Analytica Chimica Acta 858 (2015) 66–73

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A fast and effective routine method based on HS-SPME–GC–MS/MS for the analysis of organotin compounds in biota samples

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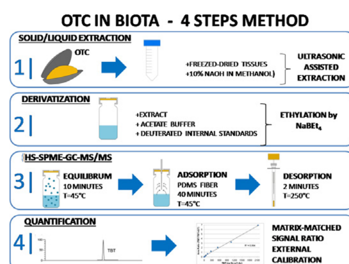
HIGHLIGHTS

- A SPME based method was validated for routine analysis of OTC in biota samples.
- Matrix-matched signal ratio external calibration is effective in SPME application.
- Remarkable analytical performances over the current OTC levels of contamination.
- SPME benefits (fast–solventless) make the method suited for routine analysis

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 25 November 2014

Keywords:
Biota
Organotin
Routine
Tributyltin
Solid phase microextraction
Calibration

ABSTRACT

This work validated an automated, fast, and low solvent- consuming methodology suited for routine analysis of tributyltin (TBT) and degradation products (dibutyltin, DBT; monobutyltin, MBT) in biota samples. The method was based on the headspace solid-phase microextraction methodology (HS-SPME), coupled with gas chromatographic separation and tandem mass-spectrometry (GC–MS/MS). The effectiveness of the matrix-matched signal ratio external calibration was tested for quantification purposes. The exclusion of matrix influences in the calibration curves proved the suitability of this versatile quantification method. The method detection limits obtained were of 3 ng Sn g^{-1} dw for all the analytes. The analysis of references materials showed satisfying accuracy under optimum calibration conditions (% recovery between 87–111%; |Z-scores|<2). The repeatability RSD% and intra-laboratory reproducibility RSD% were lower than 9.6% and 12.6%, respectively. The work proved the remarkable analytical performances of the method and its high potential for routine application in monitoring organotin compounds (OTC).

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1. Introduction

Tributyltin (TBT) was used worldwide as active biocide in antifouling paints until the 1980s, when progressively stricter regulations were adopted to control its release into the aquatic environments. The use of TBT-based antifouling products was globally banned in 2001 by the International Convention on the

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http://dx.doi.org/10.1016/j.aca.2014.11.028
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Control of Harmful Anti-Fouling System on Ships (AFS Convention [1]), which entered into force on 17th September 2008.

Despite the progressive decline of TBT concentrations in aquatic environments, following TBT-paints regulation [2], this pollutant and its degradation products (dibutyltin, DBT; monobutyltin, MBT) are still present at trace levels in marine environments almost everywhere [3]. In fact, sediments, which sequestrated huge amounts of TBT during the pre-ban period, are now acting as reservoirs of contamination [4].

The toxicity of organotin compounds (OTC; OTC = TBT + DBT + MBT) in aquatic environments is well known, especially for TBT; their potential of inducing toxic effects has been assessed in several taxa, from phytoplankton to mammals ([5], and references therein). Thus, TBT is still considered one of the most harmful toxicants for ecosystems and human health, and consequently it is listed among the priority pollutants of national legislations and international conventions (*i.e.* OSPAR Convention; Directive 2000/60/EC [6] and the daughter Directive 2008/105/EC [7]).

Several analytical methodologies based on separation techniques (gas chromatography, GC; high-performance liquid chromatography, HPLC) have been developed to assess OTC levels in aquatic environments [8]. Among them, GC is probably the most attractive choice, because of its high sensitivity and easy coupling to several detectors. However, because of the low volatility of these compounds and their presence at trace levels in many environmental compartments, the GC based methods involve laborious derivatization and preconcentration steps, which make the whole analytical procedure time- and solvent- consuming.

The solid phase microextraction (SPME) technique [9] represents a valuable alternative to extract OTC from environmental samples in a quick and efficient way. It basically relies on the use of a fused silica fibre coated with a thin layer of extraction phase (polymer) and mounted inside the needle of a syringe-like device. In most SPME applications, the analyte extraction is performed by direct immersion of the fibre into the liquid sample or its gaseous phase (headspace mode), whereas desorption occurs directly in the GC injector. The SPME technique, which integrates sampling, extraction and concentration into a single step, is solventless, environment-friendly and free of health hazards. Furthermore, compared to the more traditional GC methods, it is competitive in terms of high pre-concentration power, low interaction with matrix (when used in headspace HS- mode) and short processing time [10].

