Journal of Chromatography A, 1223 (2012) 9–14

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Critical evaluation of fiber coatings for organotin determination by using solid phase microextraction in headspace mode

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ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form 7 December 2011
Accepted 8 December 2011
Available online 16 December 2011

Keywords:
Solid phase microextraction (SPME)
Organotin compounds
Experimental design
Gas chromatography-pulsed flame photometric detection (GC-PFPD)

ABSTRACT

In the present work three different SPME fibers have been investigated for simultaneous determination of methyl-, butyl- and phenyltins by using gas chromatography-pulsed flame photometer detection (GC-PFPD). The optimal experimental conditions for each fiber were determined and the respective figures of merit were evaluated. All fiber evaluated presented similar limit of detection (sub ng L^{-1}) and requires two internal standards to reach an acceptable repeatability. However, the CAR-PDMS fiber offers the best compromise between selectivity and sensibility for determination of organotins selected. The developed method was validated for analysis of certified reference material and spiked samples, obtaining satisfactory results. Finally, some contaminated samples were analyzed demonstrating the applicability of developed method for determination of organotin compounds in the environment and for monitoring their biochemical cycle.

1. Introduction

The toxicity of organotin compounds (OTCs) is widely recognized and their toxic effects on different biological species such as aquatic organisms and mammals have been well documented [1,2]. Several constrains have been imposed to their industrial application, specially for tributyltin used as active biocide in antifouling paints, attempting to avoid pollution of different ecosystems, particularly aquatic medium [3]. Besides, recently the European Union has classified these compounds as priority pollutants in according with Water framework Directive (2000/60/EC) and Pollutant Emission Register (2000/479/EC).

Several analytical methodologies have been proposed to evaluate environmental pollution due to OTC and to monitor the effectiveness of organotin banning [4–6]. In general, they are based on a gas chromatographic separation and detection with a selective detector system, such as ICP-MS and PFPD. This approach requires a previous derivatization step to transform OTC in volatile and thermally stable compounds. The most common reagent used for this aim is sodium tetraethylborate, because it offers a relatively fast and simple way to obtain derivatized organotins in an aqueous medium [7].

On another hand, these compounds are present in environmental samples at trace levels and its determination requires sensitive analytical methodologies. Several pre-concentration procedures have been proposed based on liquid–liquid extraction (LLE) [8,9], solid phase microextraction (SPME) [10,11] and recently, liquid phase microextraction (LPME) [12] to increase sensibility. The SPME is a free-solvent technique, environment-friendly, and it presents several advantages such as a high pre-concentration power, no significant interaction with matrix when headspace mode is applied [13]. This technique has been applied for determination of butyl and phenyltins in natural water, sediments, biological samples and beverages with satisfactory results [14–17]. For organometallic analysis, several variables can be considered to improve the performance of SPME procedure such as procedure extraction (direct or headspace), sampling time, sampling temperature, thermal desorption conditions, derivatization process and nature of SPME fiber [18]. Polydimethylsiloxane (PDMS), initially proposed for volatile and non-polar compounds, is the most commonly coating applied for butyl- and phenyltin determination in various matrices [13,19]. Only two works were found in the literature proposing other SPME coatings. In the first, Le Gac et al. evaluated Carboxen-PDMS (CAR-PDMS) fiber for simultaneous determination of methyl-, butyl-, phenyl- and octyltins [14]. In the second, Bianchi et al. evaluated the figures of merit of three different SPME fibers for determination of trimethyl-, dibutyl- and tributyltin, resulting divinylbenzene-CAR-PDMS (DVB-CAR-PDMS) as the best alternative [20]. However, till today, a systematic evaluation of these different SPME coatings for organotin determination in environmental samples has not been carried out.

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doi:10.1016/j.chroma.2011.12.038

In the present work PDMS, CAR-PDMS and DVB-CAR-PDMS coatings have been evaluated and analytical performances compared for simultaneous determination of twelve organotin compounds in environmental samples including methyl-, butyl- and phenyltins in headspace mode. At best of our knowledge, no similar studies have been reported for organotin speciation analysis based on solid phase microextraction procedure.

