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Rapid determination of organotin compounds by headspace solid-phase microextraction

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Abstract

Headspace solid-phase microextraction (SPME) followed by gas chromatography (GC) coupled to pulsed flame photometric detection have been investigated for the simultaneous speciation analysis of 14 organotin compounds, including methyl-, butyl-, phenyl-, and octyltins compounds. The analytical process (sorption on SPME fibre and thermal desorption in GC injection port) has been optimised using experimental designs. Six operating factors were considered in order to evaluate their influence on the performances of a SPME-based procedure. The evaluation of accuracy, precision and limits of detection (LODs) according to ISO standards and IUPAC recommendations has allowed the method to be validated. The LODs obtained for the 14 studied organotins compounds are widely sub-ng(Sn) l^{-1}. The precision evaluated using relative standard deviation ranges between 9 and 25% from five determinations of the analytes at 0.25–125 ng(Sn) l^{-1} concentrations. The accuracy was studied throughout the analysis of spiked environmental samples. These first results show that headspace SPME appears really as attractive for organotins determination in the environment and the monitoring of their biogeochemical cycle.

Keywords: Experimental design; Organotin compounds

1. Introduction

In the 1980s, the organotin compounds were recognised for the first time as being responsible of very serious environmental contamination, and the European Union has listed them as priority pollutants. Organotin compounds are used in a lot of industrial and agricultural applications, including poly(vinyl chloride) (PVC) stabilisers, homogeneous catalysts and biocide formulations. So, their presence in the environment is due to anthropogenic uses mainly, except for the methyltins. Indeed, despite these last species being used as stabilisers or biocides and so can be released in the environment, chemical or biological processes can occur naturally as well [1,2].

The toxic effects of organotins are widely dependent on the number and nature of alkylated or arylated groups bonded to the tin atom. Recently they have been considered as possible endocrine disrupters [3]. Negative effects on environment can occur since sub ng(Sn) l^{-1} concentrations [3,4]. In these conditions, the development of analytical methods able to speciate and detect these compounds at low concentration levels in the different parts of the environment appears essential. Most of these methods combine a separation technique such as gas chromatography (GC) with element-selective detection like atomic absorption spectrometry (AAS),

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atomic emission spectrometry (AES), mass spectrometry (MS), flame photometric detection (FPD), pulsed flame photometric detection (PFPD) or inductively coupled plasma mass spectrometry (ICP-MS) [5–11]. However, before chromatographic injection, a derivatisation step has to be made in order to convert the analytes into stable forms, with preservation of their original speciation. Simultaneously, an extraction from the aqueous medium (i.e., water sample or aqueous acidic extract from solid samples) is performed. Liquid–liquid extraction (LLE) is typically used for the determination of butyl-, phenyl- and octyltin compounds [11–13]. But this process does not appear suitable to determine the most volatile methylated species, which are usually reached by methods based on purge and trap [14,15].

Recently, solid-phase microextraction (SPME) has been proposed as a promising alternative to LLE, due to its simplicity of use, high preconcentration power and the capability to analyse volatile methylated species as well as phenyltins. The determination of these last species have been used SPME in direct mode mainly (i.e., fibre placed directly into the aqueous sample) [16–18]. Despite the attractive sensitivity obtained using direct SPME, dramatic matrix effects can occur when complex samples such as biological materials are analysed [18]. Moreover the simultaneous determination of a wide range of organotins appears difficult to perform by direct mode.

The use of headspace SPME has been reported for the study of methyltins in water [19], butyltins in water, sediments or body fluids [10,20–24], triphenyltin (TPhT) in biological and vegetal samples [25]. In headspace, the extraction time is faster than in direct mode (15–30 and 40–60 min, respectively). In the literature, the 100-μm thickness polydimethylsiloxane (PDMS) coated fibre is the most employed because of its high repeatability inter- and intra-fibre. This is probably because the PDMS is constituted by a coated liquid polymeric phase and therefore extraction is mainly based on physical absorption. Coating volume also influences the method sensitivity [26]. Other commercial fibres with specific coatings are available as well. For example, using porous coated ones, an adsorption phenomenon is involved, which appears more convenient for the extraction of volatile forms. The use of thicker coatings results in longer extraction times because diffusion of the analytes is slow within the polymer extraction phase [27].

Considering all these data, headspace SPME–GC–PFPD has been investigated for the speciation of 14 organotins, including methyltins, butyltins, phenyltins, and octyltins, with the aim to decrease matrix effects and time to sorption. This work is a real challenge due at once to the number of organotins determined simultaneously and the various boiling points (b.p.) of these compounds. This paper presents the optimisation of the analytical process using experimental designs, after preliminary studies evaluating the capabilities of two different fibres. The analytical method has been validated by the simultaneous determination of organotins with very varying volatilities in environmental samples.

2. Experimental

2.1. Apparatus

A Varian 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a PFPD system with a 1079 split/splitless injector was used. The separation was carried out on capillary columns (30 m×0.25 mm I.D.) coated with methyl silicone (0.25-μm film thickness) (Quadrex, New Haven, CT, USA). Nitrogen was used as carrier gas. The oven temperature was initially held at 50 °C for 30 s, and then programmed at 10 °C/min to 200 °C and at 30 °C/min to a final temperature of 270 °C which was held for 30 s. The conditions of the detection have been described elsewhere [11].

