Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1064 (2005) 1–8
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of organotin compounds in water by headspace solid phase microextraction with gas chromatography–mass spectrometry☆

Chi-Chi Chou, Maw-Rong Lee*

Department of Chemistry, National Chung-Hsing University Taichung, Taiwan, ROC

Received 19 August 2003; received in revised form 26 February 2004; accepted 2 August 2004
Available online 24 December 2004

Abstract

This investigation evaluates headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography–mass spectrometry (GC–MS) to determine trace levels of organotins in water. The organotins were derivatized in situ with sodium tetraethylborate and adsorbed on a poly(dimethysiloxane) (PDMS)-coated fused silica fiber. The SPME experimental procedures to extract organotins in water were at pH 5, with extraction and derivatization simultaneously at 45 °C for 30 min in a 2% sodium tetraethylborate solution and a sample solution volume in the ratio of 1:1, and desorption in the splitless injection port of the GC at 260 °C for 2 min. Detection limits are determined to be in the low ng/L range. According to the analysis, the linearity range is from 10 to 10,000 ng/L with R.S.D. values below 12% except triphenyltin (24%). The proposed method was tested by analyzing surface seawater from the harbors on the Taiwanese coast for organotins residues. Some organotins studied were detected in the analyzed samples. Results of this study demonstrate the adequacy of the headspace SPME–GC–MS method for analyzing organotins in sea water samples.

Keywords: Headspace solid-phase microextraction; Organotins; Sea water; GC–MS

1. Introduction

Organotin compounds (OTs) have been extensively in recent decades in agriculture and industry as biocides, insecticides, fungicides, wood preservations, antifouling agents and polymer stabilizers. Among these, the most prominent are the trisubstituted forms tributyltin (TBT), and triphenyltin (TPhT). Tributyltin has for several years been used as an antifouling compound added to paints for use on boats. Triphenyltin is still being frequently used as a fungicide in agriculture, primarily against potato blight. Recently organotin compounds have been considered as possible endocrine disrupters [1]. Negative effects on environment can produce at low concentration even low to sub ng/L [1,2]. The migration of organotins from large harbors through the water, the illegal use of the organotin-containing antifouling paints on the boats, the desorption from contaminated sediments, or the desorption of volatile organotins are the pollution sources of organotins. TBT and TPhT, as well as their major metabolites, dibutyltin (DBT), monobutyltin (MBT) and monophenyltin (MPhT), are still found in natural water at levels that may be critical for the most sensitive organisms. Hence, a rapid, accurate, and sensitive analytical method is acquired to identify and determine the trace of these compounds in various sample matrices.

Determining of trace organotins in matrix requires the combination of a separation method, usually gas chromatography (GC) or liquid chromatography (LC), with selective and sensitive detection. Several GC analytical approaches for determining of OTs have been reported. The derivatization step, including alkylation by Grignard reagents or hydrogenation by sodium borohydride, is required to obtain OTs in appropriate forms for GC analysis. Direct aqueous-phase ethylation by sodium tetraethylborate ($NaBEt_4$) combined with GC–flame photometric detection (FPD) has been

☆ Presented at the 7th International Symposium on Hyphenated Techniques in Chromatography, Bruges, 6–8 February 2002.

* Corresponding author. Tel.: +886 4 22851716; fax: +886 4 22862547.
E-mail address: mrlee@mail.nchu.edu.tw (M.-R. Lee).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.08.166

developed for simultaneously determining of OTs and applied to the analysis of various environmental samples [3–8]. Liquid chromatography methods represent an alternative approach to OTs speciation that does not require derivatization before analysis [9,10]. All these methods offer good sensitivity but no structural information on the measured analyte. Mass spectrometry (MS) is a powerful technique for identifying compounds. However, the main limitation of LC–MS for quantification purposes seems to be related to the reproducibility of the signal, especially when dealing with complex matrices.

Proper sampling largely determines the validity of analytical samples for trace analysis. Previous investigations have set forth various types of extraction methods for OTs in water, including liquid–liquid extraction [7], solid-phase extraction (SPE) [10,11], and supercritical fluid extraction (SFE) [12–14]. Conventional extraction methods, although efficient and precise, are relatively time-consuming, because, the solvent decantation may take up to 12 h, depending on the sample matrix [7]. The organic solvents used are hazardous to human health and extremely expensive with respect to the disposal of solvents. Consequently, an alternative method was developed to reduce the extraction time, and to perform the extraction without solvent. Solid-phase microextraction (SPME) [15] can resolve many of the foregoing problems. Zhong et al. [16] detailed the underlying principles and advantages of trace organic analysis and the application of the SPME technique to extract trace organic compounds from a complex matrix. The mechanism of SPME is based on an equilibrium between the analyte concentration of the sample and that in the solid-phase fiber coating. The analytes are directly determined by thermal desorption into a gas chromatograph or desorption in the eluent stream of a high performance liquid chromatograph. To date, the application of SPME has focused mainly on organic compounds, such as pesticides, phenols, and semivolatile compounds [17–20]. However, only a few studies have addressed the SPME of water samples contaminated with organometallic species [21–25]. The use of headspace SPME has been reported for the detection of methyltins and butyltins in water, sediments or body fluids [21–25]. Gac et al. [23] used headspace SPME coupled GC–PFPD to analyze 14 organotin compounds in spiked environmental and biological samples. Their results have demonstrated that headspace SPME appears really as attractive for organotins determination in the environment and monitoring of their biogeochemical cycle.

