Improving detection limits for organotin compounds in several matrix water samples by headspace-solid-phase microextraction and GC-MS

L. Segovia-Martínez¹, A. Bouzas-Blanco¹, P. Campins-Falcó²,* A. Seco-Torrecillas¹

¹ Dpto. Ingeniería Química. Universidad de Valencia. Doctor Moliner 50. 46100. Burjassot – Valencia. Spain (E-mail: alberto.bouzas@uv.es; aurora.seco@uv.es; laura.segovia@uv.es)
² Dpto. Química Analítica. Universidad de Valencia. Doctor Moliner 50. 46100. Burjassot – Valencia. Spain (E-mail: pilar.campins@uv.es)

Abstract

Triethyltin, tributyltin, diphenyltin and triphenyltin were selected as model compounds. The method is based on an in situ ethylation and simultaneous headspace- solid-phase microextraction (HS-SPME) and gas chromatographic-mass spectrometry analysis (GC-MS). The extraction procedure was optimized studying some variables such as reaction time, salinity, sample volume and headspace volume. SPME-GC-MS and SPME-GC-FID techniques were compared; quality assurance parameters such as sensitivity, selectivity and precision were established. The proposed procedure showed limits of detection between 0.025 ng/L and 1 ng/L. The linearity was in the 0.025-5000 ng/L range. The precision expressed as relative standard deviations (RSD), were below 20%. Real wastewaters and seawaters were analysed. The method permits controlling legislated annual average values.

Keywords: Gas chromatography, mass detection, headspace solid-phase-microextraction, organotin compounds.

1. Introduction

In the 1980s, organotin compounds were recognised for the first time as being responsible of very serious environmental contamination, and consequently the European Union listed them as priority pollutants. The Directive 2000/60/EC (Water Framework Directive-WFD) is probably the most significant international legislation to be introduced in the field of water from many years [1]. WFD includes and protects different kinds of water in Europe (surface water, subterranean, transitional and coastal) with the aim to achieve and ensure a good quality for all of them. WFD includes as a priority and hazardous substance the tributyl compounds among others substances. Furthermore, Directive 2008/105/EC lays down environmental quality standards (EQS) for priority substances and certain other pollutants as provided for in WFD. The Directive 2008/105/EC establishes the extent permitted of tributyl compounds (tributyltin-cation) in inland and other surface waters, expressed as an annual average value (0.0002 μg/L) or as maximum allowable concentration (0.0015 μg/L).

Organotin compounds have been extensively used in recent decades. Several monoalkyl tins have been used as PVC stabilizers, catalysts, water repellents and fire retardants. Some dialkyl tins have been used as catalysts, stabilizers against heat and light effects in construction industry, anthelmintics in poultry management, insecticides for sheep and cattle and for packaging of food, beverages, pharmaceuticals and cosmetics. Trialkyl tins have been used as biocides in marine antifouling paints, fungicides, insecticides, mosquito larvicides, wood preservatives and industrial circulation water disinfectant [1],[2].
Organotins toxicity is dependent on the size and number of organic groups attached to the tin atom. Trialkyltins are generally more toxic than the corresponding dialky1 or monoalkyl derivatives. Within the trialkyltin compounds, the lower homologues, triethyltin and trimethyltin, have the greatest acute toxicity. Various dialky1tin and trialkyltin compounds have an immunotoxic effect. Tributyltin is particularly toxic in gastropods and molluscs. It can produce chronic toxic effects on oysters (shell deformation), mussels (growth inhibition) and marine gastropods (sterilization of females) [3], [4].

Analytical methods for organotin compounds determination wearing in mind WFD must be highly sensitive. Determination of trace organotins in water requires the combination of a separation method, usually gas chromatography (GC) or liquid chromatography (LC), coupled with highly selective and sensitive detectors, such as mass spectrometry [5]-[9], atomic absorption spectrometry [10], flame photometry [11]-[13], flame ionization detection [14]-[15].

