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Automated headspace-solid-phase micro extraction–retention time locked-isotope dilution gas chromatography–mass spectrometry for the analysis of organotin compounds in water and sediment samples

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Abstract

An automated method for the simultaneous determination of six important organotin compounds namely monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT) in water and sediment samples is described. The method is based on derivatization with sodium tetraethylborate followed by automated headspace-solid-phase micro extraction (SPME) combined with GC–MS under retention time locked (RTL) conditions. Home-synthesized deuterated organotin analogues were used as internal standards. Two high abundant fragment ions corresponding to the main tin isotopes Sn^{118} and Sn^{120} were chosen; one for quantification and one as qualifier ion. The method was validated and excellent figures of merit were obtained. Limits of quantification (LOQs) are from 1.3 to 15 ng l^{-1} (ppt) for water samples and from 1.0 to 6.3 μg kg^{-1} (ppb) for sediment samples. Accuracy for sediment samples was tested on spiked real-life sediment samples and on a reference PACS-2 marine harbor sediment. The developed method was used in a case-study at the harbor of Antwerp where sediment samples in different areas were taken and subsequently screened for TBT contamination. Concentrations ranged from 15 μg kg^{-1} in the port of Antwerp up to 43 mg kg^{-1} near a ship repair unit.

Keywords: Derivatization; Retention time locking; Isotope dilution; Organotin compounds analysis; Water; Sediment samples

1. Introduction

Because of the recent awareness of the toxicological effects of many organometallic species, organometal speciation is presently a topic of intense research. Within the class of organometallics, organotin compounds are probably the most widely spread in the environment due to their use as biocides in polymers, in the agricultural industry, as antifouling paints, etc. [1–3]. Organotin compounds degrade in the environment into more polar metabolites [4] and, for instance, tributyltin one of the most frequently used organotin additives (as tributyltinchloride or (bis)tributyltinoxide), degrades into dibutyltin (DBT) and monobutyltin (MBT). Consequently, a large diversity of organotin compounds can be detected in environmental samples [5]. Alarming toxic effects on living organisms such as disturbances in the hormonal system and even the occurrence of imposex already appearing at parts per trillion (ppt) level concentrations [6,7], show the importance of developing highly sensitive and robust analytical methods for their determination in environmental samples.

Several methods for the extraction and analysis of organotins have been described. Extraction with tropolone and *n*-hexane followed by Grignard derivatization and determination with GC–flame photometric detection (FPD) [3,8–13] is more and more replaced by the less time consuming in situ ethylation with sodium tetraethylborate ($NaBEt_4$) [14–17] followed by GC–FPD, GC–atomic

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emission detection (AED) or GC–inductively coupled plasma mass spectrometry (ICPMS) [15,17,18]. A few years ago, solid-phase micro extraction (SPME) developed by Arthur and Pawliszyn [19] in combination with GC–ICPMS was applied for the analysis of $NaBEt_4$ derivatized volatile [18] and semi-volatile [20] organotins in environmental samples. More recently, stir bar sorptive extraction (SBSE) [21], based on the same principle as SPME but with a much higher volume extracting phase (polydimethylsiloxane—PDMS) was applied for the determination of organotins in environmental samples after in situ derivatization with $NaBEt_4$ and CGC–ICPMS [22].

Accurate organotin speciation in different matrices requires the use of appropriate internal standards in order to sufficiently alleviate matrix effects and systematic errors occurring during the sample preparation steps. Tripropyltin (TPT) and tricyclohexyltin (TCyT) are the most frequently used internal standards for the analysis of organotin compounds in environmental samples [18,22]. It remains, however, questionable whether those compounds behave exactly the same as the target analytes and correct for all matrix interferences. More recently, isotope labeled standards such as isotopically enriched TBT (Sn^{117}, Sn^{118} or Sn^{119}) were introduced resulting in more reliable and accurate results [23–25] for ICPMS detection. Besides this approach, also deuterated organotin compounds can be used for internal standardization [26]. Deuterated labeled standards, however, cannot be applied in combination with element selective detectors (AED and ICPMS) but are ideal for GC–MS analysis. In this framework, we have to note that environmental laboratories are all equipped with GC–MS instrumentation and prefer this combination for organotin speciation over GC–AED or GC–ICPMS. Dealing with thousand of samples, GC–MS indeed is by far the cheapest and best-established technique in environmental laboratories.