In this study, an in situ ethylation of organotins, simultaneous solid-phase microextraction of the derivatives in a laboratory-made headspace device, followed by a gas chromatographic analysis with mass spectrometry was performed. The optimum conditions of SPME for determining organotins in water are also systematically investigated. The SPME behavior, detection limits, linear dynamic detection range and reproducibility are studied by determining the amount of organotins, to demonstrate the applicability of the proposed methods. The optimized method was then applied to the analysis of several seawater samples obtained from the harbors of Taiwan, to confirm the proposed method's effectiveness.

2. Experiment

2.1. Reagent and solution

Phenyltin trichloride ($MPhTCl_3$, 98% purity), dibutyltin dichloride ($DBTCl_2$, 97% purity), tetrabutyltin (TeBT, 98% purity) and tributyltin chloride (TBTCl, 97% purity) were purchased from Fluka (Switzerland). Monobutyltin trichloride ($MBTCl_3$, 97% purity) was obtained from ACROS (Geel, Belgium), and triphenyltin chloride (TPhCl, 95% purity) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Stock solutions of 1000 mg/L were prepared separately in methanol (Merck, Darmstadt, Germany). Further dilutions were obtained by adding methanol. All stock solutions were stored in the dark at 4 °C in a refrigerator. The solutions were renewed after six months even though no OTs degradation was noticeable. Glassware was soaked overnight in 1 M HNO_3 aqueous solutions, washed with soap, and rinsed with water. All solvents used were analytical grade. Sodium tetraethylborate ($NaBEt_4$) was purchased from Strem Chemicals (Bischheim, France). Milli-Q water (>18 MΩ) (SG Water USA, LLC, USA) was used to prepare freshly 2% (m/v) working solutions immediately before the start of the analysis.

To obtain buffer solutions with pH values between 4 and 6, suitable volumes of acetic acid were added to 16.4 g/L NaOAC. Seawater samples were collected at harbors on the Taiwanese coast and acidified on-site with HCl to pH 4, and stored at −30 °C in the laboratory [26]. Seawater samples were all analyzed within 1 week. Polyethylene flasks are known to release trace amounts of OTs, so 100 mL glass flasks were used.

2.2. Apparatus

Analysis by GC–MS was conducted using a Hewlett-Packard MS engine mass spectrometer (Palo Alto, CA, USA) with an HP 5890 Series II gas chromatograph and a split/splitless injection port. A 30 m × 0.25 mm i.d. fused capillary column DB-5 (J&W Scientific, USA) with a stationary phase thickness of 1.0 μm was used in the chromatographic analysis. The GC was operated in the splitless mode. For fiber injection, the injector port temperature was held isothermally at 260 °C. The splitless time was 1 min. The GC–MS transfer line temperature was maintained at 290 °C. The column temperature was initially set to 70 °C, programmed to rise to 190 °C at a rate of 30 °C/min, from 190 to 240 °C at a rate of 10 °C, and then from 290 °C upward at 30 °C/min. The final temperature was maintained for 0.5 min. Helium was used as a carrier gas and maintained in the electron impact (EI) ionization mode with an electron energy of 70 eV and tune to

perfluorotributylamine (PFTBA). The mass spectra were obtained at a mass-to-charge ratio scan range from 50 to 450 u to determine appropriate masses for selected ion monitoring (SIM). The EI ion source of the mass spectrometer was 230 °C. The solvent delay time was set to 3 min. Selected ion monitoring mode was used in quantitation. The dwell time was set to 30 ms for each ion.

2.3. Sampling

SPME was performed using a commercially available poly(dimethylsiloxane) (PDMS) fiber with a film thickness of 100 μm and housed in its manual folder (Supelco, Bellefonte, PA, USA). A new fiber should be conditioned before use as specified in the literature accompanying the commercial SPME products. The PDMS fibers were conditioned in the hot injection port of a gas chromatograph for 1 h at 250 °C. Each sample was stirred vigorously during the sorption step using a 8.0 mm diameter × 20.0 mm long magnetic stir bar and a stirring plate.

