ELSEVIER

Journal of Chromatography A, 846 (1999) 413–423

JOURNAL OF CHROMATOGRAPHY A

Determination of tributyltin and triphenyltin in sediments by liquid chromatography with fluorimetric detection Assessment of spiking procedures

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Abstract

A liquid chromatographic method with fluorimetric detection using fisetin as fluorogenic reagent is proposed for the determination of tributyltin (TBT) and triphenyltin (TPhT) in sediments. Ethyl acetate in the presence of an aqueous solution containing hydrochloric acid and sodium chloride is used as extracting system. This method was applied to the assessment of different spiking procedures used to evaluate the recoveries of the analytes. Variables of spiking experiments such as solvent and volume of the spiking solution, equilibration time and type of sediment were studied. The analytical method together with the proposed spiking procedure has been applied successfully to a sediment in an interlaboratory exercise organised by the European Union.

Keywords: Sediments; Tributyltin; Triphenyltin; Organotin compounds; Fisetin

1. Introduction

The widespread use of organotin compounds (OTs) has led to their entry into the environment. Tributyltin (TBT) and triphenyltin (TPhT), active agents in antifouling paints, are the most important OTs in the marine environment [1]. Recognition of their toxicity has led to the regulation of their use in most countries, and to the monitoring of OT levels in environmental samples. Moreover, since OTs tend to accumulate in sediments, this compartment is considered a potential source for the release of these compounds. Consequently, reliable analytical methods for this matrix are required in order to perform effective monitoring programs.

Determination of OTs requires the combination of a separation method, usually gas chromatography (GC) or liquid chromatography (LC), with a selective and sensitive detection. Although GC shows higher resolution than LC, the latter are simpler and, combined with inductively coupled plasma–mass spectrometry (ICP–MS) or fluorimetric detection it has been applied to determine the most relevant compounds [2–4]. One of the most difficult aspects of the analysis of OTs in complex matrices such as sediments is the extraction of the analytes, as very strong interactions between OTs and matrix occur. Moreover, extraction should be performed in mild conditions to preserve the chemical integrity of the analytes, and therefore it is difficult to achieve

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0021-9673/99/$ – see front matter
PII: S0021-9673(98)01033-4

extraction recoveries close to 100%. A large variety of solvents covering a wide range of polarities have been proposed for OT extraction from sediments. The addition of acids or complexing agents has also been considered [5]. In this paper some of the approaches are evaluated in order to select an extraction method compatible with a previously reported LC method [6] based on separation in a cation-exchange column and post-column fluorimetric detection of OT-fisetin derivatives.

In the validation and application of analytical methods, recovery studies are an essential step. Common approaches to assess recoveries are: analysis of certified reference materials, use of surrogates, isotope dilution and spiking [7]. Spiking is the most commonly applied, especially in case of compounds for which certified materials are not available, as in the case of TPhT. The steps of a spiking experiment include the addition of known amounts of analytes in a proper solvent, an equilibration time to allow incorporation of spikes into the matrix and, finally, the removal of the solvent. Subsequently, the spiked material is analysed. The main risk is that the behaviour of the added analytes may be not the same as that of the native ones. Consequently the recovery value obtained in this way is not a realistic recovery, but may be an overestimation. A systematic study of the influence of the experimental variables of the spiking process on the values of recovery factors has not been reported. Moreover, the information about spiking procedures included in published papers is often insufficient (Table 1).

Taking into account both the relevance of spiking experiments and the lack of rigorous studies on this issue, the purpose of this paper is to examine the influence of the most important spiking variables (concentration of spikes, type of solvent, time of equilibration and volume of solvent) on TBT and TPhT recoveries from sediments in order to establish some recommendations about spiking conditions.

2. Experimental

2.1. Reagents

Stock solutions (0.5 g/l tin) of triphenyltin chloride and tributyltin chloride were prepared by dissolving the compounds (Fluka, >97% purity, Buchs, Switzerland) in methanol (Baker, HPLC, Deventer, The Netherlands) and stored in dark glass bottles at 4°C. Ten-mg/l standard solutions were prepared weekly by dilution with methanol and also stored at 4°C. Subsequent dilutions were freshly prepared with methanol.

The LC mobile phase was prepared by mixing 100 ml of aqueous solution of 0.75 *M* ammonium acetate (Merck, Darmstadt, Germany) with 400 ml of HPLC grade methanol (Baker). This solution was passed through a 0.2-μm nylon membrane filter (Lida, Kenosha, WI, USA) and degassed for 10 min by a helium current.