Solid phase microextraction (SPME) was developed as a useful alternative to liquid-liquid extraction (LLE) [16], [17] or solid phase extraction (SPE), as it reduces extraction time, and no organic solvent is necessary. This technique is based on equilibrium between the analyte concentration in the solution matrix and that in the solid-phase fibre; the fibre is coated generally with a polymeric organic stationary phase. SPME with a polydimethylsiloxane (PDMS) fibre has been used to extract organotins from water samples and sediments. Even in the last years supercritical fluid chromatography has been used to the extraction of organotins [18]. The SPME sampling can be carried out in direct mode, immersed in liquid or in the headspace mode [13].

Organotins due to its low volatility need to be derivatized before being injected into the gas chromatograph. The methods of derivatization used include hydride generation with sodium borohydrate [12] or alkylation by Grignard reagent [19]. These methods have been used for long time, however, requires a strictly aprotic medium for the derivatization [20]. In the last year sodium tetraethylborate [11], [13] or sodium tetrapiropylborate (STPB) [20], [21] have been used. These compounds can be used directly in aqueous phase. Derivatization with sodium tetraethylborate (STEB) converts ionic organotins compound into non-polar volatile derivates in situ, removing the problems associated with extracting ionic compounds into an organic solvent from an aqueous matrix. In Table 1 several studies about organotins analysis by using STEB and STPB are compared, any method used HS-SPME-GC-MS. Any method could detect TBT at the legislated annual average concentration.

The aim of this work was to develop a cost-effective method to detect in several matrix waters the organotins compounds at the levels required by the legislation. HS-SPME-GC-MS is the best option as this manuscript demonstrates. Figures of merit were established and some samples of wastewater and seawaters were analysed by the optimized HS-SPME-GC-MS procedure to test the reliability of the method.

2. Experimental

2.1. Reagents and solutions
All the reagents were of analytical grade, Triethyltin bromide (TET, 97% purity), tributyltin chloride (TBT, 96% purity), diphenyltin dichloride (DPT, 96% purity), triphenyltin chloride (TPT, 97% purity) and sodium tetraethylborate (STEB, 97% purity) were purchased from Sigma-Aldrich (Steinheim, Germany). Sodium chloride and sodium acetate were obtained from VWR International Eurolab (Barcelona, Spain).

Individual standard solutions of the organotins (200 mg/L) were prepared in methanol and more diluted aqueous solutions were prepared from the most concentrated solutions. Methanol was of spectrophotometric grade (Sigma-Aldrich, St. Louis, MO, USA) and pure water was obtained by means of a Milli-Q water purification system (Millipore).

A 2% (w/v) aqueous solution of STEB was used for derivatization. STEB was kept in desiccators into a glovebag under dry nitrogen and was always manipulated in the glovebag inside of an extractor hood. The STEB solution was prepared every day taking certain amount of reagent and adding the necessary volume of pure water into a dark and sealed vial.

Sodium chloride solutions and sodium acetate buffer solution were used to adjust the salinity and the pH in the derivatization process. The buffer solution was prepared by dissolving the necessary amount of sodium acetate in pure water to get 0.1M concentration and then adding acetic acid (98% purity) to adjust the pH to 5. Solutions were kept in darkness at 5°C.

2.2. Apparatus and chromatographic conditions

Analysis by GC-FID was performed with a gas chromatographic system (Agilent Tecnologies 6890N, Palo Alto, CA, USA) coupled with a flame ionization detector and operated by the Chemstation Software (Agilent Tecnologies).

Analysis by GC-MS was conducted using a mass spectrometer (Agilent Tecnologies 5973 inert), a gas chromatograph (Agilent Tecnologies 6890N) and a split/splitless injection port and operated by MSD Chemstation Software (Agilent Tecnologies).

A 30 m x 0.250 mm i.d. capillary column HP-5MS (Agilent Tecnologies) with a stationary phase with a thickness of 0.25 µm was used for analytes separation in both systems. The carrier gas was helium.

Both gas chromatographs were operated in splitless mode and the injection port temperature was hold isothermally at 260°C. The temperature program used was as follows: initial temperature of 50°C, 15°C/min to 190 °C, 10°C/min to 240°C, 30°C/min to 290°C, hold 4 min, for a total run time of 19 minutes.