The derivatization system involves sample vials and a heating mantle. Derivatization of organotins standard solution with sodium tetraethylborate in NaOAC/HOAC buffer was achieved in aqueous solution. The 40 mL vial was used and closed using a PFTE coated septum. The reaction mixture was magnetically mixed and maintained at 45 °C using a heater mantle. The SPME needle pierced into the septum, and the fiber was exposed to the headspace. After 30 min of adsorption, the SPME fiber was inserted in the GC injection port for thermal desorption.

3. Results and discussion

3.1. Development of GC–MS

Analyzing organotin compounds directly using the GC technique is quite difficult. Since those compounds tend to be absorbed onto the packings in the chromatography column. Consequently, derivatization is required to make the organotins appropriate for GC analysis. In this study, organotins were ethylated with $NaBEt_4$ and sorbed on a poly(dimethylsioxane)-coated fused silica fiber in headspace, then desorbed in the splitless injection port of the GC.

The electron impact ionization and positive chemical ionization (CI) mass spectra for ethylation derivatives of standard organotin compounds were obtained. Independently of the ionization mode used, no molecular ions of organotin compounds are observed. The most abundant fragment ions of all organotin compounds are $[M - C_2H_5]^+$ except TBT is $[M - C_4H_9]^+$ (Fig. 1, Table 1). A series of fragment ions are generated through the successional degradations. A standard solution of organotin compounds was used to compare the responses obtained with various ionization modes of MS to evaluate the optimum ionization technique for the trace analysis of organotin compounds in water. According to the peaks

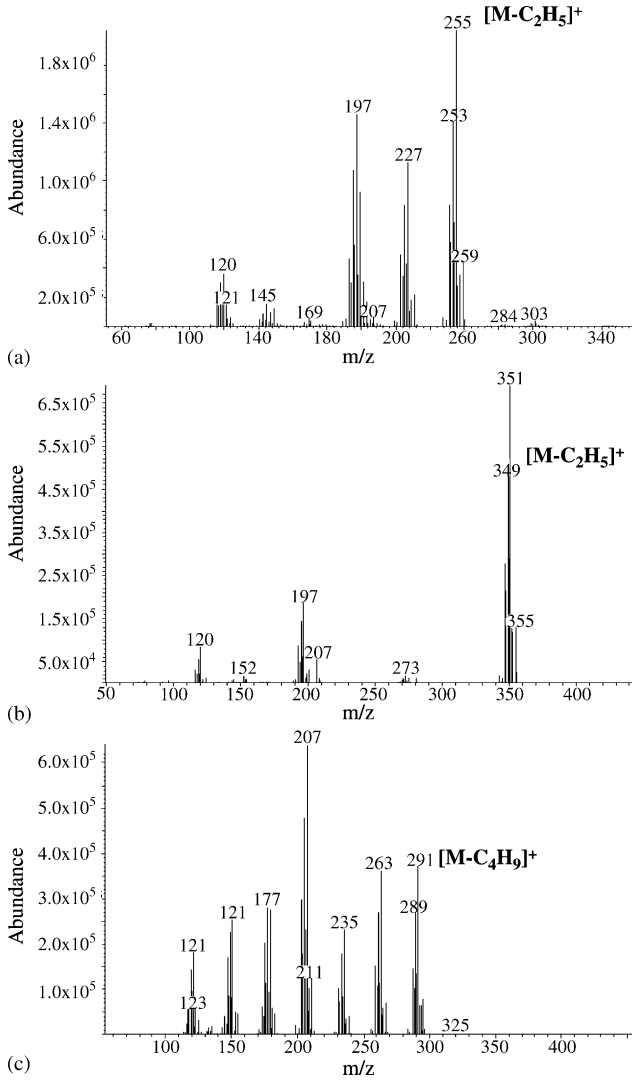

Fig. 1. Mass spectra of the derivatives of (a) MPhT (b) TPhT (c) TBT produced by EI.

areas obtained of organotin compounds, the sensitivity of EI exceeded that in the CI mode, therefore, in this study, EI was adopted to investigate the optimum conditions of SPME.

The highest sensitivity is required to monitor organotins at trace levels in the water. Quantitative analyses were

Table 1
Analytical conditions of the ethylation of organotin compounds, as determined by GC–MS with CI and EI modes

Compound	MW	t_R (min)	Selected ion (*m*/*z*)		Confirmed ion (*m*/*z*)	
			EI	CI	EI	CI
MBT	282	4.48	235	283	233	311
DBT	304	5.57	263	305	261	333
MPhT	302	6.45	255	303	253	331
TBT	326	6.69	291	327	289	355
TeBT	348	7.82	235	349	233	377
TPhT	386	12.97	351	387	349	415

performed using MS in the selected ion monitoring mode. For this purpose, characteristic ions were monitored with a dwell time of 30 ms for various groups of ions. Table 1 presents the analytical conditions for determining of the ethylation derivatives of organotin compounds with the two most common ionization modes.

