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Comparison between Headspace and Aqueous Phase Solid Phase Microextraction Method for Speciation Analysis of Butyltin Compounds in Sea Water

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ABSTRACT

Headspace and aqueous phase solid phase microextraction (SPME) mehtods for the analysis of butyltin compounds in sea water were evaluated and compared. The method detection limit (MDL) for monobutyl- (MBT), dibutyl- (DBT), and tributyltin (TBT) in sea water were detected as 3.5, 3.8, and 3.8 ng/L, respectively, by the headspace SPME method. On the other hand, the MDL for MBT, DBT, and TBT in sea water were detected as 19.2, 20.4, and 31.7 ng/L, respectively, by the aqueous phase SPME method. Butyltin compounds in seawater collected from different harbors in Taiwan had MBT in the range of 5.5-51.9, DBT <MDL-19.5, and TBT <MDL-7.8 ng/L as detected by the headspace SPME method.

Key words: solid phase microextraction (SPME), headspace, aqueous phase, butyltin compounds, sea water

INTRODUCTION

Organotin compounds have been widely used in many applications, such as fungicides, bactericides, pesticides, catalysts and polymer stabilizers[1, 2]. They are also used as biocidal additives in antifouling paints for ships, boats and fishing nets[3]. Organotins, in particular tributyltin (TBT) and triphenyltin (TPT), are considered to be dangerous chemicals because of their deteriorating effects on non target marine organisms. Previous studies have demonstrated that organotin compounds are highly toxic to marine mollusks, even at very low concentrations[4-7] and that their toxicological effects are largely dependent on the number and nature of the substituents[4,7]. Organotin compounds in the environment may be degraded to inorganic tin by various chemical or biological processes[8-10]. An understanding of the toxic effects of these organotin compounds requires the distinction of all species in the environment. Consequently, the analytical methods should be capable of distinguishing organotin compounds, and sensitive enough to detect at non-effect levels.

Gas chromatography (GC) coupled with a flame photometric (FPD) tin selective detector[11] has been developed for organotin speciation, taking an advantage of the fact that several of the derivatives (e.g. tetraethyl and hydride) are volatile and amenable to GC. Thus, it was necessary to perform extraction and derivatization steps prior to the analysis. Previously, various procedures had been developed, e.g. extraction of hydrogenated organotin compounds followed by the Grignard reaction[12], simultaneous hydridization and extraction[13], solid phase extraction followed by an *in situ* alkylation step[14], aqueous alkylation followed by liquid-liquid extraction[15], and hydride generation[16,17] or ethylation[18] combined with a purge and trap system. All of the above extraction techniques are either time requiring or using large amounts of organic solvents. Extraction and derivatization based on solid phase microextraction (SPME), a simple and solvent-free technique, offers an alternative to the current methods and can minimize the problems associated with those methods. SPME is suitable for volatile and semi-volatile compounds in the aqueous phase. Analytes are adsorbed directly from the aqueous matrix or its vapor in equilibrium into the organic phase until the equilibrium is reached. The application of SPME to determine the organic species of lead[19], mercury[20-22] and tin[22-25] has been reported.

In this study, both the headspace and the aqueous phase SPME extraction and derivatization procedures were compared for the determination of butyltin compounds in sea water before GC-FPD detection. Factors that affected the performance of the headspace and the aqueous phase SPME were also evaluated.

MATERIALS AND METHODS

I. *Reagents and materials*

Monobutyltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), and

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tripropyltin chloride (TPrT, 98%) were purchased from Aldrich (Milwaukee, WI, USA). Organotin stock standard solutions (1000 mg/L) were prepared in methanol. The solutions were generally stable for 1 year under low temperature (4˚C) and dark conditions[26]. Working standard solutions were prepared by dilution with Milli-Q H_2O weekly for 10 mg/L, and daily for 100 μg/L. These solutions were stored in the dark at 4˚C. Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals (Bischheim, France). A working standard solution of $NaBEt_4$ was prepared daily by dissolving 0.05 g of $NaBEt_4$ in 5 mL of deionized water, and stored at 4˚C in the dark. The buffer solution with pH 4.8 was a mixture of acetic acid (1 M) and sodium acetate (1 M) solution. All other solvents and reagents were analytical reagent grade or better. Artificial sea water with salinity 35 psu was prepared by dissolving 35.9 g of artificial sea salts (Aqua Crafe^{TM}, Inc., CA) in 1000 mL of deionized water.

