Journal of Chromatography A, 655 (1993) 51–56
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 043

Supercritical fluid extraction of tributyltin and its degradation products from seawater via liquid–solid phase extraction

R. Alzaga and J.M. Bayona*

Environmental Chemistry Department, C.I.D.-C.S.I.C., Jordi Girona Salgado 18–26, 08034-Barcelona (Spain)

ABSTRACT

Quantitative extraction of di- and tributyltin compounds from aqueous matrices using C_{18} liquid–solid extraction (LSE) discs, followed by *in situ* Grignard ethylation and supercritical fluid extraction of derivatized LSE discs, is demonstrated for the first time. The optimum extraction efficiency of dibutyltin and tributyltin from synthetic seawater at pH 2 was achieved by using a combination of static and dynamic extraction procedures with supercritical carbon dioxide (10 MPa, 40°C). The extraction efficiency for dibutyltin and tributyltin ranged from 92 to 102%, and the R.S.D.s ($n = 5$) were 6.6 and 8.2%, respectively. The limit of detection of tributyltin (1 l of seawater) using a capillary gas chromatograph coupled to a single-flame tin-selective flame photometric detector was 6 ng/l, while the limit of quantitation of harbour seawater was 9 ng/l. Furthermore, analysis time and solvent usage are reduced by 50 and 90%, respectively, in comparison with classical methods involving liquid–liquid extraction in the presence of complexing agents.

INTRODUCTION

Of organometallic compounds, organotins have the highest industrial output, and this has increased over the last decade as a result of the use of organotins in a large variety of applications (*i.e.* catalysts, polymer additives, agricultural biocides, antifouling paints) [1]. Because of their pattern of usage, a significant portion of organotins are released directly into the marine environment or transported from continental areas. The strong toxicity of some organotin compounds is a cause of primary concern in coastal environments owing to their deleterious effects on biota at very low concentration levels. Indeed, some of them are included in the EC list of pollutants.

Analytical procedures for the determination of organotins in environmental samples should therefore be able to differentiate the toxic parent compounds from the less toxic degradation products. Furthermore, analytical procedures should be able to reach a limit of detection (LOD) below the environmental quality target (EQT) (0.2–20 ng/l) [2].

Several analytical procedures have been developed for organotin speciation in seawater [3–5], but most of these techniques rely on multiple extraction and derivatization steps and, consequently, they are not well suited for application to monitoring programmes involving a large number of samples. Although hydride generation (HG) coupled to cryogenic trapping GC and atomic absorption spectrometry (AAS) has been widely used during the last decade [6], recent interest has been focused on the alkylation reactions owing to the higher stability of alkylated derivatives and lower matrix depen-

* Corresponding author.

0021-9673/93/$06.00

dency of these reactions [7–10]. At present, the absolute LOD of HG–GC–AAS is higher than that of other analytical techniques such as capillary GC (cGC) coupled to flame photometric detection (FPD) [11], atomic emission detection (AED) [12] or MS in the single-ion monitoring (SIM) mode [13].

In this paper, an analytical procedure using liquid–solid extraction (LSE) with C_{18} extraction discs, *in situ* ethyl-Grignard derivatization and supercritical fluid extraction (SFE) with carbon dioxide and off-line cGC–FPD determination is presented. This procedure is clearly better than sequential liquid–liquid extraction (LLE) and derivatization procedures in terms of analysis time, extraction efficiency and waste reduction due to solvent minimization during the extraction step.

The application of LSE using extraction cartridges (Carbopack, silica-C_8 and -C_{18}) for the butyltin compounds has been previously evaluated [14,15]. However, several drawbacks are associated with this method: (1) the eluting solvent may extract potentially interfering compounds from the polypropylene housing and polyethylene frit; (2) batch-to-batch sorbent variability; (3) channelling, which prevents the interaction between components of interest and the sorbent; (4) low flow-rate (<10 ml/min) and (5) suspended matter can clog the limited number of flow paths.