As reviewed by Lambropoulou et al. [11], several authors described methods using SPME in combination with GC for the quantitative determination of OTC in environmental samples. The majority of them focused on water and sediment samples [12–27], whereas few on biota, which is an important target of several monitoring programs [14,20,28]. The aforementioned studies typically use standard addition or isotope dilution methods for OTC quantification. In fact, in HS-SPME analyses of complex matrices, such as biota and sediments, the extraction by the fibre is influenced by sample-dependent matrix effects on the partition of the analytes into the three phase equilibrium (*i.e.* liquid extract, vapour phase and fibre coating). For this reason, "sample-to-sample" quantification approaches are highly recommended [29]. However, this choice is not practicable in routine analysis or by laboratories unequipped for precise isotopic measurements (ICP-MS; quadrupole MS for applying the isotope dilution mass spectrometry, IDMS [27,30]).

The main purpose of the present study was to validate a fully-automated HS-SPME–GC–MS/MS methodology suitable for routine analysis of the current levels of OTC in marine biota samples. The suitability of the matrix-matched signal ratio external calibration [31], as alternative to sample-to-sample quantification approaches, was tested. The method aims to provide valuable analytical performances and important benefits to environmental laboratories in terms of reduction of solvent consumption, processing time, costs and working effort.

2. Materials and methods

2.1. Reagents, solutions and reference materials

For OTC tissue extraction, a 10% NaOH methanolic solution was prepared (NaOH ACS-ISO, Carlo Erba Reagents, Italy; methanol HPLC-Plus gradient, Carlo Erba Reagents, Italy). A sodium acetate/acetic acid buffer solution (3.6 M, pH 5.1) was made by mixing appropriate amounts of CH_3COONa (ACS-ISO, Carlo Erba Reagents, Italy) and CH_3COOH (RPE glacial for analysis ACS-ISO, Carlo Erba Reagents, Italy). A 2% (m/v) solution of sodium tetraethylborate ($NaBEt_4$, 98%; Aldrich, Italy) was prepared immediately before use in high purity water (18 MΩ cm at 25 °C) in a closed plastic glove-bag filled with nitrogen, in order to obtain an inert atmosphere. The deionized water used throughout the study was generated on-site using a Milli-Q® Integral 5 Water Purification System (Merck Millipore, Vimodrone (MI), Italy).

MBT, DBT and TBT standards ($MBTCl_3$, 99.5%; $DBTCl_2$, 99.5%; TBTCl, 98.5%) were purchased from Chiron AS (Trondheim, Norway); deuterated internal standards (MBT-d9-Cl_3, 98%; TBT-d27-Cl, 97%) were provided by C/D/N Isotopes Inc. (Pointe-Claire, Canada). For all standards, primary stock solutions were prepared at a concentration of 1000 ng Sn μL^{-1} in methanol. From these, an intermediate working standard, containing the three analytes at concentration 1 ng Sn μL^{-1}, was prepared for calibration purposes. Similarly, a mix working solution containing both deuterated internal standards (1 ng Sn μL^{-1} in methanol) was made to be used as internal standard.

100 μm polydimethilsiloxane (PDMS) fibres for SPME, purchased from Supelco (Sigma–Aldrich, Italy), were conditioned according to Supelco's instructions before use. 20 mL headspace vials and associated screw caps with PTFE/silicone septum were purchased from Microcolumn Srl (Lissone (MB), Italy).

For validation, three reference materials were used: the ERM® Certified Reference Material 477 (CRM 477; mussel tissue) and two biota samples (mussel) from the QUASIMEME proficiency study (samples code: QSP044BT, QSP045BT; Round 72, March–June 2013; Exercise 1011, BT8).

2.2. Extraction from solid sample and derivatization

0.200 g of freeze-dried tissue (dw) was extracted by sonication (2 h) with 10 mL of extraction solution (10% NaOH in methanol). Once the extraction was completed, the supernatant was centrifuged for 15 min at 1500 rpm. 1.5 mL of supernatant were transferred into a 20 mL headspace vial containing 7 mL of acetate buffer solution. Thus, a proper volume of internal standard solution was added to each vial. Afterwards, the vials were crimped with caps provided with a PTFE lined silicone septum. The analytes were ethylated by adding 0.5 mL of a 2% solution of $NaBEt_4$.

2.3. HS-SPME and GC–MS/MS analysis

The SPME was carried out in automated mode by using a TriPlus autosampler - SPME version (Thermo Fisher Scientific Inc.), interfaced to the GC–MS (Trace GC coupled to PolarisQ Ion Trap, Thermo Finnigan). HS-SPME was performed after 10 min of incubation of the sample at 45 °C, under regular agitation (10 s intervals). The PDMS fibre was exposed in the headspace for 40 min at the same temperature and agitation conditions. Once the isolation step was completed, the fibre was desorbed for 2 min in the GC injection port (at 250 °C) equipped with a 0.8 mm (I.D.) inlet

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