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ORIGINAL PAPER

Manuel Bravo · Gaëtane Lespes · Ida De Gregori · Hugo Pinochet · Martine Potin Gautier

Determination of organotin compounds by headspace solid-phase microextraction–gas chromatography–pulsed flame-photometric detection (HS-SPME–GC–PFPD)

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Abstract A method based on headspace solid-phase microextraction (HS-SPME, with a 100-μm PDMS fibre) in combination with gas chromatography and pulsed flame-photometric detection (GC–PFPD) has been investigated for simultaneous determination of eight organotin compounds. Monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), and the semi-volatile diphenyltin (DPhT), triphenyltin (TPhT), monooctyltin (MOcT), and dioctyltin (DOcT) were determined after derivatization with sodium tetraethylborate. The conditions used for the extraction and preconcentration step were optimised by experimental design methodology. Tripropyltin (TPrT) and diheptyltin (DHepT) were used as internal standards for quantification of volatile and semi-volatile organotin compounds, respectively. The analytical precision (RSD) for ten successive injections of a standard mixture containing all the organic tin compounds ranged between 2 and 11%. The limits of detection for all the organotin compounds were sub ng (Sn) L^{-1} in water and close to ng (Sn) kg^{-1} in sediments. The accuracy of the method was evaluated by analysis of two certified reference material (CRM) sediment samples. HS-SPME–GC–PFPD was then applied to the analysis of three harbour sediment samples. The results showed that headspace SPME is an attractive tool for analysis of organotin compounds in solid environmental matrices.

M. Bravo · I. De Gregori · H. Pinochet
Laboratorio de Química Analítica y Ambiental,
Instituto de Química,
Pontificia Universidad Católica de Valparaíso,
Avenida Brasil,
2950 Valparaíso, Chile

M. Bravo · G. Lespes · M. P. Gautier (✉)
Laboratoire de Chimie Analytique,
LCABIE, UMR CNRS 5034,
Université de Pau et des Pays de L'Adour,
Avenue de l'Université, BP1155,
64013 Pau, France
e-mail: martine.potin@univ-pau.fr

Keywords Organotin compounds · Solid-phase microextraction · Gas chromatography–pulsed flame photometric detection (GC–PFPD) · Experimental design · Canonical analysis

Introduction

Organotin compounds (OTCs), especially the trisubstituted species, have been widely used as active ingredients in fungicides, pesticides, and marine antifouling agents [1]. Their extreme toxicity, especially in marine and freshwater ecosystems, have, however, resulted in numerous adverse biological effects on non-target organisms [2, 3]. Although several regulations have been implemented to control their application, especially the use of tin-based antifouling paints [4, 5], contamination of the environment by OTCs is a real problem and even potential transfer to humans by enrichment in each trophic level is under discussion [6, 7].

The different control programs have prompted the development of many analytical methods for organotin speciation. Most of these methods are based on a chromatographic separation, usually by gas chromatography (GC), then selective detection, for example flame-photometric detection (FPD) or inductively coupled plasma–mass spectrometry (ICP–MS) [8–10]. GC–FPD seems well adapted for routine use and so is employed for environmental monitoring of organotin compounds [11, 12]. The analytical procedure is based on one-step $NaBEt_4$ ethylation and liquid–liquid extraction (LLE) before GC–FPD analysis [13, 14]. This detector is simple but suffers from interference and lack of sensitivity [15, 16].

More recently, to overcome these problems, a pulsed flame-photometric detector (PFPD) has been developed commercially and marketed to replace the FPD. The main improvements result from use of a discontinuous flame connected to enable discontinuous detection, and a selective signal is obtained by using an element-specific emission profile which varies with time [17]. The corresponding analytical procedure was optimised and validated for simultaneous determination of butyl, phenyl,

and octyltin compounds in a variety of environmental samples [17, 18]. By application to different samples, for example water or sediments, the capabilities of the method based on GC–PFPD have been demonstrated [19]. Although use of LLE–GC–PFPD has been proposed in two different analytical standardised procedures [20, 21], the method is inconvenient. It can sometimes be difficult to separate the organic and aqueous phases after the ethylation–LLE procedure, especially when the sample is rich in organic matter, because co-extracted compounds result in the formation of an emulsion between the two phases. LLE also requires the use of toxic solvents and its automation is not easy to achieve.

