

# Absorption of Hydrophobic Compounds into the Poly(dimethylsiloxane) Coating of Solid-Phase Microextraction Fibers: High Partition Coefficients and Fluorescence Microscopy Images

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**The use of solid-phase microextraction with poly(dimethylsiloxane) (PDMS)-coated glass fibers for the extraction and analysis of hydrophobic organic analytes is increasing. The literature on this topic is characterized by large discrepancies in partition coefficients and an uncertainty of whether highly hydrophobic analytes are retained by absorption into the fiber coating or by adsorption to the fiber surface. We applied a new method, which minimizes the impact of experimental artifacts, to determine PDMS water partition coefficients of 17 hydrophobic analytes including chlorinated benzenes, PCBs, PAHs, and *p,p'*-DDE. These partition coefficients are several orders of magnitude higher than some reported values. Two observations strongly suggest that the retention of hydrophobic organic substances is governed by partitioning into the PDMS coating. (1) The partition coefficients are proportional with octanol/water partition coefficients. (2) The fluorescence of fluoranthene was observed to be homogeneously distributed within the polymer coating when studied by means of fluorescence microscopy. Implications of these findings for the application of solid-phase microextraction with respect to potential detection limits, with respect to biomimetic extraction, and with respect to measurements in multicompartiment systems are discussed.**

Solid-phase microextraction (SPME) was introduced in 1990 by Arthur and Pawliszyn<sup>1</sup> as an analytical technique that utilizes a small segment of fused-silica fiber with polymer coating for extraction of analytes and for the subsequent introduction to a chromatographic system. SPME has since then increasingly been used for a wide range of analytical applications, particularly for the determination of aqueous analyte concentrations. Most applications are based on the extraction of a constant analyte fraction from aqueous sample using internal or external calibration for quantification. Recently, solid-phase microextraction has been

applied to measure dissolved rather than total concentrations,<sup>2–4</sup> for the biomimetic extraction of complex mixtures<sup>5–7</sup> and to study analytes binding to protein, humic acids, or algal exudates.<sup>4,8,9</sup> These applications require a thorough understanding of the working principle of solid-phase microextraction with regard to sorption kinetics, the sorption mechanism, and the distribution coefficients ( $K_{\text{polymer, water}}$ ) between the sample and the polymer coating of the SPME fiber.

A substantial number of articles have been devoted to enhancing our understanding of the working principle of SPME. Nevertheless, no consensus has been reached on whether hydrophobic organic substances such as chlorinated benzenes, PCBs, and PAHs are retained by the polymer through surface adsorption<sup>10</sup> or through uptake into the coating.<sup>11</sup> It is further controversial whether distribution coefficients  $K_{\text{polymer, water}}$  of hydrophobic organics do increase with increasing hydrophobicity<sup>7,8</sup> or decrease with increasing molecular weight.<sup>10</sup> Improper procedure is according to Gorecki and Pawliszyn<sup>12</sup> the main cause for such discrepancies, which are most pronounced for very hydrophobic compounds (e.g., PCBs and PAHs) with high

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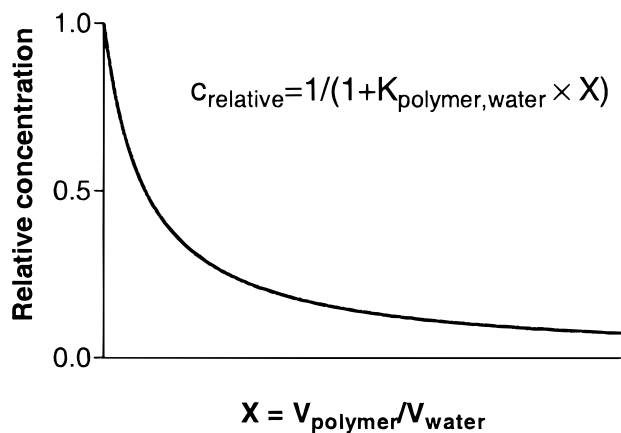


Figure 1. Decrease in aqueous concentration as a function of the added amount of SPME fiber.  $K_{\text{polymer,water}}$  is estimated by regression within a range of phase ratios ( $V_{\text{polymer,water}}/V_{\text{water}}$ ).

affinities to the fiber coating. These semivolatiles are difficult to dissolve in water and also difficult to keep in true solution, which can give rise to experimental artifacts if care is not taken. Gorecki and co-workers<sup>13</sup> concluded, therefore, that “there seems to be a pressing need to develop improved methodologies for the determination of partition coefficients of semi-volatile compounds in water”.

