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# Speciation of butyl- and phenyltin compounds in sediments using pressurized liquid extraction and liquid chromatography–inductively coupled plasma mass spectrometry

S. Chiron*, S. Roy, R. Cottier, R. Jeannot

*BRGM, Service Analyse et Caractérisation Minérale, B.P. 6009, 45060 Orléans Cedex 02, France*

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**Abstract**

A liquid chromatographic method with inductively coupled plasma mass spectrometry is proposed for the speciation of butyl- (monobutyltin, dibutyltin, tributyltin) and phenyl- (monophenyltin, diphenyltin, triphenyltin) tin compounds in sediments. After evaluation of different additives in the mobile phase, the use of 0.075% (w/v) of tropolone and 0.1% (v/v) of triethylamine in a mobile phase of methanol–acetic acid–water (72.5:6:21.5) allowed the best chromatographic separation of the six compounds. Pressurized liquid extraction (PLE) with a methanolic mixture of 0.5 *M* acetic acid and 0.2% (w/v) of tropolone was suitable for the quantitative extraction of butyl- and phenyltin compounds with recovery values ranging from 72 to 102%. This analytical approach was compared to conventional solvent extraction methods making use of acids and/or organic solvent of medium polarity. The main advantages of PLE over conventional solvent extraction are: (i) the possibility to extract quantitatively DPhT and MPhT from sediments, which could not be done by a solvent extraction approach; (ii) to preserve the structural integrity of the organotin compounds; (iii) to reduce the extraction time from several hours in case of solvent extraction techniques to just 30 min. For spiked sediments, limits of detection ranged from 0.7 to 2 ng/g of tin according to the compound. The relative standard deviations were found to be between 8 and 15%. The developed analytical procedure was validated using a reference material and was applied to various environmental samples. 

*Keywords:* Sediment; Environmental analysis; Organotin compounds

## 1. Introduction

Butyltin compounds (BTs) and phenyltin compounds (PhTs) are used worldwide mainly as antifouling agents and biocides, respectively. Due to their high toxicity toward aquatic organisms, tributyltin (TBT), dibutyltin (DBT) and triphenyltin (TPhT) compounds are included in the European Union pollutant list (EU, Directive 76/464) [1]. Moreover, monobutyltin (MBT) diphenyltin (DPhT) and monophenyltin (MPhT) compounds are also regarded as toxic pollutants and are expected at trace levels in the environment. Recent monitoring programmes have shown the presence of BTs in sea and fresh water [2,3] at concentration levels of a few ng/l. However, BTs and PhTs tend to accumulate in sediments, a compartment from which they can be released, becoming a steady source of pollution [3,4]. Consequently, reliable analytical methods for

*Corresponding author.

*E-mail address:* s.chiron@brgm.fr (S. Chiron)

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this matrix are required in order to perform effective monitoring programmes.

Various analytical procedures have been implemented for trace analysis of organotin compounds (OTs) in natural waters or sediments. Lately, direct alkylation of organotin compounds in water using either sodium tetraethylborate or tetra(*n*-propyl)borate reagents followed by their analysis by gas chromatography with selective and sensitive detection methods such as flame photometric detection (FPD) [5], pulsed-flame photometric detection (PFPD) [6], mass spectrometry (MS) [7] and to a lesser extent inductively coupled plasma mass spectrometry (ICP-MS) [8] has appeared as a method of choice for the ultra-trace (ng/l level) determination of OTs in environmental waters. However, this method may not be suitable for sediment sample analysis for the following reasons: (i) derivatized compounds are not commercially available and different derivatization yields in pure solvent and complex matrix extracts can be expected; (ii) GC analysis requires extensive and time-consuming clean-up of the extracts before injection; (iii) conventional GC detection methods, GC–FPD using a band pass filter at 610 nm or the selected-ion monitoring mode in GC–MS are not selective enough due to the coelution of the OTs with alkylated sulfur compounds [9] and due to the low-molecular masses of diagnostic ions in the electron impact ionization mode, respectively [10].

As a consequence, liquid chromatography (LC) coupled with ICP-MS [11] or fluorimetric detection after derivatization [12] has appeared as a simpler alternative approach for the determination of butyl- and phenyltin compounds in sediments. However, the number of species analysed using LC are significantly lesser than the ones analysed using GC and, to our knowledge, LC methods have not yet encompassed the whole group of BTs and PhTs. Among the different modes of LC, $C_{18}$ reversed-phase has been used for the separation of BTs. In this case, the use of a complexing agent, such as tropolone, is mandatory [13]. Addition of triethylamine in the mobile phase allows the speciation of DBT, TBT, TPhT and DPhT in sediments [14].

