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Optimization of solid-phase microextraction for the speciation of butyl- and phenyltins using experimental designs[1]

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Abstract

This paper deals with the optimization of solid-phase microextraction (SPME) for organotin speciation in water. The analytical method consists of an in situ ethylation, simultaneous solid-phase microextraction of the derivatives, followed by a gas chromatographic analysis with flame photometric detection. Experimental design methodology was used to evaluate the influence of six analytical parameters on the mean peak area (S_{mean}). The adsorption of the compounds on the SPME fibre was found to be the most important parameter and two other factors are positively significant: the adsorption time and the sample volume. The adsorption profiles and the optimal operating conditions were determined from the modelling of S_{mean}. The detection limits range from 2 to 4 ng l^{-1} (monophenyltin excepted: 18 ng l^{-1}) and linearity is from 50 to 600 ng l^{-1}. The relative standard deviations are 7–10% for five determinations. Water samples were analysed in order to verify the accuracy of the optimized method by comparing results with those obtained using a conventional solvent extraction of the ethylated organotins.

Keywords: Experimental design; Extraction methods; Organotin compounds

1. Introduction

The use of organotin products — especially trisubstituted compounds — has increased significantly in the last few decades. The ecotoxicological impacts of tributyltin (TBT) and triphenyltin (TPhT) have been demonstrated [1,2]. Contamination of marine and freshwater environments by these highly toxic species is primarily due to their use in antifouling paints [3]. Nevertheless, significant concentrations of these compounds and their metabolites have been detected in all aquatic media: waters [4], suspended matters [5], sediments [6] and biomass [7]. Recently, sewage sludge has also been recognized as contaminated [8,9].

The high toxicity of organotins at low concentration levels has stimulated the development of accurate and sensitive analytical methods for their determination. Recently, a new organotin determination procedure involving gas chromatography–flame photometric detection (GC–FPD) analysis has been proposed [10]. Before GC injection, a sodium

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tetraethylborate derivatization was performed in order to permit the analysis of the less volatile compounds such as phenyltins. The ethylated species are simultaneously extracted in a small volume of isooctane. For water analysis, the derivatization is directly applied to the sample and for solid matrices, an acidic extraction is previously carried out. Therefore, this method allows simultaneous determination of butyl- and phenyltins in all parts of the aquatic environment [10–12], and it has been applied to the analysis of various samples [13]. Considering all these points, this procedure seems to be suitable for routine analysis. However, the process remains long, because, depending on the sample matrix, the solvent decantation may require up to 8 h. Moreover, the automation of liquid–liquid extraction is not easy to achieve. So, an alternative method was envisaged to reduce the extraction time and to make it possible to automate the protocol.

Solid-phase microextraction (SPME) was chosen. The advantages of this solvent-free technique are numerous: simplicity, low cost, easy automation and reduction of analyte loss during extraction [14]. In this technique, analytes establish an equilibrium between the sample matrix and the stationary phase coated on a fused-silica fibre. Different natures of fibre are now available and analyte adsorption depends essentially on its affinity with the stationary phase and on the thickness of the coating material. After adsorption equilibrium, the fibre is thermally desorbed in the injection port of the GC system which transfers the analytes into the capillary column [15]. To date, SPME has been mainly used for the analysis of organic compounds, e.g. pesticides, phenols and volatile compounds [16–21]. But a few studies concern its application to organometallic species [22–24].

In this paper, the suitability of SPME for both butyl- and phenyltin speciation in water was examined. SPME optimization was first performed by using experimental design methodology. This statistical method allowed the systematic examination of the influence of different parameters and the control of the analytical procedure with the maximum of accuracy. The optimized method was then applied to the analysis of several environmental water samples. The results obtained were compared with spiked values and with conventional isooctane extraction.

2. Experimental

All organotin concentrations reported in this paper are expressed as the mass of tin (Sn) per mass or volume unit.