2. Experimental

2.1. Materials

For the analysis of organotin compounds, a Varian 3800 gas chromatograph (Walnut Creek, CA USA) equipped with a PFPD system, Varian 1079 split/splitless injector and a capillary column CP-Sil 5 CB (30 m × 0.25 mm × 0.25 μm; Varian, USA) with Nitrogen as a carrier gas (flow: 2 mL min^{-1}) was used. The oven temperature was initially held at 50 °C for 0.5 min, and then programmed at 10 °C/min to 200 °C and at 30 °C/min to the final temperature of 290 °C which was held for 4 min. A high transmission band filter (320–540 nm; BG 12, Schott, France) was selected to observe the emission from Sn-C, with a gate delay of 3.0 ms and a gate width of 2.0 ms.

A mechanical table with elliptical stirring (NB-101 M, N-Biotek Inc., Gyeonggi-Do, Korea) was used for the extraction of organotin compounds from solid samples and for the derivatization/extraction step. A magnetic stirrer (Cole, Parmer, USA) was used for the screening study in the derivatization/extraction.

For the SPME procedures, a manual SPME holder and fibers were obtained from SUPELCO (Bellefonte, PA, USA). The SPME fibers evaluated in this study were PDMS (100 μm thickness), CAR/PDMS (75 μm thickness) and DVB/CAR/PDMS (50/30 μm thickness). For ethylation/extraction procedure, 50 mL glass reaction vials closed with PTFE coated silicone rubber septa (SUPELCO, Bellefonte, PA, USA) were used.

2.2. Reagents and standards

High quality water (18 MΩ) obtained from a Milli-pore system (Millipore, Bedford, MA, USA) was used to prepare the solutions. The organotin standards, such as monomethyltin trichloride (MMT, 97%), dimethyltin dichloride (DMT, 97%), trimethyltin chloride (TMT, 97%), monobutiltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 96%), tributyltin chloride (TBT, 96%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), triphenyltin chloride (TPhT, 95%) and tripropyltin chloride (TPrT, 98%) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Monooctyltin trichloride (MOcT, 96%), dioctyltin dichloride (DOcT, 97%) and trioctyltin chloride (TOcT, 98%) were obtained from LGC Standards (Augsburg, Germany). Stock solutions of these reagents (1000 mg L^{-1} of tin) were prepared in methanol and stored at −20 °C in the dark. Working standards were obtained by dilution with water, weekly for solutions of 10 mg (Sn) L^{-1} and daily for 10–100 μg (Sn) L^{-1}.

Sodium acetate and acetic acid were obtained from J.T. Baker (Baker analyzed). Sodium chloride (Suprapur) was obtained from Merck and sodium tetraethylborate ($NaBEt_4$) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Aqueous ethylating solution (1%, m/v) was prepared just before a set of analysis and stored at 4 °C in the dark.

Glassware was rinsed with deionized water, decontaminated overnight in 20% (v/v) nitric acid solution and then rinsed again with deionized water.

Table 1
Experimental factors and intervals considered in (a) screening and (b) optimization steps.

(a) Screening study

Factors	Levels		Response[a]		
	−1	+1	Mean	Sum	Desirability
(A) Equilibrium time (min)	4	15	NS[b]	NS	NS
(B) Sorption time (min)	15	40	S[c]	S	S
(C) Type of agitation	Magnetic	Mechanic	S	S	S
(D) Agitation rate (rpm)	200	400	NS	NS	NS
(E) Air/water ratio	0.5	11	NS	NS	NS
(F) NaCl (%)	0	4	NS	NS	NS

(b) Optimization

Factors	Levels				
	$-\alpha$	−1	0	+1	$+\alpha$
Sorption time (min)	9.8	15	27.5	40	45.2
Agitation rate (rpm)	279	300	350	400	421

[a] This response considers the effect of each variable for three fibers.
[b] No significant at 95% of confidence.
[c] Significant at 95% of confidence.

2.3. Optimization of solid phase microextraction procedure

A Plackett-Burman design was used to evaluate the influence of factors involved in the SPME procedure in a reduced number of runs for three fibers considered in this study. The examined variables and the levels considered in this screening are presented in Table 1. All experiments was carried out using 15.0 mL of sodium acetate–acetic acid buffer solution (0.5 mol L^{-1}; pH 4.8) spiked with the appropriate amount of the analytes in a range between 0.01 and 20 ng (expressed as tin content) for each fiber and the instrumental response registered was the absolute chromatographic area obtained through GC-PFPD. Besides, in order to simplify the OTC response matrix and to find compromise conditions, different combined responses were evaluated such as mean, sum and total desirability (D) obtained as geometrical mean of individual Derringer functions for each compound (d_i). In the last case the individual desirability for OTC response were obtained by maximization (unilateral; weight factor, $s = 1$; impact factor, $I = 3$). Subsequently, a composite central design was set up for the optimization of significant experimental factors, analyzing the individual response and then applying the above mentioned desirability function. The obtained models of the regression were validated and analyzed using the analysis of variance (ANOVA). The Statgraphics plus 5.0 software package was used for the statistical and mathematical calculations involved in this study, which provided a flexible, step-by-step approach.

