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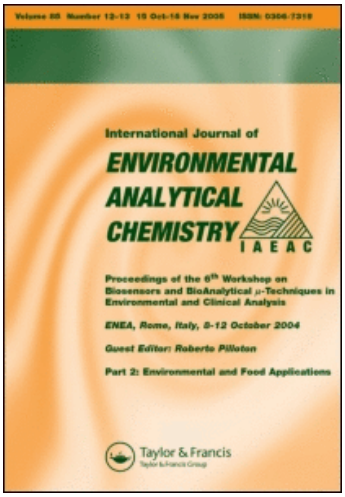

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Determination of organotins in aquatic plants by headspace SPME followed by GC-PFPD determination

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Optimal conditions of headspace solid-phase microextraction followed by gas chromatography coupled to pulsed flame photometric detection (SPME–GC–PFPD) have been investigated to validate the analysis of 11 organotin compounds in plant matrices including methyl-, butyl-, and phenyltin compounds. The extraction of organotin compounds from vegetal matrices has been carried out using optimized conditions of HCl-based extraction. The use of headspace SPME to preconcentrate the analytes allowed most of the detection limits to be obtained sub-0.5 ng(Sn) g^{-1}. The precision evaluated using RSD with six replicates ranges between 5 and 10% (except for triphenyltin: 17%). The accuracy of the method was validated on spiked or polluted vegetal samples taken from Bizerte Lagoon (Tunisia) and by comparison with classical liquid–liquid extraction (LLE). These results highlight the suitability of the selected method for organotin control in complex environmental matrices such as aquatic plants.

Keywords: Organotin compounds; Headspace solid-phase microextraction; Vegetal matrices; Validation; Algae of Bizerte Lagoon

1. Introduction

Organotin compounds (OTC) have been widely used previously as poly(vinylchloride) stabilizers, wood preservatives, biocides, and catalysts in many industrial processes [1, 2]. These numerous applications led to direct or indirect diffusion of free organotins in the environment [3]. A number of studies have demonstrated the high ecotoxicological risk of these compounds on marine ecosystems at low concentration levels, especially tributyltin (TBT) and triphenyltin (TPhT) compounds [4–6]. This situation induced the development of sensitive and accurate analytical methods for the speciation and detection of these elements in environmental matrices [7].

The most widely applied separation technique in organotin speciation analysis is gas chromatography (GC) combined with element-selective detection such as atomic

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absorption spectrometry (AAS) [8, 9], mass spectrometry (MS) [10], flame-photometric detection (FPD) [11], direct-current plasma (DCP) [12], microwave-induced plasma atomic emission spectrometry (MIP-AES) [13], inductively coupled plasma-mass spectrometry (ICP-MS) [14], and, more recently, a new generation of FPD based on a pulsed flame: the PFPD developed by Amirav and Jing about 10 years ago [15].

Prior to the instrumentation step, OTC are simultaneously derivatized into volatile GC amenable species and extracted from the matrix. Recently, a speciation procedure based on a derivatization step with sodium tetraethylborate ($NaBEt_4$) and solid-phase microextraction (SPME) has been proposed for the determination of methyl-, butyl-, phenyl-, and octyltin compounds [16]. The application of SPME to the analysis of OTC has already been reported [17–21]. This solvent-free extraction technique offers numerous advantages such as rapidity, simplicity of use, and high preconcentration power [22, 23]. Usually, two basic types of extraction mode can be performed using SPME: direct and headspace extraction. In the direct extraction mode, the coated fibre is inserted into the sample medium, and the analytes are transported directly to the extraction phase. In the headspace mode, the analytes need to be transported through a layer of air before they can reach the coating. This mode allows the decrease of matrix effects occurring with complex samples such as biological matrices and protects the fibre from damage by high-molecular-weight species [24].

In this article, optimal conditions of headspace SPME–GC–PFPD have been evaluated on algal matrices and validated for the speciation of methyl-, butyl-, and phenyltin compounds. These environmental matrices play an important role in the aquatic food chain [25] and have a completely different composition with other matrices such as sediments or animal tissues. Therefore, the development of rapid and accurate speciation procedures specific to these vegetal samples is of great interest, especially for the evaluation and quantification of the OTC transfer in marine ecosystems [26].

