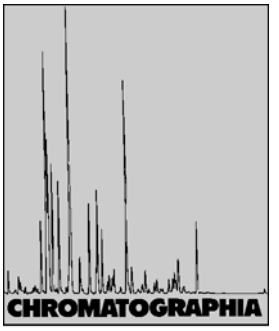
Determination of Aqueous Chlorophenols by Microwave-Assisted Headspace Solid-Phase Microextraction and Gas Chromatography



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Key Words

Gas chromatography
Electron-capture detection
Microwave-assisted headspace solid-phase microextraction
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Summary

A pretreatment technique denoted microwave-assisted headspace solid-phase microextraction (MAHS-SPME) has been designed and studied for one-step in-situ sample preparation before analysis of aqueous chlorophenols (CP). The aqueous CP are extracted on to a solid-phase microextraction fiber directly in the headspace with the aid of microwave irradiation. After collection on the SPME fiber the CP were desorbed in a GC injection port and analyzed by gas chromatography with electron-capture detection (GC-ECD). Experimental conditions (pH, addition of salt to the sample solution, microwave power and irradiation time, and temperature and time of desorption) were optimized to obtain the most efficient extraction. The results indicated that the highest extraction efficiency (recovery > 93%) and lowest *RSD* (< 8.0%) were obtained by irradiation of sample solution at pH 2 with medium-power microwaves for 5 min, and desorption at 300 °C for 3 min. Detection limits were approximately 0.1 to 2.0 μg L^{-1}. The proposed method is a very simple, rapid, and solvent-free procedure for collection of CP from complicate sample matrixes. Its application was illustrated by the analysis of trace CP in landfill leachates.

Introduction

Chlorophenols (CP) have been widely used for many agricultural, pharmaceutical, and industrial purposes, e. g. as preservative agents, pesticides, antiseptics, disinfectants, and as intermediates in chemical production [1]. They are, therefore, commonly found in contaminated surface and groundwater. In Canada CP have been found in pulp wastewater and as groundwater pollutants [2–5]. In Taiwan serious CP pollution of soil and water have been reported and are causing great concern. As a result of this extensive contamination toxic and carcinogenic chemicals such as phenol, 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP) are listed as priority pollutants by the USEPA [6–9] and a rapid, convenient, accurate, and sensitive method is required for their detection in environmental samples.

Many methods based on chromatographic techniques, including HPLC-UV [10, 11], GC-MS [12, 13], GC-ECD [14, 15], and HPLC with electrochemical detection, have been proposed for determination of CP in water, soil, or urine [16, 17]. Before chromatographic measurement, appropriate sample pretreatment is usually required for clean up or to preconcentrate the target species. Previous publications have proposed the use of a variety of extraction techniques for CP in water, including liquid-liquid extraction [14] and solid-phase extraction [17]. Although these conventional methods of extraction are efficient and precise, they are relatively time-consuming, hazardous to health (because of the use of organic solvents), and highly expensive (because of the cost of disposal of solvents) [18]. Solid-phase microextraction was, therefore, developed to resolve some these problems [19–26]. Pawliszyn et al. [21, 27] first applied SPME to the analysis of CP in water. The efficiency of extraction of CP was subsequently found to be significantly affected by the matrix of sewage samples [27]. Lee et al. [12] investigated conditions for optimum SPME of CP in landfill leachates and then analyzed the compounds by GC-MS. They reported that the matrix not only hampered diffusion of CP to the coating, but also inhibited absorption of CP by the fiber. Although extension of the extraction time has been proposed to compensate for these problems, this is, again, time-consuming. Headspace SPME (HS-SPME) was developed to avoid matrix effects, and has been applied successfully [23, 28, 29]; it is, however, suitable