3.2. Selecting of optimum conditions for SPME

As an equilibrium technique, SPME does not exhaustively extract organic compounds from an aqueous sample. The amount of analytes extracted by the coating at equilibrium is proportional to their initial concentration in the aqueous sample. The choice of an appropriate coating is very crucial to the SPME method. The chosen coating depends on the chemical nature of the analytes. Typically, derivatization always reduces the polarity of the analytes, and therefore, the use of non-polar coatings. The derivatized organotins are volatile and have a greater affinity for the apolar phase than for the polar sample matrix. As referred in the introduction, the information available in the literature was the starting point for the establishment of the method under study. The chosen fiber was 100 μm fibers coated with poly(dimethylsiloxane) which has been reported as providing a good performance for organotion compounds [15,21,22,27–29].

Usually, in GC analysis, derivatization is a feasible method for promoting chromatographic separations with by increasing the volatility of the analytes and the sensitivity and selectivity of the detector. Organotins need to be extracted from the sample and to be derivatized to a volatile species for GC analysis. Ethylation with sodium tetraethylborate was introduced by Ashby et al. [30–32]. The advantages of derivatization of OTs by the $NaBEt_4$ technique are that ethylation can occur in the aqueous phase and extraction can be performed simultaneously. The ethylation reaction is a nucleophilic reaction and the capacity of organotins to be involved in nucleophilic reactions may depend on the extent of their substitution [33]. The relative signals area counts for different organotins after derivatization were compared for using the SPME methods with direct and headspace extraction. In direct SPME, the fiber is introduced in the aqueous phase. From the results, for organotins extracted by using SPME, the sensitivity of the headspace SPME is higher by a factor of up to 11 (DBT) than that of direct SPME. Headspace SPME is more sensitive than that in direct SPME, therefore, aqueous organotins were extracted by headspace SPME in this study.

Derivatization time, derivatization temperature and amount of reagent are the main parameters that affect the efficiency of derivatization. The water samples were spiked with 10 μg/L organotins standard solution to trace the concentration of $NaBEt_4$ effect by using headspace SPME method. Various volume ratios of 2% $NaBEt_4$ solution combined with 5 mL of sample solution were used to investigate this effect (Fig. 2). The greatest derivatization obtained was the sample solution to the $NaBEt_4$ solution ratio at 1:1 (v/v).

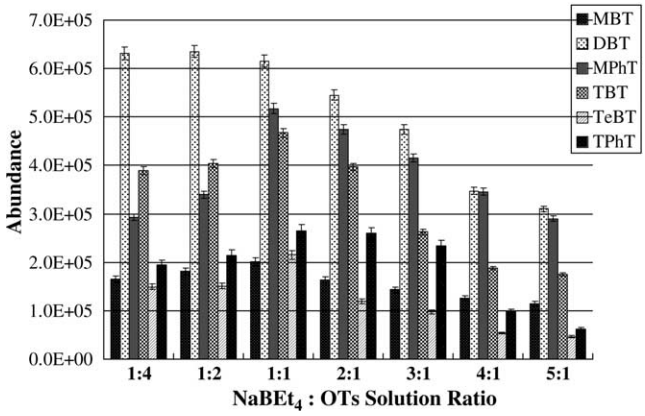

Fig. 2. Effect of the ratio of derivatizing reagent (2% $NaBEt_4$) and sample solution volume on peak areas of 10 μg/L OTs.

The amount of analytes extracted in headspace SPME heavily relies on the mass transfer of analytes through the aqueous phase to the gas phase, and then onto the fiber coating. Extraction temperature and sorption time will influence the amount of mass transfer. The sample temperature also determines the efficiency of the derivatization of organotins. In this study, the derivatization and extraction of organotins were performed simultaneously. The effect of the sample temperature was investigated by sampling standard mixtures of 100 μg/L for 30 min at various temperatures from 25 to 80 °C. The extracted amounts of organotins, except for the more volatile MBT, increased with increasing the temperatures to a maximum at 45 °C and decreased as temperature increased further. The results in Fig. 3 indicate that heating the organotins to 45 °C increased the adsorption efficiency. At higher temperature, organotins are partially desorbed from the SPME fiber coating to decrease the extraction efficiency. The variance analysis of the experimental results reveals that the peak area counts of organotins increased with the extraction time or the derivatization time from 5 to 50 min. All organotins reached equilibrium in 30 min (Fig. 4). Therefore, the extraction time or derivatization time was chosen as

