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WORKING METHODS PAPER

Comprehensive Evaluation of the Extraction Variables Affecting the Determination and Stability of Native Butyl- and Phenyl-tin Compounds from Sediment

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The effect of several extraction variables such as acid concentration and strength (e.g. for HCl and HOAc), the presence of complexing agents (e.g. tropolone, sodium diethyldithiocarbamate) in the extracting mixture, solvent polarity (e.g. hexane, toluene) and sonication time for native butyl- and phenyl-tin compounds from sediment was evaluated. A toluene–HOAc mixture (10:4) yields the highest extraction efficiency for all the analytes and minimizes the degradation of trialkyl- and triaryl-tins during the extraction under sonication. In addition, losses of underivatized monobutyltin and monophenyltin were minimized in several steps of the analytical procedure. The analytical procedure developed was validated against existing CRMs for butyltin determination. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The occurrence of organotin compounds (OTs) in the aquatic environment is of great concern. Since toxic effects on non-target marine organisms depend on tin substitution, OT speciation becomes necessary to evaluate the risk associated with the occurrence of this class of compounds.

A large number of analytical procedures for OT speciation in environmental samples, particularly sediments and biological materials, have been developed over the last decade and they have been reviewed recently.[1] However, some uncertainties have arisen about the accuracy of published analytical procedures. In most of them, spiked sediments have been used to evaluate the extraction efficiency; this might lead to recovery overestimation. Moreover, little attention has been paid to the assessment of organotin stability during the extraction procedure.

Despite the large amount of existing literature on OT speciation in sediments, only a few articles have evaluated the extraction variables which affect the recovery of organotin compounds. In those cases, the optimization of the parameters has been performed on spiked sediments and then evaluated on native matrices.[2,3] Zhang *et al.*[4] assessed the extraction efficiency of butyltins in PACS-1 using 10 different extraction procedures, but no systematic optimization was carried out. In addition, few studies have dealt with the evaluation of the extraction efficiency of phenyltin compounds from sediments,[3,5–9] even though they are widely distributed in the marine environment. The absence of CRMs for these species could be a reason for such a lack of study. To this end, the Measurements and Testing (MAT) in the 4th Framework Programme of the European Union (EU) has launched a project to develop analytical procedures and CRMs for butyl- and phenyl-tin speciation in order to improve their measurement in the marine environment.[10]

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In this study, relevant variables that could affect the extraction efficiency of native butyl- and phenyl-tin compounds from a marina sediment have been evaluated, with the aim of obtaining the optimum extraction conditions for all analytes. In order to trace the different steps of the analytical procedure, several surrogates were added before the extraction and before the derivatization. Furthermore, the degradation associated with the extraction has been carefully evaluated and some critical steps affecting the analysis of butyl- and phenyl-tin compounds have been identified. Finally, the analytical procedure developed has been cross-validated for the butyltin content in several existing CRMs.

EXPERIMENTAL

Reagents and materials

Surficial sediments were collected in the Masnou marina (NW Mediterranean) and offshore from Barcelona. They were freeze-dried, sieved through 120 μm mesh and stored in the darkness at −20 °C until analysis. PACS-1 and CRM-462 were obtained from the National Research Council of Canada (Ottawa, ON, Canada) and from the Institute for Reference Materials of the European Commission (Gheel, Belgium), respectively and were stored at 4 °C in the dark until analysis.

Monobutyltin (MBT, 95%), monophenyltin (MPhT, 98%), tricyclohexyltin (TCyT, 90%) and tripentyltin (TPeT, 98%) as chlorides were obtained from Aldrich (Milwaukee, WI, USA). Dibutyltin (DBT, 96%), tributyltin (TBT, 96%), diphenyltin (DPhT, 96%) and triphenyltin (TPhT, 95%) as chlorides were supplied by Aldrich Chemie (Steinheim, Germany). Tripropyltin chloride (TPrT, 98%) was from Merck–Schuchardt (Hohenbrunn, Germany) and tetrabutyltin (TeBT, 98%) was obtained from Fluka AG (Buchs, Switzerland). All standards were used as received. Tropolone (99%) was purchased from Sigma. Sodium diethyldithiocarbamate (NaDDC) (99%), ammonium pyrrolidinedithiocarbamate (APDC) (97%), pentylmagnesium bromide (PeMgBr, 2.0 M in diethyl ether) and ethylmagnesium chloride (EtMgCl, 2.0 M in tetrahydrofuran) were obtained from Aldrich *n*-Hexane, toluene (pesticide grade), 25% hydrochloric acid, neutral alumina and anhydrous sodium sulphate were from Merck and 99.7% and acetic acid (HOAc) was from Aldrich. All other chemicals were suitable for organic trace analysis or a higher grade.

