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Physico-chemical approach to study organotin sorption–desorption during solid-phase microextraction

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Abstract

Solid-phase microextraction (SPME) has become a real alternative to liquid–liquid extraction in the field of speciation of organometallic compounds. Despite the high performance of this preconcentration technique, matrix effects in natural samples can affect the analytical precision. In order to understand the origin of these disturbances and control the extraction step as best as possible, the sorption–desorption behaviour of organotins was studied. In the first part, this paper discusses the analytical problems encountered in the daily use of SPME due to the particular problems observed for phenyltins. The sorption profile of these compounds was modelled using experimental design methodology to confirm the first-order kinetics. Desorption of the compounds was also observed after a given time and could not be attributed to competition between organotin compounds. In the same way, butyl- and phenyltins were studied in the presence of humic substances, which acted as representatives of organic matter found in natural samples. These substances drastically decrease the extraction yields, but do not affect the sorption profile of butyl- and phenyltins.

Keywords: Experimental design; Kinetic studies; Solid-phase microextraction; Organotin compounds; Humic substances

1. Introduction

The use of solid-phase microextraction (SPME) has increased considerably in recent years in environmental analysis [1]. This quite simple preconcentration method can be implemented by direct immersion of the fibre in the sample (direct mode) or by positioning it above the solution (headspace mode). A polydimethylsiloxane (PDMS) phase has mainly been used in all fields of application of SPME. The extraction phenomenon from the liquid (or gaseous) phase to the PDMS phase has been attributed to an *ab*sorption process [2,3], corresponding to diffusion of the analytes into the stationary phase. Among other applications, PDMS-SPME has been successfully applied to the speciation of organometallic compounds (tin, lead and mercury) present at trace levels in environmental samples [4].

Despite the high analytical performance of SPME-based procedures, several authors have observed phenomena which could affect the precision and reliability of the methods developed. One of these disturbances is that equilibrium, which theoretically is expected to be achieved in the fibre–solution system after a certain sorption time, is not reached systematically. Desorption of some compounds from the fibre has also been reported in the case of multi-component solutions [5,6]. Moreover, selective extraction of some species by SPME can be dis-

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turbed in natural samples by the presence of organic matter. For example, some studies have reported that extraction yields of organophosphorus pesticides and benzene decrease in the presence of organic carbon present in samples [7,8]. The presence of organic matter such as humic substances leads to the same phenomenon and can also lengthen the time necessary to reach equilibrium between the different phases of the system [9,10]. Under these conditions, the extraction ability of PDMS fibre decreases rapidly after several immersions in turbid waters. These observations indicate that the disturbing effect of organic matter is unquestionable and that the performance of the analytical method, generally optimised with standards prepared in Milli-Q water, is directly affected.

In the case of organotin extraction, it has been observed that the responses of some compounds (particularly triphenyltin, TPhT) drastically decrease during the analysis of sediments or sewage sludge by SPME–GC–FPD (flame photometric detection) [5,11]. Therefore, the precision and reliability of the quantitation can suffer, sensitivity can decrease, and validation of the SPME-based procedure can be compromised.

Different hypotheses have been proposed to explain these phenomena: (i) co-extraction of disturbing organic substances from the matrix into the small volume of the PDMS phase; and (ii) inhibition of species diffusion from the aqueous sample into the stationary phase due to the presence of interfering compounds. Even if these analytical problems cannot be fully resolved, it is essential to identify their causes and consequences in order to overcome them as much as possible.

This work aims to describe the behaviour of organotins during SPME. First, the main disturbances which occur during environmental sample analysis were surveyed. According to these results, and in order to obtain maximum information about the influence of co-extracted organotins and organic matter, experimental designs were used. This methodology allows the experimental part to be as comprehensive as possible. Chemometrics was implemented in order to determine sorption kinetics and to evaluate sorption–desorption phenomena. According to the results obtained, this approach proved to be a powerful way to improve our understanding of the phenomena.

2. Experimental

2.1. Instrumentation

2.1.1. SPME device

The manual SPME device and the fibres were obtained from Supelco (Saint Quentin Fallavier, France). The polydimethylsiloxane phase (PDMS, 100 μm) was shown in previous work to be the most efficient phase for the simultaneous extraction of butyl- and phenyltins [5]. The temperature of the chromatographic injector for the desorption step was fixed at 270 °C according to the recommendation of the manufacturer.