A SPME holder with replaceable extraction fibres was used for extraction of organotin compounds from water samples. The fibre used in the study was coated with 100µm thickness polydimethylsiloxane (PDMS). The SPME holder and the fibres were obtained from Supelco (Bellefonte, PA, USA). A magnetic stirrer and stir bars (VWR International Eurolab) were used for the extraction.
2.3. Extraction procedures

The GC-FID system was used for optimizing variables. In all assays, the fibre was introduced in the headspace of a glass vial containing the standard samples of the organotins. Afterwards, the SPME device was placed into the GC interface and the organotins were desorbed from the fibre under static mode during 2 minutes.

The salinity was modified adding different amounts of sodium chloride, in order to study the signal variation. Sodium chloride concentration was changed from 0% to 7% (w/v) of salt. The volume of STEB 2% (w/v) solution added was 0.3 mL and 1 mL in order to examine its effect on organotin compounds extraction. The derivatization time (i.e., time since the STEB was added until the fibre was introduced in the chromatograph inlet port) was varied between 15 and 60 minutes.

The extraction variables were studied once the reaction variables were optimized. The solution volume was optimized testing some miniaturized and normal volumes using different vial sizes. The headspace volume was optimized once the solution volume was fixed.

The reaction and extraction variables previously optimized were used for the GC-MS system.

All the experiments were performed in duplicate at ambient temperature.

2.4. Analytical performance

Organotin standard solutions, prepared by dilution in water from concentrated standards previously prepared in methanol, were use to determine organotins retention time and the different analytical parameters such as detection limit, linearity and precision.

The retention time of all organotins was determined using aqueous standard solutions up to 150 µg/L of each organotin for the SPME-GC-FID system and aqueous standard solutions up to 50 ng/L of each organotin for the SPME-GC-MS system.

Solutions of 1, 2 and 5 µg/L for TPT; 0.1, 0.5, 1, 2 and 5 µg/L for TET, TBT and DPT were prepared for detection limits determination in the SPME-GC-FID system. Solutions of 0.5, 1, 2, and 5 ng/L for TET and TPT; 0.025, 0.05, 0.1, 0.25, and 0.5 ng/L for TBT and DPT were prepared to calculate detection limits in the SPME-GC-MS system.

In the SPME-GC-MS system, the mass spectrums were obtained at a mass ratio scan range from 100 to 400 m/z to determine the appropriate masses for selected ion monitoring (SIM). SIM mode was used for quantification.

Linearity and precision were determined in SPME-GC-FID system using solutions of 1, 5, 10 and 15 µg/L of TET, TBT and DPT, and solutions of 10, 15, 30 and 40 µg/L of TPT. Moreover, in SPME-GC-MS system, linearity and precision were determined using solutions between 5-5000 ng/L for TET and TPT and solutions between 1-5000 ng/L for TBT and TPT.
2.5. Analysis of real water samples

Wastewater samples and seawater samples were used to validate the developed methods. Grab wastewater samples were collected at 7 wastewater treatment plants effluents located in close proximity to the Comunidad Valenciana coast (East of Spain). Seawater samples were collected at 24 different geographical sites along the Comunidad Valenciana coast. Samples were introduced into amber bottles and kept in the fridge at 4°C till the analysis. Each sample was analysed in duplicate at all assays were carried out at ambient temperature.

Real sample analyses were carried out with 12.7 mL of water sample in a 22 mL vial. Then, 1 mL of acetate buffer and 0.3 mL of STEB were added into the vial and finally the sample was extracted in headspace for 45 minutes with constant stirring. Wastewater and seawater samples were analyzed by SPME-GC-MS. The found concentration is always characterized by the expanded uncertainty ($K = 2$) estimated with EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement [23].

3. Results and discussion

3.1. Optimization of the extraction process

Figure 1 shows the salinity effect employing normalized chromatographic signals. For all organotins studied, the signal percentage steeply decreases with salt concentration increase. The sodium chloride addition in the standard solution, within the 0% - 7% (w/v) range, revealed that the salinity negatively affects the analyte extraction efficiency. Therefore, the salt addition is not advisable. However, a final sodium chloride concentration of 3.3% (w/v), similar to that of Mediterranean waters, was used in the standards when this kind of samples was processed.

The variation of the STEB volume added did not produce any improvement in the extraction efficiency (data not shown), achieving the same results for the two volumes studied. Therefore, it seems more suitable to work with the lower amount in order to optimize the cost (see experimental section).