Glasswares were decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed trice with deionized water.

II. *Apparatus*

(I) *SPME device*

The manual solid phase microextraction (SPME) device was obtained from Supelco (Bellefonte, PA, USA). It includes a brown glass bottle (120 mL) with a silicone rubber septa coated with PTFE, and a fiber coated with 100 μm polydimethylsiloxane (PDMS).

III. *Sample Collection and Analysis*

Sea water samples were collected from the Suao, Keelung, Wuchi, Kaohsiung, and Hualien harbors in Taiwan in November 2001. These samples were acidified to pH 4.8 with acetic acid-sodium acetate buffer (1 M) immediately after sampling, and stored in the dark at 4˚C. Analyses were performed within one month after sample collection.

When the headspace SPME method was used to analyze sea water samples, 50 mL of sea water sample, 250 μL of internal standard (tripropyltin, 50 ng/L), and 100 μL of 1% $NaBEt_4$ solution were added into the bottle and then the butyltin compounds were ethyl derivatized and extracted to the fiber at 25˚C for 50 min. After extraction, the fiber was then inserted through the septum-sealed glass line of the GC injector for thermal desorption (10 min).

IV. *Instrumental Analysis*

The gas chromatograph (GC, Dani GC 1000, Italy) was equipped with a column (HP-5, 30 m × 0.25 mm i.d. × 0.25 μm film thickness, Hewlett Packard, USA) and a flame photometric detector fitted with a 610 nm optical filter. The fiber was then injected to the GC using the splitless mode. The column was programmed from 70˚C (1 min holding time) and was increased to 190˚C at 30˚C/min and to 270˚C (3 min holding time) at 15˚C/min, and was then increased again to a final temperature of 290˚C (1 min holding time) at 15˚C/min. The injector temperature was 250˚C, and the detector temperature was 290˚C. The carrier and make-up gas were nitrogen (99.998%). The hydrogen-rich flame consisted of hydrogen (200 mL/min) and air (200 mL/min).

V. *Analytical Procedure*

(I) *Derivatization and analysis*

During the headspace SPME sampling, a magnetic stirring bar, 48.5 mL of artificial sea water, and 1.5 mL of acetate buffer solution (pH 4.8) were placed in a 125-mL glass bottle. A 50-μL aliquot of sea water or the organotin solution, 250 μL of internal standard (tripropyltin, 50 ng/L), and 100 μL of 1% $NaBEt_4$ solution were added into the bottle which was to be closed immediately. The fiber was then drawn into the bottle, and situated at about 1 cm above the surface of the aqueous phase. The bottle was moved to a 25˚C water bath, where the solution was mixed for 50 min, allowing *in situ* $NaBEt_4$ derivatization and extraction to the fiber.

For the aqueous phase SPME sampling, a magnetic stirring bar, 120 mL of artificial sea water, 3 mL of acetate buffer solution, and a known quantity (10 ng/L) of tripropyltin as an internal standard were added to a 125-mL glass bottle. The bottle was then closed immediately. One hundred μL of 1% $NaBEt_4$ solution was spiked by syringe injection. Only about 2 mL of headspace was left in the bottle, which prevented the loss of analytes to the large headspace above. The remaining steps for the aqueous phase SPME sampling were as described similar to the SPME sampling of the headspace, except that the entire fiber was placed in the solution for 50 min. After the extraction, the fiber was then inserted through the septum-sealed glass line of the GC injector for thermal desorption (10 min).

(II) *Quantitation*

Organotin compounds were identified by assigning peaks in the samples to the corresponding peaks of the external standard (Figure 1). Tripropyltin (0.5 μg/L) was used as an internal standard. The tripropyltin-relative chromatographic responses (peak areas) of individual organotin compounds were calculated from the standard solutions prepared in artificial sea water.