2.1.2. Gas chromatography–pulsed flame photometric detection

Organotin compounds were separated and detected using a Varian 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a pulsed flame photometric detection (PFPD) system and a Varian 1079 split/splitless injector. A polymethylsiloxane DB-1 capillary column was used for the separation (30 m×0.25 mm, 0.25 μm) with nitrogen as carrier gas (2 ml min^{-1}). The following oven temperature program was chosen in order to allow a satisfactory separation of organotin compounds: 80 °C for the first minute, increased to 180 °C at a rate of 30 °C min^{-1}, and then to 270 °C at 10 °C min^{-1}. The final temperature was maintained for 3 min.

A filter with a wide transmission band (320–540 nm) (BG-12, Schott, France) was used to observe the emission corresponding to the molecular recombination of Sn–C. According to the tin emission profile and previous optimisation, aquisition of the signal was carried out with a gate delay of 3.0 ms and a gate width of 2.0 ms after each flame ignition. The other PFPD operating conditions were the following: temperature 350 °C, air1 (ignition chamber) 28 ml min^{-1}, air2 (combustion chamber) 20.5 ml min^{-1} and H_2 26.5 ml min^{-1}.

2.2. Reagents and standards

Monobutyltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), and triphenyltin chloride (TPhT, 95%) were purchased from Aldrich

(Milwaukee, WI, USA). Tripropyltin chloride (TPrT, 98%) was obtained from Strem Chemicals (Bischeim, France). The organotin stock solutions containing 1000 mg l^{-1} as tin were prepared in methanol and stored at +4 °C in the dark. Working standards were obtained by daily dilution of the stock solutions in Milli-Q water (18.2 MΩ).

Methanol and sodium ethanoate were purchased from Prolabo (France). Hydrochloric, nitric and ethanoic acids were obtained from Merck (Darmstadt, Germany). Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals. The ethylating solution was prepared daily by dissolving 0.02 g in 2 ml of deionised water and stored at +4 °C in the dark.

2.3. Samples

Fish tissue (whiting) obtained from a market was mixed and spiked with butyl- and phenyltins in order to obtain a concentration of 167±20 μg (Sn) kg^{-1} in the wet tissue.

Commercial humic substances (HSs) purchased from Fluka (reference No. 35069789, M_r 600–1000, ash 20%) were used as representatives of natural organic matter in sediments and soils. Although this approach has prompted much discussion in the literature, it is recognised as the easiest way to simulate a natural matrix, especially because HSs are commercially referenced [12].

2.4. Analytical procedure

2.4.1. Extraction from solid samples

Detailed operating conditions have been described previously [11,13].

For biological material, 2 g of the freshly mixed material was humidified in 2.5 ml of methanol by mechanical stirring for 2 h. Then, 12.5 ml of HCl in methanol (0.12 mol l^{-1}) was added and the mixture was stirred sonically for 1 h.

For humic substances, the extraction process usually used for sediments was used. One gram of commercial humic substances was extracted in 20 ml glacial ethanoic acid by mechanical stirring for 12 h. This process allows the HS to be treated similarly to an organic matter-rich matrix in order to obtain an acidic extract that is representative of what is usually obtained in soil or sediment analysis.

2.4.2. Derivatisation, SPME and analysis

The glass reactors used for derivatisation and SPME were obtained from Prolabo (France). The reactor volume is about 250 ml and the neck (19/26) is adapted to make the SPME needle stable during the extraction step performed by vigorous agitation. 0.5 to 2 ml of centrifuged acidic extract was directly introduced into the derivatisation reactor in the presence of a 100 ml aliquot of sodium ethanoate/ethanoic acid buffer. Ethylation was carried out using $NaBEt_4$ (0.3–0.5 ml of a 2% solution). Then, the PDMS-SPME fibre was directly plunged into the sample and the reactor was placed on an elliptic table operated at 450 rpm. After the sorption step, the fibre was directly placed into the injection port of the GC where the compounds were thermally desorbed.

2.5. Methodological approach: theory of experimental designs

Laboratory-written software (PLEX) was used to obtain the experimental designs. The experimental design methodology has found many applications in the field of analytical method optimisation. This statistical tool allows the simultaneous evaluation of the influence of various parameters, and quantitation of the effects of the factors and their interactions. This methodology is generally used with an optimisation goal. It does not always allow one to find an individual result more quickly than other optimisation methods, but it generally does so with a greater degree of certainty.

