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Determination of kinetic and retention properties of cartridge and disk devices for solid-phase extraction

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Abstract

The kinetic properties of cartridge and disk solid-phase extraction devices are determined by forced-flow liquid chromatography. Typical cartridges provide about 5–15 theoretical plates per cm of bed height and particle-loaded membranes provide about 4–9 theoretical plates for a 0.5-mm-thick membrane. It is shown that cartridge devices fail to provide their maximum trapping performance because of inadequate packing density and that the required packing density could be easily achieved in practice with particles of a standard size. The retention properties of common sorbents for extraction from water and air are characterized with the solvation parameter model. For predominantly aqueous solutions a favorable cavity term results in increased retention while polar interactions tend to reduce retention. Retention on porous polymer sorbents is more complicated because of their capacity to absorb significant amounts of the sample processing solvent resulting in solvent-dependent changes in retention properties. For trapping organic volatiles from air cavity formation and dispersion interactions are important, and in the case of Tenax its capacity for induction interactions is also significant.

Keywords: Solid-phase extraction; Retention

1. Introduction

Solid-phase extraction (SPE) is a method used to isolate and concentrate selected analytes from a gas, fluid or liquid by their transfer and interaction (sorption) to an immobilized liquid or solid-phase. After separation of the sorbent from the sample the analytes are recovered by elution using a liquid or fluid, or by thermal desorption into the gas phase. The first significant application of solid-phase extraction was the use of charcoal beds to isolate organic compounds from water to determine the types of compounds present and to assess their health effects in the early 1950s [1]. The large volume of water generally sampled (>1000 l over several days) meant that liquid–liquid extraction procedures were inappropriate. Since then a number of different sorbents and formats for SPE have been introduced, as indicated by the time line in Fig. 1.

Carbon in its various forms, was an excellent adsorbent, but was not always so willing to give up the sample it had extracted at the desorption step. The family of macroreticular porous polymers, introduced in the early 1970s, rekindled interest in both the analysis of air and water samples that eventually stretched into the analysis of biological fluids [2–4]. The macroreticular porous polymers are copolymers of styrene-divinylbenzene or acrylic esters, usually,

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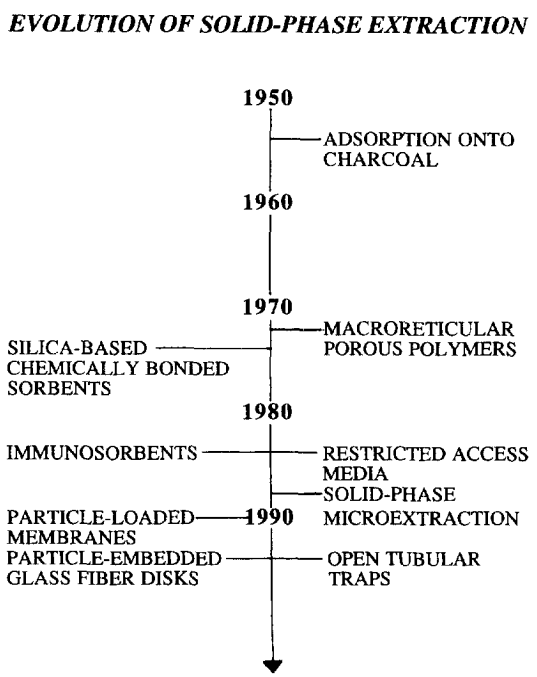

Fig. 1. Time line showing the gradual evolution of solid-phase extraction techniques.

prepared by suspension polymerization to yield particles consisting of agglomerates of randomly packed microspheres permeated by a network of holes and channels. The particles are strong (at least compared to gels) with a large surface area, had a high sample capacity, low water retention, were chemically inert, and gave high sample recoveries by solvent desorption. These properties, and a reduction in the amount of material needed for identification due to better instrumentation, resulted in the general use of small columns similar in size to those in use today. The introduction of Tenax, with its high thermal stability, was important in the evolution of sorbent trapping of air pollutants and volatile organic compounds in water for gas chromatographic analysis based on gas phase purging methods and thermal desorption for solvent-free sample introduction.

SPE became a widely used laboratory technique with the introduction of disposable sorbent cartridges containing siloxane-bonded silica particles of a size suitable for sample processing aided by gentle suction [3,5–8]. A large number of sorbents are now available including numerous siloxane-bonded materials with different functional groups, porous synthetic polymers, immunosorbents, and restricted-access media. Immunosorbents rely on bioaffinity for selective isolation of target compounds [9] and the restricted access media [5] are used to isolate small molecules in biological fluids without interference from proteins. Within their specialized application areas they represent important recent developments. Of more general interest for the purpose of this paper are the particle-loaded membranes [10], particle-embedded glass fiber disks [11], and polymer-coated fused-silica fibers (solid-phase microextraction) [12,13] introduced in the early 1990s as new formats for SPE [14,15].

The basic design of SPE cartridges has changed little since their introduction in the mid 1970s. A typical SPE cartridge consists of a short column (generally an open syringe barrel) containing a sorbent with a nominal average particle size of 50–60 μm, packed between porous metal or plastic frits. This format has several attendant disadvantages which can be briefly summarized as follows: (1) the small cross-sectional area of the extraction cartridges results in slow sample-processing rates and a low tolerance to blockage by particles and adsorbed matrix components; (2) channelling reduces the capacity of the cartridge to retain analytes; (3) sorbent properties are inconsistent from lot-to-lot and between manufacturers; (4) incomplete reversibility of the sorption of some analytes from active sorbent sites lowers their expected recovery; and (5) contamination of the isolated analytes by impurities originating from the manufacturing and packaging process. Points (3) and (4) are related to the chemistry of the sorbent and cannot be addressed by a change in format; point (5) is a matter of introducing good quality control procedures and is an avoidable problem. Points (1) and (2) have to be considered fundamental problems associated with the cartridge design that can be addressed by a change in format or by an evolutionary improvement in the standard cartridge format itself.

