Theoretical considerations on the use of solid phase microextraction with complex environmental samples

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ABSTRACT - Solid phase microextraction (SPME) is a relatively new technique for extraction of organic chemicals from aqueous matrices. However, SPME has been applied mainly to relatively clean samples and polar organic compounds. Its utility in extraction of hydrophobic organics from complex heterogeneous matrices remains to be proven, and the impact of matrix interferences needs to be quantified. In this article, the equations governing the use of equilibrium SPME for environmental samples with complex heterogeneous matrices were derived in terms of parameters commonly measured or estimated by environmental scientists. Parameterization of the SPME equations allowed for the *a priori* prediction of SPME performance as a function of analyte and sample properties, as well as experimental conditions. A theoretical evaluation of SPME was performed for a broad range of realistic scenarios using calculated equilibrium partitioning parameters, and the implications for practical applications were discussed. Potential pitfalls and errors in quantitative measurements were identified and different approaches to SPME calibration were presented. The concept of an optimum minimum volume for the analysis of heterogeneous environmental samples was presented and fully developed. Data from three previous studies were used to validate the correctness of the theoretical framework; the agreement between the measured relative recoveries of a variety of hydrophobic organic chemicals and theoretical predictions was exceptionally good. The results of this study highlight the potential for SPME to be a valuable technique for the measurement of hydrophobic organic contaminants in complex environmental samples. The SPME technique appears to be especially well suited for samples with high solids-to-water ratios and/or large sample volumes. Examples of such applications include sediment interstitial water and *in situ* field measurements, respectively.

INTRODUCTION

The analytical technique of solid-phase microextraction (SPME) was first introduced more than a decade ago by Arthur and Pawliszyn (1990), and was subsequently optimized and automated (Aurther *et al.* 1992). Since that time, SPME has evolved into a widely used alternative to more traditional methods for the extraction of organic compounds from aqueous and gaseous media. The SPME method does not require any solvent and it simultaneously extracts and concentrates organic analytes in a single step. In addition, its simplicity of use, relatively short sample processing times, the variety of available stationary phases, the ability to reuse fibers, and the potential for combining derivatization with extraction for analysis of polar analytes have made SPME a very attractive choice for a broad range of analytical applications (Pawliszyn 1997).

These aspects of SPME, among others, offer distinct advantages over conventional techniques such as liquid-liquid extraction and conventional solid-phase extraction using resin cartridges or disks. Due to its great utility, SPME has found applications in virtually every field where trace organic analytical methods are used. One field in which SPME has been used extensively is environmental analytical chemistry, where it has been applied for the analysis of hydrophobic, semi-volatile, and volatile organic analytes in surface water, wastewater, sediment porewater, and air samples (Louch *et al.* 1992, Potter and Pawliszyn 1994, Liu and Lee 1997, Stahl and Tilotta 1999, Achten and Puttmann 2000, Bernhard and Simonich 2000, Magbanua *et al.* 2000, Mayer *et al.* 2000, Black and Fine 2001, Koziel *et al.* 2001, Koziel and Pawliszyn 2001, Kim *et al.* 2002), and also for determining partitioning parameters such as Henry's Law constants (Bierwagen and Keller 2001) and octanol-water partition coefficients (Dean *et al.*

1996). Other diverse fields where SPME has been utilized include: environmental and occupational health (Asakawa *et al.* 1999); agriculture (Jia *et al.* 1998, Song *et al.* 1998, Yo 1999, Beaulieu and Grimm 2001, Cornu *et al.* 2001), food and flavor science (Bicchi *et al.* 1997, Ruiz *et al.* 1998, Lloyd and Grimm 1999, Rohloff 1999, Goupry *et al.* 2000a, Jelen *et al.* 2000, Marsili 2000, Ogihara *et al.* 2000, Sostaric *et al.* 2000, Curren and King 2001, Llompart *et al.* 2001, Tomaino *et al.* 2001, van Aardt *et al.* 2001), enology and zymurgy (Jelen *et al.* 1998, Hayasaka and Bartowsky 1999, Scarlata and Ebeler 1999, Bellavia *et al.* 2000, Vianna and Ebeler 2001), entomology (Robacker and Bartelt 1997, Monnin *et al.* 1998), ecotoxicology (Leslie *et al.* 2002), and microbiology (Vernais *et al.* 1998, Watson *et al.* 1999, Poon *et al.* 2001). Moreover, the success of SPME has also spawned the development of a number of closely related analytical techniques (Liu *et al.* 1997, Bigham *et al.* 2001, Giardina and Olesik 2001, Mullett and Pawliszyn 2001, Shen and Lee 2001, Theis *et al.* 2001, Vrana *et al.* 2001).

Although previous studies have clearly demonstrated the effectiveness of SPME as an alternative to conventional sample extraction methods, most of the development work associated with SPME has so far focused on relatively clean samples and polar organic compounds. It remains unclear whether this technique can be generally and effectively applied to the extraction of hydrophobic organic compounds in environmental samples with complex heterogeneous matrices.

The simplest and most common applications of SPME rely upon attainment of equilibrium between a sorbent-coated silica fiber and the fluid component of an aqueous sample. During an extraction, the fiber may be immersed directly into, or placed in the headspace above a sample. It can be shown that the amount ultimately sorbed by the fiber is the same for either an immersion or headspace extraction (Pawliszyn 1997). After equilibrium is attained, the fiber is removed from the system and the amount of each sorbed analyte can be accurately measured by an appropriate analytical method (usually thermal desorption-gas chromatography). The amount of analytes sorbed on the fiber is then related back to their respective concentrations in the sample via an appropriate calibration method. SPME has also been used under non-equilibrium conditions with an associated loss in sensitivity and additional complexities with respect to calibration (Vaes *et al.* 1996a; Ai 1997a, 1997c; Pawliszyn 1997; Mayer *et al.* 2000).

In contrast to the more conventional extraction methods, SPME usually does not endeavor to extract all or even most of an analyte from a sample. Indeed, SPME often extracts only a small fraction of the total analyte in a sample. It is this aspect of SPME that can make calibration problematic. Calibration in SPME is usually performed using spiked standards prepared in pure water. Problems may arise when the same calibration method is applied to the analysis of environmental samples containing a significant amount of sorbing phases. The equilibrium partitioning processes in such a complex system would render the calibration invalid.

For typical environmental samples containing significant amounts of suspended solids and/or dissolved organic matter (DOM), the assumption is that an SPME fiber would come to equilibrium with only the freely dissolved analytes in the water phase or the analytes in the vapor phase, depending on the methodology used. However, the fiber in such a sample is actually in indirect interaction with every phase in the system. For example, as an analyte is depleted from the dissolved phase by sorption to the fiber, the analyte is subsequently replenished via re-equilibration with the other phases in the sample. Therefore, significant errors are incurred if analyte concentrations in such a system are calculated using calibration relationships derived from standards prepared in pure water. Pawliszyn (1997) has pointed out that it is necessary to account for matrix effects in heterogeneous environmental samples by using the internal calibration techniques of standard addition or isotopically labeled standards. However, the standard addition method can be extremely tedious and time consuming if many samples are to be analyzed. In addition, isotopically labeled standards are usually very expensive and not available for all analytes of interest.

In order to evaluate the utility of SPME for the analysis of hydrophobic organic contaminants in heterogeneous environmental samples, it is necessary to have a thorough understanding of the behavior of the analytes in such a system before and after extraction by SPME. To this end, we re-derive the governing equations of SPME in terms of the parameters commonly measured or calculated by environmental chemists and subsequently used to understand and predict partitioning behavior of chemicals in complex environmental systems. After deriving the appropriate equations, realistic parameter values are used to theoretically evaluate the efficacy of SPME

for analyzing such systems. The analytical performance of SPME is predicted as a function of analyte polarity, fiber properties, and sample parameters. The conditions under which SPME may be effectively used for measurements of hydrophobic organic contaminants in realistic environmental samples are discussed. Finally, predictions from the derived equations are compared to previous experimental results available in the literature.

