

## Determination of Butyltin Stabilizers in PVC Using Liquid-Phase Microextraction with Electrothermal Atomic Absorption Spectrometry

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A rapid and highly sensitive method is described for the extraction and determination of di- and tributyltin in PVC samples using headspace liquid phase microextraction followed by an analysis with graphite furnace atomic absorption spectrometry (HS-LPME/GFAAS). The analytes were derivatized *in situ* with sodium tetraethylborate and concentrated in a 2  $\mu$ l microdrop of benzyl alcohol suspended from the tip of a conventional GC microsyringe. The ethylated species then were directly transferred into a graphite furnace and quantified. The extractions were carried out for 5 ml sample solution (8 ml vial) adjusted at pH 5, with derivatization at 22 °C for 15 min in a 2% sodium tetraethylborate. The experimental parameters impacting the performance of HS-LPME were also investigated. According to the analysis, the linearity range was from 5.0 to 250.0 ng l<sup>-1</sup> with a detection limit of 0.5 ng l<sup>-1</sup> for dibutyltin and from 1.7 to 170.0 ng l<sup>-1</sup> with a detection limit of 0.17 ng l<sup>-1</sup> for tributyltin. Method RSD values were below 1.5%. Finally, the analysis of spiked PVC and water samples revealed that matrix had little effect upon extraction.

**Keywords:** Organotin compounds (OTC), Headspace liquid phase microextraction (HS-LPME), Poly-vinyl chloride (PVC), Electrothermal atomic absorption spectrometry (Et-AAS)

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### INTRODUCTION

Organotin compounds (OTC) are produced at ~51,000 tonnes per annum globally [1]. They are used extensively in agriculture and industry as biocides, insecticides, fungicides, wood preservations, antifouling agents and polymer stabilizers [2]. Nowadays, one of the major applications of organotin compounds (about 70%) is as heat and light stabilizer additives in PVC processing [3,4]. The PVC polymer becomes unstable under the influence of heat and light, resulting in discoloration and embitterment. It has been established that by adding certain organotin derivatives this kind of degradation process can be prevented [5]. Today, approximately 7% of the Sn metal is used to produce organometallic derivatives [6].

The widespread commercial use of this chlorinated plastic in recent years, has led to greater direct interaction of organotins with the environment. These compounds cause serious environmental or toxicity problems [7]. The negative effects on the environment spread at concentrations even as low as sub ng l<sup>-1</sup>. Tributyltin (TBT), for example, has been identified to be responsible for the imposex syndrome in certain marine gastropods at concentrations in water of few ng l<sup>-1</sup> with a lethal concentration for the sensitive species in the range of 0.1 to 39  $\mu$ g l<sup>-1</sup> [8,9]. Other OTCs also exert strong biocidal effects, including emhigh larval mortality and severe malformation of shells in oysters, growth retardation in mussels and micro-algae, and deformities in fiddler crabs [10,11]. Hence, a rapid, efficient, and sensitive analytical method is vital to determine the trace of these compounds in various sample matrices. The procedure should include a

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reliable analytical method based on the combination of a concentration step with some selective and sensitive analysis technique. In the analysis of tin compounds, generally there is a need for a preliminary derivatization to convert the native species into less polar compounds, including alkylation by Grignard reagents or sodium tetraethylborate ( $\text{NaBEt}_4$ ) [12].

Proper sample preparation 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 [13], solid-phase extraction (SPE) [14,15] and supercritical fluid extraction (SFE) [16-18]. 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 [2]. Moreover, the extensive use of organic solvents in analytical laboratories is no longer desirable because of environmental and health concerns. In the past decade, a number of methods have been developed which are solvent free or low solvent consumption methods. Among these, solid-phase microextraction (SPME) [19] and liquid-phase microextraction (LPME) [20] have been proposed as promising alternatives to LLE due to their simplicity of use and high preconcentration power. LPME is less known and is based on a traditional liquid-liquid extraction (LLE) technique, but utilizes only small measures of organic solvent as the extracting phase [21]. The technique is rather inexpensive compared to sorbent-based approaches such as SPME or SPE. LPME has been shown to be a viable alternative sample preparation method compared to the conventional LLE [22-27]. Delivery and recovery of a few microliters of an organic solvent requires nothing special more than a GC syringe. There is a clear advantage in applying headspace sampling for compounds exhibiting high vapor pressure, as the extraction process can be significantly faster in this mode [28].