The particle-loaded membranes (PLMs) and particle-embedded glass fiber disks (PEGFDs), referred to generically as disk technology, are examples of alternative formats to the cartridge design for SPE. PLMs are available in diameters from 4 to 96 mm, are 0.5 mm thick, and consist of a web of PTFE microfibrils in which are suspended sorbent particles

of about 8 μm diameter (90% w/w for the octadecylsiloxane-bonded silica sorbent). The membranes have an homogeneous structure and are flexible. For general use they are supported on a sintered glass disk (or other support) in a standard filtration apparatus using suction to generate the desired flow through the membrane. The PEGFDs contain sorbent particles embedded in a glass fiber supporting matrix. The small diameter disks are rigid and self-supporting; the larger diameter disks are usually used with a supporting structure.

The claimed advantages of disk technology can be briefly summarized as follows: (1) shorter sample processing time due to the larger cross-sectional area of the disk and decreased pressure drop, allowing sample processing at higher flow-rates; (2) decreased plugging by particles due to the larger cross-sectional area of the disk; (3) reduced channelling resulting from the use of smaller diameter sorbents and the greater mechanical stability of the sorbent bed; and (4) cleaner extracts with lower interferences due to optimization of the bed mass to reduce non-specific matrix adsorption. Increased surface area and reduced plugging are important considerations for selecting a format for processing large sample sizes with suspended particulates, such as environmental water samples, while the better optimization of sorbent mass to reduce non-specific matrix adsorption is important in processing small samples, such as those typical of pharmaceutical applications. Stabilizing the bed by entrapping the sorbent particles addresses the problem of channelling which is the dominant cause of poor reproducibility of sampling using conventional cartridges [16].

2. Kinetic properties of cartridge and disk devices

It is difficult to study the general properties of cartridge devices by manual methods. Excising the sorbent from the cartridge and packing it into a high-performance liquid chromatography column provides the controlled environment necessary for kinetic property determinations [16,17]. For disk materials, forced-flow thin layer chromatography using an overpressured development chamber allows similar results to be obtained [11,18,19].

Table 1 summarizes the characteristic properties of some chemically bonded, silica-based, cartridge sorbents. The typical packing density of the sorbent cartridges is less than that of the liquid chromatographic columns prepared by the tap-and-fill method. The latter could be taken as a reasonable attainable density for cartridges since no special high-pressure procedures are involved in packing the liquid chromatographic column, nor are high pressures used in their evaluation. A rough calculation shows that the sorbent cartridges contain about 15–25% additional empty space on average compared to the stable column beds prepared by the tap-and-fill method. The result of inadequate packing density on SPE are:

Table 1
Characteristic properties of J.T. Baker cartridge sorbent media

Property	Cartridges				
	C_4 [a]	C_{18} (HL) [b]	C_{18} (LL) [a]	CN [c]	Diol [d]
Cartridge packing density (g/ml)	0.322	0.667	0.532	0.599	0.557
HPLC column packing density (g/ml)	0.453	0.726	0.639	0.634	0.794
Total porosity (HPLC column)	0.74	0.47	0.48	0.52	0.58
Interparticle porosity	0.60	0.41	0.36	0.41	0.41
Intraparticle porosity	0.14	0.06	0.12	0.11	0.17
Flow-resistance parameter	1100	707	–	2050	1000
Nominal pore diameter (nm)	25	6	6	6	6
Apparent particle size (μm)	46.8	55.1	40	30.3	–

[a] Seibert and Poole unpublished results.
[b] From [16], with permission.
[c] From [17], with permission.
[d] From [20], with permission.
HL: high loading; LL: low loading.

(1) variations in flow-rates between cartridges due to differences in permeability; (2) a dependence of recovery on the sample flow-rate; and (3) typical bed heights used in cartridge devices are greater than required to compensate for the heterogeneous packing structure, increasing contamination of sample extracts due to increased matrix adsorption. Some of these points are taken up later.

The intraparticle porosity values indicate a high loading of bonded phase. In particular, the high loading octadecylsiloxane-bonded sorbent is virtually non-porous. Such high loadings will not promote favorable mass-transfer kinetics, but given the intended use of the sorbents they are not objectionable, as we will show later that retention is generally more important than kinetic performance for successful sorbent extraction. A high value for the flow-resistance parameter is a general indicator of the number of particles with diameters less than the average size. Expected values are 500–1000. Only the cyanopropylsiloxane-bonded silica sorbent in Table 1 exhibits an unacceptable proportion of fine particles, resulting in poor cartridge permeability.

A plot of the observed plate height as a function of the mobile phase interparticle velocity for the chemically bonded silica cartridge sorbents is shown in Fig. 2. The plate height measurements refer to the column packing density, and are, therefore, inflated compared to expectations for a typical cartridge. The shape of the plots indicates that the main contributions to the plate height for the velocity range investigated arise from flow anisotropy in the packed bed and resistance to mass transfer. The interparticle velocity range corresponds to a flow-rate of about 3–30 ml/min for a 1 cm-diameter cartridge, and within this range there is no minimum for the plate height as well as a significant flow-rate dependence on the kinetic performance of the column. Within this flow range, the upper bound for the number of theoretical plates is generally about 5–25 theoretical plates per cm of bed height (Table 1). Additional zone dispersion caused by the lower packing density of typical cartridge devices compared with the column packing density suggests that a figure of about 5–10 theoretical plates per cm of bed height is all that can be anticipated for a typical cartridge at normal sampling flow-rates.

The characteristic properties of some octadecylsiloxane-bonded silica PLMs and a PEGFD are summarized in Table 2. The flow-resistance parameter is in the normal range indicating a reasonably homogeneous packing structure free of holes and excessive amounts of below-average-size particles. The pore volume of the sorbent is largely filled with bonded phase with the same consequences discussed for the cartridge sorbents. The interparticle porosity is similar to the values expected for a well-packed column, indicating adequate packing density for the sorbent media. The apparent average particle size is significantly smaller than that of typical cartridge sorbents as is required if significant efficiency is to be achieved with a bed height of only 0.5 mm.