The aim of this work was to construct an automated organotin analyzer by combining derivatization and automated headspace SPME analysis with state-of-the-art retention time locked (RTL)-GC–MS instrumentation for the determination of trace amounts of organotin compounds in environmental samples. Home-synthesized deuterated organotin compounds were implemented as internal standards. The method was validated and evaluated for repeatability, linearity and accuracy for both water and sediment samples. The developed method was used to evaluate, in the framework of a European TBT-remediation project, the extent of TBT contamination in sediment samples from the harbor of Antwerp.

2. Experimental

2.1. Chemicals and reagents

Mono-(MPhT), di-(DPhT) and tri-(TPhT)phenyltinchloride as well as mono-(MBT) and di-(DBT)butyltinchloride were purchased from Strem Chemicals (Newburyport, MA, USA). Tri-(TBT) and tetra-(TeBT)butyltinchloride were from Fluka Chemie AG (Buchs, Switzerland). Glacial acetic acid (99.99%) and sodium acetate were obtained from Sigma–Aldrich (Bornem, Belgium) and ethanol (Suprasolv grade) from Merck (Darmstadt, Germany). Sodium tetraethylborate ($NaBEt_4$) was purchased from Strem Chemicals or from Sigma–Aldrich. A 1% (m/v) solution of $NaBEt_4$ in Milli-Q water was freshly prepared daily. Milli-Q water was obtained by purification and deionisation of tap water in a Milli-Q plus water system (Millipore, Bedford, MA, USA). A HOAc/NaOAc buffer pH 5.3 was prepared by adding an appropriate amount of HOAc to a 0.2 M solution of NaOAc in Milli-Q water. Deuterated organotin standards (as chlorides), MBT (d9), DBT (d18), TBT (d27), MPhT (d5), DPhT (d10) and TPhT (d15) were synthesized as described elsewhere [27]. For internal standardization, a solution of ca. 5 and 0.5 mg l^{-1} in ethanol was used to spike sediment and water samples, respectively. Throughout this work, concentrations of organotin compounds are expressed as amount referring to the respective cation, except when specifically mentioned otherwise.

Stock solutions of 100 mg l^{-1} from the native organotin compounds and further dilutions were prepared in ethanol. Standard mixtures of butyltins and phenyltins were prepared separately as we observed that mixing the six organotin compounds together resulted in exchange of the butyl and/or phenyl groups, forming artifacts [27]. All standard solutions were stored in the dark at 4 °C.

Real-life organotin contaminated sediments were collected at the harbor of Antwerp, Belgium. A blank sediment sample was obtained by heating a relatively low contaminated sediment at 400 °C for 24 h. It was experimentally verified that all butyltins and phenyltins were removed at this temperature by evaporation and/or degradation to inorganic tin [28,29]. Freshly prepared blank sediment material was always analyzed before use in order to verify a sufficient low background level. For method validation, the reference material PACS-2 (marine harbor sediment) was purchased from the National Research Council of Canada (Ottawa, Ont., Canada).

2.2. Instrumentation

Analyses were performed on an Agilent 6890 GC–5973N MSD (Agilent Technologies, Little Falls, DE, USA) combination equipped with retention time locking software. A 0.75 mm i.d. SPME liner was installed in the split/splitless injector and the temperature was set at 250 °C. The column was a 30 m × 0.25 mm i.d. × 0.25 μm film thickness HP-5MS (Agilent Technologies). The oven was programmed from 50 °C (1 min) at 10 °C min^{-1} to 300 °C (4 min) and the carrier gas was helium (constant pressure 70 kPa, 41 cm s^{-1} at 50 °C). MS parameters were: transfer line 300 °C, source temperature 230 °C, MS quad temperature 150 °C, 50 ms dwell time per ion and solvent delay 5 min. Automated headspace-SPME extraction and desorption was carried out

with a Multi Purpose Sampler (MPS-2) from Gerstel GmbH (Mülheim, Germany). The extraction time and temperature were 30 min and 80 °C with a stirring rate of 500 rpm (1 min incubation time at 80 °C). Desorption time was 1 min (splitless injection) followed by 2 min bake-out time. Fibers coated with 100 μm polydimethylsiloxane (Supelco, Bellefonte, PA, USA) were used.