Headspace analysis of derivatized organotin compounds in aqueous or other matrices was found to be effective [29]. In such systems, after sampling the headspace, GC (employing a variety of different detectors) is used for the subsequent analysis in most cases [30-37]; however, because of its time-consuming nature, a powerful alternative for the analysis of organometallic compounds at low concentration levels could be atomic absorption spectroscopy.

The present work describes a new and simple procedure for the extraction and determination of di- and tri- butyltin by headspace liquid phase microextraction combined with a graphite furnace atomic absorption spectrometry (HS-LPME-GFAAS) following in situ sodium tetraethylborate derivitization. The method is so simple and quick that the overall time of extraction and determination of each sample is less than 20 min.

## EXPERIMENTAL

### Standards and Reagents

The water used for the procedural blanks and for the preparation of the solutions employed for the extraction efficiency experiments was obtained from a Milli-Q reagent water purification system (Millipore, Bedford, MA, USA). Sodium chloride, which was added to the samples before extraction, was conditioned by heating at 450 °C for 4 h before use. Organic solvents (GC grade or 99% minimum purity) used in this work were mesitylene, buthyl acecate, undecane, n-decane, toluene, benzyl alcohol and tetrahydrofuran (THF) obtained from Fluka, Buchs, Switzerland.

Standard solution ( $1000 \text{ mg l}^{-1}$ ) of dibutyltin (DBT) and tributyltin (TBT) (Merck, Darmstadt, Germany) in methanol was prepared by accurately weighing  $\sim 0.02 \text{ g}$  of analyte into 100-ml volumetric flasks and diluting to volume and stored in a refrigerator when not in use. Working solutions were prepared by sequentially diluting the stock solutions with methanol. The reagent solution was prepared by diluting a 5 ml aliquot of DBT and TBT to 100 ml. Working standard solutions in the range of  $0.02\text{-}10 \text{ mg l}^{-1}$  were prepared by dilution in methanol. Acetic acid (EM Science (Gibbstown, NJ, USA)) was purified by distillation of reagent grade feedstock in quartz still prior to use. Sodium tetra phenyl borate ( $\text{NaBPh}_4$ ) and sodium tetraethylborate ( $\text{NaBEt}_4$ ) solution 2% (m/v) were prepared daily by dissolving solid material (Aldrich Chemical, Milwaukee, WI, USA) in deionized water (DIW). A 2 M sodium acetate (Fischer Scientific, Nepean, ON, Canada) buffer was prepared by dissolving 32.81 g in 200 ml in DIW and 20 ml glacial acetic acid. The pH was adjusted to 5 with glacial acetic acid.

### Sample Preparation

0.25 g of finely ground PVC (Cat. no. 181323, CAS

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Registry Number 107-13-1), Aldrich Chemical, Milwaukee) was dissolved in 5 ml of tetrahydrofuran (THF) and then spiked with the desired amount of each analyte. 100  $\mu$ l of it was quantitatively transferred into an 8 ml vial (Sun International Trading, USA). The vials were hermetically capped with PTFE-faced silicone septum. Then, samples were subjected to extraction.

### Headspace Liquid Phase Microextraction Analysis

The experimental set-up of headspace LPME is illustrated elsewhere [20]. The extraction was carried out as follows: An aliquot of the sample solution was placed in an 8-ml headspace vial. Sodium chloride was added to the sample solution with a concentration of 30%. When 5 ml of acetate buffer solution was added, the vial was sealed with a PTFE-coated silicon rubber septum. Subsequently, 500  $\mu$ l of 2% (m/v) sodium tetraethylborate solution was injected. The solution was stirred by a magnetic stirrer with a 0.5 mm stir bar (VWR scientific, West Chester, PA, USA) at an optimized speed of 1000 rpm. The sample vial was preheated in a water bath for 15 min.