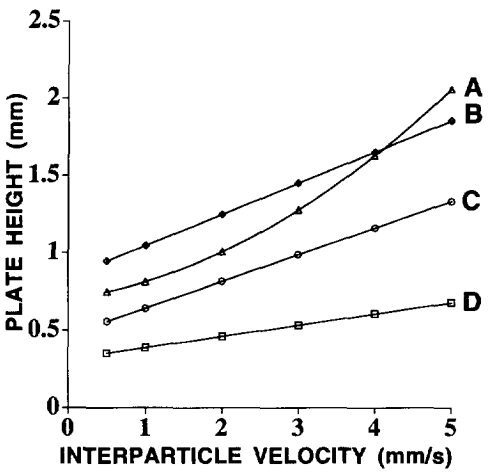

Fig. 2. Plot of the plate height against the mobile-phase interparticle velocity for the silica-based cartridge sorbents. The test compound was anthracene and the mobile-phase methanol–water (80:20 v/v). Identification: (A) butylsiloxane; (B) cyanopropylsiloxane; (C) spacer bonded propanediol; and (D) octadecylsiloxane (light loading).

The kinetic properties of a PLM are different to those of a cartridge device, Fig. 3 [19]. A minimum value for the plate height, corresponding to about seven particle diameters, is observed at an optimum interparticle velocity of 0.19 mm/s. The minimum value for the plate height is rather high and the optimum mobile-phase velocity is about an order of magnitude slower than would be expected for an ideal sorbent bed. It is possible that the web of PTFE microfibrils responsible for holding the sorbent particles in place contributes adversely to the kinetic

Table 2
Characteristic properties of octadecylsiloxane-bonded silica particle-loaded membranes and particle-embedded glass fiber disks

	Particle-loaded membranes		Particle-embedded glass fiber disk
	C_{18} [a]	C_{18} [b]	C_{18} [c]
Apparent particle size (μm)	7.7	5.8	15.3
Total porosity	0.52	0.54	0.51
Interparticle porosity	0.37	0.48	0.47
Intraparticle porosity	0.15	0.06	0.04
Flow-resistance parameter	1100	1040	970
Nominal pore diameter	6	6	8

[a] J.T. Baker brand from [19], with permission.
[b] Varian Sample Preparation Products brand from [18], with permission.
[c] Ansys brand from [11], with permission.

properties of the sorbent bed by disrupting the flow streams through the membrane and by trapping a portion of the mobile phase in the interparticle space, increasing the volume of the stagnant mobile phase and inhibiting favorable mass-transfer characteristics. Over the typical flow-rate range for a 47-mm-diameter disk with a 38 mm active sampling area, 10–100 ml/min, the particle-loaded membrane will provide 4–9 theoretical plates, with the largest value corresponding to the optimum flow-rate of about 13 ml/min (Fig. 3).

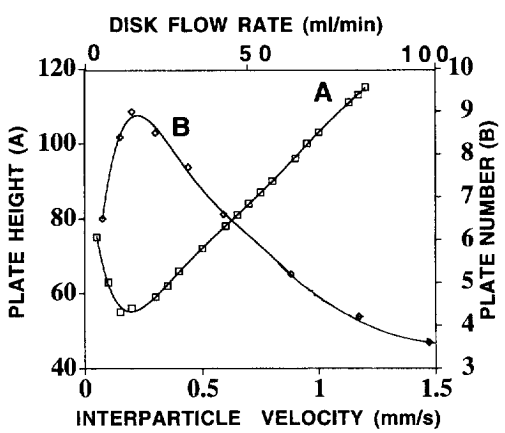

Fig. 3. Variation of the efficiency of a particle-loaded membrane as a function of the mobile-phase velocity. (A) Plot of the observed plate height (μm) as a function of the interparticle mobile phase velocity, and (B) the transformation of (A) to indicate the number of theoretical plates (N) as a function of the sample flow-rate through a 0.5 mm disk with a 38 mm-diameter active sampling area (ml/min).

3. Influence of kinetic properties on retention in solid-phase extraction

A number of models based on frontal chromatography have been proposed to account for the influence of kinetic properties on the capacity of a sorbent bed to retain an analyte [6,7,21–27]. There is a common assumption of linear chromatography, which is a reasonable beginning for the purpose of modelling, but may be inadequate for conditions of large sample sizes, competitive matrix sorption of strongly retained components, and for sorbent beds with low numbers of theoretical plates. Since adsorption isotherms at low concentration are more likely to be curved than partition isotherms, these models may be less successful at predicting results for air sampling with sorbent cartridges [28–30]. A general model we have found most useful for interpreting results from SPE was proposed by Lovkvist and Jonsson [22] to explain the sampling performance of sorbent traps with low numbers of theoretical plates. It leads to the master equation for the breakthrough volume (V_B) of a sorbent trap indicated below

$$V_B = (a_0 + a_1/N + a_2/N^2)^{-1/2}(1 + k)V_m \quad (1)$$

where a_0, a_1, and a_2 are coefficients that are characteristic of the breakthrough level summarized in tabular form in [22], N is the number of theoretical plates for the sorbent trap, k is the retention factor (capacity factor) for the analyte, and V_m is the holdup volume for the sorbent bed. Mol et al. [23]

demonstrated for open-tubular traps that for $N<1.5$ the breakthrough volume cannot be increased by increasing retention, indicating that a threshold value for minimum efficiency is required for quantitative trapping. Pankow et al. [24] have suggested that premature breakthrough for sorbent traps with low plate numbers occurs because of poor transport, that is, a lack of sufficient time for all of the analyte molecules to reach the surface of a particle before exiting the sorbent bed, and is independent of the retention capacity of the sorbent. Thus, there may be a minimum number of theoretical plates required for acceptable performance of a sorbent trap, but this number is neither well defined nor easily defined. Eq. (1) may not be applicable when $N<4$ but seems reasonable at higher values [16,31].

