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Journal of Chromatography A, 1046 (2004) 217–224
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

# Identification of sulfur interferences during organotin determination in harbour sediment samples by sodium tetraethyl borate ethylation and gas chromatography-pulsed flame photometric detection

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Received 9 January 2004; received in revised form 22 April 2004; accepted 15 June 2004

**Abstract**

Because of the high toxicity of organotin compounds and the current regulation about their applications, analytical method usable in routine analysis is required. A speciation procedure based on $NaBEt_4$ ethylation and GC-PFPD analysis has shown to be suitable for the organotin determination. Unfortunately, some matrix effects were observed during the analysis of harbour sediments from Chile. These effects were identified as the alkylation of elemental sulfur and the coelution between the organotin compounds and some dialkylsulfides. The re-optimization of GC parameters and application of solid phase microextraction (SPME) were proposed to solve these analytical problems. Certified reference materials and different harbour sediment samples were analysed in order to evaluate the suitability of the methods for organotin control in complex environment samples.


*Keywords:* Harbour sediments; Liquid–liquid extraction; Sulfur; Organotin compounds

## 1. Introduction

The ecotoxicological effects of organotin compounds (OTC) in the environment have been well recognized for some decades [1,2]. The use of alkylated and arylated tin compounds in industrial and agricultural activities has induced the contamination of different environmental compartments. Both marine and freshwater aquatic ecosystems have been strongly impacted by the organotins, especially tributyltin (TBT) and triphenyltin (TPhT), used as biocides in antifouling paints [3–6].

The triorganotins and their degradation products are accumulated in the sedimentary phase [6–8]. This phase is currently recognized as the ultimate sinking layer for the OTC in the aquatic ecosystem, from where these compounds could be released into the water column, creating a persistent ecotoxicological risk. The various environmental problems generated by the OTC have lead to the implementation of restrictions on their uses [9].

As the toxicity of OTC depends on the nature and number of organic groups bonded to the tin atom, many analytical procedures have been developed for their determination in different environmental samples [10,11]. A speciation procedure involving a simultaneous ethylation with sodium tetraethylborate ($NaBEt_4$) and a liquid–liquid extraction (LLE) has been demonstrated to be suitable for a routine organotin

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doi:10.1016/j.chroma.2004.06.076

analysis [12,13]. Solid phase microextraction (SPME) has been proposed for organotin determination, in order to increase the analytical performances of the method and eliminate some LLE inconvenients, as the high emulsion stability generated and co-extraction of organic matter [14,15]. The high preconcentration offered by the SPME has induced a great deal of interest for using it for organometallic determination at trace levels [16]. Generally, two extraction processes can be performed using SPME: direct and headspace. In the direct mode, the coated fiber is immersed into the sample while in the headspace mode, the extraction is carried out from the gaseous phase above the sample. Moreover, some matrix effects could be decreased when headspace mode is used.

The analytical methodologies for organotin determinations are currently based on gas chromatographic separation coupled to an element selective detector. The detectors commonly used are based on atomic absorption spectrometry (AAS) [17,18], microwave-induced plasma atomic emission spectrometry (MIP-AES) [19,20], inductively coupled plasma-optical emission spectrometry (ICP-OES) [21,22], inductively coupled plasma-mass spectrometry (ICP-MS) [22], mass spectrometry (MS) [23], flame photometric detection (FPD) [12,13] and more recently pulsed flame photometric detection (PFPD) [24,25].

Many instrumental and analytical improvements have been performed for the GC-MS coupling, which is still appearing essential for identifying and quantifying of various chemical species in environmental samples [26]. However, the GC-MS coupling does not provide sufficient sensitivity for the direct analysis of OTC compounds in environmental samples (e.g. water) when the ethylation with $NaBEt_4$ and LLE are used.

The FPD, proposed originally for the sensitive and selective detection of sulfur and phosphorus compounds, has been shown to be suitable for tin determination [27]. Nevertheless, high sulfur concentrations in some environmental samples such as sediment, can produce interferences during organotin determination by GC-FPD [28–30].

About 10 years ago, Amirav and Jing [31] developed a new type of FPD based on a discontinuous flame. The PFPD, initially used for sulfur, phosphorus and nitrogen determination, has been shown to outperform the conventional FPD in terms of sensitivity and selectivity. Later on the PFPD application has been extended to the determination of other elements such as arsenic, selenium, antimony, aluminium, nickel and tin [32]. Recently, a speciation procedure has been proposed for the simultaneous determination of butyl-, phenyl- and octyltins. It is based on a derivatization step with $NaBEt_4$ and GC-PFPD coupling [24]. The optimized PFPD operation conditions lead to decrease the OTC limits of detection (LODs) 25- to 50-times compared to those obtained by FPD [24].