A 2- $\mu$ l aliquot of the extracting organic solvent was withdrawn into the microsyringe. The microsyringe was then inserted into the headspace after piercing the vial septum and was suspended over the sample solution in a fixed position relative to the headspace vial. The plunger was depressed so that 2- $\mu$ l of the solvent was suspended from the tip of the syringe needle. After extraction, the drop was retracted into

the syringe. The syringe needle was removed from the sample vial, and the extract was directly transferred into the graphite furnace. All the results were determined with distilled water as a blank and treated similarly.

### Instrumentation

The extraction and injection procedures were administered using a 10  $\mu$ l microsyringe (Hamilton, Texas, USA). A circulating water bath (Optima 740, Tokyo, Japan) was used for adjusting the temperature of the sample vial, with an accuracy of  $\pm 0.1$   $^{\circ}$ C. The sample was stirred on a stirrer purchased from Hydolph (Germany) with a PTFE-coated magnetic stir bar. A Shimadzu model AA-680G atomic absorption spectrometer with a GFA-4A graphite furnace atomizer and deuterium lamp background correction was used. A tin hollow cathode lamp (Hamamatsu photonics, Kyoto, Japan) was used as a radiation source adjusted at the operating current to the value recommended by the manufacturer. High-density graphite tubes were used as atomizer. The atomic absorption signals at 286.3 nm for the Sn line were recorded on a graphic printer PR-6, at peak height and gas stop mode for quantification. The measurement conditions are given in Table 1.

### Safety Considerations

Organotin compounds are toxic substances, and  $\text{NaBeT}_4$  is highly flammable. Material Safety Data Sheets had to be consulted and essential safety precautions had to be observed

**Table 1.** Applied Conditions for Tin Determination with GFAAS System

Optimum analytical conditions					
Lamp current	7 mA				
Wavelength	286.3 nm				
Spectral bandwidth	0.2 nm				
Signal processing	Peak height				
Purge gas	Ar				
GFA heating programme					
Stage	Furnace temperature ( $^{\circ}$ C)	Mode	Time (s)	Ar flow rate (1 min $^{-1}$ )	
Drying	100	Ramp	5	1.5	
Ashing	400	Step	5	1.5	
Atomization	2300	Step	4	Gas stop	
Cleaning up	3000	Step	3	1.5	

for all the manipulations.

## RESULTS AND DISCUSSION

There are three phases involved in the HS-LPME process: sample matrix, headspace, and organic microdrop acceptor phase. First, the analyte is extracted from the matrix (sample solution) into the headspace. Then, the analyte is re-extracted into the organic microdrop suspended from the tip of the microsyringe needle. Therefore, the total process is driven by the concentration differences of the analyte between the aqueous and organic phases. Mass transfer of the analyte from the aqueous to headspace to organic microdrop continues until thermodynamic equilibrium is attained or extraction is stopped. According to this theoretical treatment, parameters that control the mass transfer of the analyte from the aqueous to organic microdrop should be assessed and optimized. The parameters that control the mass transfer include drop size, extraction time, stirring rate, addition of salt, pH, amount of  $\text{NaB}(\text{Et})_4$  and the organic solvent.

### Selection of the Extracting Solvent

To extract efficiently, several solvents differing in polarity and boiling point were screened. Solvent selectivity was evaluated for the extraction of 5 ml of a standard solution containing  $20 \mu\text{g l}^{-1}$  of the analyte, in deionized water. The stirred solution (1000 rpm) was sampled at  $25^\circ\text{C}$  for 15 min using  $2 \mu\text{l}$  of appropriate organic solvent. The results are shown in Fig. 1. It can be seen that benzyl alcohol gives the highest analytical signals; therefore, Benzyl alcohol was chosen as the extracting solvent in subsequent experiments.