The influence of kinetic properties on the retention capacity of a sorbent trap is contained in the first part of the right-hand side of Eq. (1). This contribution can be evaluated numerically for different breakthrough levels as indicated in Fig. 4. At about $N=100$ the quotient reaches about 95% of its asymptotic value for a 1% breakthrough level, $N=25$ for a 5% breakthrough level, and $N=10$ for a 10% breakthrough level. For typical sorbent cartridges and PLMs, extractions are performed with values of N that result in the breakthrough volume being less than the maximum possible under experimental conditions where the breakthrough volume is most strongly influenced by kinetic properties. These undesirable features are tolerated in contemporary practice to preserve the simplicity of sample processing by gravity or suction, and to minimize the cost of the sampling device. A cartridge packed with a 60 μm-diameter sorbent, such that it provided a plate height of 2–3 particle diameters, need only have a bed height of 1.2–1.8 cm to provide 100 theoretical plates. This illustrates the importance of maximizing the packing density of sorbent cartridges as the most straightforward approach to improving their sampling performance.

Given the low plate numbers of typical SPE devices, a flow-rate dependence of the breakthrough volume is anticipated. The form of this dependence is illustrated in Fig. 5 for an octadecylsiloxane-bonded silica PLM and a cartridge sorbent at a higher packing density than is typical of cartridges. This (probably) does not affect the form of the relationship for a typical sorbent cartridge, but results in its position with respect to the y-axis being higher than is realistic. For the PLM (38 mm sampling diameter) the breakthrough volume is not strongly affected by flow-rate in the range 10–30

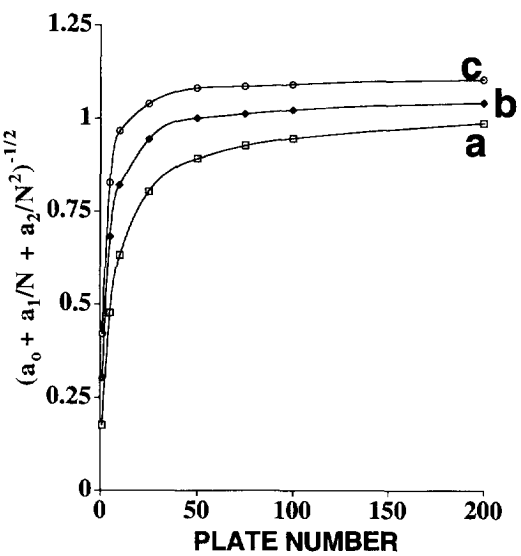

Fig. 4. Plot of the kinetic contribution to retention $[(a_0+a_1/N+a_2/N^2)^{-1/2}]$ for a sorbent trap with different numbers of theoretical plates at breakthrough levels of: (a) 1%, (b) 5%, and (c) 10%.

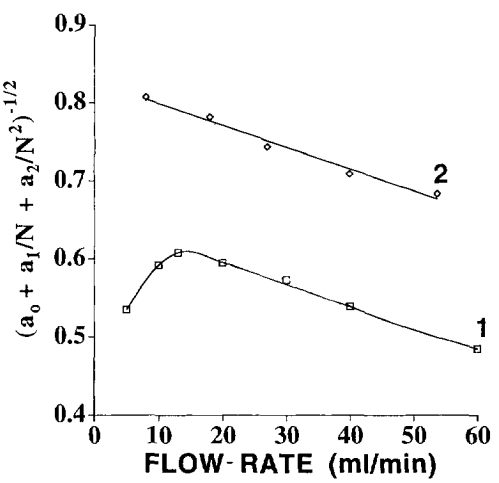

Fig. 5. The influence of the kinetic properties of an octadecylsiloxane-bonded silica sorbent trap on the breakthrough volume for: (1) a particle-loaded membrane (38 mm diameter), and (2) a well-packed cartridge (column packing density) of 13 mm diameter.

ml/min. At both higher and lower flow-rates a decrease in the breakthrough volume is expected, but the sensitivity to changes of flow-rate over ranges typically used in practice is not very great. Breakthrough volumes are more flow-rate sensitive for cartridge devices, and to obtain reproducible results the flow-rate should be controlled within reasonable limits [32]. Of course when the sample volume is significantly less than the breakthrough volume, this flow-rate dependence will not be significant, provided that the sampling device provides the minimum number of theoretical plates to prevent premature breakthrough.

4. Prediction of retention for sorbent traps

In practice an approximate value of the breakthrough volume is required in order to select the appropriate sorbent and quantity of sorbent to use to isolate and concentrate a particular analyte. The experimental measurement of breakthrough volumes is time consuming and somewhat subjective, since the breakthrough point is usually poorly defined [7]. Methods that allow the prediction of breakthrough volumes with the minimum number of experiments are, therefore, particularly attractive. The solvation parameter model provides this possibility, and, in addition, enables various sorbents to be classified according to their capacity for fundamental intermolecular interactions (selectivity), as well as estimates of elution volumes for sample recovery to be made [15,16,20,31,33,34].

For SPE from solution the appropriate form of the solvation parameter model is given by Eq. (2)

$$SP = c + mV_x/100 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H \quad (2)$$

where SP is some free energy related property of the system, such as the retention factor ($\log k$), distribution constant, or the breakthrough volume ($\log V_B$); V_x is the characteristic volume of the solute; R_2 is the solute's excess molar refraction; π_2^H is the ability of the solute to stabilize a neighbouring dipole by virtue of its capacity for orientation and induction interactions; α_2^H and β_2^H are parameters characteristic of the solute's effective hydrogen-bond acidity and hydrogen-bond basicity, respectively. The solute's characteristic volume and excess molar refraction are usually available by simple arithmetic calculation; the other solute descriptors are parameters derived from equilibrium measurements for complexation and partition processes. Solute descriptors are available for over 2000 compounds with others available as estimates by calculation [35–37]. For certain specific solutes such as anilines, sulfoxides and alkylpyridines extracted from water by sorbents capable of retaining a significant amount of water in the interphase region, a modified β_2^H solute descriptor is required [38].