THEORETICAL BACKGROUND

We consider an analyte partitioning in an aqueous system with a truly dissolved phase, a solid phase comprised of suspended solids, and a colloidal phase containing DOM. Mass balance requires that the total amount of the analyte in the system is equal to the sum of the amounts in the individual phases. The total amount, N_0, of the analyte in the system before SPME can be expressed as

$$N_0 = N_s^0 + N_{dom}^0 + N_w^0 + N_a^0 \qquad (1)$$

where N_s^0, N_{dom}^0, N_w^0, and N_a^0 are the amounts of the analyte in the solid, DOM, aqueous (truly dissolved), and air phases, respectively. After SPME is complete, we have

$$N_0 = N_s + N_{dom} + N_w + N_a + N_f \qquad (2)$$

where N_s, N_{dom}, N_w, N_a and N_f are the amounts of the analyte in the solid, DOM, aqueous and air phases, and the SPME fiber, respectively. It is commonplace in environmental chemistry to normalize contaminant concentrations in solids to the organic carbon (OC) fraction of this phase (Karickhoff 1981, Schwarzenbach *et al*. 1993). Also, DOM is most often expressed as dissolved organic carbon (DOC) because the carbon fraction is typically what is measured. Therefore, we define that: $N_s^0 = C_{oc}^0 m_{oc}$, $N_{dom}^0 = C_{doc}^0 m_{doc}$, $N_w^0 = C_w^0 V_w$, $N_a^0 = C_a^0 V_a$, $N_s = C_{oc} m_{oc}$, $N_{dom} = C_{doc} m_{doc}$, $N_w = C_w V_w$, $N_a = C_a V_a$ and $N_f = C_f V_f$, where C_{oc}^0, C_{doc}^0, C_w^0, and C_a^0 are the analyte concentrations in the solid (OC normalized), DOM (DOC normalized), aqueous, and air phases, respectively, before SPME, and C_{oc}, C_{doc}, C_w, C_a, and C_f are the analyte concentrations in the solid (OC normalized), DOM (DOC normalized), aqueous and air phases, and the SPME fiber (normalized to the polymer phase) after SPME, respectively; m_{oc} and m_{doc} are the mass of OC in the solid phase and DOC in the DOM phase, respectively; and V_w, V_a and V_f are the volumes of the aqueous and air phases, and the sorbing fraction of the SPME fiber, respectively.

When the system is at thermodynamic equilibrium, the usual partition coefficients can be used to describe the analyte distribution in the system:

$$K_{oc} = \frac{C_{oc}}{C_w} = \frac{C_{oc}^0}{C_w^0} \qquad (3)$$

$$K_{doc} = \frac{C_{doc}^0}{C_w^0} = \frac{C_{doc}}{C_w} \qquad (4)$$

$$K_f = \frac{C_f}{C_w} \qquad (5)$$

$$K_H' = \frac{K_H}{RT} = \frac{C_a^0}{C_w^0} = \frac{C_a}{C_w} \qquad (6)$$

where K_{oc}, K_{doc}, and K_f are the equilibrium partition coefficients of the analyte (solid-aqueous, DOM-aqueous, and SPME fiber-aqueous). Also, K_H and K_H' are the Henry's Law constant and the dimensionless Henry's Law constant, respectively, and R is the universal gas constant, and T is the absolute temperature.

In SPME experiments, the parameter actually measured is the amount of the analyte sorbed on the SPME fiber (N_f). Therefore, in order to determine the concentrations of analyte in the sample, it is necessary to derive a relationship between N_f with C_w^0 and N_0. Combining equations (1) – (6) yields

$$N_f = N_s^0 + N_{dom}^0 + N_w^0 + N_a^0 - N_s - N_{dom} - N_w - N_a$$

$$= C_{oc}^0 m_{oc} + C_{doc}^0 m_{doc} + C_w^0 V_w + C_a^0 V_a - C_{oc} m_{oc}$$

$$- C_{doc} m_{doc} - C_w V_w - C_a V_a$$

$$= C_w^0 (K_{oc} m_{oc} + K_{doc} m_{doc} + V_w + K_H' V_a) -$$

$$\frac{K_{oc} N_f m_{oc}}{K_f V_f} - \frac{K_{doc} N_f m_{doc}}{K_f V_f} - \frac{N_f V_w}{K_f V_f} -$$

$$\frac{K_H' N_f V_a}{K_f V_f}$$

or

$$N_f = \frac{K_f V_f (V_w + ? + K'_H V_a)}{K_f V_f + V_w + ? + K'_H V_a} C^0_w \qquad (7)$$

where $? = K_{oc} m_{oc} + K_{doc} m_{doc}$, is a matrix sorption term reflecting the effects on SPME from suspended solids and DOM. As shown later, $?$ is a key parameter for understanding how SPME experiments may be affected by various sample parameters.

For most of the hydrophobic organic compounds of interest for this study, e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, etc., the dimensionless Henry's Law constant is small, i.e., $K'_H \leq 0.05$ (Schwarzenbach *et al.* 1993). If the headspace volume is also minimized (e.g., less than 50% of the sample volume), then it can be shown that the amount of analyte in the headspace at equilibrium will be negligible compared to the rest of the system (Figure 1). Therefore, headspace terms will be omitted from all equations for the remainder of this article. Neglecting the headspace, Equation (7) becomes

$$N_f = \frac{K_f V_f (V_w + ?)}{K_f V_f + V_w + ?} C^0_w \qquad (8)$$

Equation (8) can be used to calculate the initial dissolved phase concentrations of analytes in the sample. A similar relationship can be derived for N_f and N_0:

$$N_0 = N_s + N_{dom} + N_w + N_f$$

$$= \frac{K_{oc} N_f m_{oc}}{K_f V_f} + \frac{K_{doc} N_f m_{doc}}{K_f V_f} + \frac{N_f V_w}{K_f V_f} + N_f$$

or

$$N_f = \frac{K_f V_f}{K_f V_f + V_w + ?} N_0 \qquad (9)$$

Equation (9) can be used to calculate the total concentration of analyte in a complex sample. Another useful relationship can be derived from Equation (9). If the amounts of sorbing phases in the system are insignificant (i.e., $m_{oc} \approx 0$ and $m_{doc} \approx 0$), then $?$ approaches zero and Equation (9) reduces to

$$N'_f = \frac{K_f V_f}{K_f V_f + V_w} N_0 \qquad (10)$$

Equation (10) is the most basic equation in SPME and has been successfully used for analysis of volatile organic chemicals in simple sample matrices (Pawliszyn 1997). Combining Equations (9) and (10) leads to

$$\frac{N_f}{N'_f} = 1 - \frac{?}{K_f V_f + V_w + ?} \qquad (11)$$

Equation (11) can be used to calculate the amount of the analyte sorbed on the SPME fiber in a complex sample matrix relative to the amount sorbed in a relatively "clean" sample or pure water standard of the same volume. It suggests that the presence of sorbing phases in a sample will lower the apparent recovery of the analyte. This relative recovery is, of course, an artifact due to a lack of consideration of the partitioning behavior of the analytes within the system. The extraction efficiency of SPME is the same for both cases; the lower amount of analyte extracted in the complex sample is due to a lower dissolved phase concentration in the presence of sorptive phases.

It should be noted that matrix term $?$ can be generalized to include any number of heterogeneous solid and DOM phases. The generalized form of $?$ can be expressed as:

$$? = \sum_{i=1}^{n} K^i_{oc} m^i_{oc} + \sum_{j=1}^{n'} K^j_{doc} m^j_{doc} \qquad (12)$$

where n and n' are the total numbers of solid and DOM phases, respectively. The unique aspect of the twelve equations derived thus far is that they provide a complete description of the partitioning of organic chemicals between the various phases of any heterogeneous environmental sample during an SPME extraction. Moreover, the governing equations are parameterized in terms of system qualities frequently and easily measured or estimated by environmental scientists. Such parameterization allows for a rapid interpretation of how changes in analyte, sample, and fiber properties will affect the performance of SPME in sample analysis. The ability to understand the complex equilibrium partitioning behavior of organic chemicals in heterogeneous aquatic systems using a small set of fundamental parameters has been previously demonstrated (Pankow and McKenzie 1991).