Unfortunately, some matrix effects were sometimes observed during sediment analysis, such as the appearance of unknown peaks and unusual OTC peak heights leading to some difficulties in quantitative analysis. For these reasons, a detailed study was performed.

The aims of this work were to identify the PFPD interferences with GC-MS, elucidate their origins and remove them by proposing new conditions in the analytical process. Finally, in order to verify the suitability of this process, certified reference materials and sediment samples collected in some Chilean harbours were analysed.

## 2. Experimental

### 2.1. Apparatus

For the analysis of organotin compounds a Varian 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a PFPD system and a Varian 1079 split/splitless temperature programmable injector were used. The GC separation was carried out using a capillary column DB-1 (30 m × 0.25 mm i.d.) coated with polydimethyl-siloxane (PDMS, 0.25 μm film thickness) (Quadrex, New Heaven, CT, USA). Nitrogen was used as carrier gas (flow: 2 ml $min^{-1}$). The chromatographic separation and detection parameters have been previously optimized and are precisely described elsewhere [24,25]. The column was held at 80 °C for the first minute, increased to 180 °C at the rate of 30 °C $min^{-1}$ and then to 270 °C at 10 °C $min^{-1}$. The injector was maintained at 290 or 250 °C when LLE or SPME procedure is used, respectively. The detection operating conditions have been precisely described elsewhere [24]. A high transmission band filter (320–540 nm; BG 12, Schott, France) and interference filter (610 nm; OG 590, Schott, France) was used to observe the emission corresponding to the Sn–C and Sn–H molecular bonds, respectively. According to the tin emission profile, the signal acquisition was carried out with a gate delay of 3.0 ms and a gate width of 2.0 ms after each flame ignition.

For identifying the unknown peaks, a Hewlett Packard gas chromatograph-mass selective detector (GC-MS) model HP 6890 was used, with an automatic injector, model 6890. The GC was equipped with a capillary column HP-5 (30 m × 0.32 mm i.d.) coated with a polyphenylmethylsiloxane (0.25 μm thick) (Agilent Technology, France). Ultrapure Helium was used as carrier gas, at a flow rate of 2 ml $min^{-1}$. The mass spectrometer was operated with electron impact (EI) at 70 eV as ionization potential, in positive ion mode. The transfer line was maintained at 280 °C. EI mass spectral scans ranging from 19 to 500 *m/z* were recorded at 1.59 scan $s^{-1}$. The injector temperature was held at 250 °C.

The manual SPME device was obtained from Supelco. The coated phase selected for this study was polydimethylsiloxane (PDMS, 100 μm). It was shown previously to give the best extraction yield for semi-volatile organotins, i.e. butyl- and phenyltins in direct mode [14,15].

A mechanical table with elliptic stirring KS 2502 basic (Prolabo, Fontenay Sous Bois, France) was used for the derivatization/extraction step.

### 2.2. Reagents and materials

High quality water (18 MOhm cm) obtained from a Millipore system was used to prepare all solutions (Milipore, Bedford, MA, USA).

The organotin standards such as dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%) and trioctyltin chloride (TOcT, 95%) were obtained from Sigma–Aldrich (St. Quentin Fallavier, France). Tripropyltin chloride (TPrT, 98%), monobutyltin trichloride (MBT, 95%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), triphenyltin chloride (TPhT, 95%) were purchased from Strem Chemicals and monooctyltin trichloride (MOcT, 97%), dioctyltin dichloride (DOcT, 97%) from Lancaster (Strasbourg, France). Stock solutions of these reagents (1000 mg $l^{-1}$ as tin) were prepared in methanol and stored at +4 °C in the dark. Standard working solutions (10 mg $l^{-1}$) were made weekly by diluting the stock solutions with deionized water. Standard solutions of 100 μg(Sn) $l^{-1}$ were daily prepared. They were stored in the dark a +4 °C. Elemental sulfur ($S_8$, 97%) was obtained from Sigma–Aldrich (St. Quentin Fallavier, France).

Sodium acetate, isooctane, nitric and acetic acids were purchased from J. T. Baker (Baker analysed). Sodium tetraethylborate ($NaBEt_4$) was obtained from Galab products (Geesthacht, Germany). $NaBEt_4$ was dissolved in deionized fresh water to provide a 2% (m/v) ethylating solution.

Glassware was rinsed with deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again with deionized water [15].