The manual SPME device was obtained from Supelco (Bellefonte, PA, USA). According to the literature, two fibres have been investigated: the 100-μm thickness PDMS-coated fibre and the 75-μm thickness Carboxen–PDMS (CAR–PDMS) fibre.

An elliptic stirring table KS 2502 basic (Prolabo, Fontenay Sous Bois, France) was used for derivatisation/extraction. An ultrasonic cleaner bath (Branson 2510) from Bioblock (Illkirch, France) was used for the extraction of organotins from biological material.

2.2. Reagents

All the reagents were of analytical grade and purchased from Merck Eurolab (Gradignan, France). Deionised water at 18 MΩ further purified with a Milli-Q system (Millipore) was used throughout the study. Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals (Strasbourg, France). Aqueous ethylating solution (1%, m/v) was prepared daily.

Glassware was rinsed with Milli-Q water, decontaminated overnight in 10% (v/v) nitric acid solution and rinsed again [16].

Individual organotin stock standard solutions [1000 mg(Sn) l^{-1} as tin] of monomethyltin trichloride (MMT, 97%), dimethyltin dichloride (DMT, 97%), trimethyltin chloride (TMT, 100%), tetramethyltin (TeMT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), tetrabutyltin (TeBT, 93%), and trioctyltin chloride (TOcT, 95%) (Sigma–Aldrich, St. Quentin Fallavier, France), tripropyltin chloride (TPrT, 98%), monobutyltin trichloride (MBT, 95%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), triphenyltin chloride (TPhT, 95%) (Strem Chemicals), monooctyltin trichloride (MOcT, 97%), dioctyltin dichloride (DOcT, 97%) (Lancaster, Strasbourg, France), were prepared in methanol. Stored at +4 °C in the dark, these solutions are stable for 1 year [28]. Methyltin solutions are stored in the dark at −20 °C.

Working standards were obtained by a set of weekly and daily dilutions in water. The water was Milli-Q quality (18 MΩ).

2.3. Analytical procedures

2.3.1. Extraction from biological samples

The optimisation of the extraction procedure for biological samples has been described precisely and validated elsewhere [12,29]. Briefly, amounts of 1–2 g of sample were precisely weighed and introduced into a capped 50-ml polycarbonate tube with 30 μl of a 100-μg(Sn) l^{-1} TPrT solution used as internal standard and 2.5 ml of methanol. The tube was shaken at 450 rpm for 1 h. After addition of 12.5 ml of a solution of 0.1 *M* hydrochloric acid in methanol, the mixture was sonicated for 1 h and the supernatant was taken after centrifugation.

2.3.2. Derivatisation and analysis

The derivatisation step involves the ethylation of organotin in order to obtain thermally stable tetrasubstituted species sufficiently volatile for GC separation. This step has been previously optimised and validated [11,12,29]. The derivatisation has also to be made since in case of SPME, only the ethylated species can be extracted satisfactory on the fibre.

In order to understand the behaviour of the ethylated species during headspace SPME and GC analysis, the boiling points were evaluated. For that, the corresponding retention times were measured at constant oven temperature of 100 °C for the methyl- and butyltins and 180 °C for the others. The b.p. (°C) at atmospheric pressure were calculated using the formula [30]:

$$t_R(\text{min}) = A \exp(B \text{ b.p.})$$

where $A = 0.2584$, 0.8439 and $B = 0.0210$, 0.0046 at 100 and 180 °C, respectively.

The different boiling points are reported in Table 1 (second line) and compared to those of the chloride standards (first line).

The experimental designs were made from an aqueous solution containing the 14 analytes and the internal standard over the range 0.25–125 ng(Sn) l^{-1}.

The method has been validated by analysis of

Table 1
Boiling points of the organotins (°C) at 760 mmHg pressure (1 mmHg = 133.322 Pa)

Compounds	MMT	DMT	TMT	TeMT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT	MOcT	DOcT	TOcT
In chloride form[a]	171	188	154		230	286	300–302		264–265	333–337	404	305–314	Not found	Not found
				78				285						
Ethylated	106	93	84		160	201	244		221	317	400–450	265	300–360	420–470

The precision of the determined b.p. is ±5 °C except for TPhT, DOcT and TOcT.
[a] The b.p. of the organotins were calculated at atmospheric pressure from Ref. [40].

waters and a spiked fish sample (trout Fario). In water, organotins were determinate using an 80-ml aliquot of sample, buffered to pH 4.8 with acetic acid–acetate. For the biological material, 0.5 ml of the extract was directly introduced into the derivatisation vessel containing 80 ml of buffer. In all the cases, after addition of 100 μl of the ethylating solution, the mixture was stirred on an elliptic table. This is because before headspace SPME, the analyte distribution between the both gas and liquid phases has to be in equilibrium state. So, an equilibration time has to be planned in the process. Some preliminary studies have shown such a procedure increases the SPME repeatability widely. After that, the fibre was placed in the headspace volume and the mixture was stirred on the elliptic table again. Then, the fibre is directly introduced into the GC–PFPD system for thermal desorption of the analytes.

