Theory of analyte extraction by selected porous polymer SPME fibres†

Tadeusz Górecki, Xiaomei Yu and Janusz Pawliszyn*

Department of Chemistry and Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

Received 2nd November 1998, Accepted 12th February 1999

Extraction of analytes by the new porous polymer solid phase microextraction (SPME) fibres is based on adsorption rather than absorption. The equilibrium theory developed for the liquid poly(dimethylsiloxane) (PDMS) coating does not apply to these coatings. The paper presents theoretical description of the extraction process for adsorption-type fibres, including PDMS–DVB (divinyl benzene), Carbowax–DVB and Carbowax–TR (template resin). The model is based on Langmuir adsorption isotherm. Expressions describing the amount of analyte extracted by the fibre in two- and three-phase systems are presented and discussed. The effect of selected experimental variables is discussed. In general, there is a non-linear dependence between the amount of an analyte extracted by the fibre and its concentration in a sample. The dependence can be approximated by a straight line for low concentrations only. Matrix composition can significantly affect the amount extracted. Interferences co-extracted with the analyte of interest may reduce the amount extracted and the quasi-linear range of the response. Great care should be exercised therefore when performing quantitative analysis with porous polymer SPME fibres. The phenomena discussed are illustrated on an example of benzene and 4-methyl-2-pentanone extraction from water by PDMS–DVB and Carbowax–DVB fibres.

Introduction

Solid phase microextraction (SPME) has gained widespread acceptance in many areas in recent years. It has been applied for the determination of a wide spectrum of analytes in a variety of matrices. The most widespread seems to be analysis of volatile and semi-volatile compounds in water. Examples in this area include determination of substituted benzene compounds,[1,2] volatile organic compounds,[3–5] polycyclic aromatic hydrocarbons and polychlorinated biphenyls,[6] pesticides,[7–12] phenols,[13,14] fatty acids,[15] as well as lead and tetraethyllead.[16]

There are two distinct types of SPME coatings available commercially. The most widely used is poly(dimethylsiloxane) (PDMS), which is a liquid coating. Even though it looks like a solid, it is in fact a high viscosity rubbery liquid. Poly(acrylate) (PA) is a solid crystalline coating that turns into liquid at desorption temperatures. Both PDMS and PA extract analytes *via* absorption. The remaining coatings, including PDMS–DVB (divinylbenzene), Carbowax–DVB, Carbowax–TR (template resin—DVB with uniform pore sizes) and Carboxen, are mixed coatings, in which the primary extracting phase is a porous solid, extracting analytes *via* adsorption. Similarity of the names can be very deceptive, since the fundamentals of absorption and adsorption are different. Fig. 1 illustrates the initial and equilibrium/steady-state stages of the extraction process for absorption- and adsorption-type SPME coatings. Independently of the nature of a coating, analyte molecules initially get attached to its surface. Whether they migrate to the bulk of the coating or remain at its surface depends on the magnitude of the diffusion coefficient of an analyte in the coating. Diffusion coefficients of organic molecules in PDMS are close to those in organic solvents, therefore diffusion into PDMS is relatively fast and this coating extracts analytes *via* absorption. Diffusion coefficients in poly(acrylate) are lower by about an order of magnitude, but still large enough for absorption to be the primary extraction mechanism. On the other hand, diffusion coefficients of organic molecules in the bulk of divinylbenzene and Carboxen are so small that within the time frame of SPME

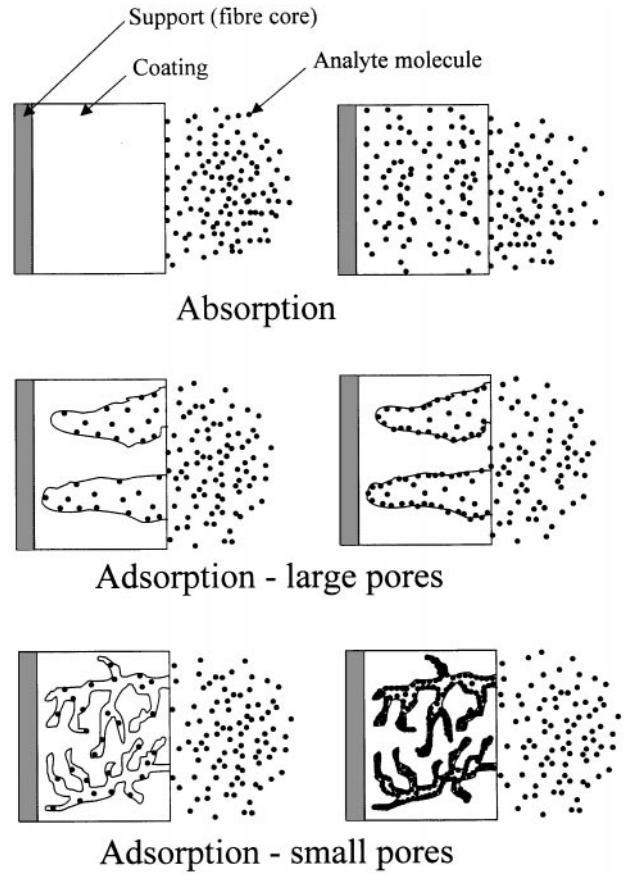

Fig. 1 Comparison of absorption and adsorption extraction mechanisms (cross-sections of the coated fibres). Diagrams on the left illustrate the initial stages of the processes. Diagrams on the right illustrate the steady-state condition.

† Presented in part at Pittcon '99, March 7–12, 1999, Orlando, Florida, USA.

analysis, essentially all the molecules remain on the surface of a coating. Should the organic molecules remain there for a very long time (measured in days or weeks rather than hours), they still might diffuse into the bulk of the coating (over very short distances). This would manifest itself during analysis as persistent carryover, difficult to eliminate even after repeated desorptions. For all practical purposes, however, adsorption is the only extraction mechanism for those coatings.

