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Temperature-controlled headspace liquid-phase microextraction device using volatile solvents

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ABSTRACT

A novel temperature-controlled headspace liquid-phase microextraction (TC-HS-LPME) device was established in which volatile solvents could be used as extractant. In this device, a PTFE vial cap with a cylindrical cavity was used as the holder of the extraction solvent. Up to 40 μl of extraction solvent could be suspended in the cavity over the headspace of aqueous sample in the vial. A cooling system based on thermoelectric cooler (TEC) was used to lower the temperature of extractant in PTFE vial cap to reduce the loss of volatile solvent during extraction process and increase the extraction efficiency. The selection of solvents for HS-LPME was then extended to volatile solvents, such as dichloromethane, ethyl acetate and acetone. The use of volatile extraction solvents instead of semi-volatile solvent reduced the interference of the large solvent peak to the analytes peaks, and enhanced the compatibility of HS-LPME with gas chromatograph (GC). Moreover, the use of larger volume of extractant solvent increases the extraction capacity and the injection volume of GC after extraction, thus improving detection limits. Several critical parameters of this technique were investigated by using chlorobenzenes (CBs) as the model analytes. High enrichment factors (498–915), low limits of detection (0.004–0.008 μg/L) and precision (3.93–5.27%) were obtained by using TC-HS-LPME/GC-FID. Relative recoveries for real samples were more than 83%.

1. Introduction

Volatile and semi-volatile organic substances in samples such as flavors in plants, food staff and drinks, tobacco leaves, and contaminants in environmental samples, usually present at low levels. The sample preparation is, therefore, a critical step on the path toward a successful quantitative measurement. Various extraction methods including liquid–liquid extraction (LLE), solid-phase extraction (SPE) are commonly used. However, LLE and SPE are tedious, labor-intensive, time consuming and require a large volume of high-purity solvents. Those solvents are often hazardous and environmentally unfriendly. The great need of using a neglectable volume solvent in analytical sample preparation has led to the development of some new methods, such as solid-phase microextraction (SPME) [1] and liquid-phase microextraction (LPME).

SPME was firstly developed by Arthur and Pawliszyn [1], which initiated the interest for microextraction techniques and achieved great success in analytical chemistry. However, the fibers of SPME are expensive, and have relatively short lifetime [2]. LPME has been proved to be a simple, inexpensive, and effective sample pre-treatment technique for the environmental and biochemical analysis [3]. The principle of LPME is based on the partitioning of analytes between sample matrices and a single drop of solvent, which is suspended at the tip of a microsyringe needle. The acceptor phase can be immersed directly in sample (DI-LPME) [3] or above for headspace extraction (HS-LPME) [4]. Because of its exceptionally low cost, simplicity of operation, and near-total elimination of the use of toxic solvents, LPME has attracted much attention in recent years [5,6].

The solvents in conventional HS-LPME should have a high boiling point and low vapor pressure in order to reduce the risk of evaporation during extraction [7,8]. The solvents in HS-LPME generally have high boiling points over 100 °C, resulting large chromatographic peak when injected into a GC with nonselective detectors, such as FID, which would seriously interfere with some target compounds of close boiling points. This problem could be solved partially by using solvents of higher boiling points, such as dodecane [9] and ionic liquids [10]. Another way is adopting dynamic HS-LPME in which solvents were shielded within the syringe barrel [11].The most effective way to reduce the evaporation of solvents is to lower the temperature of extractant [7,12–14].