A few years ago solid-phase microextraction (SPME) was proposed as a promising alternative for analysis of organometallic compounds in natural samples [22]. This solvent-free technique has numerous advantages, for example simplicity, low cost, and the possibility of on-line analysis. Analyte extraction can be achieved by placing the fibre either directly in the sample (direct mode) or in the gaseous phase above the sample (headspace mode). Although SPME in direct mode is suitable for determination of butyl and phenyltin compounds in different reference materials [23, 24], the potential of this mode has been shown to be limited, because direct contact of the sample with the fibre can lead to dramatic matrix effects (including sorption competition) and rapid fibre damage [25].

Although the headspace mode has scarcely been used for speciation of OTCs, in this mode the fibre is protected from matrix components, extraction of non-volatile interfering compounds is avoided, and the extraction time is reduced [22]. HS-SPME was recently investigated for analysis of volatile methyltin compounds and the less volatile butyltin compounds [26, 27]. PDMS and carboxen–PDMS fibres were tested. Although HS-SPME seems convenient for determination of the most volatile organotin compounds (methyltin compounds), it remains critical for the other species, especially phenyltin and octyltin compounds [26]. According to SPME theory the sorption mechanisms (mainly absorption) involved in such processes seem convenient for extraction of less volatile organotin compounds [22, 25, 28], so the development of PDMS-based HS-SPME seems important as an alternative and complementary process among the different analytical methods for speciation of organotin compounds of very different volatility and toxicity.

Such analytical development includes a first step of optimization. According to the literature, when SPME procedures have been optimised the operating variables have been studied one by one by univariate methodology [27, 29]. This classical process has important drawbacks, however, especially as it fails to consider any interaction between two or more condition and only examines a very narrow range within all possible combinations of values [30]. Experimental design methodology seems the most convenient approach for searching for the optimum conditions in a reasonable number of experiments [31].

The objective of this work was to determine the suitability of headspace-SPME for analysis of butyltin, phenyltin, and octyltin compounds by GC–PFPD. Experimental design methodology was used to determine and optimise the most important conditions. This procedure was validated by analysing certified reference materials and then applied to some environmental samples.

Experimental

Instrumentation

SPME device

The manual SPME device was obtained from Supelco (Saint Quentin Fallavier, France). The 100-μm polydimethylsiloxane (PDMS) fibre was selected for this study.

Apparatus

Chromatography was performed with a Varian (Walnut Creek, CA, USA) 3800 gas chromatograph equipped with a pulsed flame-photometric detector (PFPD) and a 1079 split/splitless injector. Compounds were separated on a capillary column (30 m×0.25 mm I.D.) coated with polydimethylsiloxane (0.25 μm film thickness) (Quadrex, New Haven, CT, USA). Nitrogen was used as carrier gas. The oven temperature was initially held at 80°C for 1 min then programmed at 30° min^{-1} to 180°C and then at 10° min^{-1} to a final temperature of 270°C which was held for 1 min [15]. The temperature of the chromatographic injector for the desorption step was fixed at 275°C, in accordance with the recommendation of the manufacturer.

The conditions used for detection have been described elsewhere [15, 24]. A filter with a broad transmission band (320–540 nm; BG 12, Schott, France) was used to observe Sn-C molecular emission. In accordance with the tin emission profile, the signal was acquired with a gate delay of 3.0 ms and gate width of 2.0 ms after each flame ignition.

A mechanical stirring table KS 2502 basic (Prolabo, Fontenay Sous Bois, France) was used for derivatisation and extraction. An ultrasonic cleaner bath (Branson 2510) from Bioblock (Ilkirch, France) was used for extraction of organotin compounds from biological materials.

