Talanta 81 (2010) 1034–1039

Contents lists available at ScienceDirect

Talanta

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

Development of a simple desulfurization procedure for the determination of butyltins in complex sediment samples using gas chromatography–pulsed flame photometric detection

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ARTICLE INFO

Article history:
Received 23 October 2009
Received in revised form 27 January 2010
Accepted 27 January 2010
Available online 4 February 2010

Keywords:
Desulfurization
Organotin compounds
Gas chromatography–pulsed flame photometric detection (GC–PFPD)
Sediments

ABSTRACT

In this study a rapid solid phase extraction (SPE) procedure was developed to minimize the effect of different sulfur species for the determination of butyltin in sediments. The organosulfur species and organotins were firstly retained on C8 cartridges and then organotins were selectively eluted and analyzed by gas chromatography–pulsed flame photometric detection (GC–PFPD). Optimal conditions for the SPE procedure were obtained using an experimental design approach. The method's accuracy was established by analyzing a certified reference material (CRM), BCR-646 freshwater sediment. The experimental values were found to be in agreement with the assigned values for butyltins. Finally, complex sediment samples collected from a Chilean harbor were analyzed using this methodology to demonstrate its analytical potential for the determination of butyltin in environmental samples.

1. Introduction

The use of organotin compounds (OTC) as fungicides, insecticides, bactericides, wood preservatives and PVC stabilizers has led to their release into the environment, resulting in the contamination of aquatic and terrestrial ecosystems [1,2].

Since the toxicity of OTC depends on the nature and the number of organic groups bonded to the tin atom, many analytical procedures have been developed for the determination of organotin in various environmental samples [3,4]. Species selective analysis of organotins is performed using a combination of a chromatographic separation, preferably gas chromatography (GC), with a sensitive and selective detection method. The pulsed flame photometric detector (PFPD) is both sensitive and selective and appears to be the best choice for analysis, especially in routine analysis because of its low cost and reduced consumption of gases [5,6]. A speciation procedure for the simultaneous determination of butyl, phenyl and octyltins involving sodium tetraethylborate ($NaBEt_4$) derivatization and GC-PFPD has been developed and validated for the analysis of environmental samples [7], such as sediments [8], sewage sludge [9] and plants [10], with satisfactory results.

Unfortunately, sulfur interference has been reported in the analysis of sulfur-rich sediment samples when flame photometric detector (FPD) or PFPD are used [11,12]. It is known that elemental sulfur in sediments is co-extracted with OTC and alkylated in the derivatization step prior to GC determination, which leads to the formation of dialkylated mono-, di- and trisulfides [13,14]. Atom selective detectors coupled with GC eliminate such sulfur interferences due to their high selectivity. However, the injection of large amounts of sulfur species can overload the stationary phase and shift the retention time, which results in the misinterpretation of data [11]. Therefore, an effective method to eliminate sulfur and organosulfur compounds is mandatory for accurate OTC determination.

Several procedures have been proposed for sulfur and organosulfur compound elimination during OTC determination in sediments when using GC [4]. Common approaches, such as irreversible adsorption of sulfur compounds on activated copper or aluminum oxide and desulfurization using tetrabutylammonium sulfite, can be used to eliminate elemental sulfur, however, organosulfur compounds cannot be quantitatively removed from extracts [4,15]. Alternative approaches, evaluated by applying laborious and time consuming Grignard alkylations, result in the satisfactory elimination of alkylsulfides, but alkylated phenyltins are irreversibly adsorbed [15]. Few studies have been conducted based on similar procedures for well established derivatization using $NaBEt_4$. Some cleanup procedures that employ Florisil or Alumina sorbent to eliminate the organic material or proteins after an ethylation step have been applied for sediment [16] and biological samples analyses [17,18]. However, these

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doi:10.1016/j.talanta.2010.01.056

approaches have failed to significantly reduce the sulfur content.

In the present study, a rapid and simple procedure is proposed for the elimination of sulfur species during butyltin determination in sediment samples using a SPE cartridge prior to the derivatization step. To the best of our knowledge, no similar approaches have been reported for butyltin determination in sediment samples.

2. Materials and methods

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 DB-5 (30 m × 0.25 mm I.D.; Quadrex, New Heaven, CT, USA) with nitrogen as a carrier gas (flow: 2 mL min^{-1}) was used. The chromatographic separation and detection parameters have been previously optimized [7,12]. 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 4.0 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 sediments and for the derivatization/extraction step.

