Journal of Chromatography A, 1217 (2010) 1891–1897

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Analysis of hexachlorocyclohexanes in aquatic samples by one-step microwave-assisted headspace controlled-temperature liquid-phase microextraction and gas chromatography with electron capture detection

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ARTICLE INFO

Article history:
Received 23 November 2009
Received in revised form 24 January 2010
Accepted 26 January 2010
Available online 1 February 2010

Keywords:
Microwave assisted
Headspace
Liquid-phase microextraction
Hexachlorocyclohexane
Water
GC-ECD

ABSTRACT

A microwave-assisted headspace controlled-temperature liquid-phase microextraction (HS-CT-LPME) technique was applied for the one-step sample extraction of hexachlorocyclohexanes (HCHs) from aqueous samples with complicate matrices, followed by gas chromatographic (GC) analysis with electron capture detector (ECD). Microwave heating was applied to accelerate the evaporation of HCHs into the headspace and an external-cooling system was used to control the temperature in the sampling zone for HS-LPME. Parameters affecting extraction efficiency, such as LPME solvent, sampling position and temperature, microwave power and irradiation time (the same as sampling time), sample pH, and salt addition were thoroughly investigated. From experimental results, the following conditions were selected for the extraction of HCHs from 10-mL water sample (pH 2.0) by using 1-octanol as the LPME solvent, with sampling done at 38 °C for 6 min under 167 W of microwave irradiation. The detections were linear in the concentration of 0.1–10 μg/L for α-HCH and γ-HCH, and 1–100 μg/L for β-HCH and δ-HCH. Detection limits were 0.05, 0.4, 0.03 and 0.1 μg/L for α-, β-, γ- and δ-HCH, respectively. Environmental water samples were analyzed with recovery between 86.4% and 102.4% for farm-field water, and between 92.2% and 98.6% for river water. The proposed method proved to serve as a simple, rapid, sensitive, inexpensive, and eco-friendly procedure for the determination of HCHs in aqueous samples.

1. Introduction

Lindane (γ-Hexachlorocyclohexane) is an organochlorine pesticide and a persistent organic pollutant (POP) that has been widely used for the control of agricultural and medical pests [1–2]. Contamination of water occurs by the use of HCH in these aspects. Because of environment-persistence, bioaccumulation and human-toxicity, lindane is listed as a pollutant of concern in EPA's Great Waters Program [3]. HCH is a mixture of alpha, beta, gamma and delta isomers. Since these isomers differ qualitatively and quantitatively in biological activity, they are required to be monitored in aquatic samples in order to assess their health risk.

Simplification, rapidity, miniaturization and eco-friendly procedures have been of interest in the development of sample pre-concentration techniques. In the past decade, solid phase microextraction (SPME) technique has been developed [4] and is widely applied as an alternative to conventional extraction methods [5–6], which are laborious, time- and solvent-consuming procedures. Meanwhile, headspace solid-phase microextraction (HS-SPME) sampling method had been introduced to eliminate interference problems commonly found in the direct immersion (DI) approach; and has been successfully applied to the determination of organochlorine pesticides through sample heating to accelerate the evaporation of analytes into headspace for sampling [7–11].

During the development of SPME techniques, miniaturization of extraction solvent was also studied in sample preparation. He and Lee [12] developed a liquid–liquid microextraction technique by using a microsyringe, called liquid-phase microextraction (LPME). Later, a porous polypropylene hollow fiber had been introduced in order to protect the solvent drop in the immersed LPME procedure [13–14]. The hollow fiber based LPME has been successfully applied to the determination of organochlorine pesticides in aquatic samples [15–17]. Similar to SPME, HS sampling is applied to substitute immersed sampling of LPME to avoid interference from complicate matrices [18–20].