The aim of the first part of this paper is to determine partition coefficients for very hydrophobic and semivolatile chemicals using a methodology that was designed to minimize the influence of experimental artifacts:

Partition experiments were performed in large flasks (1 L) as has been recommended for substances with high partition coefficients.<sup>12</sup> No Teflon was used, because it has been reported to sorb PCBs.<sup>14</sup> Partition experiments were performed at a wide range of fiber to water-phase ratios, which for each analyte includes the “robust” region at which 20–80% of the total amount is retained by the fiber. Relative aqueous concentrations were determined by conventional SPME on aqueous subsamples of flasks with and without fiber addition. Finally, partition coefficients were obtained by nonlinear regression of the aqueous concentration as a function of the added amount of fiber as illustrated in Figure 1. The fiber in the large bottle was the “object” of this experiment, whereas the fiber for the conventional SPME was used as a “sensor”. This separation of object and sensor is in contrast to most studies, where partition coefficients of a SPME fiber are based on the amount that was extracted by and thermally desorbed from that same fiber (object = sensor).

The aim of the second part of this paper is to investigate whether the sorption of hydrophobic organics is due to adsorption onto the fiber coating or due to absorption into the fiber coating. Yang and co-workers<sup>10</sup> concluded that surface adsorption is the primary mechanism controlling the partitioning of PCBs (and likely other higher molecular weight solutes) from water to SPME sorbents. Their conclusion was based on the observation that apparent partition coefficients decreased with increasing molecular volume and with increasing coating thickness. To obtain more direct evidence for the sorption mechanism, we generated

fluorescence microscopy images of SPME fibers that were exposed to fluoranthene, which fluoresces blue when excited in the UV range. We made these images of SPME fiber cross sections, because a homogeneous distribution of the fluorescence within the polymer coating would point to absorption.

## EXPERIMENTAL SECTION

**Measuring SPME Water Partition Coefficients.** An acetone spiking solution with the following substances of analytical grade was prepared: pentachlorobenzene, hexachlorobenzene, *p,p'*-DDE, phenanthrene, fluoranthene, 2,2',5,5'-PCB (No. 52), 2,3,5,6-PCB (No. 65), 2,2',4,5,5'-PCB (No. 101), 2,3,3',4,4'-PCB (No. 105), 2,3,3',5,6-PCB (No. 112), 2,3',4,4',5-PCB (No.118), 2,2',3,4,4',5'-PCB (No. 138), 2,2',4,4',5,5'-PCB (No. 153), 2,2',4,4',5,6'-PCB (No. 154), 2,2',4,4',6,6'-PCB (No. 155), 2,3,3',4,4',5-PCB (No. 156), and 2,2',3,4,4',5,5'-PCB (No. 180) (PCB numbering according to IUPAC). Ten liters of Millipore water was spiked with 2 mL of the spiking solution to obtain individual concentrations of about 100 ng/L, and this solution was agitated for 24 h before use.

Poly(dimethylsiloxane) (PDMS)-coated glass fiber was obtained from Fiberguide Industries (Stirling, NJ) with a glass core diameter of 200  $\mu\text{m}$  and a coating thickness of 15  $\mu\text{m}$  (15  $\mu\text{m}$  PDMS fiber). The volume of the polymer coating was calculated to be 10.1  $\mu\text{L}$  of PDMS/m of fiber. The fiber was cleaned by two methanol washes of 10 min and two washes with Millipore water. The fiber was then cut into pieces ranging from 0.010 to 3.00 m, and these pieces were added to eight thoroughly rinsed 1 L bottles and two 100 mL bottles. A total of 900 and 90 mL of the spiked water was added to each bottle, respectively, and the resulting PDMS to water volume ratios were 0.11, 0.34, 1.1, 3.4, 11, 34, 113, and 338  $\mu\text{L}$  of PDMS/L. These flasks and one control flask without fiber (control solution) were closed with aluminum-lined caps and placed on a one-dimensional shaker at about 40 strokes/min and at a controlled room temperature of 25  $^{\circ}\text{C}$ .