METHODS

One simple way to evaluate matrix effects is to examine the variability of the SPME analyte recovery in a heterogeneous sample (N_f) under various conditions relative to that for clean sample (N_f'), using Equation (11). Realistic values for the parameters can be used in the appropriate equations to predict the performance of SPME for a given set of sample and experimental conditions. To simplify the evaluation, the heterogeneous system to be studied is assumed to be an aqueous sample consisting of pure water and two homogeneous sorbing phases, suspended solids and DOM. The effects of ionic strength and temperature will be neglected, although it is recognized that these parameters can significantly affect partitioning behavior and SPME performance (Schwarzenbach *et al.* 1993; Pawliszyn 1997). The suspended solids are assumed to contain 1% OC (f_{oc} = 0.01) and the DOM phase can generally be assumed to contain about 50% DOC (f_{doc} = 0.5) by mass (Schwarzenbach *et al.* 1993). For simplicity, the density of the suspended solids and the DOM are assumed to be the same, that is $d_{ss} = d_{dom}$ = 1.5 g/mL.

The equilibrium partitioning parameters were calculated using correlations from the literature relating K_f, K_{oc}, and K_{doc} to K_{ow}. The specific relationships used were $K_f = 0.123K_{ow}$ (Mayer *et al.* 2000), $K_{oc} = 0.41\ K_{ow}$ (Karickhoff 1981), and $K_{doc} = 0.11\ K_{ow}$ (Burkhard 2000). It was necessary to specify a dissolved phase analyte concentration to evaluate the relative importance of considering headspace contributions to partitioning behavior in these systems. In this case, the water concentration of an analyte was estimated using a linear free energy relationship from the literature for hydrophobic organic chemicals, $\log K_{ow} = -0.85 \log C_w^{sat} + 0.78$ (Schwarzenbach *et al.* 1993). The dissolved concentrations used for the analyses were set at half the calculated saturated water concentration. Recall that the matrix term q contains both equilibrium constants and mass terms. The equations relating the concentration of suspended solids and DOC in the sample to the respective mass terms in q are

$$C_{ss} = \frac{m_{oc}}{f_{oc}V_t} \qquad (13)$$

and

$$DOC = \frac{m_{doc}}{V_t} \qquad (14)$$

where

$$V_t = V_w + \frac{m_{oc}}{f_{oc}d_{ss}} + \frac{m_{doc}}{f_{doc}d_{dom}} \qquad (15)$$

The total volume (V_t) was used because, strictly speaking, the volume of the suspended solids and DOM contribute to the total volume of the system. However, note that there are six orders of magnitude between the units typically used for expressing suspended solids and DOC concentrations and their respective densities, d_{ss} and d_{dom} (i.e., mg/L versus g/mL). Therefore, unless the masses of solids and DOM are extremely large, the volumes of these phases do not contribute significantly to the overall sample volume, i.e., $V_t \approx V_w$. Using the above equations, the performance of SPME was theoretically evaluated using a realistic range of sample, chemical, and experimental parameters.

RESULTS AND DISCUSSION

Headspace Partitioning

The importance of considering the headspace in the extraction vial as a compartment for the partitioning of organic chemicals during an SPME analysis

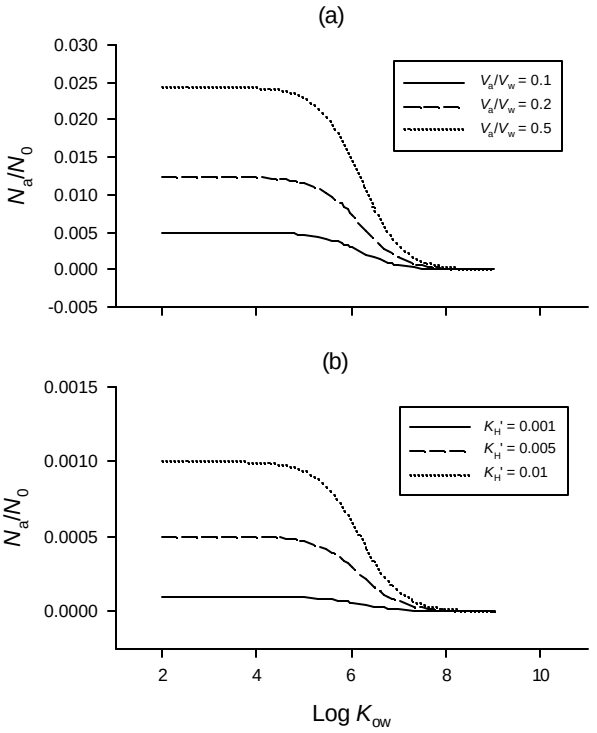

Figure 1. The ratio of analyte in the headspace air (N_a) to the total analyte in the sample (N_0) as a function of log K_{ow} and (a) the headspace to water volume ratio and (b) the dimensionless Henry's Law constant K_H'.

was evaluated. The equilibrium ratio of the amount of analyte in the headspace air (N_a) to the total amount of analyte in the system (N_0) as a function of K_{ow} and headspace/sample volume ratio is shown in Figure 1. Realistic system parameters were selected to predict the extent of analyte partitioning into the headspace. The results of this analysis show that even for compounds of low hydrophobicity, relatively high K_H', and allowing the headspace to equal the sample volume, only about 2.5% of the total analyte in the system will be in the headspace at equilibrium. Most of the compounds of interest for this study, i.e., hydrophobic organic compounds, would partition extensively into the suspended solids and DOM phases and generally have much lower K'_H values, moderate to high K_{ow}'s, and low dissolved phase concentrations. These results indicate that only an extremely small fraction of the total amount of such compounds would be in the headspace at equilibrium. Moreover, the results validate the omission of the headspace terms from the SPME governing equations.

Variability in SPME Recoveries

It is apparent from Equations (8) and (9) that complex sample matrices may significantly impact SPME measurements as q becomes significant relative to V_w. Such an illustration can be provided for the measurement of the truly dissolved phase concentration of an analyte. A comparison of Equations (8) and (9) reveals that

$$N_0 = C_w^0 (V_w + q) \quad \text{or} \quad C_w^0 = \frac{N_0}{V_w + ?}$$

In a given sample, the matrix term (q) in effect serves as a reservoir (sink and source) for analytes, and depending on the relative values of V_w and q, the concentration of an analyte in the truly dissolved phase could be substantially overestimated without consideration of the matrix effects.

The ratio of the fiber-sorbed analytes N_f/N_f' in Equation (11) can be thought of as the relative recovery of each compound as compared to a sample where matrix effects are insignificant. Equation (11) can be used to investigate the influence of sample, chemical, and experimental parameters on SPME relative recoveries. The relative recovery generally increases with increasing V_f value, but the trend levels off after V_f reaches certain values (Figure 2). Excellent relative recoveries (i.e., >90%) are predicted when using common SPME fibers with an 85-mm

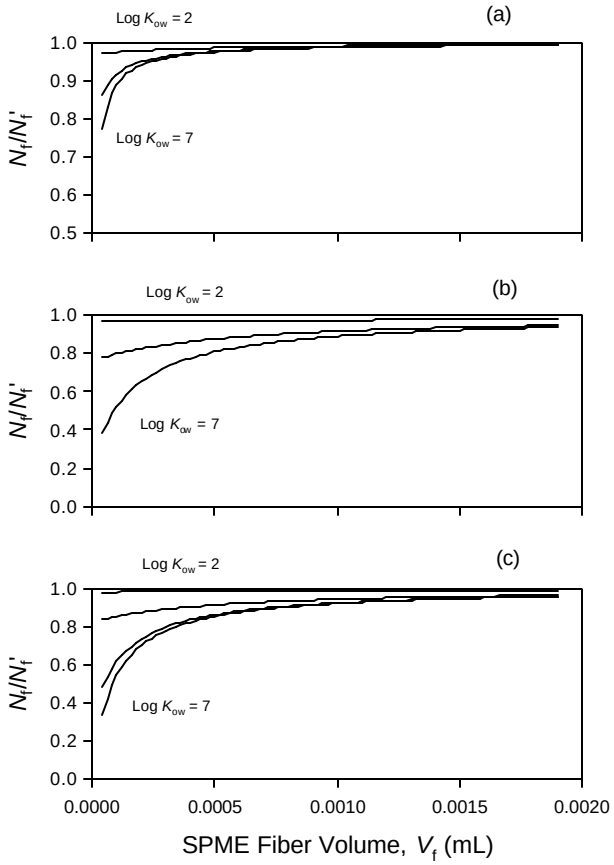

Figure 2. Variability of the SPME relative recovery (N_f/N_f') with SPME fiber volume (V_f). All curves were obtained from Equation (11) with different values for the experimental parameters: (a) V_w = 5 mL, C_{ss} = 50 mL, C_{doc} = 1 mg/L, f_{oc} = 0.01, and f_{doc} = 0.5; (b) same as (a) except for V_w (= 50 mL); and (c) same as (a) except for C_{ss} (= 500 mg/L).

