EVALUATION OF SOLID PHASE EXTRACTION LIMITS

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The Bohart-Adams equation is modified for evaluation of solid phase extraction (SPE) efficiency. A relationship between sorption conditions and sorption characteristics at SPE is described. An essential influence of sorption rate factor on the efficiency of SPE, besides the generally regarded distribution factor, is revealed. A linear decrease of solution breakthrough volume versus reciprocals of influent concentration and sorption rate factor is deduced. The SPE limits of phenol and resorcinol on a sorbent Bakerbond SDB 1 are evaluated.

Introduction

Over the past decade solid phase extraction (SPE) has emerged as a powerful tool for chemical isolation and preconcentration of contaminants. A variety of different extraction columns, so called cartridges, filled with polar, nonpolar or ionic sorbents are available. Numerous solvents are suggested to eluate sorbates from sorbent beds in the smallest volume possible. The eluates are analyzed by HPLC, GC and spectrophotometrically.

Among thousands of references to the use of the SPE [1-3] no comprehensive calculation method was found that would predict the efficiency of the concentration procedure. The common practice is to pass as much sample volume as possible through a cartridge without permitting breakthrough. As a rule, the main characteristic of the efficiency is recovery percentage. The alternative is to overload the cartridge, so that the entire sorbent is equilibrated with solute. In this case the efficiency of SPE is characterized by the distribution factor, the ratio of the solute concentrations in the stationary and mobile phases.

Capacity of any sorbent is a function of the solute, solvent and sorbent used. The published capacity of VARIAN sorbents ranges from less than 1 % to as high as 5 % of the sorbent mass [1, p. 25] and of J. T. BAKER ones even up to 10 % [2, p. 2]. Actually, it is important to assess that capacity of a sorbent is proportional with the sorbate concentration. Thus, a capacity of 5-10 % could probably be achieved when the sorbent is saturated. In diluted solutions, when preconcentration is required, capacity should be essentially lower. Furthermore, capacity would be greatly diminished by a large concentration of other compounds.

After breakthrough recovery percentage decreases with any increase of the effluent volume. Capacity factor is underestimated when the steady state condition is not attained. As a rule, SPE is needed under the range of concentrations where sensitivity of analytical methods is insufficient. In such diluted solutions it is unrealisable to get experimentally breakthrough curves and, moreover, to estimate the breakthrough and steady state points. Therefore, a concern arises that components of interest may pass through the cartridge when unknown diluted samples are tested. As well, the limits of the effluent volume are undefined under SPE.

Another factor important to an effective SPE is the flow rate of samples which allows sufficient time for sorbates to diffuse through the solution to the sorbent surface. It is recommended [1, p. 23] that the flow rate should not exceed 5-10 cm^3/min. If ion exchange is used as the extraction mechanism, a slower flow is suggested. No calculation methods have been used for predicting the boundary flow rate at SPE.

Numerous works have been published dealing with the preconcentration of monohydric phenols but none concerning that of dihydric phenols. The recovery of phenol series compounds has been studied [4-11] using ethyl-, butyl-, octyl-, octadecyl-, cyclohexyl- and phenyl-bonded phase silica sorbents as well as styrene-divinylbenzene copolymers.

The best affinity with hydroxybenzene series phenols seems to have a sorbent Bakerbond SDB 1. On a 200 mg of this sorbent, according to the "Service Method Instruction" [9], recovery of 11 phenolic compounds (hydroxybenzene and its chloro and nitro derivatives á 20 ppm) was 89-100 % from 75 cm^3 of the sample at a flow rate of 30 (!) cm^3/min.

Considering the lack of comprehensive mathematical methods for the evaluation of SPE limits, fragmentary results dealing with SPE of mono-hydric phenols and absence of any results dealing with preconcentration of dihydric phenols, the aim of this paper is to apply the bed depth-service method (BDSM) proposed by Bohart and Adams [11, p. 158] for a quantitative description of SPE efficiency. As an example, the SPE limits for hydroxybenzene and resorcinol on the sorbent Bakerbond SDB 1 are evaluated.