2.3. Sample preparation and derivatization

2.3.1. Water samples

Aqueous test samples were prepared by adding an appropriate amount of organotin standard solutions to a mixture of 5 ml Milli-Q water and 5 ml buffer solution in a closed-cap headspace vial of 20 ml. For real-life water samples, the same procedure was applied but 1 ml ethanol was added to prevent adsorption of the organotin compounds to the glass wall or to the small particles present in those samples. Subsequently, appropriate amounts of the six internal standards are added, resulting in a concentration of approximately 250 ng l^{-1}. Derivatization is performed by adding 300 μl of a 1% $NaBEt_4$ solution. The sample vials are vigorously shaken and placed in an ultrasonic bath for 10 min. The vials are then placed in the MPS-2 autosampler for headspace-SPME extraction.

2.3.2. Sediment samples

The organotin compounds are leached out according to the procedure described by De Smaele et al. [30]. One milliliter glacial acetic acid (99.99%) and 1 ml ethanol were added to 0.5 g of wet sediment sample and the sample is placed in an ultrasonic bath for 3 h. The leaching process was evaluated by repeating the extraction for different time periods and the optimum leaching time was 3 h. Appropriate amounts of deuterated internal standards were added together with, in case of spiking experiments or standard addition calibration, native organotin standards. Internal standard concentrations in the order of 100 μg kg^{-1} (ppb) were used. Afterwards, 8 ml of buffer solution was added and derivatization was performed with 500 μl of the 1% $NaBEt_4$ solution as described for the water samples. The dry mass of the sediment sample was measured by weighing after thermal treatment at 105 °C for 12 h.

3. Results and discussion

3.1. Method development

Separation of the organotin compounds is achieved on a standard HP-5MS capillary column. The method was retention time locked with tetrabutyltin (t_r = 16 min) according to the procedures described [31,32]. The locked retention times for the different target organotin compounds with their deuterated analogues are listed in Table 1.

Combining GC–MS in scan mode with the RTL screener software provides easy peak location and identification of the target organotin compounds based on their mass spectra and retention times. In ion monitoring mode, besides easy peak allocation, shifts in selected ion windows after column or instrument maintenance and in calibration curves are avoided [32,33]. Figs. 1 and 2 show the scan mass spectra obtained for each native organotin compound and its deuterated analogue, respectively. Based on these mass spectra, specific ions for ion monitoring detection were chosen in order to built up a GC–MS method that makes ultra sensitive detection possible. Two ions per solute giving the highest abundances and/or lowest background levels were selected. They are depicted in bold in Figs. 1 and 2. From the two selected ions, the highest abundant ion was used for quantification and the other one as qualifier ion. The selected ions and ion monitoring windows are included in Table 1.

Table 1
Locked retention times, windows for ion monitoring and selected ions (bold are quantification ions) for the target organotin compounds and their deuterated analogues

Organotin compound	Locked retention time (min)	SIM windows (min)	Selected ions
MBT (d9)	9.82	8.50–11.40	242, **244**
MBT	9.91	8.50–11.40	233, **235**
DBT (d18)	12.09	11.40–13.00	277, **279**
DBT	12.26	11.40–13.00	261, **263**
MPhT (d5)	13.60	13.00–13.80	316, **318**
MPhT	13.63	13.00–13.80	289, **291**
TBT (d27)	14.05	13.80–17.00	258, **260**
TBT	14.28	13.80–17.00	251, **255**
DPhT (d10)	18.83	17.00–22.00	311, **313**
DPhT	18.89	17.00–22.00	301, **303**
TPhT (d15)	23.09	22.00–25.00	364, **366**
TPhT	23.17	22.00–25.00	349, **351**

Optimum derivatization yields for the butyl- and phenyltins are obtained at a pH of 5.3 and 8, respectively [20,22]. A multi-residue method, however, requires selection of one pH only. A pH of 5.3 was chosen because this was the best compromise for both the butyl- and phenyltins [22]. Headspace SPME analysis was applied because it offered not only the fastest equilibration times and highest sensitivities, but above all because it was much more robust for enrichment from difficult matrices such as sediment samples compared to liquid SPME. Analyses were performed at different temperatures and the optimum temperature was 80 °C. Extraction at lower temperatures resulted in much lower extraction recoveries especially for TPhT. Equilibrium was almost reached for DBT (d18), TBT (d27) and DPhT (d10) in 30 min, while for TPhT (d15), equilibrium was not reached even after 60 min. Equilibrium conditions are, however, not required as long as the extraction conditions are kept constant or if labeled internal standards are used. This is the case here and moreover SPME extraction is fully automated. Extraction at 80 °C during 30 min was applied as standard operating procedure.

