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Diffusion-Based Calibration for SPME Analysis of Aqueous Samples

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When an SPME fiber is exposed for a short period of time to a flowing fluid sample, the amount of extracted analyte depends on its diffusion coefficient in the matrix medium, and it can be correlated to its concentration using a simple mathematical model. This work discusses the extension of this approach, already validated for gaseous samples and SPME fibers coated with strong adsorbent coatings, to the diffusion-based quantification of analytes present in aqueous samples. Dilute aqueous solutions of aromatic hydrocarbons were used as model samples and vials were modified to use conventional magnetic agitation with controlled tangential flow of the test solution around the fiber. It was demonstrated that, with proper selection of the stirring speed and sampling time, the same diffusion-based quantitative model used for gas samples could be employed. Under optimal conditions, the concentrations of the evaluated aromatic hydrocarbons were estimated with relative standard deviations between 0.8 and 3.6% and without deviation from the expected values within this precision range. Considering the extraction times involved, between 30 and 60 s, the approach here presented is the fastest possible technique for direct extraction of analytes from liquid samples.

The conventional SPME procedure involves exposure of the fiber to the sample or its headspace for a period of time sufficient to reach equilibrium between the analyte sorbed in the fiber coating and dissolved in the sample and subsequent desorption of the extracted material directly in the injector port of the chromatographic system. For large sample volumes, the extracted amount of analyte n is related to its concentration C_0 in the sample according to the simple relation $n = K_{fs}V_f C_0$, where V_f is the volume of the fiber coating and K_{fs} is the fiber/matrix distribution constant.[1] The distribution constant can be estimated either from extractions performed on standard solutions of the analyte or, optionally for gaseous samples, it can be calculated from chromatographic retention data.[2] These simple procedures, however, are not necessarily valid when using SPME fibers coated with mixed porous solid adsorptive coatings, such as Carboxen/PDMS and PDMS/divinylbenzene (PDMS/DVB). For most analytes, the extracted amounts (and consequently the sensitivity) with these fibers are larger when compared to liquid-coated SPME fibers.[3,4] However, the accuracy and precision of quantitative results can be deficient. These problems are related to the competition between the analytes for the adsorptive sites available in the coating and subsequent interanalyte displacement.[5]

In a recent work, Koziel and co-workers[6] postulated that, for flowing gaseous samples, short extraction times, and fibers coated with strong adsorbents, all analyte molecules reaching the fiber surface are immediately adsorbed, since the presence of a large number of nonoccupied adsorptive sites would minimize the competition between the analytes. As a consequence, the interanalyte displacement is reduced or eliminated, and the analyte uptake is controlled by its diffusion through a static boundary layer surrounding the fiber. For gaseous samples flowing with speeds up to 10 cm s^{-1}, it was demonstrated that the extracted amount n of an analyte is related to its concentration C, its diffusion coefficient in the gas phase D_g, the length L and radius b of the fiber, the effective thickness of the static boundary layer δ, and the sampling time t according to

$$C = \frac{n \ln((b + \delta)/b)}{2\pi D_g L t} \quad (1)$$

For higher sample velocities, the analyte mass uptake becomes independent from the speed and constant—i.e., independent from the sample velocity—since it is limited by its diffusion inside the pores of the adsorptive fiber coating. This model was validated and successfully applied to quantification of contaminants in indoor air using short extraction times (30 s) and PDMS/DVB fibers.[7]

Rearrangement of eq 1 leads to

$$n = \frac{2\pi D_g L}{\ln((b + \delta)/b)} Ct \quad (2)$$

Therefore, before equilibrium—where the mass uptake is con-

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(6) Koziel, J.; Jia, M.; Pawliszyn, J. *Anal. Chem.* **2000**, *72*, 5178−5186.
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trolled by analyte diffusion through the boundary layer—the extracted amount increases linearly with the extraction time.

