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New approach of solid-phase microextraction improving the extraction yield of butyl and phenyltin compounds by combining the effects of pressure and type of agitation

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Abstract

A new methodology for the simultaneous and fast solid-phase microextraction (SPME) of butyl- and phenyltin compounds, as ethylated derivates, is proposed in this paper. The effects of pressure and type of agitation during headspace SPME sampling are evaluated and discussed on the basis of thermodynamic considerations. Quantitative structure–activity relationships were used to estimate analytes partition coefficients allowing to explain the different behaviours experimentally observed. SPME sampling conditions including mechanical stirring and reduced pressure result in simultaneous higher efficiency (detection limits especially lowered for phenyltins up to a eight-fold reduction) and shorter sampling time (two-fold reduction).

Keywords: Solid-phase microextraction; Organotins; Reduced; Pressure; Mechanical agitation; Quantitative structure–activity relationships; Extraction time; Headspace

1. Introduction

Over the past 30 years, the large anthropogenic use of organotins, especially the highly toxic butyl- and phenyltin compounds, is responsible for their important occurrence in the environment [1,2]. Consequently, the presence of these compounds is more and more drastically controlled. Therefore, fast, accurate and precise analytical methods are required in order to identify and quantify these species at the levels commonly found in environmental matrices, i.e. in the range pg to ng (Sn) l^{-1}. Speciation of organotin compounds is commonly realised by coupling gas chromatography with a specific detector [3–12]. Nevertheless, sample preparation remains a critical step which requires the extraction/derivatization and preconcentration of the analytes prior to their injection in the chromatograph. Liquid–liquid extraction is traditionally used but requires high levels of often toxic organic solvents.

Solid-phase microextraction (SPME) was developed in the 1990s by Pawliszyn and co-workers [13,14] for organic compounds and further used for metallic and organometallic compounds, as reviewed by Mester et al. [15]. Nevertheless, only few teams have worked on the extraction of phenyltin compounds with SPME [16–22].

For organotin compounds, direct sampling, i.e. the fiber is directly exposed to the aqueous sample, was first proposed by Lespes et al. [16] and Aguerre et al. [17–19] but suffers from long extraction time (up to 60 min), possible matrix effects and organic matter co-absorption on the fibre [17,23].

Headspace (HS) extraction mode, i.e. the fibre is exposed in the headspace located above the sample, proposed by Zhang and Pawliszyn [24], is based on the faster diffusion of analytes in the vapor phase than in the aqueous phase if the aqueous phase is constantly stirred. HS-SPME sampling

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times could be shortened up to 40 min [20,21] with elimination of matrix effects. Nevertheless, heaviest compounds, i.e. also the less volatile ones, are less extracted.

Effects of temperature in headspace mode were also proposed to reduce extraction time [25]. But, no significant improvement in extraction time was obtained by Vercauteren et al. [22] for triphenlytin and tricyclohexyltin using a sampling temperature of 75 °C (35 min). Moreover, handling of vials is more difficult and pressure build-up inside the vial can cause some losses of sample vapor when removing the SPME needle from the vial.

Applications of new techniques of extraction such as stir bar sorptive extraction [26] or liquid phase microextraction [27] were applied to butyl- and phenyltin compounds but did not shorten extraction time (30 and 60 min, respectively including desorption time).

Hence, we propose in this paper another alternative which is the combination of SPME in HS using reduced pressure. If the pressure in the headspace is below the atmospheric pressure, extraction of analytes should be enhanced from the aqueous phase to the gaseous phase [28]. In this paper, this method was applied to butyl- (MBT, DBT, TBT) and phenyltin (MPhT, DPhT, TPhT) compounds determination. The optimisation of the critical parameters are described in details. Two stirring modes were tested both under atmospheric and reduced pressure. Analytical performances of the technique were also discussed in terms of extraction efficiency, detection limits, preconcentration time, and reproducibility.

2. Experimental

2.1. Standards and reagents

Monobutyltin trichloride (>95%), monophenyltin trichloride (>98%), diphenyltin dichloride (>96%) and triphenyltin chloride (>95%) (Aldrich), dibutyltin dichloride (>98%) and tributyltin chloride (>96%) (Merck) were used without further purification. Stock standard solutions containing 1000 mg (Sn) l^{-1} of each compound in methanol (Normapur, >99%, Prolabo) were stored in the dark at 4 °C. In these conditions, they were stable for several months [29]. Working standard solutions were prepared by dilution with Milli-Q water (Millipore, 18.2 MΩ cm) weekly for 10 mg (Sn) l^{-1} and daily for 100 μg (Sn) l^{-1}.

Sodium ethanoate (Sigma, >99%) and ethanoic acid (Merck) were used for 0.4 mol l^{-1} buffer preparation (pH = 4.75). Sodium tetraethylborate ($NaBEt_4$, 98%) was obtained from Galab (Geesthacht, Germany). Fresh 2% solutions (w/v) were prepared daily in Milli-Q water and stored at 4 °C in the dark.