**SPME Analysis.** After 3 days and again after 6 weeks, aqueous subsamples of 12 mL were transferred to 12 mL autosampler vials. Aqueous concentrations in these vials were measured by solid-phase microextraction using 7  $\mu\text{m}$  PDMS fibers from Supelco (Bellefonte, CA). These fibers were exposed to the samples for 10 min using a Varian 8200 CX autosampler (Varian, Palo Alto, CA) in the agitation mode, and they were subsequently thermally desorbed for 15 min at 250  $^{\circ}\text{C}$  in the splitless injector of a Varian 3400 CX gas chromatograph. The injector was programmed to return to the split mode after 15 min of desorption. The desorbed analytes were focused at 50  $^{\circ}\text{C}$  for 15 min on a 15 m  $\times$  0.25 mm fused-silica DB5.625 column (J&W Scientific, Folsom, CA) with a 0.25  $\mu\text{m}$  film thickness. The oven was heated at a rate of 30  $^{\circ}\text{C}/\text{min}$  to 100  $^{\circ}\text{C}$ , 5  $^{\circ}\text{C}/\text{min}$  to 175  $^{\circ}\text{C}$ , and 10  $^{\circ}\text{C}/\text{min}$  to 300  $^{\circ}\text{C}$ , where it was maintained for 5 min. Analytes were detected by means of full-scan (100–400  $m/z$ ) mass spectrometry, using a Varian Saturn 2000 ion trap (multiplier voltage 1600 V, AGC target value 15 000). Analytes were quantitated using the three most abundant  $m/z$  ratios, except for phenanthrene and fluoranthene, where only the molecular ion was used. Peak areas fell within the linear range of the GC and no statistically significant intercept was found, as confirmed by a five-point calibration using a hexane standard solution and Graphpad Prism v. 2.01 (San Diego, CA) for the linear regression.

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During the SPME analysis, every subsample was preceded by a subsample of the control solution (without fiber). Relative concentrations ( $C_{\text{relative}}$ ) were calculated as the ratio between the GC peak area of the sample and of the preceding control sample.

**Data Analysis.** Partition coefficients were derived by nonlinear regression of relative concentrations ( $C_{\text{relative}}$ ) as a function of different phase ratios ( $V_{\text{PDMS}}/V_{\text{water}}$ ),

$$C_{\text{relative}} = \frac{1}{1 + 10^{\log(K_{\text{PDMS,water}})} (V_{\text{PDMS}}/V_{\text{water}})}$$

where  $V_{\text{PDMS}}$  and  $V_{\text{water}}$  are the volumes of the fiber coating and the aqueous phase, respectively. The partition coefficients  $K$  are represented as  $10^{\log K}$ , since we expected  $\log K$  rather than  $K$  to be symmetrically distributed and in order to obtain symmetric standard error intervals for values of  $\log K$ . Regressions were performed with Graphpad Prism v. 2.01 by least squares using  $1/C_{\text{relative}}^2$  as a weight factor. Regressions were based on four to eight data points. Relative concentrations at high PDMS addition for the most hydrophobic analytes could not be obtained due to detection limits, and data points at low PDMS addition for the less hydrophobic analytes were not included since we expected them to add more error than information to the regression.

