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Journal of Chromatography A, 873 (2000) 63–71

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of butyltin species in water and sediment by solid-phase microextraction–gas chromatography–flame ionization detection

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Abstract

A procedure for determination of tetraethyltin (TeET) and tetrabutyltin (TeBT) in water by solid-phase microextraction (SPME) using the headspace approach has been developed. The method has been adapted for the simultaneous determination of mono-, di- and tributyltin species (MBT, DBT and TBT) after derivatization with sodium tetraethylborate in water and sediment samples. The analytical procedures were optimized with respect to stirring conditions, extraction time and extraction temperature. The pH and the amount of derivatizing reagent were also considered in derivatization reaction procedures. The analysis was carried out using gas chromatography equipped with flame ionization detection. The detection limits obtained for TeET and TeBT, in equilibrium conditions (room temperature for TeET and 40°C for TeBT) were 28 and 20 ng/l (as Sn), respectively. The detection limit for butyltin species in water, which was limited by signals which are non-specific for the tin compounds and the sensitivity of the FID system, was found ca. 1 μg/l (as Sn). The SPME method was validated for analysis of sediments by analyzing the certified reference material PACS-2 finding a good agreement with the certified values.

Keywords: Water analysis; Sediments; Organotin compounds; Butyltin

1. Introduction

The environmental and toxicological effects of an element greatly depend on the forms or species of the element in the original sample. Organotin compounds, in particular tributyltin (TBT), are widely used in poly(vinyl chloride) (PVC) stabilization, antifouling paints and biocides. The introduction of such compounds into the environment can cause serious problems, mainly due to the high toxicity and tendency to bioaccumulation [1]. The negative impact of butyltins on aquatic environment is well known and has led to regulation in the use of TBT-antifouling paints in several countries [2]. Nowadays, special attention is given to polluted sediment since release from sediments (which act as a long-term sink) is likely responsible for butyl concentration in waters [3].

Analytical methods for determination of organotin compounds should provide sufficient sensitivity. Most of them combine a separation technique such as gas chromatography (GC), liquid chromatography (LC) or supercritical fluid chromatography (SFC) with element-selective detection like atomic absorption spectrometry (AAS), atomic emission spec-

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0021-9673/00/$ – see front matter
PII: S0021-9673(99)01124-3

trometry (AES), mass spectrometry (MS), flame photometric detection (FPD) or inductively coupled mass spectrometry (ICP-MS) [4–6].

Many sample preparations involve acid leaching in aqueous or methanolic media by, Soxhlet extraction, stirring, shaking or sonication with an organic solvent. Complexing agents (tropolene, dietyldithiocarbamate) are often added to increase extraction yields. After extraction organotins need to be derivatized into gas chromatographable species. The methods used include hydride generation with sodium borohydrate and alkylation by Grignard reagents or sodium tetraethylborate [7–9]. Recently, supercritical fluids have been used to extract organotins, offering the advantages of reduction in preparatory steps and avoiding handling of hazardous organic solvents [10]. However, the static extraction mode, the high-pressure pump and the variable temperature for extraction are not yet standard features in this type of instruments [11].

An interesting option for the extraction of tin derivatizate species could be solid-phase microextraction (SPME). In this technique, that does not require solvents use, sampling can be carried out directly from liquid samples, from their headspace or from headspace over solid samples [12]. The headspace is more advisable when matrix could affect the determination of the target analyte. Recent works for determining organotin compounds have been used SPME directly from liquid samples [13–15]. The use of SPME sampling from headspace have been reported for determining methyltin compounds in water using GC–FPD [16], tetraethyllead and inorganic lead in water by GC–flame ionization detection (FID) and GC–MS [17] and butyltin species using GC–ICP-MS [18,19]. The last two preliminary investigations applied room temperature and extraction time of 10 min for headspace SPME extraction in the headspace mode without much effort to optimize the conditions [12].

This work is mainly focused on the suitability of SPME, sampling from headspace, for determination of semivolatile organotin compounds studying the extraction process and optimizing it. The adaptation of the procedure for determining simultaneously butyl species, after derivatization, in water and sediment samples is also presented.