Reagents and standards

Individual organotin stock standard solutions (1,000 mg (Sn) L^{-1} as tin) of dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), tetrabutyltin (TeBT, 93%), and trioctyltin chloride (TOcT, 95%) (all Sigma–Aldrich, St Quentin Fallavier, France), tripropyltin chloride (TPrT, 98%), monobutyltin trichloride (MBT, 95%), monophenyltin trichloride (MPhT, 98%), diphenyltin

dichloride (DPhT, 96%), and triphenyltin chloride (TPhT, 95%) (all from Strem Chemicals), monooctyltin trichloride (MOcT, 97%) and dioctyltin dichloride (DOcT, 97%) (both from Lancaster, Strasbourg, France), were prepared in methanol and stored at +4°C in the dark. Working standards were obtained by dilution with water, weekly for solutions of 10 mg (*Sn*) L^{-1} and daily for 100 μg (*Sn*) L^{-1} solutions. The purity of the standards was monitored by individual $NaBEt_4$ derivatisation then GC–PFPD analysis. They were stored in the dark a +4°C. The deionized water used was 18 MΩ (Millipore, Bedford, MA, USA).

Methanol and sodium acetate were purchased from Prolabo (France). Hydrochloric, nitric, and ethanoic acids were obtained from Merck (Darmstadt, Germany), and isooctane was from Fluka (Buchs, Switzerland).

Sodium tetraethylborate ($NaBEt_4$) was obtained from Galab Chemical (Strasbourg, France). Aqueous ethylating solution (2%, *m*/*v*) was prepared just before a set of analyses.

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

Analytical procedures

Extraction procedures

The extraction procedure for sediment samples has been described precisely and validated elsewhere [13, 14]. Briefly, samples were precisely weighed (0.5–1 g) and introduced into capped 50-mL polycarbonate tubes with 25 μL 100 μg (*Sn*) L^{-1} TPrT solution, used as internal standard, and 20 mL glacial ethanoic acid. The tube was shaken at 420 rpm for 12 h. The suspension was then centrifuged at 4,000 rpm and the acidic supernatant was collected.

Derivatisation and analysis

For all the matrices, 0.1 mL acidic extract was introduced directly into the derivatisation vessel, total volume 100 mL, containing 60 mL buffer solution. After addition of 50 μL ethylating solution the mixture was mechanically stirred. The fibre was then placed in the headspace volume and the mixture was stirred again. The fibre was then introduced directly into the GC–PFPD for thermal desorption of the analytes at 275°C, in splitless mode for 3 min. These desorption conditions are such that neither memory effect nor OTC degradation occur. Typical chromatograms obtained by use of this procedure are given in Fig. 1.

Samples and quantitation procedure

Three surface sediment samples were collected in two different harbours in Chile in which dry-docking and commercial harbour activities are currently conducted. The samples were freeze-dried, sieved at 63 μm (in accordance with the procedure used for preparation of the sediment CRM [32]) and stored at −20°C until analysis. For practical reasons these samples were labeled ST4, ST5, and SVF. The analytical method was validated by analysis of BCR 646 and PACS-2 sediment reference materials (respectively freshwater sediment certified for butyl and phenyltin compounds and marine sediment certified for butyltin compounds).

Organotin in marine sediments was quantified by use of the standard addition procedure. TPrT was used as both tracer and internal standard to monitor the analytes and prevent any risk of bias because of losses during the analytical procedure (from extraction to GC injection and analysis). This procedure enables matrix effects to be reduced as much as possible [15]. Each sample was extracted in duplicate. For each acidic extract two different