When the direction of the sample flow is tangential to the fiber axis, the thickness of the boundary layer in eqs 1 and 2 can be estimated by the semiempirical relationship[8]

$$\delta = 9.52(b/Re^{0.62}Sc^{0.38}) \quad (3)$$

where Re is the Reynolds number ($Re = 2ub \times v^{-1}$; u is the linear velocity of the sample and v is the kinematic viscosity of the matrix medium) and Sc is the Schmidt number ($Sc = v \times D_g^{-1}$). The equation

$$\delta = 2.64(b/Re^{0.50}Sc^{0.43}) \quad (4)$$

can be used to estimate the boundary layer thickness when the direction of the fluid sample flow is axis-symmetrical around the circumference of the fiber (as when a fiber is placed in the central position of a vial containing a magnetically stirred sample). Mathematical models, such as the one proposed by Fuller et al.[9] for diffusion in air, can be used to estimate the analyte diffusion coefficient, if experimental data regarding this parameter are not available.

This work extends the diffusion-based approach to direct and headspace extractions from aqueous samples for which the corresponding mathematical model for quantitative calculations was examined. Equation 1 was modified for aqueous matrixes, i.e., D_g was replaced with the equivalent parameter D_L—the liquid-phase molecular diffusion coefficient. As for D_g, in the absence of literature data, D_L can be calculated from[10]

$$D_L = 1.326 \times 10^{-6}/(\eta_W^{1.14}V'_B{}^{0.589}) \quad (5)$$

where η_W is the kinematic viscosity of water and V'_B is the molar volume of the analyte.

EXPERIMENTAL SECTION

Materials. *Chemicals and Supplies.* All chemicals were of analytical grade and used as supplied: benzene, toluene, ethylbenzene, and *p*-xylene (Sigma-Aldrich, Mississauga, ON, Canada) and methanol (BDH, Toronto, ON, Canada). Special caution should be exercised when working with these chemicals, since benzene is listed as known to be human carcinogen, and exposure to toluene, ethylbenzene, *p*-xylene, and methanol can result in adverse health effects and safety hazards. The SPME holder and 65-μm PDMS/DVB fibers were obtained from Supelco (Oakville, ON, Canada); the fibers were conditioned at 210 °C for 8 h prior to their use.

Sample Vials. To provide appropriate control of the velocity of the sample flowing around the fiber during the extractions using conventional magnetic stirring, the extractions were performed using 40-mL silicone-septum capped vials (Supelco) modified as shown in Figure 1. A special aluminum insert was placed between the hollow plastic cap and the septum. The SPME fiber can be introduced in the vial through narrow holes drilled in this insert, allowing accurate and precise positioning of the fiber during the extraction. The velocity u of the sample flowing around the fiber can be calculated according to[8]

$$u = 1.05\pi Nr[2 - (r/0.74R)^2] \quad (6)$$

where N is the magnetic stirrer speed in revolutions per second, r is the distance between the fiber and the center of the vial, and R is the radius of the stirring bar. Therefore, sample velocity at the fiber location can be varied by changing either the stirrer speed or the position of the fiber in the vial. Using a 1-in. Teflon-coated stirring bar (R = 1.27 cm) and a model 400S magnetic stirrer (VWR Scientific, West Chester, PA), stable agitation can be achieved with water velocities up to 75.2 cm s^{-1}, corresponding to a stirring speed of 1500 rpm with the fiber positioned at r = 0.55 cm from the center of the vial.

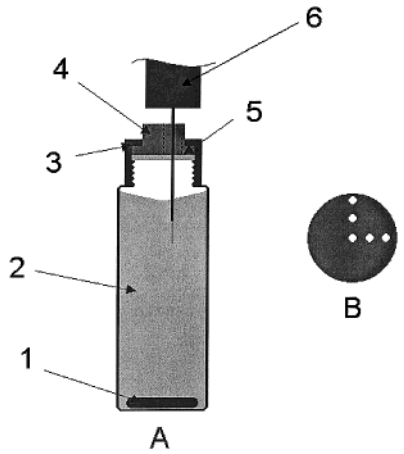

Figure 1. Modified sample vial. (A) side cut view: (1) 1-in. Teflon-coated stirring bar; (2) 40-mL glass sample vial; (3) polyethylene hollow cap; (4) aluminum insert; (5) Teflon-faced silicone septa; (6) SPME holder and & fiber. (B): aluminum insert, upper enlarged view, showing the holes for insertion of the SPME fiber.