2.3.3. Quantitation

For each sample, the chromatographic response $K_{i/is}$ of an organotin (i) relative to the internal standard (is) was calculated by standard additions. This procedure was applied to a minimum of three aliquots of either 80 ml of water or 0.5 ml of extract from biological sample. This procedure allows the matrix effects to be decreased as much as possible [31].

2.4. Chemometrics

The experimental designs were used according to Goupy [32] and Sado and Sado [33]. The design was reached by first using only two adjusting levels (minimum and maximum, noted, respectively, $+1$ and -1) for each factor. The influence of a factor was calculated and considered as significant if it was higher than experimental error. This error was evaluated from the experiment at the centre of the field (level '0'), which was done four times successively. On the basis on influent factors, linear regression was proposed as representative of the variations of responses in the whole experimental field. Because it cannot be validated, regression with second-order terms had to be proposed involving supplementary experiments (central, noted '0' and extreme levels, noted '$+\alpha$' and '$-\alpha$' with $\alpha = N^{1/4}$ of the experimental field [33]). From validated regression, the optima of the responses were calculated and graphically located using the plotting of responses curves. They allow the adjustment of the operating factors to be defined.

Precision and significance of the fitting were evaluated using, respectively, coefficient of determination (R^2) and Fisher–Snedecor test (F_{obs} in F-test). In all the used statistical tests the level of confidence is 95%, as generally recommended by the IUPAC. The calculations were made using laboratory-written software, as described by Goupy [34]. This software was previously validated owing a comparative calculation with Nemrod software (LPRAI, Marseille, France) and Statgraphics plus 5.0 [16,35].

3. Results and discussion

3.1. Preliminary studies

Before the optimisation of the different steps involved in SPME process, the chromatographic conditions (temperature programme) was also optimised. Fig. 1 shows a typical chromatogram obtained, in Milli-Q water, under the conditions described below. This method allows the 14 organotins to be analysed in less than 20 min.

CAR–PDMS and PDMS fibres were tested in order to compare the performances of extraction on the different ethylated species. As expected, CAR–PDMS fibre gives better results for methyltins and TPhT, while PDMS fibre appears more convenient for the other compounds. Because the goal of this study focuses on the best compromise for all the organotins compounds, CAR–PDMS was selected and used later on.

3.2. Optimisation of the SPME step

Mester et al. defined the most important factors affecting precision and reproducibility of the SPME measurement [27]. However, because the influence of the following ones is obvious, they were fixed accordingly:

– time between extraction and analysis: immediately,

– fibre positioning during injection: in the middle of the injector.

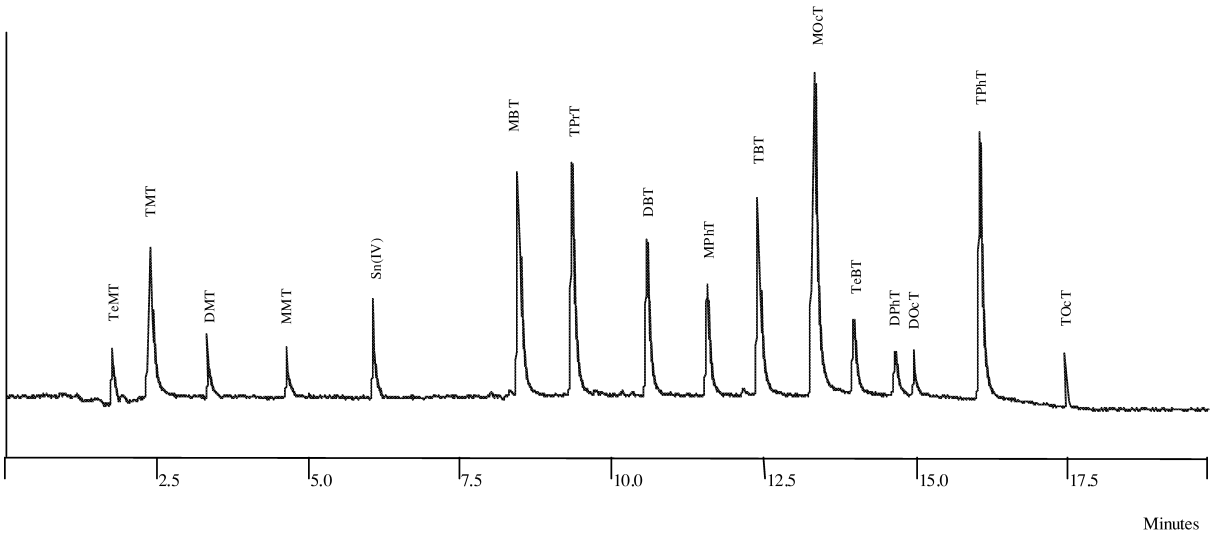

Fig. 1. Typical chromatogram of spiked water obtained by aqueous ethylation–SPME–GC–PFPD.

Because the constants of distribution between liquid and gaseous phases and between solution and SPME fibre (K_{hs} and K_{fs}, respectively) vary directly as a function of temperature, a high-temperature promotes the sorption of the analytes on SPME [36]. However, when the temperature in the reactor of derivatisation increases, the equilibrium of sorption can be shifted, leading to a desorption of the most volatile species [37,38]. Accordingly, we have decided to work at room temperature.