polymer coating, which corresponds to an effective volume of ~0.5 µL, and under the specified experimental parameters. Large SPME fiber volumes are predicted to effectively minimize the matrix interferences from suspended solids and DOM, while high K_{ow} values are expected to enhance matrix effects as more hydrophobic organic chemicals partition onto suspended solids and DOM. Increasing the sample volume while maintaining the same concentrations of suspended solids and DOM, lowers the N_f/N_f' values (Figures 1a to 1b). The same effect is observed when the concentration of suspended solids increases while maintaining the same sample volume (Figures 1a and 1c). Although using large SPME fiber volumes appears to mitigate these observed matrix effects, large fiber volumes are also expected to prolong the time required to reach equilibrium, particularly for very hydrophobic compounds (Pawliszyn 1997). Overall, it appears that the 85-µm SPME fiber is an appropriate choice for most applica-

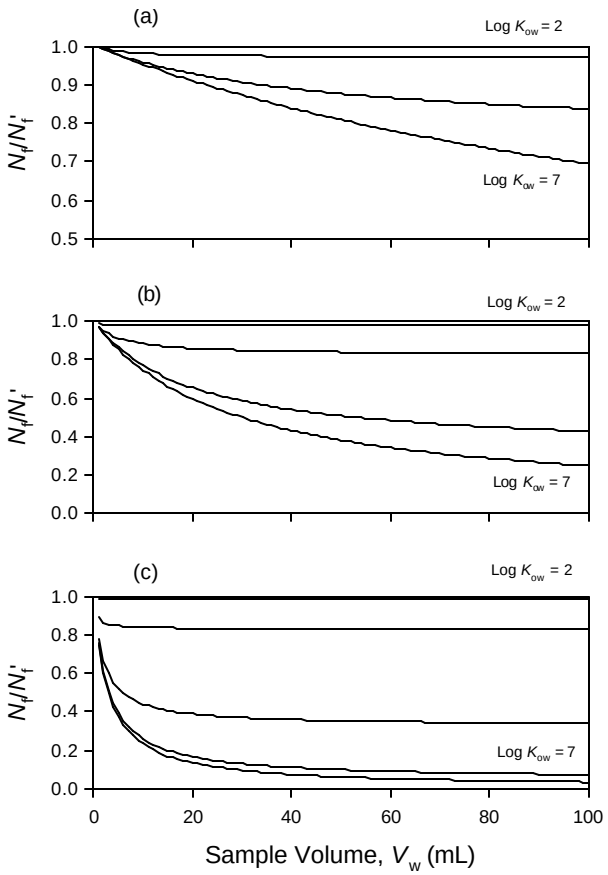

Figure 3. Variability of the SPME relative recovery (N_f/N_f') with sample volume (V_w). All curves were obtained from Equation (11) with different values for the experimental parameters: (a) C_{ss} = 50 mg/L, C_{doc} = 1 mg/L, V_f = 0.5 µL, f_{oc} = 0.01, and f_{doc} = 0.5; (b) same as (a) except for C_{ss} (= 500 mg/L); and (c) same as (a) except for C_{ss} (= 5,000 mg/L).

tions. Therefore, in all subsequent SPME assessments, a value of 0.5 µL is selected for V_f, except where otherwise specified.

Sample volume is another parameter affecting SPME experiments. It is clear from the calculated curves (Figure 3) that SPME relative recovery decreases with increasing sample volume. The reason for this trend is not readily apparent, but the explanation can be found through a detailed analysis of the governing equation. Equation (11) can be rearranged to the following form

$$\frac{N_f}{N_f'} = \frac{K_f V_f + V_w}{K_f V_f + V_w + ?} \qquad (16)$$

and similarly, q can be re-written in terms of sample volume from Equations (13)-(15),

$$q = K_{oc}\, m_{oc} + K_{doc}\, m_{doc} = K_{oc}\, f_{oc}\, C_{ss}\, V_t + K_{doc}\, DOC\, V_t$$

or for most samples,

$$q \approx K_{oc}\, f_{oc}\, C_{ss}\, V_w + K_{doc}\, DOC\, V_w \qquad (17)$$

Now, combining Equations (16) and (17),

$$\frac{N_f}{N_f'} = \frac{K_f V_f + V_w}{K_f V_f + V_w + V_w(K_{oc} f_{oc} C_{ss} + K_{doc} DOC)} \qquad (18)$$

It is evident from Equation (18) that at very small sample volumes, the water volume and matrix terms become insignificant relative to the fiber term and the ratio N_f/N_f' approaches one. As sample volume increases, the fiber term becomes increasingly less significant until the partitioning in the system is governed by the matrix term. As volume increases, eventually Equation (18) reduces to

$$\frac{N_f}{N_f'} = \frac{1}{1 + K_{oc} f_{oc} C_{ss} + K_{doc} DOC} \qquad (19)$$

Another interesting aspect of this analysis is that, for any given analyte concentration, the total amount of analyte in the system increases linearly with sample volume, which is proportional to V_w, with a slope of unity. However, as shown in Equation (18), the matrix term q is also increasing linearly with V_w, but with a slope of $K_{oc}\, f_{oc}\, C_{ss} + K_{doc}\, DOC$. In other words, the q term changes in magnitude more rapidly than the total analyte in the system as a function of sample volume if $K_{oc}\, f_{oc}\, C_{ss} + K_{doc}\, DOC$ is greater than unity. This explains the general decrease in relative recoveries with sample volume and also why the effect becomes more pronounced at high K_{ow}'s and insignificant at low K_{ow}'s.

It should be noted that the enhanced matrix effects due to increasing aqueous phase volume do not suggest the preference of using small sample volumes with SPME. As discussed later, when the sample volume reaches a certain value, the measurement of dissolved phase concentrations becomes straightforward, in that no correction for matrix effects is needed.

It should also be noted that the effects of suspended solids and DOM on the systems under evaluation are similar. All of the trends observed in the graphs would be exacerbated if the concentration of DOM were increased. For most of the analyses presented herein, the concentration of DOM was fixed and concentration of suspended solids was varied. This approach was selected for the evaluations since suspended solids vary over a larger range

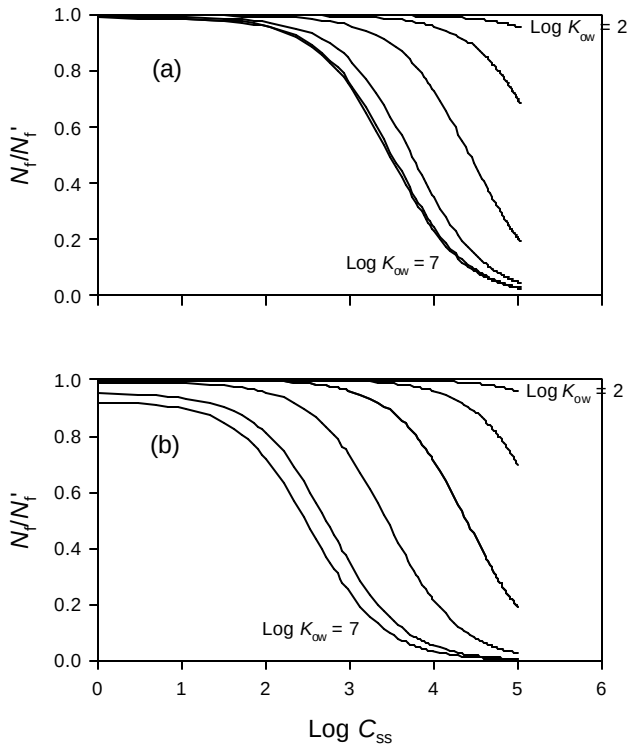

Figure 4. Variability of the SPME relative recovery (N_f/N_f') with suspended solids concentration (C_{ss}). All curves were obtained from Equation (11) with different values for the experimental parameters: (a) V_w = 5 mL, C_{doc} = 1 mg/L, V_f = 0.5 μL, f_{oc} = 0.01, and f_{doc} = 0.5 and (b) same as (a) except for V_w (= 50 mL).

of concentrations than does DOM in natural water samples. The effect of varying suspended solids concentrations on relative recoveries is shown in Figure 4.