Gas Chromatography. Analyses were carried out with a Varian Star 3400 GC-FID chromatograph equipped with a 30 m × 0.25 mm × 0.25 μm Supelco SPB-5 column and SPI; 2.0 mL min^{-1} helium at 20 psi was used as the carrier gas. The temperatures were set at 250 °C for the FID and 210 °C for the SPI, and the column oven program for all injections was as follows: 1 min hold at 60 °C, followed by a 15 °C/min ramp until 180 °C, and hold there for 3 min.

Test Solutions. For all extractions, aqueous solutions containing 500 μg L^{-1} of each aromatic hydrocarbon listed above were prepared from methanolic stock solutions by direct spiking of deionized water in the sample vials.

Methods. *Direct Liquid Extractions.* The above listed aromatic hydrocarbons solutions were extracted with PDMS/DVB fibers. Extractions were performed with magnetic stirring speeds ranging from 300 to 1500 rpm and extraction times ranging from 10 s to 15 min. Two different positions of the fiber in the aluminum insert of the modified vial were used, i.e., the center and 0.55 cm from the center. The extracted analytes were desorbed and analyzed immediately after the extraction. For these procedures, the vials

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(9) Fuller, E. N.; Schettler, P.; Giddings, J. C. *Ind. Eng. Chem.* **1966**, *58*, 19−27.
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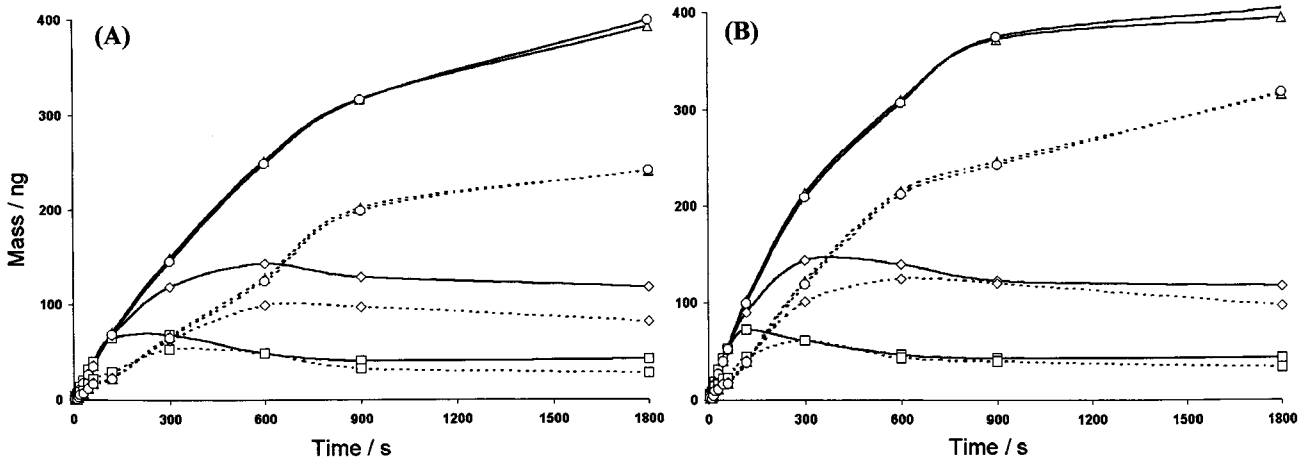

Figure 2. Extraction time profile of aromatic hydrocarbons in aqueous solution at 500 μg L^{-1} with a PDMS/DVB and stirrer speed of 600 (A) and 1200 rpm (B). Dashed line, fiber in the center of the vial (A, $u = 0.79$ cm s^{-1}; B, $u = 1.58$ cm s^{-1}); solid line, fiber 0.55 cm from the center of the vial (A, $u = 30.1$ cm s^{-1}; B, $u = 60.1$ cm s^{-1}); benzene, □; toluene, ◇; ethylbenzene, △; and *p*-xylene, ○.