2.1. Apparatus

The manual SPME device used was obtained from Supelco (Supelco, Bellefonte, PA, USA). Fibres coated with stationary phases of different natures and various film thickness were used: polydimethylsiloxane (PDMS) 100 μm, polydimethylsiloxane–divinylbenzene (PDMS–DVB) 65 μm, Carbowax–divinylbenzene (CW–DVB) 65 μm and polyacrylate 85 μm (Supelco).

A Varian 3300 gas chromatograph (Varian, Palo Alto, CA, USA) equipped with a flame photometric detector and a 610 nm optical filter (from MTO Optique Instrumentale, Massy, France) was used for this study.

Analytical parameters were optimized and precisely described elsewhere [10]. The separation was carried out on a capillary column (30 m×0.25 mm I.D.) coated with methylsilicone (0.25 μm film thickness) (Quadrex, New Haven, USA). The column temperature was held at 70°C for the first minute, increased to 190°C at the rate of 30°C min^{-1} and then to 270°C at 15°C min^{-1}. The final temperature was held for 6 min. Nitrogen was used as the carrier gas at a flow-rate of 0.7 ml min^{-1}.

The detector was operated at 290°C with an air–hydrogen flame. The flow-rates were respectively 245 and 185 ml min^{-1}.

A split/splitless injector was employed using the splitless mode.

2.2. Reagents

Tripropyltin chloride (TPT, 98%), 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 (Aldrich, Milwaukee, WI, USA). The organotin stock solutions containing 1000 mg l^{-1} as tin were prepared in methanol. When stored in the dark at +4°C, stock solutions were stable for at least one year [25]. They

were diluted weekly to 10 mg l^{-1} in water and stored in the dark at +4°C; 100 μg l^{-1} working solutions were daily prepared in water.

Methanol and sodium ethanoate were purchased from Prolabo (Fontenay sous Bois, France). Hydrochloric, nitric and ethanoic acids were obtained from Merck (Darmstadt, Germany), and isooctane from Fluka (Buchs, Germany). The deionized water used was 18 MΩ (Milli-Q filtration system) (Millipore, Bedford, MA, USA). Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals (Strem Chemicals, Newburgport, MA, USA): a working solution was made daily by dissolving 0.02 g in 1 ml of deionized water and storing in the dark at +4°C.

Glassware was rinsed with deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again.

2.3. Samples

Organotins levels were measured for samples from the Rhine, Sarre and Meuse Rivers (France). They were analyzed without any pretreatment. As soon as the samples arrived at the laboratory, they were centrifuged, acidified to pH 2 with nitric acid and stored in the dark at 4°C. Analyses were performed within five days.

2.4. Analytical procedure

2.4.1. Derivatization and analysis

A 100-ml aliquot of water sample was directly introduced into the derivatization reactor. Ethylation was carried out using $NaBEt_4$ (0.1 ml) in sodium ethanoate–ethanoic acid buffer (100 ml, pH=4.8).

For the classical ethylation/extraction, 0.3 ml of isooctane was added and the mixture was shaken at 420 rpm for 30 min. Afterwards, 2 to 3 μl of isooctane extracts were directly injected into the GC–FPD system.

For ethylation and SPME, the fibre was directly immersed into the aqueous medium, with rapid stirring. Adsorption time, sample volume and desorption parameters will be studied during the optimization of the method (see Section 3.1).

2.4.2. Quantitation

Tripropyltin was used as internal standard. The tripropyltin-relative chromatographic responses of butyl- and phenyltin compounds were calculated from standard solutions prepared in deionized water.

The internal standard procedure was then applied on three to five aliquots of 100-ml water sample.

3. Results and discussion

3.1. Factor screening

The influence of different factors and their interactions on the SPME procedure was checked by using experimental designs. According to the literature [17,23], the following parameters were preliminary considered in order to define the experimental field.