2. Experimental

2.1. Reagents

Tetraethyltin (TeET, 98% purity), tetrabutyltin (TeBT, 94% purity), butyltin trichloride (MBT, 95% purity), dibutyltin dichloride (DBT, 95% purity), tributyltin chloride (TBT, 98% purity) and sodium tetraethylborate (STEB, 98% purity) were purchased from Alfa Aesar (Ward Hill, MA, USA). Water was obtained by a NANOpure ultrapure water system (Barnstead/Thermolyne, Dubuque, IA, USA). 1000 mg/l individual standard solutions of TeET and TeBT were prepared by adding with a microsyringe 10 mg of these compounds to a preweighed 15-ml screw cap vial containing 10 ml of methanol. The other standards (1, 10 and 100 mg/l) were prepared by dilution in methanol from the most concentrated standards. Individual stock solutions of MBT, DBT and TBT (10 000 mg/l as Sn) were prepared in methanol. A mixed butyltin working solution containing 250 mg/l (as Sn) of each compound was also prepared using methanol as solvent. Dilutions in methanol of the latter solution were used as required.

STEB was kept in a desiccator. The manipulation of STEB was performed in a glovebag under dry nitrogen. The 2% (w/v) aqueous solutions using in derivatization experiments were prepared every 4 h by placing a certain amount of reagent into a preweighed 10-ml PTFE vial (tightly sealed) and adding the necessary volume of NANOpure water. Between runs, the solution was stored at 4°C.

Acetate buffers (pH 4.0, 0.1 *M*; pH 4.3, 1.5 *M*) were prepared by dissolving the appropriate amount of sodium acetate trihydrate in water, followed by pH adjustment with concentrated acetic acid.

The certified reference material (PACS-2, marine sediment) was obtained from the National Research Council of Canada (NRCC, Ottawa, Canada).

Since these organotin compounds are highly toxic they must be handled in a fume hood, wearing the appropriate clothing, rubber gloves and safety goggles. They should be kept in tightly closed containers and stored in a cool, dry, well-ventilated area. Sodium tetraethylborate may be pyrophoric in air at room temperature; therefore it has to be handled in glove box or glove bag with a dry inert atmosphere

wearing the adequate protective clothing. It should be stored in a tightly sealed container under inert atmosphere in a desiccator.

2.2. Equipment

The SPME holder and the fibers coated with 100 μm thickness poly(dimethylsiloxane) (PDMS) were obtained from Supelco (Bellefonte, PA, USA). A GC-3500 gas chromatograph equipped with septum programmable injector (SPI) and FID system (Varian Associates, Sunnyvale, CA, USA) was used in all measurements. The analyses were carried out using a 30 m×0.25 mm, 1.0 μm SPB-1 column (Supelco) and hydrogen as the carrier gas. The temperature programs used were: 40°C for 1 min, 20°C/min to 140°C, hold 2 min (for tetraethyltin) and 40°C for 1 min, 20°C/min to 220°C, hold 3 min (for the remaining organotin compounds). The injector and detector temperatures were 250°C. A personal computer interfaced to the GC system using Star 4.5 software (Varian) was used for data acquisition and processing. A VWR magnetic stirrer (VWR Scientific of Canada, Canada) and PTFE-coated stir bars were used for stirring runs. An ultrasonic cleaner bath (Branson 5210-DTH) and a centrifuge (Clay Adams Brand, Compact II) were used in the experiments with the sediment reference material.

2.3. Analytical procedures

2.3.1. Analysis of tetraethyl and tetrabutyltin in water samples

Working aqueous tetraethyl and tetrabutyltin solutions were prepared by adding the appropriate volume of one of the methanolic solutions with a microsyringe (2–20 μl) to 20 ml of NANOpure water in 40-ml amber vials sealed with PTFE-lined silicon septa (Supelco). For all the runs a stirring rate of 1200 rpm was applied. When the constant agitation was obtained, the SPME fiber was immediately exposed to the headspace over the vigorously stirred samples for predetermined times at room temperature (23°C) and at 40°C (using a constant-temperature water bath). The time was considered from the moment when the fiber was exposed. After sampling the fiber was withdrawn into the needle of the holder and SPME was placed in the GC injector. The desorption temperature was 250°C and 1 min was the desorption time for all the runs. No carryover was observed after this desorption time.

