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Journal of Chromatography A, 1094 (2005) 130–137

JOURNAL OF
CHROMATOGRAPHY A

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Organotin speciation in environmental matrices by automated *on-line* hydride generation-programmed temperature vaporization-capillary gas chromatography–mass spectrometry detection

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Received 13 May 2005; received in revised form 15 July 2005; accepted 25 July 2005
Available online 16 August 2005

Abstract

In the present contribution, a new automated *on-line* hydride generation methodology was developed for dibutyltin and tributyltin speciation at the trace level, using a programmable temperature-vaporizing inlet followed by capillary gas chromatography coupled to mass spectrometry in the selected ion-monitoring mode acquisition (PTV-GC/MS(SIM)). The methodology involves a sequence defined by two running methods, the first one configured for hydride generation with sodium tetrahydroborate as derivatising agent and the second configured for speciation purposes, using a conventional autosampler and data acquisition controlled by the instrument's software. From the method-development experiments, it had been established that injector configuration has a great effect on the speciation of the actual methodology, particularly, the initial inlet temperature (−20 °C; He: 150 ml/min), injection volume (2 μl) and solvent characteristics using the solvent venting mode. Under optimized conditions, a remarkable instrumental performance including very good precision (RSD < 4%), excellent linear dynamic range (up to 50 μg/ml) and limits of detection of 0.12 μg/ml and 9 ng/ml, were obtained for dibutyltin and tributyltin, respectively. The feasibility of the present methodology was validated through assays upon in-house spiked water (2 ng/ml) and a certified reference sediment matrix (Community Bureau of Reference, CRM 462, Nr. 330 dibutyltin: 68 ± 12 ng/g; tributyltin: 54 ± 15 ng/g on dry mass basis), using liquid–liquid extraction (LLE) and solid-phase extraction (SPE) sample enrichment and multiple injections (2 × 5 μl) for sensitivity enhancement. The methodology evidenced high reproducibility, is easy to work-up, sensitive and showed to be a suitable alternative to replace the currently dedicated analytical systems for organotin speciation in environmental matrices at the trace level.

Keywords: *On-line* hydride generation; Sodium tetrahydroborate; PTV-GC/MS(SIM); Speciation; Organotins; Dibutyltin; Tributyltin; CRM; Environmental matrices

1. Introduction

Organotin compounds have been extensively studied in the last years due to their high toxicity and remarkable impact in the aquatic environment. These compounds have been used worldwide in several areas of the human activity, particularly as components in anti-fouling paints, herbicides, fungicides and wood preservatives [1].

Tributyltin (TBT), appears as a top hazard substance in the priority pollutant lists of the European Union and United States Environmental Protection Agency, and has been included in the xenoestrogens or endocrine disrupters group, since the biocide effects observed in natural ecosystems of which the onset of *imposex* to a great number of gastropod species is a shocking example [2,3]. Shipyard docks and naval activities are in general the main sources of TBT in the estuaries and coastal waters, owing to the frequent use of anti-fouling paints, which must be carefully monitored to control the contamination level of those harmful substances. In environment, TBT can decompose into less

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doi:10.1016/j.chroma.2005.07.101

substituted compounds (e.g. dibutyltin) and usually accumulates in sediments, which act as a long-term repository and help to maintain its persistence into aquatic ecosystems [4,5].

State-of-the-art analytical methodologies currently available to monitor organotin compounds are based in liquid–liquid extraction (LLE) and solid-phase extraction (SPE) sample preparation methods for enrichment, prior to Grignard alkylation followed by injection into hot vaporization inlets of gas chromatographs having selective detectors or hyphenated to particular techniques, such as mass spectrometry [6–10]. However, the modern approaches on organotin sample preparation are more dedicated to solventless methods, such as headspace solid phase micro-extraction and stir bar sorptive extraction after in situ derivatization using sodium tetrahydroborate or tetraethylborate, followed by introduction into hot vaporization inlets and thermal desorption devices coupled to gas chromatographs, respectively [11–22]. Besides those approaches have been proved to decrease the detection limits at the ultra-trace level, they are still a bit expensive, time consuming particularly to reach optimized equilibrium conditions and for the very non-polar volatile organotins, adsorption onto sampling flask glass walls and other surfaces, is a very important phenomenon causing sometimes analyte loss and reducing sensitivity. On the other hand, sodium tetraethylborate commonly used as ethylation reagent, is very sensitive to air and moisture and must be handled under nitrogen atmosphere, which is not practical for routine analysis. Therefore, sodium tetrahydroborate is much more suitable as hydridization reagent for organotin derivatization during the experimental work, since exhibit higher stability.