The experimental design method was employed as described by Goupy [14] and Sado and Sado [15]. Instead of step-by-step data aquisition without any planning, this statistical approach suggests organised experiments in order to reduce their number and increase their reliability. According to the results obtained, an empirical mathematical modelling of the data can be performed.

First, the different study factors and their field of variation have to be chosen. The experimental field ranges between minimum and maximum levels, denoted "−1" and "+1" for each factor. On the basis of these values, an experimental matrix denoted X can be constructed, requiring 2^{N_f} experiments (N_f is the number of factors). Second, one or several responses, taken as representative of the studied phenomenon, have to be chosen. The values obtained

for each response and each experiment are collected in a matrix denoted *Y*.

Each experiment was performed once. An additional experiment in the centre of the experimental field (denoted ''0'') was carried out five to seven times. This procedure was used in order to determine the experimental precision, given by the standard deviation (σ) of the ''0'', and to adjust the different sets of results obtained during the experimental runs in the case of possible bias.

The effects of factors and interactions are presented in a matrix denoted ''*A*'' and are evaluated by a matrix calculation:

$$A = (X^t \cdot X)^{-1} \cdot X^t; Y \quad (1)$$

where X^t is the transpose of X and X^{-1} is the inverse of X.

A first-order model was first proposed and compared with the experimental results. Generally, such a multi-linear model cannot fit the response Y correctly. Therefore, it was necessary to perform complementary experiments at two levels, $+\alpha$ and $-\alpha$ ($\alpha = N^{1/4}$, where N is the number of experiments in the initial design, $\alpha > 1$), in order to extend the experimental field. The complementary experiments, added to the N initial experiments, allows a second-order model to be proposed. This quadratic model was then adjusted by stepwise, i.e. iterative, calculations allowing the progressive removal of effects with no or low significance. This statistical approach allows us to minimise the number of experiments and to determine the influence of each considered factor as well as their interactions on the studied phenomena.

3. Results and discussion

3.1. Extraction yields

Various analytical problems were reported in a previous paper dealing with optimisation of the SPME procedure for tin compounds [5]. The sorption profiles of the different organotins vs. time showed that the butyl- and phenyltins (except DPhT) suffer from slow desorption after a fibre/solution contact of 30–40 min. However, this experimental approach did not permit the determination of the causes of this desorption, which can be attributed either to self-desorption or to sorption competition between the different analytes present in the multi-component solution. In this same study, the influence of the matrix was emphasised by a study of the chromatographic responses of organotins, which varied drastically depending on the matrix analysed. Phenyltin compounds present greater variations than butyltins. This phenomenon was also dependent on the degree of alkylation of the compound, trisubstituted species (TBT and TPhT) showing the greatest variation.

In order to complete these first results and to evaluate the influence of the matrix on the sorption of organotins, the extraction yield of each tin compound in different matrices was investigated. The amount of organotin extracted into the fibre cannot be evaluated directly, since ethylation and extraction are performed simultaneously. Thus, only the ''ethylation–extraction'' yield can be estimated using the depletion experiment method described in the literature [16,17]. This method requires successive SPME extractions on the same sample and under the same conditions. The resulting data can then be fitted by a regression curve corresponding to an exponential decrease according to

$$A_i = e^{-ki} \quad (2)$$

where A_i is the amount extracted during extraction i. This relation can be linearised, allowing the evaluation of the slope k using all the data:

$$\ln A_i = -ki \quad (3)$$

Then, the percentage extracted on the fibre during the first extraction can be evaluated according to the following relationship:

$$\%\ \text{extracted} = \frac{A_1}{\sum A_i} \cdot 100 = \frac{e^{-k}}{\sum A_i} \cdot 100 \quad (4)$$

Using this methodology, successive extractions were performed in three different spiked matrices (suprapure water, fish tissue extract and an acidic extract of humic substances) in order to estimate the extraction yields for different organotins. The results are presented in Fig. 1. The ethylation–extraction yields obtained in suprapure water ranged from 10 to 60%.

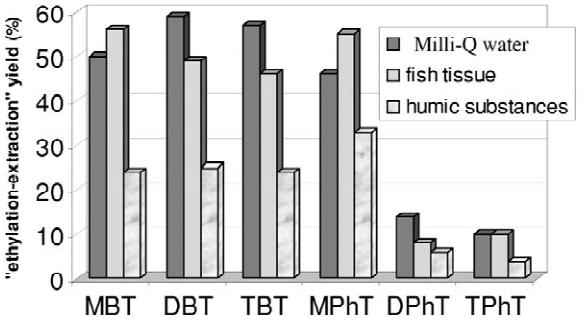

Fig. 1. Ethylation/extraction yields of butyl- and phenyltins in three matrices: suprapure water, spiked fish tissue and humic substance extract.