### Effect of the Derivatizing Reagent Concentration

Derivatization time, derivatization temperature and the amount of the reagent are the main parameters that affect the efficiency of derivatization. The water samples were spiked with  $20 \mu\text{g l}^{-1}$  organotins standard solution to trace the concentration of derivatizing reagent ( $\text{NaBEt}_4$ ) effect by using headspace LPME method. Various volume ratios of 2%  $\text{NaBEt}_4$  solution combined with 5 ml of sample solution were used to investigate this effect (Fig. 2). The greatest derivatization obtained was that of the sample solution to the  $\text{NaBEt}_4$  solution ratio at 0.16 (w/v%). The use of sodium tetra

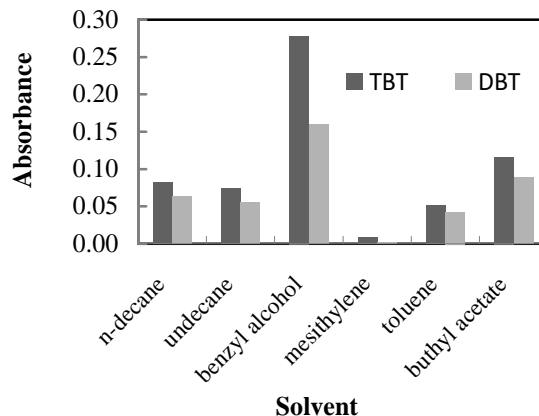


Fig. 1. Effect of extraction solvent.

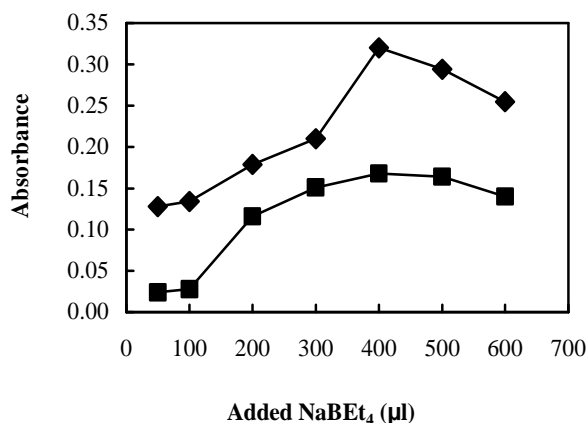


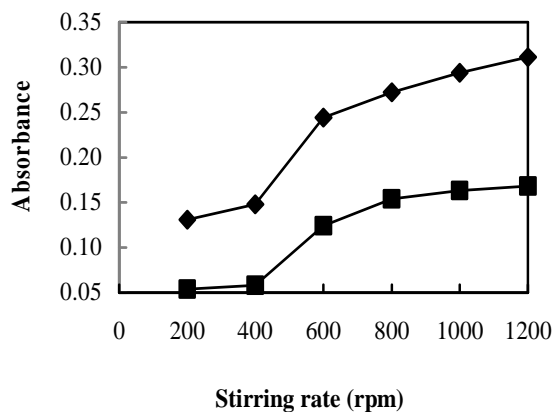
Fig. 2. Effect of the ratio of derivatizing reagent (2%  $\text{NaBEt}_4$ ) on peak areas: (◆) TBT, (■) DBT.

phenyl borate ( $\text{NaBPh}_4$ ) as a derivatization agent showed no effect on volatility of the OTs.

### Stirring of the Sample

In HS-LPME, the transport of analytes from the liquid sample to the gas phase can be improved by stirring the sample solution and hence, increasing the extraction efficiency and reducing extraction time. In our experiments, TBT and DBT standard samples were continuously agitated at  $22^\circ\text{C}$  at different stirring rates with a magnetic stir bar on a stir plate. As can be seen in Fig. 3, the peak areas of both analytes increase with an increase in the stirring rate up to 1000 rpm.

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**Fig. 3.** Effect of stirring rate on the relative peak areas: (◆) TBT, (■) DBT.

Higher stirring rates were not adopted because of spattering, which damages the drop and affects the precision and reproducibility of the extraction. Therefore, in subsequent work, a stirring rate of 1000 rpm was chosen.