2.3.2. Analysis of butyltin species in water

An appropriate amount (2 or 5 μl) of the MBT–DBT–TBT mixed standard solutions was added into a glass amber vial containing 18.5 (or 18) ml of NANOpure water and 1 ml of acetate buffer (pH 4.0; 0.1 *M*). After adding 0.5 (or 1) ml of the 2% STEB solution, the vial was immediately closed and placed on the magnetic stirrer. A working temperature of 40°C, using a water bath and a stirring rate of 1200 rpm were maintained in these runs. Sampling was carried out with SPME in the headspace for 15 min. The desorption conditions in GC were the same as for tetraethyl and tetrabutyltin.

2.3.3. Analysis of butyltin species in sediment

A 0.500-g amount of sediment was accurately weighed and placed in a 12-ml centrifugation polyethylene (PE) vial. In order to leach the organotins from the sediment, 3 ml of a mixture of 20% hydrochloric acid–methanol (1:1) was carefully added. The mixture was sonicated during 1 h (47 kHz of frequency) and centrifuged at 3200 rpm for 5 min. A 2-ml volume of the centrifuged solution was mixed with 17 ml of a sodium acetate buffer solution (pH 4.3; 1.5 *M*) in a 40-ml amber glass vial sealed with septum and placed in a water bath at 40°C for 15 min. A 1-ml volume of STEB (2%) was later added to the vial and maintained 2 min at 1200 rpm. Maintaining the same extractions conditions (1200 rpm, 40°C) the fiber was exposed to the headspace for 15 min. After sampling, the fiber was removed and inserted into the injector port. The desorption temperature and time were identical to previous ones. The standard addition technique was used to quantify the amounts of butyltin species. In the standard addition runs appropriate spikes (5, 10 or 20 μl) of the mixed butyltin solution (150 mg/l as Sn total) were incorporated to the sediment before the addition of hydrochloric acid–methanol mixture.

3. Results and discussion

3.1. Analysis of tetraethyl and tetrabutyltin in water samples

The suitability of SPME for determination of TeET and TeBT in water was first checked. These compounds were chosen taking into account the characteristics of the products obtained from the derivatization reactions with STEB (butyltriethyltin from butyltin trichloride, dibutyldiethyltin from dibutyltin dichloride and tributylethyltin from tributyltin chloride).

Both TeET and TeBT are semivolatile, nonpolar compounds with boiling points of 181°C (760 mm) for TeET and between 127 and 145°C (10 mm) for TeBT. TeET is sparingly soluble in water and TBT shows a poor solubility with an octanol–water partition coefficient (log K_{ow}) of 3.90 [20].

For the experiments involving addition of the acetate buffer solution and the derivatizing agent STEB to the aqueous solution, headspace sampling was chosen. The 100 μm PDMS fiber was selected considering its versatility and adequacy to determine methyltin compounds [16] and tetraethyllead [17] in water samples.

The extraction profiles of TeET and TeBT were first obtained. The experiments were performed with a 50 μg/l standard solution of individual compounds at room temperature (23°C). The intensity of stirring is one important parameter that affects the time profile. For headspace, stirring should be vigorous and has to be maintained constant in all experiments. The actual stirring rate required depends on the dimensions of the vial (40 ml) and the magnetic stir bar (25 mm). After several trials with 800, 1000 and 1200 rpm, the latter stirring rate was considered the most adequate. If the temperature of the sample changes a few degrees when the vial stays in contact with the stirring plate a remarkable difference in the analyte extracted may be observed. In order to avoid the potential problem of the stirring plate heating at high revolutions, especially when the stirring is fixed for long periods, a PTFE silicon septum was placed between the stirring plate and the amber vial in the experiments at room temperature.

Fig. 1 presents the amount of analyte extracted (in ng) vs. the extraction time (up to 30 min for TeET and 60 min for TeBT). Each point of the figure represents the average of three determinations. The relative standard deviation (RSD) for TeET data points was less than 6% and for TeBT was less than 10%, showing a better repeatability for the most volatile compound. It follows from the Fig. 1 that for TeET equilibrium was reached in the system after 5 min. In order to assure that the equilibrium was reached, 10 min was used in the further experiment with this compound. This extraction time was also chosen by Górecki and Pawliszyn working with 100 μg/l tetraethyllead solution [17]. The extraction time of 10 min is shorter than that of the one found by Poerschmann et al. (less than 60 min) using the fiber directly inserted in water samples [14]. Moens et al. [18] and De Smale et al. [19], extracting at room temperature, chose a sampling time of 10 min for the determination of butyl compounds. This time is adequate when working with ethyl compounds but is not sufficiently long for butyl species, which have higher affinity towards PDMS coating and hence reach the equilibrium at much longer extraction times. The behavior of butyl compounds can be understood when considering TeBT.