Of all the compounds, TPhT has the lowest yield (10%), probably because of its low diffusion coefficient from solution to the fibre, as reported previously [5]. In the samples representative of natural matrices, the extraction yield ranged from 24 to 56% for all the compounds, except DPhT and TPhT. In the biological tissue, ethylation–extraction yields were lower than those obtained in Milli-Q water, except for the monosubstituted forms. However, in the presence of fulvic acids, the yields were lower for all compounds studied, TPhT exhibiting the lowest (4%). These results confirm the disturbing effect of organic matter on the SPME extraction of organotins, particularly that of TPhT. Moreover, it is important to note that the presence of organic matter affects the extraction of trisubstituted compounds more than that of the other species. The extraction yields of TBT and TPhT decrease to 58 and 60%, respectively. MPhT is the least affected compound.

3.2. Sorption kinetics

As previous experiments have shown that organotin sorption on SPME depends on co-extracted species, extraction profiles vs. time cannot be described only by a classical kinetics approach. In this very specific context, experimental design methodology, generally used for optimisation, appeared to be the best way to quantify and fit the amount of extracted organotins most precisely and fully. The influence of several parameters can be taken into account simultaneously in a factorial design. In this way, kinetics, sorption competition and ''self-desorption'' can be studied simultaneously for each organotin compound.

3.2.1. Phenyltin mixture in suprapure water

In a first step, the sorption kinetics of organotins prepared in suprapure water were studied. In order to reduce the number of factors and focus the study on the low extraction yield of phenyltins (particularly that of TPhT), only the behaviour of the three phenyltins (MPhT, DPhT and TPhT) was considered.

Four factors were studied in an experimental field corresponding to the analytical conditions usually used in environmental analysis (sorption time and various concentrations) [5]. All the factors and the corresponding variation fields are summarised in Table 1. A fractionary design 2^{4-1} was used, where factor (1) was associated with the interaction between all the other factors (2, 3 and 4). According to the theory of chromatography, the area of the chromatographic peak is directly proportional to the amount of analyte injected and, correspondingly, to the amount of analyte extracted into the fibre. Therefore, the respective peak areas of MPhT, DPhT and TPhT were taken as the three responses to evaluate the SPME step. They were denoted A_1, A_2 and A_3, respectively. According to the results of the

Table 1
Design 1: experimental field and effect of each factor on the responses $A_1 = A$(MPhT), $A_2 = A$(DPhT) and $A_3 = A$(TPhT)

Factor	Level				Effect of each factor on		
	$(-\alpha)$	(-1)	$(+1)$	$(+\alpha)$	A_1	A_2	A_3
(1) Sorption time (min) = (234)	5	29	97	120	+	+	+
(2) [MPhT] (ng l^{-1})	5	55	200	250	+	ns	ns
(3) [DPhT] (ng l^{-1})	5	55	200	250	ns	+	ns
(4) [TPhT] (ng l^{-1})	5	55	200	250	ns	ns	+

ns, not significant; +, positive effect.

first part of the design (see the relative influence of each factor in Table 1), only the sorption time and the concentration of the compound appear to influence the corresponding responses. With regard to these results, complementary experiments at levels $-\alpha$ and $+\alpha$ ($\alpha = 4^{1/4} = 1.41$) were carried out in order to establish second-order models to fit the variations of the extracted amounts. A new matrix including only two factors on the basis of a complete design was then necessary. After analysis of the results, the following models were proposed:

$$A_1 = 2.70 + 0.40\mathbf{[1]} + 0.70\mathbf{[2]} - 0.43\mathbf{[1]}^2 \quad (5)$$

$$A_2 = 3.39 + 0.98\mathbf{[1]} + 0.74\mathbf{[3]} - 0.35\mathbf{[1]}^2 \quad (6)$$

$$A_3 = 0.25 + 0.06\mathbf{[1]} + 0.07\mathbf{[4]} + 0.05\mathbf{[1][4]} - 0.04\mathbf{[1]}^2 \quad (7)$$

They were validated statistically (precision, significance) and could describe 85 to 99% of the experimental variation. As expected, these expressions are in agreement with the quantitative relation between peak area and concentration of the species. Moreover, a quadratic term $(\text{time})^2$ systematically appeared in the three models and could be representative of a logarithmic variation, characteristic of first-order kinetics.