3.1.1. Nature of the fibre

Among the fibres commercially available, some of them are proposed with various film thicknesses such as PDMS (7, 30 and 100 μm) and PDMS–DVB (60 and 65 μm). Tutschku et al. previously showed that organotin adsorption increased with film thickness [23]. Therefore, we chose, when possible, to use only the thicker films: four fibres were thus tested (see Section 2.1). A preliminary study indicated that butyltins are better retained on apolar coatings such as PDMS and PDMS–DVB. Good adsorption was also observed on the moderately polar CW–DVB phase. Considering phenyltins, they are satisfactory adsorbed on the apolar PDMS fibre, but good results were also obtained with the CW–DVB phase, possibly owing to π–π interactions between the aromatic cycle of the analytes and the divinylbenzene polymer. On the contrary, poor sensitivity was obtained using the polar polyacrylate phase.

Hence, the PDMS and CW–DVB fibres gave the greatest peak areas for butyl- and phenyltins. Therefore, these two fibres were retained for the experimental design.

3.1.2. Stirring mode

Conventional magnetic stirring was used. Other experiments were performed with mechanical stirring, but the motion of the solution did not allow the fibre to stay continuously immersed in the aqueous sample. Consequently, magnetic stirring was retained and adjusted to the maximum rate to accelerate adsorption.

3.1.3. Sample volume

In theory, the sample volume has no significant influence on adsorption when the analyte concentration is kept constant. This parameter seemed however to be important according to the stirring rate of the solution which depends on the sample volume and on the geometry of the reactor. The sample volume was tested between 10 and 200 ml in a preliminary study.

According to the results obtained, this parameter appears to be especially influential below 100 ml. Therefore, the sample volume was studied between 20 and 100 ml in the experimental design.

3.1.4. Adsorption time

This parameter is well-known to be essential in SPME. Tutschku et al previously found that the optimal extraction time of tetrabutyltin was between 30 and 45 min [23]. However, we did not know if the adsorption equilibrium is reached for the other organotins. Consequently, this parameter was studied between 15 and 60 min.

3.1.5. Injection temperature

This parameter is particularly important when the analytes are poorly volatile [16]. Previous studies have demonstrated that below 250°C, the volatilization of phenyltins was not satisfactory [31]. So, the temperature of the injection port of the GC system was maintained at 250°C or at the maximum temperature allowed for each nature of fibre (see Table 1).

3.1.6. Desorption time

The thermal desorption of the compounds in the injection port is recognized to be instantaneous [18]. The duration of the splitless injection did not therefore need to be very long. However, the fibre is generally held for several minutes in the injection port in order to avoid memory effects. For the experimental design, injection times of between 1–2 min were considered.

3.1.7. Temperature of the laboratory

The temperature was found to have a significant negative effect on the compound adsorption [23]. So, it seems to be better to work at low temperature. However, the procedure would be easier to perform at the temperature of the laboratory (i.e. ambient temperature). So, the influence of the temperature on the analyte adsorption was checked in a range that is commonly reached in laboratories: 20–30°C.

A two-level factorial design was applied to check the influence of the factors by using the methodology described by Sado and Goupy [26,27]. It consisted of testing the combination of the levels of the different factors and their interactions with the minimum of experimentation. Two levels, expressed as coded values (+1) and (−1), were considered for each of the six studied factors (Table 1). Under these conditions, a complete factorial design would lead to 64 (2^6) experiments. According to our analytical experience and in order to reduce the number of experiments, a fractional design 2^{6-2}, leading to 16 experiments, was used [28–30]. Interactions up to second-order were considered as insignificant. The following factors were therefore connected to third-order interactions: desorption time (X_5) with the interaction adsorption time-sample volume-injection temperature ($X_2X_3X_4$), and the temperature of the

Table 1
Screening of factors: experimental field studied

Factors	Level		
	(−1)	(0)	(+1)
Nature of the fibre (X_1)	CW–DVB	–	PDMS
Adsorption time (min) (X_2)	15	37.5	60
Sample volume (ml) (X_3)	20	60	100
Injection temperature (°C) (X_4)	250	265[a]	280[a]
		257[b]	265[b]
Desorption time (min) (X_5)	1	1.5	2
Temperature of the laboratory (°C) (X_6)	20	25	30

According to the nature of the fibre: [a] PDMS, [b] CW–DVB.

laboratory (X_6), with nature of the fibre-adsorption time-injection temperature ($X_1X_3X_4$). Two experiments, noted (0−1) and (0+1) were performed respectively with the CW–DVB fibre and with the PDMS fibre at the centre of the experimental field. They were duplicated in order to determine the standard deviation. The precision of each result was then evaluated from the standard deviation by matrical calculation according to the Student *t*-test (95%).

