

Correspondence

Comments on "Adsorption versus Absorption of Polychlorinated Biphenyls onto Solid-Phase Microextraction Coatings"

SIR: Recently, Yang et al.² stated that sorption of PCBs to PDMS coated Solid-Phase Microextraction (SPME) fibers is an adsorption process. They based their conclusion on a set of experimental partition coefficients between PDMS and water.³ Yang et al.^{2,3} only determined the amount that was sorbed to the fiber and assumed the remaining part to be dissolved in the aqueous phase. They report substantial binding of PCBs to the stir bar; however, they do not take this phenomenon into account for the estimation of partition coefficients. Moreover, assuming a proportional relationship between hydrophobicity and binding to a Teflon stir bar, their data can be explained. From the analysis carried out herein, we conclude that the partition coefficients of Yang et al.^{2,3} are of insufficient quality, and cannot be used as the basis for their theory that sorption of PCBs to PDMS fibers is an adsorption mechanism. The matter of adsorption versus absorption is of great importance for the application of SPME in mixtures. If adsorption would really be the sorption process to SPME fibers, competition effects would lead to concentration- and mixture-dependent responses. These problems have not been reported since the introduction of SPME, 10 years ago.

Solid Phase Microextraction (SPME), as originally devised by Arthur and Pawliszyn,¹ is regarded as a partition extraction, i.e., compounds with hydrophobic properties tend to partition from an aqueous phase to the extraction device which consists of a polymer-coated fused silica rod. As a consequence, linear isotherms are assumed, leading to concentration-independent partition coefficients.

Recently, Yang et al.² came to the conclusion that surface adsorption is the primary mechanism controlling PCB (and likely other high-molecular-weight solutes) sorption to poly-

(dimethylsiloxane) (PDMS) coated fibers. The conclusions they draw are consistent with the data they presented, which show an inverse relationship between the *n*-octanol/water and PDMS/water partition coefficients. Nevertheless, their conclusion concerning adsorption behavior of PCBs to PDMS is counter-intuitive for a number of reasons: (1) It is very well-known that retention times on PDMS-coated gas-liquid chromatography (GLC) columns are reproducible and not dependent on the sample size, as opposed to those on gas-solid chromatography (GSC). In the former, partitioning (absorption) is the retention mechanism while in the latter it is adsorption. (2) Increasing the PDMS film thickness in GLC definitely results in longer retention times, which is in accordance with absorption. A decreasing retention time, as a result of a lower surface area, would be expected for adsorption behavior. (3) The high activity coefficients of PCBs in water ($>10^7$) suggest that these compounds are sparingly soluble in water, which suggests higher fiber/water partition coefficients.

Nevertheless, intuition should be avoided in the data analysis although it can be a trigger to reanalyze.

In this correspondence, we will show that it is very likely that the assumptions Yang et al.^{2,3} make during the measurements are incorrect and lead to a highly biased data set. First, we will discuss and explain the origin of their erratic assumptions and therefore erroneous measurements. Subsequently, their data will be reanalyzed to show that their data do not support their surface adsorption theory.

Measurements. The method Yang et al.² used to determine partition coefficients is based on the assumption that they have a complete mass balance, i.e., the sum of the amount in the aqueous phase (n_a) and in the fiber coating (n_f) equals the nominal amount (n_{tot}):

$$n_{tot} = n_a + n_f \quad (1)$$

On the basis of this assumption, the partition coefficient can be calculated according to

$$K = \frac{n_f V_a}{(C_{a,0} V_a - n_f) V_f} \quad (2)$$

where K is the partition coefficient PDMS/water, $C_{a,0}$ the concentration of the compound of interest in the aqueous phase before the extraction, and V_a and V_f the volumes of the aqueous phase and fiber coating, respectively. The amount that was sorbed to the fiber, n_f , is determined from an external calibration using solvent injection. This approach has some major drawbacks under specific circumstances, such as in the study of Yang et al.² The volume ratio of the two phases, i.e., PDMS and water, is 3268 (for the 100- μ m fiber). This actually means that at a partition coefficient of 3268, the aqueous phase will be depleted for 50%. At high partition coefficients (e.g.,

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(1) Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145–2148.