For the SPE procedures, a Visiprep™ SPE 12-port vacuum manifold, model 57030, obtained from SUPELCO (Sigal Ltda., Santiago, Chile) was used. The SPE cartridges evaluated in this study were 3 mL Bond Elut C18 (500 mg) purchased from Varian (Merck Chile, Santiago, Chile) and 3 mL-Sep Pak® Vac C8 (500 mg) from Waters (IADET, Santiago, Chile).

2.2. Reagents and materials

High quality water (18 MΩ) obtained from a Milli-pore system (Milipore, Bedford, MA, USA) was used to prepare the solutions. The organotin standards, such as dibutyltin dichloride, tributyltin chloride, tripropyltin chloride and monobutyltin trichloride, were obtained from Sigal (Santiago, Chile). Stock solutions of these reagents (1000 mg L^{-1} of tin) were prepared in methanol and stored at +4 °C in the dark. Standard working solutions were prepared daily. Glassware was rinsed with deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again with deionized water.

Sodium acetate, isooctane, nitric acid and acetic acid were obtained from Merck (Merck Chile, Santiago, Chile). Sodium tetraethylborate ($NaBEt_4$) was obtained from Galab products (Geesthacht, Germany).

2.3. Analysis of butyltins in sediment samples

The extraction procedure was based on a previously optimized procedure [19,12], 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 50 μL of TPrT (10 mg of tin) and 20 mL of glacial acetic acid. The tubes were stirred at 420 rpm for 12–14 h. For the analysis of the certified sediment sample in the presence of sulfur interferences, the sediment extract was spiked with sulfur according to previous work [12]. The SPE cartridges were then conditioned with 3 mL of hexane, 3 mL of methanol and 4 mL of deionized water at a flow rate of 1.1 mL min^{-1}. Then, 0.5 mL of the acidic extract was loaded into the C8 SPE cartridge, at a flow rate of 1.0 mL min^{-1}. Finally, non-derivatized organotins were eluted with 1 mL of HNO_3 solution (0.1 mol L^{-1} in 20% methanol at pH 1.0) at a flow rate of 1 mL min^{-1} aided by a vacuum manifold. The eluted solution was collected immediately into a 25 mL acid cleaned reactor for the ethylation process.

Table 1
Experimental factors and intervals considered in statistical significance study.

Coded factors	Factors			
	pH	Methanol (%, v/v)	Acid nature	SPE adsorbent
	A	B	C	D
Level −1	1	0	HCl	C8
Level +1	4	20	HNO_3	C18

Ethylation was carried out using $NaBEt_4$ solution (2%, w/v) in 0.5 mol L^{-1} sodium acetate/acetic acid buffer (pH 4.8) according to previously optimized conditions [20]. Then, 50 mL of the buffer solution, 500 μL of $NaBEt_4$ solution and 1 mL of isooctane were introduced into the reactor. The mixture was stirred at 400 rpm for 30 min. Two to three microliters of the organic phase was then analyzed by GC-PFPD [7].

2.4. Quantification and validation of the methodology

The standard addition method using TPrT as an internal standard (I.S.) was used for OTC quantification in sediment samples.

The surface sediment samples were collected from a harbor placed in Talcahuano city, a southern 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.

This method was validated by analyzing the BCR 646 freshwater sediment, which is certified in butyl and phenyl tins. All samples were run in triplicate.

2.5. Solid phase extraction: screening of influencing factors

The sorption study of organotin and organosulfur compounds was performed separately to elucidate the significant factors involved in the sorption for each compound. Synthetic solutions of organotin and organosulfur compounds were prepared in glacial acetic acid using known extraction conditions [21]. For organotins, a 250 ng L^{-1} (Sn) solution of MBT, DBT, TPrT and TBT was prepared in glacial acetic acid, while a mixture of organosulfur compounds was prepared by applying the extraction procedure presented in Section 2.3 to 1.0 g of elemental sulfur [12].

A two level factorial design was used to evaluate the influence of factors involved in the elution/SPE step in a reduced number of runs. To maintain satisfactory resolution, a half fraction factorial design was selected, in which the four factors were associated with non-significant, third order interactions. The examined variables and the levels considered in this screening are presented in Table 1. The instrumental response studied was the absolute chromatographic area of each butyltin obtained through GC-PFPD following the application of SPE.