Organotin chlorides and TeBT stock standard solutions were prepared at 500 mgl^{-1} (as Sn) in hexane and were stored at −20 °C. Working solutions were prepared weekly by diluting the stock solutions with hexane or acetone.

Tropolone (0.5% w/v) was dissolved directly in the solvent used for the extraction. NaDDC was prepared following the procedure described by Dirkx *et al.*[2] NaDDC was dissolved in an aqueous solution, this solution was acidified with H_2SO_4, extracted with pentane in order to recover the complexing agent in an organic solvent and a small volume of the pentane solution was mixed with hexane to give 1.5% (w/v) NaDDC in hexane.

Extraction procedure

A 2 g dry sediment intake was transferred to a glass centrifuge tube with a Teflon-lined cap previously wrapped with aluminium foil; 1 ml portions of acetone solution containing 400 and 100 ng ml^{-1} (as Sn) of TPrTCl and TCyTCl, respectively, were added as surrogates to the sample. They were vortex-stirred for 1 min and left to equilibrate for 1 h. The appropriate volume of the corresponding extraction mixture (12–20 ml; see Table 1, below) was transferred to the glass centrifuge tube containing the sample and was vortex-stirred for 1 min and then sonicated for 10 min. Following the extraction, a centrifugation at 2000 rpm was carried out. The supernatant was recovered by means of a Pasteur pipette and transferred to a glass conical vessel wrapped in aluminium foil. Extraction was repeated twice with the same volume of extraction mixture as in the first extraction, and the combined extracts were placed in the glass conical vessel. Following the extraction steps, two different procedures (A and B) were considered to remove the HOAc.

Procedure A: The solvent extract was vacuum-evaporated to dryness at 30 °C. HOAc was previously removed from the extract by liquid–liquid extraction (LLE) twice with 10 ml of Milli-Q water for 1 min. The organic phase was percolated through 2 g of activated Na_2SO_4. After solvent evaporation, the extract was reconstituted with 2 ml of hexane and spiked with TPeTCl (300 ng as tin) in hexane to assess the derivatization yield. The derivatization was performed with 2 ml of EtMgCl, with shaking for 1 min and then standing for 10 min.

Procedure B: HOAc was removed quantitatively

Table 1 Extraction conditions in the different experiments

Solvent	Acid (conn)	Solvent/acid ratio (ml:ml)	Complexing agent (%, w/v)	Extraction time (min)
Hexane	HCl (0.5%)	(10:4)	Tropolone (0.5)	10
Hexane	HCl (25%)	(10:4)	Tropolone (0.5)	10
Toluene	HCl (25%)	(10:4)	Tropolone (0.5)	10
Toluene	HOAc (99.7%)	(10:4)	Tropolone (0.5)	10
Toluene	HOAc (50%)	(10:4)	Tropolone (0.5)	10
Toluene	HOAc (99.7%)	(10:4)	Tropolone (0.5)	20
Toluene	HOAc (99.7%)	(10:4)	NaDDC (0.9)	10
Toluene	HOAc (99.7%)	(10:4)	—	10
Toluene	HOAc (99.7%)	(10:4)	—	5
Toluene	HOAc (99.7%)	(10:2)	—	5
Toluene	HOAc (99.7%)	(10:10)	—	5

from the extraction mixture by LLE repeated twice with 10 ml of 0.5% APDC aqueous solution. The organic phase was dried as described under Procedure A. The solvent extract was vacuum-evaporated to a few millilitres, at 30 °C then the extract was spiked with TPeTCl (300 ng as tin) in hexane. The derivatization was performed with 2 ml of PeMgBr, with shaking for 1 min and then standing for 10 min.