Microwave heating is applied to accelerate analyte vaporization in order to shorten the sampling time of HS-SPME [11,21]. However, when microwave heating hyphenates to HS-LPME, it results in significant evaporation of the extraction solvent, subsequently

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doi:10.1016/j.chroma.2010.01.076

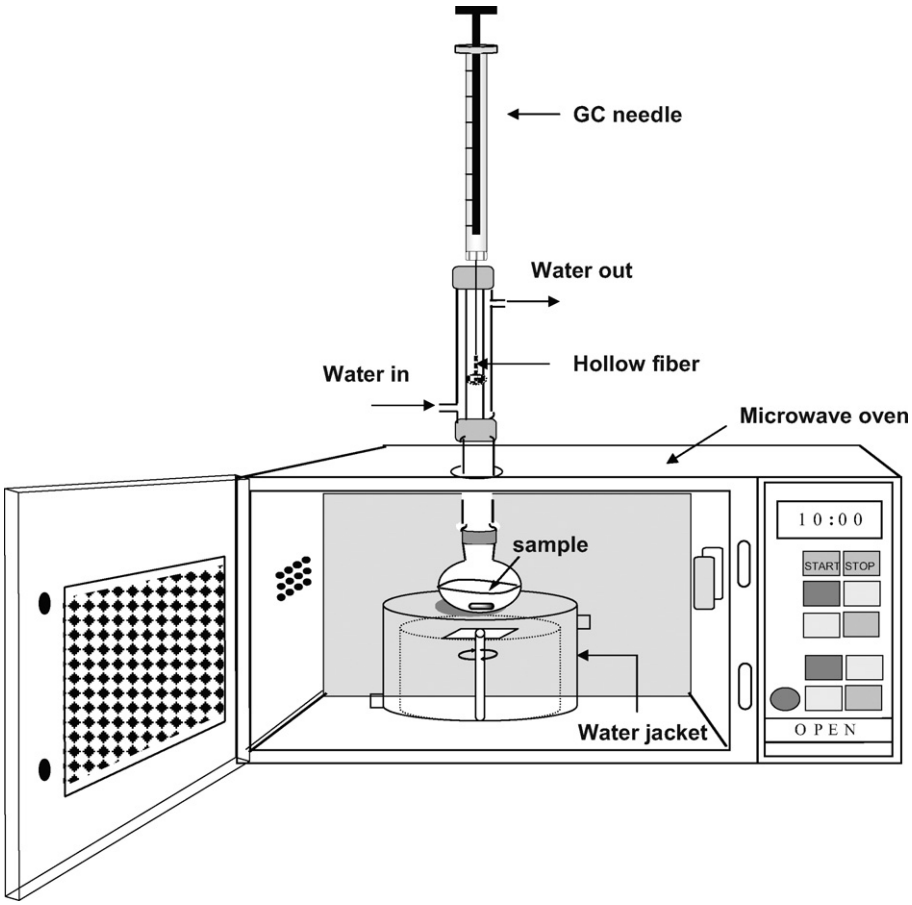

Fig. 1. Assembly of MA-HS-CT-LPME sampling system.

affecting the extraction reproducibility. In our previous study, we designed an external-cooling system to keep the temperature of the sampling point constant, which prevents the vaporization of the LPME extraction solvent [22–23]. With this external-cooling system, a dense cloud (mist) of analyte-water vapor is formed in the headspace due to the sudden cooling of vapors. In the present approach, we report here a HS-LPME sampling technique, which combines the fast microwave-assisted (MA) heating and controlled-temperature sampling (CT) for the determination of HCHs in complicated aquatic samples for effective GC determination.

2. Experimental

2.1. Reagents and solutions

Deionized water for all aqueous solutions was produced in the laboratory using the Barnstead Nanopure water system (Barnstead, NY, USA). All chemicals used in the study were of ACS reagent grade. Four isomers of HCH, α-HCH, β-HCH, γ-HCH and δ-HCH (analytical-standards grade) purchased from Dr Ehrenstorfer (Augsburg, Germany), were used for preparing standard stock solutions that were used without further purification. Standard stock solutions of 1000 mg/L HCHs were prepared individually in acetone (LC grade, Merck, Darmstadt, Germany), and diluted to 100 mg/L and 10 mg/L by using acetone. Fresh working solutions of standards were prepared by appropriate dilution with acetone. All standards and working solutions were stored at 4 °C in silanized brown glass bottles with Teflon-lined caps. Methanol, acetone, hexane, 1-octanol and n-decane of HPLC grade were obtained from Merck (Darmstadt, Germany). Ethylene Glycol and sodium hydroxide were obtained from Riedel-de Haën (Seelze, Germany). Citric acid and potassium chloride were purchased from Showa (Tokyo, Japan), hydrochloric acid (36.5%) was obtained from J.T. Baker (Phillipsburg, NJ, USA), and toluene was from Tedia (Fairfield, OH, USA). Dichlorodimethylsilane (99%) was obtained from Supelco (Bellefonte, PA, USA). High purity nitrogen (99.9995%) that was used as the carrier gas was obtained from a local supplier (Lien-Hwa, Taichung, Taiwan). River and farm-field water samples were collected from the agriculture district of Dali city (Taichung County, Taiwan).