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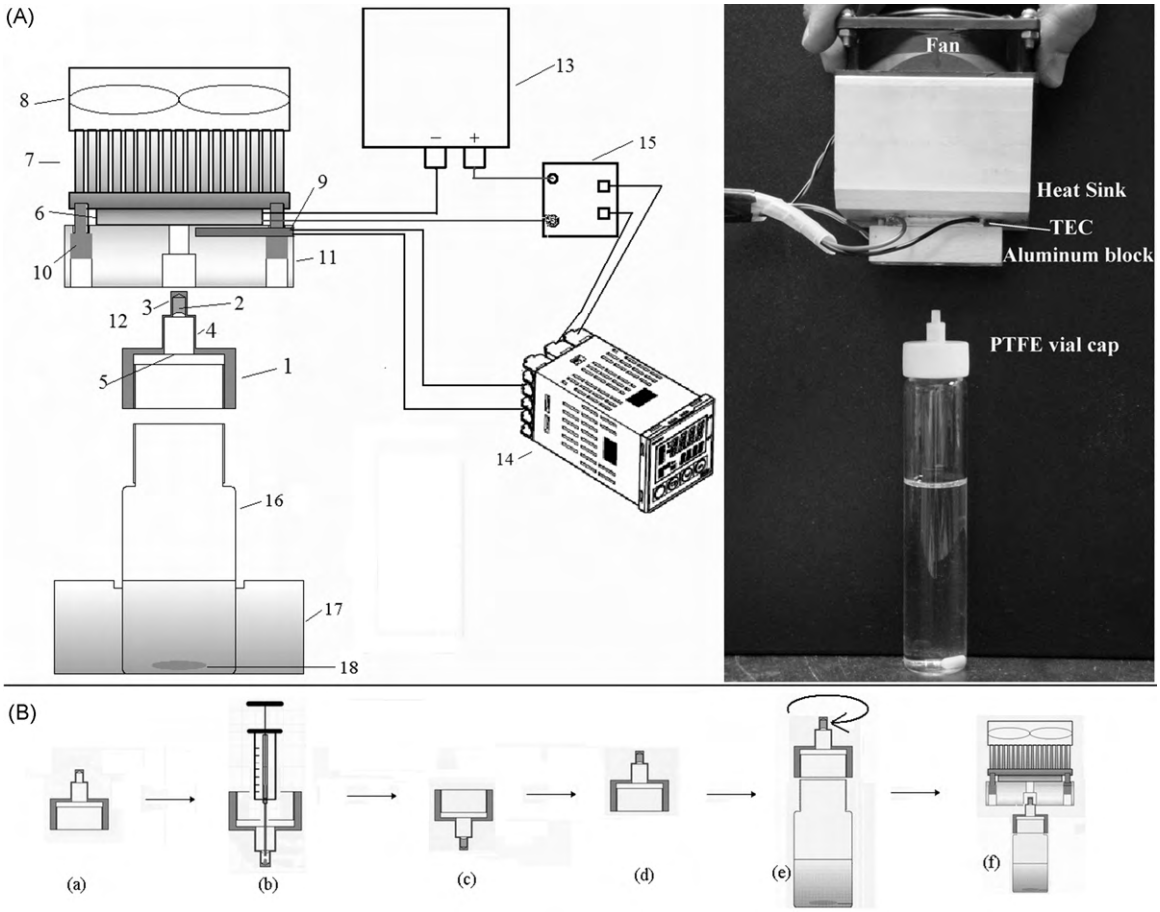

Fig. 1. (A) Schematic diagram of the temperature-controlled headspace liquid-phase microextraction apparatus (not in scale). (1) PTFE vial cap with a cylindrical cavity, (2) extractant, (3) the cavity, (4) the transit region, (5) the entrance of transit region, (6) screw threads of PTFE vial cap, (7) TEC, (8) heatsink, (9) fan, (10) Pt-100 temperature sensor, (11) nylon screw, (12) two-step hole in aluminum block, (13) aluminum block, (14) power supply, (15) digital temperature controller, (16) solid state relay, (17) cylindrical vial, (18) magnetic stirrer with water bath, and (19) PTFE stirrer. Heat insulation materials were not shown. (B) The procedure of TC-HS-LPME. (a) PTFE vial cap without extractant, (b) adding extractant, (c) PTFE vial cap with extractant, (d) the extractant suspended steadily in the cavity at the top of the cap, (e) screwing the cap onto the sample vial, (f) placing the cooling system onto the PTFE vial cap. (C) The real picture of TC-HS-LPME device.

Khajeh et al. [7] developed an apparatus with two compartment cells, in which the temperature of solvent and sample could be controlled respectively. Xu et al. [15] utilized a PCR tube to carry the solvent and reduced the temperature of solvent just only with an ice bag.