2.4. Evaluation of figures of merit

Analytical figures of merit, such as detection limit (LOD), quantification limit (LOQ) and precision (relative standard deviation, % RSD) were evaluated according IUPAC recommendations for each fiber support studied [21,22].

The accuracy of the developed methodology was assessed by the determination of butyltin compounds in a certified reference material (PACS-2). This sample was also spiked with methyl and phenyltin compounds to evaluate the recovery. For water samples, accuracy was also assessed by recovery assays for all organotin compounds considered in this study. Both samples were analyzed

in triplicate and using standard addition with TPrT or DHepT as internal standards (I.S.).

In order to evaluate precision, two different internal standards were used, such as tripropyltin (TPrT) and diheptyltin (DHepT). For this purpose, the %RSD was evaluated from an aqueous solution containing buffer and an appropriate amount of analytes, varying from 0.05 to 100 ng as tin content, depending of each organotin and fiber support.

For all organotin compounds, precision was evaluated according to relative response (analyte/I.S area-ratio) and analyses were run in triplicate.

2.5. Sample collection and treatment

Surface sediment samples were collected from a harbor placed in Iquique city, a northern city in Chile, in which dry-docking and harbor/commercial activities are currently carried out. The collected samples were freeze dried, sieved at 63 μm and stored at −20° C until analysis. These samples were labeled E15 (Caleta Riquelme) and E16 (Club de Yates).

Seawater samples were collected from coastal areas of Valparaiso bay, a place where dry-docking activities are currently carried out. An aliquot of 2.5 L was collected in clean polyethylene bottles and transported immediately to the laboratory. Then, these samples were filtered, the pH was adjusted at 2.0 with hydrochloric acid and stored at −20 °C until analysis.

2.6. Analysis of organotin speciation in environmental samples

For sediments, the extraction procedure was based on a previously optimized procedure [8,23], in which 0.5–1.0 g (±0.5 mg) of a freeze dried sample was placed into a capped 50-mL polycarbonate tube followed by the addition of 100 μL of a 500 μg (Sn) L^{-1} TPrT solution, 250 μL of a 10 mg (Sn) L^{-1} DHepT solution and 20 mL of glacial acetic acid. The tubes were stirred at 420 rpm for 12–14 h. Then, 50 μL of the acidic extract was introduced immediately into a 50-mL reactor containing 15 mL of 0.5 mol L^{-1} sodium acetate/acetic buffer (pH 4.8). Ethylation was carried out using 50 μL of $NaBEt_4$ solution (1%, w/v) in according to previously optimized conditions. The mixture was stirred at 420 rpm for 10 min on the elliptic table to reach the equilibrium state. After that, the SPME fiber was placed into the headspace volume and the mixture was stirred again during 45 min. Then, the fiber was directly introduced into the GC-PFPD system for thermal desorption of the OTC.

For seawater analysis, a 0.5–5.0 mL aliquot of sample was directly introduced into the derivatisation reactor, containing 15 mL of buffer. 100 μL of a TPrT and DHepT solution (2 μg (Sn) L^{-1} and 50 μg (Sn) L^{-1}, respectively) was added to the reactor followed by the addition of 50 μL of $NaBEt_4$ solution. HS-SPME procedure was the same used for sediment samples, detailed above.

Finally, all environmental samples were analyzed in triplicate and using standard addition with TPrT or DHepT as internal standards (I.S.).