The post-column reagent used for LC fluorimetric detection contained fisetin 5×10^{-5} *M* and Triton X-100 2.4×10^{-2} *M*. This was prepared from 2.5×10^{-3} *M* methanolic solution of fisetin (Aldrich, Steinheim, Germany) and 0.2 *M* aqueous solutions of Triton X-100 (Merck).

Ethylacetate, hydrochloric acid, sodium chloride, sodium hydrogencarbonate, anhydrous sodium sulfate (Merck, analytical-reagent grade) and methanol (Baker, HPLC grade) were used. Double-deionized water (Milli-Q, Millipore, Molsheim, France) of resistivity 18.2 MΩ cm^{-1} was used throughout.

All glassware was previously soaked in 10% nitric acid for 24 h and rinsed in double deionized water.

2.2. Apparatus

The LC equipment consisted of a Model 480 double piston pump (Ginkotek, Germering, Germany), a Ginkotek MSV 6 injection valve equipped with a 200-μl loop, and a Partisil SCX (10-μm particle size, 25 cm×4.6 mm I.D.) analytical column (Whatman, Maidstone, UK) with a guard column. Post-column reaction was achieved using a Minipuls 3 peristaltic pump (Gilson, Villiers le Bel, France). The derivatization reagent merges with the chromatographic effluent in a T-tube before its introduction into an Aminco-Bowman Series 2 spectrofluorimeter (SLM Aminco, Rochester, NY, USA) equipped with a 25-μl flow-cell (Hellma, Müllheim, Germany).

A microdigest model A301 microwave digester (Prolabo, France), a rotary mixer 34526 (Breda Scientific, Breda, The Netherlands), a centrifuge

Table 1
Summary of spiking procedures described in the bibliography applied to the determination of TBT and TPhT in sediments

Sample	Solvent (volume)	Equilibration time	Spiking level[a] (ng/g)	Recovery (%)		Ref.
				TBT	TPhT	
PACS-1	n.e.	n.e.	1250	109±7	108±2	[10]
n.e. sediment	n.e.	15 min	n.e.	93	n.a.	[9]
		24 h	n.e.	87	n.a.	
Scheldt river	Water	n.e.	5000	95	n.a.	[9]
Adriatic sea (OT-free)	Methanol	30 min shaking+overnight	160	91±10	92±11	[11]
Maggiore lake	n.e.	n.e.	3300	82	n.a.	[11]
Sewer sediment	Acetone	Some hours (thorough mixing)	n.e.	55±10	n.a.	[12]
n.e. sediment (wet)	Ethanol	n.e.	100	86±1	n.a.	[13]
			1000	98±1	n.a.	
Different procedences (9)	n.e.	n.e.	n.e.	85–93	n.a.	[8]
Rhine river	Methanol	n.e.	35–119	142	n.a.	[14]
n.e. sediment (OT-free)	Methanol	n.e.	125	103	n.a.	[15]
PACS-1	Methanol	n.e.	5000	108±12	104±16	[16]
Ontario lake (OT-free)	Hexane	15 min in the rotary evaporator	100 μg/g	108±11	n.a.	[17]
			1000	63±35	n.a.	
			200	81±31	n.a.	
			10	106±12	n.a.	
Marina sediment (OT-free)	Methanol–water (60:40) (150 μl)	24 h, refrigeration	3000	97±8	n.a.	[18]
n.e. sediment (OT-free)	Hexane	24 h at 4°C	8	100±10	n.a.	[19]
			40	92±13	n.a.	
			200	106±2	n.a.	
n.e. sediment (OT-free)	Methanol (10 ml)	(1) Shaking (2) Evaporation in the dark	3	n.e.	n.e.	[20]
n.e. sediment (OT-free)	Methanol (1 ml)	(1) 1 h agitation (2) Evaporation at room temperature	1000	97±5	n.a.	[21]
S. Diego Bay	Ethanol	Overnight at 4°C	0.3	130	n.a.	[22]
			0.5	105	n.a.	
			1.0	93	n.a.	
			1.8	102	n.a.	
PACS-1	Methanol (50–250 μl)	Solvent evaporation (5 min)	1250	109±7	108±2	[23]
CRM-462	Methanol (50–250 μl)	Solvent evaporation (5 min)	1000	99±15	75±24	[23]
RM-424	Methanol (50–250 μl)	Solvent evaporation (5 min)	1000	106±35	82±36	[23]
n.e. sediment (OT-free)	Methanol	Overnight	125	103±24	61±5	[24]

[a]Concentration as Sn. n.e.: non specified; n.a.: non analysed.