2.2. MIP-AES apparatus and GC conditions

Chromatographic separation of ethylated butyltin and phenyltin compounds was performed with an Agilent (Wilmington, DE, USA) Model 6890 Series Plus gas chromatograph equipped with a split/splitless injection port and a narrow bore injection liner (0.75 mm I.D.). Detection was achieved with an Agilent G2350A Microwave Induced Plasma Atomic Emission detector (MIP-AES) with operational parameters previously optimised in our lab [18].

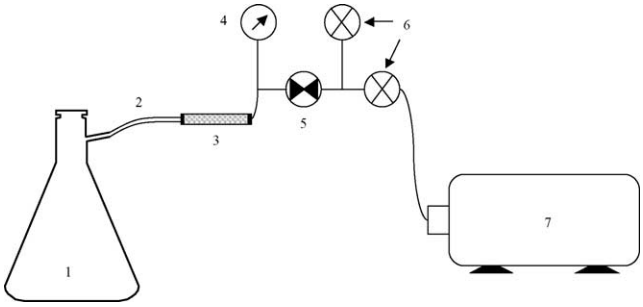

Fig. 1. Schematic of SPME device for sampling at reduced pressures: (1) modified conical flask; (2) tygon tubing; (3) water trap (soda lime and $CaCl_2$ mixture); (4) vacuum controller; (5) two-way valve; (6) vent (depression regulation); (7) vacuum pump.

2.3. SPME procedure

SPME was carried out manually with the appropriate SPME holder and 100 μm polydimethylsiloxane (PDMS)-coated fused silica fibres (Supelco, Bellefonte, PA, USA). This apolar phase is the most commonly used for organometallic compounds [15,16,21].

For the optimisation of the HS SPME procedure, modified 50 ml conical flasks were used. An open-cap vial was welded at the top of the flask allowing it to be sealed with a polytetrafluoroethylene (PTFE)-coated silicone rubber septum (Supelco, 20 mm diameter). The importance of the headspace to aqueous phase volume ratio in HS SPME sampling is well known [30–32]. Geometry of modified conical flasks was designed to allow: (i) a reduced headspace volume around the fibre while keeping the headspace to aqueous phase volume ratio constant; (ii) a larger exchange surface between headspace and sample to improve analyte transfer from aqueous to headspace phase.

A glass tube (17 mm length × 2 mm I.D.) was also welded at the neck of the flask in order to carry out HS SPME in reduced pressure conditions. In the case of HS SPME sampling at atmospheric pressure, this opening was tightly shut.

A 25 ml aliquot of the sodium ethanoate/ethanoic acid buffer was introduced in the modified conical flask. After sealing, organotins were added to obtain a final concentration of 400 ng (Sn) l^{-1} of each compound. The SPME fibre was inserted in the headspace immediately after the addition of 25 μl of $NaBEt_4$ solution. In the case of reduced pressure SPME sampling in order to minimise analyte losses, derivatization reagent was added after decreasing the pressure in the flask. A manual two way valve allowed to isolate the reactor from the vacuum pump once the depression was achieved as indicated in Fig. 1. The pump was then switched

off and the fibre was exposed to the headspace. During the sampling time, pressure did not significantly increase (less than ± 0.01 bar) for the two tested vacuum levels, i.e. 0.5 and 0.04 bar.

In HS SPME sampling, sample stirring does not affect analyte diffusion from the headspace to the fibre coating, but it accelerates the mass transfer of low volatile compounds from aqueous phase to headspace [33]. Two different types of stirring were tested: (i) using the stirrer in combination with a magnetic table, called magnetic, with the stirring rate adjusted to 600 rev min^{-1}; (ii) using the elliptical table with the stirring rate adjusted to 350 rev min^{-1}, called mechanical.

After SPME sampling, the fibre was placed into the injection port of the gas chromatograph where ethylated organotin compounds were thermally desorbed at 270 °C in the splitless mode for 1 min. Under these conditions complete desorption of all investigated compounds was assured (data not shown).

3. Results

3.1. Evaluation of HS SPME GC–MIP-AES performances

The results of extraction time studies, including sampling at 5, 10, 15, 20, 30, 40 and 60 min, are presented as the mean obtained with two different PDMS fibres. Error bars representing the relative standard deviation between the two fibers are included.

The influence of tested parameters, i.e. sample stirring type and pressure, have been evaluated by the determination of repeatability, application domain and detection limits of the whole SPME procedure.

Repeatability (RSD) is defined as the relative standard deviation calculated from five SPME samplings of aqueous samples spiked with the studied compounds at 400 ng (Sn) l^{-1}. The obtained value is given for one fibre.

The application domain (AD) of the whole procedure, including sampling and detection, has been evaluated with samples containing organotin compounds at concentrations from 40 to 2000 ng (Sn) l^{-1}. Each spike level was sampled twice.

The detection limits were evaluated according to the IUPAC specifications as:

$$\mathrm{DL} = \frac{t\sigma}{s_i} \quad (1)$$

where t, student's coefficient with $t = 3$ for a confidence interval of 99.73%, σ the height standard deviation calculated from 10 SPME sampling of the "blank", i.e. buffer and derivatization reagent, and s_i is the calibration curve slope for organotin (i), i.e. peak height/(ng (Sn) l^{-1}).