In both procedures, the excess of derivatization reagent was destroyed by adding 10 ml of Milli-Q water and then a few drops of HCl (25%), keeping the conical vessel in an ice bath. The derivatized extract was recovered and the aqueous phase was submitted to LLE twice with 2 ml hexane. Combined extracts were passed through a glass funnel containing 1 g of Na_2SO_4 and then kept overnight in the presence of 0.5 g of activated copper at −20 °C. The supernatant was purified through a glass column slurry-packed with 3 g of neutral alumina activated at 120 °C overnight. Following the elution of the sample extract, 4 ml of fresh hexane was added, followed by TeBT (300 ng as tin) in hexane as (I.S.) internal standard. Evaporation down to 1 ml was carried out under a gentle stream of N_2. Derivatized samples were stored at −20 °C until determination. Procedural blanks were processed in parallel with sediment samples.

CGC–FPD determination

Analysis of derivatized extracts was performed in

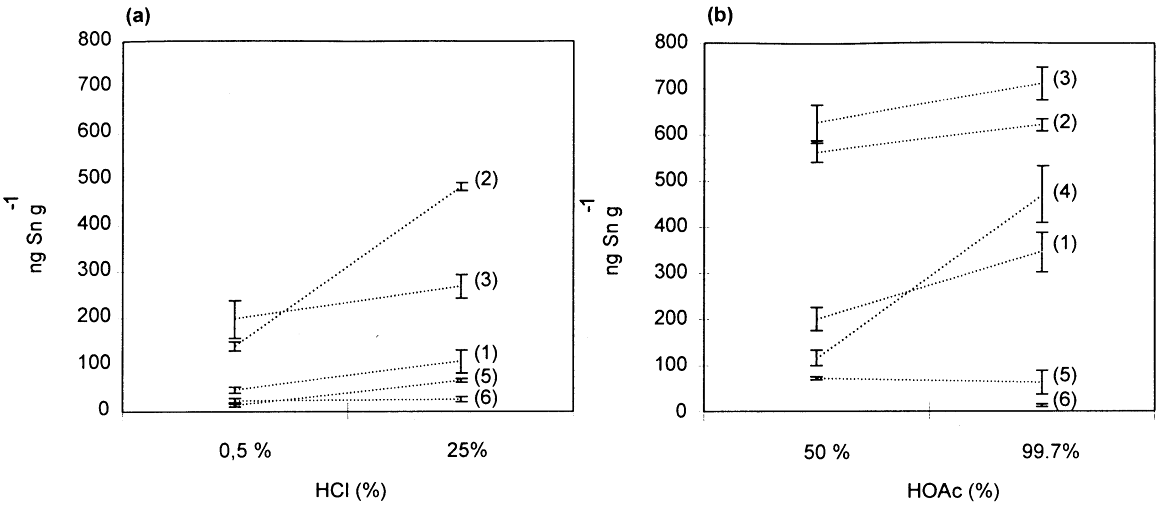

Figure 1 Effect of acid type and acid concentration on the extraction efficiency of OTs. Extractions were performed with: (a) HCl–hexane (0.5% tropolone): (b) HOAc–toluene (0.5% tropolone). The sample was a sediment from Masnou marina. Mean values and SD ($n = 3$) are represented. Compounds: (1) MBT: (2) DBT: (3) TBT: (4) MPhT: (5) DPhT: (6) TPhT.

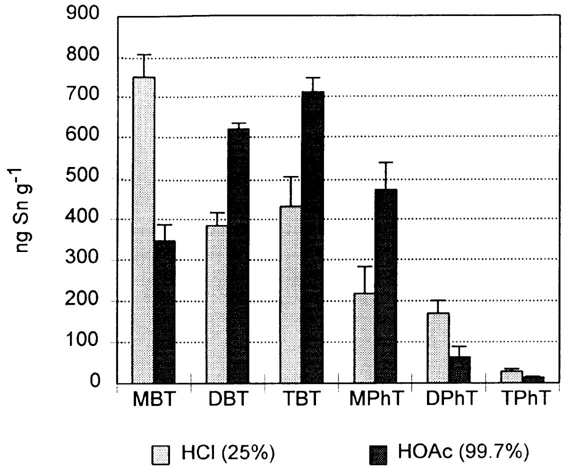

Figure 2 Effect of acid type on the extraction efficiency of OTs. Extractions were performed with acid–toluene (0.5% tropolone). The sample was a sediment from Masnou marina. Mean values and SD ($n = 3$) are represented.

