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Journal of Chromatography A, 963 (2002) 195–203

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Rapid determination of butyltin species in water samples by multicapillary gas chromatography with atomic emission detection following headspace solid-phase microextraction

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Abstract

A procedure for the rapid determination of mono-, di- and tributyltin in water samples is described. The analytes are simultaneously ethylated and concentrated on a solid-phase microextraction fibre placed in the headspace over the sample for 2 min. The ethylated species are then separated and selectively quantified in only 90 s using a multicapillary gas chromatography column combined with atomic emission detection. The influence of blank signals and sampling conditions on the sensitivity of the method is described. Detection limits of 1–5 ng/l and relative standard deviations of 6–10% at concentrations of 20 ng/l were obtained.

Keywords: Water analysis; Atomic emission detection; Detection, GC; Environmental analysis; Organotin compounds; Butyltin

1. Introduction

Tributyltin (TBT) is mainly used as a biocide especially in antifouling paints, while dibutyltin (DBT) is mainly used as a polymer stabiliser [1]. TBT, DBT and their degradation product (MBT) are harmful to several non-target aquatic organisms, because of which the use of TBT in antifouling paints has been restricted [2] and butyltin compounds have been included in the European list of priority pollutants [3]. TBT has also been identified as an endocrine disruptor, responsible for the imposex syndrome in certain marine gastropods at concentrations in water of a few ng/l [4].

The accurate identification and quantification of tin species in aqueous samples needs reliable analytical methods based on the combination of a concentration step with selective and sensitive analysis techniques. In the analysis of tin compounds, despite the need for a preliminary derivatization to convert the native species into less polar compounds, gas chromatographic techniques are more widely used than HPLC methods. The main reason is the commercial availability of more highly developed detectors and hyphenated techniques (based on GC separations), which enable the sensitive and selective determination of organotin compounds (GC–flame photometric detection (FPD) [5], GC–MS [6], GC–microwave-induced plasma atomic emission spectrometry (MIP-AES) [7,8] and, more recently, GC–inductively coupled plasma (ICP)-MS [9]).

The levels of organotin compounds in environmental water samples are usually below the detection limits of the above techniques, making necessary a

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00550-2

concentration step prior to their chromatographic analysis. One of the first alternatives was liquid–liquid extraction (LLE): organotin compounds can be extracted from water samples using a complexing agent (tropolone or sodium diethyldithiocarbamate) in combination with a non polar organic solvent, this procedure is generally followed by their derivatization with a Grignard reagent [7,10,11]. A faster option is the use of $NaBEt_4$ or $NaBPr_4$ as derivatization agents. With both reagents, alkyl derivatives are simultaneously formed in the aqueous sample and extracted into an organic solvent [12,13].

The concentration of organotin species in aqueous samples by solid-phase extraction (SPE) using C_{18}, polymeric or carbonaceous sorbents has also been carried out. Analytes can be retained on the solid sorbent either prior to their derivatization [14–16] or after being alkylated in the aqueous medium [17]. Solid-phase microextraction (SPME) has been used as a concentration technique for quantification of tin species in water [18–24], and in aqueous extracts of sediments [19,21,24,25], and biological matrices [26]. Non-polar fibres are the most often used (mainly with poly-dimethylsiloxane, PDMS, as stationary phase), and for butyltin species extraction is normally carried out at room temperature, with the fibre being placed in the headspace (HS) over the sample [19]. Recently, PDMS-coated stir bars have also been employed for the concentration of organotin compounds in aqueous samples [27]. The mass of stationary phase incorporated in the surface of a coated bar is bigger than in a SPME fibre, therefore the total amount of extracted organotin species is also higher. But unlike fibres, the coated stir bars can not be directly desorbed into a splitless injector (available in most GC systems); instead, a special thermal desorption unit is necessary.