Louch *et al.*[17] developed equilibrium theory for coatings extracting analytes *via* absorption in two-phase systems (sample and fibre coating), while Zhang and Pawliszyn extended it to three-phase systems (sample-headspace-coating).[18] A complete theory for absorption-type coatings was presented in a book by Pawliszyn.[19] Recently, Ai developed theoretical descriptions of the dynamics of non-equilibrium direct extraction,[20] as well as equilibrium[21] and non-equilibrium[22] headspace extraction. This paper presents the steady state theory of analyte extraction *via* adsorption by selected porous polymer fibres (PDMS/DVB, Carbowax/DVB, Carbowax/TR). The theory does not apply to Carboxen fibres.

Theory

Weak intermolecular interactions (and hydrophobic interactions when sampling from water)[23] play the most important role in analyte extraction by the porous polymer SPME coatings available commercially. The number of surface sites where adsorption can take place is limited. When all such sites are occupied, no more analyte can be trapped (unless it can condense into pores by the capillary condensation mechanism).[24] This means that the dependence between the concentration of the analyte in a sample and the amount of the analyte extracted from this sample by a solid SPME coating cannot be linear over broad concentration ranges. In addition, while absorption is a non-competitive process, adsorption is by definition competitive, and a molecule with higher affinity for the surface can replace a molecule with lower affinity. Thus, the amount of the analyte extracted by the fibre from a sample can be significantly affected by sample matrix composition.

The following considerations pertain to PDMS–DVB, Carbowax–DVB and Carbowax/TR coatings. No theory has been developed yet for the Carboxen coating, for which capillary condensation plays an important role. As a result, this coating behaves differently than the other coatings. For example, equilibration times for the DVB-based coatings are usually quite short. In headspace extraction of tetraethyllead (TEL) from water (25 mL sample in a 40 mL vial) these coatings reach equilibrium in less than 30 min. On the other hand, the amount of TEL extracted by the Carboxen coating increases with increased extraction time under similar conditions even after 48 h. Such a long time cannot be explained by poor mass transfer conditions—it can only result from slow filling of the pores with the condensing analyte. Consequently, the assumption that the analyte molecules can only attach themselves to active sites on the coating surface is not valid for the Carboxen coating.

The dependence between the equilibrium concentration of a compound associated with the sorbent and its concentration in the solution is commonly referred to as adsorption isotherm. It will be illustrated later in this paper that Langmuir adsorption isotherm well describes equilibrium analyte extraction by PDMS/DVB and Carbowax/DVB coatings, therefore it has been used to develop the theoretical description of the process.

In the Langmuir model, the surface has a limited number of adsorption sites that can be occupied by the sorbate. The following assumptions apply: (1) the adsorbing molecule adsorbs into an immobile state; (2) all sites are equivalent; (3) each site can hold at the most one molecule of the adsorbate, and (4) there are no interactions between adsorbate molecules on adjacent sites so that the equilibrium constant is independent of the coverage of the adsorbed species.[24] Assumption (3) means that a monolayer of the adsorbate can be formed at the surface at the most. Adsorption is treated as a reaction where a molecule A reacts with an empty site, S, to yield an adsorbed complex A_{ad}:

$$A + S \Leftrightarrow A_{ad} \quad (1)$$

At equilibrium, surface concentration of A in mol cm^{-2}, $[A_{ad}]$, is described by the following equation:

$$[A_{ad}] = [S_0]\frac{K_A[A]}{1 + K_A[A]} \quad (2)$$

where $[S_0]$ is the total concentration of active sites on the surface (maximum surface concentration of the analyte) in mol cm^{-2}, K_A is the adsorption equilibrium constant, and [A] is the concentration of A in the matrix.

It would be cumbersome to use surface concentration expressed in number of moles per cm^2 for the description of the SPME process. However, if we assume that the sorbent has a uniform pore size distribution and surface area throughout its bulk, surface concentrations can be replaced by bulk concentrations by multiplying both sides of eqn. (2) by the term Φ/V_f, where Φ is the surface area (in cm^2). Such an assumption seems reasonable in view of the fact that the fibre-to-fibre reproducibility is usually very good for fibres originating from the same batch. We can now define the concentration of the analyte on the fibre C_{fA} and the maximum concentration of active sites on the coating C_f max in the following way:

$$C_{fA} = [A_{ad}]\frac{\Phi}{V_f} \quad (3)$$

$$C_{f\,max} = [S_0]\frac{\Phi}{V_f} \quad (4)$$

We will also use the symbol C_{sA}^{∞} instead of [*A*] to denote analyte concentration in the sample at equilibrium. From these, we can define the equilibrium concentration of the analyte on the fibre, C_{fA}^{∞}:

$$C_{fA}^{\infty} = \frac{C_{f\,max}K_A C_{sA}^{\infty}}{1 + K_A C_{sA}^{\infty}} \quad (5)$$

It is evident that C_{fA}^{∞} is not a linear function of equilibrium analyte concentration in the sample, except when the product $K_A C_{sA}^{\infty}$ is much smaller than one. This may happen when either the affinity of the analyte towards the coating is low, or its concentration in the sample is very low. The reciprocal of this equation yields:

$$\frac{1}{C_{fA}^{\infty}} = \frac{1}{C_{f\,max}} + \frac{1}{C_{f\,max}K_A C_{sA}^{\infty}} \quad (6)$$

Therefore the plot of $1/C_{fA}^{\infty}$ *vs.* $1/C_{sA}^{\infty}$ should be a straight line with a slope of $1/C_{f\,max}K_A$ and an intercept of $1/C_{f\,max}$.