In order to obtain the best sensitivity for all the organotins studied, the first response considered was the average area of the chromatographic peaks, noted S_{mean}. Three compounds, tripropyltin, monophenyltin and tributyltin, lead to a less sensitive response than the others. Therefore, a second response defined as the average peak area of these three compounds was taken into account: it was noted S_1. The consideration of this response gave the priority to these less sensitive compounds.

The effect of a factor i is represented by the coefficient b_i, calculated by linear combination (Eq. (1)). The interaction between the two factors i and j is expressed as the coefficient b_{ij} (Eq. (2)). It should be considered when the effect of the first factor depends on the level of the second factor.

$$b_i = \frac{1}{n}\sum_k L_k y_k \quad (1)$$

where n is the number of experiments, L_k the level of the factor i in the kth experiment (here, −1 or +1), and y_k the response (S_{mean} or S_1) corresponding to the kth experiment.

$$b_{ij} = \frac{1}{n}\sum_k L_{ik}L_{jk}y_k \quad (2)$$

To represent the response (y), a polynomial equation can be proposed:

$$y = b_0 + \sum_i b_i X_i + \sum_{ij} b_{ij}X_iX_j + \cdots \quad (3)$$

where b_0 is the average effect, X_i the coded variable which corresponds to the factor i, and b_i the effect of the factor i on the response y.

The influence of a factor or interaction is considered as significant if the corresponding effect is higher than the precision. The effect of the factors and their interactions are described in Table 2.

Only three factors and their interactions appeared significant: nature of the fibre (X_1), adsorption time (X_2), and sample volume (X_3). The temperature of the laboratory (X_6) seemed to have a slight positive influence on the mean peak area S_{mean}.

The nature of the fibre was the most influential factor and its effects were opposed according to the considered response (S_{mean} or S_1): the CW–DVB fibre gave the highest peak areas for all of the organotins although the PDMS fibre allowed the maximum areas for tripropyltin, monophenyltin and tributyltin. Moreover, when CW–DVB fibre was used, often no peak was observed for these last compounds. Consequently, it appeared essential to consider only the response S_1 for the choice of the fibre.

The sample volume appeared less significant. This is in good agreement with the theory. In our case, the

Table 2
Screening of factors: effect of the studied factors and of the most significant second-order interactions.

Factor/Interaction	Effect on S_{mean}	Effect on S_1
Average	+4.83±0.06	+1.41±0.06
Nature of the fibre (X_1)	−0.99±0.06	+0.41±0.06
Adsorption time (X_2)	0.57±0.06	+0.23±0.06
Sample volume (X_3)	−0.47±0.06	0.01±0.06
Injection temperature (X_4)	+0.06±0.06	+0.03±0.06
Desorption time (X_5)	+0.02±0.06	−0.01±0.06
Temperature of the laboratory (X_6)	+0.09±0.06	+0.02±0.06
Nature of the fibre–Adsorption time (X_1X_2)	+0.43±0.06	+0.14±0.06
Nature of the fibre–Sample volume (X_1X_3)	+0.57±0.06	−0.04±0.06
Adsorption time–Temperature of the laboratory (X_2X_6)	+0.19±0.06	+0.04±0.06
Adsorption time–Sample volume (X_2X_3)	+0.16±0.06	+0.16±0.06

The interactions X_1X_4, X_3X_6, X_2X_4, X_3X_5, X_2X_5, X_1X_6 and X_3X_4 are found to be insignificant (i.e. $b_{ij}<0.06$).

slight influence of this factor is probably due to the geometry of the reactor and consequently also to the stirring efficiency.