### Extraction Time Profile

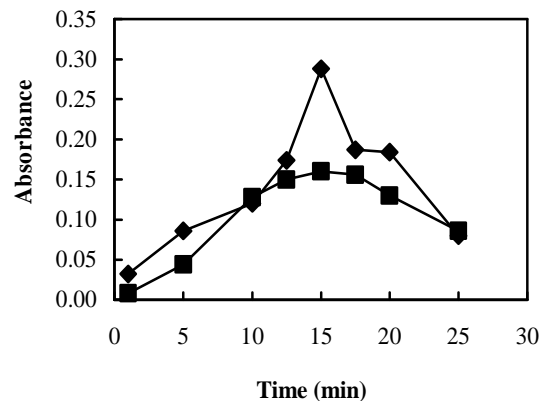
The effect of time on the extraction efficiency was examined in the range of 1-30 min at the optimized temperature (22 °C) with constant stirring speed. The peak areas increase up to 15 min and decrease at higher extraction times. Therefore, 15 min was used as the optimum extraction time (Fig. 4).

### Volume of Extraction Solvent

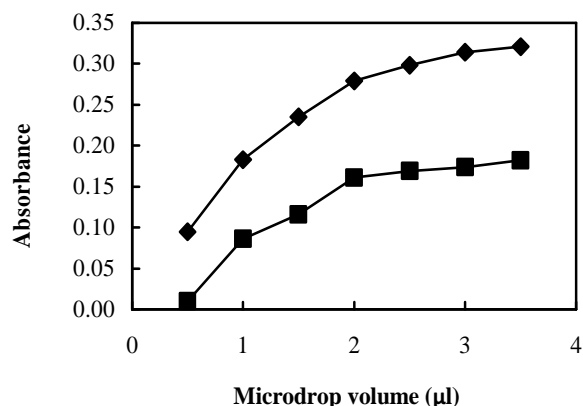
The volume of extraction solvent has great effect on the extraction efficiency. The effects of drop size on the extraction of DBT and TBT were examined in the range of 0.5 to 3.5  $\mu\text{l}$ , (the relations between the volume of the organic solvent and absorption peak areas can be seen in Fig. 5). The peak areas of both analytes increased with the organic solvent volume in the whole range of 0.5-3.5  $\mu\text{l}$ . When the volume exceeded 2.0  $\mu\text{l}$ , the drop became too unstable to suspend at the needle tip. On the basis of these facts, drop volume of 2.0  $\mu\text{l}$  was selected for the subsequent experiments.

### Extraction Temperature

Because partition coefficients are temperature dependent,

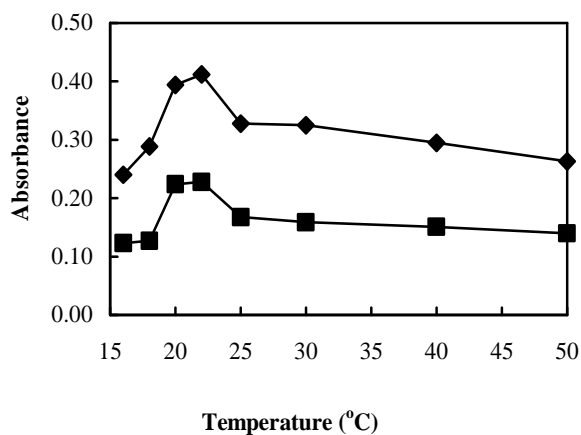


**Fig. 4.** Influence of the headspace sampling time: (◆) TBT, (■) DBT.



**Fig. 5.** Effect of organic drop volume on the extraction: (◆) TBT, (■) DBT.

there is usually an optimum temperature for HS-LPME. Temperature has a significant effect on both kinetics and thermodynamics of the extraction process. As temperature rises, more analytes are released from the aqueous matrix to the headspace, a process that results in higher analyte concentrations in the headspace, favoring the HS-LPME final determination. However, at high temperature, solvent-headspace partition coefficients decrease because the absorption step is an exothermic process. Thus, negative results can be achieved by increasing the temperature. As can be seen in Fig. 6, better results were achieved at moderate