### 2.3. Extraction and derivatization procedure

Extraction procedure from sediment samples has been previously optimized and precisely described [12,13]. Briefly, 0.5–1.0 g (±0.5 mg) of freeze-dried sample is weighed into a capped 50 ml polycarbonate tube. Then, 50 μl TPrT (10 mg(Sn) $l^{-1}$), solution used as internal standard and 20 ml of glacial acetic acid were added. The tube was shaken at 420 rpm for 12 to 14 h and centrifugated for 15 min at 4000 rpm. According to the process, i.e. LLE or SPME, 1 ml or 200 μl of centrifuged extract was directly introduced into the derivatization reactor. Ethylation was carried out using $NaBEt_4$ in 0.5 mol $l^{-1}$ sodium ethanoate–ethanoic acid buffer (pH 4.8).

For LLE, 100 ml of the buffer solution, 500 μl of $NaBEt_4$ solution and 1 ml of isooctane were introduced into the reactor. The mixture was immediately shaken at 400 rpm, for 30 min. Subsequently, 1 or 2 μl of the organic phase were injected directly into GC-PFPD or GC-MS.

For SPME extraction, the headspace mode was used. Briefly, 60 ml of the buffer solution and 50 μl of $NaBEt_4$ solution were introduced into the reactor. The mixture was shaken during 10 min. Then the fiber device was placed into the headspace phase. The mixture was shaken for 30 min at 420 rpm. After the sorption step, the fiber was directly transferred into the GC injector port where the compounds were thermally desorbed.

### 2.4. Quantitation and samples

The standard addition method using TPrT as internal standard (I.S.) was used for the OTC quantification in marine sediments.

The surface sediment samples were collected in two different harbours in Chile. In these places, the dry-docking and commercial–commercial activities are currently carried out. The samples were freeze-dried, sieved at 63 μm and stored at −20 °C until analysis.

The analytical method was validated by analysing the BCR 646 and PACS-2 sediment reference materials (respectively, freshwater sediment certified in butyl- and phenyltins and marine sediment certified in butyltins). For each sample, the extraction was duplicated. For each extract two different aliquots were ethylated. Concerning the SPME process, it was duplicated from two independent aliquots of the acidic extract.

## 3. Results and discussion

### 3.1. Matrix effect identification

#### 3.1.1. GC-PFPD approach

The PFPD technique is characterized by the additional information available from the flame chemiluminescence emission time dependence [32]. In a hydrogen-air pulsed flame the molecular emission depends on the time and it is characteristic of the involved species. This dependence allows the electronic separation of a specific emission from at once the interference and pulsed flame background emissions, as was previously discussed [24,32]. Moreover, the recorded emission profile can give any information about the elemental composition of a chromatographic peak. However, the dependence of photometric signal on the amount of the analyte is not ever linear. Quadratic relations have been reported (e.g. 400 nm analysis of sulfur compounds) [31].

In the flame, an OTC emits at typical wavelengths resulting from Sn–C bonds (blue light, 390 nm) and Sn–H bonds (red light, 610 nm). The Sn–C emission is 100–1000 times more intense than Sn–H one. The choice of a specific filter (blue and red filters for Sn–C and Sn–H emissions, respectively) allows the measurement of the desired emission. However, the Sn–C emission measurement appears less selective because sulfur emission (due to $S_2$* and presenting a quadratic relation between signal and sulfur amount) occurs at the same wavelength range. At the same wavelength, the phosphorus emission (due to HPO*) should interferer the tin determination in theory. However, this problem has never been described in the literature during the organotin determination. In the Sn–H mode, only a less intense emission of sulfur (due to HSO*) can be detected, explaining the relatively

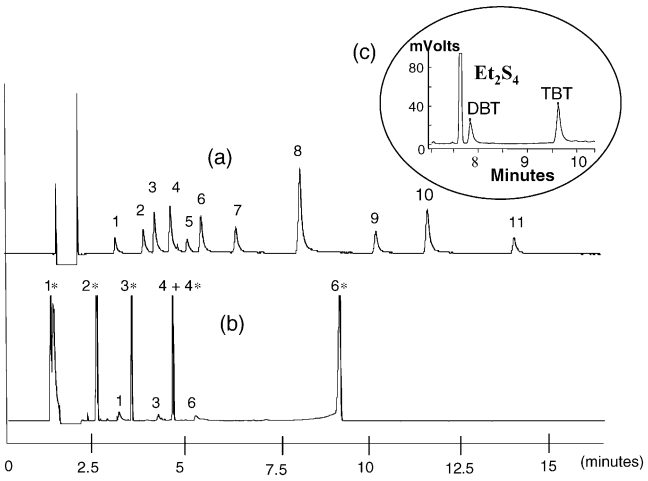


Fig. 1. Typical chromatogram obtained by LLE-GC-PFPD of an ethylated species from: (a) a standard solution of OTC, (b) An acidic extract of a harbour sediment sample. Compound identification: 1, inorganic tin; 2, MBT; 3, TPrT; 4, DBT; 5, MPhT; 6, TBT; 7, TeBT; 8, DPhT; 9, DOcT; 10, TPhT; 11, TOcT; *, sulfur compounds. (c) Chromatographic separation of DBT and $Et_2S_4$ obtained with a new temperature program.