(Heraeus Christ, Osterode am Harz, Germany) with glass tubes, a LaboRota 300 rotavapor (Resona, Germany) with a Labo-therm SW 200 thermostathic bath (Resona) and an ultrasound bath (Selecta, Abrera, Spain) were used in extraction experiments.

2.3. Procedures

2.3.1. Spiking

Two hundred μl of methanolic solutions of TBTCl and TPhTCl were added to a slurry of 1 g of dry sediment in 1.8 ml of water. After an equilibration time of at least 30 min in an orbital shaker analysis was carried out.

Alternatively, 200 μl of an aqueous solution of TBT and TPhT were added to 1 g of dry sediment and left to stand for at least 30 min before analysis.

2.3.2. Analysis

In a 40-ml glass extraction tube, 10 ml of an aqueous solution containing 2.6 *M* NaCl and 0.6 *M* HCl were added to 1 g of sediment sample. After a short manual shaking to release gases, 5 ml of ethyl acetate were added. The mixture was stirred mechanically for 30 min and then centrifuged (3000

rpm, 15 min). The organic phase was transferred with a Pasteur pipette to a 40-ml glass tube with a PTFE liner. The extraction was performed once again. Then the residue and the aqueous phase were washed in 5 ml of ethyl acetate. The pooled organic layer was washed in 7 ml of an aqueous phase containing 0.5 *M* $NaHCO_3$ and 1.3 *M* NaCl. After 2 min of shaking, the organic phase was passed through anhydrous sodium sulfate and collected in an evaporation flask. The aqueous phase was washed in 5 ml of ethyl acetate, which was dried and added to the organic extract. The extract was evaporated just to dryness in a rotary evaporator at 35°C. The residue was reconstituted with 2 ml methanol and analytes were determined by LC–fluorimetry as described elsewhere [6].

2.4. Samples

The sediments used in this study were:

(1) Two marina sediments from El Masnou, on the NW Mediterranean coast (Catalonia, Spain): SED-1 from the dry-dock and SED-2 from an inside area; both sediments were oven-dried (at 60°C for 48 h and then at 120°C for 2 h) and sieved at 63 μm.

(2) The reference material RM-424 from BCR, an industrial harbour sediment from the Sado estuary (Portugal) (SED-3).

(3) A sediment from a fluvial channel in The Netherlands supplied by the European Union as the sample for an interlaboratory exercise within the Measurement and Testing Programme (SED-4).

All sediment samples were stored at −20°C. Before analysis, samples were left at room temperature for 1 h, hand-shaken for 5 min to rehomogenise the content and then left to stand for 10 min.

SED-2 and SED-3 had TBT and TPhT levels below the detection limit of the LC-fluorimetry method. Sediment characteristics are summarized in Table 2.

3. Results and discussion

3.1. Selection of the extraction method

Six extraction procedures described in the literature were evaluated for the extraction of TBT and TPhT. The methods, summarized in Table 3, were chosen on the basis of the reported recovery values, simplicity of the procedure and compatibility with the determination technique. They make use of acids and/or organic solvents of high to medium polarity: acetic acid, methanol, 1-butanol, ethyl acetate and dichloromethane. Methods M2, M5 and M6 were slightly modified in order to make them suitable for the LC method. Thus the extracts were evaporated to dryness, either under a nitrogen stream or in a rotary evaporator, and reconstituted in mobile phase or methanol. Fig. 1 shows the results obtained when the six extraction methods were applied to SED-1, which contained incurred amounts of TBT and TPhT.

Methods M-2, M-3, M-4 and M-5 provided no significant differences between TBT concentrations, whereas M-1 and M-6 led to lower results.

In the case of TPhT, method M-6 yielded the highest concentration, whereas methods M-3, M-4 and M-5 provided slightly lower values, without significant differences between them. Finally methods M-1 and M-2 gave clearly lower values.