3. Results and discussion

3.1. Optimization of the HS-SPME procedure

In the SPME optimization, six factors were defined to evaluate their contribution to the extraction efficiency for PDMS, CAR-PDMS and DVB-CAR-PDMS fibers. A Plackett-Burman design was used to evaluate the effect of single factors considering three alternatives of response: mean, sum and total desirability of individual chromatographic areas obtained for each fiber. Considering the ANOVA of results, the three approaches led to obtain similar conclusions for three SPME coatings (see Table 1) and showed that, in decreasing order, agitation type and sorption time had a significant positive effect on the SPME efficiency, suggesting that SPME process depends of extraction kinetic. Then mechanical agitation was selected and the no-significant factors were fixed at the lower level for the next experiments.

In a second step, agitation rate and sorption time were simultaneously optimized through a central composite design obtaining the respective surface response of desirability for each coating (Fig. 1). Clearly, a constant increase of the response was observed for the three coating in the measure that the sorption time and agitation rate were increased, obtaining a maximum response for the extreme positive values of these factors (45 min and 420 rpm). Except for PDMS, the response evaluated did not attain a maximum value suggesting that the partition equilibrium is not reached on these solid phases that showing higher sorption capacity. This fact is clearly evidenced for the CAR-PDMS and it can be attributed to particular sorption mechanism of this fiber. This coating possess enough small pores to cause capillary condensation, increasing the sorption capacity and requiring long extraction times to reach equilibrium [24]. Additionally, different sorption kinetic of each organotin on SPME support can be equally attained. In previous work, it has been reported that the less volatile organotins require large extraction times to reach the equilibrium in headspace mode [25], and then, the experimental conditions estimated for desirability function can be influenced for this behavior, being different of optimum.

Finally, a typical chromatogram obtained in optimal conditions for a standard solution using CAR-PDMS coating is presented in Fig. 2A. A well resolved chromatogram can be appreciated for all organotins considered in this study, demonstrating an adequate analytical performance for separation and detection of methyl-, butyl- and phenyltins, mandatory requirement for simultaneous determination of these compounds.

3.2. Analytical performances of HS-SPME procedure

The analytical parameters of HS-SPME–GC-PFPD using the three fiber supports under optimized conditions have been exhaustively evaluated and the results are summarized in Table 2. As can be observed, the most volatile organotins (methyl-, butyltins and MPhT) present the lowest error when tripropyltin (TPrT) is used as internal standard; while the repeatability is considerably improved for less volatile organotins (DPhT and TPhT) when diheptyltin (DHepT) is applied as internal standard. The typical internal standard used in any analytical method devoted for butyl- and phenyltin determination is TPrT, and its applicability has been widely validated considering the large number of works reported using this compound. The effectiveness of DHepT to improve precision for less volatile compounds has been reported previously and it was attributed to similar sorption behavior between these compounds and internal standards [15,25].

In consideration of coating nature, the fibers present similar precision for volatiles organotins, while significant differences can be observed for less volatile, particularly for DVB-CAR-PDMS, showing the highest relative error. However, considering the applicability of this method, the objective is to propose an alternative for simultaneous determination of methyl-, butyl- and phenyltins, CAR-PDMS presents the best precision for all organotins evaluated.

According to explanation above, the figures of merit were determined by using TPrT and DHepT as internal standards. As can be seen in Table 2, the methodology evaluated based on HS-SPME is very sensitive allowing determination of organotins at the ng Sn L^{-1} level. However, comparing the performance of three fibers, the lowest detection limits (ng L^{-1}) were obtained with CAR-PDMS.