As it has been previously observed by other authors [21] detection limits are mainly controlled by contamination originating from the buffer and the derivatization reagent. In this paper, we distinguish the instrumental detection limit (IDL) and a "procedure" detection limit (PDL) that takes into account organotin signals originating from the "blank". For IDL calculation, σ value is taken as the standard deviation of the "blank" chromatogram background, while it represents the standard deviation of organotin "blank"

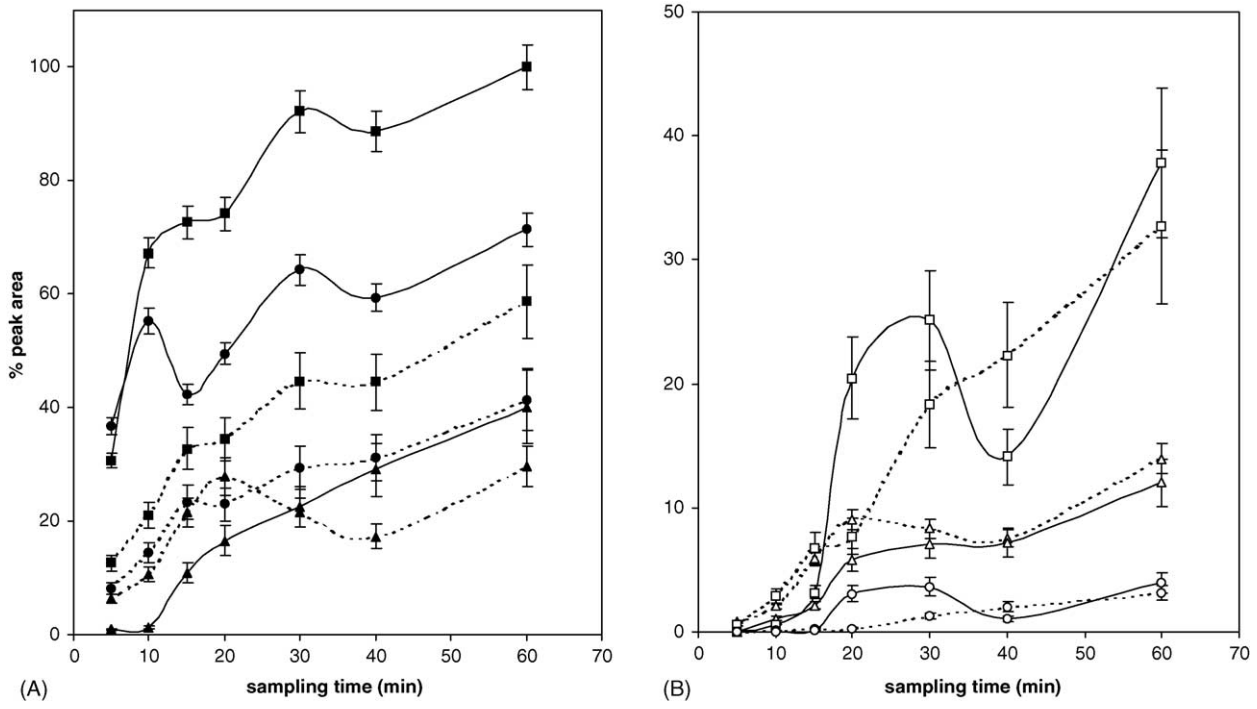

Fig. 2. HS SPME time profiles from agitated sample by magnetic (- - -) and mechanical (—) stirring under atmospheric pressure. (A) Butyltin compounds: (▲) MBT; (■) DBT; (●) TBT. (B) Phenyltin compounds: (△) MPhT; (□) DPhT; (◯) TPhT (400 ng (Sn) l^{-1} spiked aqueous sample).

Table 1
Comparison of (A) atmospheric pressure (AP) and (B) reduced pressure (RP) HS SPME GC–MIP-AED performances from mechanical or magnetic stirred sample

	Magnetic stirred sample[a]				Mechanical stirred sample[b]			
	RSD[c]	IDL[d]	PDL[d]	AD[d]	RSD[c]	IDL[d]	PDL[d]	AD[d]
(A) AP								
MBT	7	0.13	7	400	8	0.11	19	400
DBT	10	0.06	6	2000	3	0.04	3	1000
TBT	10	0.06	3	400	5	0.04	3	400
MPhT	10	1.00	1	1000	14	0.90	0.90	1000
DPhT	13	0.45	0.45	2000	6	0.30	0.30	1000
TPhT	10	0.80	0.80	2000	8	0.30	0.30	2000
	Magnetic stirred sample[e]				Mechanical stirred sample[f]			
	RSD[c]	IDL[d]	PDL[d]	AD[d]	RSD[c]	IDL[d]	PDL[d]	AD[d]
(B) RP								
MBT	13	0.10	4	400	5	0.08	11	400
DBT	11	0.07	8	400	6	0.04	6	1000
TBT	8	0.06	5	400	7	0.04	5	1000
MPhT	10	0.90	0.90	1000	17	0.50	0.50	400
DPhT	11	0.30	0.30	400	8	0.15	0.15	400
TPhT	13	0.30	0.30	1000	18	0.10	0.10	2000