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2. Experimental

2.1 *Apparatus*

A Varian 3800 GC (Walnut Creek, CA) equipped with a PFPD system and a 1079 split/splitless injector was used. The GC separation was carried out on a capillary column (Walnut Creek, CA) coated with 5% phenyl, 95% polydimethylsiloxane. The column temperature was held at 50°C for 30 s and increased to 200°C at the rate of $30^{\circ}C\,min^{-1}$ to a final temperature of 270°C, which was held for 3 min. Nitrogen was used as carrier gas, with a flow rate of $2\,mL\,min^{-1}$. The detection parameters have been described elsewhere [27].

The manual SPME device was obtained from Supelco (Bellefonte, PA). The fibre used was the 75-μm thickness Carboxen-PDMS (CAR-PDMS) fibre. For the derivatization/extraction step, a mechanical table with elliptic stirring KS 2502 basic (Prolabo, Fontenay-sous-Bois, France) was used.

2.2 *Reagents and materials*

Deionized water (18 MΩ) purified with a Milli-Q system (Millipore, Bedford, MA) was applied for the preparation of the solutions. Sodium tetraethylborate ($NaBEt_4$) was

obtained from Galab products (Geesthacht, Germany). Aqueous ethylating solution (1% m/v) was prepared daily.

Sodium ethanoate, isooctane, and nitric and acetic acids were obtained from J.T. Baker (Baker analysed, Deventer, NL). Methanol was purchased from Merck Eurolab (Gradignan, France).

The organotin stock solutions containing 1000 mg(Sn) L^{-1} of monomethyltin trichloride (MMT, 97%), dimethyltin dichloride (DMT, 97%), trimethyltin chloride (TMT, 100%), tetramethyltin (TeMT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%) (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%) (Strem Chemicals), were prepared in methanol. Methyltin solutions were stored in the dark at −20°C. The other organotin solutions were stored in the dark at +4°C.

The glassware and material for extraction were rinsed with deionized water, decontaminated for 2 days in 10% (v/v) nitric acid solution, and rinsed again before use.

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2.3 *Samples*

Aquatic plants (*Elodea*) were taken in the river Gave de PAU. Algae (*Ulva lactuca*) were collected from two different sites of the Bizerte Lagoon situated in the Tunisian country. The large harbour connected to this lagoon and the industrial activities carried out around it may affect the lagoon biodiversity by contamination with OTC compounds. Immediately after their arrival to the laboratory, the plant samples were air-dried and stored frozen at −20°C in the dark until extraction and analysis.

2.4 *Analytical procedure*

2.4.1 Extraction from the sample. The extraction procedure from plant matrices has been optimized and described elsewhere [26]. It was performed as follows: 0.5 g of dried plant powder was introduced into a 50 mL polycarbonate tube with 50 µL of a 100 µg(Sn) L^{-1} TPrT used as internal standard and 2.5 mL of ethyl ethanoate. The tubes were shaken at 400 rpm for 1 h to humidify the material. Six millilitres of 0.035 M HCl in ethyl ethanoate was then added, and the mixture was shaken for 1 h (400 rpm) and finally centrifuged at 4000 rpm for 10 min.

2.4.2 Derivatization and analysis. A 2 mL volume of centrifuged extract was directly introduced into the derivatization reactor. Ethylation was carried out using $NaBEt_4$ in a sodium ethanoate–ethanoic acid buffer (pH 4.8).

For classical liquid–liquid extraction, 500 µL of $NaBEt_4$ solution, 1 mL of isooctane, and 100 mL of the acid buffer solution were added at the same time, and the mixture was shaken at 420 rpm for 30 min. Subsequently, 1 µL of the organic phase was injected directly into GC-PFPD.

For headspace SPME extraction, 50 µL of the ethylating solution and 70 mL of buffer were introduced into the derivatization vessel. The mixture was stirred

on an elliptic table during 10 min at 400 rpm. After that, the fibre was placed in the headspace volume, and the mixture was stirred again for 30 min. Then, the fibre was directly transferred into the GC injector port for thermal desorption of the analytes. The precise operating conditions are as follows: time of sorption, 30 min; nature of the fibre, CAR-PDMS; injection temperature, 285°C and desorption time, 1.5 min [16].

2.4.3 Quantitation. TPrT was used as internal standard. The results were given in terms of relative peak areas. The TPrT-relative responses of OTC were calculated by standard additions. For each sample, the extraction was duplicated. Two different aliquots of each extract were then ethylated. This methodology allows the matrix effects to be decreased as much as possible.