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.

3. Results and discussion

3.1. Sulfur interference during butyltin analysis

Fig. 1(A) shows a typical chromatogram with sulfur interference corresponding to unknown peaks labeled 1–5*. A chromatographic signal overlapped with dibutyltin (labeled 2*), and a broad signal (labeled 5*) with a retention time greater than 9 min is evident. According to a previous study, these species have been identified as diethyl-tetrasulfide and elemental sulfur, respectively [12]. Based

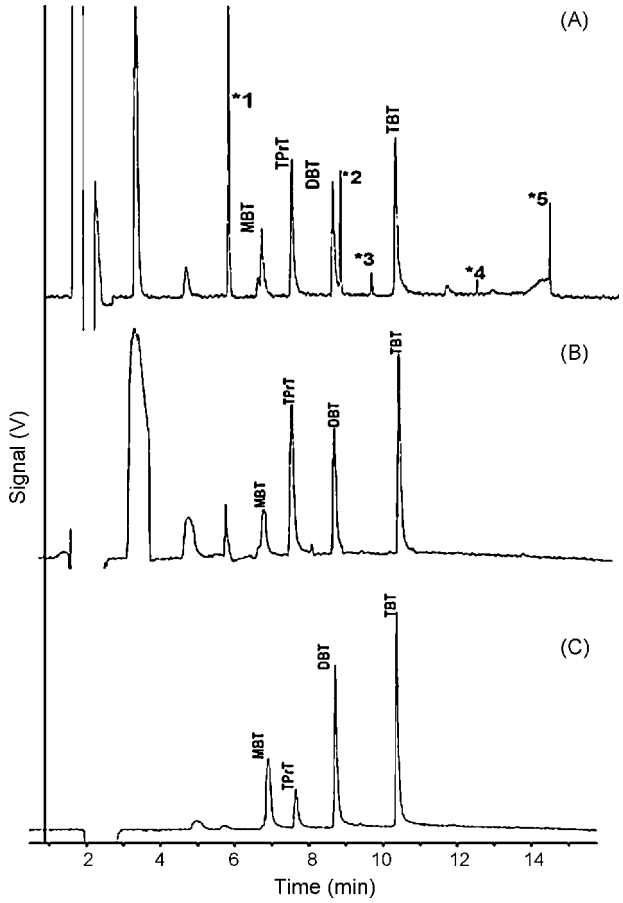

Fig. 1. Typical chromatogram obtained by LLE-GC–PFPD for an ethylated sediment sample (A) and the same sample after application of the SPE procedure using C8 (B) and C18 (C) sorbents.*Sulfur compounds.

on our experience, reliable results cannot be obtained using these conditions, especially for DBT, where the problem of co-elution is evident.

3.2. Solid phase extraction procedure development

To overcome the lack of selectivity of the PFPD detector, a simple SPE procedure was developed based on commercially available sorbents. However, it is necessary to know the sorption/elution behavior of organotin and sulfur compounds with selected SPE sorbents to find experimental conditions that allow the selective separation of these species.

3.2.1. Sorption study

The SPE sorption profiles obtained for organotins and sulfur compounds before ethylation were studied using C8 and C18 sorbents. The results obtained for organotin compounds are presented in Fig. 2(A). As expected, OTCs showed a differentiated affinity for both sorbents. For these species, a higher retention volume (1.0 mL for C8 and 1.5 mL for C18) was observed when more non-polar C18 cartridges were used. This result suggests that the retention of non-polar butyltin species formed in extraction medium (glacial acetic acid) was most likely due to a carboxylate derivative formed by the solvolysis of cationic organotin. Stable complexes of organotins and carboxylate ligands have been reported [22], and considering the low dielectric constant of glacial acetic acid with respect to water, non-covalent associations can be favored.

In contrast, for sulfur compounds, retention volumes of 1.6 and 2.0 mL were obtained for the C8 and C18 sorbents, respectively (see Fig. 2(B)). Clearly, a higher retention volume than OTC was observed using both adsorbents, which indicates differences in affinities for the SPE phase and a possible way to separate butyltins and sulfur compounds by developing a selective elution step. Although the retention mechanism is not evident, a similar retention mechanism to butyltins can be proposed for sulfur compounds. In this case, non-polar sulfur derivatives can be formed during extraction with glacial acetic acid and then retained by SPE sorbents.