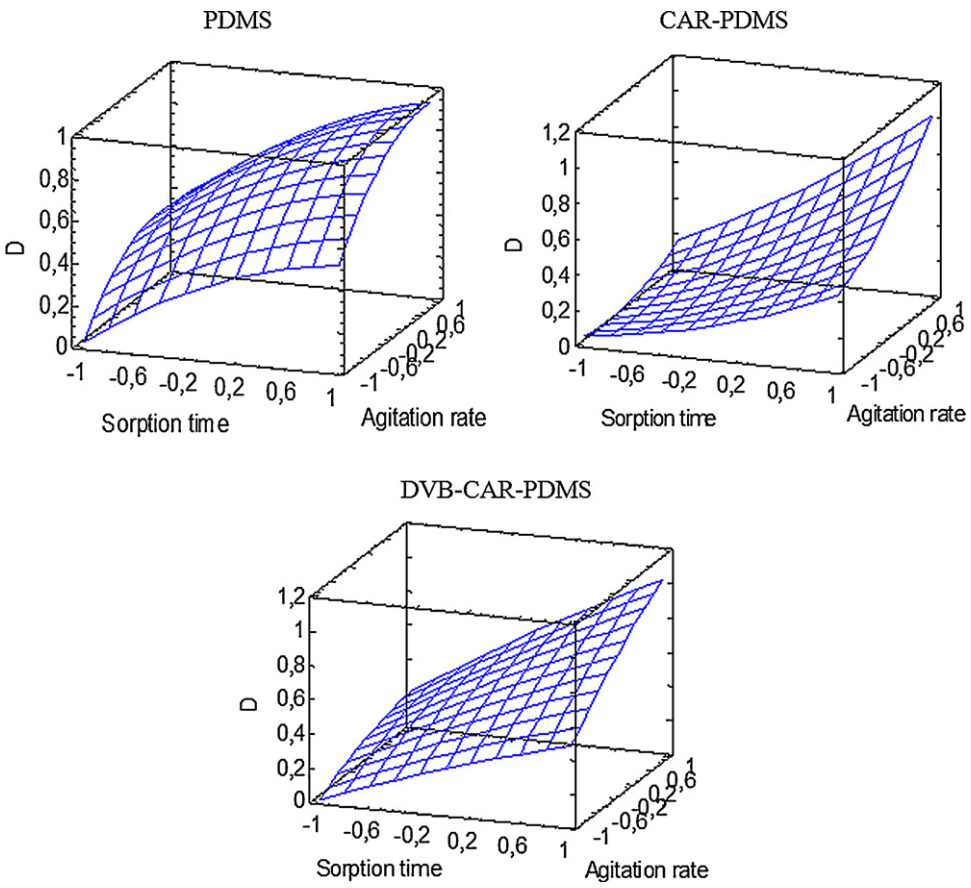

Fig. 1. Response surfaces corresponding to the desirability function obtained for each SPME coating during optimization of HS-SPME procedure. The factors optimized were agitation rate and sorption time by analyzing 12 responses simultaneously, corresponding to methyl-, butyl- and phenyltins.

These values are comparable or much lower than the former reports obtained with similar equipment [14,15,26,27]. The PDMS coatings offer figures of merits similar to CAR-PDMS, and it could be applied to resolve equivalent analytical problems.

Finally, DVB-CAR-PDMS presents the lowest sensitivity, evidenced in the highest detection limit obtained, probably due to low affinity of ethylated organotins for this polar coating. In order of figures of merit, this fiber could be considered for analysis of highly contaminated samples or when high quantities of samples are available.

3.3. Validation of analytical methodology

After optimization, the HS-SPME methodology was validated by the analysis of a certified reference material (PACS-2, certified in butyltins) spiked with methyl- and phenyltins and a seawater sample spiked with all the organotin compounds considered in this study. A representative chromatogram obtained for spiked PACS-2 is presented in Fig. 2B. Other chromatographic signals can be observed together with corresponding organotins peaks. In a previous study, these signals were attributed to ethylated-sulfur

Table 2
Analytical performances for the three fiber coatings evaluated in optimal conditions.

Fiber coating	Analytical performance	MMT	DMT	TMT	MBT	DBT	TBT	MPhT	DPhT	TPhT
PDMS	RSD(%)[a]	7	7	9	5	4	4	9	26	31
	RSD(%)[b]	23	29	23	32	30	31	27	7	6
	L.O.D. (ng)	0.36	0.73	0.39	0.01	0.01	0.01	0.03	0.11	0.11
	L.O.Q. (ng)	1.20	2.43	1.30	0.03	0.03	0.03	0.10	0.37	0.37
	Linear range (ng)	LOQ-10	LOQ-10	LOQ-10	LOQ-0.8	LOQ-0.8	LOQ-0.8	LOQ-0.8	LOQ-10	LOQ-20
CAR/PDMS	RSD(%)[a]	3	6	3	4	7	4	5	20	21
	RSD(%)[b]	21	24	26	20	24	19	18	3	8
	L.O.D. (ng)	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.11	0.13
	L.O.Q. (ng)	0.07	0.07	0.07	0.07	0.07	0.10	0.13	0.37	0.43
	Linear range (ng)	LOQ-3	LOQ-5	LOQ-3	LOQ-0.8	LOQ-0.8	LOQ-0.8	LOQ-0.8	LOQ-20	LOQ-25
DVB/CAR/PDMS	RSD(%)[a]	7	6	10	7	5	5	4	39	43
	RSD(%)[b]	36	70	26	21	54	6	32	10	6
	L.O.D. (ng)	0.04	0.17	0.45	0.11	0.06	0.10	0.17	0.64	0.99
	L.O.Q. (ng)	0.13	0.57	1.50	0.37	0.20	0.33	0.57	2.13	3.30
	Linear range (ng)	LOQ-3	LOQ-3	LOQ-6	LOQ-5	LOQ-2	LOQ-3	LOQ-2	LOQ-10	LOQ-50