From the results obtained for both compounds, we can conclude that extraction methods M-3 (ethyl

Table 2
Characteristics of the sediments ($n=3$)

	Major components[a] (%)			TOC[a] (%)	Moisture content[a,c] (%)
	SiO_2	Al_2O_3	CaO		
SED-1	54.7±0.2	15.0±0.02	5.2±0.03	2.7±0.2	2.0±0.1
SED-2	51.0±0.3	14.9±0.02	7.4±0.01	1.5±0.25	1.53±0.01
SED-3	56.6±0.1	13.2±0.02	1.1±0.0	6.4[b]	2.8±0.2
SED-4	43.8±0.3	7.4±0.02	5.4±0.01	10.6±0.2	5.7±0.1

[a]Triplicate determinations.
[b]Value taken from bibliography.
[c]Values obtained by drying at 105±1°C.

Table 3
Description of extraction methods applied to TBT and TPhT extraction; previous LC–fluorimetry determination

Method	Extraction procedure	Ref.
M-1	One g sediment+10 ml methanol. Sonication for 15 min	[25]
M-2	One g sediment+20 ml acetic acid. Stirring overnight. Evaporate to dryness. Reconstitution in mobile phase	[26]
M-3	One g sediment+10 ml aqueous NaCl+1 ml conc. HCl. Extraction with 5 ml of ethyl acetate for 30 min. Evaporation just to dryness. Reconstitution in methanol	[27]
M-4	One g sediment+50 ml HBr:water (2:3). Stirring for 1 h. Extraction with dichloromethane for 2 h. Evaporation to 0.5 ml.	[25]
M-5	One g sediment+3 ml butanol. Sonication for 30 min. Evaporation to 0.5 ml. Dilution with methanol.	[18]
M-6	One g sediment+10 ml 0.5 M acetic acid in methanol. Microwaves (70 W) for 3 min. Evaporation to dryness. Reconstitution in mobile phase	[28]

acetate in HCl medium), M-4 (dichloromethane in HBr medium) and M-5 (butanol in ultrasound) provided the best results. Since methods M-4 and M-5 are more time-consuming than method M-3, this was the extraction method chosen.

However, before its application to the assessment of the spiking process, some aspects of the analytical procedure were evaluated. Firstly, the volume of ethyl acetate and the number of extractions were varied. An increase in the volume of ethyl acetate from 5 to 7 ml did not improve the recovery for either analytes. Similarly, an increase in the number of extraction steps from two to three led to similar recoveries. Consequently, the procedure adopted consists of two extractions plus washing in 5 ml of ethyl acetate.

Because OTs are volatile, especially that of TBT, they may be lost during evaporation of the solvents (methanol or ethyl acetate), and so the influence of the evaporation step was studied. Thus, three 10-ml solutions containing 700 ng/g of TBT and 30 ng/g of TPhT were evaporated under a nitrogen stream up to different stages: before dryness (ca 0.5 ml), just to dryness and 10 min after dryness. The residue was reconstituted with methanol and injected. In the case of TPhT, no losses were observed (Fig. 2). In contrast, significant losses of TBT were observed, increasing with evaporation time (Fig. 2). In view of these results, rotary evaporation was assayed as an alternative. Solutions of both analytes in ethyl acetate and methanol were evaporated before dryness by rotary evaporation at ca 35°C. This evaporation system led to recoveries of TBT and TPhT higher than 95% in all the cases. Attention must be paid to this step and longer evaporation times should be avoided. In further experiments rotary evaporation was used.

Finally, the stability of diluted solutions of OTs in water and methanol at different storage conditions was studied. In spite of the relevance of this aspect to the accuracy of the results, no systematic study has been found. Three solutions of 300 ng/g of TBT and 30 ng/g of TPhT in each solvent were stored for 14 h at 4°C in the dark, at room temperature in the dark, and at room temperature and exposed to light. After storage, LC analysis was carried out. When water was used as solvent, solutions were diluted 5-fold with methanol. The signals of these solutions were compared with those of standards prepared in methanol or in methanol with 20% of water. From the results of these experiments, it can be concluded that both methanolic and aqueous solutions were stable in all of the conditions assayed.