Octanol/water partition coefficients ( $K_{\text{OW}}$ ) were all taken from De Bruijn and co-workers.<sup>15</sup> They were experimental values derived by the slow stirring method for pentachlorobenzene, hexachlorobenzene, *p,p'*-DDE, phenanthrene, and fluoranthene.  $K_{\text{OW}}$  values for the PCBs were estimated by a linear regression according to De Bruijn et al.,<sup>15</sup> which is based on  $K_{\text{OW}}$  values (slow stirring) of 20 PCBs and their chlorine number ( $N_{\text{Cl}}$ ):  $\log K_{\text{OW}} = 0.45N_{\text{Cl}} + 4.36$  ( $n = 20$ ,  $r^2 = 0.935$ ,  $s = 0.29$ ).

**Fluorescence Microscopy.** One liter of magnetic stirred Millipore water was spiked with fluoranthene at 40  $\mu\text{g/L}$  using 500  $\mu\text{L}$  of methanol as carrier. The fibers that were used in the partition experiments and fibers from Polymicro Technologies (Phoenix, AR) with a glass core diameter of 150  $\mu\text{m}$ , a silica cladding of 7.5  $\mu\text{m}$  (diameter 165  $\mu\text{m}$ ), and a PDMS coating of 42.5  $\mu\text{m}$  (diameter 250  $\mu\text{m}$ ) were both cut into 100 mm pieces and cleaned in methanol. These fibers were exposed to the fluoranthene solution for minutes to hours. Cleaned fibers that were not exposed to fluoranthene served as controls.

After exposure, the fibers were cut with a razor blade and were immediately studied on a Zeiss Axioskop fluorescence microscope (Oberkochen, Germany) equipped with the photunit MC100. Short fiber pieces of less than 20 mm were vertically inserted into an agar block that was placed on an object glass. The agar surface was wetted with a few microliters of water, and the fiber pieces were gently pushed into the agar by placing a cover slip on the agar block. These specimens were excited from above at an excitation wavelength of 365 nm (slit width 12 nm) for the fluorescence images, and broad spectrum transmission light was supplied from below through the agar for the bright-field images. All photos were taken with a Fuji Superia 400 film and a 25 $\times$  (oil) objective.

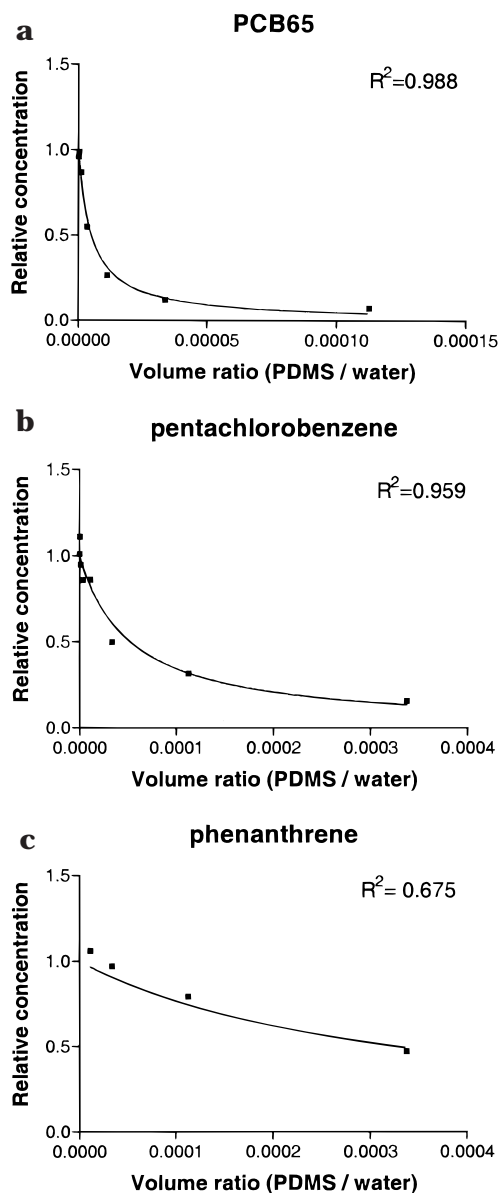


Figure 2. Relative aqueous concentrations after 3 days of contact time plotted against the added amount of SPME fiber. Three representatives were selected on the basis of their  $r^2$  values. The highest  $r^2$  was obtained for PCB 65 (panel a), the median  $r^2$  for pentachlorobenzene (panel b), and the lowest  $r^2$  for phenanthrene (panel c).