3.2. Optimization

Mathematical models were established to allow the adjustment of the operating conditions: first-order polynomials (see Eq. (3)) including the three significant factors were first proposed for each studied response (S_{mean} and S_1). Nevertheless, they could not be validated at the centre of the experimental field. Moreover, these linear models cannot describe the adsorption equilibrium and consequently they did not satisfactorily fit the adsorption profile. In order to have the possibility to postulate a more appropriate second-order model, a composite design was planned. Due to the previous results, only the most efficient PDMS fibre was used. The two most significant factors adsorption time (X_2) and sample volume (X_3) were studied. The other parameters were adjusted as follows: injection temperature (X_4): 250°C, desorption time (X_5): 1 min, and temperature of the laboratory (X_6): 30°C.

In order to define the experimental matrix of the optimization design, some complementary experiments were added to the previous factorial design. In Fig. 1, the square area represents the factorial matrix which was taken from the previous experimental design. The four other points correspond to the added experiments performed in star configuration, with levels ±1.41 allowing the best precision [27]. The experiment at the centre of the experimental field (noted 0) was performed four times.

The effects of each factor and their interactions on the mean peak areas (S_{mean} and S_1) are presented in Table 3.

From these results, mathematical models established on second-order polynomials were proposed; each response could be hence represented by Eqs. (4) and (5)

$$S_{mean} = 3.87 + 1.00(X_2) + 0.21(X_3) - 0.72(X_2)^2 - 0.71(X_3)^2 + 1.05(X_2X_3)^2 \quad (4)$$

$$S_1 = 1.94 + 0.37(X_2) - 0.28(X_2)^2 - 0.28(X_3)^2 + 0.44(X_2X_3)^2 \quad (5)$$

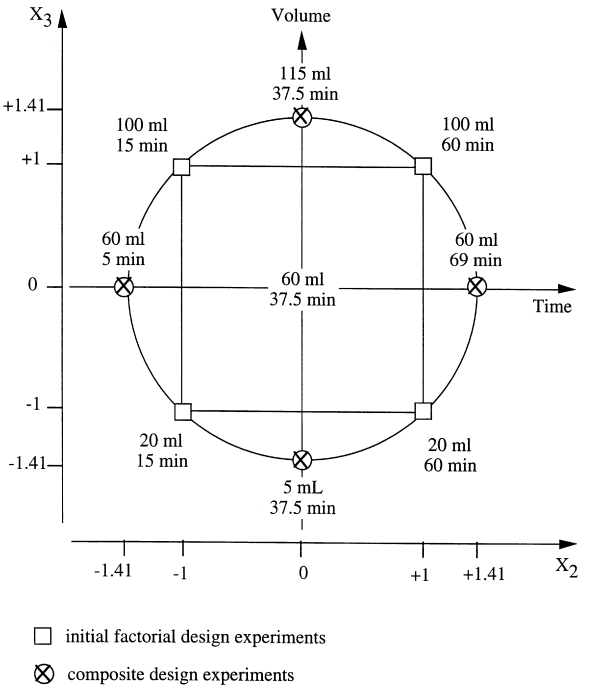

Fig. 1. Optimization: experimental field corresponding to the composite design.

where X_2 corresponds to the adsorption time, X_3 to the sample volume and X_2X_3 to their interaction.

The difference between experimental and calculated results always appears 2.5 times lower than standard deviation. So, this comparison allowed the validation of the two second-order models. Moreover, the analysis of the variance performed at 95% showed that these models were very significant, without distortion, and the correlation coefficients (R^2) between experimental and calculated data were 0.999 for both relations.