3.2. Recovery assessment by means of spiking experiments

The influence of the nature of the solvent used to add the spikes, the volume of spiking solution, the concentration of spikes, the equilibration time and

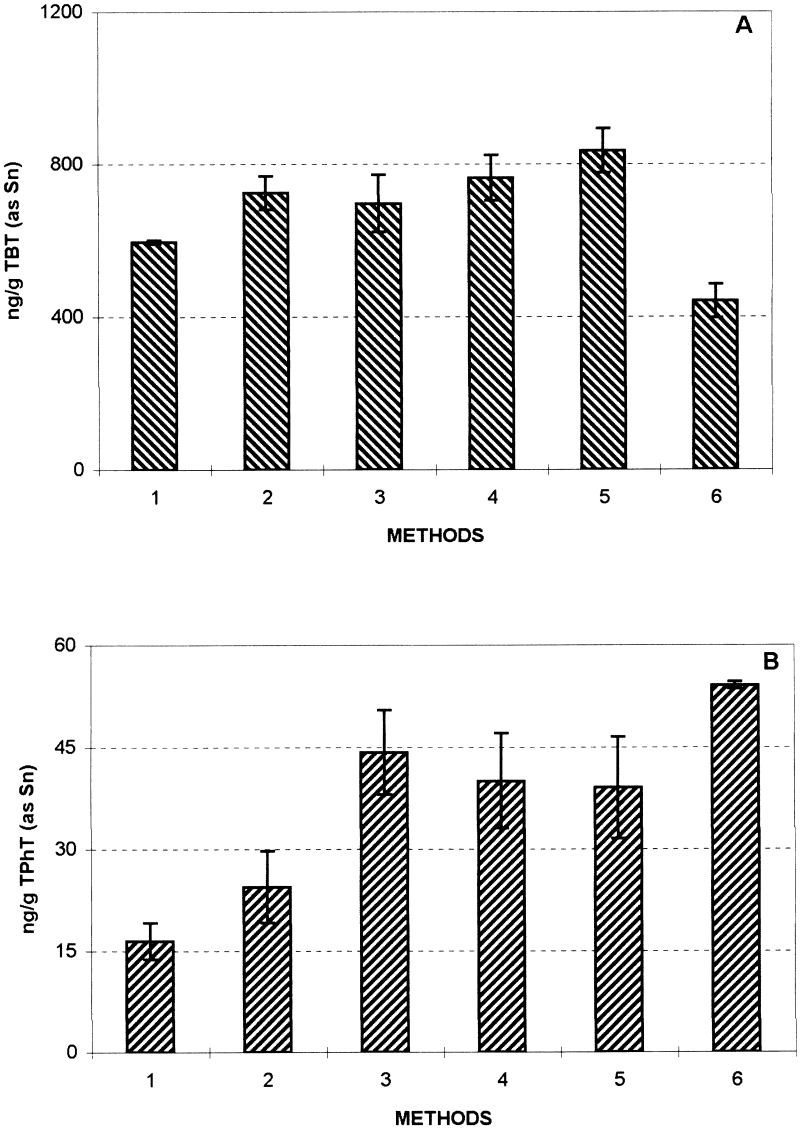

Fig. 1. Concentration of TBT (A) and TPhT (B) obtained by the extraction methods described in Table 3. Error bars indicate standard deviation.

the nature of the sediment on the recovery factors was evaluated (Table 4). Values of recovery factors were compared by means of *Z*-tests. For this purpose, standard deviations for both TBT and TPhT recoveries were estimated from large series of data obtained in our laboratory (σ_{TBT}=3.8 and σ_{TPhT}= 4.5).

In order to assess the influence of the solvent, methanol and water were chosen. Methanol is most often used in spiking experiments although water is more representative in the environment (Table 1). Less polar solvents, such as hexane, sometimes used in this kind of experiment, were discarded, because they do not facilitate the incorporation of the spikes into the sediment. These experiments were performed with SED-2. The sediment was equilibrated

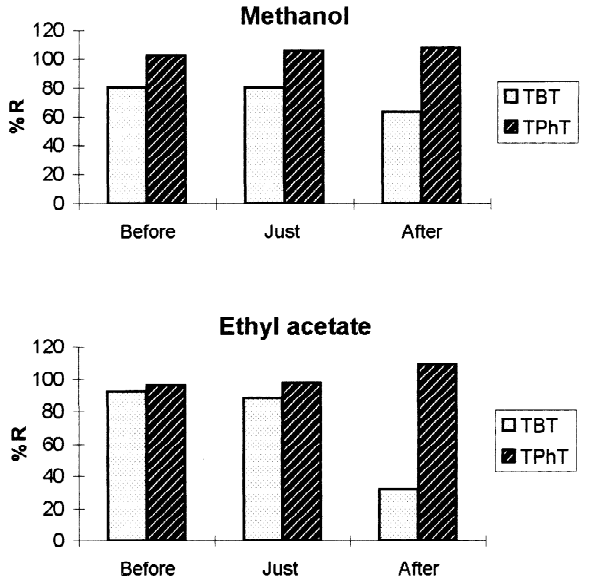

Fig. 2. Influence of the evaporation time (evaporation by nitrogen current) on the recuperation of TBT and TPhT from solutions of methanol and ethyl acetate. R=recovery.

for a period of 16 h with 2 ml of a methanolic solution of the analytes (experiment A) or the same volume of an aqueous solution with 10% of methanol (experiment C). The results indicate that spiking with the methanolic solution leads to significantly higher recoveries ($P<0.001$ for both analytes).