The derivatization time optimization was carried out after the optimum sodium chloride and the STEB values were established. Standard solutions containing a mixture of the organotins evaluated (15 µg/L of each compound, wearing in mind that the detector used was FID) were prepared in a 22 mL vial as follows: 12.7 mL of water, 1 mL of acetate buffer, 0.3 mL of STEB, 0.5 g of sodium chloride for sea water and the necessary amount of the organotin concentrated solutions. Samples were extracted during 15, 30, 45 and 60 minutes in order to get the optimum reaction time. The extraction started in headspace just after adding the STEB and with constant stirring (750 rpm) due to liquid sample agitation improves the kinetics of the derivatizing reaction and the analytes transport towards the fibre [18]. As Figure 2 shows, the optimum reaction time changes for each compound. The signal increases with the reaction time for TET, DPT and TPT but not for TBT, for which the signal drops off
after reaching an optimum at 30 minutes. Finally, within the time range considered, a 45
minutes value was considered as optimum reaction time for further work.

Other sample volume was assayed in order to minimize reagents and sample
consumptions: in a 5 mL vial were placed 2.54 mL of water, 0.2 mL of acetate buffer,
0.06 mL of STEB, and the necessary amount of standard solution in order to get 15
µg/L concentration for each organotin. Similar signals than those obtained with 22 mL
vials were achieved. Then, if necessary less volume of sample could be used.

Regarding headspace volume optimization, two solutions volumes were
prepared in a 22 mL vial size: a 14 mL solution was prepared adding, 12.7 mL of water,
1 mL of acetate buffer, 0.3 mL of STEB and the necessary amount of standard solution
in order to get a concentration of 15 µg/L (of each organotin); and a 7 mL solution
adding, 6.35 mL of water, 0.5 mL of acetate buffer, 0.15 mL of STEB, 0.2 g of sodium
chloride for sea water and the necessary standard solution so to get 15 µg/L
concentration (of each organotin). Once the solutions were prepared, the fibre was
exposed in the headspace solution during 45 minutes. Better results were obtained with
a headspace volume of 8 mL considering the response for all organotins tested (data not
shown).

The use of STEB could generate tetraethyltin, affecting on the analysis of TET
[21]. Nevertheless, this possible interference in TET analysis was not observed in this
study.

3.2. Analytical parameters

**Figure 5** shows an organotins chromatogram in the optimized conditions by use
FID detection. Figures of merit achieved from this detector are given in **Table 2**. The
detection and quantification limits were determined experimentally as the lowest
concentration giving a chromatographic peak three times the signal/noise ratio and ten
times the signal/noise ratio, respectively. The detection limits in the GC-FID system are
above the environmental quality standards established for TBT by Directive
2008/105/EC.

The first study undertook with the GC-MS system was in full scan mode in
order to find the characteristic ions and the abundance of each organotin, (**Figures 4 to
7**). The mass spectra obtained were similar to mass spectra showed by NIST library
[22]. Each organotin had different number of characteristic ions depending on its
structure. TBT showed more fragmentation than TET since its molecule is bigger and it
is more easily fragmented than DPT or TPT.

Selected quantification ions were chosen for each organotin and other
characteristic ions were also selected in order to identify each compound. **Table 3**
shows quantification and identification ions used for the studied organotins.

The SIM mode analysis was used to determine the quality assurance parameters
such as detection and quantification limits, precision and linearity. All determinations
were carried out in the optimized conditions: 3.3% of salinity (for sea water), 0.3 mL of
STEB, 45 minutes for extraction, 14 mL of solution and 22 mL total volume vials.
Figure 8 shows the chromatograms obtained in the SIM mode for each compound and Table 4 the figures of merit obtained.

The detection and quantification limits were determined as described for the GC-FID. The detection limits in the GC-MS system are quite lower than the environmental quality standards established for TBT by Directive 2008/105/EC.

3.3. Real Samples

The accuracy of method was evaluated by analysing fortified seawater and wastewater samples. The obtained recoveries were 90 ± 20 (n=12) being independent of the organotin assayed.