[a] Performances calculated for 30 min extraction time.
[b] Performances given for 20 min extraction time.
[c] Repeatability in % as defined in the text.
[d] In ng (Sn) l^{-1}, see the text for definition.
[e] Performances calculated for 15 min extraction time.
[f] Performances given for 15 min extraction time.

signal in the case of PDL. As it will appear latter, blank contamination, originating mainly from the derivatization reagent, concerns butyltin compounds and leads to an increase of their detection limit by a factor 50–175.

3.2. Mechanical versus magnetic stirring

HS SPME sampling under atmospheric pressure of ethylated organotin compounds from agitated sample at room temperature ($24 \pm 1\,^{\circ}C$) was compared for magnetic and mechanical stirring. Results are presented in Fig. 2A and B as percent peak areas with respect to maximum signal obtained, i.e. the one of DBT for 60 min extraction under mechanical stirring. Whatever the stirring type, extraction time profiles show that equilibrium is not reached even after 1 h of sampling. The positive effect of mechanical stirring on DBT and TBT extraction is obvious for the whole sampling time range. The use of a mechanical table leads to a two-fold increase of peak areas and to the improvement of reproducibility between fibers in comparison with magnetic stirring. For the

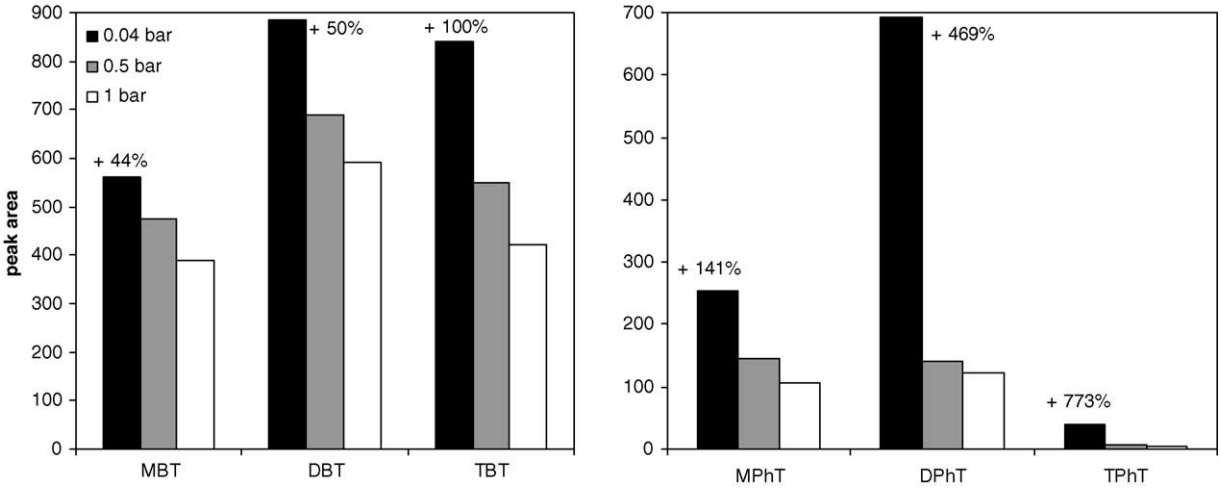

Fig. 3. Comparison of HS SPME responses obtained under atmospheric and reduced pressures sampling (400 ng (Sn) l^{-1} spiked aqueous sample, 15 min sampling, magnetic stirring). The percent gain indicated is calculated from peak areas obtained at 0.04 ($A_{0.04}$) and 1 bar (A_1) as $(A_{0.04} - A_1)/A_1 \times 100$.