In view of these results, in order to evaluate the degree of TBT and TPhT adsorption into the sediment during the equilibration period, both methanol and aqueous solutions of OTs were held in contact with SED-2 for variable periods of time. It was observed that, after an equilibration period of 30 min, neither TBT nor TPhT was detected in the aqueous solution. In contrast, no significant decrease in the concentration of either substance in the supernatant methanolic solution was observed after a contact period of 14 h. This indicates that when OTs are dissolved in methanol they are not incorporated into the sediment, and in this case, when the solvent of the spiking solution is evaporated, analytes are just deposited on the matrix surface, which make them more easily extractable. Subsequent experiments were carried out with aqueous solutions containing up to 10% of methanol.

In order to ascertain the influence of OT concentration, recovery experiments at three concentration levels, between 200 and 1500 ng/g for TBT

Table 4
Recoveries of TBT and TPhT in different spiking conditions

Experiment	Sediment	Equilibration time	Volume of spiking solution	*n*	Recovery (%)	*s*
TBT						
A	2	16 h	2 ml[a]	6	87.8	7.7
B	2	16 h	200 μl	4	64.8	2.0
C	2	16 h	2 ml	6	73.1	2.0
D	2	30 min	200 μl	6	70.7	3.4
E	2	30 min	2 ml	6	75.4	3.8
F	3	30 min	2 ml	6	80.7	1.7
G	3	16 h	2 ml	4	77.3	3.3
H	4	16 h	2 ml	11	69.7	5.4
TPhT						
A	2	16 h	2 ml[a]	6	102.3	3.5
B	2	16 h	200 μl	4	70.8	3.4
C	2	16 h	2 ml	6	82.9	4.4
D	2	30 min	200 μl	6	75.1	1.6
E	2	30 min	2 ml	4	80.1	1.4
F	3	30 min	2 ml	6	81.4	2.1
G	3	16 h	2 ml	4	80.2	7.1
H	4	16 h	2 ml	8	87.6	13.6

[a]Spikes added as a methanolic solution.

and 15 and 110 ng/g for TPhT, were carried out. Fig. 3 shows good correlations (r^2>0.99) between added and found amounts of OTs, pointing out that recovery rates did not depend on the OT concentrations in the range studied.

To study the influence of the volume of spiking solutions, two procedures were assayed. In experiments C and E, 1 g of sediment was mixed with 2 ml of the spiking solution and the slurry was shaken in an orbital shaker. In experiments B and D, 200 μl of the spiking solution were added dropwise to the sediment. In this case no slurry was formed and the sample was left to stand for the equilibration period without shaking.

For both analytes recoveries found from 2-ml spikes were higher than those obtained from 200-μl spikes, and this effect was more noticeable when equilibration time increased.