Eqn. (5) is difficult to use in practice, since it requires knowledge of the analyte concentration in the sample at equilibrium. It is more practical to determine the dependence between the initial concentration of the analyte in the sample (C_{0A}) and the amount extracted. Mass balance can be used for this purpose:

$$C_{0A}V_s = C_{sA}^{\infty}V_s + C_{fA}^{\infty}V_f \quad (7)$$

From eqn. (5), equilibrium concentration of the analyte is:

$$C_{sA}^{\infty} = \frac{C_{fA}^{\infty}}{K_A(C_{f\,max} - C_{fA}^{\infty})} \quad (8)$$

By combining eqns. (7) and (8), after a few rearrangements one gets:

$$n = C_{fA}^{\infty}V_f = \frac{K_A C_{0A}V_s V_f(C_{f\,max} - C_{fA}^{\infty})}{V_s + K_A V_f(C_{f\,max} - C_{fA}^{\infty})} \quad (9)$$

where n is the amount of the analyte extracted by the fibre at equilibrium. Eqn. (9) is an iterative dependence, since equilibrium analyte concentration on the fibre (C^{∞}_{fA}) appears on both its sides. Nevertheless, it gives an insight into the nature of analyte extraction with porous polymer coatings, as will be illustrated later. It is in fact a quadratic equation, which can be solved analytically. Of the two roots obtained, only the following has a physical meaning:

$$n = \frac{C_{f\,max}K_A V_f + C_{0A}V_s K_A + V_s - \sqrt{K_A^2(C_{f\,max}V_f - C_{0A}V_s)^2 + 2K_A V_s(C_{f\,max}V_f + C_{0A}V_s) + V_s^2}}{2K} \quad (10)$$

A discussion of this dependence is presented in the Results and discussion section of this paper. In real life situations, one can hardly assume that only one compound will be extracted by the coating. Since adsorption is a competitive process, the presence of other compounds must affect the amount of analyte A extracted by the fibre (n_A). In the following derivation, only one competing compound is taken into account. The same reasoning can be applied, however, to any number of compounds present in the sample.

The concentration of analyte A on the fibre in the presence of a competing compound B is given by the following equation:

$$C^{\infty}_{fA} = \frac{C_{f\,max}K_A C^{\infty}_{sA}}{1 + K_A C^{\infty}_{sA} + K_B C^{\infty}_{sB}} \quad (11)$$

where K_B is the adsorption equilibrium constant for compound B, and C^{∞}_{sB} is the equilibrium concentration of B in a sample. If more than two compounds were present in the sample, the denominator would contain additional $K_i C^{\infty}_{si}$ terms. Mass balance for A is again described by eqn. (7). A derivation similar to that described above yields the following relationship:

$$n_A = C^{\infty}_{fA}V_f = \frac{K_A C_{0A}V_s V_f(C_{f\,max} - C^{\infty}_{fA})}{(1 + K_B C^{\infty}_{sB})V_s + K_A V_f(C_{f\,max} - C^{\infty}_{fA})} \quad (12)$$

Eqn. (12) can be solved in the same way as eqn. (9). The only root with a physical meaning has the form:

$$n_A = C^{\infty}_{fA}V_f = \frac{C_{f\,max}K_A V_f + C_{0A}V_s K_A + V_s(1 + K_B C^{\infty}_{sB})}{2K_A} + \frac{\sqrt{K_A^2(C_{f\,max}V_f - C_{0A}V_s)^2 + 2K_A V_s(1 + K_B C^{\infty}_{sB})(C_{f\,max}V_f + C_{0A}V_s) + V_s^2(1 + K_B C^{\infty}_{sB})^2}}{2K_A} \quad (13)$$

Even though this dependence seems very complex, it can give insight into the extraction process, as will be illustrated in the Results and discussion section.

SPME extraction can be carried out by immersing the fibre in the sample (direct extraction), or by exposing it to the sample headspace. In fact, when volatile compounds are analysed, headspace extraction is the preferred mode of operation.[19] Mathematical description of the headspace extraction process is more complex than that of direct extraction, as in headspace extraction one has to deal with equilibria involving three phases: sample, its headspace, and the fibre coating. When the fibre is exposed to the headspace, partitioning of analytes occurs between the gas phase and the coating, as well as between the sample and the gas phase. Mass balance for such a system (containing one analyte only) can be written in the following way:

$$C_{0A}V_s = C^{\infty}_{sA}V_s + C^{\infty}_{hA}V_h + C^{\infty}_{fA}V_f \quad (14)$$

where C^{∞}_{hA} is the equilibrium concentration of the analyte in the sample headspace, and V_h is the headspace volume. Based on the Langmuir model, equilibrium concentration of the analyte on the fibre coating can be defined as:

$$C^{\infty}_{fA} = \frac{C_{f\,max}K_{A_h}C^{\infty}_{hA}}{1 + K_{A_h}C^{\infty}_{hA}} \quad (15)$$

where the subscript h in K_{A_h} denotes that this is the equilibrium constant for adsorption of the analyte from the gas phase (sample headspace), as opposed to the liquid phase. Equilibrium concentration of the analyte in the sample headspace is determined by dimensionless Henry's law constant K_{H_A}:

$$C^{\infty}_{hA} = K_{H_A}C^{\infty}_{sA} \quad (16)$$

Let us denote the product of K_{H_A} and K_{A_h} as K'_A. Substituting eqns. (15) and (16) into eqn. (14), after a few rearrangements, yields:

$$n = C^{\infty}_{fA}V_f = \frac{K'_A C_{0A}V_s V_f(C_{f\,max} - C^{\infty}_{fA})}{V_s + V_h K_{H_A} + K'_A V_f(C_{f\,max} - C^{\infty}_{fA})} \quad (17)$$

Analytical solution of eqn. (17) yields:

$$n = \frac{C_{f\,max}K'_A V_f + C_{0A}V_s K'_A + V_s + V_h K_{H_A}}{2K'_A} + \frac{\sqrt{K'^2_A(C_{f\,max}V_f - C_{0A}V_s)^2 + 2K'_A V_s\left(C_{f\,max}V_f + C_{0A}V_s + V_{hA}K_{H_A}\frac{V_f}{V_s}C_{f\,max} + V_h K_{H_A}C_{0A}\right) + (V_s + V_h K_{H_a})^2}}{2K'_A} \quad (18)$$