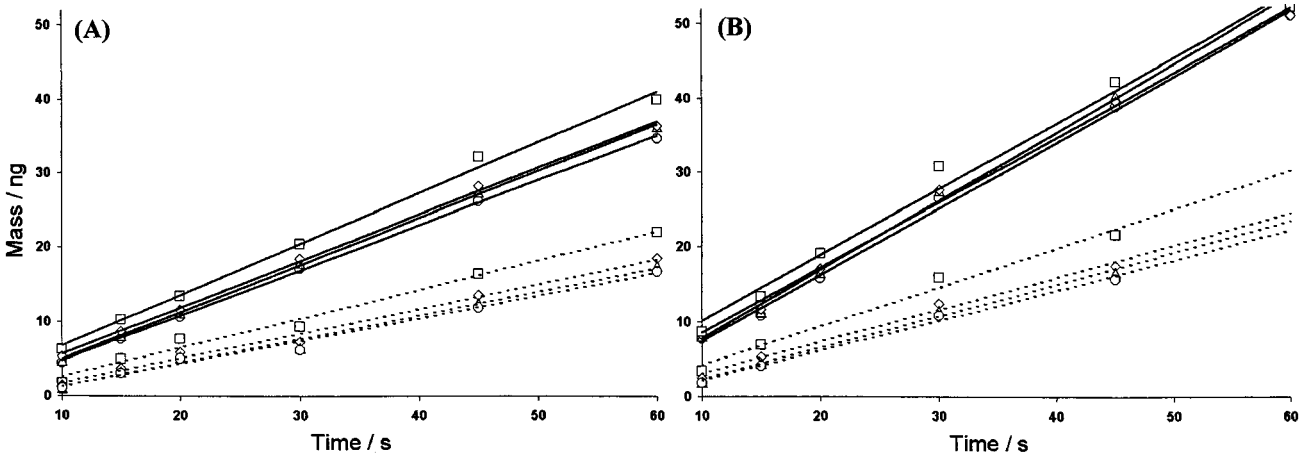

Figure 3. Linear section of the extraction time profile of aromatic hydrocarbons in aqueous solution at 500 μg L^{-1} with a PDMS/DVB and stirrer speed of 600 (A) and 1200 rpm (B). Dashed line, fiber in the center of the vial (A, $u = 0.79$ cm s^{-1}; B, $u = 1.58$ cm s^{-1}); solid line, fiber 0.55 cm from the center of the vial (A, $u = 30.1$ cm s^{-1}; B, $u = 60.1$ cm s^{-1}); benzene, □; toluene, ◇; ethylbenzene, △; and *p*-xylene, ○.

were completely filled with the test solution, eliminating any headspace left in the vials, to avoid evaporative losses of analytes that could lead to misinterpretation of the results.

Headspace Extractions. The same procedure as described above was employed for headspace extractions where only 10 mL of the test solution in the same modified 40-mL vials was used for each sample.

RESULTS AND DISCUSSION

Extraction Time Profiles for Direct Extraction. Figure 2 shows the extraction time profiles obtained for direct extraction of the aqueous solutions of aromatic hydrocarbons with different stirring and fiber positioning conditions. It can be seen that for benzene and toluene there is an increase in the extracted amounts with extraction time until a maximum is attained; further increments of time lead to reduction in the extracted masses. For ethylbenzene and *p*-xylene, a different behavior was observed; i.e., the extracted masses increased continuously without reaching any visible maximum within the time range evaluated. This pattern is consistent with what would be expected for application of solid porous polymer-coated fibers such as PDMS/DVB to samples containing mixtures of analytes.[5] Analytes present in high concentrations (500 μg L^{-1}) and with higher affinities for the adsorptive coating, such as ethylbenzene and *p*-xylene, tend to displace other substances less strongly adsorbed, such as benzene and toluene. As discussed previously, this fact prevents the use of the equilibrium conditions for quantification with such fibers.

