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Analysis of polychlorinated biphenyls in aqueous samples by microwave-assisted headspace solid-phase microextraction

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Abstract

The hyphenated technique namely microwave-assisted headspace solid-phase microextraction (MA-HS-SPME) was developed and studied for the simultaneous extraction/enrichment of polychlorinated biphenyls (PCBs) in aqueous samples prior to the quantification by gas chromatography (GC). The PCBs in aqueous media are extracted onto a solid-phase micro fibre via the headspace with the aid of microwave irradiation. The optimum conditions for obtaining extraction efficiency, such as the extraction time, addition of salts, addition of methanol, ratio of sample to headspace volume, and the desorption parameters were investigated. Experimental results indicated that the proposed MA-HS-SPME method attained the best extraction efficiency under the optimized conditions, i.e., irradiation of extraction solution (20 ml aqueous sample in 40 ml headspace vial with no additions of salt and methanol) under 30 W microwave power for 15 cycles (1 min power on and 3 min power off of each cycle). Desorption at 270 °C for 3 min provided the best detection results. The detection limit obtained were between 0.27 and 1.34 ng/l. The correlation coefficient for the linear dynamic range from 1 to 80 ng/l exceeded 0.99 for 18 PCBs.

Keywords: Headspace analysis; Solid-phase microextraction; Microwave-assisted extraction; Extraction methods; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs), were produced as complex mixtures for a variety of uses such as dielectric fluids, printing inks, paints, pesticides and many other applications, are a class of 209 discrete compounds in which 1–10 chlorine atoms are attached to the biphenyls [1]. The concern about PCBs arose from the finding that they were toxic. The toxicology of PCBs has been extensively studied in the subjects of lethality, inhibition of growth, immunotoxicity, carcinogenicity, and neurotoxicity [2]. PCBs are among organic compounds that can be found in polluted environmental media such as ambient air, soil, sediment, and water as well as in plant and animal tissues due to their chemical and physical stability and widespread use since 1930 [3].

The occurrences of PCBs in contaminated waters are usually in parts per trillion (ppt, ng/l) levels. Appropriate sample pre-treatments are usually re-

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quired to extract and concentrate the analytes prior to the chromatographic determination. Liquid–liquid extraction (LLE) consumes large amount of organic solvent to extract liter(s) of aqueous sample and is time consuming and labor intensive [4]. Solid-phase extraction (SPE) technique requires only relatively small amounts of solvent to elute the analytes from the sorbent. However, plugging, channeling, and large sample size used remain drawbacks to SPE [5,6] Subsequently, a new solid-phase microextraction (SPME) technology was developed to resolve some of the problems [7–10]. The direct immersion SPME (DI-SPME) technique was found to be significantly influenced by sample matrix [11]. Hence, headspace SPME (HS-SPME) was developed and applied successfully to avoid matrix interference for volatile compounds [12–14]. However, HS-SPME technique, which requires relatively long sampling times with low sensitivity and reproducibility, is still limited to semi-volatile compounds.

Microwave energy has been investigated and developed for the extraction of pollutants from environmental samples over the last decade. Microwave-assisted extraction (MAE) method has been applied in a number of sample preparation procedures [15–19]. Under the microwave irradiation, the temperature of the media containing ionic or polar species rises rapidly. Therefore, microwave heating has potential to be incorporated with headspace SPME technique. Coupling MAE and SPME, Wang et al. investigated the isolation of flavor components in food products [20], Lloyd and Grimm [21] and Zhu et al. [22] determined semivolatile off flavor compounds from catfish tissue, Wu and Hsieh [9] isolated the chlorinated pesticides from medicinal herbs, and Hernandez et al. analyzed herbicides in soil and water samples [23]. All the above procedures included two steps: the SPME fibre was directly immersed into the aqueous media or exposed to the headspace of the sample followed by MAE. Recently, an one-step MAE-HS-SPME was developed by Chen et al. [24]. This new method provides quick and solvent-less in situ extraction of analytical process to determine dichlorvos in agricultural products.

Analysis of PCBs in the aqueous sample with DI-SPME was reported by Pawliszyn and Potter, i.e., equilibration of tri- and penta-chlorobiphenyls can be reached in 60 min of the exposure of fibre to the sample media [25]. The extraction of 21 PCBs (di- to deca-CBs) were achieved using a 100-μm poly(dimethylsiloxane) (PDMS) fiber and gas chromatography–electron capture detection (GC–ECD). The maximum recoveries of PCBs were reached in 5 h after exposure of the fibre direct into the aqueous sample with stirring [26]. With the MultiSimplex optimization method, Cortazar et al. investigated the variables such as extraction time, extraction temperature, desorption time, desorption temperature, and addition of sodium chloride which affect the recoveries of analytes. The optimized condition used for direct immersion with the extraction temperature at 50 °C for 50 min and the desorption temperature at 270 °C for 2 min on a 30 ml aqueous sample containing 9 g NaCl in a 40-ml vial by using a 30-μm PDMS fibre was suggested [27]. Llompart et al. developed HS-SPME method for the determination of Aroclor in water samples [28]. The parameters studied were sampling time, volume of water, volume of headspace, temperature, and addition of salts. HS-SPME reached equilibrium about 4 h at 100 °C. The sensitivity obtained with HS-SPME was superior to the sensitivity of SPME by a factor 2. HS-SPME was also applied on the on-fibre photodegradation studies of PCBs [29,30].

