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Determination of organotin compounds in waters by headspace solid phase microextraction gas chromatography triple quadrupole tandem mass spectrometry under the European Water Framework Directive

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ABSTRACT

The European Union Water Framework Directive (2013/39/EU) sets very restrictive environmental quality standards for 45 priority substances and other pollutants, including organotin compounds (OTCs). Therefore, it is necessary to develop analytical methods in compliance with the environmental quality standard (EQSs) proposed to protect the aquatic environment and humans. The proposed method (HS-SPME-GC–QqQ-MS/MS) allows the determination of OTCs, i.e. monobutyltin (MBT), dibutyltin (DBT) and TBT in water in the range of few ng L^{-1}. The method is nearly full automated, sensitive and simple; it involves less reagents, reduces waste, and is less-time consuming than traditional methods for OTCs. As such, the procedure connects with the principles of green analytical chemistry. Additionally, good precision (RSD < 20%), a very low method quantification limit (MQL) (0.76 ng L^{-1} for TBT by using only 10 mL of sample) and excellent linearity (range MQL–20 ng L^{-1}) are achieved. Under these conditions, the very restrictive limits for the environmental quality standards (EQS) fixed by the 2013/39/EU Directive are achieved.

1. Introduction

Organotin compounds (OTCs), such as tributyltin (TBT), are persistent organic pollutants that are present in water samples (surface water, river water, sea water, waste water, etc.) because of anthropogenic activities (antifouling agents in ship paints, biocides in polymers, etc.). The toxicity and endocrine disruption potential of these chemicals have been demonstrated even at very low levels (<1 ng L^{-1}) [1,2]. Due to the extensive presence of OTCs in all environmental media as well as their adverse effects on human health and biota, quantitative and qualitative determination of those compounds in complex environmental matrices has become a matter of great concern. Also, these compounds are included in the list of priority substances according to the EU Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy [3]. This directive specifies annual average environmental quality standard (AA-EQS) of 0.2 ng L^{-1} TBT and a maximum allowable environmental quality standard (MAC-EQS) of 1.5 ng L^{-1} TBT for all surface waters.

Unfortunately, determination of OTCs from environmental matrices is extremely difficult owing to matrix effects and their presence in very low amounts in samples [4]. Actually, achieving a reliable determination of these compounds in the range of a few ng L^{-1} continues to be an analytical challenge.

For the analysis of OTCs, a large variety of analytical methods have been developed. Gas chromatography (GC) is the most widely used technique for speciation of OTCs [5]. Mass spectrometry (MS) [1,6–14], inductively coupled plasma mass spectrometry (ICP-MS) [15–18], atomic emission detection (AED) [19,20], flame ionization detection (FID) [8] and pulsed flame photometric detection (PFPD) [21] have been coupled to GC for the quantification of OTCs in environmental samples. Gas chromatography with mass spectrometry detection (GC–MS) in full scan and selective ion monitoring (SIM) modes has become a useful tool in organometallic compounds analysis because it offers simultaneous identification and quantitation of a large number of these compounds, including OTCs [5]. Due to excellent qualitative and quantitative abilities, GC–MS in full scan and SIM modes is commonly used to analyze unknown organic compounds in many types of samples. However the efficacy depends on the levels of interfering ions from the matrix, which can obscure the signal from the target compounds at the very low concentrations expected in environmental samples [22].

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Gas chromatography–tandem mass spectrometry (GC–MS/MS) operated in selected reaction monitoring (SRM) detection mode can provide high confidence in the identification of target analytes in complex matrices and low detection limits. Because SRM selects two sets of precursor-to-product ions, greater specificity sometimes can be achieved than when using full scan or even SIM modes [22].

A pre-concentration step typically is required because of the low concentration of the OTCs expected in environmental samples. Solid-phase microextraction (SPME), developed by Arthur and Pawliszyn in 1990 [23], has been widely used as an extraction method for OTCs [6,8–10,21,24–27]. The SPME sampling can be carried out either in the direct mode (immersed in the liquid) or in the headspace (HS) mode. Due the high volatility of OTCs in their alkylated forms, HS mode is the technique usually selected. Other procedures, also included in the group of green analytical pre-concentration procedures like SPME, have been applied to determine OTCs, e.g. stir bar sorptive extraction (SBSE) or liquid phase micro-extraction (LPME) [26]. SPME is a simple, fast and solvent-free technique, which combines extraction, concentration and sample introduction into the GC injector using one single device. Since SPME is an equilibrium-extraction method, the equilibrium time determines the maximum amount of analyte that can be extracted by the fibers, which controls the sensitivity of the method. Nevertheless, if the achieved analytical sensitivity is sufficient for a quantitative analysis, it is not necessary to reach the equilibrium [28].

Due to the low volatilities of the OTCs, a derivatization step (alkylation by Grignard reagents [29,30] or hydrogenation by sodium borohydride [31]) is required before injection into the gas chromatograph. In recent years, sodium tetraethylborate ($NaBEt_4$), sodium tetraphenylborate ($NaBPh_4$) or sodium tetra (*n*-propyl) borate ($NaBPr_4$) has been used for OTCs determination [1,4,21,26,32–34]. These derivatizing agents can be used directly in the aqueous phase which provides a great advantage. However, the use of $NaBEt_4$ and $NaBPh_4$ has a significant limitation in the simultaneous determination of ethyl and phenyl species as their use is not possible due to the loss of OTC species information. The recent introduction of $NaBPr_4$ as a derivatization reagent has significantly changed this situation [19].