The system constants in Eq. (2) are unambiguously defined, and are determined by the difference in capacity of the solvent and solvated sorbent for specific intermolecular interactions: the r constant refers to the capacity for interaction with solute n- or π-electrons; the s constant refers to the capacity to take part in dipole–dipole and dipole-induced dipole interactions; the a constant characterizes the hydrogen-bond basicity of the system (because a basic phase will interact with an acidic solute); the b constant characterizes the hydrogen-bond acidity of the system; and the m constant relates to the relative ease of forming a cavity for the solute in the bulk solvent and solvated sorbent. The sign of the system constant indicates whether the contribution is favorable for transfer to the solvated sorbent, positive value, or unfavorable, negative value, resulting in diminished retention by the solvated sorbent. The system constants for any solvated sorbent and sample solvent are determined from experimental values for the observed parameter, SP, for a group of solutes of known properties, sufficiently varied to define all interactions in Eq. (2), and of sufficient number to establish the statistical validity of Eq. (2). They are obtained by multiple linear regression analysis. It is usual for upwards of 20 measurements of SP to be used in the regression analysis for a good statistical outcome for the fit to Eq. (2). Once the system constants are known, then the retention properties in the same system for any solute with known solute descriptors are accessible by calculation through Eq. (2).

In the absence of breakthrough volume values for a large enough collection of varied solutes to meet model requirements, the easiest approach to determine the system constants is by instrumental liquid

chromatography (HPLC) using the cartridge sorbent as column packing [16,20,33] or forced-flow planar chromatography in the case of PLMs and PEGFDs [11,18]. For typical octadecylsiloxane-bonded sorbents, with a high phase loading, it is difficult to determine the retention factor with water as the mobile phase, because of the often long retention times involved and the poor peak shapes observed, even with short columns. The retention factor for water as solvent can be estimated more conveniently by a linear or second-order polynomial extrapolation of the retention factors observed at higher levels of organic solvent to zero-volume fraction of organic solvent with a binary mobile phase containing, for example, methanol. As demonstrated by the plot in Fig. 6, no general assumptions can be made about the form of the extrapolation, since the relationship is solute dependent. Full composition data is shown in Fig. 6, but when only a short range of compositions have been acquired, the choice of extrapolation method becomes arbitrary, and the intercept obtained depends on the range chosen for the extrapolation. Extrapolation can yield both good and poor values for a large solute set with no mechanism to distinguish between them. As a minimum requirement, as much data as possible should be obtained at the lowest volume fraction of organic solvent that yields acceptable separation times. For the polar

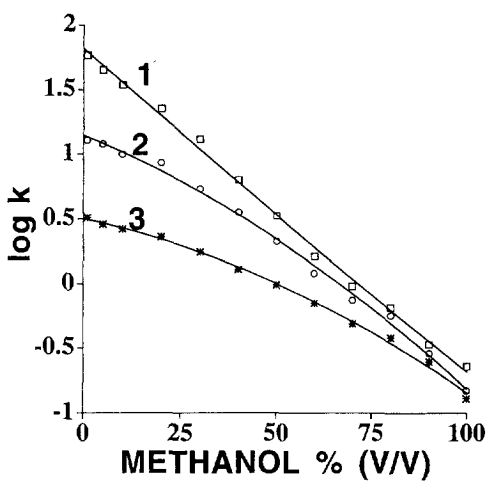

Fig. 6. Plot of the retention factor ($\log k$) against the volume fraction of methanol in a binary methanol–water mobile phase for: (1) naphthalene, (2) chlorobenzene, and (3) 1-phenylethanol for a cyanopropylsiloxane-bonded silica sorbent.

chemically-bonded sorbents experimental data can usually be acquired with less difficulty.

There is generally a linear relationship between $\log P_{oct}$ and the reversed-phase retention factor with water as solvent for closely related compounds [39]. The large pool of octanol–water partition constants ($\log P_{oct}$) can be used as a surrogate estimate for the retention factor when experimental values are unavailable [6,39]. The accuracy of literature $\log P_{oct}$ values vary considerably, often dependent on the method of measurement or calculation, adding to the uncertainty when they are used for estimating breakthrough volumes.

5. Extraction from predominantly aqueous solution

The system constants for five silica-based siloxane-bonded cartridge sorbents with a sample solvent of 1% (v/v) methanol in water are summarized in Table 3. We have chosen 1% (v/v) methanol as the reference solvent since the addition of a small amount of an organic solvent considerably improves the sample processing speed when large sample volumes are extracted and exact measurements of the retention factor with 1% (v/v) organic solvent can be made by HPLC, while, when pure water is used, peak profiles are often highly distorted. It is probably also closer to true experimental conditions since the interphase region will generally contain some methanol from the conditioning step, even when pure water is used as the sample solvent. With a small amount of organic solvent in the sample solvent the sampling conditions remain stable, while the breakthrough volume is hardly affected [32].

The general picture that emerges in Table 3 for sorbent extraction from predominantly aqueous solution is that the dominant contribution to retention is the ease of cavity formation in the solvated sorbent with a smaller contribution from electron lone-pair interactions (m constants are always positive, supported by the r constant in some cases). The driving force for retention is expulsion of the analyte from the hydrogen-bonded water network and the characteristic property that distinguishes individual solvated sorbents is their cohesion. The cyanopropylsiloxane and spacer-bonded propanediol groups are more

Table 3
System constants for J.T. Baker silica-based cartridge sorbents with 1% (v/v) methanol in water as the sample solvent; SP = log k in Eq. (2)

Sorbent	System constant					
	m	r	s	a	b	c
Butylsiloxane	3.36	0	0	−0.46	−1.53	−1.38
Octadecylsiloxane (low loading)	3.92	0	−0.11	−0.54	−1.53	−0.90
Octadecylsiloxane [a] (high loading)	5.65	0.70	−0.76	−0.40	−3.26	−1.18
Cyanopropylsiloxane [b]	2.06	0.53	0	−0.51	−1.45	−0.88
Spacer-bonded propanediol [c]	1.57	0.61	0	−0.45	−0.80	−1.05

[a] From [16], with permission.
[b] From [33], with permission.
[c] From [20], with permission.

cohesive than those with simple bonded alkyl chains resulting in less favorable conditions for solute transfer from aqueous solution (smaller m constant). Both hydrogen-bond bases and hydrogen-bond acids are less well retained than neutral molecules of a similar size because none of the solvated sorbents are competitive with water for these interactions (a and b constants are always negative). In particular, water is such a strong hydrogen-bond acid that the conditions are always less favorable for the retention of hydrogen-bond bases than for non-polar analytes. The most surprising result is the influence of dipole-type interactions on retention. For three sorbents the s constant is zero and for the other two it is negative. For the two polar bonded sorbents there is no preference for dipole-type interactions in the solvated sorbent or sample solution, a balance of properties that is difficult to explain, but suggests that the polar functional groups of the solvated sorbent are selectively solvated by water in the interphase region, negating their influence on sorbent selectivity. In the case of the octadecylsiloxane-bonded sorbents the negative s constants suggest that there is less uptake of water in the interphase region in this case and dipole-type interactions favor the most polar entity in the system, water, resulting in reduced retention.