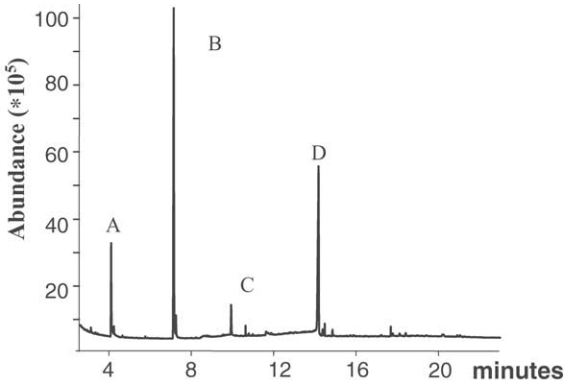


Fig. 2. Total ion GC-MS chromatogram obtained from ethylated harbour sediment extract. (For the peak identification see text.)

more selective tin detection in this mode [31]. However, even if the sensitivity and selectivity reached by using PFPD for organotin determination are better than those of the classical FPD system, the PFPD range of linearity is slightly less extended than the FPD one.

Two chromatograms are presented in Fig. 1. They were obtained for an ethylated standard solution of butyl-, phenyl- and octyltins (Fig. 1a) and ethylated sediment extract (Fig. 1b). On the second chromatogram some unknown peaks (labelled 1*, 2*, 3*) can be observed. A high DBT chromatographic signal and a broad band (labelled as 6*) with a time retention over 9 min can be noticed. Because OTC are present at low concentration in this sample, the presence of high peaks (i.e. 4 + 4* at the DBT retention time) let suspect that some interfering non-tin species occur. Moreover, from the comparison of the two chromatograms presented in the Fig. 1, coelution between DPhT and the broad band (labelled 6* in Fig. 1) is evident.

The emission profiles of these peaks were studied. This work was performed by comparison of the emission profiles from each peak of the sample and the corresponding peak (tin or sulfur species) obtained by using a standard solution. This systematic comparison established that the unknown peaks and the broad band observed in Fig. 1b corresponded to sulfur compounds. Concerning the signal at the DBT retention time, the coelution of this specie with a sulfur compound (labelled 4* in Fig. 1) was demonstrated.

### *3.1.2. GC-MS approach*

A GC-MS chromatogram obtained from the same ethylated sediment extract is presented in the Fig. 2. The ethylated-OTC signals were not detected because of the insufficient sensitivity of the mass detector compared to PFPD one. However, four intense peaks were observed. The only compound recognized by using the MS database was the peak with a retention time of 14.01 min (labelled D in Fig. 2), identified as molecular elemental sulfur ($S_8$). The identification of the other compounds was not possible by this way.

The MS spectra corresponding to the peaks with 4.01 and 7.11 min retention times, respectively (labelled A and B in Fig. 2) are presented in Fig. 3. An extensive study of the EI-spectrum presented in Fig. 3a allowed to establish that this compound corresponds to diethyldisulfide of molecular formula $Et_2S_3$. The abundance of its isotopic peaks, $M$ ($m/z$ 153.95), $M + 1$ ($m/z$ 154.95) and $M + 2$ ($m/z$ 155.95) was consistent with this molecular formula. The molecular ion for the diethyltrisulfide can be observed in the mass spectrum. Moreover, its fragmentation appears very similar to its methylated analogue, the dimethyltrisulfide [35].

The peaks at 7.11 and 9.89 min, respectively (labelled B and C in Fig. 2) can be attributed to diethyltetrasulfide ($Et_2S_4$) and diethylpentasulfide ($Et_2S_5$). These molecular formulas are consistent with their isotopic abundances ($M$, $M + 1$, $M + 2$). Even if the fragmentations of these three compounds (including $Et_2S_3$) are slightly different, the same $m/z$ fragments are observed in the corresponding spectra.