During optimization of the sample preparation procedure, several sources of contamination had to be eliminated. This is especially critical for water samples for which much lower concentrations should be measured compared to sediment

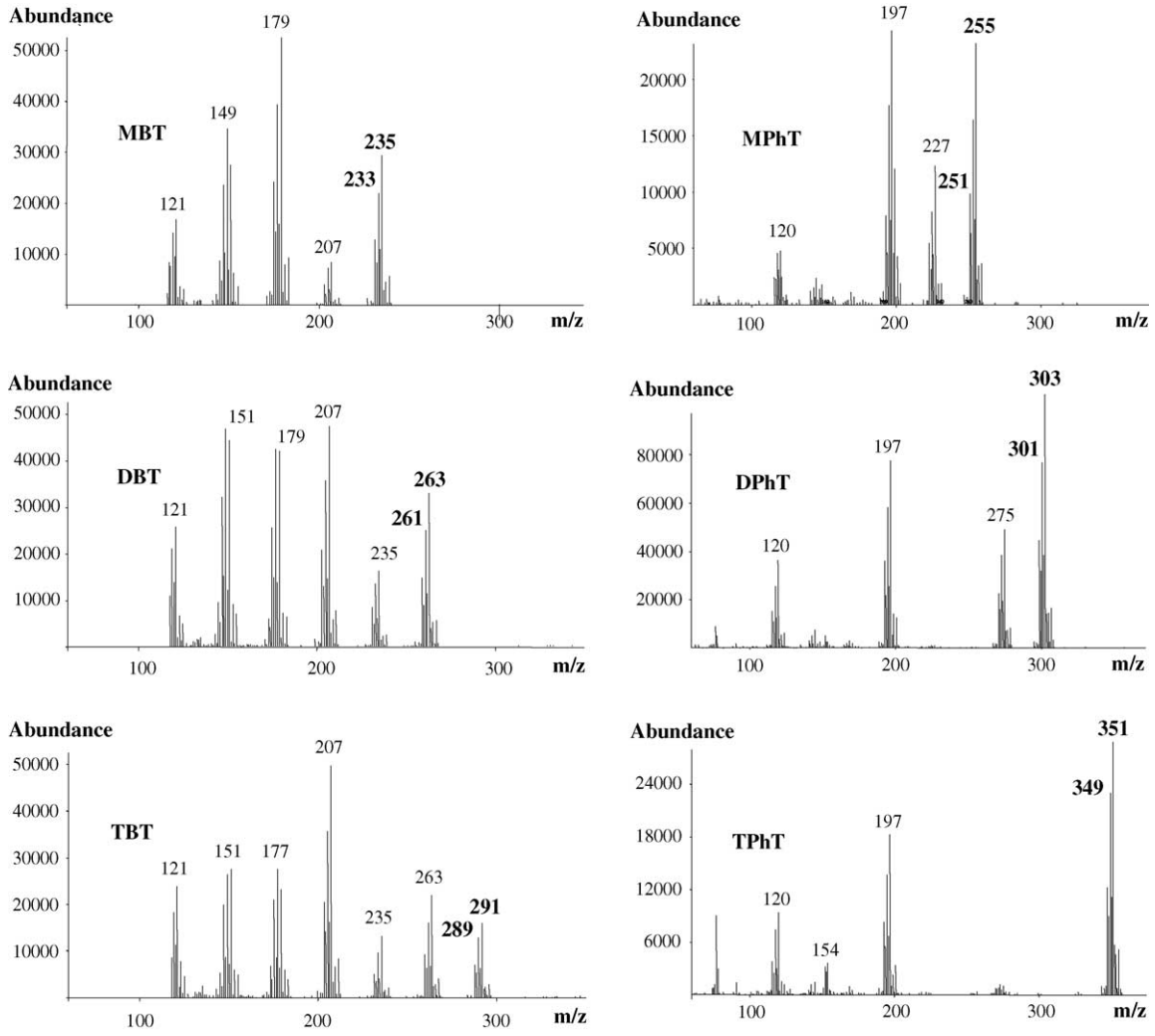

Fig. 1. Mass spectra of the six major organotin compounds with the ion for quantification and the qualifier ion depicted in bold.