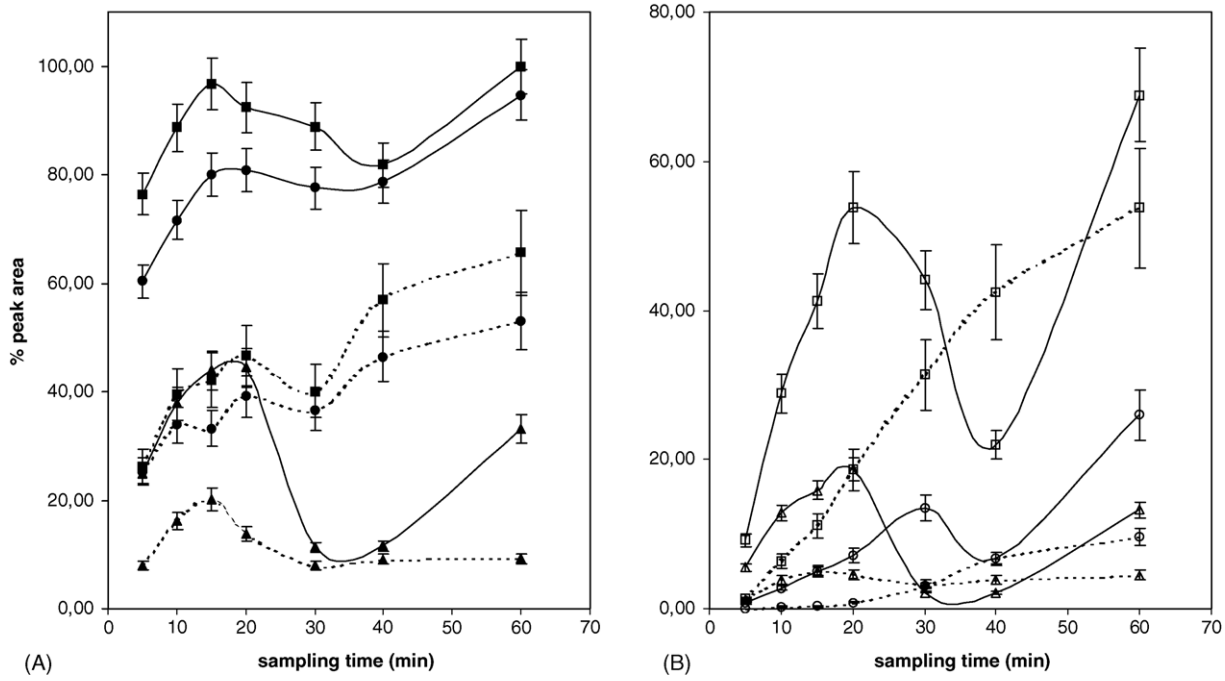

Fig. 4. Reduced pressure HS SPME time profiles from agitated sample by magnetic (- - -) and mechanical (—) stirring. (A) Butyltin compounds: (▲) MBT; (■) DBT; (●) TBT. (B) Phenyltin compounds: (△) MPhT; (□) DPhT; (◯) TPhT (400 ng (Sn) l^{-1} spiked aqueous sample).

other compounds, we cannot draw such a clear tendency. The behaviour of phenyltins is discontinuous with peak areas increasing up to a plateau at 20–30 min. After this time, desorption of DPhT and TPhT occurs while MPhT signal remains constant. Such phenomenon has been observed in direct extraction mode and was attributed to a slow self desorption of the compounds from the fiber [23].

As a compromise between sensitivity and extraction time adapted to GC analysis (15 min), sampling of 30 and 20 min were chosen for magnetic and mechanical agitation respectively. Corresponding SPME procedure performances are given in Table 1A.

3.3. Reduced versus atmospheric pressure sampling

The effect of reduced pressure SPME sampling from magnetic agitated sample was compared to atmospheric pressure sampling for two vacuum levels, i.e. 0.5 and 0.04 bar. Results are presented in Fig. 3 for an extraction time of 15 min. The positive effect of reduced pressure on SPME sampling efficiency is obvious, not only for enhanced overall sensitivity, but also for each individual organotin compound and particularly for the less volatile ones, i.e. DPhT (around five-fold enhancement) and TPhT (around eight-fold enhancement). As 0.04 bar sampling was the more efficient in extracting ethylated organotin compounds, extraction time profiles from 5 to 60 min were studied at this reduced pressure and are compared in Fig. 4A and B. The effect of sampling under 0.04 bar is obvious in particular for phenyltin compounds for which extraction is significantly enhanced. For MBT and MPhT, it appears that sampling under reduced pressure shifts individual extraction maximum to lower sampling times around 15 min. As previously noticed with mechanical stirring under atmospheric pressure (see Fig. 2), desorption of phenyltins is also observed for shorter sampling times under reduced pressure (see Fig. 4). It is also observed when sampling MBT with both agitation types.

Table 2
Variations of SPME responses as a function of sample agitation type (MA: magnetic; ME: mechanical) and sampling pressure (AP: atmospheric; RP: reduced, i.e. 0.04 bar)

Organotin	Calibration slope	Gain (%)		
	MA-AP sampling	MA-RP sampling	ME-AP sampling	ME-RP sampling
$MBTEt_3$	0.233	−12	21	61
$DBTEt_2$	0.478	−4	75	61
TBTEt	0.465	13	57	59
$MPhTEt_3$	0.030	11	10	106
$DPhTEt_2$	0.067	65	44	205
TPhTEt	0.038	133	167	500

Table 3
Estimates of solubility, saturated vapor pressure and K_{ow} for ethylated butyl- and phenyltin compounds