In this work, microwave-assisted headspace solid-phase microextraction (MA-HS-SPME) for the determination of PCBs has been developed. Parameters affecting the adsorption of analytes onto the fibre, such as extraction time, sample volume, headspace volume, salt addition effect, and methanol addition effect, have been evaluated. The proposed MA-HS-SPME shows very good linearity and sensitivity. Water-bathed headspace solid-phase microextraction (WB-HS-SPME) and MA-HS-SPME were compared at 44, 60, and 76 min extraction periods. PCB reaches the maximum recovery according to their structure, extraction time and method.

2. Experimental

2.1. Reagents and materials

Twenty congeners of PCB 18, 28, 33, 44, 52, 70, 101, 105, 118, 128, 138, 153, 170, 180, 187, 194,

195, 199, 206 and 209 (individual solution of 35 μg/ml in isooctane) were purchased from Accustandard (New Haven, CT, USA). Iso-octane and methanol (HPLC grade) were obtained from Tedia (Nashville, TN, USA). Sodium chloride (reagent grade) was obtained from Sigma (St. Louis, MO, USA). Deionized water was produced by Nanopure water system (Barnstead, Dubuque, IA, USA). Natural river water was collected at a known site of Er-Ren River in southern Taiwan.

2.2. Preparation of standard solution

A standard mixture solution containing the 20 PCBs were prepared at 1.0 μg/ml in isooctane. Artificial aqueous PCB solutions (containing 80 ng/l of each congener) were prepared by adding 80 μl of standard mixture to 1 l of deionized water. The solution was stirred for 3 days in dark at ambient temperature before extraction. Water samples in other concentrations were prepared by dilution.

2.3. MA-HS-SPME and WB-HS-SPME procedures

A 100-μm poly(dimethylsiloxane) SPME fibre with a manual holder assembly (Supelco, Oakville, Ontario, Canada) was used. All the fibers before being used in the experiments were conditioned for 1 h in the injectors of a gas chromatograph under nitrogen stream at a desorption temperature of 250 °C. An aliquot of 20 ml of water containing PCBs was placed in a 40-ml vial which was sealed with a screw cap with a PTFE-faced septum. The fibre was exposed to the headspace over the water sample. For the MA-HS-SPME procedure, the vial was placed in a cavity of Prolabo (Soxwave 100, 2450 MHz, equipped with a programmable heating power from 0 to 300 W with 5% increment) microwave apparatus and irradiated with microwave power at 30 W for a certain number of cycles (power on for 1 min and off for 3 min in each cycle) with stirring. The assembly of MA-HS-SPME is illustrated in Fig. 1. For the WA-HS-SPME, sample vial was placed in a preheated water bath at 100 °C. To obtain the highest sensitivity of PCBs, the SPME fibre was set at 4.0 cm in depth inside the GC injector port and desorbed at 270 °C for 3 min after extraction. In order to avoid possible carryover, the fibre was kept in the GC injector with split mode for 3 min before next extraction.

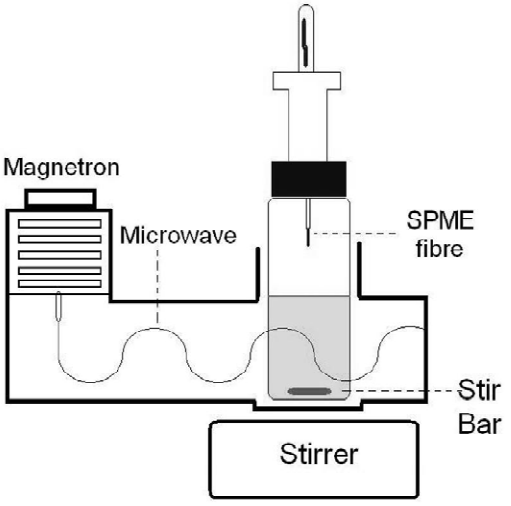


Fig. 1. Microwave-assisted headspace solid-phase microextraction assembly.

2.4. GC–ECD analysis

A Hewlett-Packard 5890 gas chromatograph, with a split/splitless injection port and an ^{63}Ni ECD system, was used for the experiments to optimize HS-SPME conditions. The injector was used in splitless mode and held isothermally at 270 °C. Separations were conducted using a HP-5MS capillary column (30 m×0.25 mm I.D., 0.25-μm film thickness, Agilent, USA). The column was held at 90 °C for 0.5 min, increased to 225 °C at a rate of 30 °C/min, ramped at 5 °C/min to 300 °C, and held for 13 min. The ECD system was maintained at 300 °C. The carrier gas was nitrogen at a flow-rate of 0.7 ml/min and the flow-rate of the make-up gas was 18 ml/min with nitrogen.

3. Results and discussion

In order to optimized the GC–ECD analysis conditions and MA-HS-SPME sampling conditions, factors potentially affecting the extraction efficiency, such as the desorption time, the desorption temperature, depth of fibre inside the GC injector, the

duration of extraction, the ratio of the sample volume to headspace volume, and the additions of sodium chloride and methanol were studied.

3.1. Thermal desorption condition

To obtain the highest response signals of the GC–ECD analysis, the thermal desorption conditions of PCBs from PDMS fibre in the GC injection port was optimized. The optimized conditions (illustrated in Fig. 2) consisted of 3 min desorption time with the fibre depth of 4.0 cm in the injector at 280 °C (in order to protect the SPME fibre as suggested by the manufacturer, lower desorption temperature is preferred, 270 °C was applied to all the experiments). Upon completion of the first analysis, the fibre was re-inserted into the injector and desorbed for another 9 min: residual PCBs detected were less than 0.7% of the first analysis.