However, with the available information, it was difficult to know if the ethylated sulfur compounds identified by GC-MS were responsible for interferences observed by GC-PFPD. Commercial standards for these ethylated compounds (i.e. $Et_2S_3$, $Et_2S_4$ and $Et_2S_5$) are not available and thus the direct identification based on the retention times of these compounds by GC-PFPD is not possible. However, these dialkylsulfides species have structurally four carbon atoms and a variable number of sulfur atoms. This fact influences their chromatographic behaviour and this property was exploited. A linear correlation between the number of sulfur atoms for the ethylated compounds identified by GC-MS and their corresponding retention times was established. Obviously, elemental sulfur was not included in this study, due to its structural differences. Presuming that the PFPD unknown peaks previously observed in Fig. 1, could be originated for the sulfur species identified by GC-MS, a similar correlation was proposed by using the GC-PFPD chromatographic

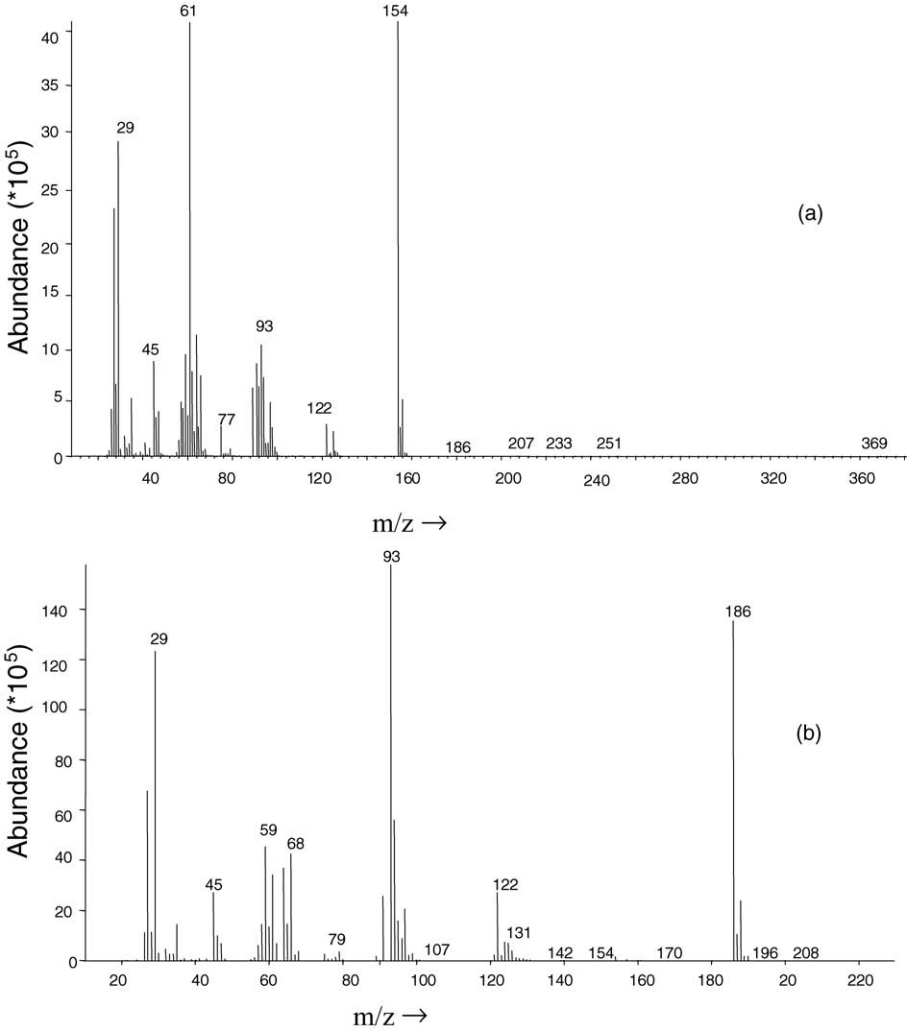


Fig. 3. EI-MS spectra of the chromatographic peaks A (a) and B (b), obtained by GC-MS from the harbour sediment extract. (For peak identification refer Fig. 2.)

peaks. These results are also presented in Fig. 4. A significant linear correlation was found in both cases. However, even when differences exist between the retention time values for both coupled systems because the chromatographic capillary columns used are not the same (DB-1 for GC-PFPD and HP-5 for GC-MS), it appears as non-significant for the elution sequence of the dialkylsulfides. So, no significant differences was observed between the slopes of the linear curves from GC-MS and GC-PFPD ($2.7 \pm 0.2$ min $NSA^{-1}$ and $2.6 \pm 0.1$ min $NSA^{-1}$, respectively), suggesting that the species detected by both chromatographic systems are the same.