Some of these disadvantages are avoided by the introduction of extraction discs (silica-C_{18}) [16], which have in fact been successfully applied to the recovery of tributyltin from seawater [17]. However, no attempts have been made to perform *in situ* derivatization and SFE, which has been a very successful approach for the extraction of polar compounds from solid matrices [18,19]. In fact, the derivatization reaction was also evaluated as carried out *in situ* on the Empore extraction disc for several reasons. Firstly, it is faster in comparison with conventional procedures involving an extended sample treatment. Secondly, derivatized organotin compounds are presumably easier to extract from the extraction disc. Finally, SFE can be coupled to other chromatographic techniques.

EXPERIMENTAL

Materials and reagents

Pesticide-grade diethylacetate, analytical-grade hydrochloric acid (32% v/v) and ethylmagnesium chloride in tetrahydrofuran (THF) were obtained from Merck (Darmstadt, Germany). Discs of 4.7 mm, Empore 3M (PTFE membrane enmeshed with 8-μm silica-C_{18}), were used for LSE. Instant Ocean was used to prepare synthetic seawater from Milli-Q-grade water (33 g/l). Natural seawater was sampled at the subsurface and bottom using a home-built system in a marina located in the N.W. Mediterranean Sea containing more than 400 moored vessels.

Standards

Monobutyltin chloride (MBT) was obtained from Aldrich (Stenheim an Albuch, Germany). Dibutyl- (DBT), tripropyl- (TPrT) and tributyltin (TBT) chlorides were provided by Fluka (Buchs, Switzerland). Stock solutions, used for cGC–FPD calibration, were prepared with *n*-hexane, while they were dissolved in acetone for water-spiking purposes at concentrations ranging from 2.3 to 4.8 μg/l.

Extraction and derivatization procedures

Samples were acidified to pH 2 with hydrochloric acid and spiked with MBT, DBT and TBT chlorides for method development purposes and with TPrT chloride as internal standard for natural seawater. Samples were kept at 4°C in the dark until analysis (less than 10 days).

Extraction discs were preconditioned in the extraction assembly using a sequential solvent elution programme with the following solvents: (a) 10 ml of ethyl acetate, (b) 5 ml of methanol and (c) 10 ml of Milli-Q water. A vacuum source was applied for 5 min during each solvent treatment until the first drops came out. The acidified sample (0.5–1 l) containing methanol (5–10 ml) was immediately transferred into the extraction assembly to avoid drying of the extraction disc. The vacuum was adjusted to keep the extraction flow-rate at 200 ml/min. Filters were dried for 1 h at room temperature, cut into small pieces and

introduced into a home-made cylindrical aluminium foil reaction cell built inside the extraction vessel. The derivatization reaction was performed with ethylmagnesium chloride (1.5 ml), keeping the extraction vessel at room temperature for 2 min. THF of Grignard reagent was removed before performing SFE, keeping the extraction vessel open at room temperature for 15 min after the derivatization step.

Instrumental analysis

SFE was carried out in an SFC 3000 series (Fisons Instruments, Milan, Italy) using 99.995% carbon dioxide (Carburos Metálicos, Barcelona, Spain). Extraction cells of 5 ml were obtained from Suprex (Pittsburgh, PA, USA). The flow-rate through the extraction vessel was adjusted with linear restrictors of different length (fused silica, 30 μm I.D. × 12–18 cm) (MicroQuartz, Munich, Germany). Derivatized organotins were collected in a vial containing 1 ml of *n*-hexane.

SFE extracts were analysed by cGC apparatus (Fisons Instruments) equipped with cold on-column injection and an FPD containing a 610-nm bandpass filter. The detector temperature was set to 225°C. A 2.5 m × 0.32 mm I.D. deactivated fused-silica tubing was coupled via a press-fitted back-connector to the analytical columns, which were a DB-5 (30 m × 0.25 mm I.D., film thickness = 0.1 μm) and a OV-1 (10 m × 0.25 mm I.D., film thickness = 0.15 μm). Column temperature was programmed from 60 to 225°C at 8°C/min, after an isothermal period of 2 min. Hydrogen was used as carrier gas at 50 cm/s. Data were acquired by a Nelson-PE interphase with a sampling frequency of 100 Hz and handled with a PS computer.