2.2. Microwave-assisted HS-CT-LPME

The microwave oven used in this work was a NE-V32A inverter system (2450 MHz, National, Taiwan) with a maximum power of 1400 W. The arrangement of the MA-HS-CT-LPME sampling system is shown in Fig. 1. In the sampling system, cooling water system from a water circulating machine (Yih Der BL-720, Taiwan) was connected to the sampling chamber to control the sampling zone temperature and a circulating water flow in the microwave oven to reduce the effective power of microwave irradiation. After modification, the effective powers of microwave irradiation of 47, 70, 116, 167 and 279 W were used in this study. To prevent leakage of irradiation, aluminum foils were attached to the inner and outer wall of the microwave oven at the interface between the microwave body and the headspace sampling apparatus. A microwave leak detector (MD-2000, Less EMF, NY, USA) was used to check the safety aspects of the equipment during the experiments.

A Q 3/2 Accurel polypropylene hollow fiber (i.d. 600 μm, thickness 200 μm, pore size 0.2 μm) was purchased from Membrana (Wuppertal, Germany). After being cleaned ultrasonically in acetone and subsequently dried, the hollow fiber was cut into segments of 1.5-cm length and kept in an organic solvent (1-octanol) in order to impregnate the pores of the hollow fiber with 1-octanol. To build up an LPME probe, about 4.0 μL of 1-octanol was taken into a conventional 10 μL microsyringe (SGE Australia, Ringwood, Australia), and injected into the hollow fiber segment (effect length 1.2 cm) mounted on the needle tip of the microsyringe. After the extraction, the extracted solvent in the hollow fiber was retracted in to the barrel of the microsyringe, before being pushed and retracted for five cycles. 1 μL of extracted solvent was used for GC-ECD analysis. The used hollow fiber was replaced by a new fiber for each extraction. All analyses were performed by adding 10 mL of the sample solution in 25-mL round bottom flasks fitted with a condenser for the external cooling of the sampling zone, along with an LPME device in the headspace as shown in Fig. 1. Prior to the experiment, all the glassware were thoroughly cleaned with soap solution, deionized water, acetone, and again deionized water. The glassware were then dried in the oven at 80 °C for about 4 h. Two sets of flasks and condensers were used alternately because the inner surfaces of flasks and condensers had to be thoroughly cleansed by acetone and deionized water between runs to prevent carryover problem from the glassware setup.

2.3. GC-ECD

The GC used in this work was a HP 5890 (Hewlett Packard, PA, USA) equipped with a split/splitless injector and an electron capture detector (ECD, ^{63}Ni). Compounds were separated on a fused silica HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) (Agilent Technologies, Palo Alto, CA, USA). Nitrogen was used as both carrier gas and makeup gas at flow rates of 1.0 and 55 mL/min, respectively. The gas chromatograph was operated in splitless mode with the injector temperature of 220 °C. The oven temperature was maintained at 120 °C for 3 min, then programmed at 20 °C/min to 160 °C held for 5 min, then at 10 °C/min to 200 °C held for 4 min, and finally 20 °C/min to 280 °C which was held for 4 min. The separated species were measured by electron capture detector held at 320 °C. A Peak-ABC Chromatography Data Handling System (Kingtech Scientific, Taiwan) was used to obtain chromatograms and to perform data calculations.

3. Results and discussion

To obtain a better extraction efficiency of the MA-HS-CT-LPME method for the analysis of HCHs by GC-ECD, parameters affecting extraction efficiency that includes selection of LPME solvent, sampling position of LPME in the headspace, microwave irradiation power and time, sample pH and salting-out effect were systematically investigated.