3.2. Extraction temperature profile of MA-HS-SPME

Owing to the lack of a temperature controller for the microwave equipment used in this study, the microwave irradiation time for power on and off was tested to maintain the extraction temperature around 100 °C. It was found that with the 30 W power on for 1 min and power off for 3 min in each cycle, the temperature rose and was maintained between 92 and 103 °C after 36 min (nine cycles).

3.3. Extraction time profile

The extraction time profile between 1 (4 min) to 25 (100 min) cycles of microwave irradiation described above for MA-HS-SPME was studied. It indicates that the number of microwave irradiation cycle to reach the maximum response for PCBs are nine cycles for tri- and tetra-chlorinated, 13–17 cycles for penta- and hexa-chlorinated, and 19–21 cycles for hepta-, octa-, nona-, and deca-chlorinated congeners. PCBs are a class of compounds that behave similarly as a function of the number of chlorine substituents. Thus, seven congeners were selected, one from each homolog (3–9 Cl-CB), to represent the extraction time profile as shown in Fig. 3. The microwave irradiation cycles needed for the maximum extraction might be due to the vapor pressure and structure of the analytes under this non-equilibrium partition mechanism. In general, the higher the vapor pressure of the analyte the less microwave irradiation needed to achieve highest response. Owing to the different extraction profiles

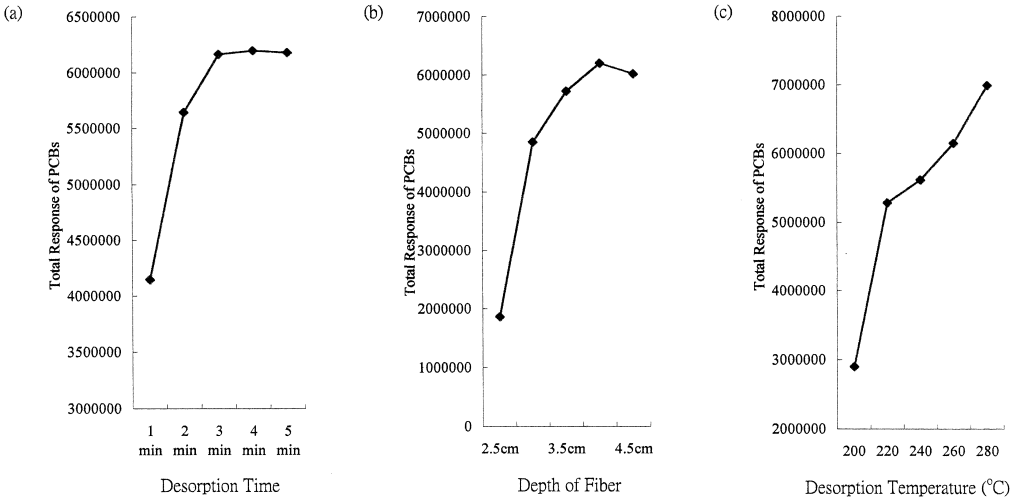


Fig. 2. Influence of time, depth of fibre, and temperature on the desorption of PCBs from SPME fibre in the injection inlet of gas chromatograph. Conditions: (a) at 270 °C in depth of 4.0 cm; (b) at 270 °C for 3 min; and, (c) in depth of 4.0 cm for 3 min. *Headspace SPME before desorption was performed on the following conditions: 20 ml of 80 ng/l PCB in distilled water was extracted at 100 °C for 60 min.

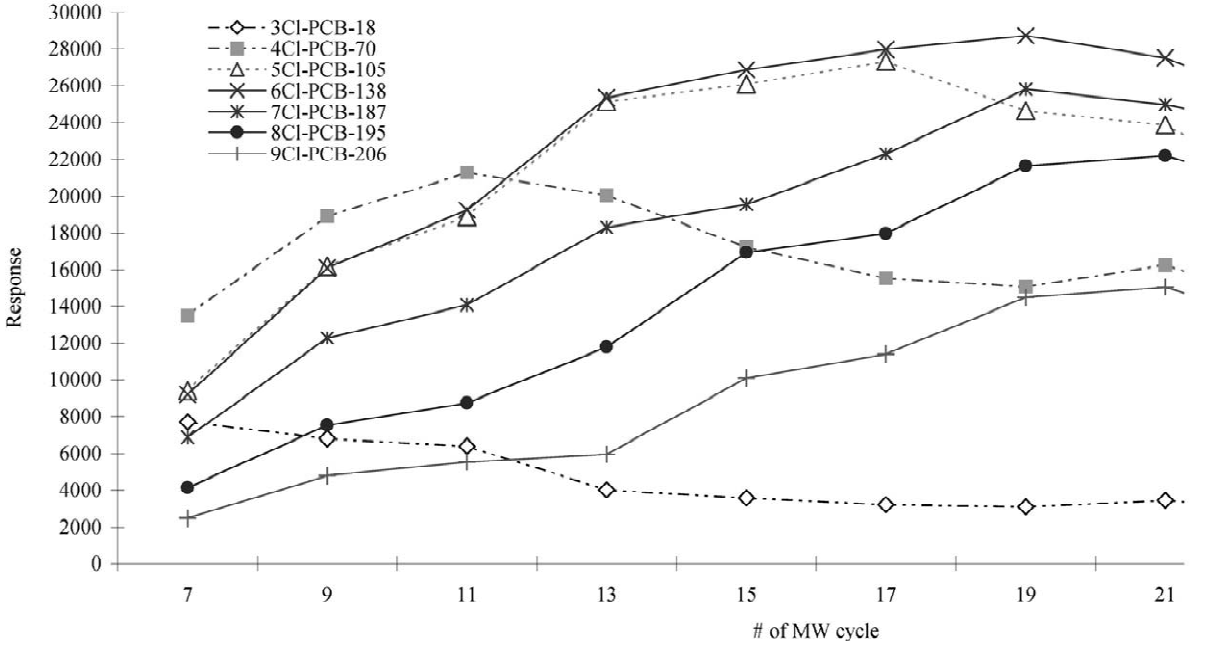


Fig. 3. Extraction time profiles of PCBs by microwave-assisted headspace solid-phase microextraction.