The extraction time profile for TeBT shows a different behavior than TeET, the curvature is shifted to the higher equilibration time. The equilibrium point (not depicted in Fig. 1) was reached after 3 h of extraction and the amount uptake by 100 μm PDMS fiber was ca. 640 ng. If the extraction time was kept at 10 min, the fiber could extract less than 20% of the amount of the equilibrium value. The long time to reach the equilibrium reduces the advantages of the headspace vs. the direct sampling. However in headspace, the equilibration time for less volatile compounds, as TeBT, can be significantly shortened by agitation, reduction of space volume and increase of the sampling temperature [21]. Although the increase of temperature can cause loss of sensitivity [22], the latter was the option chosen. New runs with a 50 μg/l of TeBT solution working at 40°C (placing the vial in a water bath to maintain the temperature) with a stirring rate of 1200 rpm were carried out. The results are also shown in Fig. 1. Each data point is the average of three determinations and the RSD was less than 8%. Under these conditions the equilibrium was reached in 30 min and the amount of analyte uptake by the fiber was ca.

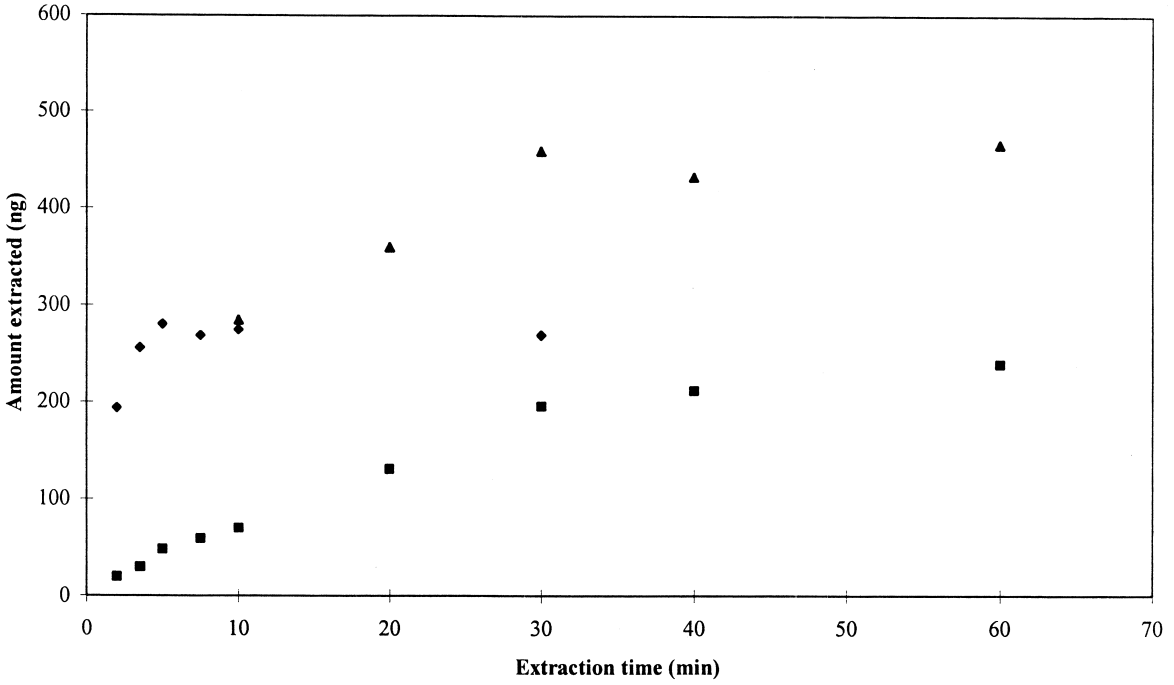

Fig. 1. Extraction time profiles for 50 μg/l of tetraethyltin (TeET) and 50 μg/l of tetrabutyltin (TeBT) aqueous solutions sampled from headspace with a 100 μm PDMS fiber. Extraction temperature: (♦) TeET – 23°C; (■) TeBT – 23°C; (▲) TeBT – 40°C.

460 ng. With these conditions a remarkable reduction in the equilibrium time was obtained.