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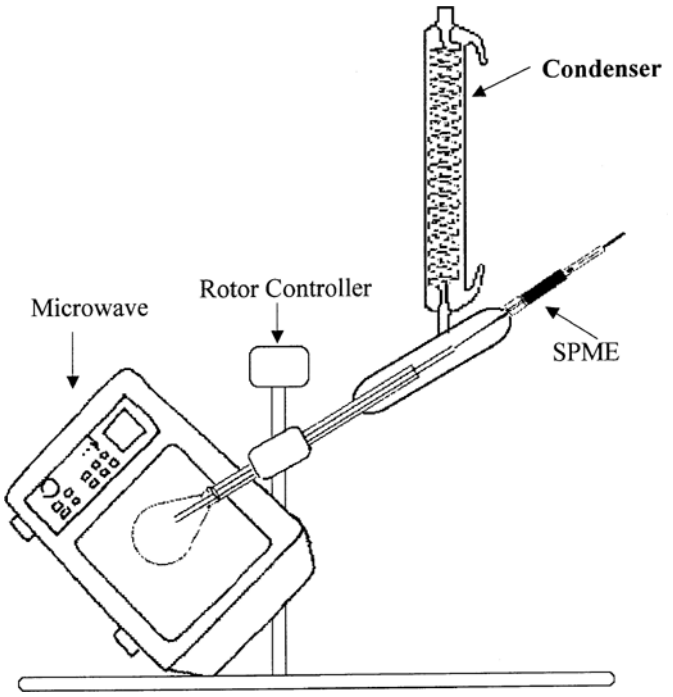

Figure 1. Schematic diagram of the MAHS-SPME apparatus.

for volatile analytes only, or sampling takes a long time and sensitivity and reproducibility are moderate – headspace sampling is limited to semi-volatile organic compounds.

In the last decade microwave energy has been investigated and widely applied in analytical chemistry to accelerate sample digestion, extraction, and the rate of chemical reactions [30–32]. As a result of the dipole rotation and ionic conductance of polar substances or ionic species under the action of microwave irradiation, the temperature of the system increases very quickly. Microwave heating also has the potential to improve SPME sampling for organic compounds, and Wang et al. [33] first combined solid-phase microextraction with microwave-assisted extraction (MAE) to investigate the isolation of flavor ingredients from food products. Hernandez et al. [34] subsequently isolated herbicides from soil and water samples and Ho et al. [35] then reported the successful isolation of organochlorine pesticides from medicinal plants. These workers used a two-step procedure, immersion of the fiber into the aqueous solution then MAE. Zhu et al. [36] used microwave-mediated distillation with SPME to determine off-flavors in catfish tissue. The fiber was immersed in the condensate to achieve sample collection.

In this study microwave energy has been used for the first time to assist one-step in-situ headspace sampling of semi-volatile organic compounds (in this work CP) by use of an SPME fiber. Microwave-assisted HS-SPME (MAHS-SPME) combined with GC-ECD has been systematically investigated to develop a simple, rapid, and solvent-free procedure for analysis of CP in wastewater.

Experimental

Chemicals and Reagents

Deionized water for all aqueous solutions was produced by means of a Barnstead Nanopure water system (Barnstead, New York, USA). All chemicals and solvents were of ACS reagent grade. 2,4-Dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) were obtained from Aldrich (Milwaukee, WI, USA), 2,4,6-trichlorophenol (2,4,6-TCP) was from TCI (Tokyo, Japan), and 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) was from Riedel-de-Häen (Hannover, Germany). Standard stock solutions (1.0 mg mL^{-1}), prepared by dissolving 0.100 g in 100 mL methanol (Mallinckrodt, Kentucky, USA), were stored at 4 °C in silanized brown glass bottles with Teflon-lined caps. Fresh working solutions were prepared by appropriate dilution of the stock solutions with methanol. Sodium chloride and sodium hydroxide were from Riedel-de-Häen. Hydrochloric acid (36.4%) was from J.T. Baker (Phillipsburg, USA). A real leachate sample was collected from Taichung landfills.