of the 20 PCBs, 15 cycles of the irradiation were selected for the further experiments.

3.4. MA-HS-SPME versus WB-HS-SPME

In the results reported by Llompart et al., HS-SPME reaches maximum extraction efficiency in 4 h at 100 °C on the extraction of Aroclor 1260 (containing >93% of penta-, hexa- and hepta-CBs) [28]. In order to make a comparison between MA-HS-SPME and WB-HA-SPME, experiments of 11-, 15-, and 19-cycles by microwave-irradiated process were compared against the results of 44-, 60-, 76-min water-bath methods and the results are presented in Table 1. With short extraction time (11 cycles, 44 min), lower MW PCBs (PCB 18–101 in elution order), have significantly higher extraction yields by MA-HS-SPME than by WB-HS-SPME. With longer extraction time (19 cycles, 76 min), the results are reversed, i.e., higher MW congeners (128–209) have better yields by MA-HS-SPME than by WB-HS-SPME. The ratio of the signal response of PCB 18 between microwave-assisted and water-bath methods was 1.52 at 44 min extraction and that of PCB 209

Table 1
Comparison of extraction efficiency between MA-HS-SPME and WB-HS-SPME

PCB no.	Ratio of extracted PCBs between MA-HSSPME and WB-HSSPME		
	MA 11 cycles	MA 15 cycles	MA 19 cycles
	WB 44 min	WB 60 min	WB 76 min
18	1.52	0.57	0.55
28	1.57	0.59	0.50
33	1.40	0.63	0.61
52	1.45	0.68	0.60
44	1.41	0.78	0.69
70	1.49	0.89	0.80
101	1.41	0.92	0.90
118	1.22	1.00	1.11
153	1.17	1.05	1.17
105	1.11	1.05	1.22
138	1.09	1.07	1.26
187	1.06	1.09	1.28
128	0.96	1.12	1.42
180	0.91	1.12	1.54
199	0.89	1.19	1.55
170	0.85	1.16	1.65
195	0.78	1.21	1.77
194	0.72	1.38	1.87
206	0.73	1.32	1.82
209	0.75	1.25	1.92

was 1.92 at 76 min extraction. According to the profile presented in Fig. 3, analysis of tri- and tetra-CBs can be accomplished in 40 min with maximum sensitivity by MA-HS-SPME. Among the six conditions (three microwave and three water-bath), the 76 min (19-cycle) microwave irradiation method provides the best extraction efficiency for the congeners containing 5 to 10 chlorine atoms (Table 1 and Fig. 3).

3.5. Effect of sample volume to headspace volume ratio

The effect of water sample volume to headspace volume ratio was investigated. Two sets of experiments, by MA-HS-SPME at 15 cycles and WB-HS-SPME at 60 min, were conducted using 40-ml vials with different ratios of sample volume to headspace volume (at constant concentration of PCBs); 5 ml/35 ml, 8 ml/32 ml, 10 ml/30 ml, 20 ml/20 ml, and 25 ml/15 ml. The recoveries are listed in Table 2. The smaller the ratio of sample volume to headspace volume, the higher the recovery observed in the results by WB-HS-SPME method. Similar trends were also observed in MA-HS-SPME for volume ratios of 5 ml/35 ml to 20 ml/20 ml. However, the recoveries increased for all the congeners at the ratio of 25 ml/15 ml. Signal response and recovery against the volume ratio for three PCBs representing light, moderate, and high-molecular mass (PCB 28, 138, and 194) was plotted in Fig. 4. Although the recovery is higher for smaller ratios of sample volume to headspace volume, the overall response is lower than those using higher sample volumes. The 25 ml/15 ml ratio gave the highest signal response. However, during the experiment, the water vapor condensation on the fibre was observed. The aqueous film may have prevented the interaction of the analytes with the fibre thus causing the failure of the experiment.

Table 2
Dependence of extraction recoveries of PCBs on the sample and headspace volume