3.2.2. Selective elution

Since underivatized OTCs interact strongly with some sorbents, polar eluents are needed to achieve quantitative recovery [4]. Several alternatives have been considered depending on the selected sorbents. For example, tropolone in hexane has been used as an eluent for C18 cartridges [23], and a mixture of ether and acetic acid was used for Florisil [24]. In the present study, the elution of OTC from SPE cartridges using a mixture of an acid solution and methanol was evaluated.

From a practical point of view, several variables must be considered to develop a selective elution for a specific compound from an SPE adsorbent, especially the nature of the organic group bonded to silica and the pH and polarity of the eluent solution. An experimental design was developed to study several factors simultaneously with a reduced number of experiments. The selected variables and their levels are presented in Table 1.

The results obtained using this experimental design are presented in a pareto chart in Fig. 3 and show that the evaluated variables had a significant effect on the elution of organotin compounds ($\alpha = 0.05$), because the standardized effect extends beyond the vertical line. However, some expected differences were found for mono- and di- or trisubstituted organotin compounds. These results suggest that a higher HNO_3 concentration and methanol content increased the elution of the less polar TBT and DBT from SPE sorbents, while a maximal elution of MBT was observed when HCl and C18 sorbents were selected. It is widely recognized that monosubstituted organotin chemistry is very different compared to di- and trisubstituted derivatives [1]. These chemical differences have been widely demonstrated for methyltins [24,25]. For butyltins, this subject has been scarcely studied, but some differences have been clearly exposed when OTC extraction from a solid matrix, such as sediments, is discussed [26,27].

Conversely, the important factors for the elution of sulfur species were evaluated only for species 1–3*, because 4* and 5* presented a non-reproducible chromatographic response. The results are presented in normal probability plots shown in Fig. 4. This figure illustrates that the pH and acid nature were significant and caused a negative effect on the sulfur elution, while methanol presents a no significant effect. According to these results, a low elution of sulfur compounds is observed when HNO_3 is selected.

Based on these results, the following conditions were selected to avoid the elution of sulfur interferences: the acid used was HNO_3, the pH was set to 1.0 and the methanol concentration was 20% (v/v).

These conditions were applied using C8 and C18 SPE sorbents, and the chromatograms obtained in both cases are presented in Fig. 1(B) and (C), respectively. Based on these figures, sulfur interferences were partially eliminated when C8 sorbent was used and were completely eliminated when C18 sorbent was used. However, as previously demonstrated, the elution of butyltins was lowest when the C18 sorbent is used, and therefore the C8 sorbent represents the best compromise between selectivity and sensitivity for butyltin analysis in the presence of sulfur interferences.

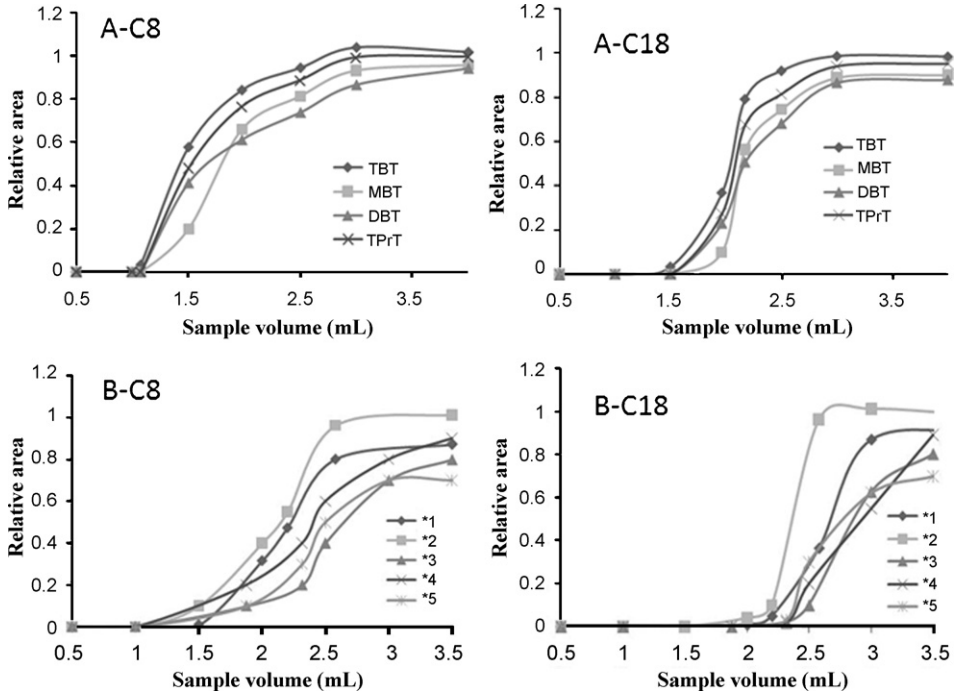

Fig. 2. Sorption profiles obtained for (A) butyltins and (B) organosulfur compounds on C8 (left) and C18 (right) sorbents.