GC-ECD

Gas chromatography was performed with a Chrompack (Middelburg, Netherlands) 9000 instrument equipped with an electron-capture detector (ECD, ^{63}Ni) and a split/splitless injector. Compounds were separated on a 30 m × 0.25 mm i. d. fused-silica capillary column coated with a 1.0 μm film of DB-5 (J&W Scientific, Folsom, CA, USA). The oven temperature was held at 60 °C for 1 min after injection then programmed at 30° min^{-1} to 180 °C, which was held for 1 min, then at 10° min^{-1} to 260 °C, which was held for 1 min, and finally at 20° min^{-1} to 300 °C, which was held for 5 min. The injector was used in splitless mode and held isothermally at 300 °C for CP desorption (3 min). The ECD was maintained at 320 °C. The carrier gas was nitrogen at a flow rate of 1.0 mL min^{-1}; the make-up gas was nitrogen at 35 mL min^{-1}; and the flow rate for the purge gas was 15 mL min^{-1}. A Chem-Lab (Taipei, Taiwan) data system was used to acquire the chromatogram and perform data calculation.

Microwave-Assisted Solid-Phase Microextraction

The microwave oven used in this work was a modified version of the Tatung (Taipei, Taiwan) 2450 MHz TMO-2030P domestic oven with a maximum power of 650 Watts. It was equipped with a cooling condenser connected to tap water and after modification the microwave power was 11, 132, 160, or 210 W for weak, medium, medium high, and high irradiation, respectively. To keep the headspace volume as small as possible a glass tube was used as a seal and to guide the vapor to the SPME fiber. The arrangement used for sampling is shown in Figure 1.

The SPME device, comprising the holder and fiber assembly for manual sampling, was obtained from Supelco (Bellefonte, PA, USA) and was used without modification. The fibers selected in this study were 1-cm long and coated with polyacrylate (film thickness 85 μm). The fibers were conditioned under nitrogen in the hot injection port of the GC at 300 °C for 2 h before use. The needle on the SPME manual holder was set at its maximum length of 4-cm in the GC injector port. A desorption temperature of 300 °C for 3 min was used obtain the highest sensitivity for CP. All analyses were performed

with a 50-mL bottle, with ground-glass connection, containing 20 mL solution. To find the optimum microwave and SPME conditions aqueous solutions (20 mL) at pH 2.0 were spiked with standard solutions (200 µL) of 2,4-DCP (100 µg mL^{-1}), 2,4,6-TCP (8 µg mL^{-1}), 2,3,4,6-TeCP (4 µg mL^{-1}), and PCP (4 µg mL^{-1}).

Results and Discussion

To optimize MAHS-SPME sampling and GC-ECD analysis, conditions affecting sampling efficiency, e. g. microwave heating power and irradiation time (fiber absorption time), pH of sample solution and the amount of salt added, and desorption temperature and time, were studied thoroughly.

Optimization of Microwave Irradiation Conditions

In this study microwave-assisted heating combined with HS-SPME was used to isolate semi-volatile CP from a complex water sample. Conditions affecting heating, including microwave irradiation power and irradiation time, were investigated. Figure 2 shows the dependence of CP recovery by the MAHS-SPME fiber on irradiation time at medium power. It is apparent that recoveries of 2,4,6-TCP, 2,3,4,6-TeCP, and PCP increase with time and become constant after irradiation for 5 min whereas for 2,4-DCP the recovery passes through a maximum at 5 min, indicating that 2,4-DCP might be lost if the irradiation time is longer than this, because of the greater volatility of CP. Figure 3 shows the dependence of CP recovery on microwave irradiation power for an irradiation time of 5 min. It is clear that medium-power irradiation results in higher recovery than weak, medium high, and high-power irradiation. It also apparent that medium-high- and high-power irradiation would lead to loss of CP to an extent depending on their volatility. Microwave irradiation at medium power for 5 min was, therefore, used to assist HS-SPME sampling.