Organotin	TSA[a]	S[b]	p[c]	K_{ow}[d] $\approx K_{fs}$	H[e] $\approx K_{hs}$	$K_{fh} = K_{ow}/H$
$MBTEt_3$	279.3	2.00×10^{-7}	2.29×10^{-4}	2.32×10^{5}	4.67×10^{1}	4.96×10^{3}
$DBTEt_2$	319.3	2.54×10^{-8}	2.42×10^{-5}	2.62×10^{6}	3.89×10^{1}	6.73×10^{4}
TBTEt	359.3	3.23×10^{-9}	2.56×10^{-6}	2.95×10^{7}	3.23×10^{1}	9.12×10^{5}
$MPhTEt_3$	276.2	2.35×10^{-7}	4.11×10^{-6}	1.92×10^{5}	7.15×10^{-1}	2.69×10^{5}
$DPhTEt_2$	313.1	3.50×10^{-8}	2.47×10^{-8}	1.80×10^{6}	2.88×10^{-2}	6.23×10^{7}
TPhTEt	350	5.22×10^{-9}	1.48×10^{-10}	1.68×10^{7}	1.16×10^{-3}	1.45×10^{10}

[a] In Å^2, calculated with individual TSA: 17.7 for Sn, 55.4 for C_2H_5, 95.4 for C_4H_9 and 92.3 for C_6H_5.
[b] In mol l^{-1}, calculated from Eq. (5).
[c] In atm, calculated from Eq. (7) and (11) for butyl and phenyl series, respectively.
[d] Calculated from Eq. (6).
[e] Calculated from Eq. (4).

From extraction time profiles obtained, sampling times of 15 min were chosen for magnetic and mechanical agitation under reduced pressure. Corresponding SPME procedure performances are given in Table 1B. By combining mechanical stirring and reduced pressure conditions, detection limits are especially lowered for phenyltin compounds up to an eight-fold reduction for triphenyltin. In the case of butyltins, procedure detection limits remain similar to the ones obtained under atmospheric pressure sampling due to enhanced blank signal when sampling under reduced pressure. HS SPME efficiency for tested extraction conditions are compared in Table 2. In addition to saving of time, combining mechanical agitation and reduced pressure results in a general enhancement of extraction yields which is the most pronounced for triphenyltin.

4. Discussion

The effects experimentally observed and detailed above can be discussed on the basis of thermodynamic considerations. Therefore, we have tried to explain the different behaviours observed for organotins under study using the equilibrium theory of SPME developed for fibres extracting analytes by absorption and the estimation of organotins partition coefficients.

4.1. Theoretical considerations

In HS SPME sampling, the amount of analyte absorbed by the fibre coating, n_f, can be expressed as [24]:

$$n_f = \frac{K_{fh}K_{hs}V_fV_sC_0}{K_{fh}K_{hs}V_f + K_{hs}V_h + V_s} = \frac{K_{fs}V_fV_sC_0}{K_{fs}V_f + K_{hs}V_h + V_s} \quad (2)$$

where V_f is the fibre coating phase volume, V_s the aqueous phase volume, V_h the headspace phase volume, C_0 the initial concentration of the analyte in the aqueous phase, K_{hs} the partition coefficient of an analyte between the headspace and aqueous phases, K_{fh} the partition coefficient of an analyte between the fibre coating and headspace phases and K_{fs} is the partition coefficient of the analyte between fibre and aqueous phases, easily connected to K_{fh} and K_{hs}.

The octanol/water partition coefficient (K_{ow}) is a good estimate of K_{fs} for methyl silicone coating as it has been previously observed by other authors [24,34], and the partition coefficient K_{hs}, is equivalent to the dimensionless Henry's constant, H. Eq. (2) can thus be rewritten as:

$$n_f = \frac{K_{ow}V_fV_sC_0}{K_{ow}V_f + HV_h + V_s} \quad (3)$$

4.2. Estimation of H and K_{ow} constants

Henry's constant can be determined from the knowledge of the saturated vapour pressure of the analyte, p (in atm with 1 atm = 1.013×10^5 Pa), and its solubility in water, S (in mol l^{-1}), [35]:

$$H = \frac{p}{SRT} \quad (4)$$

with $R = 0.08205$ atm l mol^{-1} K^{-1}, and $T = 298$ K in our case.

Physicochemical properties can be obtained from quantitative structure–activity relationships (QSARs). Solubility, saturated pressure, and K_{ow} have been successfully correlated to molecular total surface area (TSA in Å^2) for organotin compounds in the form of:

$$-\log S = 0.0224 \times \mathrm{TSA} + 0.442, \quad \text{with } S \text{ in mol l}^{-1} \quad (5)$$

$$\log K_{ow} = 0.0263 \times \mathrm{TSA} - 1.98 \quad (6)$$

$$\log p = -0.0244 \times \mathrm{TSA} + 6.0554, \quad \text{with } p \text{ in mmHg} \quad (7)$$

(p is later converted to atm, 760 mmHg = 1 atm = 1.013×10^5 Pa).

Eqs. (6) and (7) [36,37] can be used for mixed tetra alkyltin compounds, i.e. $R^1_nR^2_{4-n}Sn$, corresponding to ethylated butyltins. Eq. (5) [1,36] was firstly demonstrated for homologous tetraalkyl derivatives of Group IVA elements and further applied to mixed tetra alkyltin compounds [37]. Estimates of tetra substituted organotin TSA can be obtained with summation of mean individual TSA values for organic substituents and tin atom [1]. Values of solubility and K_{ow}

obtained applying Eqs. (5) and (6) for ethylated butyl and phenyltin compounds are presented in Table 3.