The distribution constants between the fiber and the sample under the equilibrium conditions at the two temperatures were calculated ($K_{fs}=C_f^{\infty}/C_s^{\infty}$). Three additional runs for TeET at 40°C were performed (average value, 166 ng; RSD, 4.4%). The values obtained for the two organotin compounds at room temperature and at 40°C are shown in Table 1. The K_{fs} value of TeBT is more than four-times higher than that of the K_{fs} of TeET, at the two temperatures. This indicates the higher affinity of the fiber for TeBT compound. For the two compounds, the ratio between the values of constants at 23°C and 40°C is almost the same (ca. 2). The K_{fs} values found in the present work differ from the ones given by Poerschmann et al. [14]. In the latter work the aqueous samples (containing tetraethyl and tetrabutyltin) filled the 40-ml amber vials completely and the distribution constants were calculated with the data obtained after 16 h sampling time. During prolonged sampling, analyte losses via adsorption onto sampling walls, absorption by silicone rubber septum, microbial decomposition, etc., can affect the amount of analyte extracted by SPME [21].

Table 1
Distribution constants for TeET and TeBT, K_{fs}, between a 100 μm PDMS fiber and water using headspace[a]

Analyte	Temperature	
	23°C	40°C
Tetraethyltin (TeET)	12 000 (10 min)	6100 (10 min)
Tetrabutyltin (TeBT)	55 000 (180 min)	26 000 (30 min)

[a] Extraction conditions: 50 μg/l of organotin compounds in aqueous solutions (20 ml in a 40-ml sampling vial); stirring rate 1200 rpm.

In order to check how the changes in temperature and time affected the analytical parameters (calibration range, precision and limit of detection) further runs were carried with these two organotin compounds. For TeET, the experiments were performed at room temperature for 10 min. For TeBT, three different sets of experiments were carried out: room temperature (23°C) – 10 min, room tempera-

Table 2
Calibration results for TeET and TeBT in water sampled from headspace with a 100 μm PDMS fiber

Compound	Extraction conditions	Linear range (μg/l)[a]	RSD (%)[b]	LOD (ng/l as Sn)[c]
TeET	23°C, 10 min	0.1–100	5.8	28
TeBT	23°C, 10 min	0.5–100	9.0	159
TeBT	23°C, 30 min	0.1–100	7.7	24
TeBT	40°C, 30 min	0.1–50	6.0	20

[a] Correlation coefficient higher than 0.99.
[b] Relative standard deviation for 25 μg/l of TeET and TeBT ($n=7$).
[c] Calculated considering y_b+3S_b in the calibration curve.

ture (23°C) – 30 min, and 40°C – 30 min. The calibration results for TeET and TeBT appear in Table 2.

The calibration curve for TeET in water was linear in the range checked, from 0.1 to 100 μg/l, with a correlation coefficient of 0.9982. The precision was estimated with a 25 μg/l solutions and $n=7$ samples under the mentioned temperature and time conditions. The RSD obtained was 5.8%. The limit of detection was calculated considering y_b+3S_b in the calibration curve [23]. The limit of detection (LOD) found was 28 ng/l as Sn.

The calibration curves for TeBT showed a wider linear range at room temperature. However, the precision and the LOD were better working at 40°C. At this temperature and 30 min extraction time, the calibration was linear from 0.1 to 50 μg/l with a correlation coefficient of 0.9993. The RSD, with 25 μg/l solution and $n=7$, was 6%; and the LOD obtained from the calibration curve was 20 ng/l as Sn. Although there is a loss of sensitivity working at higher temperature, at 40°C the experiments are carried out in equilibrium conditions, and this allowed better results in precision and limit of detection.

This first step showed the adequacy of SPME–GC for determination of organotin compounds TeET and TeBT. Having established the conditions for TeBT analysis, experiments with derivatization reactions were started.

3.2. Analysis of butyltin species in water

Since the volatility of butyltin compounds need to be increased, a derivatization step is necessary. Ethylation using STEB may be preferable to hydride generation [9]. One of the factors that affects the amount of the organotin compounds extracted from the samples is pH. Ceulemans et al. [24] found that for butyltin species the efficiency of the liquid–liquid extraction was better in the 4–5 pH range. Because STEB solutions are strongly alkaline, a relatively large amount of pH buffer must be added to the water samples in order to keep the adequate pH. After several runs, a pH value of 4.3 and sodium acetate–acetic acid buffer was used for this purpose. The ratio of the pH buffer was 1 ml to 20 ml of total aqueous solution.