In agreement with our experience, experimental constraint and previous studies, the following other operating parameters were fixed [9,16,18]: sample volume, 80 ml; sample study, Milli-Q water; condition of the coated fibre and its thickness, a 75-μm thickness CAR–PDMS.

A particular point is that before extraction, organotins have to be ethylated since direct sorption of non-tetrasubstituted species (cationic forms according to the pH in the reactor) is impossible. So, prior to the SPME step, a delay is required in order to have organotins under suitable forms and obtain equilibrium between liquid and gaseous phases (evaluated by K_{hs}). Accordingly, this delay has to be taken into consideration and was noted later on 'equilibration time'.

Finally, six factors were considered with a view to optimise the sorption and desorption steps. In a first experimental design (sorption on SPME fibre) four factors were taken into account: (1) the time of equilibration before sorption on the fibre, (2) the time of sorption, (3) the air–water ratio (v/v) in the reactor of ethylation/extraction and (4) the stirring rate of the sample during SPME. For the second design (thermal desorption in injection port), two factors were considered according to previous studies [9,18,38]: (1) the temperature of injector and (2) the duration of splitless injection. The corresponding experimental field is presented in Table 2. The peak heights (H) of each of the 14 organotins and internal standard were chosen primarily as representative responses of the studied process. From the deduced mathematical expressions of the fitting, the optima were evaluated as previously described.

3.2.1. Optimisation of the sorption

Because four factors were studied, a complete factorial design would have involved $2^4 = 16$ experiments. So, in order to decrease this number, a fractional design 2^{4-1} containing eight experiments was chosen. This approach involves the possible risk of uncertainties concerning the origins of the effects due to aliases (associations) between factors and interactions. In this case, the fractional design has to be planned by associating originally a factor (in the present study, 4) to the interaction having the highest

Table 2
Determination of the experimental field

	Factors/levels	$-\alpha$	-1	0	$+1$	$+\alpha$
Design 1	(1) Equilibration time (min)	1.3	4	8	12	14.7
	(2) Time of sorption (min)	3.2	10	20	30	36.8
	(3) Air/water ratio (v/v)	–	0.54	–	4	–
	(4) Stirring rate (rpm/min)	132	200	300	400	468
Design 2	(1) Temperature of injector (°C)	252	260	280	300	308
	(2) Duration of splitless (min)	0.1	0.5	1.0	1.5	1.9

α defined on the basis of $N^{1/4}=1.68$ and 1.41 for designs 1 and 2, respectively.

order (i.e., 123). So, the risk of uncertainties is decreased because, as a matter of statistical fact, higher is the order of the interaction, lower is the risk this interaction is significant [33]. The experiments of the 2^{4-1} design were performed by measuring the 15 responses H. The results obtained showed that some of these responses varied in the same way. They correspond to species having close retention times, i.e., close volatility. Thus, the responses with similar variations in the experimental field were regrouped and only the following two responses were considered and presented later on:

$$(H)_1 = \frac{(H)_{\mathrm{MMT}} + (H)_{\mathrm{DMT}} + (H)_{\mathrm{TMT}} + (H)_{\mathrm{TeMT}}}{4},$$

$$(H)_2 = \frac{(H)_{\sum \mathrm{butyltins}} + (H)_{\sum \mathrm{phenyltins}} + (H)_{\sum \mathrm{octyltins}} + (H)_{\mathrm{TPrT}}}{11},$$

$(H)_1$ corresponding to the most volatile species and $(H)_2$ to the less volatile ones.

The effects of the four factors and interactions on the two responses were calculated as described previously. They are graphically presented on Fig. 2 with the corresponding error (dotted lines indicating the level of significance). On the same figure, the aliases factor–interaction and interaction–interaction are explicitly presented. By comparison with the level of significance, factors (2), (3), and (4) appear to be very influential on the two responses. Concerning $(H)_2$ response, despite factor (1) not being intrinsically significant, its interactions with the other factors are influent.

Because factor (3) is clearly negatively influential and concerns the geometry of the reactor of ethylation/extraction, it was decided to choose the smallest reactor, allowing the smallest air–water ratio. So, all the further experiments have been performed with this reactor.

Using these results, first order models (i.e., linear) were proposed. But they could not be validated because experimental and calculated responses $(H)_1$ and $(H)_2$ were found to be significantly different, showing that the variations of the response are curved. So, an optimisation design had to be planned. Because the geometry of the reactor (factor 3) has been kept at its low level, only the three factors, 1, 2, 4 were considered later. Consequently, an optimisation design was built such that it had 15 experiments, including four ones from the fractional designs 2^{4-1}, four complementary experiments in order to have a complete design and seven additional experiments at $\pm\alpha$ and 0 levels (see Table 2). Then, non-linear models could be proposed and are presented in Table 3, Part A. The model appears as significant and precise, without any bias and so, can be statistically validated. Fig. 3 shows the three-dimensional representations of the responses $(H)_1$ and $(H)_2$ versus influential factors in the experimental field corresponding to ± 1 levels. According to these two models, two sets of optimised operating conditions (S1 and S2) have been deduced (Table 4). So, it is possible to extracted methyltins within 10 min or all the species with a sorption step of 30 min.

