Introduction

Organotins have been used in the shipping industry as protective paint coatings applied to ship’s hulls. In water, trisubstituted organotin compounds decompose in a stepwise manner to less substituted compounds, down to inorganic tin.\(^1\) They are used in the industry in the form of chloride complexes.\(^2\) Due to their toxicity at low concentrations, environmental quality standards below 20 ng/L in waterways have been issued in several countries; consequently triphenyltin and tributyltin are included in the European Union pollutant list (EU Directive 76/464).\(^2\) When analyzed by gas chromatography (GC), polar ionic organotin species need to be extracted from the sample matrices and converted into their fully alkylated and more volatile forms by derivatization, which generates sharper peaks and higher sensitivity.\(^3\) The analysis is made more difficult because no derivatized standards are commercially available so they have to be prepared in the laboratory. The extraction method used for this study included ethylation with sodium tetraethylborate (NaBE\(_t\)) followed by liquid-liquid extraction (LLE) into hexane. GC-MS analysis was performed by making a large volume injection followed by detection by Selected Ion Monitoring (SIM) on a quadrupole mass spectrometer.

Sample Prep and Derivatization

The organotin chloride standards were derivatized to their respective alkylated forms. Figure 1 shows the full scan spectrum of tributyltin chloride, which was derivatized to tributylethyltin.

The glassware consisted of a 250 mL separatory funnel, 250 mL beaker, and 3 mL conical flask. All glassware was rinsed in soap, tap water, 2% nitric acid, deionized water, and then acetone. The nitric acid rinse prevented the formation of an emulsion during the extraction phase of the sample preparation. The internal standard, triphenyl-d\(_{15}\)-tin chloride, was prepared in methanol at a concentration of 0.8 ng/µL. A 50 µL aliquot of the internal standard solution was added to the 100 mL water sample in a 250 mL separatory funnel. The organotin chloride target compounds were made in methanol at the following concentrations: 10, 1, and 0.1 ng/µL, and spiked into the 100 mL of water for preparation of the calibration standards. The samples were prepared as described in the publication by Ikonomou, as shown in Figure 2.\(^4\)
**Experimental Conditions**

The analysis of organotins was performed using a Thermo Scientific TRACE GC Ultra, TriPlus autosampler and DSQ II single quadrupole operated in electron ionization (EI) SIM mode. The following ethylated organotins were studied: butyltriethyltin, dibutylethyltin, phenyltriethyltin, tributylethyltin, diphenyldiethyltin, and triphenylethyltin. Triphenyl-d15-ethyltin was used as an internal standard. The Method Detection Limits were determined at low ppt (ng/L) levels with calibration over a working range of 10 ng/L to 5000 ng/L in water.

The BEST (Brightly Enhanced Sample Transfer) Programmed Temperature Vaporizing (PTV) injector was used. This programmable temperature vaporizor can eliminate many of the unwanted effects that can occur with traditional hot injection techniques. In the large volume injection mode the sample is injected into the liner at the boiling point of the solvent with the Split Vent open to eliminate the solvent before the sample enters the column. Once the solvent evaporation phase is completed, the PTV is rapidly heated to transfer the sample into the capillary column. A Total Ion Chromatogram (TIC) of a 20 µL injection in Full Scan of a 5000 ng/L standard is shown in Figure 3.

The full scan spectra for the triphenylethyltin and the dueterated internal standard are shown in Figures 4 and 5. Once the retention times were established, the SIM ions were entered into the instrument method.
Calibration Curve and Method Detection Limits

The preliminary evaluation of the calibration curve (10 ng/L to 5000 ng/L) was performed by making a 1 µL cold splitless injection on the PTV. The results showed poor linearity below 1000 ng/L. The 5000 ng/L standard was diluted in hexane and the calibration curve was run using a 1 µL injection and then a 20 µL injection. These results are shown in Figures 6 and 7. The chromatographic activity that was noted in the 1 µL injections was resolved by incorporating a large volume injection.

Then, the calibration curve was regenerated by spiking water at 10, 50, 100, 1000, and 5000 ng/L and analyzed by LVI with a 20 µL injection. The Method Detection limits were established by preparing replicate 50 ng/L spikes in water. The results were tabulated by multiplying the Student t value by the standard deviation as listed in Table 1 with the linear fits for each.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R² Fit</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyltriethyltin</td>
<td>0.9999</td>
<td>70</td>
</tr>
<tr>
<td>Dibutyl(2-ethyl)hexyltin</td>
<td>0.9997</td>
<td>20</td>
</tr>
<tr>
<td>Phenyltriethyltin</td>
<td>0.9896</td>
<td>188</td>
</tr>
<tr>
<td>Tributylethyltin</td>
<td>0.9996</td>
<td>28</td>
</tr>
<tr>
<td>Diphenyl(2-ethyl)hexyltin</td>
<td>0.9995</td>
<td>30</td>
</tr>
<tr>
<td>Triphenylethyltin</td>
<td>0.9888</td>
<td>9.5</td>
</tr>
<tr>
<td>Triphenyl-p-d15-ethytin</td>
<td>17% RSD</td>
<td>3% RSD</td>
</tr>
</tbody>
</table>

Table 1: Linearity and MDLs for derivatized organotins

Some typical calibration curve plots are shown in Figures 8 and 9.
Results

The analysis of organotins was performed by derivatization with sodium tetraethylborate (NaBEt4) followed by liquid-liquid extraction (LLE) into hexane. The extract was injected using a PTV in large volume injection mode and detected by 3-ion SIM. The calibration curves were all \( > 0.999 \) and the MDLs determined were in the low ng/L range. The precision for the internal standard in the MDL study was 3.5 %RSD.

Conclusion

The analysis of organotins in water was performed by doing a liquid/liquid extraction after the addition of a derivatization reagent. Minimal glassware was required and no extract concentration step was required. A LVI SIM method was developed which generated quantitation down to 10 ng/L levels. The GC-MS run time was only 13 minutes long and maintenance consisted of septum replacement after 50 injections. All of the consumables are readily available and the chromatography was not affected by the derivatization reagent.

References