The most difficult aspect of the analysis of OTs in complex matrices remains the extraction of the analytes. Various solvent extraction techniques have given good recovery values ranging from 70 to 100% for both butyl- and phenyltin compounds [15,16]. Samples are generally treated with hydrochloric acid with shaking or sonication followed by sequential non-polar solvent extraction. In an attempt to shorten the sample extraction time, supercritical fluid extraction (SFE) and microwave-assisted leaching (MAE) have been proposed. However, with MAE, PhTs are degraded to a large extent during extraction [17] and with SFE, MPhT and MBT are hardly recovered [18]. Recently, a method based on pressurized liquid extraction (PLE) has been evaluated showing good recovery values ranging from 80 up to 100% for all the BTs and PhTs with only a slight degradation of DPhT into MPhT [7].

In view of the different approaches for the analysis of BTs and PhTs in sediments, the main aims of this work were the following:

(i) to compare extraction procedures based on PLE with conventional solvent extraction procedures in order to extract butyl- and phenyltin compounds from sediments;

(ii) to develop a LC method able to separate all the butyl- and phenyltin compounds;

(iii) to assess the coupling capability of LC–ICP-MS for the analysis of butyl and phenyltin compounds in sediments.

## 2. Experimental

### *2.1. Reagents*

Tropolone, triethylamine and acetic acid were purchased from Fluka (Buchs, Switzerland). Doubly deionized water (Milli-Q, Millipore, Molsheim, France) of 18.2 MΩ resistivity was used. Stock solutions (1 mg/ml) of triethyltin, monobutyltin, dibutyltin, tributyltin, monophenyltin, diphenyltin and triphenyltin chloride (Strem Chemicals, Bischheim, France) were prepared by dissolving the compounds in gradient-grade methanol and stored in dark bottles at 4°C. Ten-mg/l solutions were prepared weekly and subsequent dilutions were freshly prepared.

### *2.2. Samples*

Reference material PACS-2 sediment with a certified content of dibutyltin and tributyltin compounds

was obtained from the National Research Council of Canada. The sediment SED 0 was used for spiking procedure. Other sediments, SED 1, SED 2 and SED 3, SED 4 were collected from French harbours and channels, respectively. They were oven-dried at 40°C and sieved and stored in the dark at −20°C before analysis. Only fractions below 150 μm were analysed. Sediment characteristics are summarized in Table 1.

### 2.3. Analytical procedures

#### 2.3.1. Spiking

Two hundred μl of a methanolic solution of BT and PhT chlorides were added to a slurry of 2 g of a sediment dissolved in 2 ml of methanol. After an equilibration time of 24 h, the solvent was eliminated with a gentle stream of nitrogen and the sediment was left to stand for at least 1 week. Prior to extraction, the water content was adjusted to 10% (w/w) and the material was allowed to swell for 1 day. Blank samples were prepared in the same way using pure methanol as spiking agent.

#### 2.3.2. Sample preparation and preconcentration

Two solvent extraction methods chosen in the literature for their performances were carried out in order to recover BTs and PhTs from spiked sediments. Briefly, in the first method [19], 2 g of sediment were stirred overnight in presence of 30 ml of acetic acid and then centrifuged (3000 rpm, 15 min). The organic phase was transferred to a 40-ml glass tube and evaporated down to 200 μl under a gentle stream of nitrogen. In the second method [16], 40 ml of an aqueous solution containing 2.6 *M* NaCl and 0.6 *M* HCl were added to a 2-g sediment sample. After manual shaking, 10 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 removed and the operation was repeated once again. The pooled organic layer was washed in 7 ml of an aqueous phase containing 0.5 *M* $NaHCO_3$ and 1.3 *M* NaCl, meanwhile the aqueous phase was washed in 5 ml of ethyl acetate. The organic extract was evaporated to dryness and the residue was reconstituted in 200 μl of mobile phase.