Most recent research on the quantification of tin compounds has focussed on the development of methods for fast, simple analysis of solid environmental matrices. Procedures have been developed in which the extraction and derivatization of organotin compounds is performed in only 2–3 min under the action of a microwave field [28,29]. The derivatized compounds are separated isothermally in less than 1 min using a GC–MIP-AES or a GC–ICP-MS system equipped with a multicapillary GC column operating at constant temperature and high carrier gas flows rates [30–32]. The complete analytical process thus takes less than 5 min. Strangely, little effort has been put into the development of similarly rapid analysis of water samples.

In this paper, a method for the fast quantification of butyltin species in water samples is described. The whole procedure (concentration plus quantification) takes less than 4 min, and allows the determination of butyltin compounds at the low ppt level. The analytes are first concentrated on a PDMS-coated fibre and then selectively determined by GC–MIP-AES using a multicapillary column. Chromatographic parameters and sampling conditions were optimised to achieve maximum sensitivity with minimum analysis time. Special attention has been paid to blank signals due to their influence on the detection limits of the proposed procedure.

2. Experimental

2.1. Apparatus

Chromatographic separations of ethylated butyltin compounds were performed with an Agilent (Wilmington, DE, USA) Model 6890 Series Plus gas chromatograph equipped with a split/splitless injection port and electronic pressure control. Detection was achieved with an Agilent G2350A atomic emission detector. Data were acquired using the Agilent Chemstation software (revision A.05). Ethylated compounds were separated on a multicapillary column consisting of approximately 920 capillaries 1 m×40 μm I.D. (0.2 μm SE-54 film thickness) purchased from Alltech (Deerfield, IL, USA). The multicapillary column, with an external diameter of 2–3 mm, was connected to the MIP-AES detector using a piece of deactivated silica tubing 30 cm×0.32 mm I.D. Helium (99.9999%) was used both as carrier gas in the column (at a constant flow of 140 ml/min, it was achieved with a gradual increase of the column head pressure from 53 to 70 p.s.i.; 1 p.s.i.=6894.76 Pa) and as make-up gas in the microwave induced plasma (270 ml/min). O_2 (99.99%) and H_2 (99.999%) were added as auxiliary plasma gases at pressures of 25 and 20 p.s.i., respectively. Microextraction fibers were desorbed at 270 °C in the splitless mode for 18 s. The GC oven

temperature was adjusted initially at 80 °C (18 s) and then increased at 100 °C/min up to 220 °C (1 min). Transfer line and cavity block temperatures were kept at 280 °C and the chromatograms monitored using the tin emission line at 303.42 nm.

A manual SPME fibre holder and 100 μm film thickness poly(dimethylsiloxane) fibres (Supelco, Bellefonte, PA, USA) were used for the concentration step. Fibres were thermally desorbed in the split–splitless injector of the gas chromatograph.

2.2. Material and reagents

Glassware used for standard preparation and for HS-SPME was cleaned using conventional detergent, rinsed with tap water and Milli-Q water, left in a 5% nitric acid bath for at least 24 h, and finally rinsed thoroughly with Milli-Q water before use. HS-SPME was performed in 20- and 100-ml glass vials sealed with PTFE-coated silicone rubber septa.

HPLC-grade methanol was obtained from Merck (Darmstadt, Germany), and glacial acetic acid and sodium acetate from Aldrich (Milwaukee, WI, USA). Buffer solutions of pH 5 were prepared by dissolving sodium acetate (1 mol/l) in Milli-Q water and adjusting to pH 5 with glacial acetic acid.

Sodium tetraethylborate ($NaBEt_4$) was purchased from Strem Chemicals (Bisscheim, France) and stored in a dry atmosphere to prevent its decomposition. Fresh 1% solutions (w/v) were prepared in Milli-Q water every 6 h.

2.3. Standards and samples

Standards of butyltin trichloride 95% (MBT), dibutyltin dichloride 96% (DBT), tributyltin chloride 96% (TBT), and tripropyltin chloride 98% (TPT) were obtained from Aldrich, stored in the freezer at −20 °C and used without further purification. Standards with concentrations in the range 2–3 mg/l were prepared by weight in methanol and stored at −20 °C for a maximum of 3 months. Dilute standards, and mixtures of butyltin species, were also prepared in methanol and stored at 4 °C for a maximum of 1 week. A TPT solution in methanol (18–20 ng/ml, as tin) was added to all samples and used as internal standard to correct for the variability of the derivatization reaction.