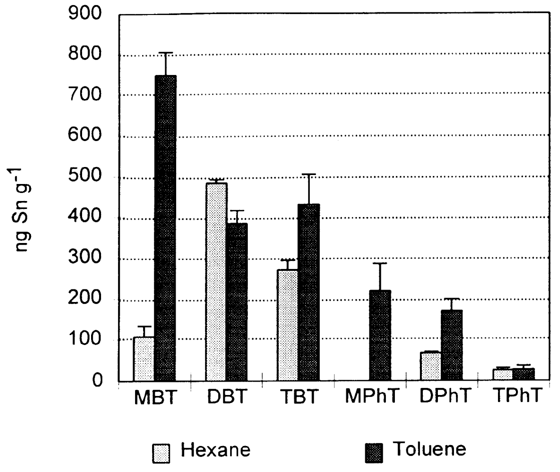

Figure 3 Effect of solvent polarity on the extraction efficiency of OTs. Extractions were performed with HCl (25%) – solvent (0.5% tropolone). The sample was a sediment from Masnou marina. Mean values and SD ($n = 3$) are represented.

duplicate using a Fisons Mega 2 Series 8560 model gas chromatograph (Milan, Italy) equipped with an AS 800 autosampler and an FPD detector (FPD 700, Fisons, Milan, Italy) containing a 610 nm bandpass filter. Injector and flame detector temperatures were held at 250 and 220 °C, respectively. A 30 m × 0.25 mm (i.d.) fused silica column coated with a film of DB-17 (J&W Scientific, Folsom, CA, USA) 0.25 μm thick was used as analytical column. The initial column temperature was held for 1 min at 60 or 100 °C for hexane or toluene, respectively, and then ramped at 10 °C min^{-1} to 280 °C where it was held for 5 min. Hydrogen at a flow rate of 3 ml min^{-1} and nitrogen at 46 ml min^{-1} were used as carrier and detector make-up gases, respectively. Flow rates of fuel detector gases were 120 ml min^{-1} of hydrogen and 80 ml min^{-1} of air. Data were acquired and processed by a Perkin-Elmer–Nelson interface connected to a PC.

Quantification

This was performed by the internal standard procedure using TeBT. Calibration plots from 25 to 400 pg for each analyte were obtained daily ($R^2 = 0.99$) (R: regression coefficient). Procedural blanks were carried out for every set of samples. All the experiments carried out in the course of developing the method were in triplicate and for method validation in quintuplicate. The RSD and recoveries of surrogates ranged from 5 to 12% and 70 to 95%, respectively.

RESULTS AND DISCUSSION

Optimization of the extraction variables

The evaluation of the extraction efficiency for OTs was performed on a sediment in which phenyl- and butyl-tin compounds had been identified previously.[6] Sonication was selected for extraction because of its widespread availability and its relatively short extraction time and low solvent usage compared with other conventional extraction techniques (e.g. Soxhlet). The effect of several extraction variables was evaluated by changing one at a time (Figs 1–4, 6). Experimental analytical conditions are listed in Table 1.

Effect of acid type and acid concentration

Hydrochloric and acetic acids were selected in this study since they can displace the different to counterions occurring in the matrix, forming either chlorides or acetates which are quite soluble in organic solvents. Both acids were evaluated at two concentrations. In general, the extraction efficiency of organotins increased with the concentration of