3.2.2. Optimisation of the thermal desorption

The two factors considered were studied in a complete factorial design involving $2^2=4$ experiments. The 15 responses H were measured in order to evaluate the efficiency of the desorption. Similarly to the previous optimisation, it can be defined the same two 'mean' responses $(H)_1$ and $(H)_2$ according

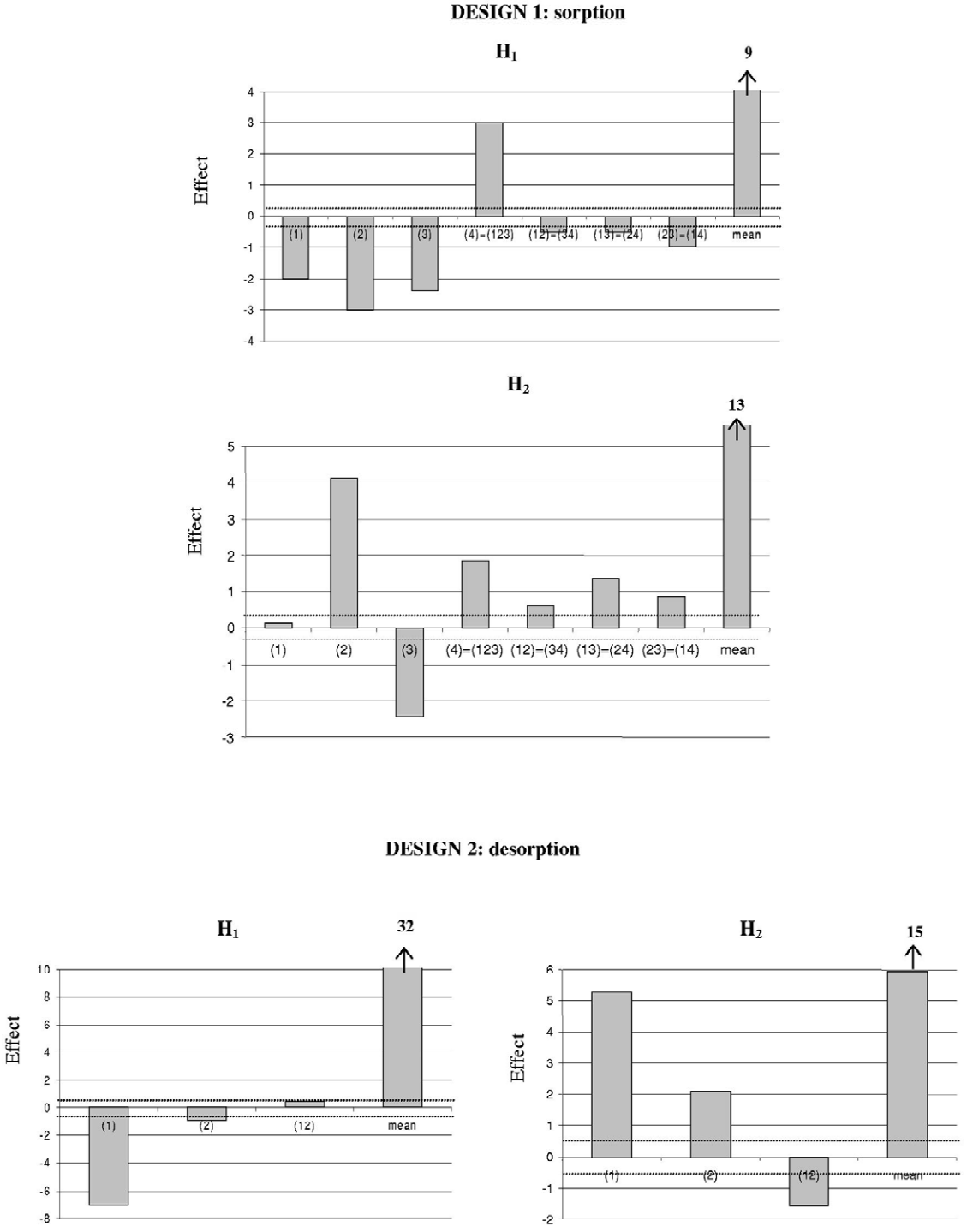

Fig. 2. Experimental design: influence of the factors on the studied responses. Dotted line: level of significance according to experimental precision.