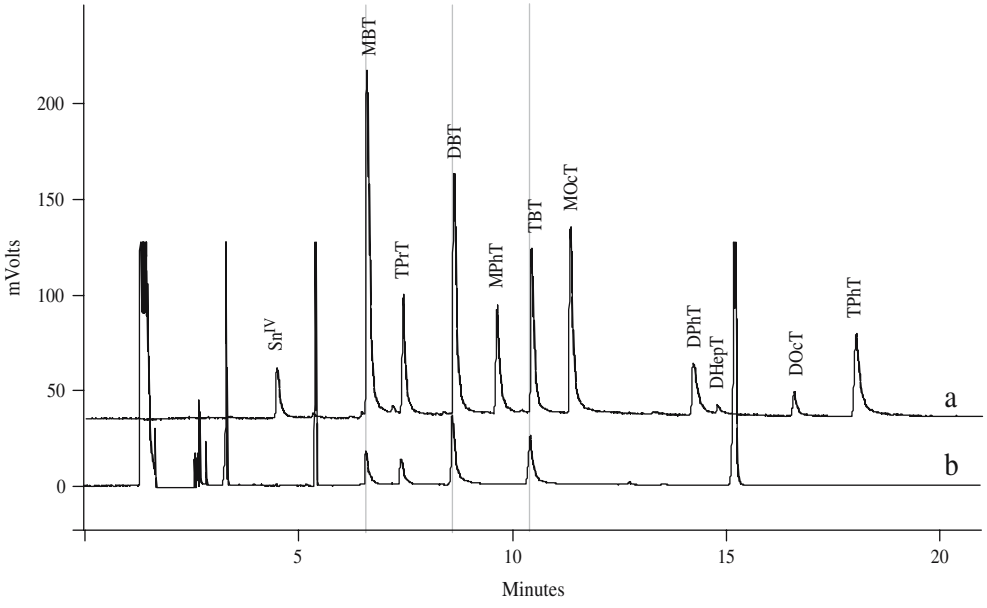

Fig. 1 Typical chromatograms obtained by HS-SPME–GC–PFPD analysis: (**a**) Aqueous standard (0.25–125 ng (Sn) L^{-1}); (**b**) PACS−2 CRM sediment

Table 1 Research on the influencing factors: 2^{4-1} experimental matrix (X)

		Level				
Factor	Coded factor	$-\alpha$[a]	−1	0	1	α
Stirring rate (rpm)	(1)	132	200	300	400	468
Sorption time (min)	(2)	3.2	10	20	30	36.8
Equilibration time (min)	(3)	1.3	4	8	12	14.7
Solution volume (mL)	(4)	–	55	65	75	–

[a] α=1.68 according to rotability

aliquots were ethylated. SPME was performed in duplicate using two independent aliquots of the acidic extract.

Experimental design

An aqueous solution containing the eight analytes (three butyltin compounds, three phenyltin compounds and two octyltin compounds) and the internal standard (tripropyltin), over the range 0.25–125 ng (*Sn*) L^{-1}, was used for the experimental designs. A factorial design with two levels of adjustment was used for the screening step. Each factor can have two adjustment values, called levels: the highest level is denoted +1 and the lowest −1 (Table 1). A fractional design was used to estimate the influential effects from a reduced number of runs. To maintain satisfactory resolution (i.e. to reduce the risk of uncertainty about the origins of the effects), the factors were associated with third-order interactions only, because these interactions are not usually significant [30, 31]. Also, by using a factorial design at two levels, a polynomial model without any square term (i.e. a "quasi-linear model" in a simple description) can be proposed to fit the variation of the response.

A supplementary experiment at the centre of the experimental field (denoted "0") was performed five times to estimate the standard deviation of the measured responses (σ). The effects of factors, interactions, and their respective precision were evaluated using the least-squares method. The effect of a factor or interaction was regarded as significant if the corresponding effect was higher than the precision.

For the optimization step, a central composite design, based on the influential factors from the previous fractional design, was used. It enables a second-order polynomial model with square terms to be proposed to adjust the possible response curvature correctly. Precision and significance of the fitted model were evaluated using, respectively, the coefficient of determination (R^2) and the Fisher–Snedecor Test (F_{obs} in the *F*-test). In all the statistical tests used the level of confidence was 95%. For the statistical and mathematical calculations involved in this study, Matlab 6.0 and Statgraphics plus 5.0 software package were used, for a flexible step-by-step approach. The response optimum was found by canonical analysis, as described by Goupy [31].

Results and discussion

As discussed in the Introduction, this work focussed on the PDMS fibre because it seems clearly more efficient for extraction of butyl, phenyl, and octyltin compounds [26]. Complementary experiments performed in this study also showed that DPhT, TPhT, and DOT were not satisfactory extracted from sediment samples by the carboxen–PDMS fibre in headspace mode. Because extraction is the crucial step of the SPME-based process [22, 26, 27], it was optimized first by focussing on screening of the factors potentially important in the process and, second, by optimization of the operating conditions of HS-SPME.