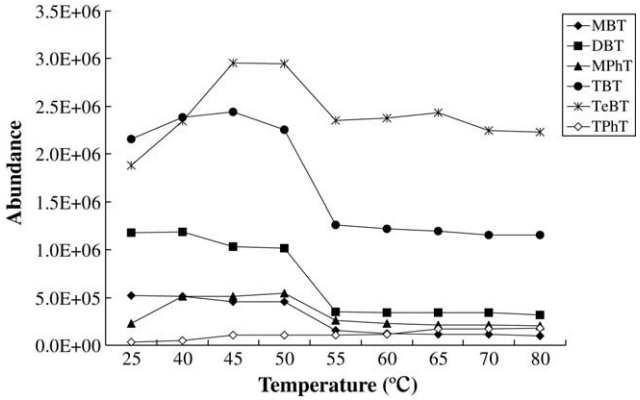

Fig. 3. Effect of absorption temperature on peak areas of organotin compounds in water produced by HS-SPME–GC–MS.

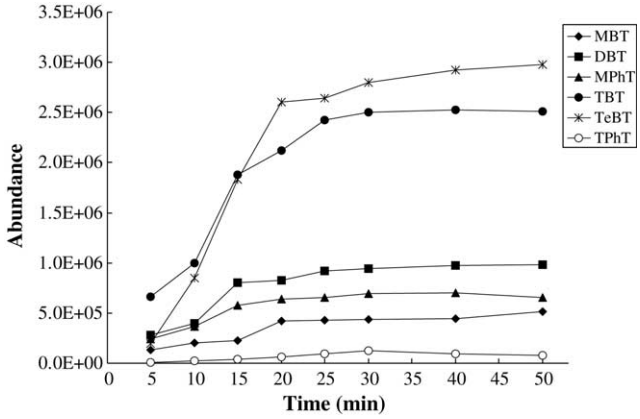

Fig. 4. Effect of extraction time on peak areas of organotin compounds in water produced by HS-SPME–GC–MS.

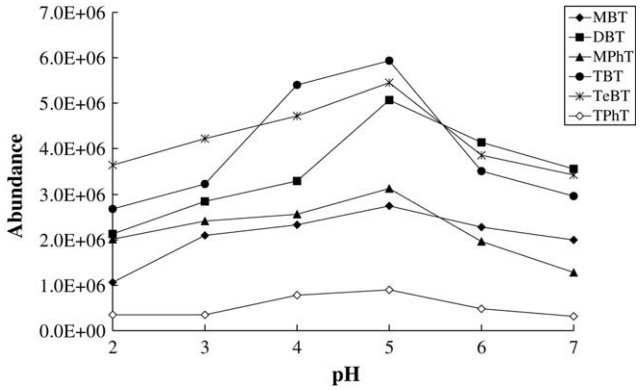

Fig. 6. Effect of pH on peak areas of organotin compounds in water produced by HS-SPME–GC–MS.

30 min to allow simultaneous extraction and derivatization of organotins in water using headspace SPME.

According to SPME theory, the volume of the gaseous phase must be minimized to obtain high sensitivity when headspace extraction is used [34]. The effects of the water sample and the headspace volumes were studied to optimize the extraction procedure of organotins. This study was performed using 40 mL vials and by increasing the volume of a fortified aqueous sample from 0.25 to 15 mL; the sample was spiked with 10 μg/L organotins. The extraction time was 30 min at 45 °C. The results show that the sample volume affects the extraction of organotins (Fig. 5). The peak area was increased from organotins sample volume of 0.25 to a maximum of 5 mL. Further experiments were performed using a 5 mL water sample.

Salting is conventionally added to the aqueous matrix to increase the amount of organotins extracted from the water [35–39]. In view of the apolar nature of the derivatized organotins, increasing the ion strength of the sample solution by addition of NaCl is expected to increase the diffusion of organotins into the headspace and increase the adsorption onto this space. The saturated NaCl solution was added with a syringe after 10 s of derivatization prior SPME extraction. Under the experimental conditions described above, the effect of NaCl concentration on the peak areas of 10 μg/L organotins was studied. The addition of salt significantly affects the extraction of TeBT meanwhile but was found not to affect the extraction efficiency of other organotins probably because the aqueous solution was already sufficiently polar and the derivatized organotins were highly hydrophobic. Further experiments were performed using saturated NaCl to extract organotins simultaneously.

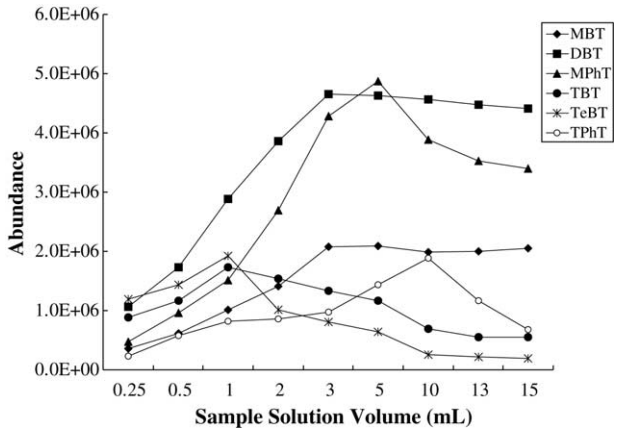

Fig. 5. Effect of sample solution volume on peak areas of organotin compounds in water produced by HS-SPME–GC–MS.