Visual inspection of the extraction profiles also shows that, for short extraction times, the relation between extracted mass and time is linear, as would be expected from eq 2. Figure 3 shows the profiles for extraction times up to 60 s and Table 1 lists the slopes of the extraction curves, as well as their correlation coefficients. For all analytes and evaluated combinations of stirring speed and fiber position, the extraction time profile is linear, as predicted by eq 2. The values of the correlation coefficients for the linear curves in the time interval up to 60 s range from 0.993 to 1.000 showing good fitting. Additionally, considering that the extraction rate is controlled by the diffusion of the analytes through a static boundary layer, the slopes of the extraction curves—corresponding to the mass uptake rate a—should be proportional to the liquid-phase diffusion coefficient D_L for each analyte. Figure 4 shows plots of the mass uptake rates obtained from the linear range of the extraction profiles as a function of

Table 1. Mass Uptake Rates a (in ng s^{-1}) and Correlation Coefficients r of the Corresponding Mass × Time Curves as Function of the Sample Speed u (in cm s^{-1}) and Diffusion Coefficient of the Analyte D_L, (in 10^{-6} cm^2 s^{-1}

	benzene		toluene		ethylbenzene		*p*-xylene	
u	a	r	a	r	a	r	a	r
0.79	0.39	0.994	0.33	0.995	0.32	0.994	0.30	0.994
1.58	0.52	0.993	0.43	0.995	0.42	0.996	0.40	0.997
30.1	0.68	0.998	0.63	0.999	0.63	1.000	0.60	1.000
60.1	0.88	0.994	0.87	0.998	0.92	0.999	0.88	0.999
D_L	10.3		9.1		8.2		8.2	

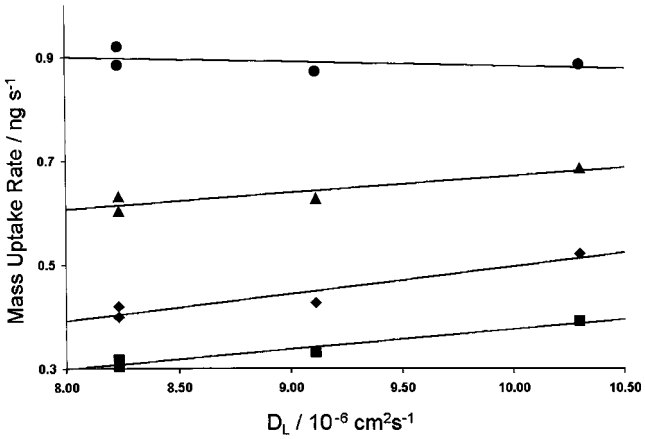

Figure 4. Dependence of the mass uptake rate a of aromatic hydrocarbons on the analyte diffusion coefficient in water D_L: u = 0.79 (■), 1.58 (◆), 30.1 (▲), and 60.1 cm s^{-1} (●).

the water liquid-phase diffusion coefficient of the analytes at different sample speeds. Except for the highest sample speed tested, i.e., u = 60.1 cm s^{-1} that is equivalent to a stirring speed of 1200 rpm and to the fiber positioned at 0.55 cm from the center of the vial, the mass uptake rate increases from the lowest for ethylbenzene and *p*-xylene ($D_L = 8.2 \times 10^{-6}$ cm^2 s^{-1}) to the highest for benzene ($D_L = 1.03 \times 10^{-5}$ cm^2 s^{-1}), as expected according to the model.

For u = 60.1 cm s^{-1}, the mass uptake rate tends to become constant and equal to 0.89 ± 0.02 ng s^{-1}; therefore, the simple model correlating adsorbed masses with concentrations described by eqs 1 and 2 cannot be applied. A possible explanation for this phenomenon can be related to the localized displacement effect theoretically discussed by Semenov et al.[11] The process of adsorption by a porous polymer-coated fiber can be considered to involve three steps—diffusion of the analyte through the matrix boundary layer, initial adsorption over the surface of the coating, displacement by the stronger bonding analytes, and migration of the analyte to the interior of the pores, where it is adsorbed by the active sites. The sample velocity causes a significant decrease of the thickness of the boundary layer (e.g., for *p*-xylene and ethylbenzene it decreases from 45 μm, for u = 1 cm s^{-1}, to 3.1 μm, for u = 75 cm s^{-1}). In these conditions, the first step of the adsorptive process (diffusion of the analyte through the boundary layer) can be assumed to be faster than the migration of the