Table 1
Characteristics of the sediments ($n=3$)

| | Major components (%) | | | Sn (ppm) | Total organic carbon (%) |
|---|---|---|---|---|---|
| | $SiO_2$ | $Fe_2O_3$ | CaO | | |
| SED 0 (for spikes) | 48 | 5.3 | 3.8 | 5 | 7.3 |
| SED 1 | 49.4 | 6.1 | 4.2 | 14 | 2.5 |
| SED 2 | 51.9 | 6.4 | 4.3 | 18 | 3.1 |
| SED 3 | 52.5 | 7.6 | 3.7 | 34 | 5.5 |
| SED 4 | 58.7 | 7.5 | 3.1 | 38 | 6.2 |

PLE was carried out with the Dionex ASE 200 device (Sunnyvale, CA, USA) equipped with a controller device. Two grams of sediment were mixed with 9 g of quartz sand. The mixtures were transferred to 11-ml extraction cells. The extraction cells were fitted with solvent and heated within 5 min to the extraction temperature (100°C). Sediment samples were extracted with five static cycles of 5 min. Between each static extraction cycle 4 ml of solvent was renewed. Various extraction conditions including 1 *M* acetic acid in methanol, 0.2% (w/v) tropolone dissolved in 0.5 *M* acetic acid–methanol and 1 *M* sodium acetate–1 *M* acetic acid in MeOH as recommended elsewhere [7] were tested. The optimal solvent was found to be methanol with 0.5 *M* acetic acid and 0.2% (w/v) tropolone. The 20–25-ml raw extract was passed through a 1 g $C_{18}$ cartridge (Supelco, Bellefonte, PA, USA) for a rapid clean-up. The cartridge was rinsed with 3 ml HPLC mobile phase in order to recover possible adsorbed OTs on the free silanol group of the $C_{18}$ cartridges. The extract was concentrated under a gentle stream of nitrogen down to 200 μl. Extracts should not be evaporated to dryness in order to avoid losses. Before injection, an internal standard (triethyltin chloride) at 1 mg/l was added to the extracts. For environmental samples, 10 g of sediments were extracted in order to ensure the representativity of the sample.

#### 2.3.3. Analysis

HPLC mobile phase was delivered by a 9010 model Varian pump running in the isocratic mode at a flow-rate of 0.9 ml/min. The mobile phase consisted of a mixture of methanol–water–acetic acid (72.5:21.5:6, v/v/v) containing 0.075% (w/v) tropolone and 0.1% (v/v) triethylamine. Separation was achieved on a 250×4.6-mm i.d TSK gel ODS-80 TM column (Interchim, Montluçon, France). The

Table 2
ICP-MS operating conditions

| | |
|---|---|
| Radio frequency power | 1350 W |
| Plasma gas | 16 l/min |
| Auxiliary gas | 0.65 l/min |
| Nebulizer gas | 1 l/min |
| Oxygen | 60 m l/min |
| Cones | Pt |
| Mass | 120 |

column outlet was connected to the nebulization device (Meinhard, type K) by means of a 5-cm polyether ether ketone (PEEK) tubing (0.5 mm I.D.). Injection volume was 50 μl. The ICP-MS system used was a Plasmaquad PQ3 (VG Elemental, Winsford, UK) equipped with a double-pass Scott spray chamber cooled at −4°C. The operating conditions are shown in Table 2. In order to prevent carbon accumulation on the sampler, the argon nebulizer gas was mixed with oxygen (6%). The tin major isotope (32.37% abundance) at $m/z$ 120 was monitored. Quantification was performed by means of an internal standard (I.S.), triethyltin. I.S. was added after the extraction step and I.S. only compensated for the uncontrolled variations in the chromatographic measurements. The triethyltin relative chromatographic responses of butyl- and phenyltin compounds were calculated from standard solutions prepared in methanol.

## 3. Results and discussion

### 3.1. Optimization of chromatographic conditions

Previous work with LC–ICP-MS, using Kromasil 100 $C_{18}$ packing material showed that the presence of tropolone (0.1%) in a methanol–water–acetic acid mobile phase increases the retention time of DBT meanwhile TBT and MBT are hardly affected. As shown in Fig. 1, the same behaviour can be observed for DPhT compound, tropolone acting therefore as a specific complexing agent of the disubstituted tin compounds. However, in presence of tropolone, separation of TBT and TPhT is not achieved, which represents the main drawback of this analytical approach. Besides, White et al. [14] demonstrated that the use of 0.1% of triethylamine in methanol–acetic acid–water mobile phase increases the retention times of TBT, as confirmed in Fig. 1 and allowed the baseline separation of DBT, TBT, DPhT and TPhT. However, in this case, DBT and DPhT are hardly retained on the column and coelute with MBT and MPhT, respectively. Combination of both