The amount of STEB added can also play an important role in derivatization experiments. In order to assure enough reactant, 0.5 ml (or 1 ml) of 2% STEB freshly prepared was used. However, with this derivatization agent some problems related to the blank value contribution appeared [17,24]. The use of silanizing glass vials and the cleaning with concentrated nitric acid improved the value of the blank. Running blank samples on a regular basis is also advisable.

As we indicated the extraction equilibrium conditions found for tetrabutyltin were: 40°C, 1200 rpm and 30 min. However, this period of 30 min is long enough to reduce the great advantage of the rapidity in the analysis using headspace SPME. Therefore, we chose to work at 40°C and reduce the extraction time to 15 min. Although, the equilibrium conditions were not reached, mainly for DBT and TBT derivatives, the SPME technique allowed to obtain adequate analytical results as we had previously check with TeBT.

The calibration curves for MBT, DBT and TBT sampled from headspace after derivatization using 2% STEB are shown in Fig. 2. The analytical results (liner range, RSD and LOD) for these three butyltin species are shown in Table 3. DBT and TBT presented linear range from 0.5–10 μg/l, for MBT the linear large was check up to 50 μg/l ($r=0.9983$). The precision was estimated by analyzing $n=5$ samples containing 5 μg/l (as Sn) of each compound. The RSD obtained was less than 10%, which is good considering the relatively complex samples. The RSDs for MBT, DBT and TBT obtained by Lespes et al. [15] working with SPME directly

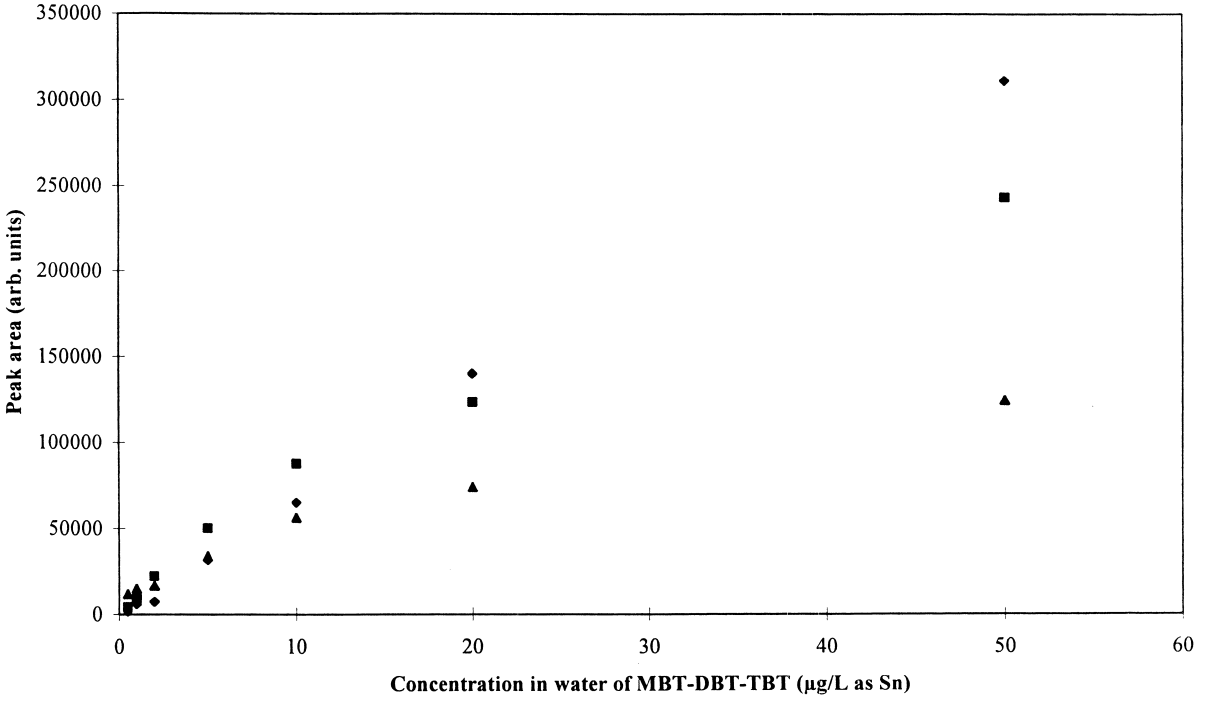

Fig. 2. Calibration curves for MBT, DBT and TBT sampled from headspace with a 100 μm PDMS fiber after derivatization using STEB: extraction conditions: 40°C, 15 min, 1200 rpm. Compounds: (♦) monobutyltin, (■) dibutyltin, (▲) tributyltin.