In order to validate these two linear models, their predictive capacity was tested. The PFPD linear model predicted a retention time of 2.78 min for diethyldisulfide ($Et_2S_2$). This compound can be observed in the chromatogram shown in Fig. 1 (labelled 2* in Fig. 1) and its identification was confirmed for the analysis of the corresponding standard. The GC-MS identification from the same isooctane extract was not possible because the solvent delay (fixed to 3 min to avoid the detector saturation). However, the same sediment sample was analysed by the solventless SPME-GC-MS. This analysis allowed the detection and identification (based in its mass spectrum) of $Et_2S_2$.

These different results lead to confirm that the PFPD-interferences are due to dialkylsulfides and elemental sulfur. The unknown peaks 2*, 3*, 4*, 5* and 6* found on the GC-PFPD chromatogram (see Fig. 1b) correspond to diethyldi-, tri-, tetra-, pentasulfide and elemental sulfur, respectively, which were previously identified by GC-MS.

### *3.1.3. Sulfur interference during organotin determination*

In order to reduce the significance these interferences, it was important to understand their origins. During the OTC determination from sediment samples the possibility of interferences due to elemental sulfur ($S^0$) occurring during Grignard derivatization-GC-FPD has been previously documented [10,29,30]. Sulfur, in the elemental state, is present in anoxic sediments because of microbiological ac-

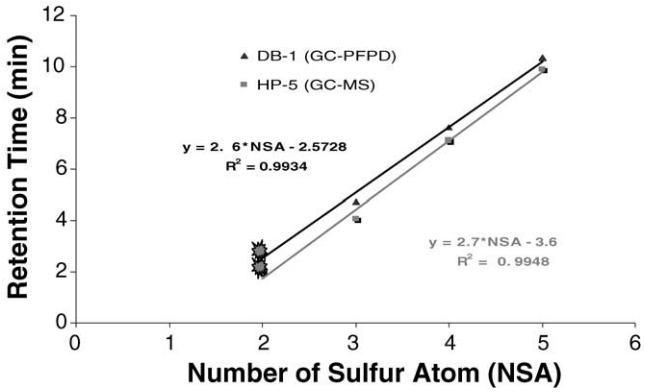


Fig. 4. Linear correlation obtained by GC-PFPD and GC-MS between the number of sulfur atoms and the retention time of the sulfur compounds identified. The '*' corresponds to an extrapolated point from the linear model.

tivities, which convert sulfate and sulfide to elemental sulfur [33].

The detection of $S^0$ in the sediment extract analysed in this work suggested that this element could be responsible of the observed interferences. So, the nature of the possible products obtained from elemental sulfur during the analytical process was studied.

A small aliquot (0.03–0.05 g) of elemental sulfur was analysed according to the analytical process previously described (see Sections 2.1 and 2.3). The organic phase obtained was analysed by GC-MS. The main peaks observed on the corresponding chromatogram were diethyltrisulfide, diethyltetrasulfide, diethylpentasulfide and elemental sulfur, similarly to those found in the ethylated extract of the sediment sample.

The same organic phase was then analysed by GC-PFPD. When the PFPD was used in Sn–C mode (emission at 390 nm), stronger signals were obtained and their retention times corresponded to the interferences previously found. If the Sn–H mode (emission at 610 nm) was used, much smaller peaks were observed, as expected for a series of sulfur compounds.

It is known that during the derivatization step of sediment extract with Grignard reagent, alkylation of $S^0$ occurs, which leads mainly to the formation of dialkyl mono-, di- and trisulfide [29,30]. In this case, the derivatization step must be carried out in a non-aqueous medium such as an organic solvent (toluene, hexane, benzene) where $S^0$ is soluble and, therefore, sulfur alkylation appears possible. For the $NaBEt_4$-ethylation two possibilities can be considered. First, the elemental sulfur co-extracted with the OTC could be ethylated in the aqueous buffer medium. However, this process does not appear probable, because the elemental sulfur is scarcely soluble in an ionic medium [34]. Moreover, the intensity of the sulfur peak is not affected by the $NaBEt_4$ concentration. So, the possible direct ethylation of $S^0$ in a buffer medium could be rejected.

The other hypothesis is that during the analytical process, $S^0$ could suffer from some chemical transformations and the corresponding products of this process can be ethylated in a buffer medium. The examination of the mass spectrum of the chromatographic band detected by GC-MS (between 7.5 and 8.5 min, see Fig. 2) in front of elemental sulfur elution shows the presence of ions below *m*/*z* 224 while the ion *m*/*z* 256 (corresponding to $S_8^+$) is missing. So, the hydrolysis of the sulfur ring during acidic extraction followed by the ethylation of the corresponding products appears as a possible physicochemical process. Moreover, it can be observed in the Fig. 2 that diethyltetrasulfide (with four atoms of sulfur) presents the most intense signal. However, the available information is not sufficient to confirm this hypothesis definitively.