## RESULTS AND DISCUSSION

**SPME Water Partition Coefficients.** The reduction of aqueous concentrations by the added amounts of PDMS-coated fiber is shown in Figure 2. We selected three regressions from the 3-day series: phenanthrene with the lowest  $r^2$  (0.68), pentachlorobenzene with the median  $r^2$  (0.96), and PCB 65 with the highest  $r^2$  (0.99). Such regressions were the bases for the calculations of partition coefficients ( $K_{\text{PDMS,water}}$ ) after 3 days and after 6 weeks of exposure (Table 1). A 6-week partition coefficient could not be obtained for phenanthrene due to analytical interference.

$K_{\text{PDMS,water}}$  values obtained at the two measurement times were generally similar, except for the most hydrophobic substances. Partition coefficients of the hexachlorinated PCBs were in average 0.34 log unit higher after 6-week exposure in comparison with the 3-day exposure; and the partition coefficient of the heptachlo-

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Table 1. PDMS/Water Partition Coefficients

compound	log $K_{OW}^a$	log $K_{PDMS,water}$			
		present study, 15 $\mu\text{m}$		Yang et al. <sup>10</sup>	
		3 days	6 weeks	7 $\mu\text{m}$ , 5 h	100 $\mu\text{m}$ , 24h
phenanthrene	4.47 <sup>a</sup>	3.48 ± 0.09			
fluoranthene	5.16 <sup>a</sup>	4.09 ± 0.04	4.26 ± 0.20		
PeClBz	5.18 <sup>a</sup>	4.28 ± 0.04	4.27 ± 0.09		
HxCIBz	5.73 <sup>a</sup>	4.77 ± 0.04	4.75 ± 0.04		
PCB 52	6.16 <sup>b</sup>	5.30 ± 0.07	5.38 ± 0.11	4.67	3.87
PCB 65	6.16 <sup>b</sup>	5.30 ± 0.06	5.35 ± 0.09		
PCB 101	6.61 <sup>b</sup>	5.58 ± 0.11	5.71 ± 0.06	4.56	3.56
PCB 105	6.61 <sup>b</sup>	5.69 ± 0.02	5.89 ± 0.03	4.56	3.42
PCB 112	6.61 <sup>b</sup>	5.57 ± 0.10	5.71 ± 0.06		
PCB 118	6.61 <sup>b</sup>	5.69 ± 0.06	5.87 ± 0.03	4.56	3.56
p,p'-DDE	7.00 <sup>a</sup>	5.73 ± 0.09	5.88 ± 0.05		
PCB 138	7.06 <sup>b</sup>	5.79 ± 0.07	6.20 ± 0.07	4.49	3.37
PCB 153	7.06 <sup>b</sup>	5.84 ± 0.08	6.16 ± 0.09	4.57	3.42
PCB 154	7.06 <sup>b</sup>	5.89 ± 0.09	6.17 ± 0.10		
PCB 155	7.06 <sup>b</sup>	5.84 ± 0.14	6.03 ± 0.15		
PCB 156	7.06 <sup>b</sup>	5.79 ± 0.07	6.28 ± 0.06		
PCB 180	7.51 <sup>b</sup>	5.85 ± 0.06	6.40 ± 0.10	4.21	2.92
log( $V_{water}/V_{PDMS}$ )		3.5–7.0		4.9	3.5

<sup>a</sup>Log  $K_{OW}$  values are all taken from ref 15; superscripts a and b denote experimental and estimated values, respectively.

rinated PCB 180 increased by 0.56 log unit. This shows that equilibrium was established within 3 days for the less hydrophobic substances, whereas equilibration times for the most hydrophobic substances exceeded 3 days.