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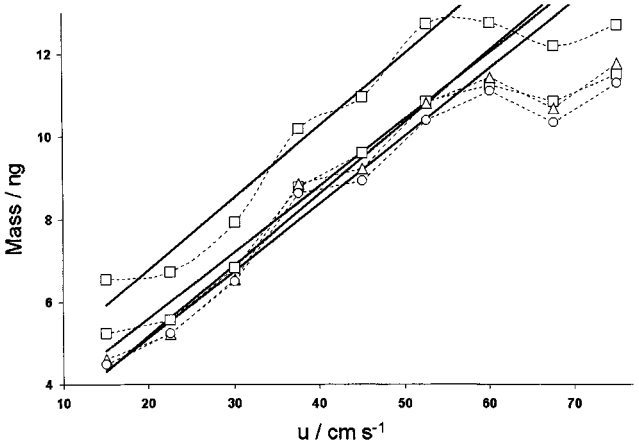

Figure 5. Effect of the sample velocity over the extracted masses of aromatic hydrocarbons in aqueous solution at 500 μg L^{-1} with a PDMS/DVB fiber and 10-s extraction time: benzene, □; toluene, ◇; ethylbenzene, Δ; and *p*-xylene, O.

molecules to the interior of the pores (third step of the process). Molecules of analytes with smaller affinity to the coating, such as benzene, can be displaced from the surface of the coating by strongly adsorbable substances such as *p*-xylene before having the opportunity to migrate to the interior of the pores. Previous observations support this hypothesis,[6] suggesting that use of coatings such as Carboxen (with larger adsorptive capacity and smaller pores) and shorter sampling times could reduce or eliminate this problem associated with very high sample velocities.

Effect of Sample Velocity in the Direct Extraction. To assess the limit of velocity where the diffusion-based extraction model is valid, 10-s extractions with sample velocity ranging from 15.0 to 75.2 cm s^{-1} were performed and the results obtained are shown in Figure 5. It can be seen that an increase in the sample velocity up to ∼50 cm s^{-1} causes an increase in the extracted mass for all analytes, as would be expected for diffusion-controlled mass uptake. This increase can be attributed to the reduction of the thickness of the boundary layer with the velocity, caused by the change in the Reynolds number used in eqs 3 and 4. For higher velocities, the extracted mass becomes much less dependent on the sample velocity and constant—further increments in the sample velocity do not cause a corresponding increase in the amount of analyte extracted per time unit. In these conditions, the diffusion of the analyte through the pores of the solid coating becomes the limiting factor in the mass uptake by the fiber,[6] as mentioned in the previous paragraph. For very high analyte concentration, saturation of the polymer might occur for longer extraction times and/or high matrix velocities, which will result in a decrease of the amount of extracted analyte by the fiber compared to predicted values.

Validation of the Diffusion-Based Model for Direct Extraction. The applicability of eq 1 to quantitative analyzes was evaluated by using it to calculate the concentrations of the aromatic hydrocarbons at several sample velocities and extraction times from 10 to 60 s. These estimates of concentrations are shown in Table 2. The model tends to underestimate the concentration of the aromatic hydrocarbons for slow sample velocities (0.79 and 1.58 cm s^{-1}) and also for sampling times up to 20 s. In these conditions, i.e., small sample velocities and/or very short extraction times, the errors can have experimental origin and could be

Table 2. Concentration Estimates of Aromatic Hydrocarbons in Water (in μg L^{-1}) as a Function of the Sample Speed u and Sampling Time t, Average Concentrations C_{av} (in μg L^{-1}), Relative Error of the Average Concentrations E, and Relative Estimate of Standard Deviation s_r

	$u = 0.79$ cm s^{-1}				$u = 1.58$ cm s^{-1}			
t (s)	B[a]	T	E	X	B	T	E	X
10	245	229	172	172	358	280	229	213
15	475	380	353	340	483	397	354	326
20	558	460	435	417	519	433	406	379
30	455	378	358	344	556	468	457	432
45	534	473	460	443	502	436	440	416
60	536	483	484	467	394	339	343	327
C_{av}[b]	508	445	434	418	484	414	413	392
E (%)[b]	1.7	−11.1	−13.1	−16.4	−3.2	−17.1	−17.3	−21.6
s_r (%)[b]	9.1	13.1	15.4	15.6	17.1	16.3	14.9	14.4

