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New approach of solid-phase microextraction improving the extraction yield of butyl and phenyltin compounds by combining the effects of pressure and type of agitation

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Abstract

A new methodology for the simultaneous and fast solid-phase microextraction (SPME) of butyl- and phenyltin compounds, as ethylated derivates, is proposed in this paper. The effects of pressure and type of agitation during headspace SPME sampling are evaluated and discussed on the basis of thermodynamic considerations. Quantitative structure–activity relationships were used to estimate analytes partition coefficients allowing to explain the different behaviours experimentally observed. SPME sampling conditions including mechanical stirring and reduced pressure result in simultaneous higher efficiency (detection limits especially lowered for phenyltins up to a eight-fold reduction) and shorter sampling time (two-fold reduction).

Keywords: Solid-phase microextraction; Organotins; Reduced; Pressure; Mechanical agitation; Quantitative structure–activity relationships; Extraction time; Headspace

1. Introduction

Over the past 30 years, the large anthropogenic use of organotins, especially the highly toxic butyl- and phenyltin compounds, is responsible for their important occurrence in the environment [1,2]. Consequently, the presence of these compounds is more and more drastically controlled. Therefore, fast, accurate and precise analytical methods are required in order to identify and quantify these species at the levels commonly found in environmental matrices, i.e. in the range pg to ng (Sn) l^{-1}. Speciation of organotin compounds is commonly realised by coupling gas chromatography with a specific detector [3–12]. Nevertheless, sample preparation remains a critical step which requires the extraction/derivatization and preconcentration of the analytes prior to their injection in the chromatograph. Liquid–liquid extraction is traditionally used but requires high levels of often toxic organic solvents.

Solid-phase microextraction (SPME) was developed in the 1990s by Pawliszyn and co-workers [13,14] for organic compounds and further used for metallic and organometallic compounds, as reviewed by Mester et al. [15]. Nevertheless, only few teams have worked on the extraction of phenyltin compounds with SPME [16–22].

For organotin compounds, direct sampling, i.e. the fiber is directly exposed to the aqueous sample, was first proposed by Lespes et al. [16] and Aguerre et al. [17–19] but suffers from long extraction time (up to 60 min), possible matrix effects and organic matter co-absorption on the fibre [17,23].

Headspace (HS) extraction mode, i.e. the fibre is exposed in the headspace located above the sample, proposed by Zhang and Pawliszyn [24], is based on the faster diffusion of analytes in the vapor phase than in the aqueous phase if the aqueous phase is constantly stirred. HS-SPME sampling

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times could be shortened up to 40 min [20,21] with elimination of matrix effects. Nevertheless, heaviest compounds, i.e. also the less volatile ones, are less extracted.

Effects of temperature in headspace mode were also proposed to reduce extraction time [25]. But, no significant improvement in extraction time was obtained by Vercauteren et al. [22] for triphenlytin and tricyclohexyltin using a sampling temperature of 75 °C (35 min). Moreover, handling of vials is more difficult and pressure build-up inside the vial can cause some losses of sample vapor when removing the SPME needle from the vial.

Applications of new techniques of extraction such as stir bar sorptive extraction [26] or liquid phase microextraction [27] were applied to butyl- and phenyltin compounds but did not shorten extraction time (30 and 60 min, respectively including desorption time).

Hence, we propose in this paper another alternative which is the combination of SPME in HS using reduced pressure. If the pressure in the headspace is below the atmospheric pressure, extraction of analytes should be enhanced from the aqueous phase to the gaseous phase [28]. In this paper, this method was applied to butyl- (MBT, DBT, TBT) and phenyltin (MPhT, DPhT, TPhT) compounds determination. The optimisation of the critical parameters are described in details. Two stirring modes were tested both under atmospheric and reduced pressure. Analytical performances of the technique were also discussed in terms of extraction efficiency, detection limits, preconcentration time, and reproducibility.