inserted in water samples were in the range 8 to 11%. The RSDs for butyltin compounds after derivatization using headspace ranged from 5 to 14% [18] and from 10 to 25% [19]. In the present work the LOD reached for the three compounds was ca. 1 μg/l. The LOD was calculated considering y_b+3S_b for each calibration curve [23] with range of 0.5–10 μg/l. These results allow the use of the method to highly contaminated water samples. Since the work has been carried out using GC–FID, the use of more specific detection methods for tin,such as FPD, MS, ICP-MS or AES could achieve greater sensitivity and lower detection limits.

According to the previous results, the same methodology should be applicable to the determination of butyltin species in other environmental samples which higher organotin contents, such as sediments.

Table 3
Calibration results for MBT, DBT and TBT in water sampled from headspace with a 100 μm PDMS fiber after derivatization with STEB

Compound	Extraction conditions	Linear range (μg/l)[a]	RSD (%)[b]	LOD (μg/l as Sn)[c]
MBT	40°C, 15 min	0.5–10	9.4	1.0
DBT	40°C, 15 min	0.5–10	9.6	1.2
TBT	40°C, 15 min	0.5–10	8.7	0.9

[a] Correlation coefficient higher than 0.99.
[b] Relative standard deviation for 5 μg/l of MBT, DBT and TBT (n=5).
[c] Calculated considering y_b+3S_b in the calibration curve.

3.3. Analysis of butyltin species in sediment

In order to check the usefulness of the method we chose the certified reference material PACS-2. The first efforts were focused to the effective separations of butyltins from the sediment using a suitable medium and the postseparation reaction of the analytes with STEB.

The initial step of the procedure involved the leaching of organotin compounds from the sediment. Results presented in several works, using certified material, have shown the difficulties in sample

preparation, mainly the accurate determination of MBT [25]. Ceulemans and Adams [26] concluded that the combination of a strong acid and a polar solvent was necessary for an effective extraction of MBT from the sediments. After several tries with different mixtures of methanol and 20% HCl acid the mixture (1:1, v/v) was the most efficient. The sonication time was also checked and the final time was fixed in 1 h. This sonication time is also used by other researchers [27].

In the derivatization–extraction step we found that the leaching solution was extremely acidic. Hence, the concentration of the sodium acetate buffer had to be modified (1.5 *M*) and a higher amount of this new buffer (17 ml) had to be added to maintain the pH. With these modifications the pH was maintained at a value of 4.3 during the derivatization process.

Since the trustworthiest assessment of the recovery is achieved using the standard additions method, 0.25, 0.50 and 1.0 μg of each compounds (as Sn) were added to the sediment sample. Table 4 shows the results for determination of MBT, DBT and TBT in reference material. The data, average of three independent sediment samples, are presented as μg Sn/g dry weight. Good agreement with the certified values for DBT and TBT were observed. The *t*-test showed no significant differences at 0.05 level [23]. The amount of these two compounds represent more than 90% of the certified amount. These results are comparable to others obtained with more complex techniques as SFE [11], LC–ICP-MS coupled with ultrasonic nebulization [28], or SPME extraction followed by GC–ICP-MS determination [18,19]. The precision for DBT and MBT, using SPME–GC (FID), was better than the ones given with certified values. In the PACS-2 reference material the value for MBT is only indicative. The value of MBT obtained with SPME–GC was higher than the indicative one. Other researchers using organic solvent extraction and STEB derivatization [25,26] and SPME with GC–ICP-MS [18,19] have also reported higher results for MBT than that of the indicative value.

Table 4
Results for the determination of butyl species in the certified reference sediment PACS-2 measured by SPME–GC (FID) using the standard addition method

Compound	μg/g (as Sn)	
	Certified	Determined
TBT	0.98±0.13	0.89±0.10
DBT	1.09±0.15	0.99±0.05
MBT	0.3[a]	0.80±0.13

[a] MBT value is only indicative.