	Recovery (%)									
	MA-HS-SPME, volume ratio[a]					WB-HSSPME, volume ratio[b]				
	5/35 ml	8/32 ml	10/30 ml	20/20 ml	25/15 ml	5/35 ml	8/32 ml	10/30 ml	20/20 ml	25/15 ml
PCB-18	8.4	6.3	5.3	3.9	4.5	14.2	12.5	9.7	6.9	6.2
PCB-28	7.3	6.0	5.1	4.1	4.9	14.8	12.0	9.4	7.1	6.7
PCB-33	10.1	7.8	6.5	4.9	5.7	15.8	13.2	10.2	7.8	7.3
PCB-52	15.7	10.5	8.6	6.5	7.3	19.3	14.4	12.5	9.6	9.0
PCB-44	12.6	11.8	10.0	7.7	8.7	19.1	15.7	12.7	9.9	9.0
PCB-70	13.3	11.8	10.4	8.5	9.6	19.9	14.9	12.7	9.6	9.1
PCB-101	14.9	11.8	10.5	8.8	9.7	21.6	14.3	12.3	9.6	9.3
PCB-118	17.9	13.6	12.6	10.4	12.2	26.1	16.2	14.0	10.4	10.2
PCB-153	17.9	12.8	11.9	10.2	12.3	25.7	14.7	13.0	9.8	9.6
PCB-105	19.8	15.4	14.2	11.7	13.7	25.8	17.5	15.7	11.1	10.9
PCB-138	18.3	14.4	13.5	12.0	14.5	27.0	16.4	15.0	11.2	11.1
PCB-187	17.1	12.4	11.6	10.7	13.7	25.2	14.0	12.6	9.8	9.9
PCB-128	21.0	16.3	15.3	13.2	15.9	27.1	17.7	16.7	11.8	11.8
PCB-180	20.6	13.2	12.3	11.4	15.3	27.8	14.7	13.9	10.2	10.3
PCB-199	18.3	11.9	10.3	11.3	14.1	23.4	12.2	12.4	9.5	9.8
PCB-170	20.7	13.5	12.5	11.9	15.9	25.8	14.7	14.9	10.3	10.6
PCB-195	17.5	10.2	9.5	9.9	13.9	19.8	10.9	11.6	8.2	8.4
PCB-194	18.7	9.9	9.1	8.8	12.5	16.0	8.7	9.4	6.4	6.5
PCB-206	14.8	7.1	7.0	6.9	9.3	12.0	6.7	7.6	5.2	5.3
PCB-209	11.6	4.8	5.7	5.4	6.1	11.6	5.8	6.5	4.3	4.4

*At constant sample concentration.
[a] Extraction condition: 15 cycles of microwave irradiation.
[b] Extraction condition: water bath at 100 °C for 60 min.

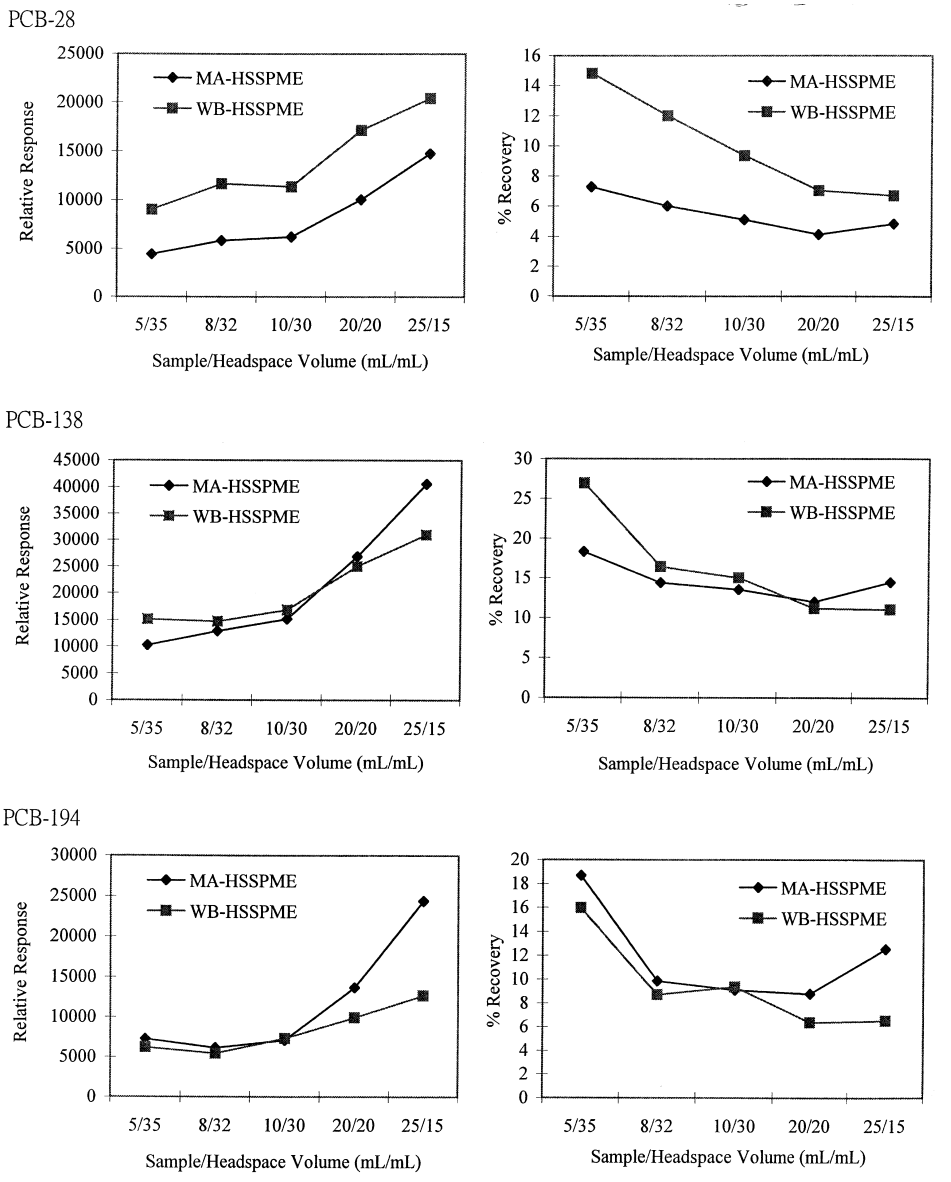


Fig. 4. Dependence of extraction efficiency expressed in terms of signal response and percent recovery on the sample to headspace volume ratio at constant concentration.