The iso-response curves were then plotted and are presented in Figs. 2 and 3. We can see that the two responses S_{mean} and S_1 have similar profiles. It is also confirmed that the adsorption time (X_2) is very significant, whereas the sample volume (X_3) appears little influential, especially in the range 40–100 ml where the reactor geometries are similar. The adsorption is however significantly lower when a small volume (6 ml) is used. It could be supposed that the stirring is less efficient in this case than when larger volumes are involved. It can also be pointed out that this assumption is only valid in the field of this study

Table 3
Optimization: effects of the factors and interactions

Factor/Interaction	Effect on S_{mean}	Effect on S_1
Average	+1.95±0.25	+3.87±0.44
Adsorption time (X_2)	+0.37±0.09	+1.00±0.16
Sample volume (X_3)	+0.03±0.09	+0.21±0.16
Adsorption time–Sample volume (X_2X_3)	−0.11±0.12	+0.07±0.22
$(X_2)^2$	−0.28±0.15	−0.72±0.27
$(X_3)^2$	−0.28±0.15	−0.71±0.27
$(X_2X_3)^2$	+0.44±0.18	+1.05±0.31

which concerns manual SPME with magnetic stirring. It cannot be therefore easily transposed to the automated SPME device, where smaller volumes are used and where the stirring is performed by fibre vibration.

Whatever the volume (in the range 20–100 ml), it is therefore possible to plot a single kinetic adsorption curve (Fig. 4). This curve shows that the equilibrium is reached after approximately 60 min when all the organotins studied are considered. This equilibrium time is longer than the 30 min reported by Tutschku for butyltins [23]. This is due to the adsorption equilibrium of phenyltins which is reached more slowly (around 60 min) (Fig. 5). According to this study, it can be assumed that the adsorption equilibrium of butyltins is reached after 20 min (Fig. 5).

Therefore, the final operating conditions can be defined: they correspond to an extraction of a 100 ml water sample with a 100 μm PDMS fibre over 60 min.

3.3. Analytical performances

The performances were determined, according to

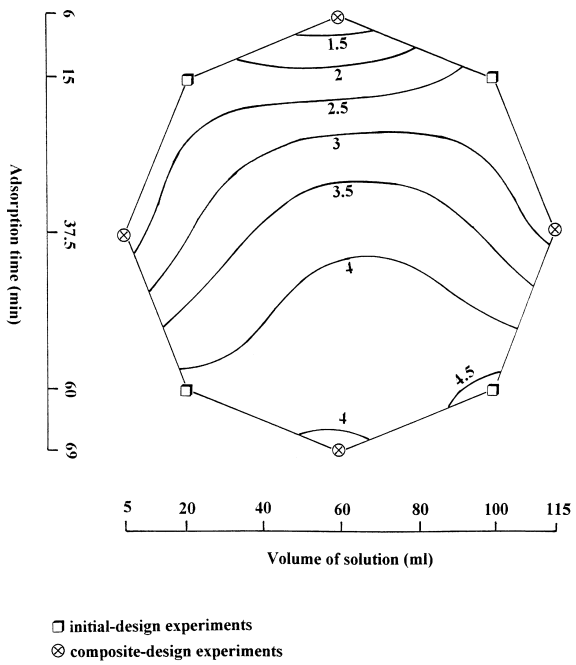

Fig. 2. Iso-response curves for mean peak area of butyl- and phenyltins (S_{mean}).

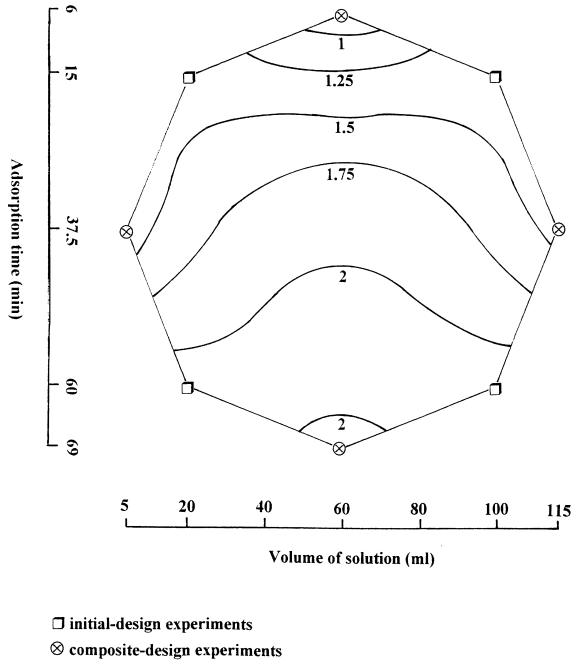

Fig. 3. Iso-response curves for mean peak area of tripropyl-, monophenyl- and tributyltin compounds (S_1).