Fiber Selection and Microwave-Assisted Headspace Extraction

Because the CP studied are polar species, the polar polyacrylate fiber was selected

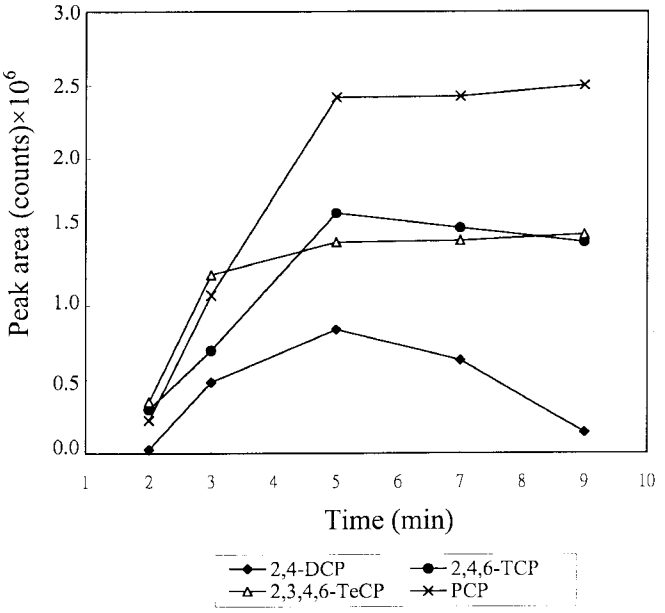

Figure 2. Dependence of recovery of CP on irradiation time at medium microwave power.

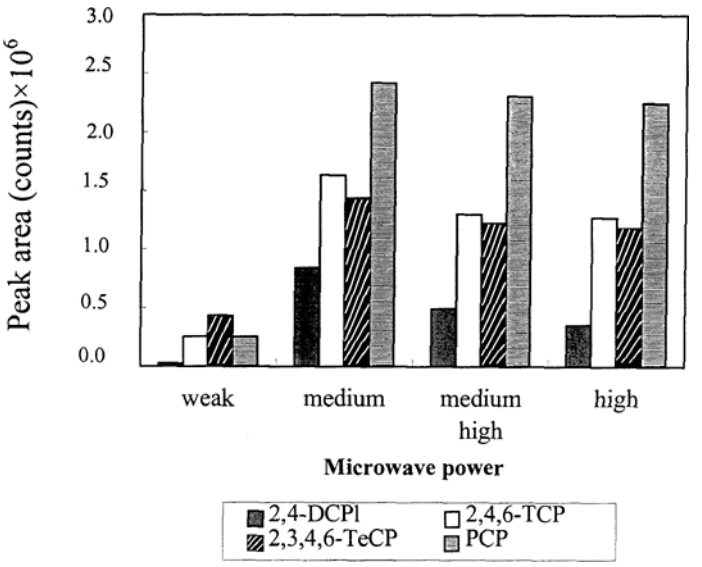

Figure 3. Dependence of recovery of CP on microwave irradiation power for 5-min irradiation time.

for extraction. The HS-SPME extraction process involves dynamic partition among the SPME fiber, headspace, and sample solution. Because HS-SPME sampling was combined on-line with microwave irradiation the rapid increase in temperature increases the vapor pressures of the CP, promoting absorption of the CP by the fiber. As shown by Figure 2, exposure of the fiber to the headspace for 5 min resulted in maximum absorption of the CP under the action of medium-power microwave irradiation. It is worth remarking that the quantity absorbed by the fiber did not increase significantly after microwave irradiation, so the fiber was withdrawn from the sampling assembly and injected into the GC-ECD system immediately after 5-min exposure in the headspace during microwave irradiation.