Water samples (Milli-Q, tap water or seawater) were placed in 20 or 100 ml vials, spiked with the internal standard solution, and with different volumes (from 0 to 400 μl) of a standard containing MBT, DBT and TBT (around 20 ng/ml as tin for each compound) in methanol. The pH was adjusted to 5 with the sodium acetate acetic acid buffer solution (1 ml of 1 *M* buffer per 10 ml of sample), and the vial was immediately closed and shaken manually for 2 min. 1 ml of the $NaBEt_4$ solution was added through the PTFE-coated silicone rubber septum using a 1 ml glass syringe, and the SPME fibre was exposed to the headspace vapour for 2 min at room temperature (18–20 °C). The extracted analytes were then thermally desorbed from the fibre in the GC injector.

3. Results and discussion

3.1. Optimisation of the chromatographic conditions

Multicapillary columns have previously been used (in combination with MIP-AES detection) for fast isothermal separation of several groups of organometallic compounds in a few seconds (maximum 1 min). A fast automatic injection device and an injection port operating in the split mode have usually been used to ensure narrow injection bands [30–32]. Since, thermal desorption from a SPME fibre is a relatively slow injection technique, analytes need to be refocused in the head of the chromatographic column to achieve acceptable peak widths. An oven temperature programme must therefore be used: during desorption from the SPME fibre the column must be maintained at a relatively low temperature, and when the injection period terminates, it must be heated as fast as possible to achieve rapid chromatographic separations of the butyltin species.

For the optimisation of the chromatographic conditions an oven heating rate of 100 °C/min (the highest rate possible in the gas chromatograph) and a constant head column pressure of 53 p.s.i. (365 kPa) were initially fixed. The first parameter considered in the optimisation was the desorption time. A SPME fibre was exposed in the HS of a 20-ml vessel

containing 10 ml of Milli-Q water spiked with the butyltin species at concentrations of 200 ng/l. The analytes were then desorbed at 270 °C for consecutive periods of 6 s (with the injector in splitless mode) until, at the third iteration, no MBT, DBT or TBT peak was observed in the corresponding chromatogram. The optimal desorption time at 270 °C, was therefore taken to be 18 s.

The second factor optimised was the temperature of the oven during desorption of the fibre. Values between 40 and 160 °C were used, and after finishing desorption (18 s, with the injector in splitless mode) the column was heated to 220 °C at 100 °C/min. Increasing the initial temperature reduced retention times (Fig. 1A), but above 80 °C broadened the peaks (Fig. 1B). An initial oven temperature of 80 °C was therefore selected. Using this temperature programme (80 °C for 18 s, 100 °C/min to 220 °C), chromatographic separation of ethylated butyltin species is achieved in less than 2 min.

The sensitivity of the MIP-AES detector to organotin compounds depends heavily on the total make-up flow, which is the sum of column and auxiliary plasma flows. The optimal value is 260–270 ml/min [31]. With conventional 0.25 or 0.32 mm I.D. capillary columns the contribution of the carrier gas to the total make-up flow is negligible (0.8–2.0 ml/min). However with the multicapillary one, working at the constant head pressure of 53 p.s.i. (365 kPa) the column flow reduces from 140 to 85 ml/min, when the oven pass from 80 to 220 °C. This variation caused a significant reduction in the total make-up flow and thus a loss in sensitivity. To avoid this problem, we decide to work in the constant column flow mode (140 ml/min). The gas chromatograph gradually increased the pressure from 53 to 70 p.s.i., when the oven pass from 80 to 220 °C, to ensure this constant flow. Under this regimen, retention times (see Fig. 2) are even slightly shorter than those obtained with a constant head pressure of 53 p.s.i. (Fig. 1A).