Wastewater sample analysis revealed the presence of DPT at detection limit level in two samples. Detection of DPT in wastewater could be derived from its use as plasticizer.

The analysis of seawater samples revealed the presence of DPT and TBT. DPT was detected and quantified in one sample, reaching a concentration of 0.14 ± 0.04 ng/L. TBT was found at detection limit level in eleven samples. Moreover, TBT was detected and quantified in a sample grabbed in close proximity to a harbour. The TBT concentration in this sample was 1.3 ± 0.3 ng/L. This value is below the maximum allowable concentration permitted by Directive 2008/105/EC but is above the annual average value permitted. Hence, periodical sampling campaigns should be needed in order to evaluate, in the long term, the water chemical status regarding TBT.

4. Conclusions

The HS-SPME-GC-MS method is a cost-effective method with adequate figures of merit for the study of the presence of organotins in environmental water samples. The detection limits achieved with the proposed method are far below of concentration levels established in Application of EU Water Framework Directive (DMA 2000/60/EC).

The proposed method allows detect organotin compounds in water samples at concentration of pg/L with low sample and solvents volumes. Table 1 shows that this method offers the best detection limits with the less time and volume for all studied organotins.

Acknowledgments

This research was financially supported by The Government of the Region of Valencia (Generalitat Valenciana), within the research project “Application of EU Water Framework Directive 2000/60/EC on endocrine disrupters and other priority substances in coastal areas in the Region of Valencia”. Also the project CTQ2008-01329/BQU has contributed.
References

List of Tables.

Table 1. Selected methods for speciation of organotin compounds in water

Table 2. SPME-GC-FID analytical parameters

Table 3. Quantification and characteristics ions of the analyzed compounds

Table 4. SPME-GC-MS analytical parameters
Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LOD (ng/L)</th>
<th>Pre-treated Procedure</th>
<th>Technique</th>
<th>Derivatizing Reagent</th>
<th>Total Analysis Time (min)</th>
<th>Sample Volume (mL)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TET</td>
<td>48.8</td>
<td>SPME</td>
<td>GC-FID</td>
<td>STEB</td>
<td>30</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>TBT</td>
<td>0.5</td>
<td>SPME</td>
<td>GC-MS</td>
<td>STEB</td>
<td>45</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>7-29</td>
<td>LLE</td>
<td>GC-HRMS</td>
<td>STEB</td>
<td>90</td>
<td>100</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>HS-SPME</td>
<td>GC-PFPD</td>
<td>STEB</td>
<td>50</td>
<td>80</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td>SPME</td>
<td>GC-FID</td>
<td>STEB</td>
<td>30</td>
<td>18</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>0.525</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STEB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>0.55</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STPB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>DPT</td>
<td>7-29</td>
<td>LLE</td>
<td>GC-HRMS</td>
<td>STEB</td>
<td>90</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>26.37</td>
<td>HS-SPME</td>
<td>GC-PFPD</td>
<td>STEB</td>
<td>50</td>
<td>80</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>0.465</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STEB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>0.44</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STPB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>TPT</td>
<td>7-29</td>
<td>SPME</td>
<td>GC-MS</td>
<td>STEB</td>
<td>45</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>4.6</td>
<td>LLE</td>
<td>GC-HRMS</td>
<td>STEB</td>
<td>90</td>
<td>100</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>SPME</td>
<td>GC-FPD</td>
<td>STEB</td>
<td>60</td>
<td>100</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>SPME</td>
<td>GC-ICPMS</td>
<td>STEB</td>
<td>45</td>
<td>40</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>0.63</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STEB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>0.39</td>
<td>HS-SPME</td>
<td>GC-AED</td>
<td>STPB</td>
<td>40</td>
<td>40</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