Thermal Desorption Temperature and Desorption Time

For optimum separation efficiency and resolution, it is possible that a minimum time is required for thermal desorption. Because the CP have a wide range of boiling points (209–210, 246, 275, and 309 °C for 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, and PCP, respectively) and are unstable at high temperatures the optimum desorption temperature and desorption time in

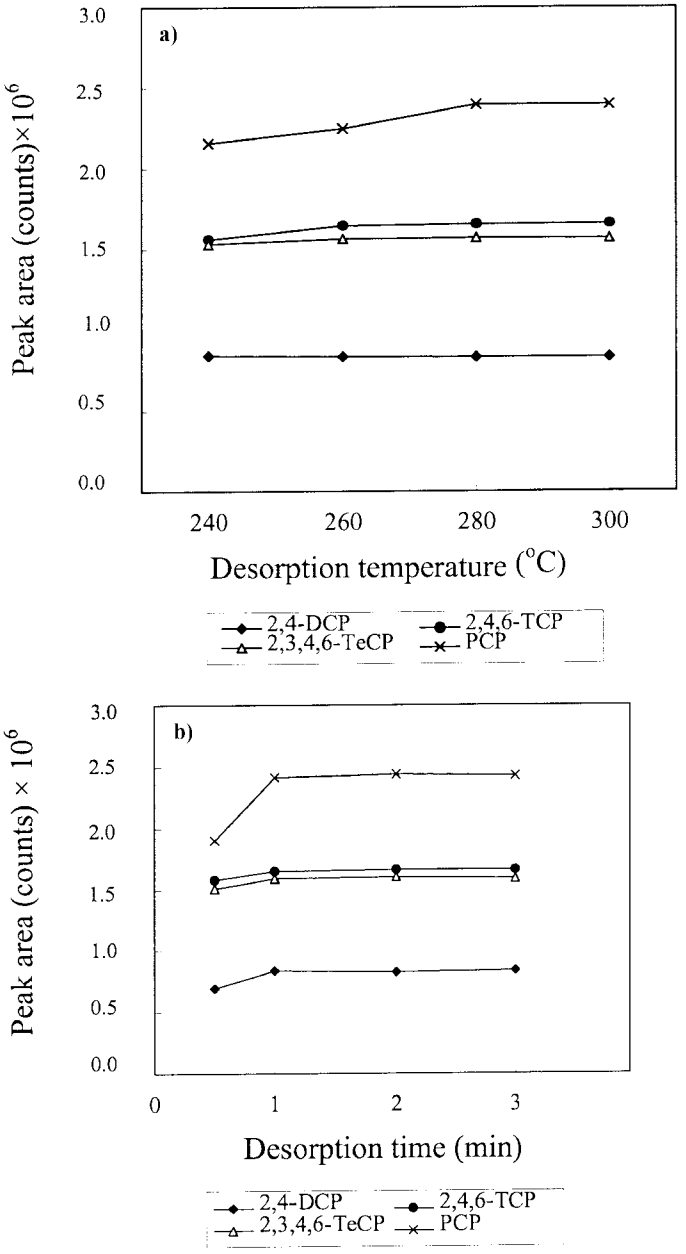

Figure 4. (**a**) Effect of desorption temperature on detection signal (peak area). (**b**) Effect of thermal desorption time on detection signal.

Table I. Results from analysis of CP in landfill leachate and in spiked samples.

Species	Amount in leachate ($\mu g\,L^{-1}$)	Spike concn ($\mu g\,L^{-1}$)	Recovery (%)	RSD^b (%)
2,4-DCP	ND[a]	250	93.2	1.65
		125	86.2	5.41
2,4,6-TCP	ND	16.0	104.4	1.87
		8.0	96.6	1.67
2,3,4,6-TeCP	ND	8.0	96.8	6.39
		4.0	105.5	2.39
PCP	0.8	8.0	95.5	2.02
		4.0	109.1	4.88

[a] Not detectable; detection limits are 2.0, 0.3, 0.2, and 0.1 $\mu g\,L^{-1}$ for 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, and PCP, respectively; [b] $n = 5$.