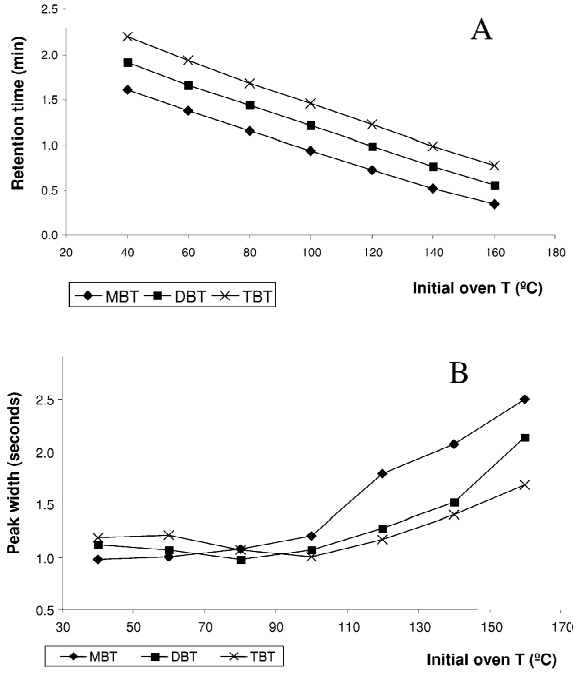

Fig. 1. Influence of the initial oven temperature on the retention times (A) and the peak widths (B) of MBT, DBT and TBT.

3.2. Optimisation of the SPME parameters

3.2.1. Extraction time

Fig. 3 shows the effect of fibre exposure time on the yield of the microextraction at room temperature. Since only butyltin species were considered in this study the fiber was placed in the headspace over the sample. For these semivolatile species it has been proved that the kinetic of the headspace extraction is

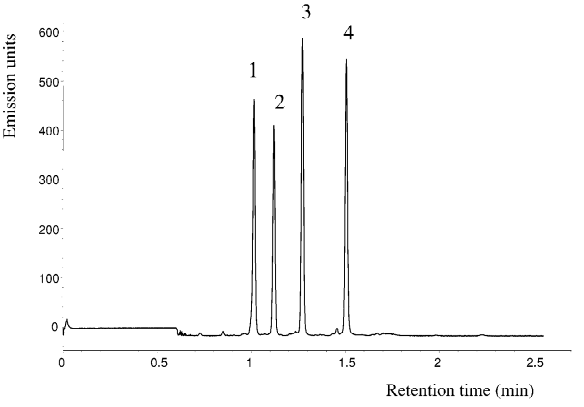

Fig. 2. Chromatogram obtained under optimal detection conditions for a sample of 10 ml of Milli-Q water spiked with 200 ng/l of each compound. 1=MBT, 2=TPT (I.S., ≈200 ng/l), 3=DBT, 4=TBT.

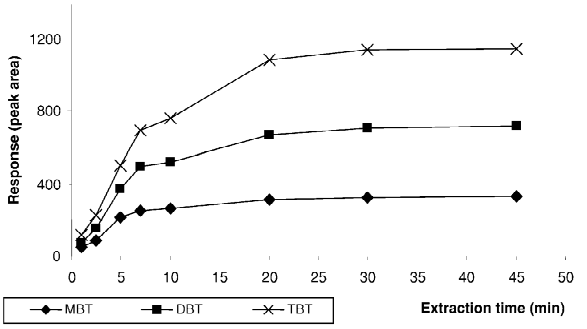

Fig. 3. Influence of the headspace sampling time, at room temperature, on the response to MBT, DBT and TBT (20 ng/l as tin) spiked over 80 ml of Milli-Q water.