Table 3
Validation of the modelling

	Assignation	Responses	
		$(H)_1$	$(H)_2$
Part A: design 1 optimisation of the sorption			
	Mean	**+3.9±0.5**	**+27±1**
Main	(1)	**−0.2±0.1**	**+1.5±0.4**
characteristics:	(2)	**−2.3±0.2**	**+4.8±0.4**
	(4)	**+3.3±0.2**	**+7.3±0.4**
	(12)	**−0.7±0.2**	**+0.9±0.5**
Coefficients	(14)	−0.0±0.2	**+0.9±0.5**
of the models	(24)	**+1.0±0.2**	**+1.9±0.5**
	(1)[b]	**+1.8±0.2**	−0.1±0.6
	(2)[b]	**+2.1±0.2**	**−2.6±0.6**
	(4)[b]	**+3.7±0.2**	**−2.2±0.6**
Significance	Total fitting $(F_{obs})^b$	97	286
Precision	Determination coefficient (R^2)	0.938	0.977
Part B: design 2 optimisation of the desorption			
Main	Mean	**+30±1**	**+18±1**
characteristics:	(1)	**−5.5±0.5**	**+5.1±0.5**
	(2)	**−1.0±0.5**	**+3.1±0.5**
Coefficients	(12)	+0.5±0.7	**−1.3±0.7**
for the models[a]	(1)[b]	**+3.0±0.8**	**+1.3±0.8**
	(2)[b]	−0.0±0.8	**−2.0±0.8**
Significance	Total fitting $(F_{obs})^b$	1040	320
Precision	Determination coefficient (R^2)	0.933	0.978

[a] Significant values in bold characters.
[b] Positive statistical tests: $F_{obs} > F_{tab\ (95\%)}$.

to the volatility and the behaviour of the organotins during desorption.

The effects of the factors and interactions evaluated on these two responses are presented on Fig. 2. Factor 1 (temperature of injector) and factor 2 (duration of the splitless) are very positively significant on $(H)_2$. At the opposite, factors 1 and 2 have a negative effect on $(H)_1$ while interaction 12 is less significant.

The optimisation design involved five supplementary experiments (see Table 2). Non-linear models could be proposed and are presented in Table 3, Part B. The 3D representations of the response $(H)_1$ and $(H)_2$ versus influential factors are plotted in the experimental field corresponding to ±1 levels (Fig. 3). According to the nature of the organotins, the temperature of injector and splitless duration were found to have different effects. Consequently, two sets of optimised operating conditions were deduced and are given in Table 4 (last two lines).

3.3. Analytical performances

These were determined, according to the S1 and S2 operating conditions described above, by using standard solutions and tripropyltin as internal standard. The limits of detection (LODs) were calculated according to IUPAC recommendations ($2\sigma t/A$, where t is the coefficient of Student in a interval of confidence of 95%, σ the standard deviation of baseline according to the retention time of the organotins compounds and A the sensitivity (slope) obtained from the corresponding calibration curve). The LODs and the repeatability (relative standard deviation, RSD) are presented in Table 5. The relative standard deviation was evaluated from 1 to

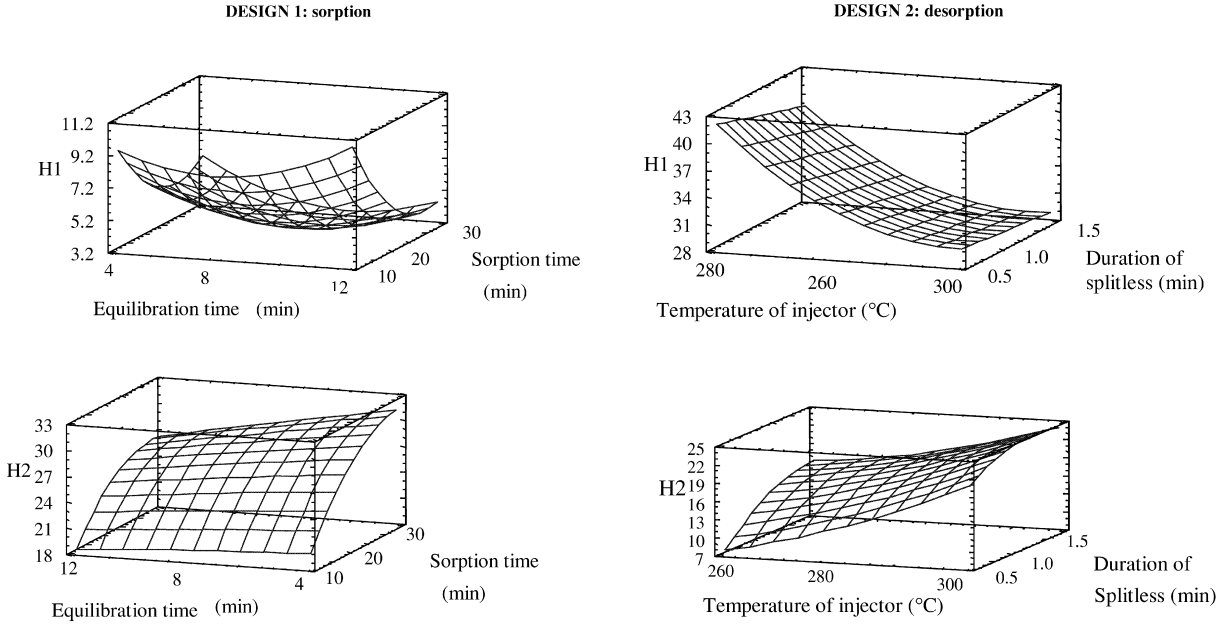

Fig. 3. Optimisation–response curves of the studied responses.