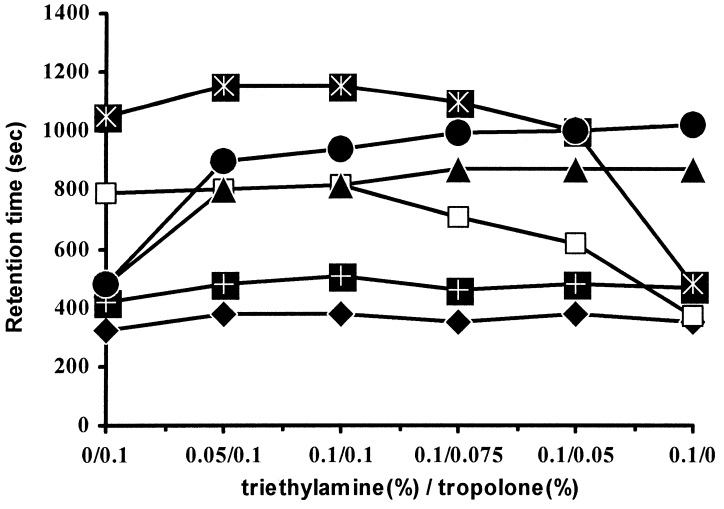


Fig. 1. Effect of the composition ratio of triethylamine to tropolone present in the LC mobile phase on the separation of BTs and PhTs compounds. Mobile phase: methanol–water–acetic acid (72.5:21.5:6, v/v/v). (◊) monophenyltin; (□) diphenyltin; (△) triphenyltin; (+) monobutyltin; (*) dibutyltin; and (●) tributyltin.

additives in the mobile phase logically allows the baseline separation of the six compounds, as shown in Fig. 2a. A ratio of tropolone–triethylamine of 0.075% (w/v):0.1% (v/v) has given the highest resolution between the six compounds. Use of acetonitrile gave somewhat thinner chromatographic peaks as compared to methanol but poorer stability of the plasma was noticed. Furthermore, methyltin compounds, other potential pollutants in sediment and generated by biological activity [20] were tested in order to evaluate possible interferences. Methyltin eluted with a retention time of 250 s while the dimethyltin peak overlapped the MPhT peak bringing about possible overestimation of the MPhT results. Finally, when elemental tin was injected in the chromatographic system, it was steadily released from the analytical column prompting a possible higher background level in the chromatograms when it is present at high concentrations (>30 mg/l) in the extracts.

### *3.2. Optimization of the extraction conditions*

Two solvent extraction procedures, described in the literature and making use of acids and/or organic solvent of medium polarity (ethyl acetate) have been chosen according to their efficiency and have been evaluated for the extraction of BTs and PhTs from a spiked sediment. Method 1 referred to an extraction with acetic acid while method 2 referred to an extraction with ethyl acetate after digestion of the matrix with an hydrochloric acid solution. Those conventional extraction methods were compared with an PLE using methanol with 0.2% (w/v) tropolone and 0.5 *M* acetic acid as extracting solvent (method 3). Table 3 depicts the recovery values obtained with the three different extraction methods. As far as solvent extraction methods are concerned, results for BTs were in accordance with those found in the literature [16,19]. Method 1 was not suitable for the extraction of PhTs as already described [21]. Method 2 yielded to good recovery values for BTs and TPhT but lower recovery values of MPhT and DPhT were noted, as illustrated in Fig. 2b. Previous results [7] using PLE with 1 *M* acetic acid–1 *M* sodium acetate showed good recovery values ranging from 90 to 100% for all BTs and PhTs compounds. Applying the same experimental conditions, lower recovery values were found in case of MBT and MPhT (63 and 27%, respectively; results not shown). No degradation of MPhT and MBT into inorganic tin was observed as confirmed by the derivatization of the extract with $NaBEt_4$ and the subsequent analysis of elemental tin by GC–MS. MBT and MPhT were therefore not completely extracted. This result can be explained by the way the spiking was done. As a rule, a spiking experiment includes the addition of known amounts of analytes in a solvent, an equilibration time to allow incorporation of spikes into the matrix and finally the removal of the solvent [22]. However, in Ref. [7], the spiking procedure consisted in distributing the standard solution over the sediment. The recovery value obtained in this way may not be realistic and may entail an overestimation [21]. Use of a higher amount of acetic acid clearly entailed the degradation of DPhT into MPhT and probably into inorganic tin. This option was therefore discarded. Finally, 0.2% tropolone was found to be the best option to increase the extraction yields of both MPhT and MBT to 92 and 93%, respectively. The role of a complexing agent to enhance the extraction of monoalkyltin compound is once more endorsed. The monoalkyltin compounds should undergo strong specific interaction such as surface complexation and ionic interactions in solid matrices. Dirty extracts were obtained and a clean-up step was required before analysis. A mere clean-up involving $C_{18}$ cartridges has turned out to be sufficient in order to eliminate the more apolar interferences and to avoid the bandbroadening of the first eluting peaks in the LC chromatograms. As a conclusion, PLE has appeared as a unique tested method capable of quantitatively extracting DPhT and MPhT from spiked sediments. PLE allowed better recovery values than that permitted by solvent extraction methods. The stability of the extracts was investigated. Extracts were stocked in the dark at 4°C. Even in these conditions, rapid degradation of PhTs compounds was observed, more in particular DPhT into MPhT. As a consequence, the analysis must take place within a week after extraction.