Modification of Bed Depth-Service Time (BDST) Model

An important problem regarding the SPE method is the volume of a sample solution that would guarantee quantitative retention of sorbates. According to Bohart and Adams [11], sorption exhaustion curves, so called bed depth-service time (BDST) curves, can be described by the equation

$$\ln (C_0/C - 1) = \ln [\exp(KND/v) - 1] - KC_0t \tag{1}$$

where t - service time, min

v - linear flow rate, cm/min

D - depth of sorbent bed, cm

K - rate constant, cm^3/µg min

N - sorbent capacity, µg/cm^3

C_0 - influent solute concentration, µg/cm^3

C - effluent solute concentration, µg/cm^3

For predicting the effluent volume at the breakthrough point, we suggest modifying the Equation (1) into a bed depth-service volume (BDSV) model. For that aim the following replacements are introduced:

$$v = w/S = wdD/G \tag{2}$$

$$t = V/w \tag{3}$$

and

$$\ln [\exp(KND/v - 1)] = KND/v \tag{4}$$

where w - volume flow rate, cm^3/min

S - cross-section area of cartridge, cm^2

d - density of sorbent layer, g/cm^3

G - mass of sorbent, g

V - volume of effluent, cm^3

The last approximation is held true, when the effective sorbents with a high value of K and N are used at preconcentration.

Thereupon, the volume V can be calculated from the equation

$$V = NG/dC_0 - (w/KC_0) \ln (C_0/C - 1) \tag{5}$$

The preconcentration by SPE is needed when we have very diluted solutions. As a rule, in such solutions the adsorption equilibrium can be described by a linear isotherm

$$N = kC_0 \tag{6}$$

where k is the dynamic distribution factor, (µg cm^{-3})$_s$ /(µg cm^{-3})$_l$.

Therefore, prescripting the value of ratio C_0/C and the maximal value for C, as $C(\max)$, the Equation (5) must represent the following simple relationship:

$$V(\max) = A - BwC_0^{-1} \tag{7}$$

where

$$A^{1)} = kG/d \tag{8}$$

and

$$B = (1/K)\ln (C_0/C(\max) - 1) \tag{9}$$

At high flow rates, sorption rate is limited by internal diffusion. In this case K is constant for a sorbate-sorbent system, and the Equation (7) expresses a plane of $V(\max)$ versus w and $1/C_0$.

In most cases, the sorption rate is limited by external diffusion. In this case the value of K is proportional with the linear flow rate [12]

$$K = fv = fw/S \tag{10}$$

where f - rate factor, $cm^2/\mu g$.

Consequently, a linear relationship between the maximum admissible volume of a solution and $1/C_0$ under low flow rates can be expressed by

$$V(\max) = A - B'/C_0 \tag{11}$$

where

$$B' = (S/f)\ln [(C_0/C(\max) - 1)] \tag{12}$$

The Equations (7) and (11) explain the limits of SPE. It is remarkable that when the initial concentration of the solute decreases, the maximum volume to be concentrated decreases all the more than lesser is the rate factor. $V(\max)$ approaches the capacity characteristic of the sorbent bed, A, when the value of the sorption rate characteristic Bw/C_0 or B'/C_0 is trivial. So, only under very favourable conditions is $V(\max)$ virtually independent of the value of flow rate as well as of the influent solute concentration. Under unsuitable conditions A can be even smaller than Bw/C_0. It means that when $C_0 < B'/A$, the solute comes out of the cartridge with the first drops of the effluent. In turn, the effluent concentration is limited by the prescribed effluent volume V as

$$C_0 = B'/(A - V) \tag{13}$$

[1)] When the approximation (4) is not valid, intercept $A = w(KC)^{-1} \ln [\exp(KNG/wd) - 1]$.