Screening design

The screening step enables determination of the factors which affect the method. The choice of variables to be considered for optimization depends on the physicochemical and kinetic processes involved [22]. In headspace mode, two phenomena are involved. First, the analytes originally present in the gaseous phase are extracted directly into (or on to) the fibre. The less volatile compounds present in the aqueous medium are then transferred to the gaseous phase and finally extracted into (on to) the fibre. Volatile species are therefore extracted faster than semi-volatile species because the first are present at higher concentrations in the headspace gaseous phase.

Moreover, because the OTC must be derivatized to obtain volatile and thermally stable species for the GC separation, an ethylation is performed in the same step as extraction. It is well known that this reaction is widely pH-dependant. It has been clearly established that the optimum pH ranges from 4.5 to 5 [33, 34]. Because no ambiguity remains about the effect of pH on OTC ethylation yields, it was decided to keep this condition constant. The amount of ethylating reagent is also a crucial condition to check, because the matrix can consume it. A large excess of $NaBEt_4$ excess, typically 1:2 (*v*/*v*) 2% ethylating solution–

Table 2 Effects of factors and interactions considered in the screening study

Factors and interactions	Assignation	Effect±error
Mean	–	**94±4**
(1)	Stirring rate	**30±4**
(2)	Sorption time	**31±4**
(3)	Equilibration time	**7±4**
(4)	Sample volume	−2±4
(12)+(34)	–	**6±4**
(13)+(24)	–	−1±4
(14)+(23)	–	2±4

Significant effects are given in bold characters

acidic extract, is usually sufficient to ensure quantitative ethylation. This is why, after checking the quantitative properties of the ethylation, this process was not considered for optimization [21]. Because the ethylation reaction is very rapid compared with the extraction [13, 14], it is possible that the limiting factor in the kinetics of ethylation–SPME corresponds to the transfer of the ethylated OTC between the different phases [22, 29]. Some preliminary experiments on the sorption profile performed with different ethylation times for the organotin compounds confirmed this hypothesis.

The literature describes SPME as an equilibrium technique. [22, 27] Two approaches are possible in the extraction procedure. The first consists in extracting the species before their distribution equilibrium between the involved phases [35]; the second enables the highest extraction yield possible to be achieved, by allowing equilibrium to be reached [25]. Obviously, method sensitivity depends on the amount of analyte extracted into the polymer film and so is expected to depend on both time and sample volume [36]. In accordance with these different observations, SPME at the equilibrium was chosen.

The variables selected for screening were:

- *Stirring rate* (x_1). Previous work has shown that mechanical stirring results in the highest extraction efficiency, by favouring convective mass transfer between the liquid and gaseous phases [24].
- *Sorption time* (x_2). This seems very important in OTC speciation analysis in which very low concentrations must be determined.
- *Equilibration time* (x_3). This affects the distribution of the ethylated species between the gaseous and liquid phases and also affects SPME repeatability.
- *Sample volume* (x_4). The headspace-to-sample volume ratio affects the distribution of analytes between the phases involved, because the extraction kinetics depend on the headspace capacity.

In agreement with our experience and previous discussion of SPME procedures the following operating conditions were fixed: volume of $NaBEt_4$, 50 μL (2% *v*/*v*); SPME, PDMS (100 μm) fibre; temperature, room temperature.

Finally, on the basis of the four factors considered for optimization of the sorption step, a 2^{4-1} fractional factorial design was used for screening. This design was built by aliasing the factor (4) with the third-order interaction (123). The experimental runs were conducted in duplicate and in randomized order to avoid systematic error.

To obtain the best sensitivity for all the organotin compounds the amounts of OTC extracted must be regarded as responses to evaluate the efficiency of the process. Previous work has shown that the area of the chromatographic peak of each organotin compound is representative of the quantity of each species extracted [24, 25]. So, the peak areas of MBT, DBT, TBT, MPhT, DPhT, TPhT, MOcT, and DOcT were taken as responses. Unfortunately, TOcT was not detected, probably because of its low volatility. It was, therefore, subsequently decided to not consider this compound.