Table 4
Optimised operating conditions

	Factors/species involved	S1: Me	S2: all species
Design 1	(1) Equilibration time (min)	4	10
	(2) Time of sorption (min)	10	30
	(3) Air/water ratio (v/v)	0.54	0.54
	(4) Stirring rate (rpm/min)	400	400
Design 2	(1) Temperature of injector (°C)	260	285
	(2) Duration of splitless (min)	1.0	1.5

Table 5
Analytical performances of the headspace SPME-based method: S1, S2

	TeMT	TMT	DMT	MMT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT	MOcT	DOcT	TOcT
LOD (ng(Sn) l^{-1})														
S1	0.35	0.08	0.01	0.05										
S2	0.50	0.14	0.03	0.08	0.04	0.02	0.07	4.25	0.01	11.34	0.01	0.03	17	56
RSD (%) (n=5)														
S1	24	16	16	18										
S2	25	20	18	22	9	11	19	24	16	15	21	15	19	17

125 ng(Sn) l^{-1} standard solutions. The LODs (between 0.02 and 56 ng(Sn) l^{-1}) allow most of the compounds to be determined sub-0.2 ng(Sn) l^{-1}. The performances obtained by using S1 and S2 are very close. LOD are evaluated over the whole analytical process, i.e., especially considering the both ethylation and extraction yields. It can be expected that the most volatile compounds are more quantitatively extracted on headspace SPME fibre, leading to obtain the lowest LODs. However, it is not verified for some species such as MMT (see Table 1). The tetrasubstituted organotins have also higher LODs. In case of TeMT, this is probably because it has a very low boiling point and some losses can be expected. This hypothesis is confirmed by the fact it has also the highest RSD (about 25%). TeBT, DPhT, DOcT and TOcT give high LODs as well, because of their high boiling points (>280 °C). TPhT has a low limit of detection while its boiling point is high (400–450 °C). These results have been confirmed by performing several sets of experiments in order to calculate several times the LODs for each compound. Consequently, and even if the result concerning TPhT is unexpected and difficult to explain, it was obtained from reliable experimentation. Particular behaviour of sorption of TPhT has been already noted in the case of direct SPME using PDMS fibre [18]. However, in the present study the mechanisms of sorption on CAR–PDMS fibre are not well known, few studies being reported in the literature. Competitions of sorption or phenomenon of saturation of the fibre have to be taken into consideration. Moreover, some authors underline that these particular phenomena are enhanced when the time of extraction is more than a few minutes [38].

Despite these observations, the different limits of detection obtained are in agreement with the concentration levels that should be determined in environmental waters, according to the ISO project concerning organotin speciation in water [39]. The repeatability appears also to be satisfactory for a reliable quantitative analysis.

3.4. Application to organotin speciation in water and biological sample

The method was applied to the analysis of spiked Milli-Q water and fish, and non-spiked natural water.

Table 6
Determination of organotin compounds in different spiked samples

	Milli-Q water [Concentrations in ng(Sn) l^{-1}]									
	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT	MOcT	DOcT	TOcT
Spiked values	2.5±0.1	0.25±0.01	2.5±0.1	6.0±0.3	2.5±0.1	25±1	1.20±0.06	2.5±0.1	25±1	25±1
Found values	2.8±0.3	0.26±0.03	2.0±0.5	5±1	3.0±0.5	22±3	1.5±0.3	2.4±0.4	28±5	26±4
RSD (%)	11	12	25	20	17	14	20	17	18	16
	Fish (Trout Fario) [Concentrations in ng(Sn) g^{-1} dry]									
	TeMT	TMT	DMT	MMT						
Spiked values	13.3±0.7	7.2±0.4	0.50±0.02	7.2±0.4						
Found values	17±3	8±1	0.42±0.08	8±1						
RSD (%)	20	13	19	14						
	Natural waters [Concentrations in ng(Sn) l^{-1}]									
	TeMT	TMT	DMT	MMT	MPhT	MOcT				
(1) Artenay										
Found values	1.3±0.3	0.18±0.02	1.0±0.1	16±2	0.24±0.03	nd				
RSD (%)	23	11	10	12	12	–				
(2) Saint Lyé										
Found values	d	d	0.23±0.04	14±2	nd	6±1				
RSD (%)	–	–	17	14	–	16				
(3) Le Nan										
Found values	19±5	0.22±0.04	0.71±0.02	7.8±0.8	0.19±0.02	nd				
RSD (%)	26	18	3	10	10	–				

d, detected; n.d., not detected.

The results are presented in Table 6. The spiked and found values appear to correlate in an interval of confidence of 95% (Student *t*-test). So, these analysis can be considered as conform and analytical method as accurate. The SPME was also applied to the analysis of natural waters from three pools in the centre of the France (last part of Table 6). Methyltin compounds, MPhT and MOcT were detected. The presence of these two last compounds in waters at low concentration clearly indicates either a slight contamination, probably from domestic organotin-based products or biomethylation phenomena. The levels of concentrations determined in all these samples (0.2–25 ng(Sn) l^{-1}) and the precision of the results (RSD$<$16% generally) show the suitability of the headspace SPME-based procedure for environmental analysis. It can be especially noticed that in the case where biological tissue was studied, no matrix effect was observed. This is not the case by using direct mode SPME [18,38], and so headspace mode really appears to be a promising procedure.