### 3.2. Analytical solutions

In this work, the coelution between some organotins and sulfur compounds was demonstrated. This analytical problem have been previously reported during the OTC determination by Grignard pentylation-LLE-GC-FPD [29,30]. For the LLE, different clean-up and desulfurization procedures have been proposed [10]. However, the recovery of butyltins reaches 80% while the phenyltin compounds are not stable during the desulfurization step [29]. For these reasons, two different alternatives were evaluated in order to allow a reliable quantitative analysis. First, the re-optimization of the separation parameters was performed. Second, in order to decrease the matrix effects and increase the selectivity of organotin extraction, the SPME in headspace mode (HS-SPME) was used.

#### 3.2.1. Optimization of separation parameters

In order to resolve the coelution problem a re-optimization of the GC parameters was carried out. First, a different temperature program was applied. It is based on a constant temperature rate at 10 $min^{-1}$. A partial chromatogram obtained with this temperature program from a sediment extract is presented in Fig. 1c. As it can be observed, the separation re-optimization allows the resolution increases, while the coelution between DBT and $Et_2S_4$ is totally eliminated. However, the coelution of diphenyltin (DPhT) and elemental sulfur is still present and remains critical for its determination when the LLE procedure is used.

#### 3.2.2. Application of the HS-SPME

The solid phase microextraction (SPME) has been proposed as an interesting alternative for organotin determination [14,15,22]. Its application in the headspace mode (HS) has been proposed for the analysis of complex samples, because in this condition the fiber has not any direct contact with the sample, allowing some matrix effects to be avoided.

Fig. 5 shows a chromatogram obtained by HS-SPME-GC-PFPD from the same sediment sample analysed previously by LLE-GC-PFPD. This figure shows that even if the sulfur compounds are present, the HS-SPME based process improves resolution, especially for DPhT and elemental sulfur. In this last case, the SPME uses eliminates completely the coelution found with LLE.

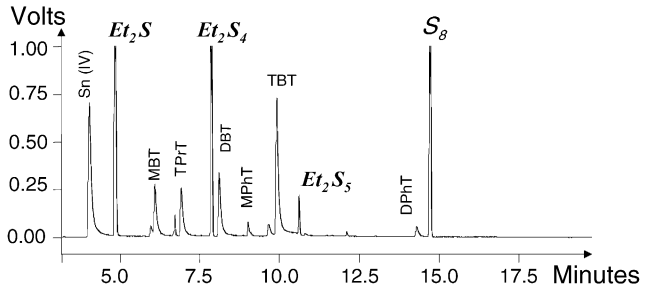


Fig. 5. SPME-GC-PFPD chromatogram obtained from the acidic extract of a harbour sediment sample.

### 3.3. Validation and applications

The determination of butyl- and phenyltins in certified sediment materials (CRMs) and three harbour sediment samples was preformed using LLE- and SPME-GC-PFPD. Due to the lack of CRMs of harbour sediments, freshwater and marine sediments (BCR 646 and PACS-2, respectively) were selected to be studied. However, the analysis of these CRMs has been previously carried out and the presence of the sulfur compounds identified in this work was not detected in any reference material. So, in order to verify the suitability of the methodology, both reference materials were analysed in the presence of these interferences. For that, the acidic extracts obtained for PACS-2 and BCR 646 were spiked each with 0.5 ml of the extract obtained from the acidic extraction of elemental sulfur. The analyses were performed by GC-PFPD. Table 1 shows that all the experimental values are in good agreement with the certified ones. However, for the PACS-2 analysis, the value found for MBT is higher than the indicative value for both LLE and HS-SPME. This fact has been already noted by several authors [22,36]. The results obtained for the analysis of BCR 646 by LLE-GC-PFPD are not presented. This is because the determination of the diphenyl- (DPhT) and monophenyltin (MPhT) was not possible by this process due to some intense interference signals. In the case of DPhT, the coelution with elemental sulfur did not allow the integration of the chromatogram. For MPhT, its determination in the presence of the interferences produced erratic results. So, for the further analysis of sediments with high sulfur concentrations, the PFPD could be critical for the phenyltin determination, especially when the LLE method is performed.

