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Short communication

Determination of tributyltin in environmental water matrices using stir bar sorptive extraction with *in-situ* derivatisation and large volume injection-gas chromatography–mass spectrometry

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ABSTRACT

Stir bar sorptive extraction with *in-situ* derivatization using sodium tetrahydridoborate ($NaBH_4$) followed by liquid desorption and large volume injection-gas chromatography–mass spectrometry detection under the selected ion monitoring mode (SBSE($NaBH_4$)$_{in\text{-}situ}$–LD/LVI-GC–MS(SIM)) was successfully developed for the determination of tributyltin (TBT) in environmental water matrices. $NaBH_4$ proved to be an effective and easy *in-situ* speciation agent for TBT in aqueous media, allowing the formation of adducts with enough stability and suitable polarity for SBSE analysis. Assays performed on water samples spiked at the 10.0 μg/L, yielded convenient recoveries (68.2 ± 3.0%), showed good accuracy, suitable precision (RSD < 9.0%), low detection limits (23 ng/L) and excellent linear dynamic range (r^2 = 0.9999) from 0.1 to 170.0 μg/L, under optimized experimental conditions. By using the standard addition method, the application of the present methodology to real surface water samples allowed very good performance at the trace level. The proposed methodology proved to be a feasible alternative for routine quality control analysis, easy to implement, reliable and sensitive to monitor TBT in environmental water matrices.

1. Introduction

Over the past three decades, organotin compounds have been widely used in several industrial and agricultural applications. Organotin compounds are mainly used as fungicides, biocides, wood preservatives and polyvinyl chloride stabilizers. Among them, tributyltin (TBT) has been extensively used as a biocide agent in antifouling paints of ship hulls, harbor structures and aquaculture nets [1]. Owing to their numerous applications, these compounds are continuously released into marine and fresh water environment leading to its contamination. Toxic effects of organotin compounds on aquatic organisms and mammals are well known, such as induction of the imposex effect, *e.g.*, superimposition of male sexual characteristics on female organisms [2,3]. Due to the fact that organotin compounds have high bioaccumulation potential, control of contamination levels in environmental samples is necessary [4]. As a consequence, several water quality criteria and legislative restrictions have been adopted in order to control the usage of these compounds. The Marine Environmental Protection Committee proposed a global prohibition on the application of organotins as biocides in antifouling systems on ships by January 2008 [5].

For many years, researchers have been focused on the determination of organotin compounds from many different types of matrices. Nevertheless, the quantification of these compounds in environmental samples has been considered a very difficult task, since they had shown instability and usually occur at the trace level [6]. Therefore, new sensitive and cost-effective methodologies are still demanded for organotin speciation in particular using gas chromatography–mass spectrometry (GC–MS), once it is the hyphenated system commonly used in many laboratories and allows the unequivocal identification through the mass spectral features. Among the analytical schemes usually proposed, liquid–liquid extraction, solid-phase extraction and solid-phase micro extraction (SPME) with derivatization followed by GC–MS have been currently used for the determination of organotin compounds in environmental and biological matrices [7–9]. More recently, stir bar sorptive extraction (SBSE) has been successfully employed as a novel sample preparation technique, based on the same principles as those of SPME, particularly for enrichment and sensitive determination of priority organic pollutants, including organotins, in water samples but also in many other matrices [10–16]. Besides the noteworthy performance demonstrated by SBSE for TBT speciation, the analytical approaches claim also to be an

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in-situ derivatization step compatible with the hot injection by GC analysis [16]. Even so, most of those derivatisation agents such as some borate derivatives (*e.g.* sodium tetraethylborate) are neither stable nor easy to manipulate. So far, sodium tetrahydridoborate ($NaBH_4$) has been accepted as a much more simple and effective chemical agent to produce organotin adducts prior to GC–MS analysis [17]. Furthermore, $NaBH_4$ exhibits a remarkable stability and an easier practical approach in comparison to other derivatization agents.

The present contribution aims the development of a novel and easy analytical strategy for TBT speciation by combining SBSE with *in-situ* derivatization using $NaBH_4$, followed by liquid desorption and large volume injection-gas chromatography–mass spectrometry under the selected ion monitoring mode (SBSE $(NaBH_4)_{in\text{-}situ}$–LD/LVI-GC–MS(SIM)). The performance of the proposed methodology was evaluated in terms of accuracy, precision, linearity and detection limits. The application to environmental water matrices is also addressed.