4. Conclusion

The statistical approach used in this work to optimise the SPME step has provided reliable analytical results. The determination of organotins by ethylation/headspace SPME followed by the GC-PFPD has been demonstrated to be an efficient, rapid and simple technique to analyse simultaneously 14 organotins. Low limits of detection [sub-0.2 ng(Sn) l^{-1} for most species] can be reached. The first applications made on environmental samples have demonstrated the reliability of the analysis, without any noticeable matrix effect. So, headspace SPME appears as convenient for the organotin determination in environment and monitoring of their biogeochemical cycle. Further applications will have to be made in order to confirm the high potential of this method.

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References

[1] O.F.X. Donard, J.H. Weber, Nature 332 (1988) 339.
[2] Y.K. Chau, P.T.S. Wong, O. Kramar, C.A. Bengert, in: Proc. Int. Conf. Heavy Metals Environ. Amsterdam, 1980.
[3] K. Fent, Crit. Rev. Toxicol. 26 (1996) 1.
[4] R.J. Maguire, Appl. Organomet. Chem. 1 (1987) 475.
[5] D.S. Forsyth, C. Cleroux, Talanta 38 (1991) 951.
[6] R. Lobinski, F.C. Adams, Spectrochim. Acta B 52 (1997) 1865.
[7] M. Azena, M.T. Vasconcelos, Anal. Chim. Acta 458 (2002) 231.
[8] I. Meriowsky, R. Brandsch, J. Ejlertsson, J. Environ. Qual. 30 (2001) 1604.
[9] S. Aguerre, G. Lespes, V. Desauziers, M. Potin-Gautier, J. Anal. At. Spectrom. 16 (2001) 263.
[10] G.B. Jiang, J. Y Liu, K.W. Yang, Anal. Chim. Acta 41 (2000) 67.
[11] Ch. Bancon-Montigny, G. Lespes, M. Potin-Gautier, J. Chromatogr. A 896 (2000) 149.
[12] C. Carlier-Pinasseau, A. Astruc, G. Lespes, A. Astruc, J. Chromatogr. A 750 (1996) 317.
[13] K. Fent, M.D. Muller, Environ. Sci. Technol. 25 (1991) 489.
[14] R. Reuther, L. Jaeger, B. Allard, Anal. Chim. Acta 394 (1999) 259.
[15] C. Pecheyran, C. Quétel, C.R. Lecuyer, O.F.X. Donard, Anal. Chem. 70 (1998) 2639.
[16] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[17] J. Poerschmann, F.D. Kopinke, J. Pawliszyn, Environ. Sci. Technol. 31 (1997) 3629.
[18] S. Aguerre, C. Bancon-Montigny, G. Lespes, M. Potin-Gautier, Analyst 125 (2000) 263.
[19] Y. Morcillo, Y. Cai, J.M. Bayona, J. High Resolut. Chromatogr. 18 (1995) 767.
[20] E. Millan, J. Pawliszyn, J. Chromatogr. A 873 (2000) 63.
[21] L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, P. Sandra, Anal. Chem. 69 (1997) 1604.
[22] L. Dunemann, H. Hajimiragha, J. Begerow, Fresenius J. Anal. Chem. 363 (1999) 466.
[23] N. Cardellicchio, S. Giandomenico, A. Decataldo, A. Di Leo, Fresenius J. Anal. Chem. 369 (2001) 510.
[24] J. Carpintero Botana, I. Rodriguez Pereiro, R. Cela Torrijos, J. Chromatogr. A 963 (2002) 195.
[25] J. Vercauteren, A. De Mester, T. De Smaele, F. Vanhaecke, L. Moens, R. Dams, P. Sandra, J. Anal. At. Spectrom. 15 (2000) 651.
[26] C. Haberhauer-Troyer, M. Crnoja, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 366 (2000) 329.
[27] Z. Mester, R. Sturgeon, J. Pawliszyn, Spectrochim. Acta Part B 56 (2001) 233.

[28] G. Lespes, C. Carlier-Pinasseau, M. Potin-Gautier, M. Astruc, Analyst 121 (1996) 1969.
[29] C. Carlier-Pinasseau, G. Lespes, M. Astruc, Environ. Technol. 18 (1997) 1179.
[30] D. Amouroux, E. Tessier, C. Pécheyran, O.F.X. Donard, Anal. Chim. Acta 377 (1998) 241.
[31] C. Montigny, G. Lespes, M. Potin-Gautier, J. Chromatogr. A 819 (1998) 221.
[32] J. Goupy, in: La Méthode des Plans d'Experiences, Dunod, Bordas, Paris, 1988.
[33] G. Sado, M.C. Sado, in: Les Plans d'Experiences, Afnor, Afnor Technique, Paris, 1991.
[34] J. Goupy, Plans d'Expérience pour Surface de Réponse, Dunod, 1999.
[35] www.statgraphics.com
[36] M. De Fatima Alpendurada, J. Chromatogr. A 889 (2000) 3.
[37] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[38] S. Aguerre, thesis, University of Pau, Pau, France, 2001.
[39] ISO/TC 147/SC 2N 0569, Water Quality, Determination of Selected Organotin Compounds, Gas Chromatographic Method, 2002.
[40] Handbook of Chemistry and Physics, CRC Press, xxth ed., 1975–1976.