A common feature to all of these analyses is that N_f/N_f' remains close to unity while sample parameters vary over a wide range of values when $\log K_{ow} \leq 3$ (Figures 2-4). This emphasizes that matrix effects are only important for compounds of significant hydrophobicity. This is why SPME has been used widely and very successfully for the extraction of volatile organic compounds which have relatively low K_{ow} values (Stahl and Tilotta 1999, Achten and Püttmann 2000, Black and Fine 2001).

Potential Calibration Errors

Quantitative analytical measurements require calibration. In SPME experiments, either external or internal calibration can be used. As demonstrated above, the presence of a heterogeneous matrix may significantly affect the SPME relative recovery and hence any quantitative measurement in SPME experiments. Therefore, it is important to understand how measurement errors are associated with calibration methods in SPME quantitative measurements. Unfortunately, this issue has not been discussed in many previous SPME studies.

External calibration remains widely used in SPME experiments due to its simplicity. Although the response of a specific analytical detector to a specific analyte may vary, the variation may be small enough to satisfy the accuracy objectives. Alternatively, multiple experiments can be conducted to obtain a statistical average of the response. External calibration can be performed using two different approaches. In the first approach, calibration standards are prepared in clean water and analyzed by SPME to obtain response factors (RFs). Measurement errors result from the matrix difference between the calibration standard solutions and real samples. In this case, the measurement errors can be estimated using Equation (11), and expressed in percent of error (%E) as follows:

$$\% \text{ E} = \frac{100\ ?}{K_f V_f + V_w + ?} \qquad (20)$$

In the second approach, the RFs of target analytes are acquired by direct injection of calibration standards (e.g., prepared in an appropriate organic solvent) into the analytical instrument. To estimate the measurement errors stemming from matrix effects under such a scenario, the measured dissolved phase concentration of an analyte with and without any matrix interference can be compared using Equation (8). When the matrix term is ignored, we can have from Equation (8)

$$N_f = \frac{K_w V_f V_w}{K_w V_f + V_w} C_0 \qquad (21)$$

Combining Equations (8) and (21) yields

$$\frac{C_0}{C_w^0} = \left(1 - \frac{?}{K_f V_f + V_w + ?}\right) \frac{(V_w + q)}{V_w} \qquad (22)$$

Equation (22) indicates that C_0/C_w^0 is always greater than unity, i.e., the truly dissolved phase concentration of the analyte is always overestimated using this type of external calibration without consideration of matrix effects. It is possible to estimate the maximum error that can be incurred by allowing q to become very large. As q approaches infinity, C_0/C_w^0 approaches $1 + K_f V_f/V_w$, which is the maximum

possible error using this type of external calibration.

Measurement errors with internal calibration are much more difficult to estimate as compared to external calibration. The reason for this is that the matrix effects need to be corrected for both the target analyte and internal standard in an internal calibration method. In an internal calibration approach, target analytes and internal standards are prepared in either pure organic solvent or clean water to make calibration solutions (typically with five levels of concentration for each analyte). These calibration solutions are either injected directly into the analytical instrument or extracted first by SPME and then desorbed into the analytical instrument to obtain relative response factors (RRFs) for the analytes.

The best internal standard calibration approaches are to use either isotopically substituted standards of the target analytes or a standard addition approach. However, care must be taken to allow enough time for the system to reach equilibrium prior to performing an analysis. Even so, differences in sorption behavior between recently spiked and aged field samples could still introduce substantial measurement errors (Langenfeld *et al*. 1996). These so-called "aging effects" or slow desorption kinetics could contribute to serious measurement errors even under the best possible experimental conditions.

Optimization of Sample Volume

An approach to optimizing sample volume has been introduced by Pawliszyn (1997). The approach is based on the fact that when the sample volume reaches a certain value, the absorption of an analyte onto the SPME fiber would have little impact on the dissolved phase concentration of the analyte in the sample. After this point, the sensitivity of SPME does not increase with further increase in the sample volume. Using a similar conceptual approach, the sample volume for a heterogeneous system can be optimized. Equation (5) is rearranged to yield

$$N_f = K_f V_f C_w \qquad (23)$$

where C_w is the analyte concentration in the dissolved phase after SPME. Combining Equations (8) and (23),

$$\frac{C_w}{C_w^0} = \frac{V_w + ?}{K_f V_f + V_w + ?} \qquad (24)$$

It is evident from Equation (24) that if the sample volume is increased, eventually there will be a volume such that $(V_w + q) >> K_f V_f$, and the ratio of the dissolved phase analyte concentration after SPME to the initial dissolved phase analyte concentration, C_w / C_w^0, will approach unity. At this point, SPME sensitivity in the heterogeneous system is maximized and the pre-extraction concentration in the dissolved phase is reflected in the amount of the analyte sorbed to the fiber. Other investigators have recognized the existence and implications of this relationship in heterogeneous SPME, and have even utilized this so-called "nondepletive extraction" mode in their research without fully developing it on a theoretical basis (Vaes *et al*. 1996b, Mayer *et al*. 2000). We will fully develop the concept here by proposing that the dissolved phase volume at which $C_w \approx C_w^0$ be defined as the critical volume, V_c, and that the ratio C_w / C_w^0 be defined as the critical ratio, r_c. It is clear that the critical ratio can never be exactly unity, because the $K_f V_f$ term can never be zero. Therefore, the parameter r_c can be defined by the user to achieve any desired degree of accuracy. A mathematical expression for the critical volume may be derived from a variation of Equation (24)

$$r_c = \frac{V_c + ?}{K_f V_f + V_c + ?}$$

that can be solved for V_c,

$$V_c = a\, K_f V_f - q \qquad (25)$$

where $a = r_c/(1 - r_c)$. In Equation (25), q is also a function of V_c and needs to be expressed explicitly in terms of V_c and other experimentally measurable parameters. The true total system volume from Equation (15) can be re-written as

$$V_t = \frac{V_c}{1 - \frac{C_{ss}}{d_{ss}} - \frac{DOC}{d_{dom} f_{doc}}} \qquad (26)$$

Using the definition of q we have

$$q = K_{oc} m_{oc} + K_{doc} m_{doc} = K_{oc} C_{ss} f_{oc} V_t + K_{doc} DOC\, V_t$$

$$= (K_{oc} C_{ss} f_{oc} + K_{doc} DOC) \left[\frac{V_c}{1 - \frac{C_{ss}}{d_{ss}} - \frac{DOC}{d_{dom} f_{doc}}} \right] \qquad (27)$$

Combining Equations (25) and (27) and solving for V_c we have

$$V_c = \frac{aK_f V_f}{1 + \dfrac{K_{oc}C_{ss}f_{oc} + K_{doc}DOC}{1 - \dfrac{C_{ss}}{d_{ss}} - \dfrac{DOC}{d_{dom}f_{doc}}}} = \frac{aK_f V_f}{1 + \beta} \quad (28)$$

where

$$b = \frac{K_{oc}C_{ss}f_{oc} + K_{doc}DOC}{1 - \dfrac{C_{ss}}{d_{ss}} - \dfrac{DOC}{d_{dom}f_{doc}}}$$

The parameter b is composed of variables that are measurable experimentally and/or easily estimated. The expression for b may be simplified if the concentrations of suspended solids and DOC are very small compared to their densities, i.e., $C_{ss}/d_{ss} << 1$ and $DOC/d_{dom}f_{doc} << 1$. As previously mentioned, this condition is satisfied for most environmental samples. Therefore, b can be approximated as

$$b = K_{oc}\, C_{ss}\, f_{oc} + K_{doc}\, DOC$$

For simplicity, the conceptual development here has been limited to a three-phase system of water, suspended solids, and DOM. However, it is straightforward to extend Equation (28) to include any number of matrix phases. Figures 5a and 5b depict the variation in logV_c with logK_{ow} for r_c = 0.99 (1% error) and 0.90 (10% error), respectively. Comparison of Figures 5a and 5b shows that V_c decreases significantly for a relatively small relaxation in the required accuracy. Also noteworthy is that the critical volume is smaller for samples with larger amounts of suspended solids after K_{ow} exceeds a certain value. Highly hydrophobic organic compounds partition extensively to the suspended solids and DOM that effectively become a large reservoir for these chemicals. As a result, the amount of an analyte partitioning onto the SPME fiber would be compensated by desorption of the analyte from this reservoir. Figure 5 also indicates that the critical volume can be very small for compounds with low K_{ow} values. This further explains why SPME has been so successful in the measurement of relatively polar and/or volatile organic chemicals.