The results obtained for the three surface sediment samples collected from two harbours from Chile are presented in Table 2. Only butyltins were found in all the analysed samples. The concentrations found by using both methodologies are of the same order of magnitude. However, the TBT concentration appears systematically higher when the SPME was used. Considering that SPME-based method requires a smaller amount of sample than LLE and the fiber has no contact with the aqueous phase, so that matrix effects are considerably decreased. It can explain the difference between these results.

The DBT and MBT concentrations appear higher when the LLE is applied to ST4 and ST5 analyses. These samples gave rise to the most severe analytical difficulties due to sulfur interferences and a noisy baseline was observed on both chromatograms. It was suspected that these higher values correspond to an over-estimation of MBT and DBT

Table 1
Determination of OTC in certified sediments samples (marine sediment, PACS-2 and freshwater sediment, BCR 646) by LLE- and SPME-GC-PFPD

| Sample | Analytical method | Concentration (ng(Sn) $g^{-1}$ (dry mass) $\pm$ $\sigma$[a]) | | | | | |
|---|---|---|---|---|---|---|---|
| | | MBT | DBT | TBT | MPhT | DPhT | TPhT |
| BCR 646 | SPME-GC-PFPD | 429 ± 35 | 344 ± 23 | 171 ± 12 | 59 ± 8 | 13 ± 2 | 6 ± 1 |
| | Certified | 411± 81 | 392 ± 46 | 196 ± 33 | 42 ± 11 | 16 ± 3 | 10 ± 4 |
| PACS-2 | LLE-GC-PFPD | 566 ± 46 | 1013 ± 99 | 931 ± 154 | – | – | – |
| | SPME-GC-PFPD | 560 ± 30 | 1037 ± 41 | 879 ± 59 | – | – | – |
| | Certified | 300[b] | 1090 ± 150 | 980 ± 180 | – | – | – |

[a] $\sigma$, standard deviation ($n$ = 4).
[b] Indicative value.

Table 2
Determination of OTC in different harbour sediment samples by LLE- and SPME-GC-PFPD

| Sample | Analytical method | Concentration (ng(Sn) $g^{-1}$ (dry mass) $\pm$ $\sigma$) | | |
|---|---|---|---|---|
| | | MBT | DBT | TBT |
| ST4 | LLE | 24 ± 2 | 120 ± 11 | 331 ± 23 |
| | SPME | 16 ± 2 | 97 ± 3 | 354 ± 30 |
| ST5 | LLE | 10 ± 1 | 35 ± 3 | 88 ± 7 |
| | SPME | 6.1 ± 0.5 | 19 ± 1 | 117 ± 6 |
| SVF | LLE | 44 ± 3 | 90 ± 4 | 186 ± 2 |
| | SPME | 49 ± 1 | 97 ± 3 | 196 ± 10 |

concentration when LLE-GC-PFPD is used and it can be attributed to the different components of the matrices. Both ST4 and ST5 sediment samples were collected from the same harbour in the South of Chilean coast, where dry-docking and the fishery-exploitation activities are currently carried out. The FV-sample came from a harbour where mainly commercial activities are performed. So, the matrix components appear to play a fundamental role in the differences of observed analytical behaviors.

In summary, the method has been validated by analysing two certified material sediments in presence of sulfur interferences.

## 4. Conclusion

The first part of this study has allowed the identification of the main matrix effects observed during the analysis of harbour sediment samples. Elemental sulfur was found as mainly responsible for these effects. This element appears to react to dialkylsulfides during the analytical process. Due to impaired high concentrations of sulfur, the selectivity of PFPD is overcome. The mechanism leading to form dialkylsulfides appears very complex and a hypothesis based on the hydrolysis of $S^0$ ring during the acidic extraction has been proposed.

The main consequence of the lack of selectivity of the detector was the coelution of some OTC and the sulfur compounds. The re-optimization of separation parameters and the HS-SPME application together allowed the resolution increasing and complete elimination of coelution problems.

The analysis of reference sediments allowed the validation of the methodology even in the presence of sulfur compounds. Finally, the organotin determination in some sediment matrices has confirmed the convenience of the $NaBEt_4$ ethylation-GC-PFPD for controlling the organotin contamination in all parts of the aquatic environment. Nevertheless, in samples with high sulfur concentrations, the LLE presents some limitations for phenyltin determination. In this case, the HS-SPME appears as a promising alternative with a high sensitivity and sufficient selectivity for the organotin determination by GC-PFPD in complex samples.

## Acknowledgments

The authors acknowledge the Program ECOS-CONICYT (Scientific cooperation project between France and Chile, action C01E010) for financial support. Manuel Bravo thanks to Conicyt and the French Government for the fellowships conceded.

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