samples. Glassware should be properly cleaned, high purity solvents and chemicals (especially ultra pure glacial acetic acid) should be used and Milli-Q water should be freshly prepared. Small background levels of monobutyltin, dibutyltin and diphenyltin are, however, difficult to avoid. MBT and DBT contamination originates from the laboratory environment (plastic tubing, rubber teats, etc.) while the $NaBEt_4$ derivatization reagent appeared to be the cause of the DPhT background level. Variable DPhT background levels were measured when using different batches of the derivatization reagent or from different suppliers. Blank runs should be regularly performed to check on background levels. Taking the necessary precautions, the background level in aqueous media could be reduced to $5\,ng\,l^{-1}$ for MBT, DBT and DPhT while TBT, MPhT and TPhT did not suffer from background contamination. For water samples the limit of quantitation for MBT, DBT and DPhT was therefore set at $15\,ng\,l^{-1}$ and not at the 10 S/N level (see Section 3.2).

Fig. 3 shows a chromatogram of a low level ($\pm 60\,ng\,l^{-1}$) spiked Milli-Q water sample. The deuterated internal standards were spiked at a range of $250\,ng\,l^{-1}$. Note that the deuterated species of MBT, DBT, TBT and TPhT are baseline separated from the non-deuterated species.

3.2. Figures of merit

Milli-Q water was spiked with $250\,ng\,l^{-1}$ of the deuterated internal standards and with the native organotin compounds in the range 10–$1000\,ng\,l^{-1}$ (nine-point calibration) and analyzed as described. Regression coefficients between 0.9967 and 0.9998 were measured. Blank sediment samples were spiked in a 1–$1000\,\mu g\,kg^{-1}$ range (five-point calibration) with a fixed concentration of the deuterated internal standards ($100\,\mu g\,kg^{-1}$) giving regression coefficients between 0.9981 and 0.9994. Good linearity was only possible with the deuterated standards. Using TPT or TCyT as internal standards, the linearity was poor.

Table 2 presents data on repeatability over a one day and a 6-month period for spiked Milli-Q water samples at 200 and $500\,ng\,l^{-1}$, respectively, and for a spiked sediment sample