The fact that V_c decreases with increasing amounts of solids has important implications for environmental applications. It suggests that SPME should be particularly effective for the measurement of hydrophobic organic compounds in sediment interstitial water, where extremely high solids-to-water ratios prevail. Also, the large critical volumes required for samples with low suspended solids and/or DOM concentrations suggest that SPME should be most useful for *in situ* field measurements. However, it remains to be demonstrated that equilibrium between SPME fibers and large media volumes (e.g., 10 – 100 L for water) can actually be achieved in the field. If equilibrium can be achieved, the dissolved phase concentration of the analyte in the sample medium is approximately the same before and after SPME and can be calculated using $C_w = N_f/V_f K_f$. Such an approach can be applied to both air and water sampling.

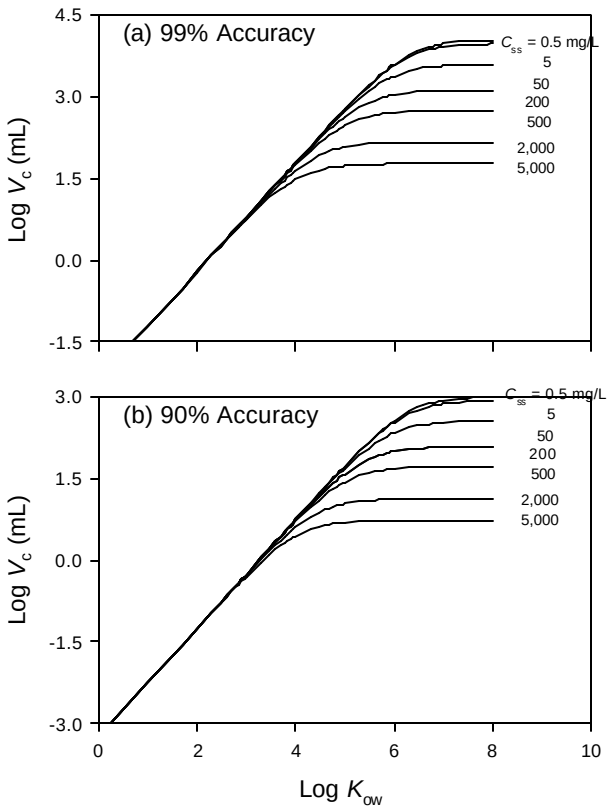

Figure 5. Variation of critical volume (logV_c) with log K_{ow} obtained from Equation (28): (a) a = 0.99 or 99% accuracy and (b) r_c = 0.90 or 90% accuracy. V_w = 5 mL, V_f = 0.5 µL, C_{doc} = 1 mg/L, f_{oc} = 0.01, and f_{doc} = 0.5.

Sensitivity Evaluation of SPME

Since the total amount of an analyte sorbed on the SPME fiber is used for quantitative measurement, the SPME fiber serves as both an extractor and a concentrator. Hence, low detection limits may be achievable even with a small sample volume. Figure

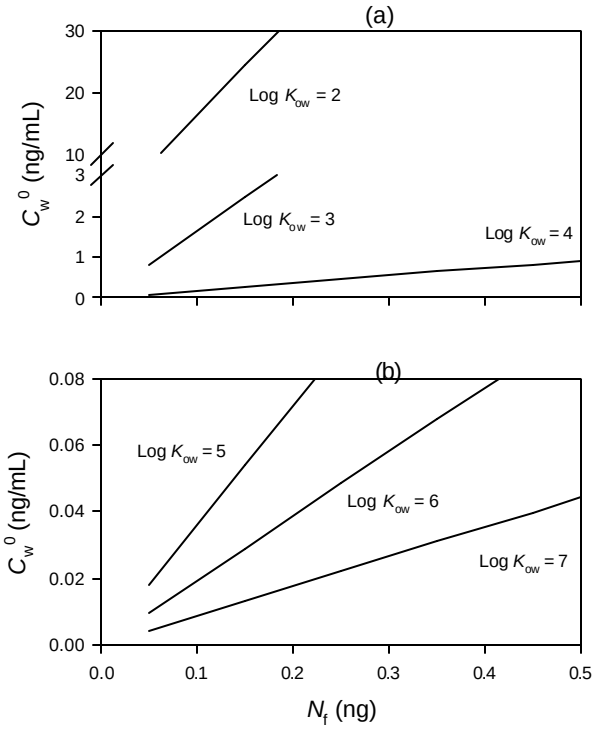

Figure 6. Correlation of dissolved phase concentration (C_w^0) with the amount of the analyte sorbed on the SPME fiber (N_f): (a) log K_{ow} = 2, 3, and 4 and (b) log K_{ow} = 5, 6, and 7. V_w = 5 mL, V_f = 0.5 µL, C_{ss} = 1 mg/L, C_{doc} = 1 mg/L, f_{oc} = 0.01, and f_{doc} = 0.5.

6 shows the correlation between the analyte concentration in the truly dissolved phase (C_w^0) and the amount of the analyte that can be collected from the SPME fiber (N_f) at the low ranges of C_w^0 and N_f values. Given the typical minimum amount of an organic compound measurable with a gas chromatography-mass spectrometry system, e.g., about 0.1 ng on the column, the detection limit ranges from 4 ng/mL for logK_{ow} = 2 to as low as 0.01-0.02 ng/mL for logK_{ow} = 6 and 7. To achieve the same maximum sensitivity using conventional extraction methods, 10 L of sample would be required for final extract volume of 1.0 mL and an injection volume of 1.0 mL. The detection limit with SPME can be further improved as the sample volume increases to where $V_w > V_c$, as previously stated. In this case, the $C_w^0 = N_f/K_f V_f$ and using the given values of N_f, K_f, and V_f, the lowest detection limit can be estimated by 1,626/K_{ow} (ng/mL). For highly hydrophobic organic compounds, the best detection limit can be extremely low.

Similarly, condensation of the analyte on the SPME fiber can be estimated using Equation (8) at the high ranges of C_w^0 and N_f values (not shown). For highly hydrophobic organic compounds, virtually all of the analyte amount in a sample could be extracted by SPME given a sufficient SPME fiber capacity and adequate extraction time. By selecting appropriate SPME fibers, the SPME technique may be combined with compound-specific isotope ratio GC/MS to enhance the use of isotopic signatures in environmental studies. A limited number of such applications have been published, but all were focused on volatile organic compounds (Goupry *et al.* 2000b).

Calibration of SPME Experimental Parameters

The key to the successful application of SPME in chemical analysis is a diligent calibration of the SPME device and sample matrix. There are two sets of parameters that need to be calibrated before actual samples may be extracted by SPME. The first set is $K_f V_f$, which can be calibrated in two steps. In the first step, a series of calibration standards prepared in organic solvent are injected directly into the analytical instrument. The RF of a specific analyte is the slope of the plot of A *versus* $C\,V_{inj}$, where A is the peak area (response) for a particular analyte, C is the concentration of the analyte in the analytical standard solution, and V_{inj} is the injection volume. Once the RF is determined, the second step is to prepare another set of standard solutions in clean water and analyze these solutions by SPME. From Equation (10) we have

$$\frac{A'}{\mathrm{RF}} = \frac{K_f V_f V_w}{K_f V_f + V_w} C_w^0 \qquad (29)$$

where A' is the peak area from the analytical instrument related to C_w^0. The slope (defined as S) of the plot A'/RF *versus* C_w^0 is therefore associated with $K_f V_f$ by $S = K_f V_f V_w/(K_f V_f + V_w)$ and solving for $K_f V_f$,

$$K_f V_f = \frac{S V_w}{V_w - S} \qquad (30)$$

If V_f is accurately known (generally given by the manufacturer), the distribution coefficient, K_f, of the analyte can be calculated.