the hot GC injector were investigated to obtain an acceptable result. Figure 4a shows the effect of desorption temperature on detection signal (peak area). It is apparent that for PCP the peak area increased up to 280 °C and then remained constant, that for 2,4,6-TCP and 2,3,4,6-TeCP it increased up to 260 °C and then remained constant, and that for 2,4-DCP there was no significant increase in this temperature range. To ensure that other contaminants did not remain on the fiber after desorption, the desorption temperature was set at 300 °C. Figure 4b depicts the effect of thermal desorption time on peak area. It indicates that 2 min is sufficient for desorption at 300 °C. To prevent and remove possible memory effects the fiber was left in the liner for a further 1 min after thermal desorption. After this period no significant blank values were observed, and so no further regeneration of the fiber was necessary, and a total of 3 min was required for each thermal desorption.

Effect of Sample pH on Extraction

Sample pH is often adjusted to enhance extraction efficiency in conventional liquid-liquid extraction, solid-phase extraction, and solid-phase microextraction. Figure 5 shows the effect of sample matrix pH on extraction efficiency (peak area). It is apparent that peak area decreases at pH > 3.0 for PCP and 2,3,4,6-TeCP, at pH > 4.0 for 2,4,6-TCP, and remains constant at pH 2.0–7.0 for 2,4-DCP. In general, the species are volatile only in their neutral (molecular) forms. The pK_a of PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP, are 4.74, 5.22, 7.24, and 7.25, respectively, so the sample solution was adjusted to pH 2.0 before MAHS-SPME to obtain the best extraction efficiency.

Effect of Addition of Salt

The salting-out effect often improves recovery in conventional extraction processes. In direct-immersion SPME addition of salts to the aqueous sample solution has been found to reduce the solubility of CP and to enhance the amounts extracted [13, 28]. NaCl or Na_2SO_4 is usually added to the aqueous sample for this purpose. Some discrepancies have, however, been observed and no direct relationship between extraction efficiency and salt addition has been discovered [37–41]. In this study NaCl at different concentrations (0 to 3.0 M) was added to the aqueous sample to determine the effect on extraction. The results indicated that addition of salt had no significant effect on ex-

traction efficiency. Salts were not, therefore, added to the sample solution before MAHS-SPME extraction.

Validation of the Method

To test the suitability of the proposed MAHS-SPME-GC-ECD method for quantitative determination of CP, standard solutions were used for calibration by subjecting them to the complete analytical procedure, i. e. MAHS-SPME and thermal desorption from the fiber into the chromatograph. An ECD chromatogram obtained from the CP standards under the chromatographic conditions described above is shown in Figure 6. Calibration plots were constructed over the concentration ranges 0.52–12.5, 0.52–12.5, 1.04–24.0, and 15.6–37.4 $\mu g L^{-1}$ for PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP, respectively. Good linear relationships were obtained between peak area and quantity injected; the respective correlation equations and correlation coefficients were $y = 593000x + 51200$, $y = 246000x + 60600$, $y = 63900x - 3400$, and $y = 1620x + 30300$, and 0.9987, 0.9979, 0.9993, and 0.9965. Detection limits, calculated on the basis of three times the average background noise divided by the detection sensitivity (slope of calibration plot), were 0.1, 0.2, 0.3, and 2.0 $\mu g L^{-1}$ for PCP, 2,3,4,6-TeCP, 2,4,6-TCP, and 2,4-DCP, respectively. The precision of the method was estimated by performing eight extractions of sample solutions at pH 2.0 each spiked with all the CP studied at the concentrations given in the experimental section. Precision varied between 3 and 8% *RSD*, which should be satisfactory for determination of CP in waste water

To examine the suitability of the method for determination of CP in real samples, a leachate sample was collected from Taichung landfill and analyzed. From Table I it is apparent that only PCP (0.8 $\mu g L^{-1}$) was detected. Results obtained from MAHS-SPME extraction, thermal desorption, and GC-ECD analysis, under the optimum conditions proposed, of leachate samples spiked with two concentrations of each of the CP (in their linear dynamic ranges) are also listed in Table I. The recoveries were 86.2–93.2%, *RSD* 1.65–5.41%, for 2,4-DCP, and 95.5–109.1%, *RSD* 1.67–6.39%, for PCP, 2,3,4,6-TeCP and 2,4,6-TCP. These values are acceptable in environmental analysis of complex matrixes. Figures 7a and b show chromatograms of CP obtained from real leachate and from spiked samples.