3.6. Addition of salt and methanol

Addition of salt often improves efficiency in conventional extraction processes. Enhancement of the extracted quantity was observed in the addition of ionic salts to sample solution in the DI-SPME [13,31]. In some studies, no direct relation between extraction efficiency and salt addition was proven [32–34]. Sodium chloride at various concentrations (from 0 to 20%) was added to the water sample to observe its effect on extraction efficiency. Fig. 5 shows the profile of the effect of salt addition on the

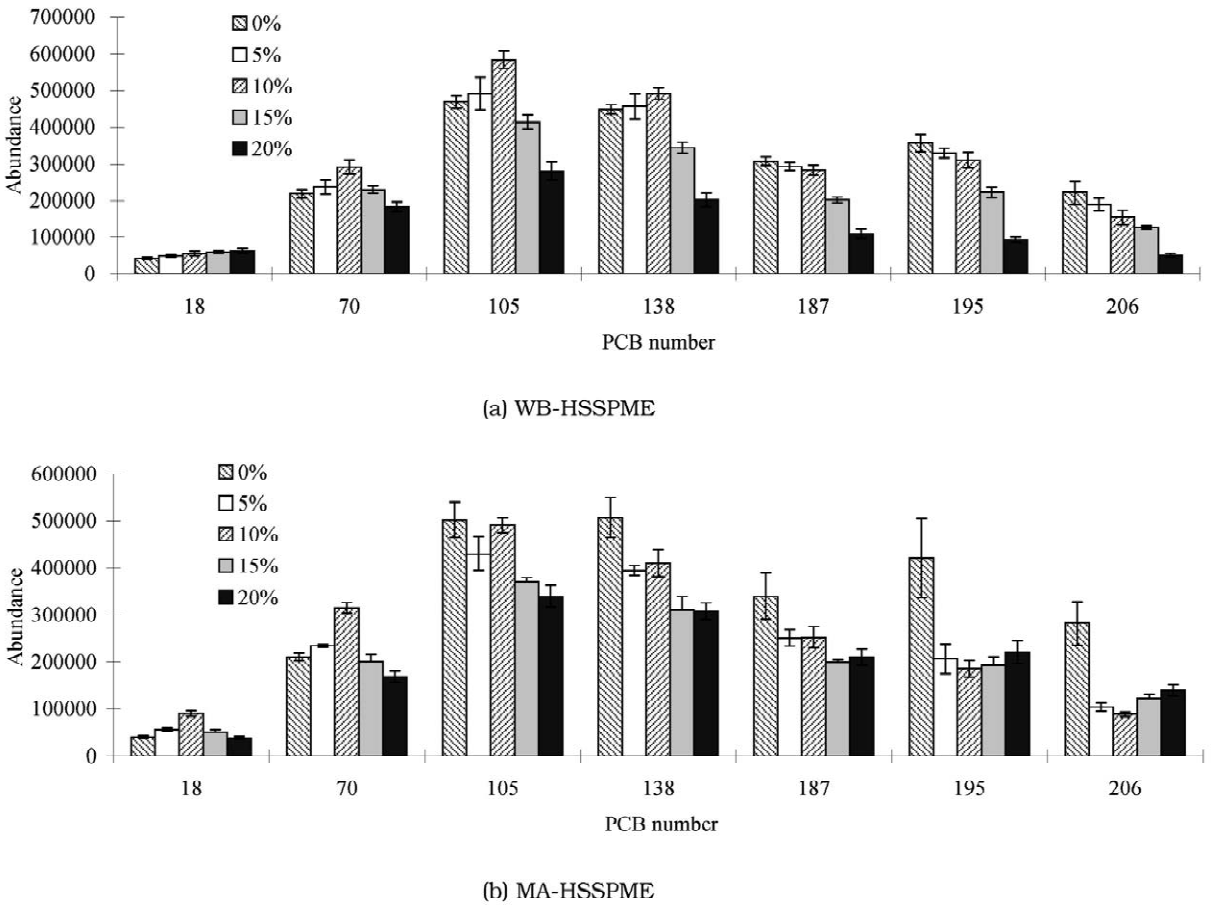


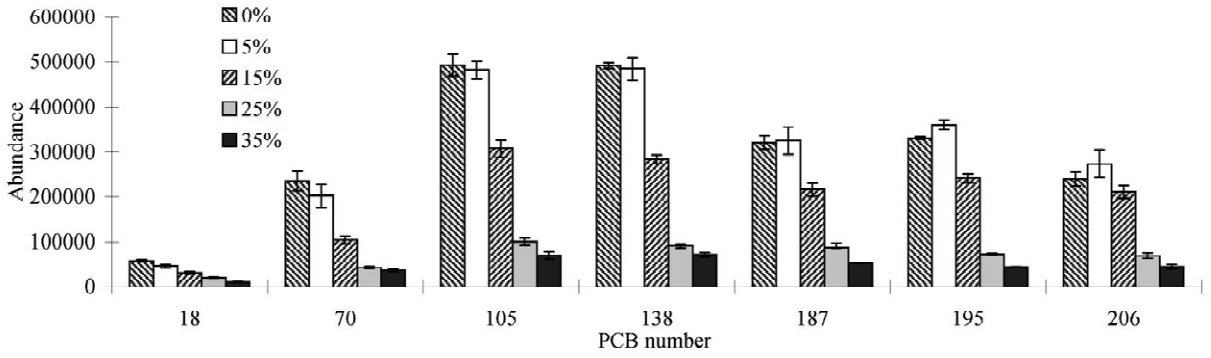
Fig. 5. Effect of sodium chloride addition to the PCBs extraction efficiency by (a) WB-HS-SPME and (b) MA-HS-SPME.