The other parameter that must be determined is q. The standard addition method can be used to accomplish the task. In this method, various amounts of the target analyte are added to at least five sample replicates with their matrix being representative of the actual samples, and the spiked samples are analyzed by SPME. The peak areas from the analytical instrument can be plotted against the added amounts of the analyte. The intercepts of the plot are the

native amount (on the *x* axis) of the analyte in the sample replicates and the peak area (on the *y* axis) associated with the native amount, respectively. The peak area is then converted to the amount of the analyte sorbed on the SPME fiber, N_f, using the RF of the analyte obtained using external calibration as described above. Since $K_f V_f$ has been acquired using Equation (30), the value of q can be calculated using Equation (9). Alternatively, if great accuracy is not required, then the individual parameters within q can be estimated using well-established linear free energy relationships. If it is desirable to know the individual contributions of the different sorbing phases, the suspended solids may be filtered out or removed by centrifugation and the filtrates re-analyzed using the same standard addition method described above. This would allow determination of the value of $K_{doc}m_{doc}$. The value of $K_{oc}m_{oc}$ can be obtained by subtracting $K_{doc}m_{doc}$ from q. Obviously, if m_{oc} and m_{doc} are accurately determined, K_{oc} and K_{doc} can be calculated accordingly.

Comparison to Experimental Studies

The introduction of the matrix term (q) into the SPME theory provides the opportunity to account for matrix effects in SPME analysis. We conducted a comparison of the theoretical treatment presented above with available experimental data to demonstrate the validity of our approach to accounting for matrix effects. The selection of experimental data was no easy task, since many previous studies did not provide sufficient details on SPME experimental parameters. After sorting out numerous publications on SPME, we chose the experimental data from three studies by Potter and Pawliszyn (1994), Langenfeld *et al.* (1996), and Chen *et al.* (1998). These data involve mainly hydrophobic compounds with a wide range of K_{ow} values.

In the study by Potter and Pawliszyn (1994), the sample was primarily treated wastewater spiked with naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}. A 15-μm fused-silica fiber with $V_f \approx 0.0616$ μL was used for SPME extraction. The total sample volume was 40 mL (not exactly the same as V_w). The concentration of suspended solids was not given, but a similar sample from the study by Langenfeld *et al.* (1996) had C_{ss} = 1,460 mg/L. Other parameters not given are assumed to have the following values: f_{oc} = 0.1, f_{doc} = 0.5, *DOC* = 2.5 mg/L, and $d_{ss} = d_{dom}$ = 1.5 g/mL. These assumptions are reasonable for wastewater samples.

Langenfeld *et al.* (1996) analyzed four types of water samples. Samples from the Red River (Grand Forks, ND) contained a concentration of suspended solids at 430 mg/L (C_{ss}) and the fraction of organic carbon was estimated to be 0.0512 (f_{oc}). Samples from the Little Missouri River (Medora, ND) had C_{ss} = 1,450 mg/L and f_{oc} = 0.0069. Wetland samples were obtained from a prairie pothole (Larimore, ND) with C_{ss} = 825 mg/L and f_{oc} = 0.0327. Finally, treated wastewater was obtained from the City of Grand Forks secondary wastewater treatment holding pond with C_{ss} = 1,460 mg/L and f_{oc} = 0.0164. The authors indicated that either a 100-μm or 7-μm film thickness PDMS fiber was used in SPME experiments. It is not clear which fiber was used in the experiments presented here, but we used a V_f value corresponding to the 100-mm film thickness fiber in our calculation. In addition, we assumed that f_{doc} = 0.5, *DOC* = 1 mg/L, and $d_{ss} = d_{dom}$ = 1.5 g/mL.

In the study by Chen *et al.* (1998), spiked food plant samples were analyzed with phorate, diazinon, methyl parathion, and ethion as target analytes. This sample contained 75% water and 25% plant tissues. Assuming $d_{ss} = d_{dom}$ = 1.0 g/mL, the effective suspended solid concentration was 250 g/L. The total sample volume was 5.0 mL with the aqueous phase volume (V_w) being 3.75 mL. A 100-μm fused-silica fiber was used, equivalent to $V_f \approx 0.66$ μL. Additional parameters are assumed as: f_{oc} = 0.01, f_{doc} = 0.5, *DOC* = 0.1 mg/L. Both the OC and DOC concentrations are presumably low in the sample.

All of the above parameters, along with the assumptions $K_f = 0.123K_{ow}$ (Mayer *et al.* 2000), $K_{oc} = 0.41K_{ow}$ (Karickhoff 1981), and $K_{doc} = 0.11K_{ow}$ (Burkhard 2000), were substituted into Equation (11) to derive theoretical predictions. The experimentally measured parameters were the relative recoveries of the target analytes from the spiked field samples compared to spiked clean water (Potter and Pawliszyn 1994, Langenfeld *et al.* 1996, Chen *et al.* 1998). The agreement between the measured values from Potter and Pawliszyn (1994) and Chen *et al.* (1998) and theoretical predictions is excellent (Table 1). The theory not only predicts the trends of the relative recoveries for two different types of compounds, but also matches the measured values quantitatively. It is remarkable that the extremely low recoveries for chrysene-d_{12} (Potter and Pawliszyn 1994) and ethion (Chen *et al.* 1998) are well predicted by the theoretical treatment (Table 1). Comparison between the experimental data from Langenfeld *et al.* (1996) and

Table 1. Comparison of experimental results with theoretical predictions.

Analyte	LogK_{ow} [a]	Measured[b] (%)	Predicted[c] (%)
(1) Potter and Pawliszyn (1994)[d]			
1,4-Dichlorobenzene-d_4	3.38	78 (92)	87.3
Naphthalene-d_8	3.35	100 (120)	88.1
Acenaphthene-d_{10}	3.92	96 (112)	66.6
Phenanthrene-d_{10} (low)	4.45	34 (33)	37.1
Phenanthrene-d_{10} (high)	4.63	34 (33)	29.1
Chrysene-d_{12} (low)	5.61	8 (8)	5.2
Chrysene-d_{12} (high)	5.80	8 (8)	3.8
(2) Chen *et al*. (1998)[e]			
Phorate	3.92	12.8 (±6.1)	9.4
Diazinon	3.30	25.7 (±19.8)	27.7
Methyl parathion	3.32	23.5 (±17.3)	26.8
Ethion	5.07	2.4 (±1.5)	2.2

[a] K_{ow} values for polycyclic aromatic hydrocarbons are from Mackay *et al.* (1992); high and low values indicate a range of K_{ow} values from various sources.
[b] Measured as relative recoveries (%) in real samples compared to spiked clean samples.
[c] Calculated using Equation (11) with $K_f = 0.123K_{ow}$ (Mayer *et al.* 2000), $K_{oc} = 0.41K_{ow}$ (Karickhoff 1981), and $K_{doc} = 0.11K_{ow}$ (Burkhard 2000); other parameters are given in the text.
[d] The numbers in the parentheses are measured values from duplicate analyses.
[e] The numbers in the parentheses are standard deviations from five measurements for each analyte.

Table 2. Comparison of experimental results (Langenfeld *et al.* 1996) with theoretical predictions.

		Red River Water		Little Missouri River Water		Wetland Water		Treated Sewage	
	Log K_{ow} [a]	Measured[b]	Predicted[c]	Measured[b]	Predicted[c]	Measured[b]	Predicted[c]	Measured[b]	Predicted[c]
Naphthalene	3.35	66 (18)	98.0	78 (19)	99.1	78 (21)	97.6	54 (21)	97.8
Phenanthrene (low)	4.45	67 (16)	80.5	97 (14)	89.9	90 (4)	77.1	80 (16)	79.1
Phenanthrene (high)	4.63	67 (16)	73.7	97 (14)	85.9	90 (4)	69.6	80 (16)	72.0
Anthracene	4.45	66 (±14)	80.5	96 (11)	89.9	87 (3)	77.1	77 (12)	79.1
Fluoramthene (low)	4.90	64 (19)	61.7	95 (8)	77.7	81 (10)	56.8	69 (18)	59.7
Fluoramthene (high)	6.50	64 (19)	21.2	95 (8)	36.8	81 (10)	18.0	69 (18)	19.8
Pyrene (low)	4.50	58 (12)	78.7	93 (9)	88.9	80 (8)	75.1	66 (15)	77.2
Pyrene (high)	5.22	58 (12)	47.2	93 (9)	65.9	80 (8)	42.2	66 (15)	45.0
Benz[a]anthracene (low)	5.50	46 (19)	36.7	77 (21)	55.7	72 (6)	32.1	46 (23)	34.7
Benz[a]anthracene (high)	5.91	46 (19)	26.9	77 (21)	44.4	72 (6)	23.1	46 (23)	25.3
Chrysene (low)	5.61	27 (27)	33.4	44 (23)	52.1	42 (5)	29.1	29 (27)	31.6
Chrysene (high)	5.80	27 (27)	28.9	44 (23)	46.9	42 (5)	25.0	29 (27)	27.2
Benz[a]pyrene (low)	5.95	33 (25)	26.3	60 (21)	43.6	60 (21)	22.6	25 (14)	24.7
Benz[a]pyrene (high)	6.50	33 (25)	21.2	60 (21)	36.8	62 (5)	18.0	25 (14)	19.8