3.1. Selection of LPME solvent

For the LPME method, solvent is selected based on volatility (losses will occur due to evaporation during headspace sampling), solubility to analytes and material of hollow fiber (polypropylene) and its retention behaviors in chromatographic column. The physical properties of n-hexane, decane, toluene, 2-octanol and 1-octanol were screened. Toluene, decane and 1-octanol were selected and examined. Fig. 2 demonstrates the relative extraction efficiency of toluene, decane and 1-octanol as LPME solvent for the extraction of 1 μg/L of α-HCH, γ-HCH and δ-HCH, and 10 μg/L of β-HCH under microwave irradiation of 167 W for 6 min. Results indicated that 1-octanol had the highest HCH sampling efficiency

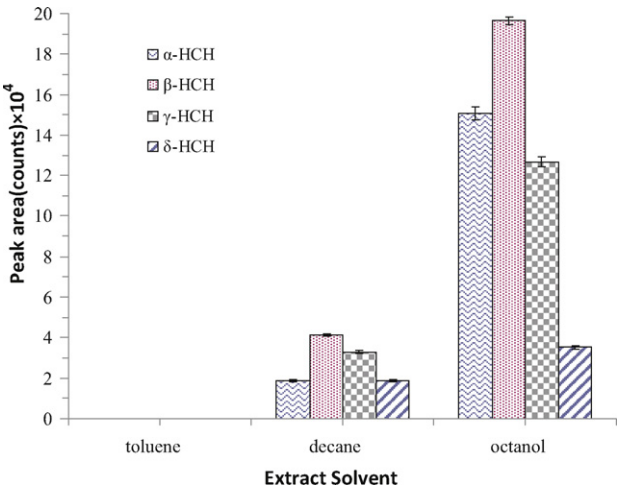

Fig. 2. Relative extraction efficiency of toluene, decane and 1-octanol as LPME solvent. Concentration: 1 μg/L of α-, γ-, δ-HCH, 10 μg/L of β-HCH. Conditions: 167 W of microwave irradiation power for 6 min. Test number: $N = 5$.

than toluene and decane, and was thus used for further experiments.

3.2. Sampling position of LPME in headspace

In the proposed method, microwave heating improves the vaporization of HCHs and water from the sample matrix into the headspace, and a circulating cooling water jacket was designed to control the temperature of sampling zone. Through the cooling of the vaporized analyte and water vapors, a cloud vapor (mist) zone (CVZ) was observed in the headspace (cooling jacket), which was applied as a mark to identify the sampling position for LPME sampling. Therefore, it is important to control the CVZ formation and sampling position in the headspace through the cooling temperature. Position of the LPME hollow fiber tip was examined in the window of upper end edge, center, lower end edge and 1-cm below lower end edge of the CVZ in the headspace to obtain the maximum extraction efficiency by using 1 μg/L of α-HCH, γ-HCH and δ-HCH, and 10 μg/L of β-HCH in aqueous solution. The respective corresponding temperatures of these positions were 35, 37, 38 and 45 °C and they were measured by a digital thermal-couple thermometer. From a series of tests, it was found that maximum extraction efficiency of all four HCH isomers were obtained when sampling was done at the position of the lower end edge of the CVZ (temperature was 38 °C). Therefore, the LPME hollow fiber tip position was selected at the lower end edge of CVZ for subsequent analyses.

3.3. Selection of microwave irradiation conditions

In this study, microwave heating was applied to accelerate the vaporization of the HCHs from the water sample into the headspace for MA-HS-CT-LPME sampling. Microwave irradiation was examined at effective powers of 47, 70, 116, 167 and 279 W from 3 to 7 min for 1-octanol-HS-CT-LPME sampling of 1 μg/L of α-HCH, γ-HCH and δ-HCH, and 10 μg/L of β-HCH in aqueous solution. Experimental results as demonstrated in Fig. 3 indicate that the effective irradiation power of 167 W gave better extraction efficiency than the others for all target HCHs. When microwave was irradiated at 47 and 70 W, no CVZ was observed and only trace quantities of HCHs were detected due to the insufficient energy for vaporizing HCHs into headspace and for the HCHs to reach the sampling area. Conversely, when microwave was irradiated at 279 W, the extraction solvent vaporized continuously after 6 min irradiation. Fig. 4 illustrates the relative HCHs extraction quantity