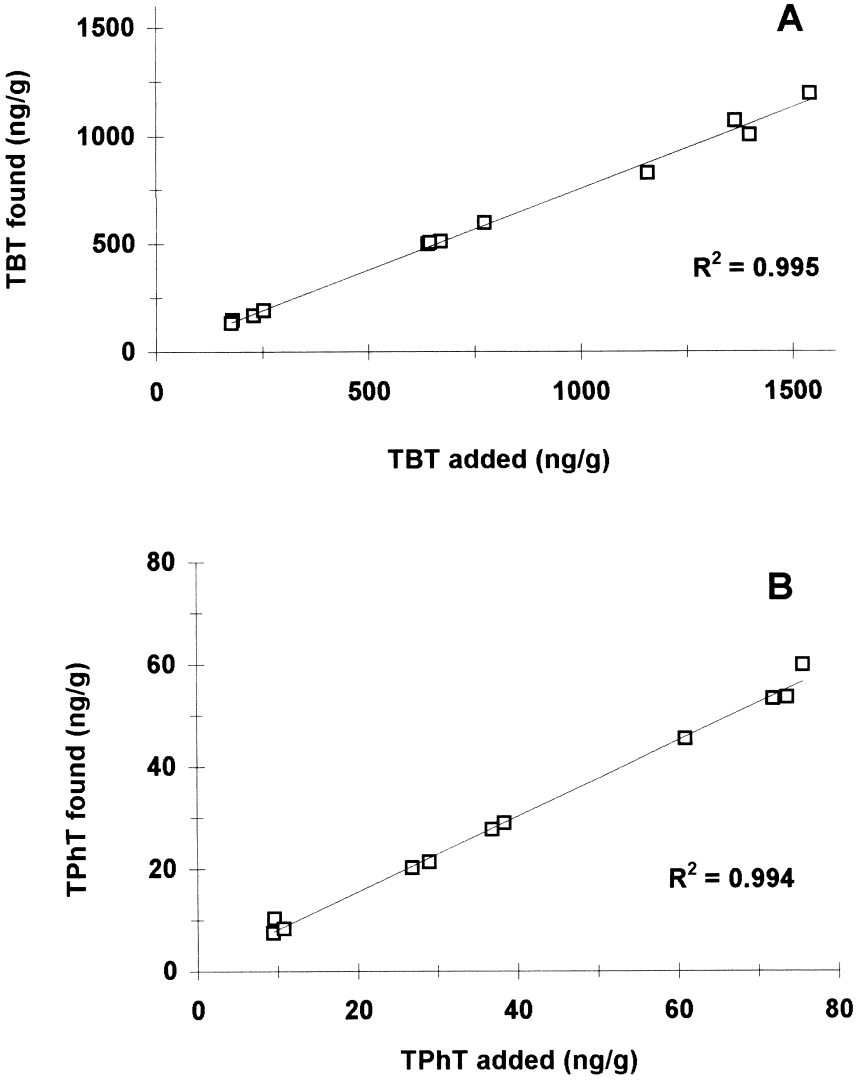

Fig. 3. Recovery experiment graph at different concentrations for TBT (A) and TPhT (B). Correlation factors for the regression lines are indicated in the graphs.

The statistical analysis of the data confirmed these observations. Thus, by comparing the results of experiments B and C, which correspond to an equilibration time of 16 h, a significant effect of spiking volumes on the recoveries of both TBT and TPhT was detected ($P<0.001$). Differences are less significant for an equilibration time of 30 min. Thus, at 95% confidence level, TBT recovery seems to be affected by the spiking volume ($P=0.03$), whereas in the case of TPhT no volume effect was detected ($P=0.08$). However, both P values (0.03 and 0.08) are close to the critical value.

Although there is no obvious explanation for the decrease in recovery rates at low spiking volume, differences could be related with the different kind of interactions that can occur between the added analytes and the matrix when a slurry is formed (2 ml) or in a 'dry' scenario (200 μl).

The influence of equilibration time for a spiking volume of 2 ml can be evaluated by comparing the results of the pairs of experiments C–E, and F–G. No significant differences were observed for either TBT or TPhT ($P>0.05$ in all cases).

The effect of equilibration time was also studied using 200 μl spiking volume (experiments B and D). There was a time effect for TBT ($P=0.02$) but not for TPhT ($P=0.14$).

From these results we adopted a spiking methodology based on the formation of a slurry with 2 ml of an aqueous solution of standards, since these conditions seem more similar to those found in the environment, where the sediment is slowly polluted. As the equilibration time did not have a significant effect, 30 min was selected for convenience, but longer periods can be used. If water is not compatible with the extraction methodology to be used, a microvolume of spiking solution would be a better choice, in order to avoid water evaporation and possible analyte losses.

Finally, in order to study the influence of the sediment, the recovery values obtained when spiking three different matrices were compared (experiments