The solvation parameter model allows the influence of solute size and capacity for polar interactions on retention to be identified. Representative data for some varied solutes on the five cartridge sorbents are summarized in Table 4. There are no general circumstances for which selection of one of the polar bonded sorbents would provide increased retention compared to the octadecylsiloxane-bonded sorbents with water as the sample solvent. This is because the higher cohesion of the polar bonded sorbents is never adequately compensated for by their capacity to compete with water for polar interactions. When the desire is to increase retention (obtain a larger breakthrough volume) for extraction from water, a heavily loaded octadecylsiloxane-bonded sorbent is the best choice. For large molecules, which have a breakthrough volume well in excess of the sample volume, a polar bonded sorbent might be a better choice to enhance recovery in a small volume of solvent. The above considerations apply only to predominantly aqueous samples. There is scant data available for extraction with non-aqueous solvents, but in this case there is a general levelling of the ease of cavity formation in the solvated sorbent and sample solvent (m constant small or insignificant) and retention is dominated by the sorbent's capacity for polar interactions, in contrast to the situation with predominantly aqueous sample solvents [20].

The solvation parameter model does not contain any terms to account for electrostatic interactions. Ionized silanol groups may retain bases by an ion-exchange mechanism causing increased retention that would not be predicted by the model. This is also a cause of poor analyte recovery, that has been noted for pharmaceutical compounds, unless a competing base is added to the elution solvent [40,41].

The solvation parameter model provides a method

Table 4
Contribution of intermolecular interactions to retention of some varied solutes on five chemically bonded cartridge sorbents

Compound	Sorbent	Contribution to log k						Predicted log k
		$(mV_x/100)$	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$b\beta_2^H$	c	
n-Propylbenzene	C_{18} (HL)	6.44	0.42	−0.38		−0.49	−1.18	4.81
	C_{18} (LL)	4.46		−0.06		−0.23	−0.90	3.27
	C_4	3.82				−0.23	−1.38	2.22
	CN	2.20	0.33			−0.22	−0.88	1.44
	Diol	1.79	0.37			−0.12	−1.05	0.99
Benzonitrile	C_{18} (HL)	4.92	0.52	−0.84		−1.08	−1.18	2.34
	C_{18} (LL)	3.41		−0.12		−0.50	−0.90	1.89
	C_4	2.93				−0.51	−1.38	1.04
	CN	1.68	0.40			−0.49	−0.88	0.71
	Diol	1.37	0.45			−0.26	−1.05	0.51
Acetanilide	C_{18} (HL)	6.29	0.61	−1.06	−0.20	−2.18	−1.18	2.28
	C_{18} (LL)	4.37		−0.15	−0.27	−1.03	−0.90	2.02
	C_4	3.74			−0.23	−1.03	−1.38	1.11
	CN	2.15	0.47		−0.26	−0.98	−0.88	0.50
	Diol	1.75	0.53		−0.23	−0.54	−1.05	0.47
Phenol	C_{18} (HL)	4.38	0.56	−0.78	−0.24	−0.98	−1.18	1.76
	C_{18} (LL)	3.04		−0.10	−0.32	−0.47	−0.90	1.25
	C_4	2.60			−0.28	−0.47	−1.38	0.47
	CN	1.49	0.43		−0.31	−0.44	−0.88	0.29
	Diol	1.22	0.49		−0.27	−0.24	−1.05	0.15
2-Hexanone	C_{18} (HL)	5.47	0.09	−0.52		−1.66	−1.18	2.20
	C_{18} (LL)	3.79		−0.07		−0.78	−0.90	2.04
	C_4	3.25				−0.78	−1.38	1.09
	CN	1.87	0.07			−0.75	−0.88	0.31
	Diol	1.52	0.08			−0.41	−1.05	0.15

C_{18} = octadecylsiloxane; C_4 = butylsiloxane; CN = cyanopropylsiloxane; Diol = spacer-bonded propanediol; HL = high loading and LL = low loading.

to identify appropriate conditions for matrix simplification by selecting a wash solvent to remove matrix components with the analytes remaining immobilized and to select an elution solvent to concentrate the analytes into a small solvent volume. As can be seen from Eq. (1), the above conditions are readily predicted from a knowledge of the holdup volume for the device and the retention factor of the analyte in the selected solvent. Effective concentration requires that the holdup volume for the sorbent trap be small and the volume of eluting solvent, or wash solvent, can then be predicted in multiples of the holdup volume from a knowledge of the retention factor. As can be seen from Fig. 7 there is a smooth but unpredictable relationship between the system constants and solvent composition. However, once such a plot is established, the retention factor is accessible for any solvent compositions by simple arithmetic. Conditions for selective matrix simplification are normally expected to be found towards the region represented by the center of the plot, and favorable elution conditions towards the right-hand side. The variations of the system constants for any sorbent are, of course, solvent dependent, so that if several solvents are to be evaluated then an equal number of plots as solvents selected will be required. This is not particularly time consuming if the data is obtained by HPLC.