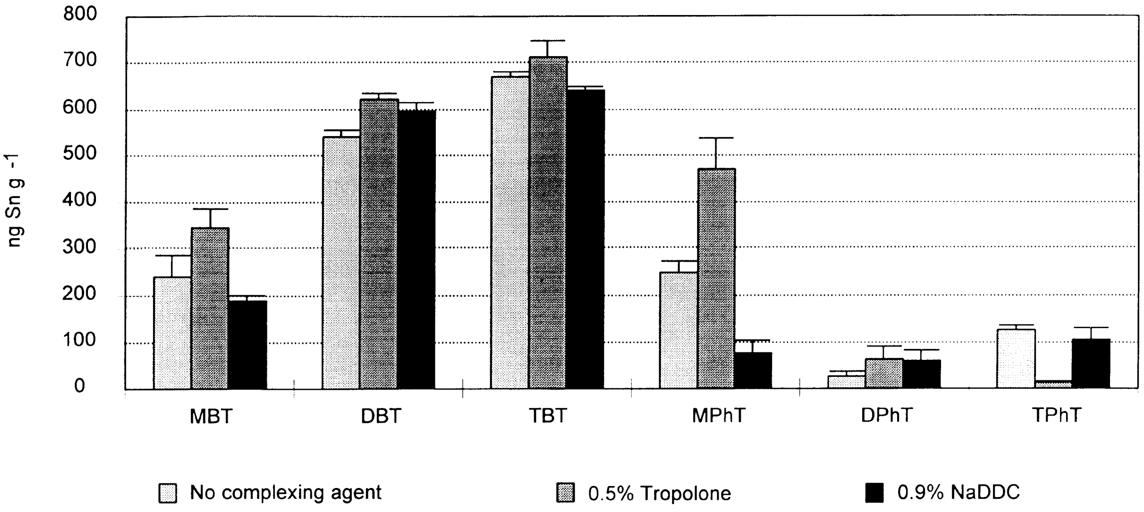

Figure 4 Effect of complexing agents on the extraction efficiency of OTs. Extractions were performed with HOAc (99.7%)–toluene. The sample was a sediment from Masnou marina. Mean values and SD ($n = 3$) are represented.

acid used (Figs 1a and 1b). The intercomparison between the two acids revealed that glacial HOAc yielded better recoveries for TBT and DBT, whereas a decrease in their extracted amounts paralleling an important increase in MBT extraction arose from the use of concentrated HCl (25%) (Fig. 2). This result could be attributable to a process of degradation of TBT and DBT which led to the formation of MBT. Conversely, phenyltins showed a different behaviour related to the degradation according to the acid strength. Whereas no degradation seemed to take place in the presence of concentrated HCl (25%), the MPhT concentration increased when pure HOAc was used (Fig. 2). However, by using dilute HOAc (50%) the amount of MPhT extracted decreased greatly; therefore the high concentration of HOAc could be responsible for the increase in MPhT extraction.

Effect of solvent polarity

Two solvents with different solvating characteristics were evaluated: *n*-hexane and toluene, both in the presence of HCl (25%) and tropolone as complexing agent (Fig. 3). Toluene was more efficient than *n*-hexane, especially for the monosubstituted compounds MBT and MPhT. In fact, MPhT could not be extracted at all in the presence of *n*-hexane. These results show that a solvent of higher polarizability is needed in order to favour the extraction of the more polar organotins. Chau *et al.*[11] reported some of the advantages of using toluene over more polar solvents: (1) it has a limited water miscibility, and (2) in spite of its high boiling point, the solvent peak emerges well before OTs in gas chromatography.

Effect of complexing agent

The effect of tropolone and NaDDC was evaluated in the presence of HOAc and toluene (Fig. 4). Tropolone was more efficient than NaDDC for butyltin compounds and MPhT. However, NaDDC led to a similar extraction efficiency for TPhT compared with the situation in the absence of complexing agents. On the other hand, tropolone led to a decay in the recovery of TPhT. These results can be interpreted in terms of the lack of effect of complexing agents on to acetates which are already soluble in the toluene used during the extraction.

Effect of extraction time

Three extractions were performed sequentially with two different extraction times (10 and 20 min) by using toluene–tropolone–HOAc. No increase in the extraction efficiency was observed to correspond with the extraction time increase. Therefore, we experimented with a reduction in extraction time to 5 min per extraction, but maintaining the three sequential extractions. A fourth extraction was also performed and it was analysed separately in order to confirm the total release of OTs from the matrix. No OTs were found in the last extraction, which led