**Fig. 6.** Extraction efficiencies obtained at various extraction temperatures: (◆) TBT, (■) DBT.

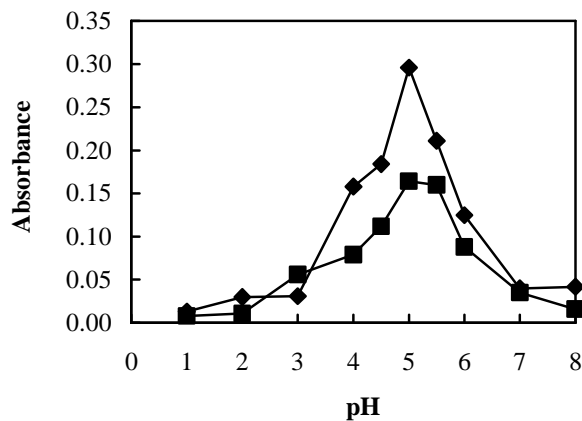
extraction temperatures. In subsequent measurements, the sample vial temperature was held at 22 °C.

### pH

The optimum pH for in situ derivatization and headspace extraction is principally dependent on the alkylation reaction. According to various reports, ethylation of OTs with NaBEt<sub>4</sub> is more favorable at a pH range 4-6 although there are some disagreements about the exact optimum [19]. A series of acetate buffer solution buffers (pH adjusted using acetic acid) in the donor phase was investigated by extracting 20 µg l<sup>-1</sup> concentrations of each analyte at 1000 rpm stirring speed at room temperature. A plot of the relative peak area versus extraction time (Fig. 7) showed that the best results were obtained for an extraction pH of 5 which is in agreement with values found by other researchers [2,19].

### Ionic Strength Influence

The effect of increasing the ionic strength of the water sample was examined by adding NaCl. An amount of NaCl up to 0.3 g ml<sup>-1</sup> was added to the spiked water samples at a concentration level of about 1 g ml<sup>-1</sup> for the analytes studied. The largest peaks were obtained when salt was added in an amount that caused saturation at the extraction temperature and so it was adopted in the subsequent experiments (*i.e.*, 0.3



**Fig. 7.** Effect of sample pH: (◆) TBT, (■) DBT.

g ml<sup>-1</sup>). The addition of salt to the sample matrix decreased the solubility of the analyte in the sample matrix, allowing more analyte to move to the sample headspace and enhancing the extraction efficiency.

### Detection Limits, Precision, and Linearity

The limits of detection of LPME used to determine organotins in water heavily relies on the amount of derivatized analytes adsorbed by extracting microdrop and the sensitivity of the GFAAS. The linearity, limits of detection and precision were calculated when the optimum conditions for the headspace LPME-GFAAS procedure were established. The linearity of the headspace LPME method was examined by extracting the spiked organotins samples ranging from 1.24 to 300 ng l<sup>-1</sup>. Triplicate injections were performed. Table 2 presents the linear ranges and the square of the correlation coefficients ( $r^2$ ) obtained for both compounds. Based on 3 S<sub>b</sub>, detection limit of 0.50 ng l<sup>-1</sup> (DBT) and 0.17 ng l<sup>-1</sup> (TBT) were obtained. The precision (RSD) for five replicate determinations of 120 ng l<sup>-1</sup> of each compound was 1.2 and 1.3%, respectively. The enrichment factor, defined as the ratio of C<sub>0</sub>/C<sub>v</sub>, where C<sub>0</sub> is the concentration of analytes in the organic phase after extraction and C<sub>v</sub> is their original concentration in the aqueous phase, was calculated using the average of the three trials obtained for 120 ng l<sup>-1</sup> concentration

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**Table 2.** Linear Range, Limits of Detection, Precision and Extraction Efficiency for *in situ* Ethylation/HS-LPME-GFAAS Method