### *3.3. Performances of the analytical method*

The performances of the proposed analytical method in terms of precision, limit of detection (LODs)

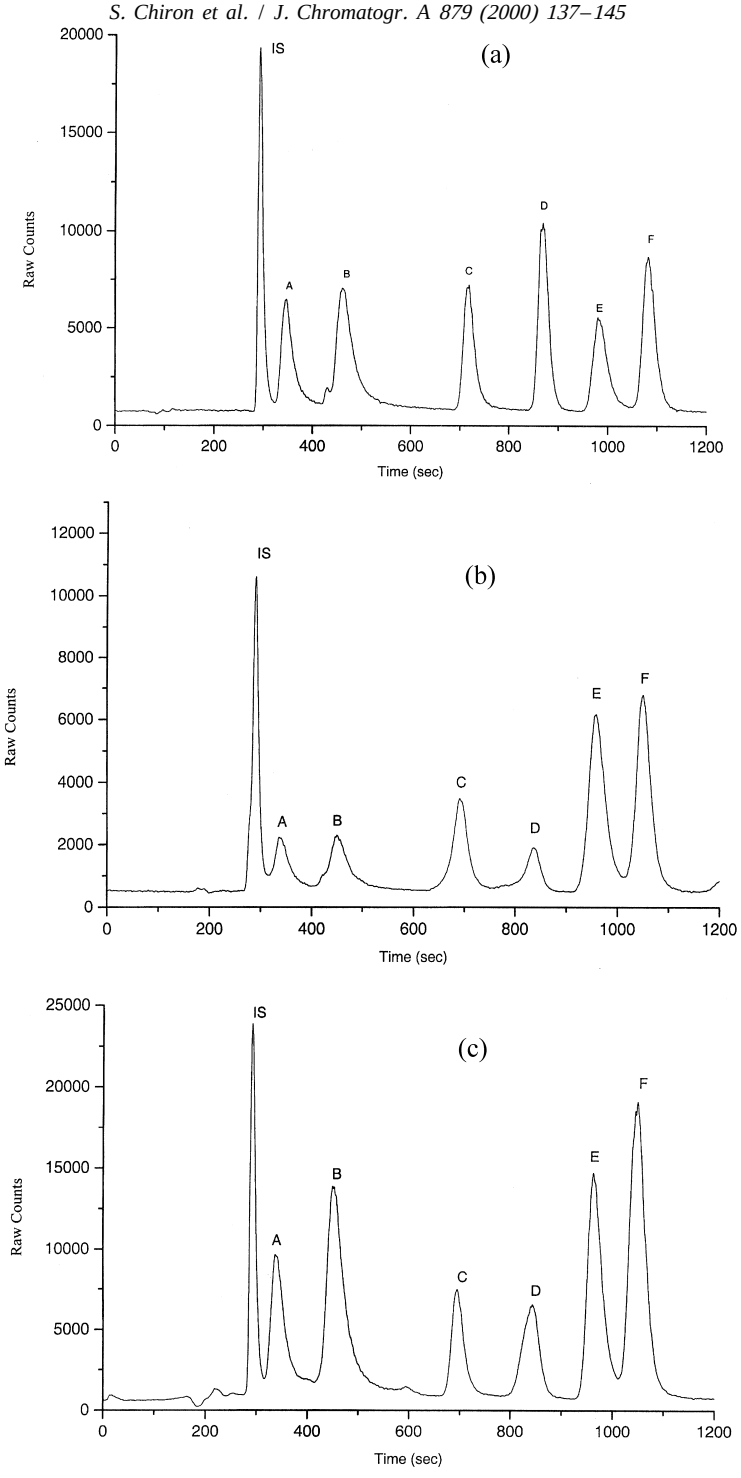


Fig. 2. (a) Chromatogram of a mixture of standards, 50 ng each. (b) Chromatogram obtained after solvent extraction (method 2) of a spiked sediment. (c) Chromatogram obtained after extraction of a spiked sediment by PLE (method 3). Spiking level: BTs, 1 μg/g; PhTs, 0.5 μg/g. For more details see Section 2. (A) Monophenyltin; (B) monobutyltin; (C) triphenyltin; (D) diphenyltin; (E) tributyltin; (F) dibutyltin. I.S. concentration is 1 μg/ml in chromatograms (a) and (c) and 0.5 μg/ml in chromatogram (b).

Table 3
Recoveries and relative standard deviations determined from spiked sediments and using different methods

| | Method (1)[a] | | Method (2)[a] | | Method (3)[a] | | LODs[b] |
|---|---|---|---|---|---|---|---|
| | Recovery (%) | RSD (%) | Recovery (%) | RSD(%) | Recovery (%) | RSD (%) | |
| MBT | 52 | (16) | 62 | (20) | 93 | (13) | 2 |
| DBT | 61 | (12) | 99 | (11) | 102 | (8) | 0.7 |
| TBT | 82 | (8) | 98 | (9) | 95 | (10) | 1 |
| MPhT | 23 | (32) | 52 | (18) | 92 | (15) | 2 |
| DPhT | 11 | (28) | 34 | (15) | 72 | (14) | 0.7 |
| TPhT | 35 | (22) | 95 | (12) | 98 | (9) | 1 |

[a] Method 1: 30 ml acetic acid stirring overnight. Method 2: 10 ml aqueous NaCl+1 ml concentrated HCl; extraction twice with 5 ml ethyl acetate. Method 3: PLE with methanol+0.5 *M* acetic acid+0.2% (w/v) tropolone. For more details see Section 2.