Preliminary analysis of the results from the experimental design revealed that the chromatographic peak areas obtained for the eight OTCs varied in the same way in all the experiments. The responses were therefore regrouped and only the following response, called the mean response (R) was studied subsequently:

$$R = \frac{\sum S_{\text{Butyltins}} + \sum S_{\text{Phenyltins}} + \sum S_{\text{octyltin compounds}}}{8} \quad (1)$$

where $\Sigma S_{\text{Butyltin compounds}}$, $\Sigma S_{\text{Phenyltin compounds}}$, and $\Sigma S_{\text{octyltin compounds}}$ are the total amounts of the respective groups of compounds.

Consideration of this mean response also led directly to operating conditions which were a compromise for all the compounds and reduced the complexity of the mathematical calculations. For each factor, the levels selected are presented in Table 1. The effects of the factors and their interactions were calculated and are summarized in Table 2. These results show only three factors have an effect—stirring rate (1), sorption time (2), and equilibration time (3). The significant difference between the modelled response (i.e. mean 94±4) and that measured (i.e. experiment "0", 107±6) at the centre of the experimental field suggested that variation of the response was curved and meant the "quasi-linear" model fitting the response could not be validated.

That equilibration time (3) is significant supports the hypothesis that the kinetics of species distribution between the aqueous and gaseous phases plays a role in the SPME process. In the same way, the solution volume (4) has no significant effect. These observations lead to postulates that in this system:

1. the sorption capacity of the SPME fibre is such that the amounts of the species remaining present in the gaseous phase are higher than those on (in) the fibre, and
2. preliminary equilibration before extraction favours the presence of the analytes in the gaseous phase.

Finally, factor (4) was fixed at 55 mL (level −1) and the other three factors only were considered for optimization.

Modelling and optimization

Model validation

On the basis of the fractional factorial design 2^{4-1}, a central composite design was built. For that, a complete factorial design 2^3 was rebuilt from the 2^{4-1} and two supplementary levels corresponding to the star points (noted±α) added to determine the square coefficients of the second-order polynomial model. The value of α was chosen according to the rotatability criteria, i.e. $\alpha=N^{1/4}=1.682$ [30, 31]. The corresponding surface response, obtained from the calculated effects and their uncertainty, is presented in Fig. 2. On the basis of the significant coefficients, the model was

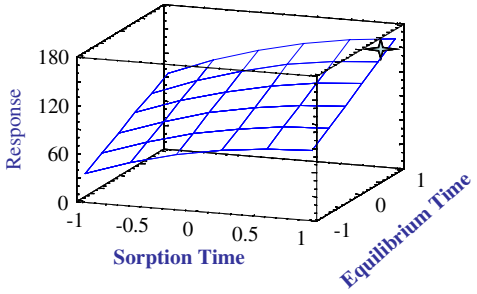

Fig. 2 Response-surface plot showing the effect of equilibration time and sorption time on the response studied

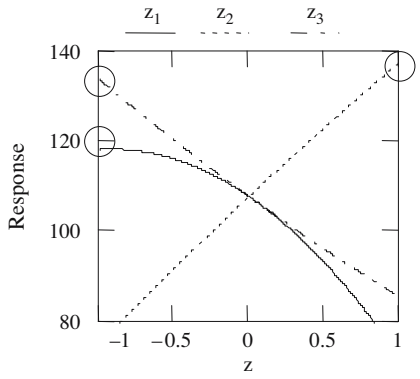

Fig. 3 Variation of the response over the canonical axes referenced to a stationary point

proposed and statically checked. Analysis of variance (ANOVA) performed for a confidence interval of 95% showed that the model was very significant (P-value=1.64×10^{-4}, i.e.<0.05), without any bias (P-value=0.335, i.e. >0.05) and correlates with experimental data precisely (R^2=0.998, i.e. 99.80% of the variation of the experimental response can be explained by this model). The Durbin–Watson test (D–W=2.434, i.e. >2) confirms there is no bias, because no residues correlation is detected. Finally, the model was statistically validated and could be used for optimization.