	$u = 30.1$ cm s^{-1}				$u = 60.1$ cm s^{-1}			
t (s)	B	T	E	X	B	T	E	X
10	461	418	398	381	266	266	269	259
15	505	460	455	436	276	253	253	243
20	497	464	476	454	295	276	278	266
30	505	493	509	487	317	298	309	297
45	527	500	517	494	290	285	302	290
60	492	483	513	491	268	275	298	286
C_{av}	508	492	513	491	292	286	303	291
E (%)	1.6	−1.6	2.6	−1.8	−41.6	−42.8	−39.5	−41.7
s_r (%)	3.6	1.7	0.8	0.8	8.4	4.1	1.8	1.9

[a] B, benzene; T, toluene; E, ethylbenzene; X, *p*-xylene. [b] Average concentrations, errors, and estimates of standard deviation calculated for the range between $t = 30$ s and $t = 60$ s.

attributable to variations either in the exact position of the SPME fiber inside the vial or in the extraction time (which was measured manually). In the case where the fiber is placed in the center of the vial, a small deviation in its position can cause a large relative deviation in the sample velocity. For very fast sampling, it could be also considered that there is not enough time to the complete wetting of the fiber coating. Furthermore, since the mathematical dependence described for eq 1 relies on the existence of a laminar flow of sample around the fiber,[6] these errors could be caused by perturbations in the flow lines caused by the introduction of the SPME fiber. For $u = 60.1$ cm s^{-1}, all concentrations are also underestimated. This was expected since this velocity is greater that the limit of ~50 cm s^{-1} previously mentioned. For a sampling velocity of 30 cm s^{-1} (which is within in the range of applicability of the diffusion-based model) and sampling times between 30 and 60 s, concentrations can be accurately estimated using eq 1. The differences between the average experimental values and the predicted concentration (500 μg L^{-1}) ranged from −1.8 to +2.6%.

The precision (defined as the relative standard deviation of the concentrations in the range) ranged from 0.8 to 3.6% for the same data subset. This precision is comparable to conventional SPME and satisfactory for analytical work. The sensitivity for very short sampling times is reduced when compared to equilibrium techniques. This can be illustrated by the extraction time profiles for 30-s sampling shown in Figure 2 where the extracted amount is 5−35% of the maximum possible when equilibrium is reached, depending in the analyte and experimental conditions. However,

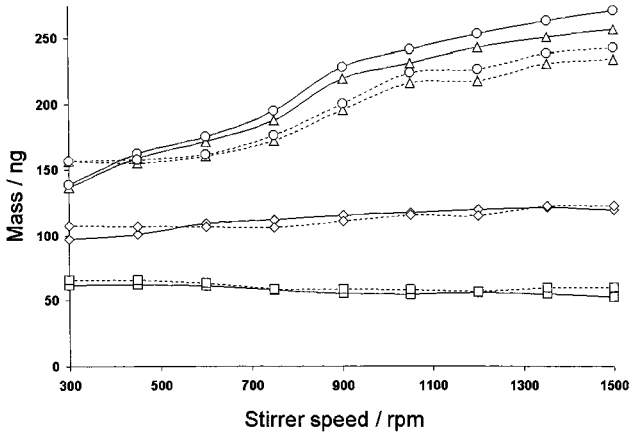

Figure 6. Dependence of the extracted masses of aromatic hydrocarbons on the stirring speed for headspace extractions. Dashed line, fiber in the center of the vial; solid line, fiber 0.55 cm from the center of the vial; benzene, □; toluene, ◇; ethylbenzene, △; and *p*-xylene, O.

this approach has several advantages, e.g., reduction or elimination of interanalyte displacement effects, that can compensate for this loss of sensitivity.