[a] K_{ow} values for polycyclic aromatic hydrocarbons are from Mackay *et al.* (1992); high and low values indicate a range of K_{ow} values from various sources.
[b] Measured as relative recoveries (%) in real samples compared to spiked clean samples. The numbers in the parentheses are percent relative standard deviation from five duplicate measurements.
[c] Calculated using Equation (11) with $K_f = 0.123K_{ow}$ (Mayer *et al.* 2000), $K_{oc} = 0.41K_{ow}$ (Karickhoff 1981), and $K_{doc} = 0.11K_{ow}$ (Burkhard 2000); other parameters are given in the text.

theoretical predictions is also reasonably good (Table 2). The measured values for benz[a]anthracene, chrysene, and benz[a]pyrene are substantially larger than theoretical predictions with the samples from the Little Missouri River and wetland water (except for chrysene from the Little Missouri River samples). Another noticeable discrepancy between the experiment and the theoretical treatment is the consistently lower measured recoveries of naphthalene relative to the predicted values (Table 2). Due to the success of the theoretical treatment for other compounds, we speculate that the high recoveries for benz[a]anthracene, chrysene, and benz[a]pyrene and low recoveries for naphthalene (Langenfeld *et al.* 1996) likely resulted from factors other than the SPME process.

The above comparison indicates that low experimental recoveries of hydrophobic chemicals observed in many previous studies are probably not due to the flaws of the SPME methods. Instead, they might be a result of severe matrix interferences that were not accounted for.

Final Considerations

Two other aspects of SPME remain largely unaddressed in the theoretical considerations above, namely physical interferences with the diffusion between the SPME fiber and the sample matrix by high levels of DOM or unusual matrix properties and non-equilibrium SPME. Since absorption and desorption of an analyte with the SPME fiber are no different from a normal physical diffusion process, it is expected that physical blockage by matrix phases sorbed to the fiber surface may adversely affect the accuracy of SPME measurements. This problem may be partially resolved by applying agitation to the SPME fiber. This is the approach taken by Varian Inc. (Walnut Creek, CA) in their autosampler for gas chromatography applications, which vibrates the fiber at high frequency during the extraction/equilibration step. Another way of eliminating matrix interferences is to perform headspace SPME. However, if diffusion across the air-water interface is slow, or the target analytes have a low K_H, then equilibration times may become excessively long. In the end, the SPME technique may be deemed inappropriate for certain sample matrices if the matrix effects cannot be mitigated and the accuracy of SPME measurements consistently falls short of data quality objectives.

The theoretical treatment of SPME has so far dealt with equilibrium partitioning only. In practical applications, the time for the system to reach an equilibrium state may be extensively long for chemicals with high K_{ow} values. It may therefore be desirable to conduct non-equilibrium SPME, but still be able to quantify the analyte concentration using the simple proportional correlations between N_f and C_w^0 or N_0, as described in Equations (8) and (9). This issue has been addressed with the assumption of a steady-state diffusion for the SPME partitioning process; however, the treatment was valid only for clean matrices (Ai 1997d, 1997b). The quantitative relationship between N_f and C_0 (or N_0) in a complex sample matrix would be extremely involved and is beyond the scope of the present article. Only a qualitative assessment is discussed below.

When the concentrations of interfering materials (e.g., suspended solids and DOM) become significant, the SPME process involves multi-phase interactions. The diffusion of an analyte into the SPME fiber causes a thermodynamic imbalance between the aqueous phase and the interfering phases, resulting in a net flow of the analyte from the interfering phases to the aqueous phase. Kinetically, two scenarios need to be considered: (1) sorption of the analyte onto the SPME fiber is the limiting step and (2) desorption of the analyte from one of the interfering phases is the limiting step. In the first scenario, the diffusion of the analyte from the interfering phases to the aqueous phase is presumably an equilibrium process. The relationship between N_f and C_w^0 (or N_0) takes a similar form as that derived by Ai (1997c); the difference is the expression of the sample volume which now becomes $V_w + q$. For the second scenario, sorption of the analyte onto the SPME fiber is an equilibrium process and N_f is related to C_w by $N_f = K_f C_w$, but C_w is kinetically determined by desorption of the analyte from the interfering phase to the aqueous phase. The amount of the analyte sorbed onto the SPME fiber would be largely compensated by that desorbed from the interfering phase controlling the diffusion kinetics. The relationship between N_f and C_w^0 (or N_0) in the second scenario also takes a similar form as in the first scenario, but the kinetics is mainly determined by the properties of the interfering phase instead of those of the SPME fiber.

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GLOSSARY

N_0	Total amount of the analyte in a closed system
N_s^0	Total amount of the analyte in the solid phase before SPME
N_{dom}^0	Total amount of the analyte in the DOM phase before SPME
N_w^0	Total amount of the analyte in the aqueous phase before SPME
N_a^0	Total amount of the analyte in the air phase before SPME
N_s	Total amount of the analyte in the solid phase after SPME
N_{dom}	Total amount of the analyte in the DOM phase after SPME
N_w	Total amount of the analyte in the aqueous phase after SPME
N_a	Total amount of the analyte in the air phase after SPME
N_f	Total amount of the analyte on the SPME fiber after SPME
C_{oc}^0	Equilibrium concentration (normalized to organic carbon) of the analyte in the solid phase before SPME
m_{oc}	Mass of organic carbon in the solid phase
C_{doc}^0	Equilibrium concentration (normalized to dissolved organic carbon) of the analyte in the DOM phase before SPME
m_{doc}	Mass of dissolved organic carbon in the DOM phase
C_w^0	Equilibrium truly dissolved concentration of the analyte in the aqueous phase before SPME
V_w	Volume of the aqueous phase
C_a^0	Equilibrium concentration of the analyte in the air phase before SPME
V_a	Volume of the air phase
C_{oc}	Equilibrium concentration (normalized to organic carbon) of the analyte in the solid phase after SPME
C_{doc}	Equilibrium concentration (normalized to dissolved organic carbon) of the analyte in the DOM phase after SPME
C_w	Equilibrium truly dissolved concentration of the analyte in the aqueous phase after SPME
C_a	Equilibrium concentration of the analyte in the air phase after SPME
C_f	Equilibrium concentration of the analyte on the SPME fiber after SPME
V_f	Volume of the SPME fiber (polymer coating phase)
K_{oc}	Equilibrium partition coefficient of the analyte between the solid phase (normalized to organic carbon) and the aqueous phase
K_{doc}	Equilibrium partition coefficient of the analyte between the DOM phase (normalized to dissolved organic carbon) and the aqueous phase
K_f	Equilibrium partition coefficient of the analyte between the SPME fiber and the aqueous phase
K_H'	Dimensionless Henry's Law constant
K_H	Henry's Law constant
R	Universal gas constant
T	Absolute temperature
q	Matrix term, defined as $K_{oc}\, m_{oc} + K_{doc}\, m_{doc}$ or in general $\sum_{i=1}^{n} K_{oc}^{i} m_{oc}^{i} + \sum_{j=1}^{n'} K_{doc}^{j} m_{doc}^{j}$, where n and n' are the total numbers of solid and DOM phases, respectively
N_f'	Total amount of the analyte on the SPME fiber after SPME with absence of matrix interferences
f_{oc}	Organic carbon fraction in the solid phase
f_{doc}	Dissolved organic carbon fraction in the DOM phase
d_{ss}	Density of the solid phase

d_{dom}	Density of the DOM phase
K_{ow}	Octanol-water partition coefficient
C_{ss}	Concentration of suspended solids in the system
DOC	Concentration of dissolved organic carbon the system
V_t	Total sample volume
V_c	Critical volume at which non-depletive SPME occurs
r_c	Critical ratio at which the critical volume is defined
a	Defined as $r_c/(1 - r_c)$
b	Defined as $(K_{oc}C_{ss}f_{oc} + K_{doc}DOC)/(1 - C_{ss}/d_{ss} - DOC/d_{dom}f_{doc})$