Another disadvantage of HS-LPME is that it requires careful and elaborate manual operation because of the dislodgment and instability of solvent drop. Due to the small contact surface, the volume of solvent is always less than 5 μL and the instability of solvent limits the extraction performance. In order to load more solvent and improve the stability of solvent drop, PTFE tube [16] and hollow fiber [17] were used to mount on the needle, and up to 20 μL 1-octanol can be loaded.Thermoelectric cooler (TEC) is one of the most attractive temperature manipulation semiconductor because they are small solid state heat pumps that can convert electrical energy into a temperature gradient, known as the "Peltier effect", without any moving part or refrigerant. With the advantages of low cost, small size, environmental safety, fast temperature response and reasonable power consumption, TEC has been applied in many miniaturized analytical devices, such as cold trap for atmospheric VOCs [18], SPME [19], cryogenic chromatography [20] and microfluidic devices [21]. However, there is no relevant report on use of TEC on HS-LPME so far.

In this report, we developed a temperature-controlled headspace liquid-phase microextraction (TC-HS-LPME) method, which uses volatile organic solvents as extractants, such as acetone, dichloromethane and ethyl acetate (Fig. 1). The extractants were suspended in the small cavity of a PTFE vial cap. Because of the low surface energy of PTFE, a variety of solvents and larger volume of solvent could be suspended in the PTFE vial cap. An extractant cooling system based on TEC was used to lower and control the solvent temperature precisely. The temperature of solvents could be cooled down to −15 °C, resulting in lower vapor pressure and higher extraction efficiency. The extraction could be extended to a feasible time in a relatively more stable state. To the best of our knowledge, the organic solvents of high vapor pressure at room temperature have never been applied in conventional HS-LPME ever before. The TC-HS-LPME/GC-FID method and the device were evaluated using several volatile solvents as extractants and chlorobenzenes (CBs) as model analytes. The selection of CBs as model compounds are based on the fact that CBs have been commonly used as industrial solvents, pesticides, dielectric fluids, and chemical intermediates, but now, CBs are well known hazardous to health and have been ranked as priority pollutants by the US Environmental Protection Agency (EPA) [22].

2. Experimental

2.1. Instruments

GC chromatograph used in this study was an Agilent 6890N (Wilmington, USA) system equipped with a cold on-column injec-

tor (COC) in "track-oven" mode and a flame ionization detector (FID). A deactivated retention gap (5 m × 0.53 mm i.d. fused-silica pre-column), coupled with a 30 m × 0.53 mm i.d., 0.6 μm OV-1701 crosslinked fused-silica capillary column (Dalian Scien-Tech Instrument Inc., Dalian, China) was used for separation. The analytes were injected with a 10-μL microsyringe (Shanghai, China) through COC injector. The retention gap technique was used to inject a large volume of solvent into GC [23,24]. A constant flow (5 mL/min) of hydrogen was used as the carrier gas. The chromatographic conditions were as follows: initial oven temperature 40 °C and held for 6 min, programmed at 10 °C/min to 100 °C, programmed at 15 °C/min to 150 °C, programmed at 20 °C/min to 230 °C, and hold for 5 min. The temperature of FID was kept at 280 °C.

Sample solutions were held in 60-mL cylindrical vials. A magnetic stirrer DF-101S (Gongyi, China) and a stirrer bar (10 mm × 4 mm) were employed for stirring the sample during extraction. A Pt-100 temperature sensor (Φ4 mm × 30 mm) was used to monitor the actual temperature of the extractant solvents. An Omron E5CN digital temperature controller (Tokyo, Japan) was used to control the temperature of the extractant solvents in proportional-integral-derivative mode. A 50-μL microsyringe (Shanghai, China) was used to measure and add volatile extractants into the PTFE vial cap.

2.2. Reagents and aqueous samples

Acetonitrile, dichloromethane, methanol and hexane were all of HPLC grade (Tedia, Portland, USA). Ethyl acetate and acetone (Fisher, Pittsburgh, USA) were of pesticide grade. Monochlorobenzene (CB), 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB) were obtained from Shanghai Chemical Reagent Co. (Shanghai, China). Deionized water used in this experiment was Wahaha purified water (Hangzhou, China). Sodium chloride was purchased from Shenyang Chemical Reagent Co. (Shenyang, China). Tap water collected from our laboratory, pond water obtained from Dalian Institute of Chemical Physics and wastewater from Malan River (Dalian, China) were used to carry out the relative recovery studies as real water samples. The water samples filtered with 0.45 μm cellulose acetate membrane filters (Millipore, Billerica, USA) were stored in a refrigerator at 4 °C and analyzed within 48 h of sampling.