RESULTS AND DISCUSSION

Development of SFE of butyltins from extraction discs

Previous studies have shown that SFE of organotin chlorides requires significant amounts of modifiers for their quantitative recovery from solid matrices [20]. Furthermore, the restricted volatility of those compounds makes it necessary to perform a derivatization step prior to GC determination [9]. Therefore, in this paper we have explored the introduction of derivatization step prior to extract desorption (Fig. 1), aiming to obtain quantitative recoveries of organotin compounds by SFE with neat carbon dioxide and to proceed with the GC analysis of the recovered extract.

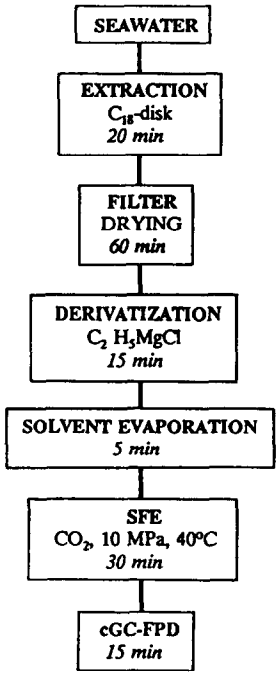

Fig. 1. Analytical scheme, showing the time consumed at each analytical step.

Therefore, the SFE of derivatized organotins was optimized using a standard mixture containing MBT, DBT and TBT, as the ethylated derivatives. The standard solution was spiked directly onto the Empore silica-C_{18} extraction disc and extracted by the dynamic method or by a combination of static and dynamic methods, using different extraction volumes of supercritical carbon dioxide. The extraction temperature was kept constant at low values (40°C) to minimize analyte degradation during the extraction period. At the same time, pressure was also kept relatively low (10 MPa) in order to enhance the extraction selectivity of organotin compounds from other sample components. Furthermore, higher pressures lead to higher flow-rates, which

could favour losses of the more volatile butyltin components, already extracted, from the collecting vial.

In order to evaluate whether, under the extraction conditions used (40°C, 10 MPa), losses of butyltins occur from the collection vial, we exposed a solution of ethylated butyltins to a stream of carbon dioxide, simulating the extract collection during the extraction process. Under these conditions, no losses of butyltins were observed in the range of extraction volumes evaluated. Consequently, extract collection vials were kept at room temperature.

The extraction efficiency of butyltins from spiked extraction discs was evaluated first in the dynamic mode according to the volume of carbon dioxide passed through the vessel. Extraction rates were dependent on the compound and on the extraction volume of carbon dioxide (Fig. 2). Thus, while MBT reached its highest extraction rate at the beginning of the extraction period, DBT presented a recovery maximum at higher extraction volumes. Conversely, TBT recovery steadily increased with extraction volume, but no maximum was apparent in the range of extraction volumes evaluated.

Therefore, the kinetics of desorption of each butyltin from the extraction disc are completely different and may depend on the hydrophobicity of the compound, since the contribution of compound vapour pressure is negligible at the low temperatures and moderate densities used during the extraction. Thus, the less hydrophobic components (*i.e.* MBT and DBT) are desorbed from the extraction disc faster than the more hydrophobic components (*i.e.* TBT).

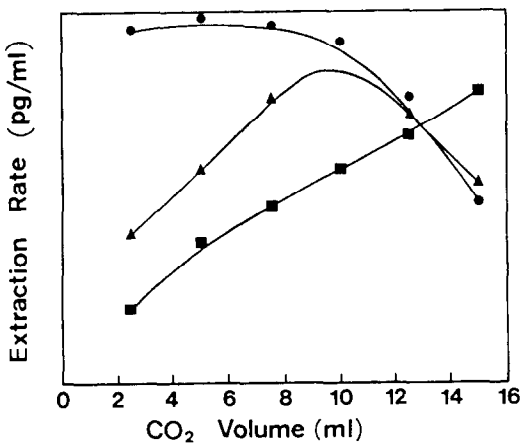

Fig. 2. Extraction rates of ethylated organotin derivatives from spiked extraction discs by dynamic SFE (10 MPa, 40°C) according to the volume of carbon dioxide used during the extraction. ■ = TBT; ▲ = DBT; ● = MBT.

