalent to a tangential sample velocity of 25.5 cm/s (calculated with Eq. (1) under the actual geometric conditions). Fig. 2 shows the extraction time profiles of the four compounds tested. The standard deviations of extracted amounts (determined at 60 s) are below 9% for all components. With fibre 1, we extracted much smaller amounts of benzene in comparison to the other compounds/fibres. The reason remains unclear. A change in the microstructure of this fibre coating, e.g. due to over-heating, cannot be excluded. Another possible reason for the reduced mass uptake of fibre 1 with benzene, a competitive adsorption process, is implausibly by taking into consideration the behaviour of the two other fibres and the very short extraction times.

From the data points between 30 and 60 s, that is the range of applicability of the diffusion-based calibration model stated in [2], we have calculated the initial mass uptake rates of the different fibres by least-square approximation. These values are summarised in Table 1 together with those reported by Sukola et al. [2] under similar conditions. Only the mass uptake rate for benzene with fibre 1 is comparable with the previous published result. Interestingly, the uptake rates for toluene, ethylbenzene and *p*-xylene are much higher with that fibre. This fact again points to a possible change in the extraction behaviour of the coating of fibre 1 (used already 40 times before this study). The differences in the uptake rates obtained with fibres 2 and 3 are insignificant. They are considerably higher than those previously published. These large discrepancies

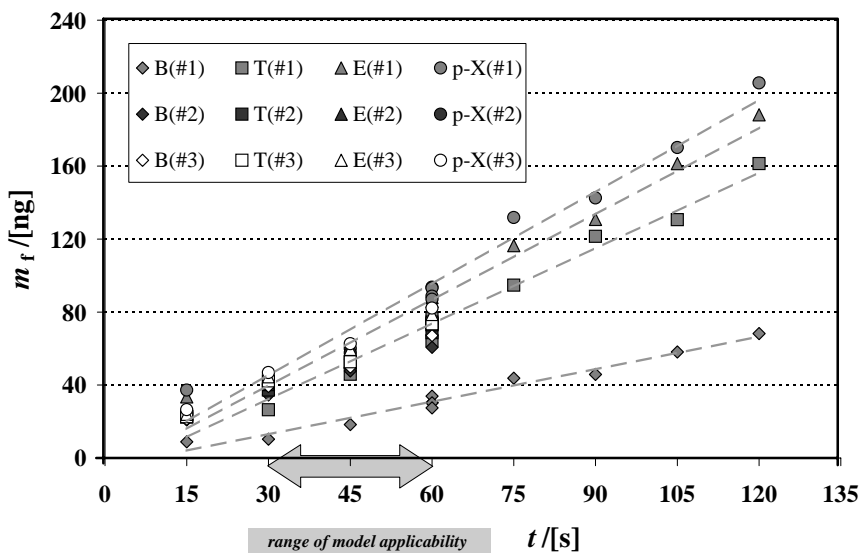


Fig. 2. Extracted amount of BTEX with the PDMS–DVB fibres 1, 2, and 3 vs. extraction time ($c_{W(0)} = 500 \mu\text{g/l}$; $u = 25.5 \text{ cm/s}$).

Table 1
Initial mass uptake rates^a of PDMS–DVB fibres from aqueous solution (sample velocity $u = 25.5$ cm/s) and their standard deviation (in brackets)

Substance	$D_W \times 10^5$ (cm ² /s)	Experiment series (fibre no.)	$\Delta m_f / \Delta t$ (ng/s)
Benzene	1.16	1	0.69 (± 0.09)
		2	0.87 (± 0.13)
		3	0.93 (± 0.13)
		Sukola et al. [2] ^b	0.68
Toluene	0.97	1	1.56 (± 0.18)
		2	1.03 (± 0.15)
		3	1.04 (± 0.20)
		Sukola et al. [2] ^b	0.63
Ethylbenzene	0.92	1	1.53 (± 0.21)
		2	1.04 (± 0.17)
		3	1.14 (± 0.08)
		Sukola et al. [2] ^b	0.63
<i>p</i> -Xylene	0.79	1	1.65 (± 0.15)
		2	1.04 (± 0.16)
		3	1.18 (± 0.07)
		Sukola et al. [2] ^b	0.60
Chlorobenzene	0.90	2	1.25 (± 0.18)
<i>o</i> -Dichlorobenzene	0.82	2	1.44 (± 0.21)
<i>p</i> -Dichlorobenzene	0.82	2	1.54 (± 0.21)

The diffusion coefficients in water, D_W , at 25 °C are taken from [7].