[b] LODs are reported as Sn. Spiking level of TBT, DBT, MBT: 1 μg/g. Spiking level of TPhT, DPhT, MPhT: 0.5 μg/g.

and linearity were evaluated by analysing spiked sediments with amounts of BTs and PhTs encompassing the range of interest that is between 1 ng/g and 10 μg/g. The detector was at least linear over four orders of magnitude with coefficients of determination $r^2>0.995$. The LODs are calculated using method 3 as extraction method and are shown in Table 3. LODs were calculated from a signal-to-noise ratio of 3:1. LODs ranged between 0.7 and 2 ng/g of tin according to the compound. Relative standard deviation (RSD) values between 8 and 15% were obtained at spiking level of 100 ng/g ($n=5$) and precision was not improved as compared to solvent extraction procedures, as shown in Table 3. In order to assess the accuracy of the method, the contents of butyltin compounds were determined in the currently available reference material PACS-2. Results are reported in Table 4. MBT, DBT and TBT concentrations of 634±82, 1020±82 and 920±92 ng/g, respectively, were measured in PACS-2 sediment ($n=5$), using method 3 as the extraction method. DBT and TBT concentrations were in perfect agreement with the certified values (1090±150 and 980±130 ng/g, respectively), whereas the concentration of MBT exceeded the indicated value by a factor of 2.1. Besides, PACS-2 contains TPhT and DPhT at concentration levels of 80±8 and 43±5 ng/g, respectively. Interferences have hampered the exact quantitation of MPhT.