2.4.4 Spiking. The dried plant material was reduced to powder and spiked by the addition of a methanolic solution of MMT, DMT, TMT, TeMT, MBT, DBT, TBT, TeBT, MPhT, DPhT, and TPhT. Then, the mixture was homogenized for 2 h and finally dried under a gentle flow of nitrogen overnight (12 h). After the spiking procedure, extraction of OTCs from the samples was started.

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3. Results and discussion

3.1 *Method validation*

The method was validated according to the AFNOR regulation XP T 90-210 [28].

3.1.1 Calibration curve and linearity. The linearity of the responses was examined by the injection of several spiked vegetal samples. The linear regression equations were obtained using the least-squares method. An adequacy test to the linear model was carried out to verify the regression model validity and the calibration field [28]. The corresponding results (expressed by the calculated ratios F_1 and F_{nl}) were compared with the critical Fisher values (VC_1 and VC_{nl}, respectively) for a risk level α of 0.01. The test is interpreted into two stages:

- if $F_1 > VC_1$, the regression model can be considered as acceptable;
- if $F_{nl} \leq VC_{nl}$, the selected calibration field can be validated, and the model error is insignificant.

In our case, $VC1 = 9.33$ and $VC_{nl} = 6.93$ [28]. All the results related to the organotins calibration curves and linearity are summarized in table 1. The results show that the regression models and the calibration fields are acceptable for all the OTCs. The regression coefficient for each compound is greater than 0.99 (table 1).

3.1.2 Precision, detection, and quantification limits. Detection limits (LD) and quantification limits (LQ) were calculated respectively as three and 10 times the standard deviation of the blank (obtained from the calibration curve) divided by the sensitivity ($LD = 3s(a_0)/a_1$, $LQ = 10s(a_0)/a_1$) [28] (table 2).

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Table 1. Linearity parameters of headspace SPME–GC–PFPD-based method in spiked aquatic plants.

	MMT	DMT	TMT	TeMT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT
Linearity field ($ng\,g^{-1}$)	8–25	3–25	2–25	2–25	1–8	2–20	1–10	10–60	10–300	20–300	200–1500
Slope (a_1)	0.0184	0.0222	0.0151	0.0075	0.6043	0.0209	0.0384	0.0015	0.0271	0.0012	0.0002
$s(a_1)$[a]	0.0003	0.0003	0.0002	0.0001	0.0046	0.0003	0.0005	0.0000	0.0003	0.0000	0.0000
Intercept (a_0)	–	–	–	–	0.0555	–	–	0.0001	–	0.0043	–
(a_0)	0.0110	0.0096	0.0038	0.0001	–	0.0009	0.0042	–	0.0526	–	0.0058
$s(a_0)$[b]	0.0058	0.0044	0.0027	0.0012	0.0246	0.0037	0.0030	0.0007	0.0442	0.0013	0.0046
R^{2c}	0.9955	0.9977	0.9982	0.9984	0.9992	0.9967	0.9974	0.9978	0.9986	0.9994	0.9917
F_l	2791	5285	9219	9060	17,609	3727	5791	5823	9037	28,645	1492
F_{nl}	0.31	0.19	2.28	1.07	0.99	0.11	1.41	0.33	0.54	2.94	0.23

[a]Standard deviation of the slope ($n=4$).
[b]Standard deviation of the blank.
[c]Correlation coefficient.

Table 2. Precision, detection and quantification limits of the SPME–GC–PFPD-based method in spiked aquatic plants.

	MMT	DMT	TMT	TeMT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT
LD ($ng\,g^{-1}$)	0.35	0.16	0.27	0.48	0.21	0.49	0.12	1.5	2.9	6.7	40
LQ ($ng\,g^{-1}$)	2.6	1.6	1.5	1.6	0.5	1.7	0.67	4.8	14.3	14.1	200
RSD%[a]	9	5	7	6	5	8	6	7	9	10	17

[a]$n = 6$.

The precision of the proposed method is expressed in terms of relative standard deviation (RSD%). In order to test the precision of the overall process, six consecutive injections of a spiked vegetal extract from 4 to 500 ng(Sn) g^{-1} were carried out (table 2).