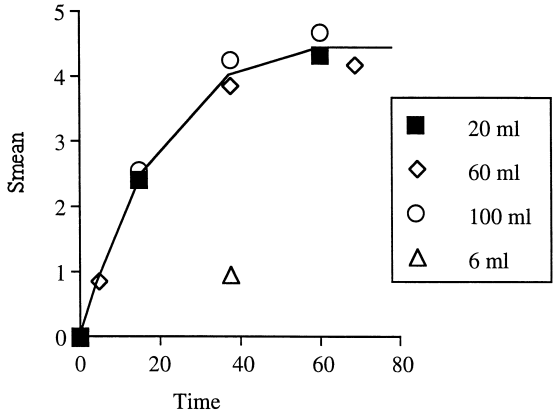

Fig. 4. Adsorption kinetics: variation of the mean peak area of butyl- and phenyltins (S_{mean}) as a function of time for different sample volumes.

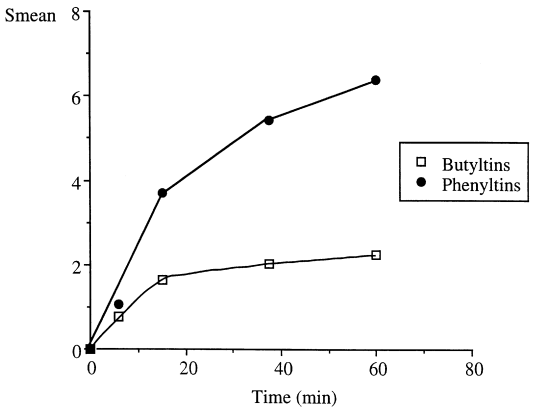

Fig. 5. Adsorption profiles for butyl- and phenyltins.

the operating conditions described above, by using standard solutions and tripropyltin as an internal standard.

The detection limits (DL) (according to the IUPAC

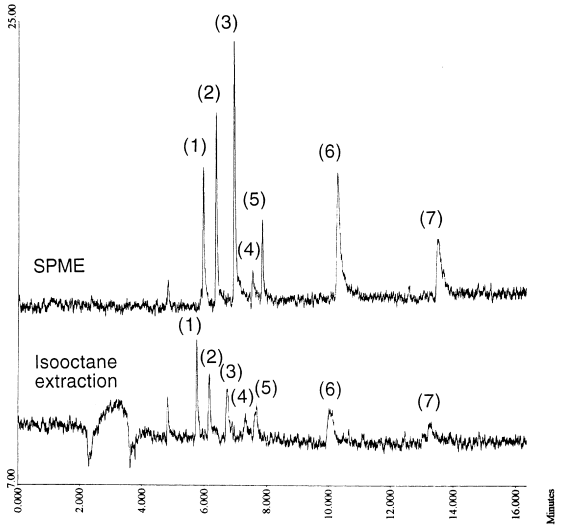

Fig. 6. Chromatograms corresponding to the ethylation–SPME–GC–FPD and to the ethylation–isooctane extraction–GC–FPD analysis of a spiked synthetic water (100 ng l^{-1} of each compound). (1) MBT, (2) TPT, (3) MPhT, (4) DBT, (5) TBT, (6) DPhT, (7) TPhT.

specifications, 3σ) and the repeatability (relative standard deviation, RSD) are presented in Table 4. The relative standard deviations were evaluated from 100–250 ng l^{-1} standard solutions. The relative peak areas were found to be linear in the concentration range 50–600 ng l^{-1}.