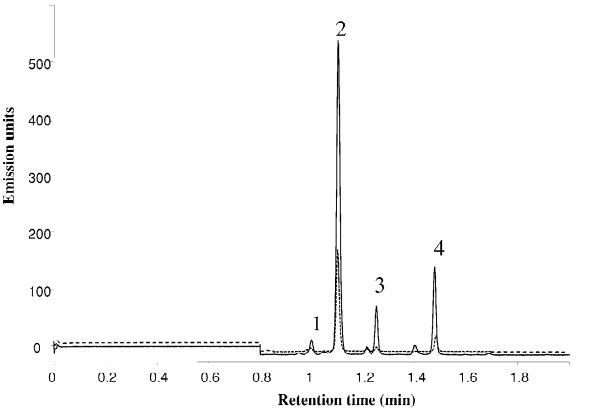

Fig. 4. Blank chromatograms for 80 ml of Milli-Q water samples. TPT was added as internal standard at the level of 20 ng/l. 1=MBT, 2=TPT (I.S.), 3=DBT, 4=TBT. (- - -) Extraction time 2 min; (—) extraction time 10 min.

faster than when the fiber is dipped directly in the water sample [19]; however, it should be noted that if the determination of the less volatile phenyl tin compounds is also considered the fiber should be placed directly in the water sample. Experiments were carried out at room temperature using 80-ml samples of Milli-Q water spiked with the butyltin compounds at concentrations of 20 ng/l. The kinetic curves show that for MBT and DBT equilibrium between sample and fibre is essentially achieved within 7 min, but for TBT a longer exposure is necessary. In principle, the maximum sensitivity in the determinations will be obtained when the equilibrium between the concentration of each compound in the sample and the extraction fibre is reached. However, we found that the sensitivity of this method was not controlled by the total amount of each analyte concentrated on the microextraction fibre, but by the signal for each compound (MBT, DBT and TBT) in the blank. Fig. 4 shows chromatograms of unspiked Milli-Q water samples obtained after extraction times of 2 and 10 min. The presence of MBT, DBT and TBT in the blanks was detected with samples of ultra-pure water from different laboratories, even without adjusting the pH of the sample with the buffer solution. The fact that the signals of both spiked and unspiked samples increased with fibre exposure time means that overall sensitivity was only marginally affected by this variable, thus an exposure time of 2 min was chosen as standard in order to minimise the total duration of the analytical procedure. The origin of the contamination is probably the derivatization reagent. Several authors have reported a similar problem in the analysis of butyltin species in water samples, and they also pointed to $NaBEt_4$ as one of the source of blank signals [19,33,34]. Moreover, in our laboratory, organotin compounds has been analysed in sediments and biological materials at the μg/g level for the last 3 years, therefore additional contribution of environmental contamination to blank signals can not be rejected. Whatever the source of this contamination was, it remained quite stable from blank to blank (results not shown); therefore, it increased the quantification limits of the analytical procedure but it did not prevent us to analyse butyl tin compounds in real samples, which contain these compounds over a given concentration level.

3.2.2. Sample volume

Fig. 5 shows the influence of the sample volume on responses (peak area) for MBT, DBT and TBT in Milli-Q water samples with addition of these compounds at the level of 20 ng/l and without addition. In all cases 1 ml of $NaBEt_4$ solution was added to the samples and the fibre was placed in the headspace for 2 min. The chromatographic response to MBT, DBT and TBT in the spiked samples increased with their volume (so with the total amount of these compounds in the sample), however blank signals remained constant. The sensitivity of the analytical procedure therefore increased with sample volume, and in all further experiments a sample volume of 80 ml was accordingly used.