*a estimated value.
STEB: sodium tetraethyl borate. STPB: sodium tetrapropyl borate
### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>LODs (µg/L)</th>
<th>$b_0 \pm s_0$ (µg/L)</th>
<th>$b_1 \pm s_1$ (µg/L)</th>
<th>$r^2$</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TET</td>
<td>0.1</td>
<td>7 ± 7</td>
<td>6.9 ± 0.8</td>
<td>0.9756</td>
<td>8</td>
</tr>
<tr>
<td>TBT</td>
<td>0.1</td>
<td>4 ± 9</td>
<td>11.2 ± 0.9</td>
<td>0.9860</td>
<td>9</td>
</tr>
<tr>
<td>DPT</td>
<td>0.1</td>
<td>-4 ± 9</td>
<td>5.1 ± 0.3</td>
<td>0.9918</td>
<td>4</td>
</tr>
<tr>
<td>TPT</td>
<td>1</td>
<td>-6 ± 8</td>
<td>6.1 ± 0.5</td>
<td>0.9961</td>
<td>12</td>
</tr>
</tbody>
</table>

LOD: detection limits. $b_0$ and $b_1$: parameters of calibration curve peak area vs concentration. $r^2$: determination coefficient. RSD: relative standard deviation for 10 µg/L (n=3).

### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantification ion</th>
<th>Chemical formula</th>
<th>Chemical formula</th>
<th>Characteristic ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>TET</td>
<td>179</td>
<td>SnEt$_2$H</td>
<td>149</td>
<td>SnEtH$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>207</td>
<td>SnEt$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>151</td>
<td>SnEtH$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>177</td>
<td>SnBuH$_2$</td>
</tr>
<tr>
<td>TBT</td>
<td>291</td>
<td>SnBu$_3$</td>
<td>121</td>
<td>SnH$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>207</td>
<td>SnEtBuH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>235</td>
<td>SnEt$_2$Bu</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>263</td>
<td>SnEtBu$_2$</td>
</tr>
<tr>
<td>DPT</td>
<td>303</td>
<td>SnEtPh$_2$</td>
<td>197</td>
<td>SnPhH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>275</td>
<td>SnPh$_2$H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>281</td>
<td>SnEt$_3$Ph</td>
</tr>
<tr>
<td>TPT</td>
<td>351</td>
<td>SnPh$_3$</td>
<td>197</td>
<td>SnPhH</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>LODs (ng/L)</th>
<th>$b_0 \pm s_0$ (µg/L)</th>
<th>$b_1 \pm s_1$ (µg/L)</th>
<th>$r^2$</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TET</td>
<td>1</td>
<td>(3 ± 3) x 10$^5$</td>
<td>(5.6 ± 0.1) x 10$^6$</td>
<td>0.9967</td>
<td>11</td>
</tr>
<tr>
<td>TBT</td>
<td>0.025</td>
<td>(4 ± 4)x 10$^4$</td>
<td>(2.3 ± 0.1) x 10$^6$</td>
<td>0.9940</td>
<td>9</td>
</tr>
<tr>
<td>DPT</td>
<td>0.025</td>
<td>(3 ± 5) x 10$^4$</td>
<td>(1.0 ± 0.1) x 10$^6$</td>
<td>0.9831</td>
<td>20</td>
</tr>
<tr>
<td>TPT</td>
<td>0.5</td>
<td>(1 ± 1) x 10$^4$</td>
<td>(0.5 ± 0.1) x 10$^6$</td>
<td>0.9971</td>
<td>12</td>
</tr>
</tbody>
</table>

LOD: detection limits. $b_0$ and $b_1$: parameters of calibration curve peak area vs concentration. $r^2$: determination coefficient. RSD: relative standard deviation for 5 ng/L (n=3).
List of Figures.

**Figure 1.** Effect of salinity in the GC-FID system. TET (■), TBT (▲), DPT (♦) and TPT (x)

**Figure 2.** Effect of reaction time between analytes and STEB. TET (■), TBT (▲), DPT (♦) and TPT (x)

**Figure 3.** FID chromatogram for a solution containing 15 μg/L of each organotin

**Figure 4.** Mass spectrum for TET in scan mode at 10 μg/L

**Figure 5.** Mass spectrum for TBT in scan mode at 10 μg/L

**Figure 6.** Mass spectrum for DPT in scan mode at 10 μg/L

**Figure 7.** Mass spectrum for TPT in scan mode at 10 μg/L

**Figure 8.** Selected ion monitoring for studied organotins at 5 ng/L for TET, TBT and DPT and at 10 ng/L for TPT. See table 3.
Figure 1

Figure 2.

Figure 3
Figure 4

Figure 5

Figure 6

Figure 7

Figure 8