This paper describes the development of a new method for the reliable qualitative and quantitative determination of OTCs in water samples, which has improved considerably the detection and quantification limits regarding other methods published to fulfill the regulatory requirements set out by the Water Framework Directive (WFD). For this purpose, 10 mL of water sample were extracted by HS-SPME with in situ derivatization using $NaBPr_4$. Moreover, two mass analyzers: the ion trap (IT-MS) and triple quadrupole (QqQ-MS) operating in full scan and SRM modes were validated and compared. GC coupled with a triple quadrupole MS/MS operated in SRM mode is becoming the standard in ultra-trace analysis because of its sensitivity and specificity. The proposed HS-SPME-GC–QqQ-MS/MS method achieves the very restrictive limits of environmental quality standards (EQS) established by the 2013/39/EU Directive [3]. To the best of our knowledge is the first time that these restrictive limits are reached using HS-SPME-GC–QqQ-MS/MS.

2. Experimental

2.1. Chemical and reagents

Monobutyltin (MBT) trichloride 95%, dibutyltin (DBT) dichloride and tributyltin (TBT) chloride were obtained from Sigma–Aldrich (Steinheim, Germany). Stock standard solutions of OTCs (1000 mg L^{-1}) were prepared in methanol (SpS-Super purity Solvent from Romil, Cambridge, UK). Stock standard solutions were stored in the dark at 4 °C. For method optimization, aqueous working solutions between 0.2 and 20 ng L^{-1} were prepared daily by appropriate dilution of the stock standard solutions in ultrapure water of 18 MΩ cm resistance (Milli-Q Water Purification System, Millipore, Bedford, MA, USA).

Tetrabutyltin (TeBT) was used as internal standard (Sigma–Aldrich, Steinheim, Germany).

Sodium tetrapropylborate ($NaBPr_4$) was obtained from ABCR GmbH & Co (Karlsruhe, Germany). A fresh $NaBPr_4$ solution of 1% (w/v) was prepared daily in 2% NaOH solution (w/v) purchased from Panreac (Barcelona, Spain).

A HOAc/NaOAc buffer of pH 5 was prepared by adding an appropriate amount of glacial acetic acid (Sigma–Aldrich, Steinheim, Germany) to a 0.2 M solution of sodium acetate traceSELECT for trace analysis (Sigma–Aldrich, Steinheim, Germany) in milli-Q water.

2.2. HS-SPME-GC–QqQ-MS/MS procedure

Derivatization with $NaBPr_4$ was carried out in aqueous solutions at pH 5. Highest derivatization yields for all compounds under study were obtained at pH around 5, which is in agreement with the literature [1,6,10,25]. For headspace SPME sampling, 10 mL of sea water, a fixed volume of the mixed organotin standard solutions and internal standard were placed in a 20 mL glass vial. 100 μL of 1% (w/v) $NaBPr_4$ solution and acetate buffer solution (pH 5) were added until a final volume of 12 mL. The vial was immediately capped, placed in the auto-sampler, and the HS-SPME step was performed by exposing the fiber to the solution headspace at a fixed temperature (60 °C) and time (30 min).

To minimize interferences and organotin contamination, the use of glassware, reagents, solvents or the number of sample manipulation were kept to a minimum.

SPME fibers of 65 μm polydimethylsiloxane divinylbenzene (PDMS/DVB) were supplied by Supelco (Bellefonte, PA, USA). Fibers were conditioned in the injection port of the GC for 0.5 h at 300 °C before use. The entirely automated extractions were performed by a Triplus auto-sampler mounted on the GC–MS system (Thermo-Finnigan, Waltham, MA, USA). The SPME accessory kept the vial agitated by oscillation and at a fixed temperature (60 °C) during the extraction step (30 min). After extraction, the fiber was thermally desorbed for 5 min in the liner of the GC injector port at 300 °C.

The analysis was carried out using a Thermo-Finnigan Trace GC chromatograph and coupled to a triple quadrupole mass spectrometer (TSQ Quantum XLS). Separation was carried out on a DB-XLB column (60 m × 0.25 mm × 0.25 μm) (J&W Scientific, Folsom, CA, USA). Injector temperature was 300 °C in PTV splitless injection. GC program started at 70 °C for 2 min, followed by a temperature rate of 15 °C min^{-1} to 270 °C and held at this temperature for 1 min. Ion source temperature was 250 °C, transfer line temperature was 300 °C. SRM was the detection mode selected.

The standard addition method was used for quantification. Tetrabutyltin (TeBT) was used as internal standard to correct possible variations in the instrumental determination.

2.3. Chromatographic determination by GC–MS and GC–MS/MS

Gas chromatography was performed with a Thermo-Finnigan (Waltham, MA, USA) Trace GC equipped with a Combi PAL autosampler, PTV injector and coupled to an ion trap mass spectrometer (Polaris Q). The system was operated in electron impact mode (EI; 70 eV).