The organotins detection limits ranged from 0.12 to 40 ng(Sn) g^{-1}. The use of headspace SPME followed by GC-PFPD detection allows most of the OTCs to be determined sub-0.5 ng(Sn) g^{-1}. Such low detection limits, especially for methyl- and butyltins, have not been reported previously for plant matrices [26, 29].

The most volatile compounds do not necessarily have the lowest LDs, probably because of their very low boiling points leading to some losses of analytes.

Phenyltin compounds have the lowest affinity for the CAR/PDMS fibre, especially TPhT (LD = 40 ng g^{-1}), this is probably because the CAR/PDMS fibre has a specific coating that appears more convenient for the extraction of volatile and small analytes [24, 30, 31]. The carboxen coating is based on an adsorption phenomenon, which is a competitive process. Since there are a limited number of sites to which analytes can bind, analytes of a lower affinity for the coating can be displaced by analytes of a higher affinity for the coating [31]. Consequently, the signal detection of the less volatile and larger forms such as TPhT (boiling point: 400–450°C, molecular weight 385.5 [32]) might be affected.

The limits of quantification ranged between 0.5 and 200 ng g^{-1}. These results confirm those results obtained with detection limits and show once again the poor affinity of TPhT for the CAR/PDMS fibre. The precision of the selected method is satisfactory for all the studied species (RSDs of 5–10%), except for TPhT (RSD = 17%). The peak integration might be more unpredictable for this OTC because of its weak response.

3.1.3 Accuracy. The accuracy expresses the closeness of agreement between the value found and the value that it is accepted as a reference value. To test the accuracy of the method, a non-polluted aquatic plant (verified by GC-PFPD), collected from the river Gave de Pau (France), was spiked with a methanolic solution of OTCs at concentrations varying between 5 and 600 ng(Sn) g^{-1}. A satisfactory correlation can be noted between the spiked values and the values determined by the analytical procedure (table 3). Therefore, these analyses can be considered as conforming and the selected method as accurate.

3.2 *Applications*

The method was applied on two polluted algal samples collected from the Bizerte Lagoon (Tunisia) according to the quantitation procedure described previously. The determination of OTCs in the algae was performed using headspace

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Table 3. Accuracy of SPME–GC–PFPD-based method in spiked vegetal samples.

	Concentration (ng(Sn) g^{-1} (dry mass) ± standard deviation[a])										
	MMT	DMT	TMT	TeMT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT
Spiked values	12.5 ± 0.6	12.5 ± 0.6	12.5 ± 0.6	12.5 ± 0.6	5.0 ± 0.2	12.5 ± 0.6	5.0 ± 0.2	50 ± 2	50 ± 2	125 ± 6	600 ± 30
Found values	12.2 ± 1.0	12.5 ± 0.6	12.3 ± 0.8	12.6 ± 0.8	4.9 ± 0.2	12.5 ± 0.7	4.8 ± 0.3	51 ± 4	49 ± 4	129 ± 13	577 ± 95

[a] $n = 3$.