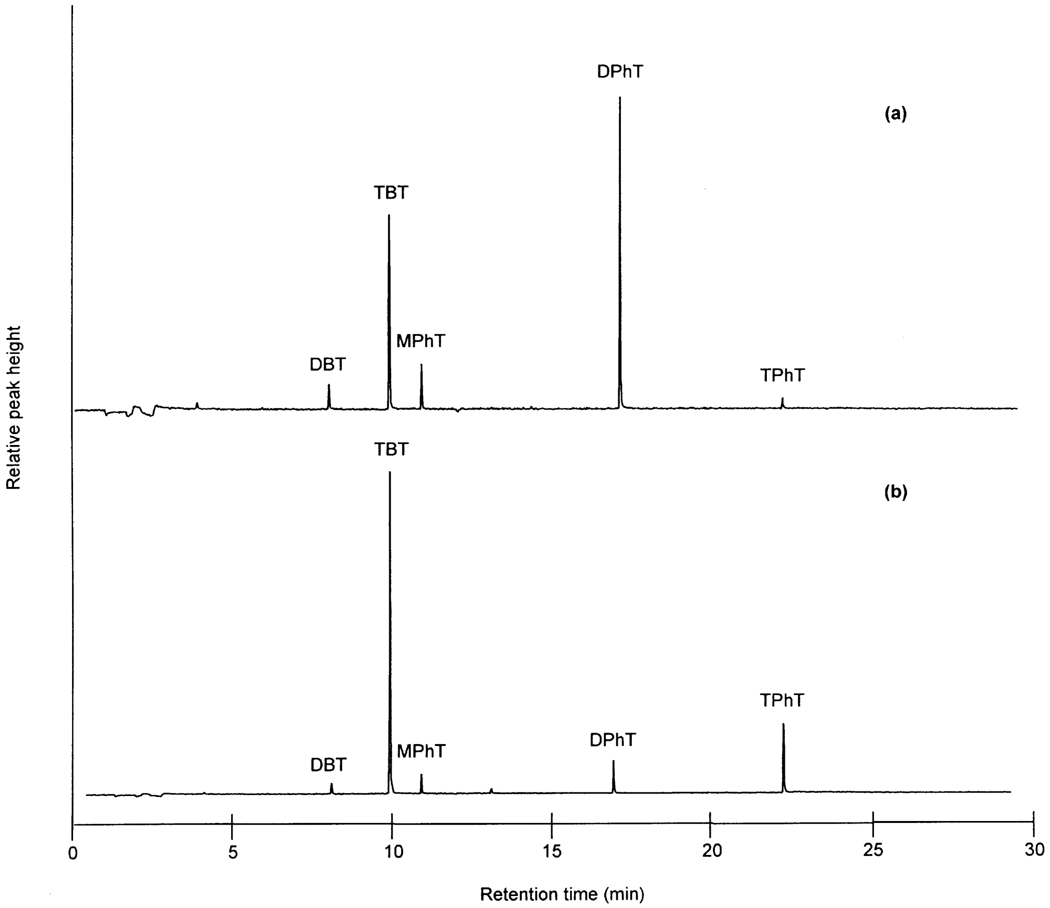

Figure 5 Chromatograms of a sediment spiked with TBT and TPhT and leached overnight with: (a) HCl (25%) and (b) HOAc (99.7%). After leaching, extraction was performed with toluene.

us to conclude that several extractions with fresh extraction mixture during a short extraction time are more effective than a single longer extraction, which minimizes the chances of to degradation.

Assessment of the stability of organotin compounds during extraction

OTs are moderately stable in most environmental compartments. Half-lives are estimated to be from days to several weeks in water, up to several years in sediments.[12–16] Stability studies according to the storage conditions and sample preparation (e.g. drying of sediments) have been carried out.[17] Special attention to these constraints has been already paid in the development of candidate reference materials (CRMs). However, the chances of OT degradation during the extraction procedure have scarcely been investigated.

In the present study, the different behaviour shown by butyl- and phenyl-tin compounds under the same extraction conditions (e.g. according to the acid strength and the complexing agent; see ‘Optimization of the extraction variables’) could indicate that degradation processes promoted either by the acid or the complexing agent could be taking place during the extraction. Therefore, a sediment free of organotin compounds was spiked with standard solutions of TBT and TPhT in acetone and extracted under different conditions to find out whether degradation products of parent OTs were formed. First, we evaluated the degradation process associated with acid extraction. To this end, a sediment was leached with acid overnight as described in the literature; some recent procedures based on HOAc extraction still employ long leaching times.[18,19] DBT, MPhT and mainly DPhT were obtained after leaching the sediment with acid (HCl or HOAc) overnight at room temperature (25 °C) and extracting it with toluene. TPhT degradation was highly significant when HCl was used since it was almost completely converted to its degradation products (Fig. 5). However, the most surprising results are those related to the use of tropolone as a complexing agent in a toluene–HOAc extraction mixture. It was found that none of the TPhT spiked could be recovered, whereas a peak of DPhT was identified (about 10% of the amount of TPhT). The complete loss of TPhT could be associated with a dismutation process which led to the formation of one molecule of DPhT and one of inorganic tin, similarly to that reported for trimethyltin in presence of tropolone (Trop) under mild conditions (Craig *et al.*[20]):

$$2(CH_3)_3SnTrop \longrightarrow (CH_3)_4Sn + (CH_3)_2Sn(Trop)_2 \quad [1]$$

This reaction led to a degradation process which does not depend on the extraction conditions, and thus the amount of TPhT extracted during different experiments was similar, except when NaDDC was used or in the absence of a complexing agent.