Optimization

Optimization was performed by canonical analysis, which enables the fitted second-degree surface to be transformed into a simpler form, so the optimum is found easily [31]. Thus, the response (S) as a function of the three influential factors, i.e. (1), (2), and (3), can be represented by three curves, each as a function of one coordinate denoted z (i.e. z_1, z_2, and z_3, respectively). From each curve, the maximum of the corresponding factor can be deduced. A typical graphical representation obtained is presented in Fig. 3. According to this figure the coordinates $z_1=-1$, $z_2=1$, and $z_3=-1$ indicate where the response is maximum. This point corresponds to an equilibration time of 12 min, a sorption time of 30 min, and a stirring rate of 400 rpm.

Analytical performance

The analytical performance was determined, under the operating conditions described above, by using standard solutions and tripropyltin as internal standard. The limits of detection (LOD) obtained for the whole process (i.e. ethylation–headspace SPME–GC–PFPD) by use of this method were calculated in accordance with IUPAC specifications (3σ). Although methods for simultaneous determination of butyl, phenyl, and octyltin compounds by an SPME procedure are scarce, their analytical performance is compared in Table 3. The LOD obtained in this work are lower than those of methods previously reported, whether using direct or HS-SPME, although the procedure described by Aguerre et al. results in a significantly lower LOD when extraction is performed in direct mode [24]. Nevertheless, although the times taken to perform these direct and HS- SPME methods are not very different, taking into consideration the total time for sample preparation, matrix effects are more likely in direct mode, as previously observed for analysis of complex matrices [25]. The mean LOD obtained by use of HS-SPME is in good agreement with the concentrations likely to occur in environmental samples.

Repeatability was determined for chromatographic area relative to that of tripropyltin (TPrT), used as internal standard (IS). The results are presented in Table 3 in order of retention time. It is apparent that with this internal standard repeatability is best for the less volatile compounds (DPhT, DOcT, and TPhT). This problem has been previously emphasized by Le Gac et al. [27]. In this work the use of another, less volatile, internal standard, diheptyltin (DHePT), was tested. As is apparent from Table 3, the repeatability is especially improved for the less volatile compounds, i.e. triphenyltin and dioctyltin. Obviously, the repeatability obtained for the most volatile analytes (from MBT to TBT) is better with TPrT than with DHePT, which confirms that an internal standard of similar volatility must be chosen for determination of a given OTC.

Validation and applications

The HS-SPME–GC–PFPD method was then validated by analysis of two certified reference materials (CRMs) and applied to three harbour sediment samples.

Certified reference materials

Freshwater and marine sediments (BCR646 and PACS-2, respectively) were selected for study. PACS-2 is certified for its butyltin content (TBT, DBT, and MBT) whereas BCR 646 is certified for its butyltin and phenyltin (TPhT, DPhT, and MPhT) content. The Table 4 shows that all experimental values are in good agreement with certified values except that the value found for MBT in PACS-2 is higher than the certified value. This has already been reported by several authors—the concentration of MBT has

Table 3 Comparison of the limits of detection (LOD; ng (Sn) L^{-1}) and repeatability of some SPME-based procedures for determination of organotin compounds

Extraction Mode		fibre	MBT	DBT	MPhT	TBT	MOcT	DPhT	TPhT	DOcT	Ref.
HS-SPME GC–PFPD	LOD (ng Sn L^{-1})	Carboxen	0.04	0.02	0.01	0.07	0.03	11	0.01	17	[27]
	RSD (%)	PDMS	9	11	16	9	15	15	21	19	
SPME–GC–FPD	LOD (ng Sn L^{-1})	PDMS	2	2	1	4	ND	2	3	ND	[23]
	RSD (%)		11	8	7	11	ND	8	9	ND	
SPME–GC–FPD	LOD(ng Sn L^{-1})	PDMS	0.004	0.001	0.008	0.001	ND	0.013	0.2	ND	[24]
	RSD (%)		3	3	9	5	ND	8	16	ND	
HS-SPME–GC–PFPD	LOD (ng Sn L^{-1})	PDMS	0.02	0.05	0.003	0.02	0.01	0.01	0.73	0.4	This work
	RSD (%) [a]		2	8	10	5	4	24	9	21	
	RSD (%) [b]		15	18	23	20	9	9	8	11	
	Linearity (pg)		LOQ-600	LOQ-600	LOQ-800	LOQ-600	LOQ-600	LOQ-600	LOQ-800	LOQ-600	

[a]Tripropyltin as internal standard (IS)
[b]Diheptyltin as IS
ND—not determined, LOQ—limit of quantification

ranged from 500 to 2,000 ng (*Sn*) g^{-1} depending on the detector used [37–39]. Blank analysis was performed to verify there was no contamination by MBT, with satisfactory results. Unfortunately, no study has yet explained this discrepancy.