The water to PDMS volume ratio was varied between 3000 and 9 000 000, which facilitated the precise determination of  $K_{PDMS,water}$  values ranging from 3000 to 2 500 000. Yang and co-workers<sup>10</sup> reported partition coefficients for PCBs that were 0.7–3.5 log units lower than the values of our study (Table 1). Their partition coefficients are likely underestimated, since they were obtained in small vials (2 mL) and at phase ratios ( $V_{PDMS}/V_{water}$ ) that are unsuitable for the determination of high partition coefficients.<sup>12</sup> An additional factor that might have caused the low partition coefficients of Yang and co-workers<sup>10</sup> are Teflon-coated stir bars that sorb PCBs.<sup>14</sup> Such sorption will cause underestimation of partition coefficients when they are based on measurements of the PDMS sorbed fraction only and when assuming the remaining part to be completely dissolved.<sup>11,13</sup> Sorption to the test flasks, evaporation, and degradation cannot be ruled out in the present study either, which makes these processes potential sources for artifacts. However, the impact of such artifacts is kept at a minimum due to the selected combination of test vessel (low sorbing, large) and analytes (moderately volatile, very persistent). Further, partition coefficients were estimated by a regression within a wide range of phase ratios. This reduces the impact of analyte losses on the estimated partition coefficients, because relative concentrations within the robust region of 20 and 80% have the strongest force on the curve fitting.

PDMS/water partition coefficients were plotted against the respective octanol/water partition coefficients in Figure 3. The slope and the  $r^2$  of the regression in the double-log plot are both very close to unity, which is equivalent to proportionality between  $K_{PDMS,water}$  and  $K_{OW}$ . This indicates that the partitioning in the PDMS/water system mainly is controlled by the hydrophobicity of the tested nonpolar analytes and not by specific interactions between the analyte and the PDMS coating. This is in good

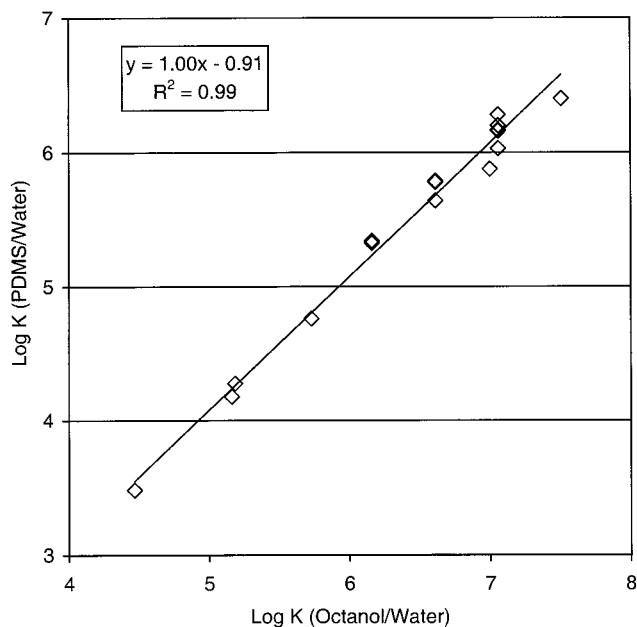


Figure 3. PDMS/water partition coefficients plotted against reported octanol/water partition coefficients.<sup>15</sup> Average partition coefficients (3 days and 6 weeks) were selected for log  $K_{OW}$  of up to 6.7, and 6 week partition coefficients were selected for the more hydrophobic compounds.

agreement with our hypothesis that analytes partition into the polymer coating.

**Fluorescence Microscopy.** Fibers that have been exposed to fluoranthene showed a strong blue fluorescence emission from the polymer coating, whereas this blue color was absent in control fibers that have not been exposed to fluoranthene (see Figure 4). This fluoranthene fluorescence was similar in color and brightness to that observed for fluoranthene-loaded octadecyl Empore disks in earlier studies.<sup>16</sup> The fluorescence was homogeneously distrib-