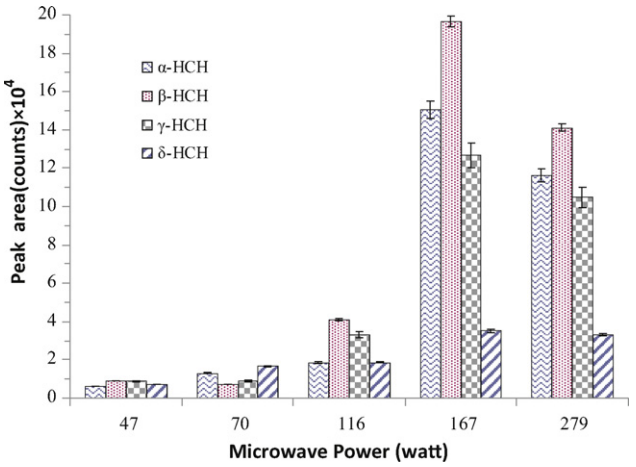

Fig. 3. Influence of microwave irradiation power on the extraction. Microwave powers 2–6 are 47, 70, 116, 167 and 279 W, respectively. Concentration: α-, γ-, δ-HCH 1 μg/L, β-HCH 10 μg/L. Test number: $N = 5$.

(related to detection peak area) by the present MA-HS-CT-LPME in varying irradiation times with the effective power of 167 W. It can be seen that the relative extraction quantities of the four HCH isomers increased significantly at the beginning of microwave irradiation, reached maximum levels at 6 min, and decreased after that. It is worthy to notice that the relative β-HCH extraction quantity increased sharply from 5 to 6 min, and decreased sharply after that. Among the four HCH isomers, β-HCH had the lowest vapor pressure (3.02 mPa at 20 °C) and the highest water solubility. During microwave heating, HCHs were vaporized with water into the headspace and reached the sampling zone and got adsorbed on the LPME probe. HCHs that were adsorbed on the hollow fiber surface got diffused into the extraction solvent (1-octanol) and a pseudo-water-film was competitively coated on the hollow fiber surface after 6 min irradiation, which retarded the extraction of HCHs from the vapor flux that might back-extract HCHs from the hollow fiber surface to the water film due to the distribution. This phenomenon is more obvious for β-HCH, which has the highest water solubility among the four HCH isomers. Furthermore, the quantity of HCHs condensed on the glassware walls turned out to be increasing significantly with microwave heating time, thus decreasing the extraction quantity of HCHs on the LPME probe. Therefore, microwave irradiation with effective irradiation power of 167 W for 6 min was optimum for the one-step MA-HS-CT-LPME sampling for target HCHs in water sample.

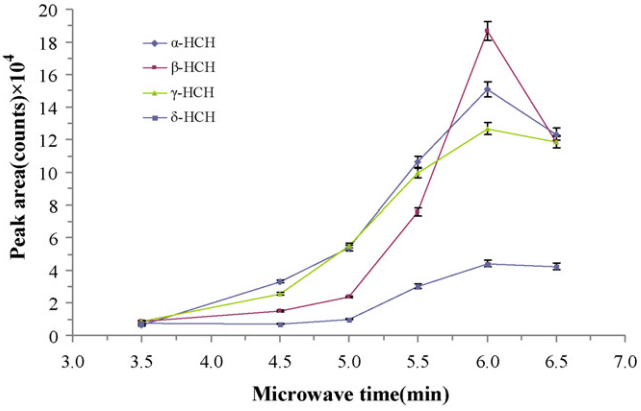

Fig. 4. Extraction quantity at different microwave irradiation time. Power: 167 W; Concentration: α-, γ-, δ-HCH 1 μg/L, β-HCH 10 μg/L. Test number: $N = 5$.

3.4. Influence of sample pH and salt addition on extraction

Sample pH is often adjusted to enhance the extraction efficiency of liquid–liquid extraction, solid-phase extraction and immersed solid-phase microextraction due to the partition of analytes in their neutral (molecular) forms, which were considered favorable to the hydrophobic phase. Although the HCHs are in neutral forms in aqueous solution, perchloro-organic compounds are usually unstable in extreme pH conditions under light irradiation. In order to examine the stability of HCHs during microwave irradiation, the sample solutions' pH that ranged from 2 to 9 was investigated. Experimental results indicate that the extraction efficiency decreased slightly when pH increased from 2 to 7 and obviously from 7 to 9, which reflects the decomposition of HCHs in alkaline condition under microwave irradiation. Therefore, pH of the water sample was adjusted to 2.0 before carrying out the MA-HS-CT-LPME process in order to ensure that all HCHs were stable during microwave irradiation. Salting-out effect was also applied to improve the extraction efficiency of HCHs in MA-HS-CT-LPME. However, when 0.5–2.0 M NaCl was added to the water sample to investigate the salting-out effect, there was no significant influence on the extraction efficiency of HCHs in MA-HS-CT-SPME. Therefore, salt was not added into the aqueous samples in the proposed method.