Taking into account that usually the total volume of the system (*e.g.*, sample vial) is fixed, we can define $a = V_h/V_s$, and eliminate V_h by substituting it with aV_s:

$$n = \frac{C_{f\,max}K'_A V_f + C_{0A}V_s K'_A + V_s(1 + aK_{H_A})}{2K'_A} + \frac{\sqrt{K'^2_A(C_{f\,max}V_f - C_{0A}V_s)^2 + 2K'_A V_s(C_{f\,max}V_f + C_{0A}V_s + aK_{H_A}V_f C_{f\,max} + aV_s K_{H_A}C_{0A}) + V_s^2(1 + aK_{H_a})^2}}{2K'_A} \quad (19)$$

When more than one compound is extracted from the sample headspace, derivation similar to those above yields the following equation for analyte A extracted by the fibre:

$$n_A = C^{\infty}_{fA}V_f = \frac{K'_A C_{0A}V_s V_f(C_{f\,max} - C^{\infty}_{fA})}{V_s(1 + K'_B C^{\infty}_{sB}) + aV_s K_{H_A}(1 + K'_B C^{\infty}_{sB}) + K'_A V_f(C_{f\,max} - C^{\infty}_{fA})} \quad (20)$$

where $K'_B = K_{Bh}K_{H_B}$.

The analytical solution of eqn. (20) is as follows:

$$n_A = \frac{C_{f\,max}K'_A V_f + C_{0A}V_s K'_A + V_s(1 + K'_B C^{\infty}_{sB})(1 + aK_{H_A}) + \sqrt{K'^2_A(C_{f\,max}V_f - C_{0A}V_s)^2 + 2K'_A V_s(1 + K'_B C^{\infty}_{sB})(C_{f\,max}V_f + C_{0A}V_s + aK_{H_A}V_f C_{f\,max} + aV_s K_{H_A}C_{0A}) + V_s^2(1 + K'_B C^{\infty}_{sB})^2(1 + aK_{H_a})^2}}{2K'_A} \quad (21)$$

This dependence is very complicated, and it is not immediately clear when looking at eqn. (21) how the particular terms affect

the amount extracted. Nevertheless, it can be used relatively easily to model equilibrium extraction conditions for various sets of input variables, as will be illustrated in the Results and discussion section.

Experimental

All the reagents were of analytical reagent grade. Benzene was purchased from Caledon Laboratories (Ontario, Canada), while i-propanol and 4-methyl-2-pentanone from Aldrich Chemical Co. (Milwaukee, WI). SPME holder and fibres (PDMS–DVB and Carbowax–DVB) were purchased from Supelco (Bellefonte, PA).

Aqueous standard solutions of benzene and 4-methyl-2-pentanone were prepared from primary dilution standard solutions of the analytes in methanol. Concentrations of the primary dilution standard solutions were such that 25 μL of a given solution added to 25 mL of water produced the desired concentration of the aqueous standard. In this way, the amount of methanol in each aqueous standard was constant. Aqueous standard solutions were prepared in 40 mL amber vials (Supelco). They were stirred during extraction with a digital magnetic stirrer (VWR model HPS 400, VWR Scientific of Canada, Ltd., Mississauga, ON) at 1200 rpm. Extraction was carried out from sample headspace. Extraction times were set in such a way that they were slightly longer than equilibration times of the analytes. For benzene, extraction time was 2 min, and for 4-methyl-2-pentanone it was 12 min.

All analyses were performed using a Varian Star 3500 GC (Varian Associates, Sunnyvale, CA) equipped with a 30 m × 0.25 mm × 0.25 μm SPB-5 column (Supelco). The column was equipped with a 1 m fused silica precolumn. Hydrogen at 20 psi was used as the carrier gas. Injector temperature was held at 210 °C for SPME injections, and was temperature programmed from 55–250 °C at 250 °C min^{-1} for syringe injections. Flame ionization detector (FID) was held at 250 °C. Oven temperature program for SPME injections was the following: 35 °C for 1 min, ramped to 120 °C at 15 °C min^{-1}, held for 1 min. For syringe injections, the initial oven temperature was 55 °C.

Detector response factors were determined by injecting 0.5 μL of standard methanolic solutions of benzene (0.995 μg mL^{-1}) and 4-methyl-2-pentanone (0.887 μg mL^{-1}). The same benzene solution was used for quality control injections performed at least daily.

Results and discussion

Fig. 2 presents calibration curves obtained for i-propanol in the presence of 4-methyl-2-pentanone (methyl-isobutyl ketone; MIBK).[25] Sampling was carried out from sample headspace with a PDMS/DVB fibre [for details, see ref. (25)]. The affinity of MIBK for the fibre coating was much higher than the affinity of i-propanol. As long as MIBK concentration remained low (10 times lower than the concentration of i-propanol; points represented by squares), the calibration curve remained linear up to ~75 μg L^{-1}, and the deviation from linearity at higher concentrations was not very significant. However, when MIBK concentration at each point was equal to that of i-propanol (circles), the dependence could be approximated by a straight line only up to ~25 μg L^{-1}. Moreover, at higher MIBK concentrations, displacement of i-propanol was evident. The amount of i-propanol extracted from the sample at 150 μg L^{-1} was lower by almost 50% when MIBK concentration was also 150 μg L^{-1}, compared to the case when it was 15 μg L^{-1}. Fig. 2 illustrates therefore that the presence of interfering compounds can affect both the amount extracted and the linear range of the method for porous polymer fibres.