RESULTS AND DISCUSSION

I. *Reproducibility, Recovery, and Detection Limits*

When a fixed concentration (0.025 μg/L for the

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headspace and 0.5 μg/L for the aqueous phase SPME method) of tripropyltin was spiked as an internal standard to sea water containing different concentrations of butyltin compounds, the relative response factor (RRF, ratio of the peak area of butyltin compound and its concentration versus the peak area of tripropyltin and its concentration) was used for correction of the analytical performance. RRF values of butyltin compounds using the headspace SPME method were 1.10 ± 0.13 to 1.79 ± 0.13. RRF values of butyltin compounds using the aqueous phase SPME method were 0.40 ± 0.01 to 0.81 ± 0.01 (Table 1).

The average recoveries of the butyltin compounds were from 95.4% to 111.7% (n = 3), with the relative standard deviation ranging from 17.7% to 22.1% for the headspace SPME method. The highest average recovery was obtained in DBT. The method detection limit (MDL) is the lowest concentration which an established method can detect a compound from the matrix under 99% confidence level. In this study the method detection limit (MDL) for MBT, DBT, and TBT were 3.5 ng/L, 3.8 ng/L, and 3.8 ng/L respectively by the headspace SPME method. While by the aqueous phase SPME method (Table 2), the average recoveries of the butyltin compounds ranged from 91.3% to 103.7% (n = 3), with the relative standard deviation between 14.6% and 24.3%. The highest average recovery was also obtained in DBT. The MDL for MBT, DBT, and TBT were 19.2 ng/L, 20.4 ng/L, and 31.7 ng/L, respectively. Thus, the MDL obtained with headspace SPME for MBT, DBT, and TBT in sea water were lower than those obtained with the aqueous phase SPME for MBT, DBT, and TBT. The relative standard deviation of the recovery rates by either headspace (17.7%-22.1%) or aqueous phase (14.6%-24.3%) extraction method was higher than the 7-10% reported by Lespes *et al*.[27] and the 2-14% reported by Jiang *et al*.[28]. The reason for the high relative standard deviation observed in this study was unclear. Components of the artificial sea salts or condition of the fibers of the SPME devices might have some effects on it.

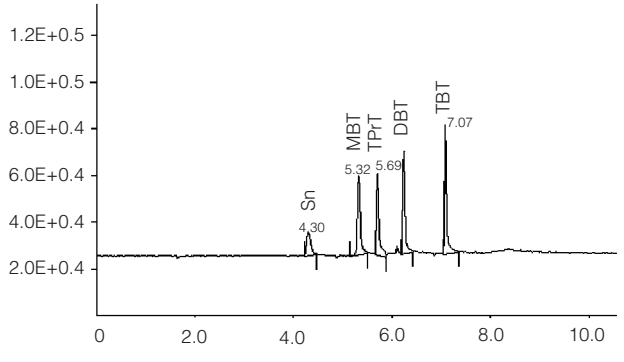

Figure 1. Chromatogram of the spiked organotin compounds followed by aqueous phase SPME-GC/FPD. Compound identification: 1, MBT; 2, TPrT; 3, DBT; 4, TBT.

II. *Effects of Temperature and Adsorption Time*

Sodium tetraethylborate derivatization was performed in order to permit the analysis of less volatile compounds such as butyltin compounds. As the derivatization reaction (for example, tributyltin $Sn(C_4H_9)_3Cl$ is ethylated to ethyltributyltin $Sn(C_4H_9)_3(C_2H_5)$) can be carried out rapidly in the aqueous phase[29,30] and the ethylated products are volatile (e.g. boiling point of $Sn(C_2H_5)_4$ is 160°C), it was expected that the ethylated products can be extracted simultaneously. In this study, the time required for ethylation and the partitioning of the butyltin derivatives between the fiber coating and the matrix using the headspace and the aqueous phase SPME extraction methods at different temperature were investigated in order to get the optimum conditions. Figure 2 shows the time profile of the in situ ethylation and