3.5. Calibration features of the proposed method

The suitability of the proposed MA-HS-CT-LPME coupled to the GC-ECD method for quantitative determination of HCHs was examined by adding standard HCHs' solutions in the sample matrix (5 μg/L of α- and γ-HCH and 50 μg/L of β- and δ-HCH in 10 mL water) and subjecting them to the complete treatment process, i.e. MA-HS-CT-LPME and GC-ECD analysis. A chromatogram of the spiked aqueous samples that was obtained under the conditions described in the Section 2.3 is demonstrated in Fig. 5(a). Four HCH isomers are well resolved within 18 min. Calibration plots for quantities of HCHs in the ranges listed in Table 1 were found to have good linearity with correlation coefficients in the range 0.9928–0.9987. Calibration plot data are listed in Table 1. Detection limits were calculated when three times the standard deviation of the detection signal for the lowest concentration ($n = 7$) in the calibration plot was divided by the detection sensitivity (slope of calibration plot), and the detection limits were 0.05, 0.4, 0.03 and 0.1 μg/L for α-, β-, γ- and δ-HCH, respectively. Precision was estimated by performing five extractions of sample solutions spiked with concentrations for calibration, and ranged from 7.5 to 11.2, 8 to 13.6, 4.3 to 10.1 and 5.2 to 11.5% RSD for α-, β-, γ- and δ-HCH, respectively. It showed satisfactory results for HCHs determination in water samples. Parameters of calibration plots built up by direct injection of quantities of HCHs are also listed in Table 1. It can be seen that the detection limits of HCHs with the present method are much lower than those with the direct injection process. This is due to the enrichment of HCHs achieved through the proposed process. When 1 μg/L of α-, γ- and δ-HCH and 2 μg/L of β-HCH in water were used as spiked samples, after the proposed sampling with 3.5 μL octanol-HS-CT-LPME and 1 μL taken for GC-ECD determination, the enrichment factors were 137, 96, 143 and 88 for α-, β-, γ- and δ-HCH, respectively. It has the potential to increase the detection quantity (reflect to enrichment factors after calculation) by injecting higher quantity of the extractant for analysis.

3.6. Analysis of HCHs in environmental samples

To examine the applicability of the method for HCHs determination in aqueous samples, river water and farm-field water samples