^a Least-square estimate of data points between 30 and 60 s.

^b Determined at $u = 30.1$ cm/s.

cannot be explained by possible, but certainly small, differences in the hydrodynamic conditions because we followed the original work closely with respect to the dimensions of the vial and the stirrer, the off-centre fibre insertion and the sample volume. The real cause could be differences in the determination of the absolute amounts adsorbed at the fibre and should be addressed in future work under consideration of [8] and consequential application of statistical tests.

From the quantified absolute amount of the analyte trapped with the SPME fibre, m_f , at a certain exposure time t one can estimate the concentration in the sample, c_W , (according to [2]) by the following equation:

$$c_W = \frac{m_f \ln(b + \delta)}{2\pi D_W L t} \quad (3)$$

In Table 2, we have listed the averages of the concentrations, c_W^{av} , estimated with this equation by inserting the m_f values determined after sampling times between 30 and 60 s (at $u = 25.5$ cm/s) and their relative errors, E , with respect to $c_{W(0)} = 500$ $\mu\text{g/l}$. The relative prediction errors are by an order of magnitude higher than reported in [2] and, moreover, analyte-specific and fibre-dependent. (The last aspect was not addressed in the study by Sukola et al. [2]. Nevertheless, it can have some importance for practical applications.) If we exclude our results with fibre 1, E seems to be correlated with the diffusion coefficient of the analyte. However, additional investigations with other initial concentrations and also with other analytes should be performed for drawing definite conclusions.

Table 2

Average of concentration estimates c_W^{av} (calculated from the model with m_f values determined for $u = 25.5$ cm/s and $c_{W(0)} = 500$ $\mu\text{g/l}$ at sampling times between 30 and 60 s) and their relative error, E

Substance	Experiment series (fibre no.)	c_W^{av} ($\mu\text{g/l}$)	E (%)
Benzene	1	224	-55
	2	462	-8
	3	526	+5
Toluene	1	485	-3
	2	563	+13
	3	621	+24
Ethylbenzene	1	528	+6
	2	617	+23
	3	691	+33
<i>p</i> -Xylene	1	611	+22
	2	669	+34
	3	783	+57
Chlorobenzene	2	764	+53
<i>o</i> -Dichlorobenzene	2	882	+76
<i>p</i> -Dichlorobenzene	2	911	+82

3.2. Application of short-term SPME to selected chlorobenzenes from water

Using fibre 2, we extracted chlorobenzene, *o*- and *p*-dichlorobenzene from aqueous test solutions choosing again a constant time of 60 s but different stirrer speeds. We obtained the similar velocity dependence for the amounts extracted as with BTEX (Fig. 3). Also a linear time dependence of fibre uptake was obtained between 30 and 60 s

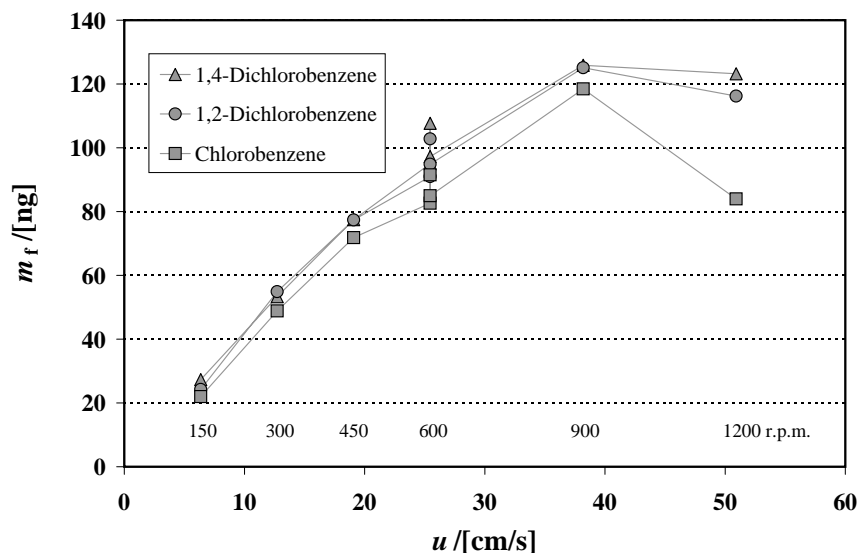


Fig. 3. Extracted amount of selected chlorobenzenes with PDMS–DVB fibre 2 vs. tangential sample velocity ($c_{W(0)} = 500 \mu\text{g/l}$; $t = 60 \text{ s}$).