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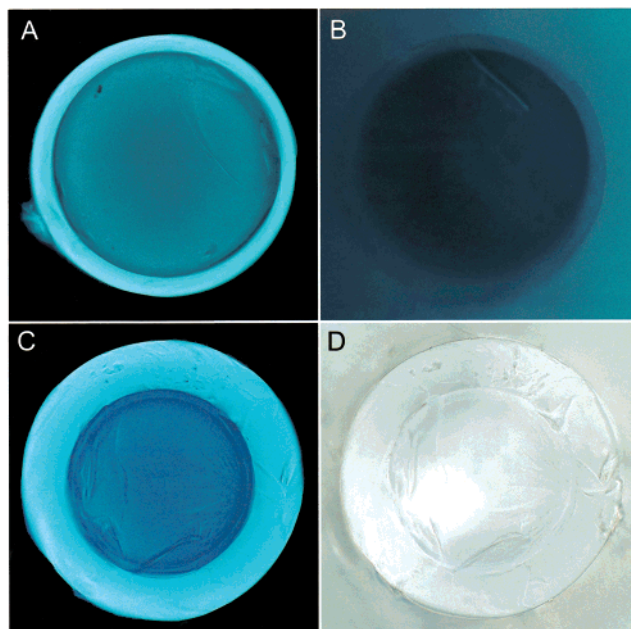


Figure 4. Microscopy images of glass fiber cross sections. Panel a: fluorescence image of 15  $\mu\text{m}$  PDMS glass fiber after 20-h exposure to fluoranthene. Panel b: fluorescence image of clean 15  $\mu\text{m}$  PDMS glass fiber. Panel c: fluorescence image of a 42.5  $\mu\text{m}$  PDMS glass fiber after 20-h exposure to fluoranthene. Panel d: bright-field image of same specimen as used for panel c.

uted within the entire thickness of the polymer coating, which is particularly evident in the fiber with the thicker coating of 42.5  $\mu\text{m}$ . This homogeneous fluorescence was observed right after placing the specimen under the microscope, which was 30–120 s after the cutting and within less than 30 s after placing the cover slip on the specimen. This is strong evidence that fluoranthene diffuses into the polymer coating and that fluoranthene is retained by means of absorption.

A homogeneous fluorescence was observed for extraction times ranging from 5 min to 20 h, whereas the partition experiment suggests that extraction of fluoranthene is incomplete after 5 min. These two observations are not in contradiction. They suggest diffusion in the PDMS coating to be sufficiently fast to render diffusion through the stagnant aqueous boundary layer the rate-limiting step for the extraction, which agrees well with earlier studies.<sup>4</sup> It has to be noted that PDMS is a liquid-phase polymer with an uniquely high permeability.<sup>17,18</sup> Reported diffusion coefficients in PDMS ( $(1-3) \times 10^{-6} \text{ cm}^2/\text{s}$ <sup>17,19</sup>) are actually only 1 order of magnitude below typical diffusion coefficients in water.

**Sorption Mechanism.** Proportionality between  $K_{\text{PDMS,water}}$  and  $K_{\text{OW}}$  values for 17 nonpolar aromatic organics including PCBs, chlorobenzenes, *p,p'*-DDE, and PAHs within the log  $K_{\text{OW}}$  range of 4.5–7.5 was observed in the first part of this study. Fluoranthene was one of these analytes, and the fluorescence of fluoranthene was observed to be homogeneously distributed within the polymer coating of freshly cut fiber cross sections. Proportionality between  $K_{\text{PDMS,water}}$  and  $K_{\text{OW}}$  values would have been very unlikely, unless only one mechanism is governing the retention of all tested

analytes. These observations consequently suggest that the retention of all tested analytes was governed by absorption into the PDMS coating. The absorption hypothesis is further supported by the behavior of higher molecular weight solutes (MW > 200) in PDMS-coated GC columns,<sup>11</sup> which generally is characterized by noncompetitive and concentration-independent retention. This is in accordance with Chiou and co-workers,<sup>20,21</sup> who applied noncompetitive and concentration-independent sorption as an indication for absorption of nonionic organic compounds into soil organic matter.

**Implications for SPME Applications.** The glass fibers used in the present study were not of chromatographic grade, because the partitioning experiment and the microscopy work demanded a few meters of fiber. Such amounts were at the time of the experiments not available in the chromatographic grade. The findings concerning trends in partition coefficients and the sorption mechanism are expected to be fully valid for the PDMS fibers that are normally used in analytical chemistry. The actual values might differ between PDMS coatings, because the properties of a polymer depends both on its monomers and on its cross-linking.