Analyte	Linear equation	Square of the correlation coefficient ( $r^2$ )	LOD ( $\text{ng l}^{-1}$ )	Linear range ( $\text{ng l}^{-1}$ )	RSD (%)	Enrichment factor (%)
Dibutyltin	$y = 4.245x + 0.131$	0.958	0.50	5.0-250.0	1.2	60
Tributyltin	$y = 12.409x + 0.09$	0.991	0.17	1.7-170.0	1.3	105

**Table 3.** Results (Based on Five Replicate Analyses) of Determination of OTC in PVC Polymer Samples

Analyte	Concentration added ( $\mu\text{g l}^{-1}$ )	Relative recoveries (%)	Precision (RSD,%)
TBT	9.1	103	1.5
	92.0	101	1.2
	165.0	103	1.2
DBT	13.6	101	0.8
	145.0	102	1.4
	245.0	102	1.3

level. As shown in Table 2, the target analytes could be preconcentrated up to 105-folds.

### Quantification of OT's in PVC

The experimental parameters in HS-LPME technique were studied in spiked samples of 5% w:v solution of the PVC in tetrahydrofuran (THF). The experimental parameters were also studied in de-ionized water, and relative recovery studies were made. Since LPME is an equilibrium technique and not an exhaustive one, the term "recoveries" can be ambiguous. Here, instead of absolute recovery, relative recovery [38] determined as the ratio of the concentration found in spiked solution of the polymer and deionised water samples, spiked with the same amount of analytes, was calculated. The quantitative results given in Table 3 show that the method was accurate and reliable and could be applied to the determination of OTC's in real samples.

### CONCLUSIONS

The research reported here has demonstrated the feasibility

of applying the HS-LPME/GFAAS system as a very promising technique to determine the amount of organometallic compounds in real samples at  $\text{pg ml}^{-1}$  levels without the need for any sophisticated device. In addition to having extremely great sensitivity, the method is environmentally friendly because only a small measure of a non-toxic solvent is used. Compared to other micro-extraction methods, HS-LPME affords much better precision to the values obtained recently for SPME-GC-FPD, DLLME-GC-FPD and HS-SPME-GC-FPD [9,20]. It yields lower detection limits ( $0.17 \text{ ng l}^{-1}$  for TBT and  $0.5 \text{ ng l}^{-1}$  for DBT) for the tested analytes compared to  $4\text{-}21 \text{ ng l}^{-1}$  obtained by LLE-GC-FPD or SPME-GC-FPD ( $2\text{-}18 \text{ ng l}^{-1}$ ) for the determination of the same analytes in aqueous samples [8,20]. Only GC-MIP-AES-based procedures for the quantification of organotin compounds in water samples afford a better limit of detection (*i.e.*,  $100 \text{ pg l}^{-1}$ ) [8]. Adequate linearity and the absence of matrix effects indicated that the proposed method could be used for screening organotins in virtually all complex matrices.