The sorption profiles of the three phenyltins at a concentration of 145 ng (Sn) l^{-1}, corresponding to level ''0'', are shown in Fig. 2. As the preliminary experiments suggested, desorption from the fibre to the solution can be observed after a certain extraction time, different for the different species. This phenomenon is important for MPhT and TPhT in the studied experimental field. According to the results of the experimental design, this desorption effect cannot be attributed to competitive sorption between organotins, since the concentrations of the other compounds do not influence the results. Only the TPhT sorption model presents an interaction term between time and the amount of analyte. Thus, TPhT desorption is faster and greater when its concentration decreases. This confirms the observation that the sorption time has to be relatively short in order to avoid a decrease of the ethylation–extraction yield of TPhT.

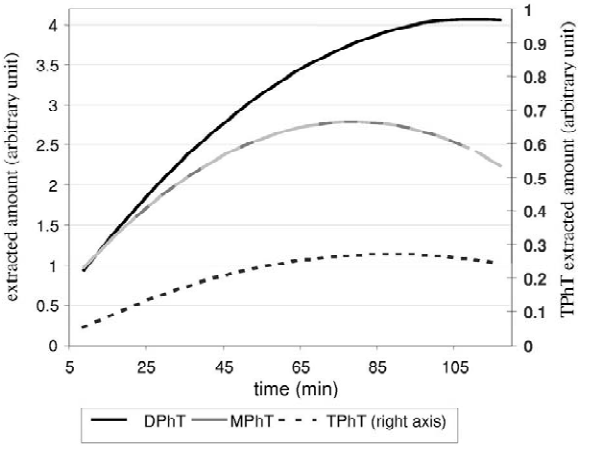

Fig. 2. Sorption profiles of phenyltins according to the polynomial models of design 1.

3.2.2. Modelling of the kinetics

Numerous authors [2,4] consider sorption in SPME to have first-order kinetics, but only very few works have studied these phenomena. In order to validate our models, experimental sorption and desorption profiles were established for each species using the experimental results obtained from the experimental design. Experimental and calculated profiles on the basis of first-order kinetics were then compared.

According to the theory of kinetics [18], the different parameters of a first-order reaction (see Table 2) can be expressed relative to the following different variables: X_s and X_f, which represent the species in the solution and the fibre, respectively; t, the time; $[X]_{s,t=0} = a$, concentration of analyte X in solution at $t = 0$; $[X]_{f,t} = x$, concentration of analyte X in the fibre at time t; t_{max}, time when desorption begins (called the desorption time below); x_{max}, concentration of the species at t_{max}.

The values of the kinetics rate constants were calculated using the numerical values of the polynomial models (5)–(7). Because of the late desorption in the chosen experimental field, the value of the corresponding constant could not be calculated with precision and was only estimated for MPhT and TPhT. The different parameters (kinetic rate constants, desorption time) and the kinetic equations are reported in Table 3.

According to the sorption and desorption constants

Table 2
First-order kinetics: parameters and equations

Sorption				Desorption			
	X_s	$\rightarrow$	X_f		X_f	$\rightarrow$	X_s
$t = 0$,	a,			t_{max},	x_{max},		$a - x_{max}$,
$t < t_{max}$,	$x_{max} - x$,		x,	$t > t_{max}$,	$x_{max} - x$,		x
t_{max},	$a - x_{max}$,		x_{max}				

Kinetics rates

(a) $-\dfrac{d[X]_{s,t}}{dt} = \dfrac{d[X]_{f,t}}{dt} = k_1[X]_{s,t}$

where k_1 is the sorption rate constant (min^{-1})

(b) $-\dfrac{d[X]_{f,t}}{dt} = k_2[X]_{f,t}$

where k_2 is the desorption rate constant (min^{-1})

(c) $\dfrac{dx}{dt} = k_1(x_{max} - x)$

after integration:
(e) $x = x_{max}(1 - e^{-k_1 t})$

(d) $-\dfrac{d(x_{max} - x)}{dt} = k_2(x_{max} - x)$

after integration:
(f) $x = x_{max}[1 - e^{-k_2(t - t_{max})}]$

k_1 and k_2, it appears that desorption is much slower than sorption. It is interesting to note that the higher the sorption rate k_1 [k_1(MPhT) > k_1(TPhT) > k_1(DPhT)], the shorter the desorption time t_{max}. Moreover, the ethylation–extraction yield of the various species seems to be directly correlated with the sorption kinetics. Indeed, MPhT which has the highest sorption rate is also the compound with the highest ethylation–extraction yield (46%) among the three species. In the same way, DPhT and TPhT present lower extraction yields (14 and 10%) and also have slower kinetic rates.