Changes in the sample matrix yielded significant differences in the signal intensities of analytes with various structures, obtained by the SPME method. The variation in the pH from 2 to 7 was monitored to examine how pH affects the extraction of organotins in aqueous solution (Fig. 6). The results indicated that the extraction increased with pH to a maximum at pH 5, and, then, declined as the basicity of solution further increased. The pH value of the solution influences the efficiency of derivatization. The results indicated that the derivatization of organotins with $NaBEt_4$ was found to be most effective at pH 5, which is in agreement with values found by other research groups [14,26,40–44]. Therefore, the pH of the solution was adjusted to 5 in all studies reported herein.

The desorption time and desorption temperature determine the amount of analytes desorbed from the fiber coating, as determined by the SPME method [21–23,45]. Desorption time was investigated within a range of 0.3–5 min, by leaving the fiber in the injector for an increasing period of time and maintaining the temperature of the injector at 260 °C. The desorption of the organotins increased with desorption time and reached a maximum after 2 min. The monitored desorption temperature ranged from 200 to 270 °C. According to the results, the peak area of all organotins increased slightly with the desorption temperature. All organotins exhibited complete desorption at a temperature of 260 °C. Therefore, a 2 min desorption time and 260 °C desorption temperature were used in all experiments. The mass chromatogram of

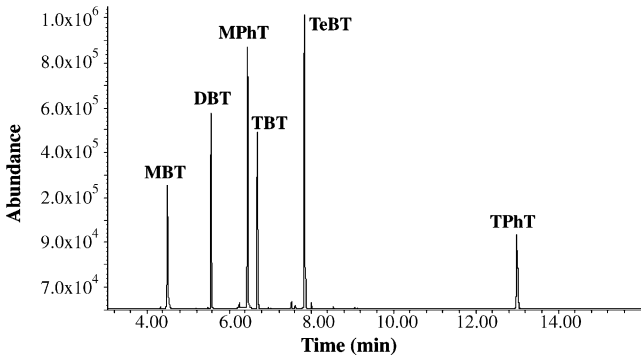

Fig. 7. Mass chromatogram of a water sample containing 10 μg/L organotins produced by HS-SPME–GC–MS.

a water sample containing 10 μg/L organotins produce by SPME–GC–MS was shown in Fig. 7. All the peaks of organotins are sharp and separated.

3.3. Linear range, limits of detection and precision

The limits of detection of SPME used to determine organotins in water heavily relies on the amount of derivatized analytes adsorbed by coating on the fiber and the sensitivity of the GC–MS. The linearity, limits of detection and precision were calculated when the optimum conditions for the headspace SPME–GC–MS procedure were established. The linearity of the headspace SPME method was examined by extracting the spiked organotins samples ranging from 10 to 10,000 ng/L. Triplicate injections were performed. Table 2 presents the linear ranges and the square of the correlation coefficients (r^2) obtained for each compound. The studied organotins in water were analyzed, and SPME was linear over approximately three orders of amounts, with linear correlation coefficients above 0.997 in all cases.

The linear range experiments provided the necessary information to estimate the limit of detection (LOD), based on the lowest detectable peak with a signal-to-noise ratio of three. The EI ionization of MS was used to determine the detection limits of organotins. Additionally, comparing with full scan, the SIM mode is performed by MS in quantitative analysis to increase the sensitivity. In general, the most abundant ion is used for the ion of monitoring; the specific ion is used as the confirmed ion. The signal is obtained by measuring the peak area over the scans during the elution of organotins in the GC. Under the experimental conditions, LODs were between 0.4 and 4.6 ng/L, as listed in Table 2. The forgoing results indicate that headspace SPME is available for extracting trace organotins from water.

The precision of the headspace SPME method was evaluated by analyzing eight extractions from an aqueous solution of all studied organotins at a concentration of 50 μg/L. The results reported in Table 2 show that the relative standard deviation (R.S.D.%) of different concentrations for repeatability ranged from 3% (monobutyltin) to 24% (triphenyltin). Therefore, the derivatization of organotins in situ with sodium tetraethylborate, and their sorption on a poly(dimethylsiloxane)-coated fiber in headspace SPME were deemed acceptable for determining trace organotins in water.