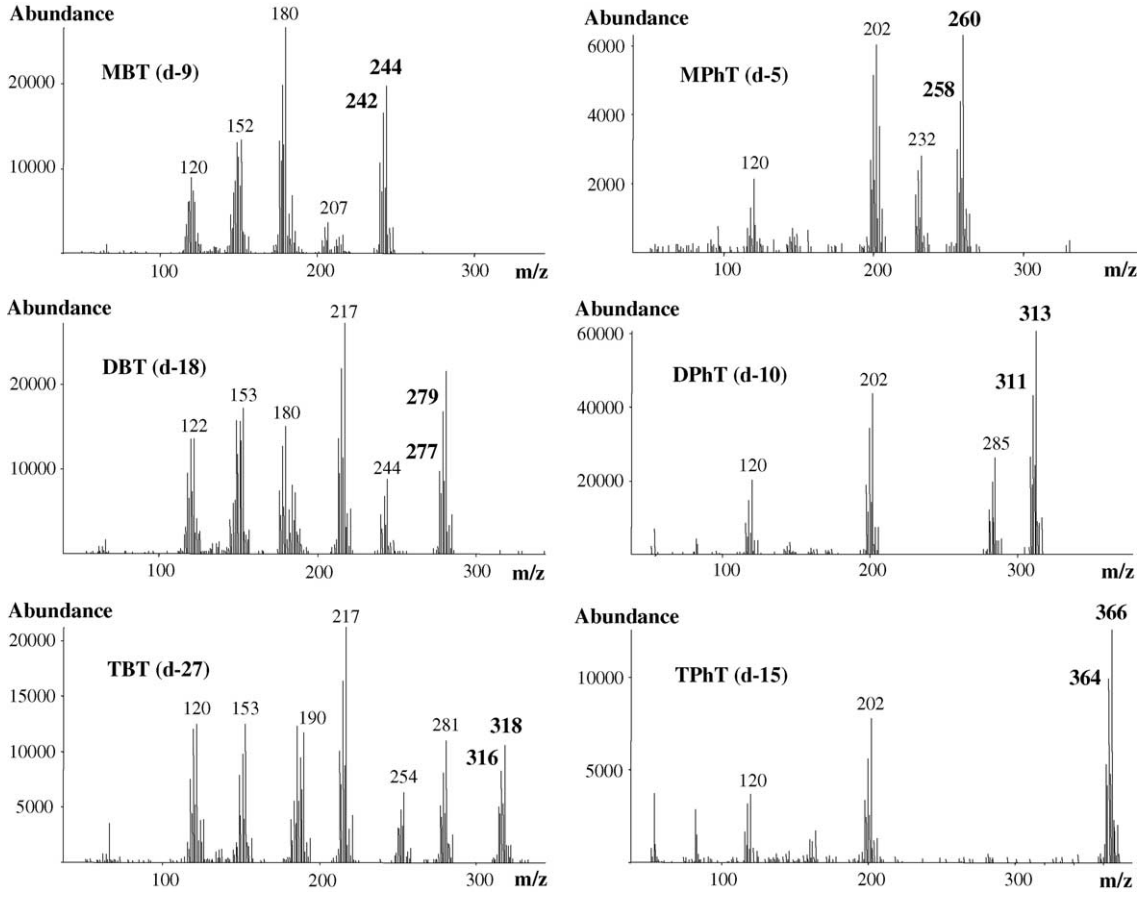

Fig. 2. Mass spectra of the deuterated organotin standards with their quantitative SIM ion and qualifier ion depicted in bold.

at 100 μg kg^{-1}. Good R.S.D. values were obtained for both phenyltins and butyltins illustrating the robustness of the method.

The limit of detection (LOD—3 S/N) for each of the six organotin compounds was determined in a Milli-Q water sample spiked with a low amount of these compounds resulting in peaks close to the LOD values (Table 3). Background concentrations for MBT, DBT and DPhT were taken into account in order to obtain a correct LOD. LOD tests for sediment analysis were performed on a spiked blank sediment sample. Higher LOD values are found for the phenyltin compared to the butyltin compounds. Matrix suppression for phenyltins indeed was noted for the sediment samples resulting in lower absolute recoveries compared to aqueous samples. This does not impose problems by using the deuterated internal standards. Relative recoveries (spike versus internal standards) for all organotin solutes range from 98 to 117% (Table 2).

Fig. 4 shows a chromatogram of the PACS-2 marine harbor sediment that is certified for TBT. Values reported for MBT and DBT are considered less reliable because they are not based on the results of at least two independent methods. Table 4 presents the concentrations measured for MBT, DBT and TBT, expressed as μg kg^{-1} Sn, together with the 95%

Table 2
Repeatability within day and within 6 months for water and sediment samples

Organotin compound	Within day repeatability		Within 6 months repeatability		Sediment recovery (%)
	(A) Water, R.S.D. (%) $n = 6$, 200 ppt	(B) Sediment, R.S.D. (%) $n = 6$, 100 ppb	(A) Water, R.S.D. (%) $n = 6$, 500 ppt	(B) Sediment, R.S.D. (%) $n = 8$, 100 ppb	
MBT	6.36	3.89	8.42	3.83	100.6
DBT	3.74	4.76	8.92	4.07	98.1
TBT	2.34	1.73	8.58	2.93	105.6
MPhT	4.18	4.06	6.40	5.90	101.2
DPhT	2.28	4.27	5.68	9.82	107.8
TPhT	2.90	4.14	6.01	8.00	116.6

Table 3
LODs and LOQs in water and sediment samples

Organotin compound	Water samples		Sediment samples	
	LOD ng l^{-1} (ppt)	LOQ ng l^{-1} (ppt)	LOD μg kg^{-1} (ppb)	LOQ μg kg^{-1} (ppb)
MBT	0.8	15	0.3	1.0
DBT	0.6	15	0.3	1.0
TBT	0.4	1.3	0.4	1.3
MPhT	0.8	2.6	1.4	4.6
DPhT	0.5	15	0.7	2.3
TPhT	1.1	3.6	1.9	6.3

Table 4
Analysis of organotins in PACS-2 sediment sample

Organotin compound	($C_x \pm 2$ s) μg kg^{-1} as Sn		R.S.D. (%) $n = 6$
	Certificate concentrations	Concentration	
MBT	450 ± 50[a]	562 ± 24	2.27
DBT	1090 ± 150[a]	775 ± 96	6.21
TBT	980 ± 130[b]	929 ± 32	1.78

[a] Information value.
[b] Certificate value.