Fig. 3 presents the superposition of the sorption profiles obtained with both approaches for the three phenyltins. The good agreement obtained allows us to confirm the hypothesis of first-order kinetics for the sorption part. Unfortunately, the desorption phenomena cannot be fitted with the same precision. Only a rough description of this phenomenon can be observed in Fig. 3. The validity of the use of experimental designs to describe sorption–desorption phenomena is, however, confirmed.

3.2.3. Mixture of butyl- and phenyltins in the presence of humic substances

With regard to the matrix effects occurring during the analysis of natural samples, a second kinetics study was carried out to consider the SPME of organotins in the presence of organic matter as an additional parameter. Six organotins (butyl- and

Table 3
Design 1: kinetic approach: calculation of kinetic parameters

	MPhT	DPhT	TPhT
Sorption			
k_1 (min^{-1})	0.049	0.028	0.033
$\log x_{max}$	0.446	0.645	−0.564
R^2	0.980	0.987	0.992
Sorption kinetics	$x = 2.793(1 - e^{-0.049t})$	$x = 4.076(1 - e^{-0.028t})$	$x = 0.273(1 - e^{-0.033t})$
Desorption			
t_{max} (min)	79	111	89
k_2 (min^{-1})	−0.003	–	−0.003
Desorption kinetics	$x = 2.793[1 - e^{0.003(t - t_{max})}]$	–	$x = 0.273[1 - e^{0.003(t - t_{max})}]$

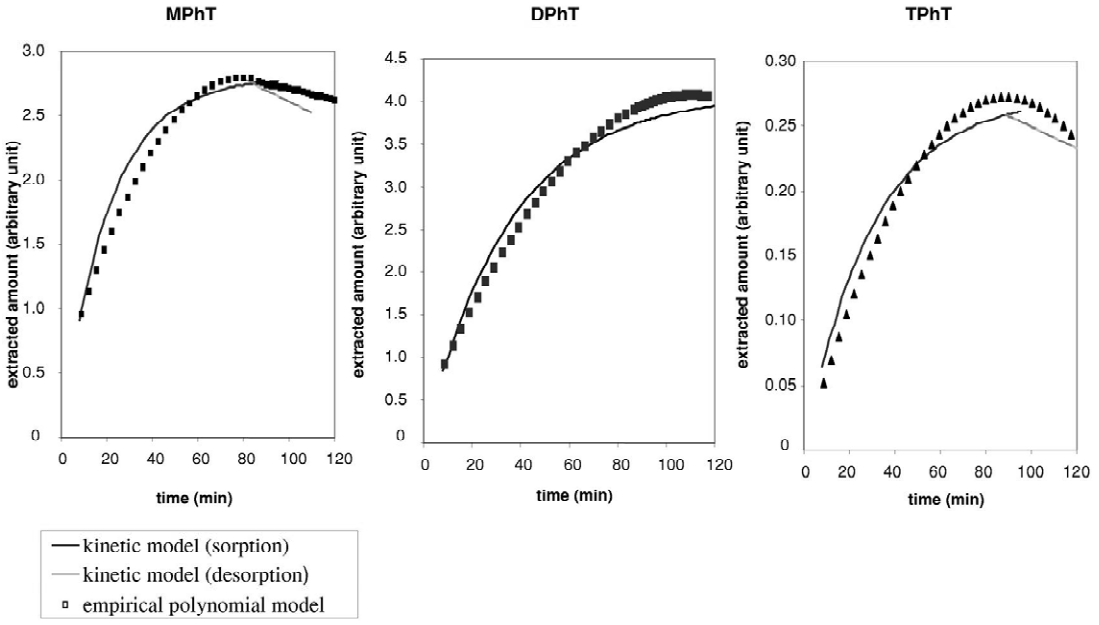

Fig. 3. Superposition of kinetic models and empirical polynomial models.

phenyltins) were considered in order to evaluate, as accurately as possible, the influence of organic matter (OM) on the whole SPME extraction procedure. Commercial humic substances were submitted to the same acidic extraction procedure used for sediments in order to simulate the impact of these compounds on the SPME step. The volume of this acidic extract [denoted V(HS)] added to the ethylation reactor was chosen as a supplementary factor in a second experimental design. Therefore, eight factors were considered in the experimental field described in Table 4. A fractionary design 2^{8-4}, which associates four of the eight factors with second-order interactions, was realised. Similarly to the first design, the peak areas relative to each organotin were chosen as responses. The influence of each factor on the responses is given in the second part of Table 4.