3.4. Headspace SPME–GC–MS of complex real-world samples

The effectiveness of the proposed method in determining organotins in real samples was tested by analyzing surface seawater samples. Organotins, especially tributyltin, have for many years been used as an antifouling compounds added to paints intended for boats. Herein, organotins are enriched in seawater. Seawater samples were collected from harbors on the Taiwan coast acidified on-site using HCl to pH 4, before being stored at −30 °C in the laboratory. Seawater samples were all analyzed within 1 week. The headspace SPME was operated under the determine optimum conditions. Triplicate analyses were performed. The results (Table 3) show that organotins were present in all surface seawater samples, except that from Taichung harbor. The concentration of organotins ranged from 16 ng/L (triphenyltin) to 298 ng/L (tetrabutyltin) in the seawater near Taichung's muddy shore. The results demonstrate the suitability of the headspace SPME–GC–MS approach for analyzing trace organotins in seawater samples.

Table 2
Linear range, limits of detection, and precision for in situ ethylation/HS-SPME–GC–MS method

Compound	Linear equation	Square of the correlation coefficient (r^2)	LOD (ng/L)	Linear range (ng/L)	R.S.D. (%)[a]	R.S.D. (%)[b]	R.S.D. (%)[c]
Monobutyltin	$Y = 199.99X + 186337$	0.9985	0.6	10–10000	19	6	3
Dibutyltin	$Y = 267.89X + 440490$	0.9979	0.4	10–10000	14	12	6
Monophenyltin	$Y = 342.68X + 63542$	0.9982	1.5	10–10000	13	11	4
Tributyltin	$Y = 214.32X + 267202$	0.9990	0.5	10–10000	20	18	7
Tetrabutyltin	$Y = 435.4X + 81946$	0.9990	1.2	10–10000	13	10	7
Triphenyltin	$Y = 8.7286X + 8911$	0.9979	4.6	10–10000	24	19	16

[a] Relative standard deviation for 50 ng/L of organotins ($n = 8$).
[b] Relative standard deviation for 500 ng/L of organotins ($n = 8$).
[c] Relative standard deviation for 50 μg/L of organotins ($n = 8$).

Table 3
Concentration of organotin species in surface seawater (ng/L)

Real water sample	Monobutyltin (ng/L)	Dibutyltin (ng/L)	Monophenyltin (ng/L)	Tributyltin (ng/L)	Tetrabutyltin (ng/L)	Triphenyltin (ng/L)
Taichung harbor	ND[a]	ND	ND	ND	ND	ND
Taichung muddy shore	54 ± 3	102 ± 12	48 ± 6	277 ± 30	298 ± 28	16 ± 4
Kaohsiung harbor	ND	83 ± 9	ND	216 ± 23	186 ± 17	ND
Kaohsiung sand beach	ND	25 ± 3	ND	107 ± 11	86 ± 9	ND
Keelung wharf	65 ± 6	160 ± 19	ND	287 ± 27	ND	ND
Su-Ao harbor	99 ± 8	24 ± 2	148 ± 16	34 ± 4	64 ± 7	ND

The samples were collected at harbors around the Taiwanese coast and filtered with 0.2 μm nylon 66 membrane filter. Three times replicated measurements.
[a] ND: not detected.

4. Conclusion

This investigation demonstrates that HS-SPME is a precise, means of reproducibly analyzing trace organotin compounds from aqueous samples. Better chromatographic shapes and sensitivity were obtained by derivatizing organotins using one-step simultaneous direct in situ aqueous ethylation using sodium tetraethylborate. The derivatization efficiency was highest in achieved in headspace derivatization with 2% sodium tetraethylborate solution and a sample solution volume ratio of 1:1. The method is precise and can be used over a wide linear range. Detection limits at below ng/L level of organotin compounds in aqueous samples are achieved. Moreover, the feasibility of applying the HS-SPME–GC–MS system to determine the amount of organotin compounds in real seawater samples in Taiwan harbors was tested. Concentrations of organotins were detected to range from 16 ng/L (triphenyltin) to 298 ng/L (tetrabutyltin). The proposed method offers a low level sensitivity in determining trace amounts of organotins in seawater samples containing a high degree of interference.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under contract no. NSC 90-2113-M-005-029 and no. NSC 91-2113-M-005-025.