Headspace Extraction. Figure 6 illustrates variations of the extracted masses in the headspace of a 500 μg L^{-1} aqueous solution of aromatic hydrocarbons with the stirring speed, using an extraction time of 10 s and different positions of the SPME fiber inside the vial. For benzene and toluene, the extracted amount remained constant with the stirring speed and fiber position. For other analytes, i.e., ethylbenzene and *p*-xylene, an increase in the extracted mass for greater stirring speeds was observed. For these substances, only a slight increase of the amount extracted also occurs when the fiber is placed 0.55 cm away from the center of the vial. The evaluation of these results should take into account that, for the headspace extraction, two distinct mass-transfer steps are occurring simultaneously, i.e., from the liquid phase to the headspace and from the headspace to the fiber. Since the extracted masses are similar for benzene and toluene, it indicates that the variations in the stirring speed of the sample matrix do not generate an equivalent variation in the convection currents in the headspace. For more volatile analytes, which are characterized by high Henry's law constant, the relative independence of the extracted masses with increase of the agitation speed indicates that the capacity of the headspace is high compared to the fiber capacity and the diffusive process is fast enough to prevent depletion of the headspace even at small stirring speeds.

However, the increase in the extracted masses observed for the less volatile analytes with increasing stirring speeds indicates that the mass transfer at the sample matrix/headspace interface is similar to the mass transfer at the matrix/fiber interface. The mass-transfer rates of ethylbenzene and *p*-xylene are controlled by their diffusion through the boundary layer present at the water/headspace interface. It is interesting to note that there is a statistically significant difference between position of the fiber in the headspace and amount of ethylbenzene and *p*-xylene extracted. When the fiber is located in the vicinity of faster moving sample matrix (away from the vial center), the amount extracted is higher compared to the center position. These data indicate that, during

extraction, the analyte concentration is substantially depleted in the vicinity of the fiber. Thinner diffusion boundary layer present in off-center position facilitates faster mass transport of analytes and more effective elimination of the depletion compared to the center position.

CONCLUSIONS

This work demonstrated that, using a very simple apparatus (a modified glass vial and a standard magnetic stirrer), diffusion-based calibration can be applied to SPME analysis of aqueous samples. Careful choice of experimental conditions, i.e., sample velocity and extraction time, allows the quantification of aromatic hydrocarbons. Good accuracy and precision should result when extraction times as short as 30−60 s are used. Such accurate results could not be obtained using conventional equilibrium or long preequilibrium SPME analysis with solid polymers, due to interanalyte displacement effects.[5,6] In addition, there is no need for calibration curves since the concentration of the analytes can be directly calculated by applying the mathematical model described in the introduction. This requires that constants such as the diffusion coefficients are known or calculable. The use of stronger adsorbent fibers such as Carboxen can also partially compensate for the loss of sensitivity by using longer extraction times. Also, the possibility of using very short extraction times and elimination of need of calibration makes this approach particularly suitable for field use, if coupled to a portable GC for the separation and detection of the analytes.[12]

It should be pointed out that the approach shown here provides the fastest possible methodology to perform direct extractions from aqueous solutions. In addition, although this concept of diffusion-based extraction was tested and validated for SPME, it is reasonable that it could be easily extended for application to other analogous sample preparation techniques, as single-drop microextraction,[13] in-tube SPME,[14] and others.

According to the eq 2, sensitivity of the technique is dependent on the agitation speed (that should be constant and within the range mentioned in Effect of Sample Velocity in the Direct Extraction above) and the contact area between the extraction phase and the sample matrix. This fact should be taken in account for the application of the technique and designing fast sampling devices based on this principle. In some situations, e.g., determination of contaminants in natural water streams, the sample may be already flowing at a speed adequate to the application of the technique and a simple exposure of the fiber to the water stream for a controlled period of time would be enough to perform the diffusion-based quantification. The flow velocity can be measured and corrected for in the final result. For static aqueous samples or in conditions where a natural flow is not constant or measurable, it would be necessary to design field agitation devices that are able to generate well-controlled flow velocities or collect an aliquot in a sealed vial and expose the fiber to the sample using some positioning device, such as that described in Figure 1, which would provide a constant flow of water around the fiber. The arrangement shown in this figure presents the simplest approach to render such a controlled sample velocity. However, the use of devices where the sample is driven by propeller or simple peristaltic pumps as those employed in flow injection analysis could be also considered. The design and testing of these alternative projects are presently being carried out.

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