On the basis of these results, toluene–HOAc was selected as the optimum extracting mixture. Tropolone and NaDDC were discarded as complexing agents since they do not increase the organotin recoveries substantially (see ‘Effect of complexing agent’). The volume of HOAc in toluene was optimized to increase the extraction efficiency of triorganotins and to minimize the formation of degradation products. An increase in the acid volume from 2 to 4 ml slightly improved the recoveries of both triorganotins, and negligible concentrations of diorganotins were identified. However, when 10 ml of HOAc was used, the recoveries of the triorganotin compounds, especially TBT, were lower, leading to the formation of degradation products (Fig. 6). The composition of the extraction mixture was fixed at 10 ml of toluene and 4 ml of HOAc for 2 g of sediment and the extraction time was reduced to 5 min per extraction since this was found to be sufficient to release OTs from the matrix.

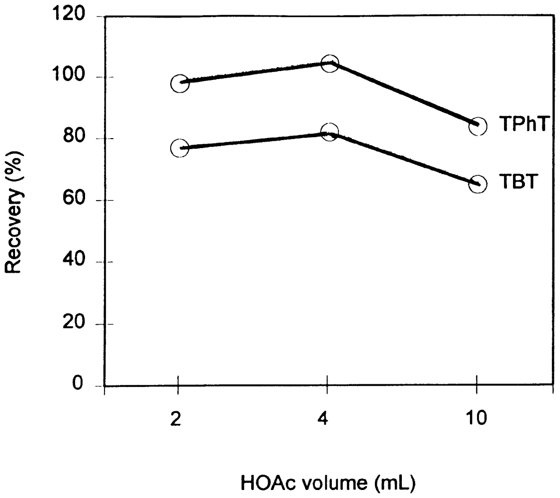

Figure 6 Effect of HOAc volume on the recoveries of TBT and TPhT. Extractions were performed with HOAc (99.7%)–toluene. The volume of toluene was 10 ml in all cases. The sample was a spiked marine sediment.

Optimization of post-extraction steps

Following the optimization of the extraction procedure, the influence of post-extraction steps in the determination of OTs was evaluated. When HOAc is used in the extraction, the removal of the acid from the extraction mixture is imperative. Otherwise, rotary evaporation could be difficult, and acid remaining in the extract can have a detrimental effect on the derivatization reaction. In several experiments, the extract was partitioned with Milli-Q water in order to remove HOAc from the extraction mixture (see the Experimental section, ‘Procedure A’). However, the analysis of the aqueous HOAc phase obtained from the extraction of a sediment spiked with butyl- and phenyl-tin compounds showed that *ca* 50% of MBT was partitioned into that aqueous phase. A second approach, using an aqueous solution of 0.5% APDC instead of water alone, was applied successfully (see the Experimental section, ‘Procedure B’). It is believed that APDC forms neutral complexes with OTs which enhance their partitioning into the solvent phase.[21]

It was therefore decided to perform an LLE on the toluene–HOAc extract with the aqueous solution of APDC in order to remove the acid. Moreover, on the basis of a recent study showing the possibility of losses during the concentration steps,[22] evaporation to dryness was avoided. Therefore, the pentylation reaction was performed directly on the toluene extract after drying it with Na_2SO_4. Hexane was kept as eluent in the alumina clean-up step, because the solvent evaporation