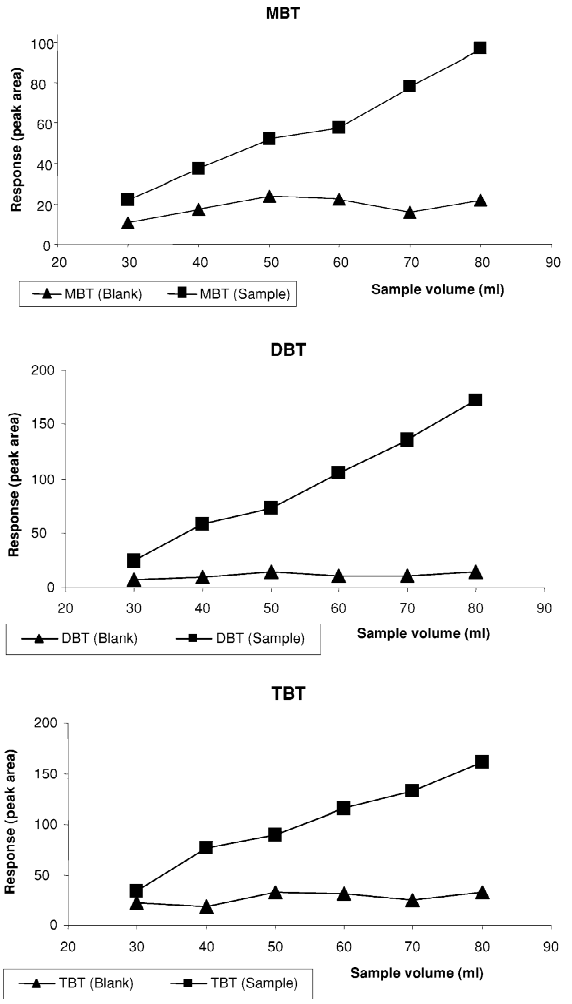

Fig. 5. Influence of sample volume on the response to MBT, DBT and TBT in Milli-Q water samples, with and without addition of the analytes at concentrations of 20 ng/l.

3.3. Analytical performance

The linearity of the response was studied using samples of Milli-Q water spiked with standards of MBT, DBT and TBT in methanol at seven concentration levels between 5 and 100 ng/l. Each solution was prepared in duplicate, and all were spiked with TPT at 20 ng/l. Correlation coefficients higher than 0.995 were obtained for the determination of MBT, DBT and TBT, after correction with the internal standard signal.

Detection limits were estimated as three times the mean peak area for MBT, DBT and TBT in five consecutive blank chromatograms. Values of 5, 1.5 and 1 ng/l (as tin) were obtained for MBT, DBT and TBT, respectively. These detection limits are similar or better than those obtained using different pre-concentration techniques followed by GC–MIP-AES analysis (Table 1). Furthermore, all of these methods require longer and tedious pre-concentration steps decreasing the number of samples processed by unit of time. Total processing time (extraction plus quantification) is an important parameter in environmental control laboratories, where a huge number of samples have to be processed every day. On the other hand, the detection limits of the present method are similar to those of previously reported procedures based on the combination of SPME with gas chromatography using different detection techniques, despite they employ sampling times at least 5 times longer. Only the procedure described by Aguerre et al. give significant lower detection limits after a sampling period of 1 h [24] (Table 2). Furthermore, methods in Tables 1 and 2 employ around 7–10 min for the chromatographic separation of butyltin species, whereas the multicapillary column takes only 90 s.

The reproducibility and the repeatability of the procedure were evaluated with samples of Milli-Q water spiked with the studied compounds at 20 ng/l. The repeatability of determinations performed using TPT as internal standard varied between 1.6 and 3.2%, and the reproducibility between 6 and 11% (Table 3). These figures shows that contribution of blank signals to MBT, DBT and TBT peak areas was very reproducible.

3.3.1. Matrix effect

In SPME methods the amount of each analyte concentrated on the fibre can be affected by the composition of the sample. Table 4 compares the response to TPT in Milli-Q water (with and without addition of sodium chloride), tap water and seawater spiked with 20 ng/l of this compound. TPT was chosen for this comparison because it has never been found in real samples and was not detected in blanks. These results show that the yield of the extraction in Milli-Q, tap and sea water is similar and it is also unaffected by the ionic strength of the solution, which is in agreement with the results of Moens et al. [19].