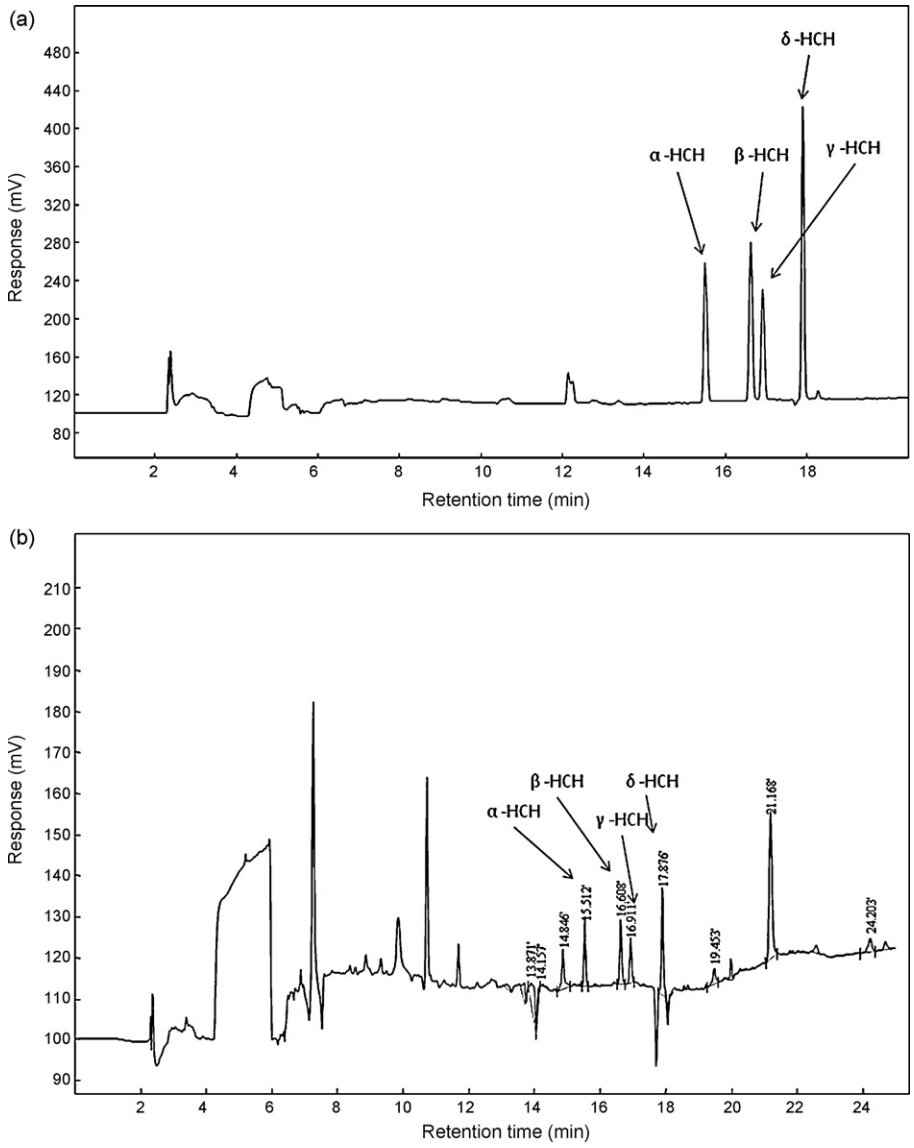

Fig. 5. (a) Chromatogram of HCHs standard solution by the proposed method, 5 μg/L of α-, γ-HCH and 50 μg/L of β-, δ-HCH in 10 mL sample solution (at pH 2); LPME with 1-octanol for 6 min under 167 W microwave power. (b) Chromatogram of HCHs spiked in the farm-field water by the proposed method. Sample: 0.5 μg/L of α-, γ-HCH and 5 μg/L of β-, δ-HCH. Other conditions are as in (a).

were collected from the agriculture district in Dali city and subsequently analyzed using the proposed method. The results are presented in Table 2, and no significant amount of interested HCHs was detected in the water samples. Recovery was examined by spiking 0.5 μg/L of α- and γ-HCH and 5.0 μg/L of β- and δ-HCH in water samples, and subjecting the spiked samples to the proposed MA-HS-CT-LPME extraction and GC-ECD analysis. Fig. 5(b) illustrates the HCHs' chromatogram in the spiked farm-field water. Peaks of α-HCH, β-HCH, γ-HCH and δ-HCH, respectively, that were shown in chromatogram, were also confirmed by GC-MS. Recover-

Table 1
Calibration parameters of HCHs by direct injection and the proposed methods.

Analytes	Concentration ranges (mg/L)	Linear equations	Linearity (R^2)	Detection limits (μg/L)	RSD% (N = 5)
By direct injection					
α-HCH	0.01–1.0	$Y = 2555664X - 59527$	0.9985	4	2.0–4.2
β-HCH	0.02–2.0	$Y = 1681142X - 22595$	0.9990	7	2.7–4.9
γ-HCH	0.01–1.0	$Y = 2183157X - 146$	0.9992	4	1.9–4.3
δ-HCH	0.01–1.0	$Y = 2346063X - 33611$	0.9991	4	2.3–4.3
Analytes	Concentration ranges (μg/L)	Linear equations	Linearity (R^2)	Detection limits (μg/L)	RSD% (N = 5)
By proposed method					
α-HCH	0.1–10	$Y = 169601X - 294$	0.9987	0.05	7.5–11.2
β-HCH	1–100	$Y = 19545X - 393$	0.9977	0.4	8–13.6
γ-HCH	0.1–10	$Y = 140309X - 353$	0.9986	0.03	4.3–10.1
δ-HCH	1–100	$Y = 35294X - 330$	0.9928	0.1	5.2–11.5

Table 2
Analytical results of HCHs in aquatic samples and the recovery in, spiked samples analyzed by the proposed method.