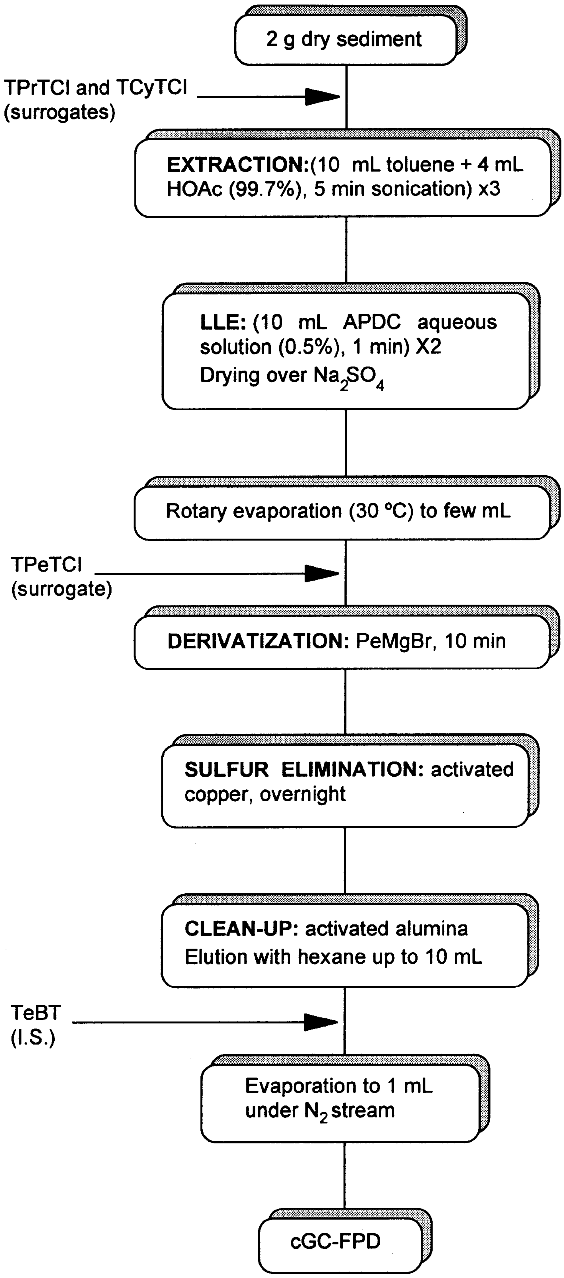

Figure 7 Flow diagram for the developed analytical procedure.

under a stream of N_2 could be too time-consuming if toluene was used as eluent. Pentylated derivatives were also preferred since they are less prone to undergo losses during the solvent evaporation steps.[22]

Validation of the analytical procedure

The developed method was applied to the determination of OTs from two existing CRMs which contain different concentrations and organic matter. Accordingly, PACS-1, highly polluted marine harbour sediment, and CRM-462, coastal sediment with intermediate pollution, were analysed following the procedure described in Fig. 7.

PACS-1

The results obtained for TBT and DBT are in comfortable agreement with the certified values for these compounds (Table 2). However, for MBT a 280% higher value, compared with that certified, was obtained. Some authors have also reported higher values of MBT for PACS-1 and it has been attributed to the current improvements in organotin determination since the certification of PACS-1.[11,23,24] In fact, many analytical procedures that allow an accurate determination of DBT and TBT fail in the determination of MBT.[4]

CRM-462

In order to evaluate the accuracy of the method developed in a sediment with medium pollution, the CRM-462 was determined. Concentrations obtained for DBT and TBT are in agreement with the certified value (Table 2), although a slightly lower value was obtained for DBT. It could be attributable to the lower concentration levels in this CRM.

CONCLUSIONS

An analytical procedure for the determination of butyl- and phenyl-tin compounds from sediment has been developed by optimizing the most relevant extraction variables (acid strength, solvent polarity, complexing agent and extraction time). Degradation during extraction was studied and obviated by optimizing the ratio between the solvent and the acid. In addition, several critical steps following the extraction were identified, such as acid removal and solvent evaporation. An intermediate partitioning step with an aqueous solution of APDC was developed in order to remove the HOAc from the extract before the evaporation stage.

The analytical procedure developed was validated against two different CRMs, PACS-1 and CRM-462. All the results obtained fall within the

Table 2 Results of the validation of the developed analytical procedure

	PACS-1			CRM-462		
	Certified value (ng Sn g^{-1})	Extracted amount [a] (ng Sn g^{-1})	Recovery (%)	Certified value (ng Sn g^{-1})	Extracted amount[a] (ng Sn g^{-1})	Recovery (%)
MBT	280 ± 170	784 ± 64	280	NC[b]	98.7 ± 9.3	—
DBT	1160 ± 180	951 ± 21	82	63 ± 8	43.9 ± 5.5	70
TBT	1270 ± 220	1163 ± 31	92	24 ± 6	23.7 ± 2.4	99

[a] Mean and SD ($n = 3$) are presented as extracted amount.
[b] NC, not certified.

certified value, except MBT for PACS-1, which had a 280% recovery compared with the certified value; that could be attributable to the improvement in the extraction efficiency of the developed analytical technique. The advantages of the developed analytical procedure are its simplicity, the short extraction time, the low volume of solvents and acids required and the widespread availability of the necessary instrumentation.

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