Table 5 summarizes the system constants for PLMs containing octadecylsiloxane-bonded silica [31] and a porous polymer (styrene-divinylbenzene type) sorbent [34]. The solvated octadecylsiloxane-bonded sorbent is less competitive than the solvated porous polymer sorbent for interactions of a dipole-

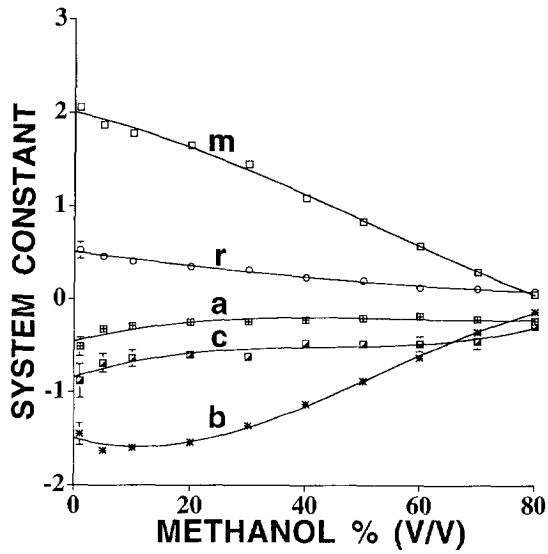

Fig. 7. Variation of the system constants of the solvation parameter model with composition of the water–methanol mobile phase for a cyanopropylsiloxane-bonded silica sorbent for solid-phase extraction.

type (*s* constant) but is a stronger hydrogen-bond acid (*b* constant) and hydrogen-bond base (*a* constant) than the methanol solvated porous polymer. The *m* constants are similar for both sorbents. The porous polymer sorbent shows significant solvent effects; it has a greater affinity for the sample processing solvent than water, and is more flexible than the silica-based sorbents permitting the polymer to swell by selective sorption of the organic solvent added to the sample to aid processing. The experimentally determined breakthrough volumes were observed to vary by up to an order of magnitude for the different sample processing solvents (some examples are appended to Table 5) [34]. The *m* constant for the solvated porous polymer sorbent cover a wide range, 5.09 to 7.20, indicating that the uptake of organic solvent by the polymer has a considerable influence on the ease of cavity formation, and quite probably, also changes in the phase ratio of the sampling system. Thus, as a rough measure of the influence of differences in cohesion of the solvated sorbent on the breakthrough volume, the term $[c+mV_x/100]$ is used. Table 6 provides an indication of the relative contribution of size and polar interactions to the breakthrough volume of a few varied solutes. Propan-2-ol and methanol are the preferred sample processing solvents for toluene because of the more favorable cavity term. Polar interactions are less important. Cyclohexanone is similar in size to toluene but is a much stronger hydrogen-bond base and has a significant capacity for dipole-type interactions. Methanol and acetonitrile are now the preferred sample processing solvents because they provide a more favorable system *b* constant. Benzonitrile is slightly larger than toluene and cyclohexanone, but has a larger capacity for dipole-type interactions and is a weak hydrogen-bond base. In this case methanol is the preferred sample processing solvent because the methanol-solvated sorbent is a weaker hydrogen-bond acid then the propan-2-ol-modified sorbent; propan-2-ol, however, would be preferred for larger solutes with similar hydrogen-bond basicity.

The choice of sample processing solvent to maximize the breakthrough volume on porous polymer PLMs can now be made in a rational way using the solvation parameter model. In the general case propan-2-ol is the favored solvent if a varied group of solutes are to be extracted, or the general choice is to be restricted to a single solvent for other reasons. Increasing solute size favors propan-2-ol over the other sample processing solvents because of the favorable cohesion properties of the propan-2-ol solvated sorbent. Solvent effects may also influence breakthrough volumes for heavily loaded octadecylsiloxane-bonded silica sorbents, but the differences in this case are subtle and not of practical significance.

Comparing the retention properties of the porous polymer PLM to those of the octadecylsiloxane-bonded silica PLM, the breakthrough volumes are larger for the porous polymer sorbent, in some cases by a significant amount, Table 7. The lower cohesion of the solvated porous polymer favors retention compared to the octadecylsiloxane-bonded sorbent, and the difference in cohesion is generally sufficient to compensate for the different capacity for polar interactions. Even for phenol, a small molecule which is a strong hydrogen-bond base and hydrogen-bond acid, the overall balance of properties still favors the porous polymer, but its breakthrough volume is still comparatively small. For solutes of a similar type to phenol, sorbent extraction is restricted

Table 5
System constants for a porous polymer and octadecylsiloxane-bonded silica particle-loaded membranes. SP = log V_B in Eq. (2). The sample processing solvent is 1% (v/v) in all cases

Sorbent	Processing solvent	System constants					
		m	*r*	*s*	*a*	*b*	*c*
Porous polymer	Methanol	5.16	0.81	−0.65	−1.85	−2.93	−0.77
	Acetonitrile	5.72	−0.26	−0.35	−1.17	−2.81	−1.19
	Tetrahydrofuran	5.09	0	0	−0.92	−4.19	−1.00
	Propan-2-ol	7.20	0.41	−0.34	−1.50	−4.53	−2.10
C_{18} silica	Methanol	5.14	0	−0.92	−1.05	−2.24	−1.23

Influence of sample processing solvent (1% v/v in each case) on the breakthrough volume for a porous polymer (STY–DVB) sorbent

Solute	Breakthrough volume (cm^3)			
	Acetonitrile	Tetrahydrofuran	Propan-2-ol	Methanol
Anisole	575	300	1750	1300
Acetophenone	475	125	1000	1000
Benzaldehyde	190	65	250	465
Benzonitrile	200	100	425	500
Nitrobenzene	300	250	1000	900
Methyl benzoate	1250	300	2700	2750
Phenol	17.5	12	20	20
4-Chlorophenol	90	150	300	120
Acetanilide	95	25	100	75
2-Phenylethanol	150	25	100	200
Hexan-1-ol	450	65	275	200
1-Nitropentane	2000	700	2900	1100
Propyl propanoate	1400	200	1250	750

Table 6
Contribution of different intermolecular interactions to the breakthrough volume for the porous polymer particle-loaded membrane

Solvent	Contribution to log V_B				Predicted V_B (cm^3)
	$([mV_x/100]+c)$	rR_2	$s\pi_2^H$	$b\beta_2^H$	
Toluene					
ISP	4.070	0.246	−0.177	−0.634	3199
MeOH	3.652	0.487	−0.338	−0.412	2449
ACN	3.712	−0.156	−0.182	−0.393	957
THF	3.362			−0.587	596
Cyclohexanone					
ISP	4.099	0.165	−0.292	−2.537	27
MeOH	3.673	0.326	−0.559	−1.641	63
ACN	3.735	−0.105	−0.301	−1.574	57
THF	3.383			−2.346	11
Benzonitrile					
ISP	4.171	0.304	−0.377	−1.494	402
MeOH	3.724	0.601	−0.722	−0.967	433
ACN	3.792	−0.193	−0.389	−0.927	192
THF	3.433			−1.383	112