Analyte	Sample conc.	Spiked quantity (μg/L)	Measured quantity (μg/L)	Recovery[b]%	RSD[b]%
Field water					
α-HCH	ND[a]	0.5	0.44	88	5.8
β-HCH	ND	5	4.32	86.4	8.9
γ-HCH	ND	0.5	0.48	96	8.7
δ-HCH	ND	5	5.12	102.4	11.5
River water					
α-HCH	ND	0.5	0.47	94	7.9
β-HCH	ND	5	4.61	92.2	12.6
γ-HCH	ND	0.5	0.48	96	6.2
δ-HCH	ND	5	4.93	98.6	6.5

[a] ND: Not detectable; Detection limits are 0.05, 0.4, 0.03 and 0.1 μg/L for α-, β-, γ- and δ-HCH, respectively.
[b] $n = 3$.

Table 3
Comparison of the MA-HS-CT-LPME–GC-ECD with other methods.

	Solvent used (mL)	Sample quantity (mL)	Extraction time (min)	LOD (ng/L)	Reference
MA-HS-CT-LPME-GC–ECD	0.004	10	6	30–100	This method
Immersed HF-LPME-GC–MS	0.005	5	30	17–29	[24]
LLE-GC–ECD	3750	800	–	–[a]	[25]
SPE-GC–ECD	0.08	10	–	30–80	[26]
SPME-GC–MS	0	4	30	12–80	[27]
Fiber-in-tube microextraction-GC–ECD	0.008	8	30	2–12	[28]

[a] Not mentioned.

ies of the HCHs in farm-field water were calculated by subtracting the measured quantity of sample from the measured quantity of spiked sample, divided by the spiked quantity and recoveries varied from 86.4 to 102.4% with 5.8 to 11.5% RSD, and in river water varied from 92.2 to 98.6% with 6.2 to 12.6% RSD, as listed in Table 2. This accuracy and precision is deemed acceptable in environmental analysis. With the addition of 0–1% of humic acid in the spiked farm-field water, no significant interference of humic acid on the HCHs measurement was observed. In addition, humic acid was precipitated when pH was adjusted to 2, and it was found that microwave heating also decreased the interaction between humic acid and HCHs.

3.7. Comparison of the proposed method with other methods

The extraction of HCHs by the proposed method was compared with the immersed LPME method for the GC analysis of the field water sample (10 mL) spiked with 0.5 μg/L of α- and γ-HCH, and 5 μg/L of β- and δ-HCH. The chromatogram of HCHs from the immersed LPME method was found to be more complicate than that from the MA-HS-CT-LPME method for the spiked field water. It indicates that some other species in field water matrix were also extracted by the immersed LPME method. Although four HCH isomers were well resolved in the chromatogram, the response signals were smaller than those obtained by the proposed method even though the immersion methods' extraction times were longer (25 min *vs.* 6 min). In comparison with MA-HS-SPME, no carryover problem occurred in the MA-HS-LPME method due to the fact that the hollow fiber was disposable. Although the segment of hollow fiber (1.5-cm length) is disposable and μL-level of 1-octanol was used in each run of sampling, the cost of expendables used in LPME is still much lower than the cost of SPME fiber spared in each run of sampling (if used 100 runs). Table 3 demonstrates the comparison of the proposed method with other methods. It can be seen, the proposed method has comparable performance to other methods in the quantity of sample and solvent used, as well as the detection limit, with the shortest sampling time. Therefore, it can be an alternative method to analyze HCHs in aqueous samples.

4. Conclusion

In this study, the proposed MA-HS-CT-LPME method is found to be an effective and much improved analytical procedure for the analysis of HCHs by GC-ECD. From the results of the applicability test for HCHs determination in the water samples**,** the present approach is found to be a simple, rapid, sensitive, inexpensive and eco-friendly procedure to determine analytes from complicate aqueous samples.

Acknowledgments

The authors thank the National Science Council of Taiwan under grant of NSC-96-2113-M-005-0021-MY3 and National Chung Hsing University for financial supports.

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