Consequently, the dynamic extraction mode evaluated was not considered to be feasible for the quantitative extraction of all of the compounds of interest because the extraction volumes of carbon dioxide required are too large. Thus, a combination of static and dynamic extraction modes was tried. In this operational mode, quantitative extraction of all of compounds of interest was achieved by combining 1 ml of dynamic, 10 ml of static and 10 min of dynamic. Consequently, this extraction procedure was used further for the desorption of butyltins from the LSE discs.

Development of in situ organotin ethylation on the extraction disc and LSE of butyltins in seawater

Derivatization reaction on the Empore extraction disc was also evaluated so that thereafter SFE of the extraction disc could be performed without any kind of extract transfer. Taking into account the low solubility of the Grignard reagent (ethylmagnesium chloride) in the supercritical carbon dioxide, the derivatization reaction was previous performed at atmospheric pressure before the SFE. This derivatization reaction was performed within the extraction vessel, keeping the extraction disc covered with the derivatization reagent. The derivatization reaction was quantitative after 15 min of reaction time, and no cross-alkylation reactions were detected under these conditions.

In order to evaluate the extraction efficiency of Empore extraction discs, synthetic seawater was spiked with organotin chlorides at the ppb level. Fig. 3 shows a typical cGC–FPD chromatogram of an SFE extraction corresponding to a standard mixture used in the development of the method. Remarkably, satisfactory results were achieved in the cases of DBT and TBT (Table I). However, MBT exhibited poorer extraction efficiency and reproducibility, which

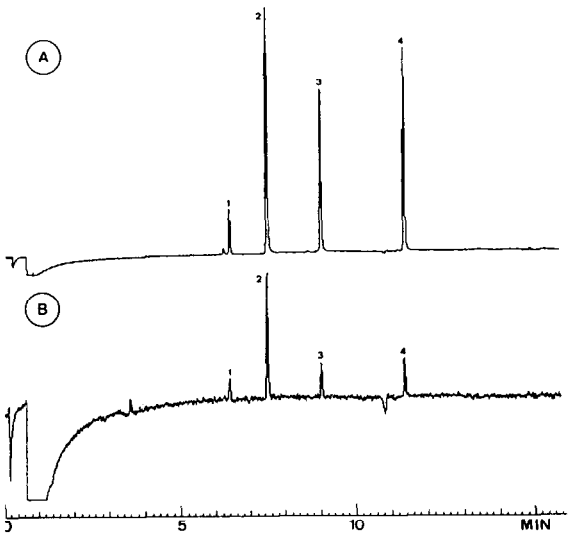

Fig. 3. cGC–FPD of SFE extracts isolated from (A) spiked synthetic seawater and (B) a real harbour water sample. Peaks: 1 = monobutyltin; 2 = tripropyltin; 3 = dibutyltin; 4 = tributyltin (analysed as ethyl derivatives).

could be attributed to its lower retention on the Empore extraction disc, or stronger adsorption on it. In preliminary work carried out using acetyl acetate as extraction solvent of the Empore disc, as described previously [17], MBT and DBT chlorides were not eluted from the disc. However, application of *in situ* derivatization reaction in the disc with the Grignard reagent coupled to SFE enables a quantitative recovery of DBT and to a lesser extent MBT. Following the derivatization reaction, they are easily desorbed because the polarized Sn–Cl bond is replaced by the less polar Sn–C, enhancing the solubility in the supercritical CO_2. Consequently, the poorer extraction recovery for MBT (Table I) may be attributable to a lower derivatization yield in the extraction membrane. Similar results have been found in an on-column or *in situ* derivatization ethylation using sodium tetraethylborate [21].

The LOD of the whole analytical procedure for TBT by extracting 1 l of water was estimated to be as low as 6 ng/l (Table II), which is satisfactory in terms of environmental quality target issued by most of national environmental protection agencies [2].