extraction efficiency. An increase of the extraction efficiency was observed for low MW congeners at the 10% addition of salt by both MA-HSSPME (observed increase on tri- and tetra-CBs) and WB-HS-SPME (observed on tri- to hexa-CBs) methods. However, with the addition of salt, a significant decrease in the extraction efficiency was observed on high MW congeners by the microwave irradiation technique. Hence, salt addition for the extraction is not recommended.

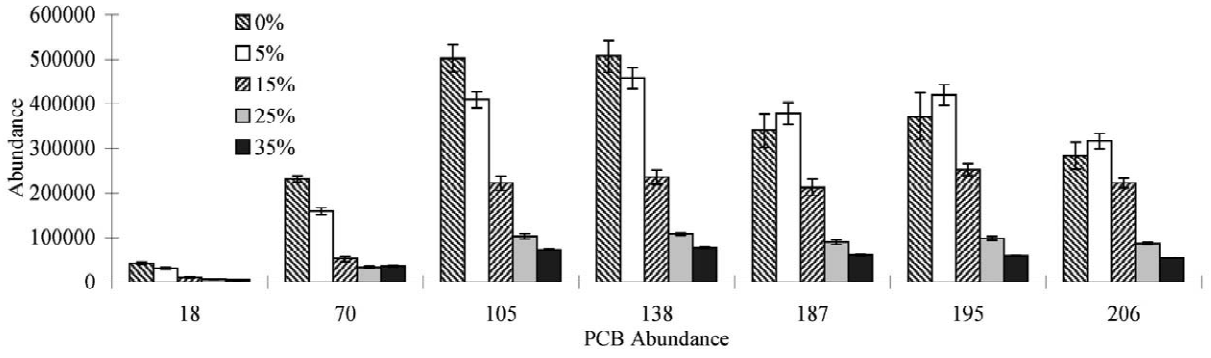
Glass adsorption of the solutes might give an unsatisfactory recovery in the extraction using sorptive technique. Adding a small portion of organic solvent is an effective way of minimizing this effect, which might be particularly pronounced in the analysis of apolar compounds in water [35,36]. For this work, water samples were modified by the addition of 5, 15, 25, and 35% of methanol. The results are shown in Fig. 6. Both extraction techniques show similar trends. In general, the extraction efficiency of PCB 18–128 (in elution order) decreases with the addition of methanol and that of PCB 180–209 increases with the best efficiency achieved at 5% addition of methanol. The overall, trend suggests the addition of methanol does not significantly improve the recovery of the congeners.

3.7. Validation of the method

The MA-HS-SPME extraction condition using 20 ml of water sample in a 40-ml vial with 15-cycle microwave irradiation was used to test the applicability of the proposed method for quantitative determination of aqueous PCBs. A calibration study was performed by spiking deionized water with PCBs to give 1, 10, 20, 40, and 80 ng/l. The



(a) WB-HSSPME



(b) MA-HSSPME

Fig. 6. Effect of methanol addition to the PCBs extraction efficiency by (a) WB-HS-SPME and (b) MA-HS-SPME.

five-point calibration curve was found to have good linearity with correlation coefficient greater than 0.985 for all analytes (in which 15 of the 20 PCBs are greater than 0.995). The detection limit of the 20 PCBs, which were calculated using three times the average background noise level divided by the slope of calibration plot, ranged from 0.27 to 1.34 ng/l.

Because of lack of availability of the reference PCB-contaminated aqueous samples, a natural water sample was collected from a river in southern Taiwan. No PCB was found in the river water by the proposed microwave irradiation method. Therefore, spiked samples, at concentrations of 10, 20, 40, and 80 ng/l, were prepared by adding the PCBs standards onto the river water which were agitated for 3 days at ambient temperature before extraction took place. Relative recoveries calculated on the basis of MA-HS-SPME for the spiked standard water sample are listed in Table 3. Large relative standard deviations (RSD) were observed in low concentration samples for recoveries of the first five eluted congeners (PCB 18, 28, 33, 52, and 44) due to interference as shown in Fig. 7. The recoveries of PCB 70 to 170 in the spiked river water, with RSD ranged from 8 to 16%, were in a good agreement with those in the standard aqueous water samples. Relatively lower recoveries were found in higher chlorinated congeners (PCB 194, 206, and 209) which may be due to the matrix interference, the adsorption of analyte onto the suspended particulate, or other interaction of analyte with sample matrix in the real water.