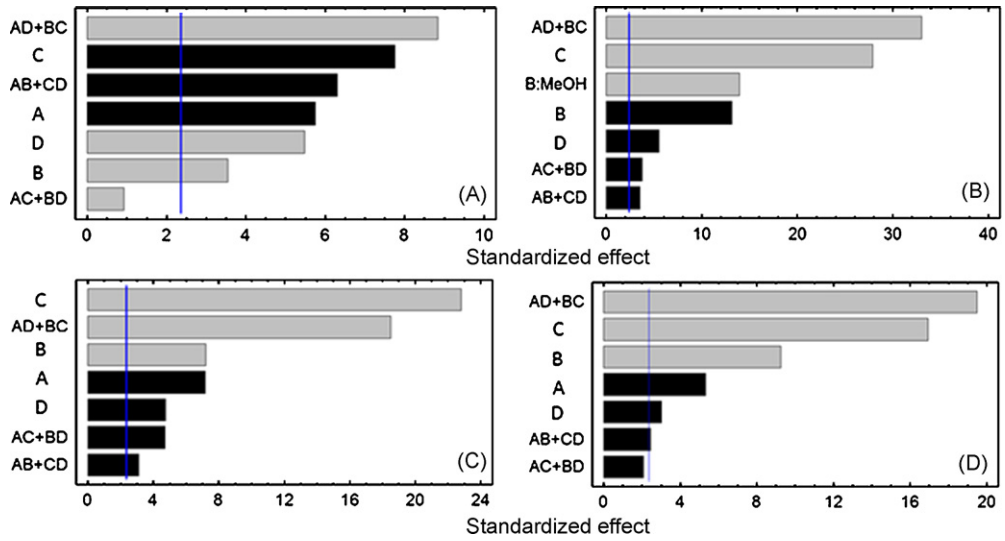

Fig. 3. Pareto charts obtained for (A) MBT, (B) DBT, (C) TBT and (D) TPrT in the significance study of several factors on SPE elution. The variables with positive and negative effects are represented by black and grey bars, respectively.

3.3. Validation and applications

The determination of butyltins in certified sediment materials (CRMs) and three harbor sediment samples with high sulfur interferences were performed using the proposed methodology (SPE followed by LLE-GC–PFPD) and compared with classical LLE-GC–PFPD. Due to the lack of CRMs of harbor sediments, the freshwater sediment (BCR 646) was selected to test the analytical

Table 2
Determination of butyltin in certified sediment samples (freshwater sediment BCR 646) by SPE–LLE-GC–PFPD and comparison with LLE-GC–PFPD method.

Sample	Analytical method	Concentration in [ng (Sn) g^{-1} (dry mass) $\pm \sigma$[a]]		
		MBT	DBT	TBT
Certified freshwater sediment (BCR 646)	LLE-GC–PFPD	465 ± 49	382 ± 26	198 ± 15
	SPE–LLE-GC–PFPD	437 ± 27	368 ± 16	172 ± 13
	SPE–LLE-GC–PFPD[b]	459 ± 31	355 ± 23	179 ± 21
	Certified values	412 ± 81	393 ± 46	196 ± 33

[a] σ is the standard deviation ($n = 3$).
[b] Spiked with sulfur interferences.