In order to evaluate breakthrough volumes in a realistic manner, different volumes of harbour seawater (surface and bottom) containing high levels of dissolved organic carbon were extracted. Fig. 4 shows a typical cGC–FPD chromatogram of a harbour water extract obtained with the OV-1 column, which enables resolution between TBT and the interference eluting as a negative peak. This compound was identified as di-*tert.*-butylmethylphenol by GC–MS and co-eluted in the 5% phenyl-substituted methypolysiloxane column.

On the other hand, no significant concentration differences between DBT and TBT were obtained from the extraction of 500–1000 ml of seawater, since the variation in the results fell within the S.D. of the analytical procedure (Fig. 4). Conversely, MBT exhibited larger variability according to the extracted volume, which could be attributed to the lower extraction recoveries for this compound (Table I). Higher water extraction volumes were not evaluated because the extraction period required was too long and

TABLE I

EXTRACTION EFFICIENCY AND REPRODUCIBILITY OF BUTYLTIN COMPOUNDS EXTRACTED BY LSE–DERIVATIZATION–SFE FROM SPIKED SYNTHETIC SEAWATER

	MBT	DBT	TBT
Recovery (%)[a]	69.9	91.8	102.0
S.D.[b]	12.2	6.1	8.4
R.S.D. (%)	17.4	6.6	8.2

[a] Spiking was performed at the low μg/l level.
[b] $n = 5$.

TABLE II

LIMIT OF DETECTION (LOD) OF THE WHOLE ANALYTICAL PROCEDURE[a]

	MBT	DBT	TBT
LOD	16	7	6

[a] It corresponds to 1000 ml of harbour water, concentrating the extract to 0.5 ml.

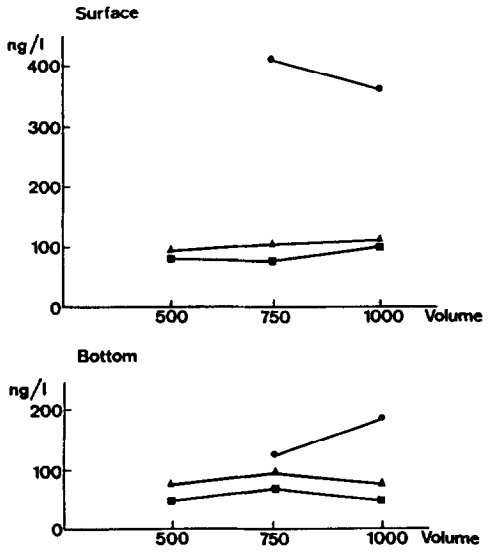

Fig. 4. Concentrations of butyltin compounds relative to the volume of extracted natural harbour water. ● = MBT; ▲ = DBT; ■ = TBT.

because the LOD of this technique meets with the most widely accepted EQT (20 ng/l).

CONCLUSIONS

LSE or butyltin compounds using C_{18} extraction discs has general advantages over LLE methods, *i.e.* solvent reduction, on-board extraction during sampling and extract storage. Also, LSE with extraction discs has advantages over LSE with cartridges: higher breakthrough volumes, less artifact formation and faster extraction rates. In the case of LSE extraction discs, artifacts are not apparent with tin-selective FPD if the proper conditioning is carried out. Another advantage of the use of extraction discs is the feasibility of "*in situ*" derivatization reaction, enabling the SFE of organotin compounds under mild conditions (CO_2, 40°C, 10 MPa) and, consequently, giving clean extracts that can be analysed directly without any further treatment. Finally, the procedural minimization of sample handling and intermediate steps leads to an enhancement of sensitivity and reproducibility and analysis time reduction. Further research is in progress in order to improve the MBT extraction from seawater.

ACKNOWLEDGEMENTS

Funding was provided by the CICYT from the Spanish National Plan for Research and Development (Grant AMB92-0218). One of us (R.A.) kindly acknowledges a predoctoral fellowship from CONACYT (México).

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