Comparison to reference values is difficult since to our knowledge, they have never been experimentally evaluated. Calculated values can be checked against comparable literature values. Considering octanol/water partition coefficients, Arnold et al. have evaluated K_{ow} constants for chloride, perchlorate, bromide and nitrate complexes of TBT and TPhT [38]. From these results, we can calculate for each complex, the ratio of TBT to TPhT K_{ow} which is close to 3. For ethylated TBT and TPhT, the ratio of K_{ow} obtained from QSAR is around 2, which is in the same order of magnitude and supports QSAR estimations of octanol/water partition coefficients for mixed ethyl-, butyl- or phenyltins.

In the case of solubility, it decreases with increasing number of substituents within butyl and phenyl series. They are of the same order of magnitude between butyl- and phenyltins which is in agreement with reported experimental values [1].

To estimate saturated vapour pressures, Eq. (7) was modified for phenyltins, to account for their lower volatility compared to butyltins. Chromatographic retention times were converted to boiling temperatures in first approximation, T_b (°C), which were correlated with TSA within each organotin series, giving following relationships:

$$T_b = 1.1577 \times \mathrm{TSA} - 116.01, \quad \text{for ethylated phenyltins} \quad (8)$$

and

$$T_b = 0.4687 \times \mathrm{TSA} + 39.408, \quad \text{for ethylated butyltins} \quad (9)$$

For ethylated butyltins Eq. (7) was applied to calculate corresponding saturated vapour pressures, p. Combining Eqs. (7) and (9) gives for butyltin compounds:

$$\log p = -0.052 \times T_b + 8.0897 \quad (10)$$

Combining Eqs. (8) and (10), it comes for phenyltins series:

$$\log p = -0.0602 \times \mathrm{TSA} + 14.122 \quad (11)$$

As reported in Table 3, the trend in the saturated vapour pressures is the same for both butyl- and phenyltin series, accounting for the decreased volatility of ethylated organotins in going from mono- to tri-substituted compounds. It is more pronounced in phenyltin series compared to butyltins. Comparison with literature data is also quite difficult, vapour pressures have been reported for $(C_6H_5)_4Sn$ ($0.16–1.2 \times 10^{-13}$ atm) [1], $(C_2H_5)_4Sn$ (10^{-3} atm) [39] and $(C_4H_9)_3SnOAc$ (3.55×10^{-6} atm) [1]. Even though these values refer to compounds different from those under study, the trend and order of magnitude of estimated vapour pressures for mixed ethylated butyl- and phenyltins seem in good agreement. Moreover, using Eq. (11) established in this paper and Eq. (7) respectively, the calculated vapour pressures of $(C_6H_5)_4Sn$ and $(C_2H_5)_4Sn$ are 8.9×10^{-13} and 2.2×10^{-3} atm, values which are close to those reported in the literature [1] supporting the use of such QSARs.

4.3. Connection with experimental results

From calculated solubilities and saturated vapour pressures, Henry's constants were estimated (see Table 3). In butyltin series, H is in the same order of magnitude (H ($MBTEt_3$)/H (TBTEt) = 1.44) while it decreases by a factor 50 in the phenyltin series from mono- to tri-substituted tin. This indicates that in the case of butyltins, the three compounds should be similarly distributed between the aqueous and headspace phases when equilibrium is reached. Hence the amount of analyte sorbed onto the fibre should mainly depends on its coating to headspace partition coefficient, K_{fh}, which can be expressed as $K_{fh} = K_{ow}/H$ (see calculated values in Table 4). The evolution of K_{fh} in the butyltin series should then be more or less the same as the K_{ow} variation, indicating that sorption should increase from mono- to tributyltin. Calculated K_{fh} values for phenyltin series are all superior to butyltin's ones, that should be manifested in higher sorption of phenyl- compared to butyltins if no kinetic limitation occurs.

From estimates of the partition coefficients, the amount of each organotin absorbed at equilibrium by the fibre coating can be calculated based on Eq. (3). Values reported in Table 4 show that absorption should increase from mono- to tri-substituted organotin, and that phenyltin compounds should be better extracted than their corresponding butyltin

Table 4
Calculation of ethylated organotin amounts (mol) extracted by the fibre coating and comparison with experimental ratios obtained for homologous organotins within butyl and phenyl series (considering 60 min sampling)

Organotin	n_f[a]	% Extracted[b]	Ratio	From n_f	Experimental[c]
$MBTEt_3$	6.636×10^{-12}	7.9	$MBTEt_3$/$MPhTEt_3$	0.11	2.73 ± 0.86
$DBTEt_2$	4.516×10^{-11}	53.6			2.29 ± 0.30
TBTEt	7.917×10^{-11}	93.9	$DBTEt_2$/$DPhTEt_2$	0.55	2.22 ± 0.60
$MPhTEt_3$	5.912×10^{-11}	70.2			1.34 ± 0.16
$DPhTEt_2$	8.230×10^{-11}	97.7	TBTEt/TPhTEt	0.94	15.60 ± 3.56
TPhTEt	8.404×10^{-11}	99.8			4.56 ± 1.28