The most important implication of the very high partition coefficients for highly hydrophobic substances is the potentially very low detection limits. The highest concentration in the fiber coating at a given aqueous concentration is reached when the coating had time to equilibrate in an infinite bath (no depletion). The partition coefficients can in this situation be viewed as the concentration factor between the dissolved aqueous concentration and the concentration in the fiber coating that is introduced in the injector of the chromatograph. Potential detection limits ( $C_{\text{pot. det. limit, water}}$ ) can then be calculated according to

$$C_{\text{pot. det. limit, water}} = \frac{n_{\text{detection}}}{V_{\text{PDMS}} K_{\text{PDMS,water}}}$$

where  $n_{\text{detection}}$  denotes the required analyte amount for the detector and  $V_{\text{PDMS}}$  denotes the volume of the polymer coating.  $K_{\text{PDMS,water}}$  values for PCBs ranged between 200 000 and 2 500 000, and this leads to potential detection limits of 4 to 50 pg/L (ppq), when  $n_{\text{detection}}$  is assumed to be 1 pg and PDMS volume to be 0.1  $\mu\text{L}$ . Nevertheless, it has to be noted that such detection limits rarely are reached due to limited extraction times and to limited sample volumes. Such a nondepletive equilibrium extraction of PCB 180 with 0.1  $\mu\text{L}$  of PDMS would, for instance, require about 2 L of aqueous sample, and the extraction would take days to weeks.

A recent application of solid-phase microextraction is “biomimetic extraction”, which aims at simulating biotic body burdens of complex mixtures. This approach was initially developed as an extraction method with solid-phase extraction disks (C18 Empore disks).<sup>22</sup> The application of SPME for this purpose was introduced by Parkerton and Stone,<sup>5</sup> and it was further developed by Verbruggen and co-workers<sup>7</sup> as a tool to mimic the accumulation in lipid membranes. This approach assumes that the amount of hydrophobic organics retained at equilibrium by the SPME fiber

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(22) Verhaar, H. J. M.; Busser, F. J. M.; Hermens, J. L. M. *Environ. Sci. Technol.* **1995**, *29*, 726–734.

is a good mimic for the amount that can accumulate in lipid membranes. Hydrophobic organic substances partition into lipid membranes, and membrane/water partition coefficients increase with increasing hydrophobicity. To mimic the membrane/water system, SPME water partition coefficients should increase with increasing hydrophobicity as well, and absorption should preferably be the mechanism that governs the retention by the polymer coating. The findings of the present study thus confirm some crucial assumptions for the biomimetic extraction of hydrophobic organics with SPME.

Finally, the sorption mechanism is also crucial for equilibrium SPME in multicompartiment systems. The chemical potential of an analyte in a multicompartiment system (including a SPME fiber) is by definition the same in all compartments when the system is completely equilibrated.<sup>23</sup> The amount that is absorbed by the fiber coating will be controlled by this chemical potential, and it will be independent of the matrix around the fiber. Gorecki and Pawliszyn<sup>12</sup> addressed this for closed flasks with headspace, where the amount of the analyte extracted by the fiber at equilibrium is the same, independent of whether the fiber is located in the headspace or in the liquid. Equilibrium SPME extractions in multicompartiment systems thus allow the estimation of concentra-

(23) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental organic chemistry*; J. Wiley: New York, 1993.

tions in any of the compartments, when the extraction can be carried out in a manner that does not affect the system (no depletion) and when the appropriate partition coefficient is available. Dissolved aqueous concentrations in multicompartiment systems can for instance, be determined based on an equilibrium extraction in any of the compartments:

$$C_{\text{dissolved, aqueous}} = C_{\text{SPME, equilibrium}} / K_{\text{SPME, aqueous}}$$

Equilibrium SPME thus offers the opportunity to determine dissolved aqueous concentrations in complex matrixes such as sediment or sludge, and the presented partition coefficients in this paper are a good basis for this kind of application.

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