[a] Relative standard deviation evaluated using tripropyltin as Internal standard.
[b] Relative standard deviation evaluated using diheptyltin as internal standard.

Table 3
Determination of organotin compounds in a certified sediment sample (PACS-2) and in spiked seawater sample.

	PACS-2 ng (Sn) g^{-1} dry weight[a]				Spiked seawater ng (Sn) L^{-1} [b]			
	Certified or spiked value	Value found			Spiked value	Value found		
		PDMS	CAR/PDMS	DVB/CAR/PDMS		PDMS	CAR/PDMS	DVB/CAR/PDMS
MBT	600[c]	587 ± 30	597 ± 32	616 ± 31	100	94 ± 5	103 ± 4	96 ± 5
DBT	1047 ± 64	1075 ± 39	1080 ± 47	1019 ± 25	100	94 ± 4	101 ± 7	96 ± 6
TBT	890 ± 105	910 ± 32	879 ± 25	846 ± 28	100	102 ± 5	95 ± 4	106 ± 6
MMT	500	375 ± 25	443 ± 14	425 ± 25	150	131 ± 8	139 ± 9	130 ± 10
DMT	500	395 ± 30	415 ± 31	455 ± 21	150	137 ± 9	142 ± 7	130 ± 9
TMT	500	351 ± 18	391 ± 24	435 ± 27	150	135 ± 9	127 ± 10	132 ± 8
MPhT	600	612 ± 21	609 ± 18	562 ± 18	200	203 ± 12	209 ± 15	182 ± 10
DPhT	700	675 ± 31	659 ± 20	669 ± 19	200	205 ± 12	194 ± 10	191 ± 11
TPhT	700	678 ± 65	659 ± 38	629 ± 49	250	256 ± 12	241 ± 13	230 ± 9

[a] PACS-2 sample was spiked with methyl- and phenyltins at indicated concentration.
[b] Seawater sample was spiked with butyl-, methyl- and phenyltins at indicated concentration.
[c] Indicative value.

Table 4
Determination of organotin compounds in environmental samples.

	MMT	DMT	TMT	MBT	DBT	TBT	MPhT	DPhT	TPhT
Sediments [concentrations in ng (Sn) g^{-1} dry]									
E 15 Caleta Riquelme	N.D.	N.D.	N.D.	234 ± 10	116 ± 4	512 ± 19	N.D.	N.D.	N.D.
E 16 Club de Yates	N.D.	N.D.	N.D.	412 ± 13	471 ± 21	1017 ± 37	N.D.	N.D.	N.D.
Sea waters [concentrations in ng (Sn) L^{-1}]									
Molo	18 ± 3	8.7 ± 0.5	N.D.	N.D.	N.D.	55 ± 2	N.D.	N.D.	N.D.
Dique	12 ± 1	9.1 ± 0.8	N.D.	N.D.	N.D.	72 ± 4	N.D.	N.D.	N.D.

N.D., not detected.

compounds and represent a potential interference when the PFPD is used in tin speciation analysis [9]. These species are not detected when classical liquid–liquid extraction probably due to low sensitivity of this technique compared to SPME. However, for conditions used in this work, these signals do not represent an inconvenient to quantify organotins and reliable results could be obtained.

The results obtained after analysis of these samples are presented in Table 3. As can be seen, the found values are statistically similar ($p < 0.05$) to certified and spiked levels for both samples, except that the values found for methyltins in sediments are lower than spiked values. The determination of methyltins in environmental samples using SPME has been scarcely reported in literature and to propose an explanation for these results is not evident. However, some sources of this bias can be revised. Considering the lower boiling point of methyltins, an eventual loss of these compounds can occur during application of SPME procedure. The evaluation of other internal standards could be corrected this inconvenient. However, other standards commercially available were evaluated (i.e. monoheptyltin and tetrapropyltin) and no significant improvements are reached. Additionally, the low recovery can be equally attributed to uncompleted thermal desorption in injection step, phenomenon commonly reported with the CAR-PDMS fiber [24]. However, the systematic analysis of fiber-blanks (direct injection of fiber after previous injection of a sample) between samples was carried out without detection of memory effect.