According to the results of the first part of the design (i.e. experiments at levels ''−1'' and ''+1''),

Table 4
Design 2: experimental field and effect of each factor on the responses $A_1 = A$(MPhT), $A_2 = A$(DPhT), $A_3 = A$(TPhT), $A_4 = A$(MBT), $A_5 = A$(DBT), $A_6 = A$(TBT)

Factor	Level				Influence of factors					
	$(-\alpha)$	(-1)	$(+1)$	$(+\alpha)$	A_1	A_2	A_3	A_4	A_5	A_6
(1) Sorption time (min)	5	34	91	120	++	++	+	+	++	
(2) [MPhT] (ng l^{-1})	10	55	145	190	+					
(3) [DPhT] (ng l^{-1})	200	300	500	600	++	++				
(4) [TPhT] (ng l^{-1})	200	300	500	600	−−	−	++			
(5) [MBT] (ng l^{-1})=(123)	10	55	145	190			+	++		
(6) [DBT] (ng l^{-1})=(124)	10	55	145	190			+		++	
(7) [TBT] (ng l^{-1})=(134)	10	55	145	190			+			++
(8) V(HS) (μl)=(234)	10	100	300	400		−−	−−	−−	−−	−−

+, Positive effect; −, negative effect; others are not significant. V(HS), volume of acidic extract of humic substances added to the ethylation/SPME reactor.

the sorption time appears as a clearly significant factor for all the responses, except for the extracted amount of TBT, which seems to reach its sorption equilibrium outside the experimental field, i.e. in less than 35 min. The amount of humic substances *V*(HS) added to the medium has a high negative influence on the responses of all compounds except MPhT. Peak areas appear systematically as a function of the concentration of the compound in solution and the amount of humic substances. The concentrations of other organotin compounds have a significant effect only on the responses of MPhT, DPhT and TPhT. However, no mutual interactions exist between these compounds. Therefore, these phenomena cannot be attributed to sorption competition.

The large number of factors considered in this experimental design makes it difficult to evaluate all the respective influences between the factors. Therefore, in order to interpret the results as best as possible, only the factors with the greatest influence were kept for the complementary experiments and the modelling. This approach allows us to obtain individual models for each species. These models were validated statistically and can explain 75 to 98% of the phenomena. The three-dimensional sorption profiles of each organotin as a function of time and amount of humic substances are presented in Fig. 4. All concentrations were arbitrarily fixed to level "+1".

The important influence of organic matter on the SPME procedure was confirmed by the empirical modelling. From these profiles, a signal decrease can be evaluated between level "−1" (i.e. 200 μl of humic substances) and level "+1" (i.e. 300 μl of humic substances). It can be seen that ethylation–extraction yields decrease as a function of the degree of substitution of the organotin. Indeed, responses for the monosubstituted organotins are the least affected by the presence of humic substances (no signal decrease for MPhT, 75% decrease for MBT). The diminution is higher for di- and trisubstituted compounds (81% for TPhT, 100% for TBT, 93% for