References

[1] K. Fent, Crit. Rev. Toxicol. 26 (1996) 1.
[2] R.J. Maguire, Appl. Oragnomet. Chem. 1 (1987) 475.
[3] C. Carlier-Pinasseau, G. Lespes, M. Astruc, Appl. Organomet. Chem. 10 (1996) 505.
[4] C. Carlier-Pinasseau, A. Astruc, G. Lespes, M. Astruc, J. Chromatogr. A 750 (1996) 317.
[5] C. Carlier-Pinasseau, G. Lespes, M. Astruc, Talanta 44 (1997) 1163.
[6] C. Carlier-Pinasseau, G. Lespes, M. Astruc, Environ. Technol. 18 (1997) 1179.
[7] C. Montigny, G. Lespes, M. Potin-Gautier, J. Chromatogr. A 819 (1998) 221.
[8] G. Lespes, C. Carlier-Pinasseau, M. Potin-Gautier, M. Astruc, Analyst 121 (1996) 1969.
[9] C.F. Harrington, G.K. Eigendorf, W.R. Cullen, Appl. Organomet. Chem. 10 (1996) 339.
[10] E. González-Toledo, R. Compañó, M.D. Prat, M. Granados, J. Chromatogr. A 946 (2002) 1.
[11] K. Mizuishi, M. Takeuchi, T. Hobo, J. Chromatogr. A 800 (1998) 267.
[12] V. Lopez-Avila, Y. Liu, W.F. Beckert, J. Chromatogr. A 785 (1997) 279.
[13] Y. Cal, R. Alzaga, J.M. Bayona, Anal. Chem. 66 (1994) 1161.
[14] Y. Cal, J.M. Bayona, J. Chromatogr. Sci. 33 (1995) 89.
[15] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[16] Z. Zhong, M.J. Yang, J. Pawliszyn, Anal. Chem. 66 (1994) 844A.
[17] K.J. Hageman, L. Mazeas, C.B. Grabanski, D.J. Miller, S.B. Hawthorne, Anal. Chem. 68 (1996) 3892.
[18] R.F. Dias, K.H. Freeman, Anal. Chem. 69 (1997) 944.
[19] M.R. Lee, Y.C. Yeh, W.S. Hsiang, B.H. Hwang, J. Chromatogr. A 806 (1998) 317.
[20] B.H. Hwang, M.R. Lee, J. Chromatogr. A. 898/2 (2000) 245.
[21] L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, P. Sandra, Anal. Chem. 69 (1997) 1604.
[22] E. Millán, J. Pawliszyn, J. Chromatogr. A 873 (2000) 63.
[23] M.L. Gac, G. Lespes, M.P. Gautier, J. Chromatogr. A 999 (2003) 123.
[24] L. Dunemann, H. Hajimiragha, J. Begerow, Fresenius J. Anal. Chem. 363 (1999) 466.
[25] I. Arambarri, R. Garcia, E. Millán, Chemosphere 51 (2003) 643.
[26] C.G. Arnold, M. Berg, S.R. Muller, U. Dommann, R.P. Schwarzenbach, Anal. Chem. 701 (1998) 3094.
[27] M.N. Sarrion, F.J. Santos, M.T. Galceran, J. Chromatogr. A 819 (1998) 197.
[28] C. Haberhauer-Troyer, M. Crnoja, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 366 (2000) 329.
[29] S. Tutschku, M.M. Schantz, S.A. Wise, Anal. Chem. 74 (2002) 4694.
[30] J. Ashby, P.J. Craig, Appl. Oranomet. Chem. 5 (1991) 173.
[31] J. Ashby, P.J. Craig, Sci. Total Environ. 78 (1989) 219.
[32] J. Ashby, S. Clark, P.J. Craig, Anal. At. Spectrom. 3 (1988) 735.
[33] R. Morabito, P. Massanisso, Trends Anal. Chem. 19 (2000) 113.
[34] R. Eisert, J. Pawliszyn, Critic. Rev. Anal. Chem. 27 (1997) 103.
[35] Z. Mester, R.E. Sturgeon, Environ. Sci. Technol. 36 (2002) 1198.
[36] E. Graupera, C. Leal, M. Granados, M.D. Prat, R. Compañó, J. Chromatogr. A 846 (1999) 413.
[37] K. Fent, J. Hunn, Environ. Sci. Technol. 25 (1991) 956.
[38] J. Poerschmann, F.D. Kopinke, J. Pawliszyn, Environ. Sci. Technol. 31 (1997) 3629.
[39] K. Inaba, H. Shiraishi, Y. Soma, Water Res. 29 (1995) 1415.

[40] H. Tao, R.B. Rajendran, C.R. Quetel, T. Nakazato, M. Tominaga, Anal. Chem. 71 (1999) 4208.
[41] R. Eiden, H.F. Schőler, M. Gastner, J. Chromatogr. A 809 (1998) 151.
[42] G.B. Jiang, F.Z. Xu, F.J. Zhang, Fresenius J. Anal. Chem. 363 (1999) 256.
[43] I. Rodriguez, M. Santamarina, M.H. Bollain, M.C. Mejuto, R. Cela, J. Chromatogr. A 774 (1997) 379.
[44] N.S. Thomaidis, F.C. Adams, T.D. Lekkas, Mikrochim. Acta 136 (2001) 137.
[45] M.R. Lee, Y.S. Song, B.H. Hwang, C.C. Chou, J. Chromatogr. A 896 (2000) 265.