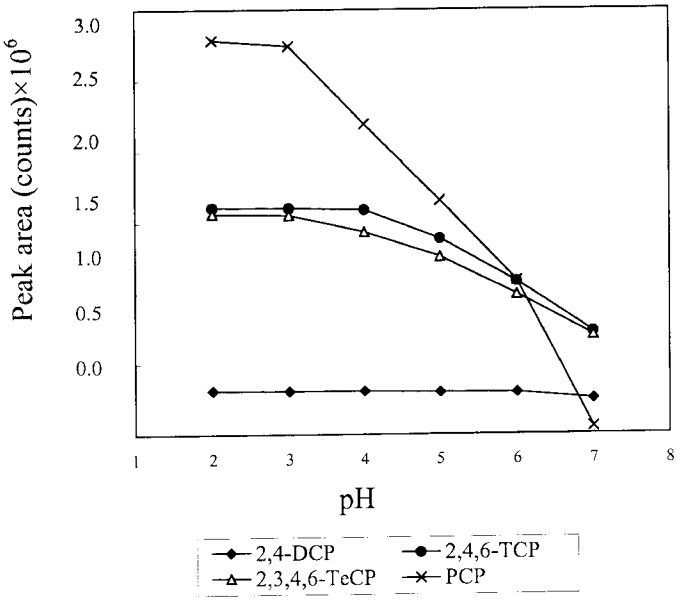

Figure 5. Effect of sample matrix pH on extraction efficiency.

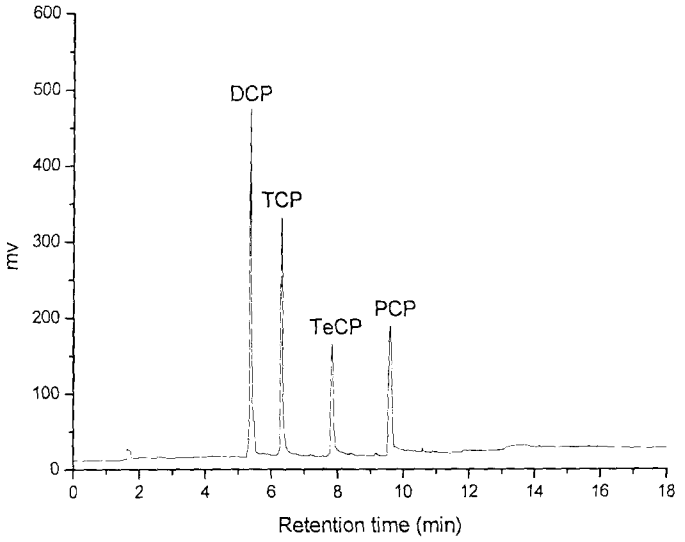

Figure 6. Chromatogram obtained from a standard solution of CP by use of the proposed method. Concentrations: DCP, 10 mg L^{-1}; TCP, TeCP, and PCP, 20 $\mu g L^{-1}$.

Table II. Comparison of analytical results obtained by use of microwave irradiation and water-bath heating.

Species	Microwave irradiation	Water-bath heating[a]
2,4-DCP	839345[b]	798764
2,4,6-TCP	1631913	567852
2,3,4,6-TeCP	1434255	ND
PCP	2418864	ND

[a] 95 °C for 5 min; [b] peak area count.