(2) Yang, Y.; Hawthorne, S. B.; Miller, D. J.; Liu, Y.; Lee, M. L. *Anal. Chem.* **1998**, *70*, 1866–1869.

(3) Yang, Y.; Miller, D. J.; Hawthorne, S. B. *J. Chromatogr., A* **1998**, *800*, 257–266.

100 000) the aqueous concentration after the extraction will be very low, which leads to a relatively high uncertainty in the estimate of the partition coefficient and thus very wide confidence intervals. Additionally, effects of sorption to the glass wall, volatilization, and all other loss processes that might seem of minor importance at high concentrations can suddenly become very important. These issues have been thoroughly discussed by Górecki et al.^{4,5}

Yang et al.^{2,3} were partly aware of these pitfalls, and therefore, they silanized the vials, used relatively new and clean fibers, and used new spin bars for every vial to prevent carryover. Concerning the spin bars, they report severe carryover. "Despite the 5 min acetone cleaning, up to 5% of the original PCBs were found in subsequent blanks."³ Note the plural form of blank. This indicates that substantially more than 5% was sorbed to the spin bar in the original vial. Although they show that binding to the spin bar is a major problem, they do not realize how important this observation is and how it affects their partition coefficients. Apparently, a certain amount (n_{sb}) of their chemical is bound to the stir bar, and therefore, eq 1 should be written as a three-phase system.

$$n_{\text{tot}} = n_a + n_f + n_{sb} \quad (3)$$

As a result, the concentration in the aqueous phase was lower than they assumed. The effect of this assumption can be shown by a simple example for an arbitrary chemical with a true partition coefficient of 1 000 000. Considering that for some PCBs they had 5% carryover in subsequent blanks after cleaning the stir bar for 5 min in acetone, it is not unreasonable to assume that 15% were actually bound to the spin bar. It can be shown that, in this situation, a measurement would result in a partition coefficient of 17 000, which is an underestimation of more than a factor of 50.

Additionally, assuming that binding of PCBs to the Teflon is significant, and that the amount in the aqueous phase is negligible ($n_a \approx 0$) in comparison with the amount on the fiber and the stir bar (which is true for partition coefficients higher than 100 000), we can, using the data of Yang et al.,³ calculate the percentage of each PCB which is presumably bound to the stir bar. From eq 2 and the partition coefficients that were described for the 100- μm PDMS-coated fiber,² we can derive which percentage of the total amount is actually sorbed to the fiber. Subsequently, we can calculate which percentage will be sorbed to the stir bar (for, if $n_a \approx 0$, then $n_{\text{tot}} = n_f + n_{sb}$). These data are shown for all PCBs in Table 1, together with *n*-octanol/water partition coefficients.⁶ Simple linear regression shows that the correlation coefficient (r^2) between the estimated amount sorbed to the stir bar and $\log K_{ow}$ is 0.87. In our opinion, a proportional relationship between hydrophobicity and binding to Teflon is, considering the high activity coefficients of PCBs in the aqueous phase, more likely than an inverse relationship between hydrophobicity and sorption to PDMS. Moreover,

Table 1. Data for $\log K_{ow}$, Measured $\log K_{PDMS}$, and the Calculated Concentration on the Fiber and the Stir Bar

PCB no.	$\log K_{ow}^5$	$\log K_{PDMS}^2$ for 100- μm PDMS fiber	% on fiber ^a	% on stir bar ^b
8	5.51	4.07	80	20
18	5.60	4.02	78	22
28	5.60	3.94	74	26
44	6.00	3.88	72	28
52	6.10	3.86	71	29
66	5.80	3.93	74	26
77	6.10	3.92	73	27
101	6.40	3.57	55	45
105	6.30	3.50	51	49
118	6.30	3.52	52	48
126	6.30	3.26	38	62
128	7.00	2.97	24	76
138	6.70	3.36	43	57
153	6.90	3.40	45	55
170	6.70	2.92	21	79
180	7.20	2.94	22	78
187	6.92	3.19	34	66
195	7.50	2.71	14	86
201	7.50	2.99	24	76
206	7.90	2.48	9.0	91
209	8.30	2.40	7.7	92