Table 1. The relative response factor (RRF) values for the butyltin compounds in sea water using the headspace and aqueous phase SPME extraction methods

Organotin	Headspace						Aqueous phase					
	Amount of organotin compounds (ng/L)					Ave. ± SD	Amount of organotin compounds (ng/L)					Ave. ± SD
	5	25	100	250	500		50	100	300	500	1000	
MBT	1.30	1.17	0.95	1.06	1.01	1.10 ± 0.13	0.82	0.82	0.81	0.81	0.81	0.81 ± 0.01
DBT	1.94	1.68	1.80	1.89	1.64	1.79 ± 0.13	0.62	0.62	0.56	0.56	0.62	0.60 ± 0.03
TBT	1.60	1.52	1.71	1.68	1.57	1.62 ± 0.08	0.37	0.37	0.42	0.41	0.41	0.40 ± 0.01

Table 2. Method detection limits and recoveries for the butyltin compounds in sea water using the headspace and aqueous phase SPME extraction methods

	Organotin	Spiked (ng/L)	Measured (n = 3) (ng/L)	Recovery (%)	MDL[a] (ng/L)
Headspace	MBT	50	47.7 ± 11.1	95.4 ± 22.1	3.5
	DBT	50	55.9 ± 8.9	111.7 ± 17.7	3.8
	TBT	50	55.4 ± 9.6	110.8 ± 19.1	3.8
Aqueous phase	MBT	500	472.0 ± 76.3	94.4 ± 15.3	19.2
	DBT	500	518.5 ± 121.5	103.7 ± 24.3	20.4
	TBT	500	456.5 ± 73.0	91.3 ± 14.6	31.7

[a]MDL: method detection limit.

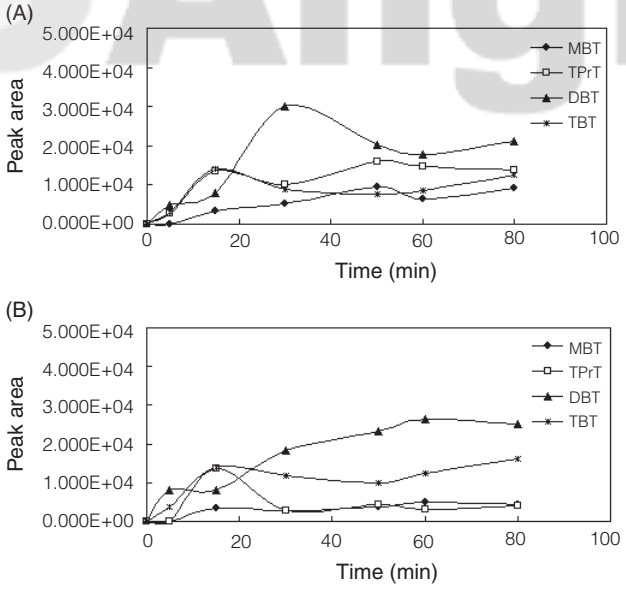

Figure 2. Time profile of the peak areas for MBT, DBT, TBT, and TPrT using the headspace SPME extraction method (A) at 25˚C (B) at 35˚C. Butyltin and propyltin compounds (0.5 ng) were spiked to 50 mL of sea water.