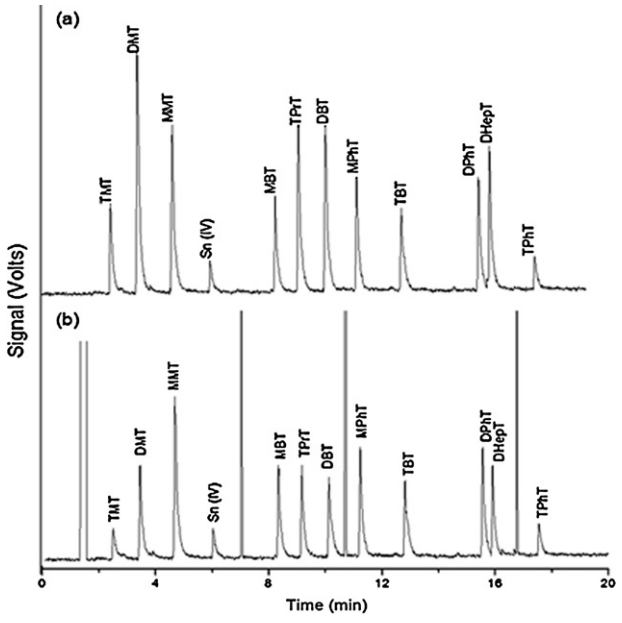

Fig. 2. Typical chromatogram obtained by HS-SPME–GC-PFPD using CAR/PDMS coating in the optimal conditions for (a) A synthetic standard solution and (b) PACS-2 CRM sediment spiked with methyl- and phenyltins.

3.4. Applications to environmental samples

The three fibers evaluated offers similar figures of merit to quantify organotins in environmental samples. However, considering precision and detection limits, CAR/PDMS fiber appears as the best alternative for simultaneous analysis of these compounds and it was selected for posterior analysis.

In this way, the validated methodology was applied to the analysis of marine sediments and sea waters from impacted zones in the Chilean littoral, such as Iquique and Valparaíso harbors. The values obtained are presented in Table 4. The presence of butyltins, especially TBT, in sediments samples is clearly noted with levels varying from 116 to 1017 ng g^{-1} suggesting a recent contamination due to the use of tin-based antifouling paints.

The HS-SPME was also applied to the analysis of sea waters from the bay of Valparaíso, where methyl- and butyltin compounds were detected. The presence of butyltins in these samples, especially TBT, indicates a noticeably contamination derived from harbors activities. Whereas the presence of MMT and DMT may be attributed to biomethylation phenomena of inorganic tin [28]. The levels of concentration of these organotin compounds in sea waters is very

low, ranged between 9 and 72 ng (Sn) L^{-1} demonstrating the suitability of the HS-SPME procedure for organotin speciation in these environmental samples.

4. Conclusions

The analytical performance of three SPME fibers was critically evaluated. In optimal conditions, the fibers PDMS, CAR-PDMS and DVB-CAR-PDMS present similar figures of merit, allowing determination of OTC at sub ng (Sn) L^{-1}. However, CAR-PDMS showed the lowest detection limit and highest precision, appearing as the best choice for the simultaneous determination of methyl-, butyl- and phenyltins in environmental samples with low organotin levels. In accordance with figures of merit, PDMS and DVB-CAR-PDMS could be proposed as an alternative to CAR-PDMS for analysis of contaminated samples.

Analysis of certified reference materials and environmental samples demonstrated the suitability of the method, seems to be a convenient method for the determination of organotins compounds in the environment and for monitoring their biochemical cycle.

Finally, in comparison with classical approaches such as solid-phase extraction or liquid–liquid extraction, the proposed methodology based on SPME required a little sample size to obtain reliable results, producing low waste quantities and demonstrating to be an effective environment-friendly analytical tool.

Acknowledgements

The authors gratefully acknowledge FONDECYT (Project 11080197). Aníbal Valenzuela thank CONICYT for the doctoral fellowship grant.

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