^a Calculated from K_{pdms} in this table and eq 2. ^b Calculated as 100% - (% on fiber).

when we use this relationship to predict the partition coefficients for benzo(a)anthracene and benzo(a)pyrene, we obtain (for the 100- μm PDMS fiber) 9163 and 3095, respectively. This is in good agreement with the data from Yang et al.² (they find 6710 and 2980, respectively).

Data Analysis. The data from Yang et al.^{2,3} consist of a considerable set of partition coefficients between PDMS-coated fibers, with a film thickness of 7 and 100 μm , and water of mostly PCBs of varying hydrophobicity (from PCB#8 to PCB#209). For both fibers, partition coefficients decrease with increasing hydrophobicity. The ratio between the two volume-based partition coefficients of the two fibers increases from 3 (for the least hydrophobic) to 22 (for the most hydrophobic). Additionally, the ratio between the surface-based sorption coefficients increases from 0.28 to 2.3 (from least to most hydrophobic). On the basis of the fact that adsorption coefficients are more similar (ratios closer to unity) than the volume-based partition coefficients, Yang et al.² conclude that adsorption is more likely to be the sorption mechanism than absorption.

This conclusion is a plausible explanation of the ratios between the sorption coefficients. Nevertheless, the actual values of the ratios that they find for the most hydrophobic compounds are more interesting. First of all, an adsorption mechanism would suggest the ratio between the surface-normalized sorption coefficients of 1. Instead, Yang et al.² observe a steady increase to as high as 2.3. A calculation of the ratios of the surfaces and volumes of the fibers gives 2.4 and 23.5, respectively. These numbers are very similar to the ratios which Yang et al.² find for the partition coefficients, and this implies that an equal amount of the PCBs was sorbed to both fibers. The most straightforward explanation for this observation is not an adsorption mechanism. Because of

(4) Górecki T.; Pawliszyn, J. *Analyst (Cambridge, U.K.)* **1997**, 122, 1079.

(5) Górecki T.; Khaled, A.; Pawliszyn, J. *Analyst (Cambridge, U.K.)* **1998**, 123, 2819–2824.

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binding to the stir bar, only a limited fraction of the added PCBs was supposedly available for sorption, and both fibers virtually depleted this available fraction. This leads to aforementioned ratios of volume- and surface-based partition coefficients, i.e., 23.5 and 2.4, respectively.

General Remarks. The matter of adsorption versus absorption is of great importance for the applications of SPME in nonsingle compound solutions, i.e., any mixture. Competition effects would lead to concentration measurements, which will be highly dependent on the constitution of the solution. Remarkably, these effects have not been reported in the literature. Moreover, if adsorption were the primary sorption mechanism, the data from Yang et al.^{2,3} would be doubtful since these data are measured in a mixture.

In conclusion, the method that was used by Yang et al.^{2,3} was inadequate to determine PDMS/water partition coefficients of highly hydrophobic substances because of two reasons. (1) The phase ratio ($V_{\text{water}}/V_{\text{PDMS}}$) was too low for the determination of high partition coefficients (e.g., 1 000 000) that can be expected in case of an absorption process. (2) The measurement of only the SPME-bound fraction, while assuming the remaining part to be completely dissolved, makes the approach

highly susceptible to experimental artifacts. This is particularly the case when testing PCBs in small vials and with Teflon coated stir bars that by the same researchers were reported to bind PCBs. Such an experimental setup requires the analytical confirmation of aqueous concentrations in order to generate trustable partition coefficients. Therefore, we conclude that the partition coefficients from Yang et al.^{2,3} are of insufficient quality, and that they should not be regarded as evidence for the adsorption theory.

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Received for review January 29, 1999. Accepted
September 27, 1999.

AC990102B