2. Experimental

2.1. Standards and reagents

Monobutyltin trichloride (>95%), monophenyltin trichloride (>98%), diphenyltin dichloride (>96%) and triphenyltin chloride (>95%) (Aldrich), dibutyltin dichloride (>98%) and tributyltin chloride (>96%) (Merck) were used without further purification. Stock standard solutions containing 1000 mg (Sn) l^{-1} of each compound in methanol (Normapur, >99%, Prolabo) were stored in the dark at 4 °C. In these conditions, they were stable for several months [29]. Working standard solutions were prepared by dilution with Milli-Q water (Millipore, 18.2 MΩ cm) weekly for 10 mg (Sn) l^{-1} and daily for 100 μg (Sn) l^{-1}.

Sodium ethanoate (Sigma, >99%) and ethanoic acid (Merck) were used for 0.4 mol l^{-1} buffer preparation (pH = 4.75). Sodium tetraethylborate ($NaBEt_4$, 98%) was obtained from Galab (Geesthacht, Germany). Fresh 2% solutions (w/v) were prepared daily in Milli-Q water and stored at 4 °C in the dark.

2.2. MIP-AES apparatus and GC conditions

Chromatographic separation of ethylated butyltin and phenyltin compounds was performed with an Agilent (Wilmington, DE, USA) Model 6890 Series Plus gas chromatograph equipped with a split/splitless injection port and a narrow bore injection liner (0.75 mm I.D.). Detection was achieved with an Agilent G2350A Microwave Induced Plasma Atomic Emission detector (MIP-AES) with operational parameters previously optimised in our lab [18].

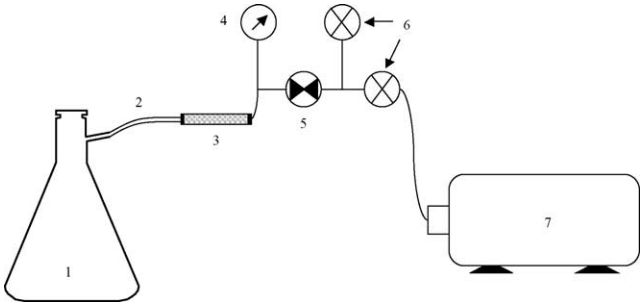

Fig. 1. Schematic of SPME device for sampling at reduced pressures: (1) modified conical flask; (2) tygon tubing; (3) water trap (soda lime and $CaCl_2$ mixture); (4) vacuum controller; (5) two-way valve; (6) vent (depression regulation); (7) vacuum pump.

2.3. SPME procedure

SPME was carried out manually with the appropriate SPME holder and 100 μm polydimethylsiloxane (PDMS)-coated fused silica fibres (Supelco, Bellefonte, PA, USA). This apolar phase is the most commonly used for organometallic compounds [15,16,21].

For the optimisation of the HS SPME procedure, modified 50 ml conical flasks were used. An open-cap vial was welded at the top of the flask allowing it to be sealed with a polytetrafluoroethylene (PTFE)-coated silicone rubber septum (Supelco, 20 mm diameter). The importance of the headspace to aqueous phase volume ratio in HS SPME sampling is well known [30–32]. Geometry of modified conical flasks was designed to allow: (i) a reduced headspace volume around the fibre while keeping the headspace to aqueous phase volume ratio constant; (ii) a larger exchange surface between headspace and sample to improve analyte transfer from aqueous to headspace phase.

A glass tube (17 mm length × 2 mm I.D.) was also welded at the neck of the flask in order to carry out HS SPME in reduced pressure conditions. In the case of HS SPME sampling at atmospheric pressure, this opening was tightly shut.

A 25 ml aliquot of the sodium ethanoate/ethanoic acid buffer was introduced in the modified conical flask. After sealing, organotins were added to obtain a final concentration of 400 ng (Sn) l^{-1} of each compound. The SPME fibre was inserted in the headspace immediately after the addition of 25 μl of $NaBEt_4$ solution. In the case of reduced pressure SPME sampling in order to minimise analyte losses, derivatization reagent was added after decreasing the pressure in the flask. A manual two way valve allowed to isolate the reactor from the vacuum pump once the depression was achieved as indicated in Fig. 1. The pump was then switched