Finally, it is probable that slight degradation of TBT occurred in the reference material.

Surface sediment samples collected from two harbours in Chile were analysed. The results are compared with those obtained by an alternative procedure based on classical liquid–liquid extraction (LLE), which has been previously optimised and validated [17]. The results are also presented in Table 4. Butyltin compounds (only) were detected in all the samples analysed. The concentrations obtained by use of both methods are of the same order of magnitude. Differences probably arise because matrix effects are substantially reduced in HS-SPME–GC–PFPD, which requires a smaller amount of acidic extract than LLE and in which the fibre has no direct contact with the aqueous phase. Sediment samples ST4 and ST5 were both collected from the same harbour on the South Chilean coast, where dry-docking and the fishery-exploitation activity are currently conducted, whereas sample SVF comes from a port where activities are mainly commercial. Finally, the amounts of organotin compounds found, especially TBT compounds, emphasise there is significant contamination of Chilean harbours, with possible environmental consequences.

Table 4 Determination of OTC in certified sediment samples (freshwater sediment BCR 646 and marine sediment PACS 2) by LLE- and SPME–GC–PFPD

Sample	Analytical Method	Concentration in ng (Sn) g^{-1} (dry mass) $\pm \sigma^a$ *[in ng g^{-1} (dry mass) $\pm \sigma^a$]*					
		MBT	DBT	TBT	MPhT	DPhT	TPhT
BCR 646	HS-SPME-GC–PFPD	429±35 *[636±52]*	344±23 *[676±45]*	171±12 *[419±29]*	59±8 *[98±13]*	13±2 *[30±5]*	6±1 *[18±3]*
	Certified values	411±81 *[610±120]*	392±46 *[770±90]*	196±33 *[480±80]*	42±11 *[69±18]*	16±3 *[36±8]*	10±4 *[29±11]*
PACS-2	HS-SPME-GC–PFPD	560±30 *[830±44]*	1037±41 *[2039±81]*	879±59 *[2153±144]*	<LOD	<LOD	<LOD
	Certified values	300 *[445]*[b]	1090±150 *[2143±295]*	980±180 *[2400±441]*	<LOD	<LOD	<LOD
ST4	HS-SPME-GC–PFPD	24±2 *[36±3]*	120±11 *[236±22]*	331±23 *[811±56]*	<LOD	<LOD	<LOD
	LLE-GC–PFPD	16±2 *[24±3]*	97±3 *[191±6]*	354±30 *[867±74]*	<LOD	<LOD	<LOD
ST5	HS-SPME-GC–PFPD	10±1 *[15±2]*	35±3 *[69±6]*	88±7 *[216±17]*	<LOD	<LOD	<LOD
	LLE-GC–PFPD	6.1±0.5 *[9.0±0.7]*	19±1 *[37±2]*	117±6 *[287±15]*	<LOD	<LOD	<LOD
SVF	HS-SPME-GC–PFPD	44±3 *[65±4]*	90±4 *[177±8]*	186±2 *[456±5]*	<LOD	<LOD	<LOD
	LLE-GC–PFPD	49±1 *[73±2]*	97±3 *[191±6]*	196±10 *[480±24]*	<LOD	<LOD	<LOD

[a]σ is the standard deviation (n=4)
[b]Indicative values

Conclusion

Determination of organotin compounds by ethylation–HS SPME then GC–PFPD is an efficient, rapid and simple technique for simultaneous analysis of the nine organotin compounds selected. Experimental design methodology enabled accurate determination and optimization of conditions affecting the headspace SPME procedure. Detection limits reached sub ng (*Sn*) L^{-1} levels for most of the organotin compounds. Analysis of certified reference materials and environmental sediment samples demonstrated the suitability of the method. Headspace SPME seems to be a convenient method for determination of organotin compounds in the environment and for monitoring their biogeochemical cycle.

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