[a] Calculated from Eq. (3), $V_f = 6.12 \times 10^{-7}$ l, $V_s = 2.510^{-2}$ l, $V_h = 3.5 \times 10^{-2}$ l, $C_0 = 3.37 \times 10^{-9}$ mol l^{-1}, H and K_{ow} from Table 3.
[b] % extracted with respect to initial 8.42×10^{-11} mol.
[c] Mean ratios calculated from peak areas considering both agitations, first line for atmospheric pressure sampling and second one for reduced pressure sampling.

compounds. For the discussion and comparison with experimental results, it has not to be forgotten that these values refer to an estimation of the amount of analyte sorbed when: (1) individual sampling is performed, (2) equilibrium is reached. Moreover, the thermodynamic constants, H and K_{ow}, govern the equilibrium concentrations of the analyte between coating, sample and headspace phases, but the kinetic aspect of partition processes is not taken into account. Experimentally, sorption of DBT and TBT is upper than sorption of MBT whatever be extraction conditions. The results obtained when sampling at atmospheric pressure indicate that DBT is better extracted than TBT under both magnetic and mechanical stirrings with the exception of 5 min extraction time. The ratio of DBT to TBT sorbed onto the coating as predicted by Eq. (3) equals 0.57. Using experimental corresponding peak areas for each sampling time, we find a ratio DBT/TBT of 1.4 ± 0.1 which is constant under magnetic or mechanical stirring (with the exception of 5 min mechanical agitation sampling which gives a ratio of 0.8). This value is very close to the ratio of estimated Henry's constants, i.e. $H(\mathrm{DBTEt_2})/H(\mathrm{TBTEt}) = 1.2$, which could indicate that: (1) under atmospheric pressure, extraction of $\mathrm{DBTEt_2}$ and TBTEt is mainly limited by their distribution between aqueous and headspace phases and; (2) this distribution is similarly modified for ethylated DBT and TBT with the two types of agitation. These hypotheses are supported by experimental results obtained under reduced pressure sampling. In that case the ratio DBT/TBT = 1.17 ± 0.08, is coming closer to Henry's constants ratio of 1.2, that could be due to the progress of analytes partition to the headspace in reduced pressure conditions. When considering phenyltin series, Eq. (3) predicts a similar order of magnitude for extraction of di- and tri-phenyltins at equilibrium. Experimentally and under atmospheric pressure sampling, the TPhT signal never exceeds those of MPhT and DPhT whatever be the agitation. A upper signal of triphenyltin compared to monophenyltin is observed only when sampling under reduced pressure and extraction times longer than 30 min. These experimental observations are indicative of the slow kinetic of TPhT partition processes (i) to the headspace and (ii) to the coating.

To evaluate the effect of sampling under reduced or atmospheric pressure, on homologous butyl- and phenyltins, their peak areas ratios were calculated at 60 min sampling under both pressure conditions. For each sampling pressure condition, the values, reported in Table 4, represent the mean obtained with both agitations. Their comparison with theoretical equilibrium ratios, i.e. calculated from n_f values, shows that butyl/phenyl homologues ratios decrease when SPME sampling is realised under reduced pressure, drawing near to equilibrium expected ratios. This tendency is all the more pronounced as substitution degree is increasing. The kinetic model developed by Zhang and Pawliszyn [24] to study the diffusion process involved in HS SPME predicts longer equilibration times for analytes with the same K_{ow} and smaller H constant. For butyl/phenyl homologues, phenyl compounds should then take longer times to achieve equilibrium than butyl compounds. The evolution of butyl/phenyl homologues ratios, reported in Table 4, indicates that the amount of analyte extracted is increased when sampling under reduced pressure even if equilibrium is not reached. Therefore HS SPME under reduced pressure has potential for the analysis of semivolatile organotins compounds.

5. Conclusion

The use of an elliptical table and/or a reduced pressure can enhance the ability of weakly volatile organotin compounds to partition into the headspace, resulting in considerable improvement of HS-SPME procedure. For phenyltin compounds, detection limits are lowered so far as eight-fold, in half the time compared with classical sampling, i.e. magnetic stirring and atmospheric pressure. Sampling with mechanical stirring alone results in decreasing detection limits up to a factor 2.5 compared to magnetical agitation, with still shorter extraction time (20 instead of 30 min). Considering the series of butyltin compounds, the HS-SPME improvement arising from these alternative sampling conditions, is mainly based on a saving of time holding satisfactory detection limits of classical sampling. As it has been already discussed by several authors, organotin signals (mainly butyltins) originating from $\mathrm{NaBEt_4}$ reagent are actually the main limiting factor of the procedure. Work is actually in progress in our lab to improve the quality of commercial reagents.

Finally, HS SPME under mechanical agitation and reduced pressure implies some technical modifications compared to traditional sampling but represents a valuable approach for the simultaneous determination of butyl- and phenyltins, including higher sensitivities and shorter extraction time.

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