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A simple, low cost GC/MS method for the sub-nanogram per litre measurement of organotins in coastal water

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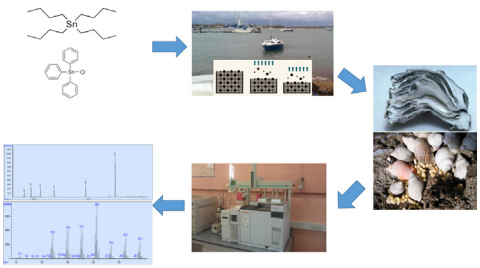
GRAPHICAL ABSTRACT



ABSTRACT

Tributyltin (TBT) is a legacy pollutant in the aquatic environment, predominantly from its use in anti-foulant paints and is listed as a priority hazardous substance in the European Union's Water Framework Directive (WFD). Measuring low concentrations of TBT and other organotins (e.g. monobutyltin (MBT), dibutyltin (DBT), diphenyltin (DPhT) and triphenyltin (TPhT)) at sub ng/L concentrations in coastal waters using standard laboratory instrumentation is very challenging. Conventional, low injection volume gas chromatography/mass spectrometry (GC/MS) combined with liquid-liquid extraction typically achieves limits of detection for TBT ~10 ng L^{-1}. We describe a simple, programmed temperature vaporisation-large injection volume (50 μL), GC/MS selected ion monitoring method for measuring DBT, TBT, DPhT and TPhT in coastal waters at lower concentrations.

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Quantification of MBT was not possible using these injection volumes but was achieved using a 10 μL injection volume together with a reduced injection speed.

This new approach offers:

- When using a 50 μL injection, limits of detection = 0.70 ng L^{-1} and limits of quantification = 2.1 ng L^{-1} for TBT were achieved in derivatised standards.
- Recoveries of TBT and TPhT from coastal water >97%.
- Time consuming, off-line sample pre-concentration methods are unnecessary.

ARTICLE INFO

Method name: Measurement of organotins in coastal water using GC/MS

Keywords: Organotins, Tributyltin, Coastal water, Gas chromatography/mass spectrometry, Large volume injection, Liquid-liquid extraction, Ethylation

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Method details

Safety protocol

Organotin compounds are toxic and harmful to the environment, requiring care in use [1]. Sodium tetraethylborate ($NaBEt_4$) is spontaneously flammable in air and produces toxic fumes when added to water. Great care must be exercised when using these compounds and adequate control measures put in place to manage risks before performing the method described in this article. For example: (1) Standards and solutions must be handled in a fume hood fitted with a carbon filter. (2) Purchasing small quantities (~1 g) of $NaBEt_4$, negating the requirement for weighing out and reducing its exposure time to air. (3) Waste stock standards (as non-derivatised analogues) disposed of as 'chlorinated organotin waste'.

Preparation of glassware

Glassware is treated using the procedure described in Ref. [2]. Briefly, glassware is cleaned using a 10% Decon-90 solution at 85° C (Decon Laboratories Ltd., Hove, UK), followed by soaking in hydrochloric acid (HCl, 12 M) for 24 h. Afterwards, glassware is rinsed with water, then methanol and dried (60° C). This procedure gives low procedural blanks for all organotins measured.

Reagents and standards

Chemicals (analytical grade or better) are from Fisher Scientific Ltd. (Loughborough, UK) unless specified. Deionised water (>15 MΩ cm, Purite Ltd., Thame, UK) is used as the laboratory water. Salts of the organotins (butyltin trichloride 97%, dibutlytin dichloride 97%, tributyltin chloride 95%, diphenyltin dichloride 98%, triphenyltin chloride 95%) are used to make stock standards (1 g L^{-1}) in methanol (LC–MS Chromasolv®, Sigma-Aldrich, Poole, UK) with storage and expiry dates as per manufacturer's instructions. From these an intermediate stock solution is prepared at 1.0 mg L^{-1} and further diluted to give a working standard solution of 0.05 mg L^{-1} (as organotin cation equivalents). Tripropyltin (TPrT) chloride (2.0 mg mL^{-1} in dichloromethane) internal standard is diluted in methanol (1.0 mg L^{-1}, as cation equivalent). Standards are stored in amber vials at 4° C and sealed with foil-lined caps and are stable for 6 months under these conditions. Sodium acetate buffer solution (1 M, pH 4.20 ± 0.1) is used to control the pH of samples during derivatisation. Here, 136 g of sodium acetate trihydrate is added to a volumetric flask (1 L) and dissolved in water (500 mL). Glacial acetic acid (200 mL) is added slowly and then the solution diluted to volume using water. The buffer solution is stable for 6 months when stored at room temperature.

Organotins are ethylated using 1% (*m/v*) $NaBEt_4$. In a fume hood, a vial of $NaBEt_4$ (1 g, 97%) is filled to the neck with water and the slurry rinsed (4–5 separate washings) into a volumetric flask (100 mL) to