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## REFERENCES

- [1] M.G. Ikonou, M.P. Fernandez, T. He, D. Cullon, *J. Chromatogr. A* 975 (2002) 319.
- [2] C.C. Chou, M.R. Lee, *J. Chromatogr. A* 1064 (2005) 1.
- [3] R.J. Maguire, *Appl. Organomet. Chem.* 1 (1987) 475.
- [4] M. Hoch, *Appl. Geo. Chem.* 16 (2001) 719.
- [5] V. Yngve, US Patent 2219463, 1940.
- [6] O.F.X. Donard, R. Pinel, in: R.M. Harrison, S. Rapsomanikis (Eds.), *Tin and Germanium, Environmental Analysis Using Chromatography Interfaced with Atomic Spectroscopy*, Wiley, New York, 1989.
- [7] V. Kaur, A.K. Malik, N. Verma, *J. Sep. Sci.* 29 (2006) 333.
- [8] J.C. Botana, I.R. Pereiro, R.C. Torrijos, *J. Chromatogr. A* 963 (2002) 195.
- [9] K.M. Attar, *Appl. Organomet. Chem.* 10 (1996) 317.
- [10] T. Horiguchi, H. Shiraishi, M. Shimizu, *Appl. Organomet. Chem.* (1997) 451.
- [11] R. Babu Rajendran, H. Tao, A. Miyazaki, R. Ramesh, S. Ramachandran, *J. Environ. Monit.* 3 (2001) 627.
- [12] J. Ashby, S. Clark, P.J. Craig, *J. Anal. At. Spectrom.* 3 (1988) 735.
- [13] C. Montigny, G. Lespes, M. Potin-Gautier, *J. Chromatogr. A* 819 (1998) 221.
- [14] E. Gonzalez-Toledo, R. Compano, M.D. Prat, M. Granados, *J. Chromatogr. A* 946 (2002) 1.
- [15] K. Mizuishi, M. Takeuchi, T. Hobo, *J. Chromatogr. A* 800 (1998) 267.
- [16] V. Lopez-Avila, Y. Liu, W.F. Beckert, *J. Chromatogr. A* 785 (1997) 369.
- [17] Y. Cai, R. Alzaga, J.M. Bayona, *Anal. Chem.* 66 (1994) 1161.
- [18] Y. Cai, J.M. Bayona, *J. Chromatogr. Sci.* 33 (1995) 89.
- [19] G.A. Zachariadis, E. Rosenberg, *Talanta* 78 (2009) 570.
- [20] A.P. Birjandi, A. Bidaria, F. Rezaei, M.R. Milani-Hosseini, Y. Assadi, *J. Chromatogr. A* 1193 (2008) 19.
- [21] M. Kaykhaii, S. Nazari, M. Chamsaz, *Talanta* 65 (2005) 223.
- [22] M. Kaykhaii, M. Ghassaban, Y. Sehri, *Chemia Analityczna* 52 (2007) 3.
- [23] M. Kaykhaii, M. Moradi, *J. Chromatogr. Sci.* 46 (2008) 413.
- [24] F.J.P. Pereira, C. Bendicho, N. Kalogerakis, E. Psillakis, *Talanta* 74 (2007) 47.
- [25] C. Denga, Y. Maob, F. Hua, X. Zhang, *J. Chromatogr. A* 1152 (2007) 193.
- [26] M. Kaykhaii, M. Mirbalouchzahi, *Environ. Monit. Asses.* 147 (2008) 211.
- [27] L. Vidal, C.E. Domini, N. Grane, E. Psillakis, A. Canals, *Anal. Chim. Acta* 592 (2007) 9.
- [28] M. Chamsaz, M.H. Arbab-Zavar, S. Nazari, *J. Anal. At. Spectrom.* (2003) 1279.
- [29] H. Shioji, S. Tsunoi, H. Harino, M. Tanaka, *J. Chromatogr. A* 1048 (2004) 81.
- [30] C. Bancon-Montigny, P. Maxwell, L. Yang, Z. Mester, R.E. Sturgeon, *Anal. Chem.* 74 (2002) 5606.
- [31] N. Cardellicchio, S. Giandomenico, A. Decataldo, A. Di Leo, *Fresenius J. Anal. Chem.* 369 (2001) 510.
- [32] G.B. Jiang, J.Y. Liu, *Anal. Sci.* 16 (2000) 585.
- [33] G.B. Jiang, J.Y. Liu, K.W. Yang, *Anal. Chim. Acta* 421 (2000) 67.
- [34] J.Y. Liu, G.B. Jiang, Q.F. Zhou, K.W. Yang, *J. Sep. Sci.* 24 (2001) 459.
- [35] E. Millan, J. Pawliszyn, *J. Chromatogr. A* 873 (2000) 63.
- [36] L. Yang, Z. Mester, R.E. Sturgeon, *J. Anal. At. Spectrom.* 17 (2002) 944.
- [37] S. Tutschku, M.M. Schantz, S.A. Wise, *Anal. Chem.* 74 (2002) 4694.
- [38] M. Kaykhaii, M. Rahmani, *J. Sep. Sci.* 30 (2007) 573.