2. Materials and methods

2.1. Chemicals and standards preparation

All reagents and solvents were of analytical grade and used with no further purification. HPLC-grade methanol (MeOH, 99.9%), acetonitrile (ACN, 99.9%), acetone (DMK, 99.5%) and ethyl acetate (EtOAc, 99.9%) were purchased from Panreac (Spain). The tributyltin chloride (TBT, $Sn(C_4H_9)_3Cl$; 96%) was purchased from Sigma-Aldrich (Germany). Sodium chloride (NaCl, 99.9%) was obtained from AnalaR (England). $NaBH_4$ and *n*-pentane (*n*-C_5, 99%) were purchased from Riedel-de-Haën (Germany). Ultra-pure water was obtained from milli-Q water purification systems (USA). A stock solution of TBT (1108.0 mg/L) was prepared by dissolving 27.7 mg of TBT in 25 mL of MeOH. To study the derivatization step and instrumental evaluation, a TBT hydride (TBTH) working standard solution was daily prepared through the pre-derivatization by adding 300 μL of 4% (w/v) $NaBH_4$ followed by incubation at room temperature and diluted to the desired concentration. For *in-situ* derivatization, method optimization, validation and real matrix assays, derivatization solutions (40.0 mg/L) were prepared by mixing 0.12 mg of $NaBH_4$ to a final volume of 3 mL with ultrapure water. Environmental water samples were collected with PVC bottles from the Tagus river in three naval docks (Santa Apolónia, Parque das Nações and Alcântara) in the metropolitan area of Lisbon (Portugal). All the samples were filtrated (Whatman No1 filters, USA) and stored at −4 °C before used.

2.2. Experimental set-up

The stir bars (Gerstel, Germany) coated with 10 mm in length and 0.5 mm film thickness of PDMS (24 μL) were pre-conditioned before use by treating them with ACN during 20 min. In a typical assay, 30 mL of ultrapure water with 40% MeOH spiked with 200 μL TBT working standard at different concentrations (0.1–170.0 μg/L) and 300 μL of the derivatization solution were introduced into glass flasks already contained the stir bar. The assays were performed with 4 h extraction time and 1250 rpm agitation speed. For back-extraction, the stir bars were removed from the samples, placed into a 2 mL vial with insert containing 200 μL of the desorption solvent (*n*-pentane), ensuring their total immersion prior to ultrasonic treatment (15 min) at a constant temperature (25 °C). After back-extraction, the stir bars were removed and the vials were resealed and placed on the autosampler prior to GC–MS analysis. For real sample assays, 30 mL with 40% MeOH were used, for which 300 μL of derivatization solution and spiked TBT working standard were used, following by the same procedure described before in triplicate. Control and blank assays were also performed in triplicate using the same procedure without spiking.

2.3. Instrumentation settings

Large volume injection GC–MS analysis were carried out on an Agilent 6890 Series gas chromatograph equipped with a 5973 N mass selective detector (USA). A programmed temperature vaporization (PTV) injector with a septumless sampling head (Gerstel, Germany) operating in the solvent vent mode (vent time 0.30; flow 150 mL/min; pressure 0 psi; purge 60 mL/min at 2 min), for which the inlet was programmed from −20 °C (0.35 min) to 300 °C at a rate of 600 °C/min and subsequently reduced to 200 °C at a rate of 50 °C/min. The injection volume was 5 μL. GC analysis were performed on a TRB-5MS (30 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column (5% diphenyl, 95% dimethylpolysiloxane; Teknokroma, Spain) using helium as carrier gas maintained in the constant pressure mode (19.6 psi) at an average velocity of 54 cm/s. The oven temperature was programmed from 70 °C (2 min) at 20 °C/min to 250 °C (held for 5 min) [16].

The transfer line, ion source and quadrupole temperatures were maintained at 280, 230 and 150 °C, respectively and a solvent delay of 5 min was selected. Electron ionization was performed at 70 eV and mass spectra in the full scan acquisition mode were recorded in the range 35–550 Da. In the selected ion-monitoring acquisition (SIM) mode, target ions (*m/z* 121, 179 and 235) were selected according to the mass spectra characteristic features obtained in the full-scan mode and by comparison with Wiley's library reference spectral bank (G1035B; RevD.02.00). Data recording and instrument control were performed by the MSD ChemStation software (G1701 CA; ver.C.00.00; Agilent Technologies).

3. Results and discussion

3.1. In-situ derivatization and instrumental conditions

Since the very beginning, the derivatization step, involving the reaction of TBT with $NaBH_4$, was carefully examined in MeOH media. According to literature [16,18], preliminary experiments showed that $NaBH_4$ provided good specificity for TBT derivatization, as depicted in Fig. 1a. Even so, we also tested the peak areas against the incubation time to foresee the TBT derivatization progress with $NaBH_4$. Fig. 1b depicts the response obtained showing that after 60 min the TBTH ($Sn(C_4H_9)_3H$) is completely

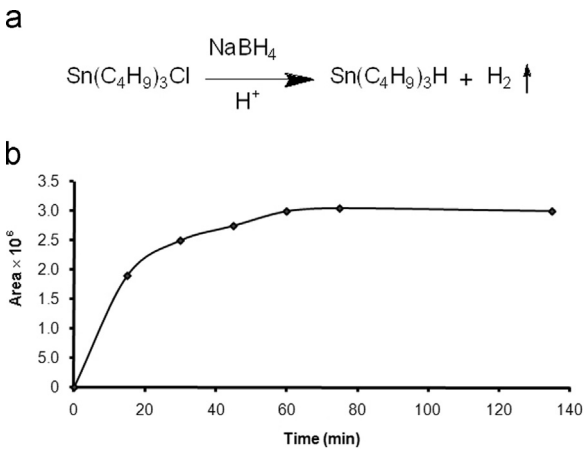

Fig. 1. Scheme of the derivatization involving TBT with $NaBH_4$ (a) and reaction progress plot obtained by LVI-GC–MS showing the peak areas (TBTH) against incubation time (b).