Table 1 illustrates the effect of the interfering compound on the amount of the analyte extracted from the sample for the PDMS–DVB and Carbowax–DVB fibres. In this experiment, the concentration of the interfering compound was kept constant for all the analyte concentration levels. It is evident from this table that in all cases the presence of the interfering compound caused a reduction in the amount of the analyte extracted by both fibres. In general, the effect of MIBK on the extraction of

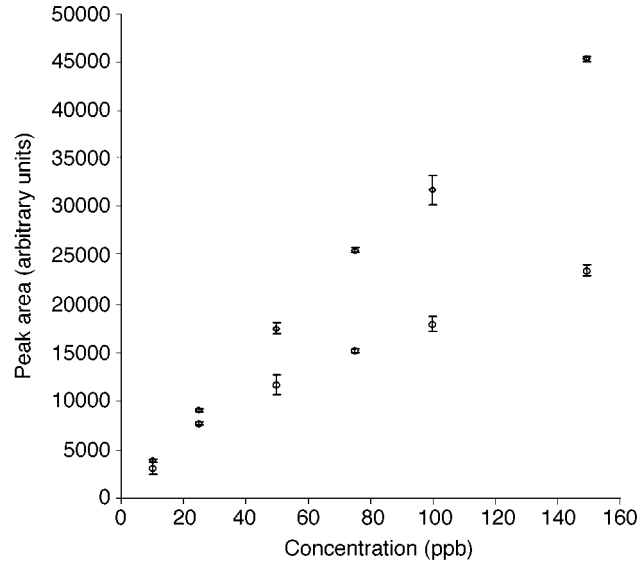

Fig. 2 Calibration curves for i-propanol in the presence of methyl-isobutyl ketone (MIBK) (PDMS/DVB fibre, headspace sampling). Squares—MIBK concentration 10 × lower than i-propanol concentration; circles—MIBK concentration equal to i-propanol concentration; error bars represent ± one standard deviation of the measurement.

Table 1 The effect of an interfering compound on the amount of analyte extracted by the fibre. Extraction of benzene in the presence of MIBK, and extraction of MIBK in the presence of benzene

	Mass of analyte extracted by the fibre/ng											
	PDMS/DVB fibre						Carbowax/DVB fibre					
	Benzene			MIBK			Benzene			MIBK		
Analyte concentration/ μg L^{-1}	No MIBK	3.5 mg L^{-1} MIBK	Difference (%)	No benzene	0.85 mg L^{-1} benzene	Difference (%)	No MIBK	5 mg L^{-1} MIBK	Difference (%)	No benzene	0.85 mg L^{-1} benzene	Difference (%)
85	104	80	23	39	22	43	31	23	27	6	3	50
350	296	243	18	122	76	38	87	67	23	20	12	40
850	481	435	10	228	153	33	209	166	20	43	28	35
1700	792	704	11	343	249	27	292	218	25	69	51	26
3450	1097	1005	8	502	397	21	471	431	8	114	86	25

benzene was less pronounced than the effect of benzene on the extraction of MIBK (note that in benzene extraction MIBK concentration was higher than benzene concentration in all but the most concentrated samples). This can be easily explained taking into account that MIBK revealed lower affinity to the fibres examined than benzene did. As a result, benzene effect on MIBK extraction was more significant even at lower concentrations (0.85 mg L^{-1}).

Eqn. (6) predicts that the plot of $1/C_{fA}^{\infty}$ *vs.* $1/C_{sA}^{\infty}$ should be a straight line. This was verified for headspace extraction of methyl-isobutyl ketone (MIBK) and benzene. For the Carbowax/DVB fibre, the dependences were linear, with R^2 values of 0.9992 and 0.9933 for MIBK and benzene, respectively. For the PDMS/DVB fibre, the R^2 values were 1.000 and 0.9954, respectively. The high R^2 values indicate that within the concentration ranges examined, the Langmuir isotherm model is suitable for the description of analyte adsorption on the fibres examined. The slopes of the lines were proportional to $1/C_{f\,max}K'_A$ (where $K'_A = K_{A_h}K_{H_A}$), while the intercepts to $1/C_{f\,max}$. The latter allowed estimation of $C_{f\,max}$. For the PDMS–DVB fibre, the estimated values were 33.3 and 14.3 μmol mL^{-1} for benzene and MIBK, respectively. For the Carbowax/DVB fibre, those values were 16.8 and 5.0 μmol mL^{-1}. The differences between the estimates obtained for the same fibres with two different compounds are not surprising in the light of the fact that the fibres also extracted water. Even though it had much lower affinity to those fibres than the organic molecules, it was present in the headspace in concentrations higher by orders of magnitude than the analytes of interest. Thus, it was able to compete for the active sites on the surface, and effectively reduced their number [see the discussion of eqn. (12)]. Additionally, standard aqueous solutions contained also methanol in concentrations much higher than those of the analytes. In spite of its very good aqueous solubility, the amount of methanol extracted by the fibres was significant. Of the two analytes of interest, benzene had higher affinity to the coatings examined, therefore the reduction in the effective number of active sites was less significant for this compound.

Determination of the 'true' $C_{f\,max}$ value would require conditions bearing little resemblance to those usually encountered in SPME. To make sure that only one compound is sorbed, it would be necessary to expose the fibre to vacuum containing pure vapors of an organic compound, since it cannot be excluded that even permanent gases can cause effective reduction of the number of active sites. For these reasons, estimation of K'_A was not carried out, since no meaningful results were expected.

The form of eqn. (9) is very similar to that of the equation for n when coatings extracting analytes by absorption rather than adsorption are used:[19]

$$n = \frac{KC_{0A}V_sV_f}{V_s + KV_f} \qquad (22)$$

where K is the partition coefficient of the analyte between the sample and the coating. The main difference between eqn. (9) and (22) is the presence of the fibre concentration term ($C_{f\,max} - C_{fA}^{\infty}$ in the numerator and denominator of eqn. (9) (also, note that the meaning of K_A is entirely different than that of K: K_A is adsorption equilibrium constant, while K is the partition coefficient). For very low analyte concentrations on the fibre, it can be assumed that $C_{f\,max} >> C_{fA}^{\infty}$. For this condition to be fulfilled, analyte concentration in the sample and/or its affinity for the fibre must be very low. When these requirement(s) are met, a linear dependence should be observed. If, however, the amount of the analyte on the fibre is not negligible compared to the total number of active sites, the dependence cannot be linear any more.