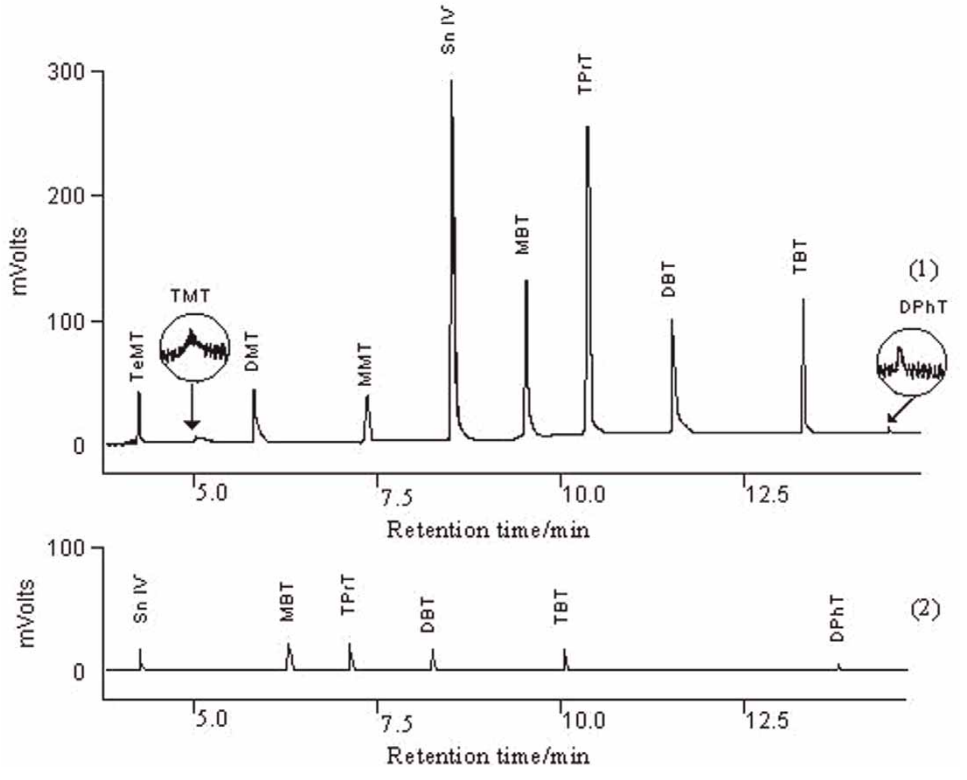

Figure 1. Chromatograms of a polluted algal sample obtained after (1) SPME and (2) LLE–GC–PFPD.

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SPME- and LLE-GC-PFPD. Typical chromatograms obtained for the most polluted sample are shown in figure 1.

These chromatograms are intentionally presented with the same scale to show the differences between the respective responses. The methyltin compounds determined by SPME were not detected by LLE (figure 1). Moreover, the peak areas obtained for butyltin compounds after headspace SPME extraction are 10–100 times higher than those obtained after LLE extraction. Moens *et al.* [33] found that headspace SPME provided approximately 300-fold better sensitivity for butyltin compounds than conventional liquid–liquid extraction. These results demonstrate the limitations of LLE in comparison with SPME and show the high concentration factor of the latter extraction type, even in complex environmental matrices such as algae. The algal butyltins concentrations using both procedures are of the same order of magnitude (table 4).

No methyltin compound was detected by LLE. On the other hand, mono-, di-, and tetramethylated OTCs were determined at very low concentrations by SPME–GC–PFPD. This is not the case for DPhT, which was determined only when conventional liquid–liquid extraction was used. This result is the logical consequence of the high DPhT detection limit obtained by SPME extraction (table 1). This is probably due to OTC competitions of sorption on the CAR/PDMS fibre. The presence of butyltin and DPhT compounds in the algal samples might be the consequence of the release

Table 4. Determination of OTC in algal polluted samples by LLE and SPME–GC–PFPD.

Sample	Analytical method	Concentration (ng(Sn) g^{-1} (dry mass) ± standard deviation[a])							
		MMT	DMT	TMT	TeMT	MBT	DBT	TBT	DPhT
ST1	LLE	nd	nd	nd	nd	7.8 ± 0.4	5.1 ± 0.2	11.9 ± 1.0	1.3 ± 0.2
	SPME	4.8 ± 0.3	3.5 ± 0.3	nd	2.9 ± 0.2	8.7 ± 0.5	5.6 ± 0.3	11.0 ± 0.4	nd
ST2	LLE	nd	nd	nd	nd	18.5 ± 0.7	26.7 ± 0.9	18.3 ± 0.8	5.0 ± 0.5
	SPME	4.1 ± 0.2	6.0 ± 0.3	d	7.5 ± 0.6	19.8 ± 0.7	27.9 ± 0.8	16.9 ± 0.8	d

[a] $n = 3$.
d: detected; nd: not detected.

of antifouling paints used on boats or the discharge of domestic and industrial wastes. Methyltin compounds are probably the result of algal biomethylation.

4. Conclusion

The headspace SPME followed by GC-PFPD detection appears to be a promising procedure for the speciation of OTCs in plant matrices. The validation of the analytical method showed low detection limits for most species (sub-0.5 ng(Sn) g^{-1}). Nevertheless, the TPhT response can be affected by the presence of co-extracted matter. Compared with conventional liquid–liquid extraction, the headspace SPME provided approximately 10–100-fold better sensitivity for butyltin compounds. The applications of SPME to spiked or polluted aquatic plants have demonstrated the reliability of the analysis and confirmed its suitability to control the organotin pollution in all types of environmental matrices.

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