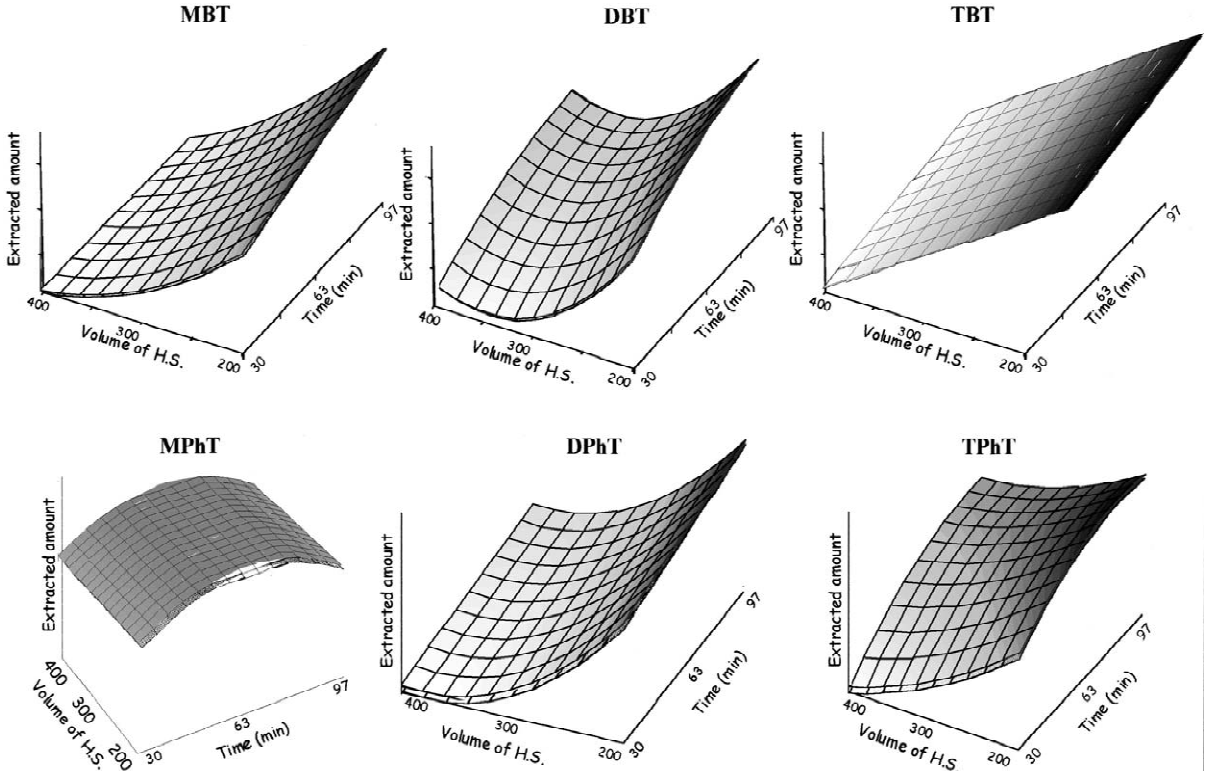

Fig. 4. Extracted amount as a function of time and volume of humic substances (HS) (design 2).

DBT and 94% for DPhT). The analytical procedure includes a one-step ethylation–extraction step. If ethylation was the step mainly affected by the presence of organic matter, monosubstituted forms would be the most affected. However, the present results demonstrate the opposite. Therefore, extraction into SPME fibre is probably the limiting step of the process.

From this second kinetics study, the same self-desorption of organotins was observed. The necessary time to reach sorption equilibrium remains the same, independent of the amount of humic substances. Therefore, the presence of organic matter does not affect the time required to reach equilibrium between the aqueous solution and the fiber, only the amount of organotin extracted by SPME. Two hypotheses could explain these observations:

(i) Organotin standards and humic substances could interact in the medium and tin compounds would no longer be available for SPME extraction. This phenomenon would be more important when the amount of humic substances is high.

(ii) A part of the humic substances present in a natural matrix would have a high affinity for the polydimethylsiloxane phase. Then, the stationary phase volume available for organotin compounds would be reduced when the amount of organic matter is high. In the same way, the distribution coefficient ''solution/fibre'' corresponding to each organotin could be affected by the potential sorption competition between the analytes and the humic substances. Diffusion coefficients in the solution could also be reduced in these complex matrices. All these additional factors could explain the decrease in the amounts of the sorbed organotins. Under these conditions, the phenomenon could be attributed to a ''decreased sorption of organotin''.

4. Conclusion

The physico-chemical approach of organotin sorption proposed in this study has allowed us to better understand the matrix effects observed during solid-phase microextraction. Moreover, experimental design, used in an original way, appears to be a powerful tool to describe physico-chemical phenomena.

In all the studied matrices, desorption phenomena cannot be attributed to competition between organotins. A correlation was observed between the time when desorption begins and the kinetic rate of the compound. In the presence of humic substances, the sorption profiles of organotins are not modified. Only the ethylation–extraction yield seems to be reduced; TBT and TPhT being the most affected. According to these results, it appears essential to work under routine conditions with a relatively short (<45 min) sorption time in order to minimise analytical problems.

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