4. Conclusion

Determination of PCBs in aqueous sample by the proposed MA-HS-SPME coupled with GC–ECD has

Table 3
Relative recoveries of PCBs from the spiked river water

Retention time (min)	Congener number	% Relative recovery (RSD, %, $n=3$) on the basis of spiked deionized water			
		Spiked level			
		80 ng/l	40 ng/l	20 ng/l	10 ng/l
7.24	PCB-18	67(23)	62(25)	57(31)	57(29)
7.97	PCB-28	101(18)	101(13)	127(21)	143(33)
8.14	PCB-33	122(15)	107(21)	151(26)	156(27)
8.57	PCB-52	137(13)	122(18)	127(17)	137(38)
9.03	PCB-44	112(11)	125(13)	136(15)	138(21)
9.97	PCB-70	111(15)	118(12)	116(13)	114(16)
10.75	PCB-101	116(10)	108(8)	110(11)	121(19)
13.06	PCB-118	113(16)	115(13)	106(11)	107(15)
13.95	PCB-153	108(11)	113(7)	115(9)	114(13)
14.16	PCB-105	109(9)	116(12)	123(17)	101(16)
15.11	PCB-138	104(13)	111(10)	106(15)	95(14)
15.79	PCB-187	101(14)	109(8)	104(12)	94(10)
16.25	PCB-128	99(8)	110(11)	110(14)	97(9)
17.88	PCB-180	96(11)	99(15)	108(9)	94(11)
18.42	PCB-199	97(16)	96(18)	103(16)	94(21)
19.10	PCB-170	88(12)	106(14)	114(10)	98(13)
20.87	PCB-195	80(8)	103(10)	101(13)	93(18)
21.63	PCB-194	72(13)	77(12)	82(11)	76(15)
23.09	PCB-206	66(11)	77(10)	68(16)	65(17)
24.26	PCB-209	61(9)	67(13)	70(15)	69(18)

Extraction condition: 20 ml aqueous sample in a 40-ml vial irradiated by microwave for 15 cycles at 30 W of power.

been described. The developed method provides acceptable sensitivity, precision and linearity in a wide range of concentrations with the detection limit at sub-nanogram per liter of sample. In most of the environmental sample analyses, a group of pollutants are extracted and determined simultaneously. The time required to reach the equilibrium condition for maximum signal response is analyte dependent and usually takes hours to achieve for semi-volatile analytes. To keep sampling times reasonably short, working in non-equilibrium condition was suggested: the basis of the established dynamic HS-SPME model indicates that in non-equilibrium and non-steady-state mass transfer conditions a proportional relationship exists between the adsorbed analyte and its initial concentration in the sample matrix [37]. The situation of the described MA-HS-SPME is even more complex due to the fluctuation in temperature (the gas temperature sensor of the microwave equipment could not be incorporated with the HS-SPME assembly for the experiment) during the extraction process, non-continuous microwave power supply, and changes of the dielectric behavior of the sample matrix at different temperature. However, a linear relation between extracted analytes and their initial concentrations was observed. The MA-HS-SPME apparatus equipped with an appropriate temperature sensor to control the temperature more precisely might improve the performance of this technique. The proposed method is viable and shows slightly better extraction efficiency than conventional heating techniques.

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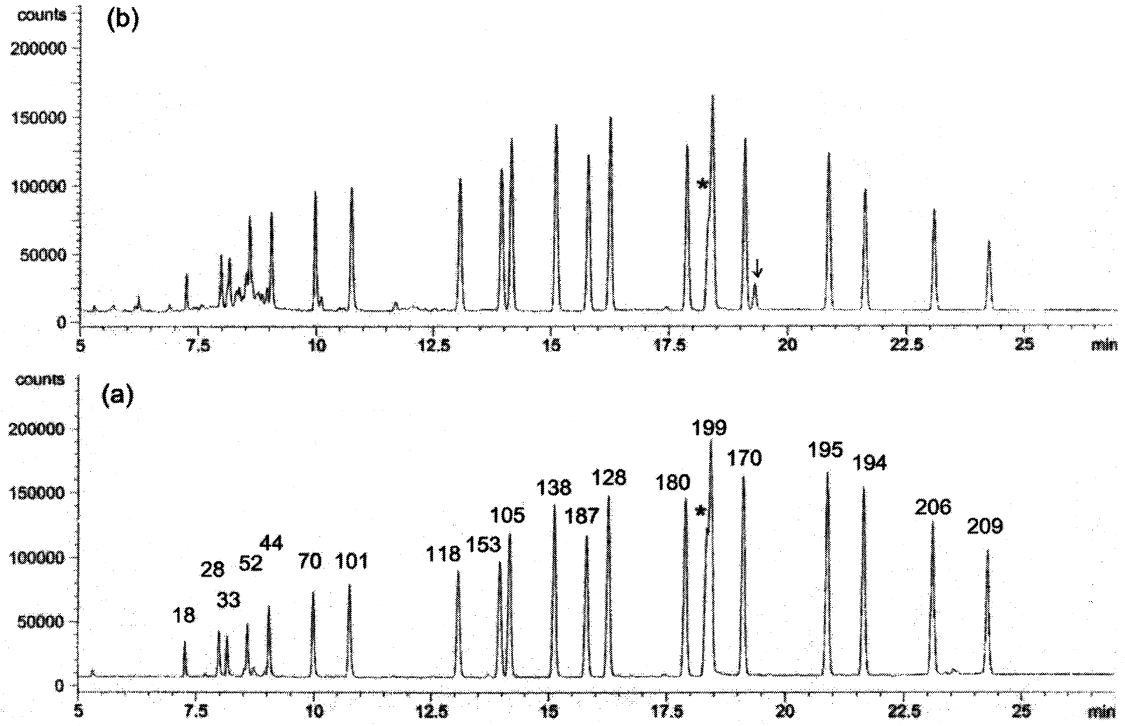

Fig. 7. Chromatograms of MA-HS-SPME of PCBs spiked (a) deionized water sample and (b) river water sample (*, SPME artifact; ↓, signal observed in un-spiked river water).

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