It can be noted that the detection limits are approximately two times lower with SPME than with isooctane (Table 4). SPME leads therefore to a better sensitivity than the solvent extraction, with the exception of monophenyltin. This can be also easily observed on the chromatograms presented in Fig. 6. The average detection limit obtained with SPME (5 ng l^{-1}) is in good agreement with the concentration

Table 4
Analytical performances of the ethylation-SPME–GC–FPD

		MBT	DBT	TBT	MPhT	DPhT	TPhT	Mean
SPME	Detection limit (ng l^{-1})	2	2	4	1	2	3	5.2
	Repeatability (%) ($n=5$)	11	8	11	7	8	9	9
Isooctane	Detection limit (ng l^{-1})	8	5	4	21	7	11	9.3
	Repeatability (%) ($n=5$)	6	11	11	7	8	9	8.5

levels that should be determined in environmental waters. The repeatability appears also to be satisfactory for quantitative analysis (Table 4).

3.4. Application to organotin determination in spiked water and environmental samples

In order to check the accuracy of the procedure, SPME was applied to the analysis of a synthetic water spiked with known levels of organotins. The results obtained are presented in Table 5. A good correspondence was achieved between the spiked values and the SPME results for all the compounds. The application of SPME for the quantitative analysis of organotins was verified with the analysis of three different natural river waters. The concentrations obtained were compared with those determined by using the conventional isooctane extraction. The results are reported in Table 5.

For each sample, the same organotins were identified by both methods, with comparable concentrations and precision, despite the low pollution level. Nevertheless, SPME appears more powerful than isootane extraction because, in several cases, some compounds were quantified after SPME whereas they are only qualitatively detected after the conventional extraction. This is the case for mono- and diphenyltins determined in the Sarre river water. This phenomenon may be explained by matrix effects which seem to increase the detection limits in real waters when the isooctane extraction is used. On the contrary, matrix effects seem to have a poor influence on the sensitivity obtained after SPME, in the case of the samples studied.

However, first results obtained from the analysis of sewage sludge indicated that the response after SPME was drastically affected by this more complex matrix. Therefore, depending on the sample matrix, the quantitation of organotins should be carefully studied, whatever the extraction technique used.

4. Conclusion

After optimization of the operating conditions by using experimental designs, the first applications of SPME to the analysis of environmental water samples demonstrated the suitability of this new extraction method in the determination of organotin compounds. Therefore, it could be considered as an interesting alternative to isooctane extraction. Thus, low detections limits (ng l^{-1} level) were obtained. The method is also very rapid compared to solvent extraction: for example, the analysis of a water sample can be performed within 1 h. SPME is also easy to use and can be automated by using the commercially available sampler. This latter could allow a more reproducible procedure and routine speciation of butyl- and phenyltins. In this field, the application of SPME to various samples such as sediment, biota or sewage sludge is now in progress

Table 5
Determination of organotin compounds in water samples

Sample	Analytical method	Concentrations in ng l^{-1} ($\pm\sigma$)					
		MBT	DBT	TBT	MPhT	DPhT	TPhT
Synthetic water	[a]		130±11	130±14	260±20	240±22	240±21
	Spiked values		150±20	150±20	250±20	250±20	250±20
Rhine river water	[a]	19±4	14±2	nd	nd	nd	nd
	[b]	19±1	<10[c]	nd	nd	nd	nd
Sarre river water	[a]	8±1	nd	nd	20±3	15±0	nd
	[b]	15±1	nd	nd	<15[c]	<15[c]	nd
Meuse river water	[a]	10±5	12±2	nd	nd	4±1	10±0
	[b]	14±3	<10[c]	nd	nd	<15[c]	11±3

[a] Ethylation–SPME–GC–FPD.
[b] Ethylation–isooctane extraction–GC–FPD.
[c] Quantitation limit.
nd, not detected.

in order to extend the application range of the method.

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