Eqn. (12) indicates that the amount of analyte A extracted from the sample containing more than one compound (n_A) must be lower than n from eqn. (9), as there is an additional term in the denominator of eqn. (12), which can only be greater than one. The difference does not have to be dramatic if the second term in the denominator of eqn. (12) is much larger than the first one, which can occur when the interfering compound is either present at a very low concentration, and/or is characterized by low affinity to the coating. In all other cases, one can expect that n_A will be significantly lower than n.

What is less obvious when looking at equation eqn. (12) is the fact that adsorption of interfering compounds affects also the linear range of the calibration curve. The term C_{sB}^{∞} is the equilibrium concentration of B. Unless the volume of the sample is very large, in which case the equilibrium concentration of B is practically equal to its initial concentration, C_{sB}^{∞} depends on the initial concentration of B and A in the same complex way in which C_{sA}^{∞} depends on C_{0A} and C_{sB}^{∞} (thus C_{0B}). Incorporating this dependence into eqn. (12) would make it very complex. Instead, we can picture this dependence in the following way: when B adsorbs on the surface of the coating, it reduces the number of adsorption sites available for A. This means that, effectively, $C_{f\,max}$ is lower for A, hence the non-linearity becomes significant at lower concentrations of A compared to the case when the sample contains no interfering compounds.

Compared to eqn. (9), eqn. (1) contains an additional term in the denominator, $V_hK_{H_A}$. Since this term can only be equal to or greater than 0, at equilibrium the amount of the analyte extracted from the sample headspace can only be equal to or lower than the amount extracted directly from the sample. It is obvious therefore that sensitivity in headspace sampling is usually lower than in direct sampling. To minimize the sensitivity loss, headspace volume should be kept small. On the other hand, headspace sampling eliminates many matrix-related problems, and is usually faster.[19] Compared to SPME with liquid coatings, eqn. (17) contains the same additional term as eqn. (9), *i.e.*, $(C_{f\,max} - C_{fA}^{\infty})$. The consequences are similar to those described for eqn. (9). Linear response can be expected only for equilibrium concentrations on the fibre that are much lower than $C_{f\,max}$.

From eqn. (20), it is clear that the presence of additional compounds which are co-extracted from the headspace reduces the amount of analyte A extracted by the fibre, unless those compounds are present at very low concentrations in the sample at equilibrium, and/or the product of their Henry's law constant and adsorption equilibrium constant for extraction from the gas phase is very small. Again, it is not immediately obvious when looking at this equation that additional compounds present in the headspace affect also the linear range of the method. For explanation of this phenomenon, see the discussion of eqn. (12) above.

Fig. 3 illustrates the predicted (theoretical) dependence of the amount of the analyte extracted by the fibre *vs.* the initial concentration of the analyte in the sample for direct extraction when a single analyte is present in the sample, for three different equilibrium constant (K_A) values. The plots were determined using eqn. (10). At low analyte concentrations, the dependencies can be approximated by straight lines. At higher concentrations they cease to be linear, and finally they level off when all active sites on the fibre surface are occupied by the analyte molecules. The shapes of the isotherms, and particularly their linear ranges, depend strongly on the K_A value. When it is large (see the curve for K_A = 1 000 000), the response remains practically linear until the fibre becomes saturated with the analyte. After this point, the curve levels off rather abruptly. When K_A is low (see the curve for K_A = 10 000), the initial quasi-linear range is narrower, but n changes with the initial analyte concentration C_{0A} in a broader concentration range.

Fig. 4 presents the theoretical dependence of the amount of analyte n extracted by the fibre on the initial concentration of the analyte in the sample for a single analyte and direct extraction,

for three different $C_{f\,max}$ values. It is clear that the concentration of active sites on the fibre has a profound effect on linearity of the response. The higher the number of active sites, the broader is the linear range of the isotherm. This is quite obvious when looking at eqn. (9). When $C_{f\,max}$ is high, the value of the difference ($C_{f\,max} - C^{\infty}_{fA}$) is very close to $C_{f\,max}$ for a broader range of C^{∞}_{fA} values than when $C_{f\,max}$ is low. For illustration purposes, the $C_{f\,max}$ value estimated for the PDMS/DVB fibre with benzene (33.3 μmol mL^{-1}) corresponds to ~2.6 g L^{-1}.

Fig. 5 presents the theoretical relationship between the amount of analyte *A* extracted by the fibre and the initial concentration of the analyte in the sample when two compounds are present in the sample (direct extraction), for three different K_B values. It is intuitively obvious that when the interfering compound has high affinity for the fibre coating, the displacement effects are more pronounced. Indeed, Fig. 5 illustrates that for the same C_A, n_A decreases when K_B increases. When the affinity for the fibre coating is similar for both compounds, the displacement effect is not very significant, especially when the concentration of the interfering compound(s) is low (see the curve for K_B = 10 000). On the other hand, when K_B is high, displacement is significant. It should be emphasized that, as already mentioned in the discussion of eqn. (12), the curves in Fig. 5 illustrate the effect of *equilibrium* concentration of the interfering compound in the sample on the amount of analyte *A* extracted by the fibre. When all other parameters are constant, for a given (small) volume V_s, the higher is the K_B value, the lower is the equilibrium concentration of *B* for the same initial concentration C_{0B} (*i.e.*, more compound is extracted when the affinity for the coating is higher). In order for C^{∞}_{sB} to be the same for the three curves in Fig. 5 corresponding to the case of two compounds that undergo extraction, the initial concentration of *B* would have to be higher for higher K_B values. The curves do not illustrate therefore directly what is the effect of the interfering compound(s) when K_B changes, while C_{0B} remains constant.