So far, hydride generation has been widely accepted as a simple and effective method to produce organotin hydrides prior to *on-line* cryogenic trapping followed gas chromatographic separation and quartz furnace atomic absorption spectrophotometric detection [23–25]. In spite of organotin derivatives being significantly more volatile and peak shapes been greatly improved with reduced tailing in the course of chromatographic analysis, low yields during in situ hydride generation can occur, particularly when organic and inorganic interferences are present in environmental matrices [26].

Sullivan et al. [27], proposed the *on-line* hydride generation using a sodium tetrahydroborate packed reactor inside the hot injector port of a gas chromatograph, which showed good performance for organotin speciation in biota matrices. By incorporating the derivatization step into the inlet of the analytical instrument, much time can be saved and previous sample preparation enrichment can be conventional (e.g. SPE) and simplified, experimental errors such as loss of volatiles and low derivatization yields can be avoided, the amounts of derivatising agent and analytical steps reduced and the analytical performance increased. Furthermore, automation is another potential benefit for *on-line* hydride generation through an autosampler and if a programmable temperature-vaporizing inlet is used, the sensitivity can be greatly improved by large volume injection [28–31].

The aim of the present study is to assess whether automated *on-line* hydride generation using a programmable temperature-vaporizing inlet followed by capillary gas chromatography coupled to mass spectrometry (PTV-GC/MS), is a suitable method for organotin speciation in environmental matrices at the trace level. The methodology is evaluated in terms of the *on-line* hydridization yields and speciation using sodium tetrahydroborate as derivatising agent, an automatic liquid sampler, a configured multi-method sequence and data acquisition controlled by the instrument's software. Optimization studies were carried out in order to foresee the most important parameters that could affect the analytical performance, including precision, linearity and limits of detection. Finally, the analytical validation of the methodology to monitor environmental matrices is tested through in-house standards and a certified reference material (CRM), including assays on water and sediment matrices, respectively.

2. Experimental

2.1. Reagents and standards

All solvents and reagents used had analytical grade. Ultra grade HCl (37%, Merck), methanol, ethyl acetate and hexane (for HPLC, Merck) were used. Sodium tetrahydroborate ($NaBH_4$; 95%) was obtained from Riedel-de Haën, for which freshly 4% aqueous solutions were daily prepared. Tropolone (99%), dibutyltin dichloride (DBT; 96%) and tributyltin chloride (TBT; 96%) were supplied from Sigma–Aldrich. A stock standard methanolic solution of DBT (0.8 mg/ml) and TBT (0.8 mg/ml) was used for method development and calibration studies, as well as for in-house spiked water assays. A standard mixture of DBT and TBT hydrides was prepared into a vial by dilution of 10 μl of the stock solution in 0.5 ml of hexane, following the addition of $NaBH_4$ powder and closed with a seal using a hand crimper prior to agitation by vortex (Velp Scientifica, Zx^3).

A certified reference material for DBT and TBT in coastal sediments (Community Bureau of Reference, CRM 462, Nr. 330; Certified value—DBT: 68 ± 12 ng/g and TBT: 54 ± 15 ng/g on dry mass basis) kept at −30 °C was used for the sediment assays [32]. Deionised water was obtained from Milli-Q water purification systems.

2.2. Experimental set-up

In sediment assays, to each accurate weight (1 g; Mettler Toledo AG135) of CRM after a previous preparation according with the instructions for use (the material was re-homogenized manually for 5 min and each sample analyzed was dried in an oven at 100 °C for 4 h) [32], 30 ml of deionised water having 5% of HCl were added and the