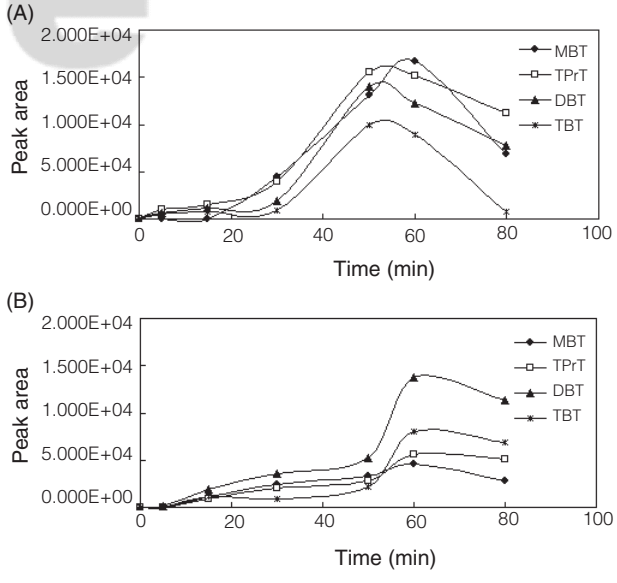

Figure 3. Time profile of the peak areas for MBT, DBT, TBT, and TPrT using the aqueous phase SPME extraction method (A) at 25˚C (B) at 35˚C. Butyltin and propyltin compounds (25 ng) were spiked to 120 mL of sea water.

extraction of MBT, DBT, TBT, and TPrT obtained by using the headspace SPME sampling method at 25˚C and 35˚C. The results indicated that different ethylated butyltin species had different reaction and extraction equilibration time. The equilibration time was approximately 50 min, 30 min, 10 min, and 10 min for ethylated MBT, DBT, TBT, and TPrT, respectively at 25˚C (Figure 2A). Gorecki and Pawliszyn[19] reported that the partition coefficient between the fiber coating and the headspace gas phase (K_1), and the partition coefficient between the gas phase and liquid phase (K_2) are involved in the extraction process in the headspace SPME mode. The total constant of the process $K = K_1 K_2$ depends on both the volatility of the compounds and the fiber affinity. The equilibration time was shorter for TBT and TPrT than for DBT and MBT. This might be because ethylated TBT and TPrT have a higher vapour pressure, and are more volatile, which let them enter the headspace and reach equilibration with the fiber faster than ethylated DBT and MBT.

No significant differences were found in the reaction and extraction equilibration time needed for the ethylated butyltin compounds at 35˚C (Figure 2B). However, the peak area of butyltin compounds obtained at 35˚C was slightly lower than those obtained at 25˚C (Figure 2). Although, when the temperature increases, analytes released from the matrix to the headspace (K_2) will increase, but the ability of the fibers to adsorb analytes (K_1) will decrease[31].

Figure 3 shows the time profile of the in situ ethylation and extraction of MBT, DBT, TBT, and TPrT obtained using the aqueous phase SPME sampling method at 25˚C and 35˚C. Reaction and extraction equilibration time needed was approximately 60 min for MBT, and 50 min for DBT, TBT, and TPrT at 25˚C (Figure 3A). The equilibration time for MBT, DBT, TBT, and TPrT was 60 min at 35˚C (Figure 3B). The hydrophobicity of MBT is lower than that of DBT and TBT, possibly results in a longer equilibration time within the fiber than other butyltin compounds. Equilibration time for the butyltin compounds at 35˚C was longer than at 25˚C. The peak area of butyltin compounds obtained at 35˚C was also lower than those obtained at 25˚C (Figure 3). This was probably due to faster desorption of butyltin compounds at higher temperature. In addition, the shorter reaction and extraction equilibration time observed from the headspace method was probably a result of faster diffusion of butyltin compounds in the vapor phase than in the aqueous phase.

III. *Linear Concentration Ranges of the Aqueous Phase and the Headspace SPME Method*

The concentration range for MBT, DBT, and TBT derivatives showing a linear ratio with the internal standard was 0-0.5 μg/L (R^2 = 0.9811) by the headspace SPME extraction method (Figure 4). The concentration range which showed linear ratio with the internal standard for MBT, DBT, and TBT derivatives was 0-1 μg/L (R^2 = 0.9956) by the aqueous phase extraction method (Figure 5). Thus the aqueous phase extraction method has wider linear range than the headspace extraction method.