Table 7
Contribution of different intermolecular interactions to the breakthrough volume of some varied compounds using an octadecylsiloxane-bonded silica (C_{18}) and porous polymer (PP) sorbent

Compound	Sorbent	Contribution to log V_B					Predicted V_B (cm^3)
		$([mV_x/100]+c)$	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$b\beta_2^H$	
Benzene	C_{18}	2.450		−0.478		−0.336	43
	PP	2.925	0.494	−0.338		−0.440	438
Naphthalene	C_{18}	4.347		−0.846		−0.448	1130
	PP	4.829	1.085	−0.598		−0.586	53 703
Nitrobenzene	C_{18}	3.350		−1.021		−0.739	39
	PP	3.825	0.706	−0.722		−0.967	700
2-Hexanone	C_{18}	3.746		−0.626		−1.142	95
	PP	4.225	0.110	−0.442		−1.494	251
Phenol	C_{18}	2.754		−0.819	−0.630	−0.694	4
	PP	3.229	0.652	−0.579	−1.110	−0.908	19
Benzamide	C_{18}	3.771		−1.380	−0.515	−1.501	2
	PP	4.251	0.802	−0.975	−0.907	−1.963	16

to small sample volumes, because none of the common sorbents can compete with water for polar interactions, and for small solutes the cavity term is unable to compensate for this effect. In these circumstances it might be beneficial to use ion-exchange or to derivatize the sample to improve its extractability.

6. Sorbent trapping from air

The transfer of a solute between a solvent and solvated sorbent is assumed to occur in such a way that dispersion interactions in both phases are approximately equal and self-cancelling. This cannot be true for transfer from the gas phase, and Eq. (2) must be modified to account for the additional analyte-sorbent dispersion interactions in the condensed phase, Eq. (3) [42,43]:

$$SP = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (3)$$

The contributions of cavity formation and dispersion interactions are represented by the $l \log L^{16}$ term, where $\log L^{16}$ is the distribution constant for the analyte between a gas and hexadecane at 298 K. The latter can be determined directly by gas chromatography or by a number of calculation methods; numerous values are available in table form for volatile organic compounds [44]. Application of Eq. (3) to retention data on carbon and Tenax yields the results summarized in Table 8. Polar interactions are not important for retention on Carbotrap, a form of graphitized carbon black, with retention dominated by the l constant, representing the contribution from cavity formation and dispersion interactions. Retention is reduced by electron lone pair–lone pair interactions (negative r constant). The retention properties of Carbotrap are different to graphite, which is rather weakly polarizable, has significant hydrogen-bond basicity, and a lower capacity for dispersion interactions. The results for Carbotrap and graphite serve to illustrate the wide range of properties common to different forms of carbon, and provide some insight into why the trapping characteristics of different carbon materials can differ by so much.

Dispersion interactions supported by dipole-type interactions are the main forces contributing to retention on Tenax. Electron lone pair–lone pair repulsion contributes unfavorably to retention. The dominance of dispersion interactions and the sorbent's capacity for induction interactions resulting from its polarizability are anticipated from the structure of Tenax, a polymer of 2,6-diphenylene oxide. The weak hydrogen-bond acidity, observed in some correlations in Table 8, is difficult to rational-

Table 8
System constants for sorbents used to trap volatile organic compounds from the gas phase; experimental data was fitted to Eq. (3)

Sorbent	Temperature (°C)	SP	System constant						Statistics for the fit [a]				Reference for data
			l	*r*	*s*	*a*	*b*	*c*	*R*	S.E.	*F*	*n*	
Carbotrap	0	$\log V_g^0$	2.65	−2.27	0	0	0	−4.73	0.97	0.88	318	38	[43]
Graphite	25	$\log K_g^0$	0.46	−0.27	0.86	0.94	0	−0.86	0.97	0.15	124	36	[45]
Tenax GC	10	$\log V_B$	0.97	0	1.07	0	0.31	−1.32	0.98	0.23	120	27	[46]
Tenax GC	20	$\log V_g$	1.39	−0.61	1.26	0	0	−2.54	0.98	0.34	647	104	[47]
Tenax GC	20	$\log V_R$	1.41	−0.37	0.73	0	0.48	−3.31	0.99	0.20	566	51	[48]
Tenax GC	20	$\log V_R$	1.40	−0.45	0.62	0	0	−2.87	0.98	0.21	251	31	[49]
Tenax GC	20	$\log V_g$	1.01	−0.52	0.47	0.54	0	−2.11	0.99	0.15	122	16	[50]
Tenax TA	20	$\log V_B$	1.35	−0.54	0.55	0.36	0.43	−2.18	0.99	0.23	967	102	[51]

[a] R = correlation coefficient; S.E. = standard error in the estimate; F = F statistic; n = number of solutes.

ize with the polymer's structure, and presumably is an indication of impurities or structural heterogeneity in some samples of the polymer. Most of the data used for the fits in Table 8 are compiled from a number of sources, employing different experimental techniques, and this, combined with the anticipated variation in properties from different batches of sorbent, probably accounts in large part for the variations observed in the system constants. The data in Table 8 indicates the power of the solvation parameter model to characterize sorbent properties as a rational basis for selection and direct further synthesis of new materials with customized properties.

7. Conclusions

Solid-phase extraction has developed as a largely empirical method of sample preparation viewed in contemporary terms as an economical replacement for liquid–liquid extraction and liquid–gas extraction with favorable characteristics for automation. The theoretical models presented in this paper provide a more purposeful approach to understanding the fundamental aspects of the technique. They provide a rational basis for the design of sampling devices, a simple means to standardize sorbents based on their retention characteristics, the basis on which to build models to predict retention for different sorbents, a means of identifying new sorbents with sampling properties that set them apart from materials already available, and an approach to developing expert systems to predict the optimum sampling conditions for any analyte.

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