4. Conclusions

This study supports the great potential of the SPME, using headspace, in the analysis of organotin pollutants. This technique can be used for direct determination of tetraethyl and tetrabutyltin and for the simultaneous determination, after derivatization, of butyl species in water and sediments. For the analysis of highly contaminated sediments the use of a simple experimental setup (GC–FID) allows results comparable to those obtained using more complex and expensive instrumentation. Since the work have been carried out using GC–FID, the use of more specific and sensitive detection methods such as FPD, MS, ICP-MS or AES could achieve greater sensitivity and lower detection limits.

Acknowledgements

The Spanish Ministry of Education and Culture has provided financial support to E.M. for her sabbatical leave at the University of Waterloo during 1997/1998 academic year. The work was supported by Natural Sciences and Engineering Research Council of Canada, National Research Council of Canada, Supelco and Varian.

References

[1] K. Fent, Crit. Rev. Toxicol. 26 (1996) 1.
[2] R.J. Hugget, M.A. Unger, P.F. Seligman, A.O. Valkirs, Environ. Sci. Technol. 26 (1992) 232.
[3] R. Ritsema, T. de Smaele, L. Moens, A.S. de Jong, O.F.X. Donard, Environ. Pollut. 99 (1998) 271.
[4] R. Lobinski, F.C. Adams, Spectrochim. Acta B 52 (1997) 1865.
[5] M. Abalos, J.M. Bayona, R. Compañó, M. Granados, C. Leal, M.D. Prat, J. Chromatogr. A 788 (1997) 1.

[6] L. Ebdon, S.J. Hill, C. Rivas, Trends Anal. Chem. 17 (1998) 277.
[7] Y. Cai, S. Rapsomanikis, M. O Andreae, Anal. Chim. Acta 274 (1993) 243.
[8] F.M. Martin, C.M. Tseng, C. Belin, P. Quevauviller, O.F.X. Donard, Anal. Chim. Acta 286 (1994) 343.
[9] S. Rapsomanikis, Analyst 119 (1994) 1429.
[10] J.M. Bayona, Y. Cai, Trends Anal. Chem. 13 (1994) 327.
[11] Y.K. Chau, F. Yang, M. Brown, Anal. Chim. Acta 304 (1995) 85.
[12] J. Pawliszyn, Solid Phase Microextraction, Theory and Practice, Wiley–VCH, New York, 1997.
[13] S. Tutschku, S. Mothes, R. Wennrich, Fresenius J. Anal. Chem. 354 (1996) 587.
[14] J. Poerschmann, F. D Kopinke, J. Pawliszyn, Environ. Sci. Technol. 31 (1997) 3629.
[15] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[16] Y. Morcillo, Y. Cai, J.M. Bayona, J. High Resolut. Chromatogr. 18 (1995) 767.
[17] T. Górecki, J. Pawliszyn, Anal. Chem. 68 (1996) 3008.
[18] L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, P. Sandra, Anal. Chem. 69 (1997) 1604.
[19] T. De Smaele, L. Moens, P. Sandra, D. Dams, Mikrochim. Acta 130 (1999) 241.
[20] M.L. Richardson, S. Gangolli, in: The Dictionary of Substances and Their Effects, Royal Society of Chemistry, Cambridge, 1994, p. 288 and 344.
[21] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[22] T. Górecki, J. Pawliszyn, Analyst 122 (1997) 1079.
[23] J.C. Miller, J.N. Miller, in: Statistics for Analytical Chemistry, 2nd Edition, Ellis Horwood, Chichester, 1988, Chapters 3 and 5.
[24] M. Ceulemans, R. Lobinski, W.M.R. Dirkx, F.C. Adams, Fresenius J. Anal. Chem. 347 (1993) 256.
[25] J. Szpunar, M. Ceulemans, V.O. Schmitt, F.C. Adams, R. Lobinski, Anal. Chim. Acta 332 (1996) 225.
[26] M. Ceulemans, F.C. Adams, Anal. Chim. Acta 317 (1995) 161.
[27] M. Ceulemans, S. Slaets, F.C. Adams, Talanta 46 (1998) 395.
[28] H. Yang, S. Jiang, Y. Yang, C. Hwang, Anal. Chim. Acta 312 (1995) 141.