Comparison with Water Bath HS-SPME

In Table II results from determination of CP by the proposed MAHS-SPME method are compared with those from a stirring water-bath HS-SPME method (at 95 °C – temperature restricted by the boiling point of water). It is apparent that the efficiency of extraction of 2,4-DCP by the water-bath method was 96% that for the proposed MAHS-SPME method whereas for 2,4,6-TCP the efficiency of the water

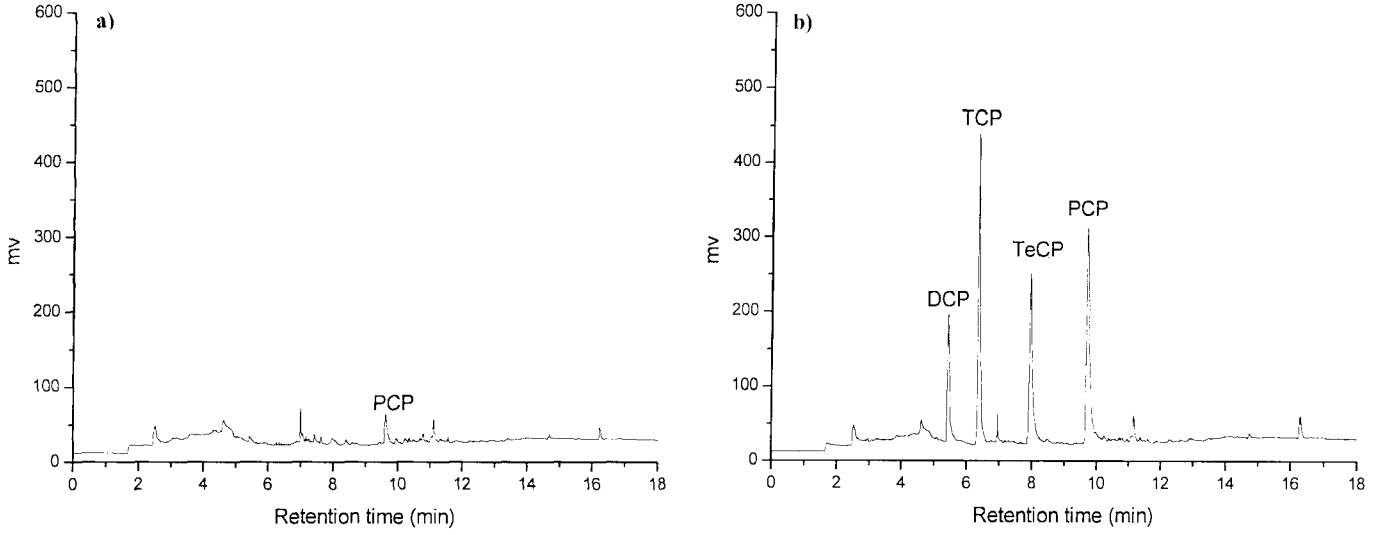

Figure 7. Chromatograms obtained from CP in (**a**) a real leachate sample and (**b**) a leachate sample spiked with 125 μg L^{-1} DCP, 8 μg L^{-1} TCP, and 4 μg L^{-1} TeCP and PCP.

bath method was only 35% that for the proposed MAHS-SPME method. PCP and 2,3,4,6-TeCP were not detected by use of the water-bath HS-SPME method. It is clear that with water bath HS-SPME detection of low-boiling species such as 2,4-DCP is comparable with that of the proposed MAHS-SPME method, but that the latter also enabled extraction of high-boiling semi-volatile organic species such as PCP, 2,3,4,6-TeCP and 2,4,6-TCP.

Conclusion

This paper reports the analysis of aqueous CP by MAHS-SPME-GC-ECD and determination of the optimum conditions. A complete analytical procedure is proposed. The proposed MAHS-SPME method has been shown to be suitable for analysis of CP in environmental water samples and has the advantages of being fast, convenient, precise, accurate, and organic solvent-free.

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