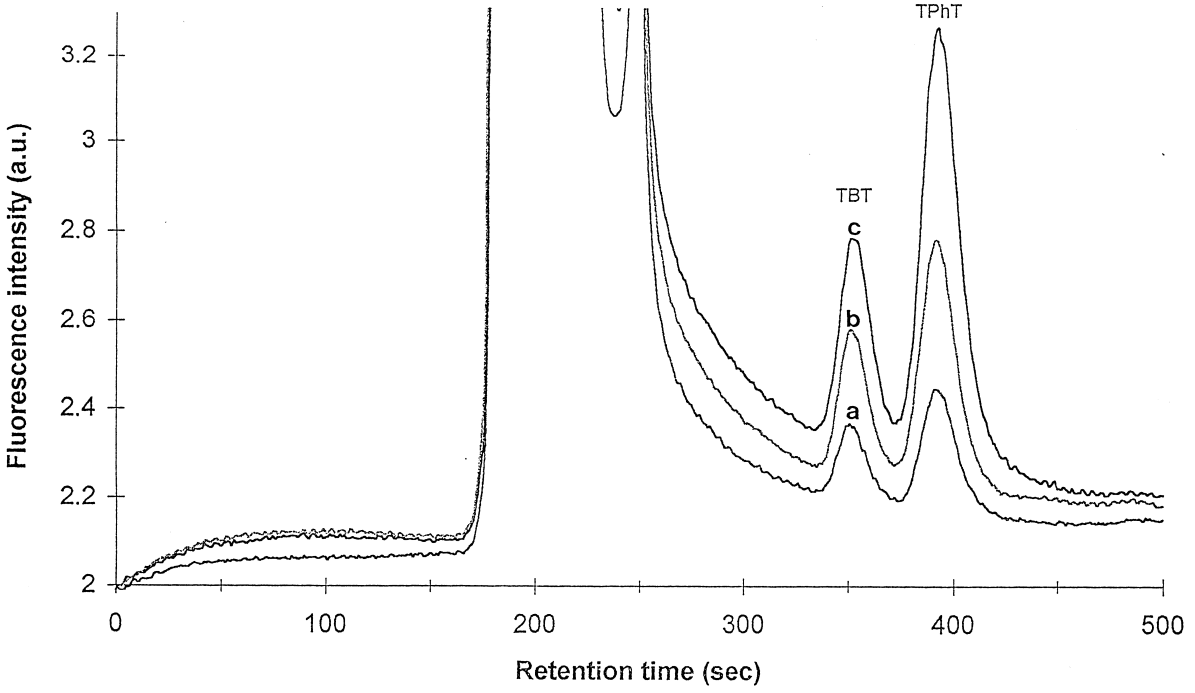

Fig. 4. Chromatograms of (a) an unspiked sample; (b) a sample spiked with 200 ng/g of TBT and 13 ng/g of TPhT; (c) a sample spiked with 400 ng/g of TBT and 32 ng/g of TPhT.

Table 5
Quantitation of TBT and TPhT in a freshwater sediment using ethyl acetate extraction and LC–fluorimetry

	Concentration[a] (ng/g as Sn)	
	TBT	TPhT
Day 1 (n=3)	457±19	18±3
Day 2 (n=2)	424±19	20±6
Day 3 (n=3)	379±12	17±1
Day 4 (n=3)	432±16	14±1
Day 5 (n=2)	411±16	18±5
Mean value±s	424±30	19±4
Interlaboratory mean value	527±147	27±7

[a]Concentrations corrected by recovery.

C, G and H). The analysis of variance (ANOVA) of the results of these experiments showed of a significant effect of the sediment on TBT recovery (P= 0.024), but no influence was observed for TPhT. Other authors have also reported that OT recoveries can be affected by the sediment matrix [8,9]. In this study an attempt to correlate sediment characteristics with this behaviour did not lead to firm conclusions. However, the results indicate that, if accurate results are needed, the analyte recoveries should be determined before applying a known extraction methodology to an unknown sediment matrix.

3.3. Analysis of a freshwater sediment within an interlaboratory exercise

The selected extraction method was applied to extract TBT and TPhT from a strongly polluted sediment from a Dutch channel. The sediment was supplied by the European Union for an interlaboratory exercise previous to the certification of OTs in a candidate reference material.

Firstly, recoveries were evaluated by means of spiking experiments at three concentration levels, according to the proposed procedure; chromatograms are shown in Fig. 4. The results obtained were 66.8 and 88.6% for TBT and TPhT, respectively.

Replicate determinations of the sediment were performed on the same day and also on different days. The results obtained, the mean values and the interlaboratory means are given in Table 5. The precision of our results is within the group of the most precise laboratories. The mean values fall into the ranges defined by the standard deviations of the interlaboratory means.

Acknowledgements

The authors thank the CICYT (AMB98-0327) and the CIRIT (SGR97-394) for supporting this study. They also thank Dr J.M. Bayona (Department of Environmental Chemistry CID-CSIC, Barcelona) for supplying RM-424.

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