when the stirrer speed is set to 600 rpm, i.e. with a tangential sample velocity of 25.5 cm/s. The initial uptake rates of the test substances are also contained in Table 1. They are slightly higher than for BTEX. This shows in principle the transferability of the diffusion-based calibration method for SPME to other analytes. But the accuracy of prediction with the model equations is worse compared to BTEX as can be seen in Table 2. Also here, an extended study is required to examine this findings.

3.3. Sensitivity analysis with the parameters of the basic model

By simple spreadsheet calculations (with MS-Excel), we performed a sensitivity analysis with the parameters of the basic model for the diffusion-based calibration of SPME (Eqs. (1)–(3)) which could be afflicted with errors. The variations were carried out in succession and the deviations from the originally predicted concentration was used as the measure of the parameter influence. The upper and lower limits of parameter variations and the resulting concentration deviations are summarised in Table 3. The parameter variations are chosen according to practical experiences for the geometrical dimensions of fibre and vial (b , L , r , R) and based on plausible and relatively broad tolerances for the other parameters. The largest influence is exerted by the boundary layer thickness, δ , followed by the tangential sample velocity at the SPME fibre, u . Both parameters cannot be determined directly but must be estimated by semi-empirical relationships (Eqs. (1) and (2)). The length of the fibre coating, L , is a third important parameter but its influence as a source of error can be eliminated if their measurements are carried out using a microscope. Because of the dominant influence of the boundary layer thickness, we performed some iterative calculations with different δ values to minimize the

Table 3

Sensitivity analysis with the parameters of the basic model (Eqs. (1)–(3)) which could be afflicted with errors

Parameter value	Variation	Δc_W (%)
$b = 0.012 \text{ cm}$	0.011 to 0.013	5 to –5
$L = 1.0 \text{ cm}$	0.9 to 1.1	11 to –9
$N = 10/\text{s}$	9.8 to 10.2	1 to –1
$r = 0.50 \text{ cm}$	0.45 to 0.55	3 to –2
$R = 1.0 \text{ cm}$	0.95 to 1.05	2 to –2
$D_W = 1.16 \times 10^{-5} \text{ cm}^2/\text{s}$	1.06×10^{-5} to 1.26×10^{-5}	6 to –5
$u = 25.5 \text{ cm/s}$	20 to 30	15 to –9
$\delta = 1.17 \times 10^{-3} \text{ cm}$	1.5×10^{-3} to 0.9×10^{-3}	27 to –22

The variations were performed in succession and the deviation from the originally predicted concentration was used as a measure of parameter influence.

error in the concentration predicted with Eq. (3). To achieve this, δ must be set, substance-specifically, to values of 3.3–4.0 μm instead of 10.2–11.7 μm . To include this finding in the basic model, it is necessary to change the exponent on Sc in Eq. (2) from originally 0.38 to 0.5. However, this empirical modification requires verification by additional fibre uptake experiments and hydrodynamic investigations.

4. Conclusions

It has been shown that the mass uptake of the PDMS–DVB fibres depends linearly on the speed of the sample stirring not only for BTEX but also for the tested chlorobenzenes. This confirms in principle the transferability of the diffusion-based calibration method for SPME to other analytes. A serious limitation for future applications can be the questionable fibre-to-fibre comparability of results (in terms of determined mass uptake rates). This issue should

be addressed in a future study. The accuracy of concentration prediction with the diffusion-based calibration model can be improved considerably by a well-founded modification of the semi-empirical relationship for the estimation of the boundary layer thickness, δ . The empirical modification proposed here for Eq. (2) must be confirmed by additional investigations. In addition, it would be desirable to have some experimental observations on the real hydrodynamic flow pattern around a SPME fibre.

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