Estimation of K and N

To calculate the effluent limit volume or the limit concentration for a quantitative SPE, the data for N and K are needed. Taking for granted that during a SPE the values of N, K, C_0 and w are constants, Equation (5) should depict a linear relationship between experimental results Z and V:

$$Z = a - bV \tag{14}$$

where

$$Z = (w/C_0) \ln (C_0/C - 1) \tag{15}$$

and

$$a = KNG/(dC_0) \tag{16}$$

Therefore, the values of K and N can be calculated from the slope b and intercept a of the rectilinear plot of Z versus V:

$$K \equiv b \tag{17}$$

and

$$N = adC_0/(bG) \tag{18}$$

Supposing that the Henry isotherm (6) is kept, the values of a and b can be estimated by conducting some SPE procedures at higher C_0 being tested without any preconcentration. If a sample under preconcentration is characterized by a high concentration of other compounds, we recommend using that sample as a matrix solvent when the breakthrough curve is built.

Recovery

Integration of the expression for breakthrough curve:

$$C = C_0(e^{P - QV} + 1)^{-1} \tag{19}$$

where

$$P = fkC_0G(dS)^{-1} \tag{20}$$

and

$$Q = fC/S \tag{21}$$

in boundary conditions $V = 0$ and $V = V$ yields the total mass (ΣM) of sorbate in the effluent volume V

$$\Sigma M = \int_0^V CdV = C_0[V + Q^{-1}\ln(1+e^{P-QV})(1+e^P)^{-1}] \tag{22}$$

The recovery α is expressed as follows:

$$\alpha = 1 - \Sigma M(C_0 V)^{-1} \tag{23}$$

Substituting the Equations (20)-(22) into (23), the recovery is as follows:

$$\alpha = f^{-1}C^{-1}\ln\{[1 + \exp(fkC_0G(dS)^{-1} - fC_0VS^{-1})] \times \tag{24}$$

$$\times [1 + \exp(fkC_0G(dS)^{-1}]^{-1}\}$$

Experimental

As an example, the SPE efficiencies for hydroxybenzene (Ph) and resorcinol (R) were evaluated following the above described BDSV model.

The cartridge Bakerbond SDB 1 [9] was selected as the best one for hydroxybenzene series phenols among those studied in [4-11].

Flow rate was held constant during an experiment by a peristaltic pump. The inner cross-section of cartridges was 1 cm^2.

The concentration of Ph and R was estimated colorimetrically [13, 14].

All extractions were carried out as follows. The cartridge was first conditioned by the addition of 5 + 5 cm^3 of ethyl alcohol which was allowed to set for 5 min before being drawn off. The cartridge was then flushed with 5 + 5 cm^3 of 0.01M HCl. The pH of solutions was adjusted to 2-2.5. Samples for analysis were taken after every 10 cm^3 when SPE of R was tested and after every 50 cm^3 when that of Ph was done. Finally the sorbate was eluted with 5 + 5 cm^3 of ethyl alcohol. Both portions were allowed to remain in the cartridge for 5 min before being drawn off.

The conditions of the experiments were the following: G - 0.2 g, d - 0.354 g/cm^3, C_0 - 1.0 mg/dm^3 (Ph) and 0.963 mg/dm^3 (R), w - 4.22 cm^3/min (Ph) and 3.29 cm^3/min (R).

Results

The elution percentage of retained solutes achieved 90 % in both experiments, and was not detailed in this study.

Breakthrough curves were generated plotting the remaining concentration of solute versus the effluent volume (Table 1, columns V and C).

The experimental results demonstrate a considerable difference between SPE efficiency of Ph and R. The many times larger breakthrough volume for Ph than that for R, proves the substantially higher capacity of SDB 1 for the less hydrophilic sorbate, Ph.