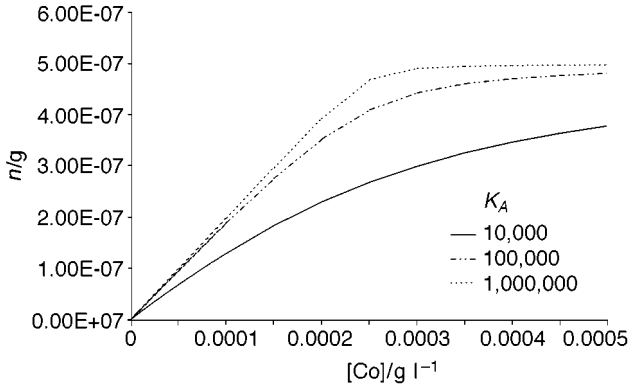

Fig. 3 Amount of analyte extracted by the fibre *vs.* initial concentration of the analyte in the sample for a single analyte and direct extraction, for three different equilibrium constants. Assumptions: $C_{f\,max}$ = 1.0 g L^{-1}, V_f = 0.5 μL, V_s = 2 mL.

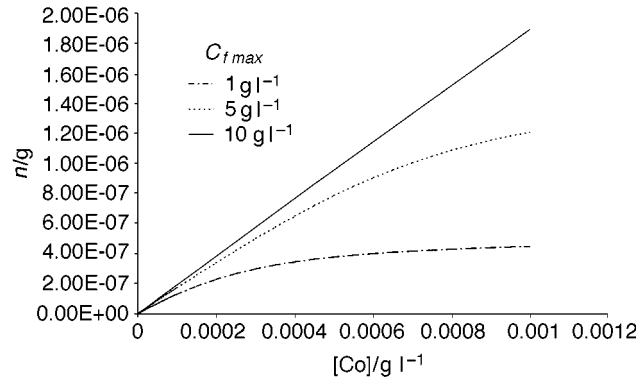

Fig. 4 Amount of analyte extracted by the fibre *vs.* initial concentration of the analyte in the sample for a single analyte and direct extraction, for three different $C_{f\,max}$ values. Assumptions: K_A = 10 000, V_f = 0.5 μL, V_s = 2 mL.

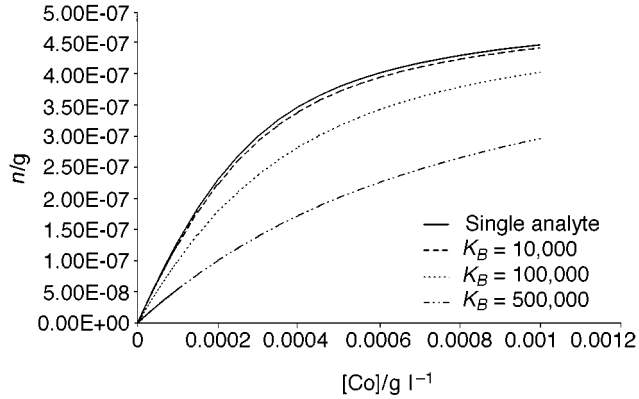

Fig. 5 Amount of analyte A extracted by the fibre *vs.* initial concentration of the analyte in the sample when two compounds are present in the sample (direct extraction), for three different K_B values. Assumptions: $C_{f\,max}$ = 1.0 g L^{-1}, K_A = 10 000, V_f = 0.5 μL, V_s = 2 mL, = 10 μg L^{-1}.

Fig. 6 illustrates a similar dependence for constant K_B (= 100 000) and three different C^{∞}_{sB} values. It should be noted that in this case C^{∞}_{sB} is proportional to C_{0B}. It is clear from Fig. 6 that the amount of analyte *A* extracted by the fibre decreases when the concentration of the interfering compound increases. This is intuitively obvious, since at higher concentrations of interfering compound(s), a larger fraction of adsorption sites is occupied, therefore fewer sites are available for analyte *A*.

Fig. 7 presents relationships between the amount of the analyte extracted by the fibre and the initial concentration of the analyte in the sample for a single analyte extracted from headspace. The total volume of the system (sample plus its headspace) was set to 40 mL, with the sample volume of 15 mL. Henry's law constant value of K_H = 1 was assumed for the calculations. The amount extracted decreases with decreasing K_A value, and so does the initial linear range. The shapes of the relationships do not change much when the sample volume is increased or K_H is decreased (not illustrated). The amount extracted increases slightly when sample volume increases, with the change being the most pronounced for analytes with the lowest K_A. The amount extracted increases also when K_H decreases, due to the fact that lower K_H value means that the headspace capacity for the analyte is lower (*i.e.*, at equilibrium fewer analyte molecules are present in the headspace of the sample, therefore more molecules are available for the coating

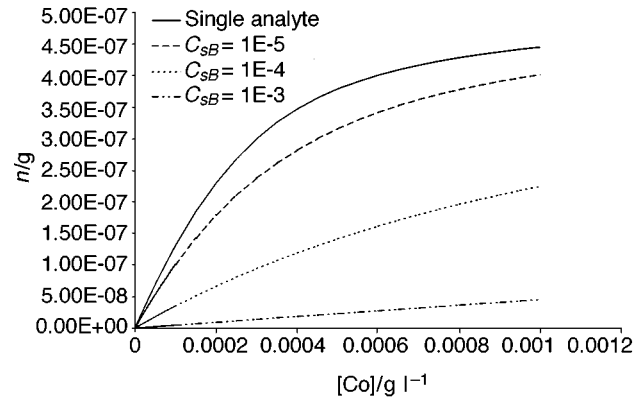

Fig. 6 Amount of analyte A extracted by the fibre *vs.* initial concentration of the analyte in the sample when two compounds are present in the sample (direct extraction), for three different C^{∞}_{sB} values. Assumptions: $C_{f\,max}$ = 1.0 g L^{-1}, K_A = 10 000, V_f = 0.5 μL, V_s = 2 mL, K_B = 100 000.

phase, since the total number of molecules in the system remains constant).

The courses of the relationships between the amount of analyte A extracted by the fibre and the initial concentration of the analyte in the sample when two compounds are present in the sample and extraction is carried out from sample headspace are very similar to those presented in Fig. 5 for direct sampling, therefore will not be discussed herein.