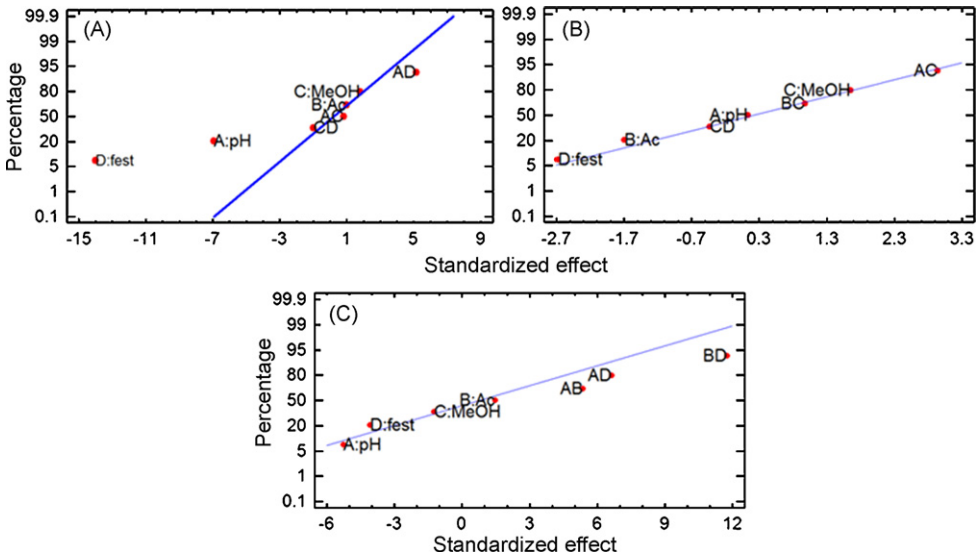

Fig. 4. Normal probability plots of sulfur compounds (A) 1*, (B) 2* and (C) 3* obtained in the significance study of several factors in SPE elution.

Table 3
Butyltin determination in complex sediment samples by LLE-GC–PFPD and developed SPE–LLE-GC–PFPD.

Sample	Analytical method	Concentration in [ng (Sn) g^{-1} (dry mass) $\pm \sigma$[a]]		
		MBT	DBT	TBT
San Vicente S1 (SV-S1)	LLE-GC–PFPD	168 ± 11	N.I.[b]	246 ± 32
	SPE–LLE-GC–PFPD	159 ± 15	193 ± 13	239 ± 33
San Vicente S3 (SV-S3)	LLE-GC–PFPD	89 ± 14	N.I.[b]	150 ± 15
	SPE–LLE-GC–PFPD	91 ± 7	156 ± 22	146 ± 11
San Vicente SA (SV-SA)	LLE-GC–PFPD	174 ± 14	N.I.[b]	563 ± 30
	SPE–LLE-GC–PFPD	185 ± 23	313 ± 28	533 ± 22
San Vicente SB (SV-SB)	LLE-GC–PFPD	199 ± 30	N.I.[b]	385 ± 12
	SPE–LLE-GC–PFPD	189 ± 19	292 ± 16	381 ± 17

[a] σ is the standard deviation ($n = 4$).
[b] No integrated due strong overlapping with sulfur compounds.

performance of the proposed methodology. However, sulfur interferences have not been reported in the analysis of this sediment sample. To solve this problem, the acid extract was spiked with sulfur interferences to evaluate the ability of this method to quantify butyltins in the presence of sulfur interferences. The results are presented in Table 2 and show that all the experimental values are in agreement with the certified values, even in the presence of sulfur interferences.

Finally, the results obtained for surface sediment samples collected from a harbor site located in Chile are presented in Table 3. Only butyltins were found in the analyzed samples, and the concentration values found for both methodologies were statistically comparable ($\alpha = 0.05$). For DBT, its determination was only possible when the proposed SPE procedure is applied.

4. Conclusions

The main consequence of the lack of selectivity of the PFPD detector was the co-elution of the organotin and sulfur compounds. The developed SPE procedure led to an increase in the chromatographic resolution, and the problem of co-elution was completely eliminated. The application of the experimental design methodology provided information on the significant factors involved in the SPE procedure and highlighted some chemical processes involved in reversible retention mechanisms presented by OTCs on the solid sorbents evaluated.

The analysis of reference sediment allowed us to validate the method and to assure the reliability of the proposed analytical procedure. Finally, organotin determination in various sediment matrices confirmed the convenience of the $NaBEt_4$ ethylation-GC–PFPD method for controlling organotin contamination in all parts of the aquatic environment. However, in extremely sulfur-charged samples, this methodology presents some limitations for OTC determination. For butyltins, the application of SPE appears to be a promising alternative to overcome the selectivity of the PFPD detector for organotin determination in complex solid samples.

Acknowledgements

The authors gratefully acknowledge FONDECYT (project 11080197) and Internal Project from Pontificia Universidad Católica de Valparaíso (project DI 0.37.105/2008) for financial support.

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