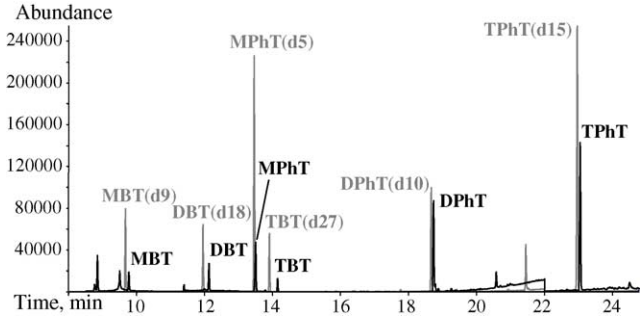

Fig. 3. Chromatogram of a water sample (Milli-Q) spiked at ca. 60 ng l^{-1} (DPhT 200 ng l^{-1} and TPhT 100 ng l^{-1}; deuterated internal standards were added at 250 ng l^{-1}).

confidence limits calculated on six replicates. R.S.D. values are given as well. For TBT, the measured concentration was in good agreement with the certified concentration and with the value reported by Monperrus et al. [23] determined with GC–ICPMS using isotopically enriched TBT (Sn^{117}).

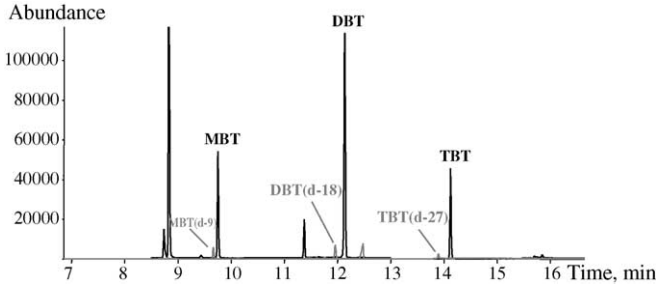

Fig. 4. Chromatogram of the PACS-2 marine harbor sediment material containing TBT as certified organotin compound and with MBT and DBT reported as information values. Deuterated internal standards were added in a concentration of 100 μg kg^{-1}.

3.3. Case-study of the harbor of Antwerp

The developed method was applied for sediments in the harbor of Antwerp within the framework of the European TBT-remediation project. Sediment samples were taken in the whole area of the harbor and analyzed with headspace-SPME–GC–MS. Alarming high concentrations (up to 50 mg kg^{-1}) were found in the area where wet and dry docks are situated (Fig. 5). This was expected because the ships are stationed here for maintenance work, often including repainting of the ship hull with TBT antifouling paint. In contrast to the very high TBT concentrations found in the sediment samples, water samples taken in this area contain relatively low concentrations of TBT (50–150 ng l^{-1}). This

Fig. 5. TBT concentrations in sediment samples from the wet and dry docks of Antwerp Ship Repair, Antwerp harbor, Belgium.

clearly proves the high adsorption affinity of TBT on sediment. Nowadays, TBT pollution of harbors is mainly considered a problem of sediment contamination and less of water contamination. Care should, however, be taken because low ng l^{-1} level concentrations in water samples can be toxic for several living organisms [34].

4. Conclusion

Derivatization with sodium tetraethylborate followed by automated headspace-SPME–RTL-GC–MS in the ion-monitoring mode provides a sensitive and accurate method for the simultaneous determination of the most important butyl- and phenyltin compounds in water and sediment samples. The use of deuterated organotin compounds as internal standards largely contribute to the robustness of the method. The method was validated for water and sediment samples with excellent figures of merit. Advantages of the proposed procedure in comparison with other analytical methods used for organotin analysis are the simple sample preparation, fully automated headspace-SPME extraction and the relatively low instrument investment cost (GC–MS compared to GC–ICPMS and/or GC–AED). The method was intensively tested for TBT screening of sediments in the harbor of Antwerp and in some areas, especially where ship maintenance is performed, TBT concentrations up to 50 mg kg^{-1} were detected.

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