Conclusions

Adsorption is a competitive process, therefore matrix composition, as well as extraction conditions, all affect the amount of analyte extracted by the fibre. This makes quantitative analysis using solid coatings more difficult compared to liquid coatings. The equilibrium theory developed for selected porous polymer coatings (PDMS/DVB, Carbowax/DVB) presented here sheds light on the effect of a number of experimental variables on the amount of the analyte extracted by the fibre coating. The theory applies also to Carbowax/TR coatings, which chemically are Carbowax/DVB coatings. In general, porous polymer coatings can be expected to perform well for relatively clean matrices or matrices of constant composition, provided that the concentration of the analyte of interest is low (otherwise, the quasi-linear range of the calibration curve can be easily exceeded and non-linear calibration is required). Special strategies can be applied when interfering compounds with high affinity to the coating are present in the sample (see ref. 25). It should be remembered that in most practical cases, one has to deal with systems where more than one compound undergoes adsorption on the fibre coating (*e.g*., the analyte of interest plus water, trace organics accompanying the analyte, *etc*.)

Carboxen coating is a special case. It extracts analytes *via* adsorption, therefore general description of the extraction process is similar to that for porous polymer coatings. The main difference is that the pores in Carboxen are small enough to cause capillary condensation to occur. As a result, one cannot talk about reaching equilibrium when Carboxen fibres are used. Also, quite obviously, one of the basic assumptions of the Langmuir isotherm model stating that the surface of the adsorbent can be covered by a monomolecular layer of analyte molecules at the most is not fulfilled, therefore the model presented herein is not applicable to Carboxen coatings.

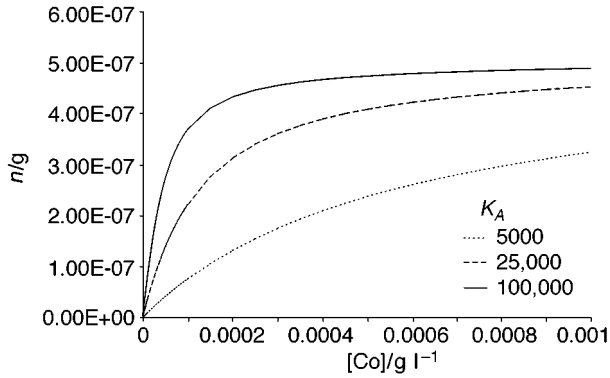

Fig. 7 Amount of analyte extracted by the fibre *vs*. initial concentration of the analyte in the sample for a single analyte and headspace extraction, for three different K_A values. Assumptions: V_f = 0.5 μL, $C_{f\,max}$ = 1 g L^{-1}, V_s = 15 mL, V_h = 25 mL, K_H = 1.

References

1 C. L. Arthur, L. M. Killam, S. Motlagh, M. Lim, D. W. Potter and J. Pawliszyn, *Environ. Sci. Technol.*, 1992**, 26**, 979.
2 B. L. Wittkamp and D. C. Tilotta, *Anal.Chem.* 1995, **67**, 600.
3 C. L. Arthur, K. Pratt, S. Motlagh, J. Pawliszyn and R. P. Belardi, *J. High Resolut. Chromatogr.*, 1992, **15**, 741.
4 J. J. Langenfeld, S. B. Hawthorne and D. J. Miller, *Anal. Chem.*, 1996, **68**, 144.
5 T. Nilsson, F. Ferrari and S. Facchetti, *Proc. 18th Int. Symp. on Capillary Chrom.*, Hüthig Verlag, Germany, Riva del Garda, 1996, p. 618.
6 D. Potter and J. Pawliszyn, *Environ. Sci. Technol.*, 1994**, 28**, 298.
7 A. A. Boyd-Boland and J. Pawliszyn, *J. Chromatogr.*, 1995**, 704**, 163.
8 R. Eisert, K. Levsen and G. Wuensch, *J. Chromatogr.*, 1994**, 683**, 175.
9 P. Popp, K. Kalbitz and G. Oppermann, *J. Chromatogr.*, 1994**, 687**, 133.
10 X. Lee, T. Kumazawa, T. Taguchi, K. Sato and O. Suzuki, *Hochudoku*, 1995, **13**, 122.
11 K. N. Graham, L. P. Sarna, G. R. B. Webster, J. D. Gaynor and H. Y. F. Ng, *J. Chromatogr.*, 1996**, 725**, 129.
12 T. Górecki, R. Mindrup and J. Pawliszyn, *Analyst*, 1996, **121**, 1381.
13 K. Buchholz and J. Pawliszyn, *Anal. Chem.*, 1994, **66**, 160.
14 B. Schaefer and W. Engewald, *Fresenius' J. Anal. Chem.*, 1995, **352**, 535.
15 L. Pan, M. Adams and J. Pawliszyn, *Anal. Chem.*, 1995, **67**, 4396.
16 T. Górecki and J. Pawliszyn, *Anal. Chem.*, 1996, **68**, 3008.
17 D. Louch, S. Motlagh and J. Pawliszyn, *Anal. Chem.*, 1992, **64**, 1187.
18 Z. Zhang and J. Pawliszyn, *Anal. Chem.*, 1993**, 65**, 1843.
19 J. Pawliszyn, *Solid Phase Microextraction*, John Wiley & Sons, Inc., New York/Chichester/Brisbane/Toronto/Singapore, 1997, ch. 3, p. 43.
20 J. Ai, *Anal. Chem*., 1997, **69**, 1230.
21 J. Ai, *Anal. Chem*., 1997, **69**, 3260.
22 J. Ai, *Anal. Chem*., 1998, **70**, 4822.
23 R. P. Schwarzenbach, P. M. Gschwend and D. M. Imboden, *Environmental Organic Chemistry*, John Wiley, New York/Chichester/Brisbane/Toronto/Singapore, 1993, ch. 11, p. 255.
24 R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley, & Sons, Inc., New York/Chichester/Brisbane/Toronto/Singapore, 1996.
25 T. Górecki, P. Martos and J. Pawliszyn, *Anal. Chem.*, 1998, **70**(1), 19.

Paper 8/08487D