Table 1
Comparison of different GC–MIP-AES-based procedures for the quantification of organotin compounds in water samples

Compounds	Sample volume (ml)	Extraction technique	Derivatization reagent	Detection limits (ng/l)	Ref.
Butyl and phenyltin	50	LLE (hexane)	$NaBEt_4$	0.1[b]	[12]
Butyl and phenyltin	50	SPE, C_{18} [a]	$NaBEt_4$	0.1[b]	[33]
Butyl, methyl and diphenyltin	100–250	LLE (hexane:tropolone)	EtMgBr	10–15	[11]
Butyl and methyltin	1500	LLE (pentane:NaDDTC)	PeMgBr	NA	[36]
Butyl and phenyltin	100	LLE (hexane)	$NaBEt_4$	17–33	[35]
Butyl and phenyltin	100	LLE (hexane)	$NaBPr_4$	3–12	[13]
Butyltin	4	Direct SPME (PDMS fibres)	$NaBEt_4$	≈20	[20]
Butyltin	80	Headspace SPME (PDMS fibres)	$NaBEt_4$	1–5	This work

NA, not available.
[a] Derivatization of polar compounds on the stationary phase of the sorbent cartridge.
[b] Calculated for an injection volume of 25 μl.

Table 2
Comparison of the analytical performance of published SPME-based procedures for the analysis of butyltin compounds in water samples

Sample volume (ml)	Extraction time (min)	Extraction temp. (°C)	Sampling	Detection limits (ng/l as tin)	Detection technique	Ref.
20	15	40 °C	Headspace	≈1000	GC–flame ionization detection	[18]
25	10	RT	Headspace	0.3–2	GC–ICP-MS	[19,21]
4	45	RT	Direct sampling	≈20	GC–MIP-AES	[20]
100	20	RT	Direct sampling	2–4	GC–FPD	[23]
100	60	RT	Direct sampling	0.006–0.03	GC–FPD	[24]
80	2	RT	Headspace	1–5	GC–MIP-AES	This work

RT, room temperature.

Table 3
Repeatability and reproducibility in the determinations of MBT, DBT and TBT in water samples using TPT as internal standard

Compound	RSD (%)	
	Repeatability (n=3)	Reproduciblity (n=9, three samples on each of 3 days)
MBT	2.2	6.3
DBT	1.6	8.6
TBT	3.2	10.5

Sample volume 80 ml (Milli-Q water), added concentration 20 ng/l, extraction time 2 min.

3.4. Application to a real sample

There is at present no available certified reference material for organotin compounds in water samples. Validation of new analytical methods can therefore only be carried out by comparison with previously described procedures. Table 5 lists the levels of MBT, DBT and TBT in a sample of seawater collected in a bay with intense shipyard activity in Northwest Spain. The sample was taken in a glass

Table 4
Comparison of the response to TPT (20 ng/l as tin) spiked over Milli-Q (with and without addition of sodium chloride), tap and seawater samples (three replicates were analysed for each sample)

Sample	Mean signal (peak area)	RSD (%)
Milli-Q water	245.3	7.8
Milli-Q water (50 g/l of NaCl)	250.8	9.2
Milli-Q water (125 g/l of NaCl)	253.1	6.3
Tap water	241.0	1.7
Seawater	230.6	11.7

Table 5
Results of the determination of butyltin species in a seawater sample

Compound	Concentration (ng/l)	
	This work	LLE (Ref. [12,35])
MBT	203±16	179±3
DBT	603±68	535±13
TBT	439±49	410±32

vessels and was analysed ($n=3$) without filtration, by both the proposed procedure and a published method involving a liquid–liquid extraction protocol [12,35]. A good concordance was observed between results obtained with both methods.

4. Conclusions

The optimised procedure combines a microextraction step with the use of a multicapillary gas chromatography column and MIP-AES detection for the determination of butyltin compounds in less than 4 min. Because of its simplicity, rapidity and remarkable analytical characteristics (linearity, reproducibility and detection limits) the described method is a useful approach for the daily monitoring of MBT, DBT and TBT in environmental water samples. Since the detection limits appear to be determined by the purity of the $NaBEt_4$, they improvement will require the use of a cleaner borate.

Acknowledgements

This work has been supported financially by the Spanish DGICT (project REN 2000-0984HIP) and the Xunta de Galicia (PGIDT 01 PXI23701PN). JCB is indebted to the Xunta de Galicia for a doctoral grant.

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