IV. *Sample Analysis*

The headspace SPME method was applied to the analysis of sea water obtained from the Suao, Keelung, Wuchi, Kaohsiung, and Hualien harbors in Taiwan. Table 3

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Table 3. MBT, DBT, and TBT concentrations in sea water from 5 harbors in Taiwan (ng/L)

Sample	MBT	DBT	TBT	TBT/total butyltin
Suao	14.0 ± 2.1	<MDL	<MDL	---[a]
Keelung	5.5 ± 1.4	6.9 ± 1.1	<MDL	---
Wuchi	17.3 ± 3.8	7.5 ± 1.8	<MDL	---
Kaohsiung	51.9 ± 11.4	19.5 ± 4.1	7.8 ± 1.2	0.10
Hualien	29.7 ± 5.3	14.7 ± 3.7	7.0 ± 1.6	0.14

[a]Under detection limit.

lists the analytical results of sea water samples obtained from these harbors. Butyltin compounds in these sea water samples were in the range of 5.5-51.9, <MDL-19.5, and <MDL-7.8 ng/L, respectively. In general, MBT had the highest concentration of the butyltin compounds in the sea water, followed by DBT and TBT. In a previous report, the ratio of the TBT to total butyltin concentration of a water sample was used as an approximate measure of the extent to which the TBT has undergone degradation[30]. A higher TBT/total butyltin concentration ratio indicates little degradation of TBT or recent input of TBT to the water system. In this study we found that the TBT/total butyltin concentration in sea water samples from habors in Taiwan were 0.1-0.14, which were lower than the ratio (0.49-0.74) found in sea water in the other study[32]. This may indicate that the degradation of butyltin compounds had occurred in sea water from the habors in Taiwan.

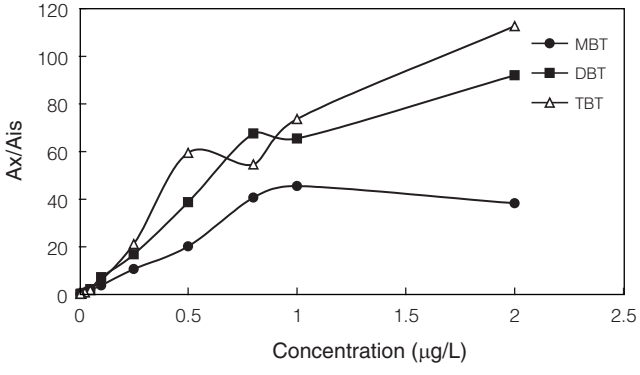

Figure 4. Profile of the linear concentration ranges for MBT, DBT, and TBT with the internal standard (TPrT) using the headspace SPME extraction method. Ethylation and extraction time was 50 min at 25˚C. Ax/Ais: the ratio of the peak area of the target compound (MBT, DBT , and TBT) and the internal standard (TPrT).

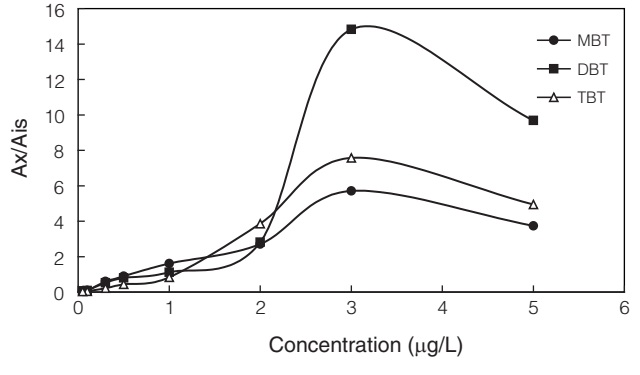

Figure 5. Profile of the linear concentration ranges for MBT, DBT, and TBT with the internal standard (TPrT) using the aqueous phase SPME extraction method. Ethylation and extraction time was 50 min at 25˚C. Ax/Ais: the ratio of the peak area of the target compound (MBT, DBT, and TBT) and the internal standard (TPrT).

CONCLUSIONS

The headspace and aqueous phase SPME methods were developed and compared for the extraction and quantitative analysis of ultra trace levels of butyltin compounds in sea water. The results showed that MDL for MBT, DBT, and TBT in sea water obtained using the headspace SPME method were lower than those obtained using the aqueous phase SPME method. Butyltin compounds in sea water from the harbors varied within 60 ng/L, which probably reflects source differences and degradation.

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