### *3.4. Determination of BTs and PhTs in environmental samples*

The proposed method was applied to environmental samples representing (i) a great range of concentration levels and (ii) two different types of

Table 4
Results on PACS-2 reference material, harbour and channel sediments[a]

| | PACS 2[b] (ng/g) | PACS 2[c] (ng/g) | SED 1 (ng/g) | SED 2 (ng/g) | SED 3 (ng/g) | SED 4 (ng/g) |
|---|---|---|---|---|---|---|
| MBT | 300[d] | 634±82 | 316(332)[e] | 251(298) | 136(162) | 121(138) |
| DBT | 1090±150 | 1020±82 | 1037(1028) | 671(680) | 1057(1068) | 221(232) |
| TBT | 980±130 | 920±92 | 820(812) | 1052(1048) | 31(26) | 31(39) |
| MPhT | n.d.[f] | n.f.[f] | n.f. | n.f. | n.f. | n.f. |
| DPhT | n.d. | 43±5 | n.f. | n.f | n.f. | n.f. |
| TPhT | n.d. | 80±8 | n.f. | 126(134) | n.f. | n.f. |

[a] All values are in ng/g of dried sediments.
[b] Certified values.
[c] Obtained values.
[d] Indicative values.
[e] Values within brackets represent the concentration of the species after subtracting a 300-ng/g spike.
[f] n.d., not determined; n.f., not found.

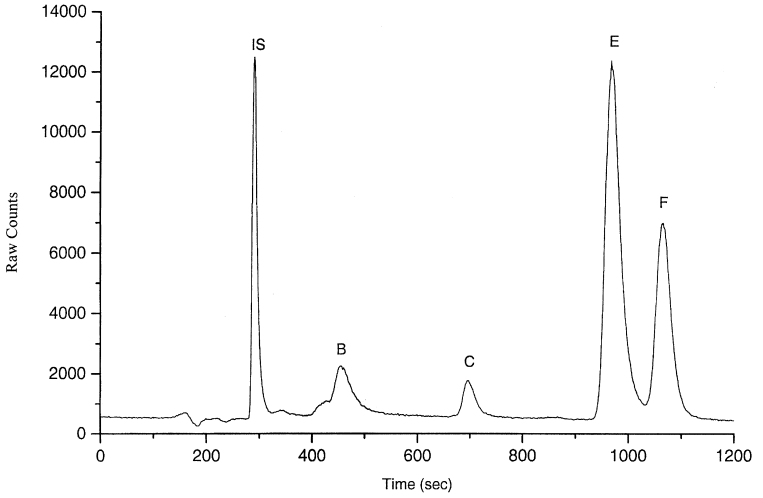


Fig. 3. Chromatogram corresponding to the analysis of a real harbour sediment. (B) monobutyltin, (C) triphenyltin, (E) tributyltin and (F) dibutyltin at concentration levels of 251±33, 126±11, 1052±100 and 67±5 4 ng/g, respectively.

sediment matrices: harbour and channel sediments (see Table 1). Fig. 3 shows a typical chromatogram obtained after extraction of 10 g of a harbour sediment containing MBT, TPhT, TBT and DBT at concentration levels of 251±33, 126±11, 1052±100 and 671±54 ng/g, respectively. Besides, in order to ensure the quantified concentrations in the unspiked sediments, the sediment was also fortified with 300 ng/g of each compound. All results are shown in Table 4. While there is a good agreement between fortified and unspiked results for TBT, DBT and TPhT, there is a slight overestimation of the MBT results, resulting from a slight matrix effect. In this way, the applicability of the analytical method for monitoring purposes in sediments was clearly demonstrated.

## 4. Conclusions

A method has been developed for the LC separation of MBT, DBT, TBT, MPhT, DPhT and TPhT followed by mass spectrometric detection using an ICP interface. This method involved both the use of tropolone and triethylamine as additives in the mobile phase. In this work, the applicability of PLE, as an extraction tool for routine extraction of BTs and PhTs from sediments has been demonstrated. The use of a complexing agent, such as tropolone is mandatory in order to extract MBT and MPhT species which may undergo strong ionic interaction and/or surface complexation in complex matrices. The main advantages of PLE over conventional solvent extraction were: (i) the possibility to extract DPhT and MPhT from sediments, which could not be done by a solvent extraction approach; (ii) to preserve the structural integrity of the BTs and PhTs compounds; (iii) to reduce the extraction time from several hours (10 h in case of acetic acid extraction) to just 30 min. The selectivity of extraction is not enhanced as compared to solvent extraction and a clean up of the extract is always required before LC analysis. However, this methodology can be regarded as cost effective in order to achieve monitoring programmes. The applicability of PLE for the extraction of other organometallic species such as organoarsenic compounds in polluted soils is currently assessed in our laboratory.

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