Table 1. **Values of Z for Breakthrough Curves**

Resorcinol			Phenol		
V, cm^3	C, μg/cm^3	Z, cm^6/min μg	V, cm^3	C, μg/cm^3	Z, cm^6/min μg
120	0.048	10.1	450	0.026	15.3
130	0.086	7.93	500	0.082	10.2
140	0.130	6.32	550	0.149	7.35
150	0.173	5.19	600	0.222	5.29
160	0.218	4.20	650	0.314	3.30
170	0.280	3.03	700	0.422	1.33
180	0.332	2.19	750	0.530	−0.51
190	0.403	1.12	800	0.655	−2.71
200	0.478	0.05	850	0.763	−4.93
210	0.517	−0.51	900	0.859	−7.63
220	0.540	−0.83	950	0.918	−10.2
240	0.655	−2.58	1000	0.959	−13.3
260	0.733	−3.96	1050	0.969	−14.5
280	0.790	−5.19			
300	0.829	−6.23			
400	0.922	−10.6			

Table 2. **SPE Characteristics for Phenol and Resorcinol on Bakerbond SDB 1**

Symbol for the characteristic	Equation Number	Unit	Phenol	Resorcinol
a	13	cm^6/min μg	3.25 ± 0.7	21.7 ± 0.5
$b \equiv K$	13	cm^3/min μg	0.0449 ± 0.009	0.109 ± 0.003
f	10	cm^2/μg	0.0105	0.0331
N	17	μg/cm^3	1280	339
k	6	(μg/cm^3)$_s$/(μg/cm^3)$_l$	1280	350
A^{*1}	11(8)	cm^3	720	200
B'^{*2}	11(12)	μg	209	66

*1 When $G = 0.2$ g.
*2 When $C_0/C = 10$.

For estimation of SPE characteristics the function Z (Equation (14)) was plotted against the effluent volume (Table 1, columns V and Z). The results show that for Ph the relationship is a straight line, as it has been assumed theoretically. For R, the slope, equivalent to rate constant K, decreases when $Z \to 0$. The transition of the sorption characteristics during the procedure indicates that the SPE mechanism of R is

complicated. As far as the breakthrough is of interest, the values of Z and V from the first linear part of the function Z were turned to account only. The lower limit of C was prescribed as 10 % of C_0 by the precision of the test procedure.

The characteristics found (Table 2) prove that the second OH group in the molecule of phenolic compound (R instead Ph) decreases distribution factor k 3.7 times and increases the sorption rate factor 3.2 times. The maximum admissible volume to be concentrated without losses of sorbate can be calculated by a simple equation:
for Ph

$$V(\max) = 720 - 209/C_0 \tag{25}$$

for R

$$V(\max) = 200 - 66/C_0 \tag{26}$$

By Equations (25) and (26) it is easy to find that for Ph and R the immediate breakthrough of the sorbate occurs when C_0 is, respectively, 0.29 mg/dm^3 or less and 0.33 mg/dm^3 or less. For example, if the effluent volume is prescribed to be 200 cm^3, the critical concentration limit for Ph should be 0.40 mg/dm^3, but there could not be any C_0 that would provide the complete retention of R.

Conclusions

1. The Bohart-Adams bed depth-service time (BDST) equation was modified to evaluate the efficiency of solid phase extraction (SPE). A relationship between solute influent and effluent concentrations, flow rate, solution volume, cartridge cross-section, sorbent mass and density was described. A method to estimate distribution factor k and sorption rate factor f for the relationship derived was proposed.

2. A linear fall of the solution volume at breakthrough versus reciprocals of the effluent concentration and sorption rate factor was deduced.

3. The values of k and f at SPE for hydroxybenzene (Ph) and resorcinol (R) were estimated. The capacity factor for more hydrophobic Ph is much higher than that for R (correspondingly 1280 and 350 (mg dm^{-3})$_s$/(mg dm^{-3})$_l$). On the contrary, the sorption rate factor on SDB 1 is higher for the more hydrophilic sorbate (correspondingly 0.033 cm^2/µg for R and 0.0105 cm^2/µg for Ph).

4. The commercial cartridge studied, containing 0.2 g SDB 1, enables preconcentration of Ph and R only when the effluent concentration is above 0.3 mg/dm^3. To guarantee a complete retention of these phenols when concentration is lower, mass of the sorbent should be increased and the cross-section of the cartridge should be decreased, or a sorbent with higher capacity and sorption rate should be found.

Acknowledgement

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