2.3. Preparation of standard solutions

Stock standard solutions of CBs were prepared in acetonitrile at concentrations of 1000 and 10 mg/L, then maintained at 4 °C. A mixed standard solution with 1 mg/L of each CB was prepared every week from 10 mg/L stock standard solutions. Working solutions were prepared by dilution of the mixed standard solutions with deionized water.

2.4. TC-HS-LPME apparatus

The PTFE vial cap with a cylindrical cavity is shown in Fig. 1(A). The cavity (6 mm × 3 mm i.d.) was used as extractant holder, and the cylindrical part (8 mm × 7 mm i.d.) was used as a transition region between the cavity and the headspace area. Because of the low PTFE surface energy, the inner diameter of the cavity was 3 mm in order to hold the extractant stably when the PTFE vial cap is inverted. The thickness of the wall of the cavity was 0.5 mm in order to reduce the thermal resistance between the cooling system and extractant. The volatile solvent suspended at the headspace of samples was cooled down to prevent fast evaporation. Because the temperature of both extractant and the transition region was kept at subzero, the water vapor was condensed and solidified at the entrance and the inner wall of this region and could not mix with the extractant. The transition region was served as the separation channel between water vapor and analytes at subzero temperature. This design allows the use of water-soluble solvents such as acetone as extractant.

The extractant cooling system was constructed based on TEC unit as the cooling source. The classical "sandwich" structure was used to conduct cold and heat produced by the TEC. A heat sink with two screwed holes and a fan combination were used to dissipate the heat generated by the hot side of the TEC. An aluminum block was attached to the cold side of the TEC by two nylon screws fixed on the screwed holes of heat sink, and then the hot side of the TEC was attached to the heat sink. A two-step hole in aluminum block, which was matched with the two-step cylindrical dimension of the PTFE vial cap, providing a cooling source for the extractant. In order to increase the heat conductivity, both sides of TEC and the surface of the two-step hole on the aluminum block were sealed with heat conduct silicone. A Pt-100 resistance temperature sensor was embedded in the aluminum block to monitor the temperature of the cold side of the TEC. Heat-insulating material was conglutinated on the surface of aluminum block to prevent thermal losses and the condensation and freeze of atmospheric water.

2.5. TC-HS-LPME procedure

Before starting the extraction, the temperature of magnetic stirrer was set at 70 °C and the extractant cooling system at −10 °C, respectively. A 40 mL of aqueous solution spiked at a known concentration of CBs was placed in a 60-mL cylindrical vial containing a PTFE stirrer bar. The PTFE vial cap was placed upside down to set the cavity at the bottom, and 20 μL of extractant was added into the cavity. The PTFE vial cap with extractant was then inverted again and screwed onto the sample vial. The cooling system was then placed on top of the vial cap. The extractant stays at the top during extraction. The cooling system decreased the temperature of extractant rapidly till preset value. The analytes were partitioning between the headspace, the organic solvent and the sample at two different temperatures. After extraction, the PTFE vial cap was unscrewed from the sample vial and then placed upside down. 10 μL of the extractant was taken by a 10-μL microsyringe, and injected into the GC for analysis. The PTFE vial cap was rinsed with methanol to avoid cross-contamination, and then dried at 100 °C for 10 min. The clean vial cap was ready for the next extraction. The procedure is demonstrated in Fig. 1(B).

3. Results and discussion

3.1. Materials of vial cap

Different polymers such as polytetrafluoroethylene (PTFE), polypropene (PP) and polyvinylchloride (PVC), had been used to make the vial cap of the same dimension as described in Fig. 1. Solvents including acetone, dichloromethane, ethyl acetate, methanol and hexane were tested to find out the most suitable material for holding solvent at room temperature. 20 μL of each solvent was added into the cavity of each vial cap, and the vial cap was then screwed on the sample vial and proceeds extraction. Experiments showed that the PTFE vial cap can hold more kinds of solvents than that made of other polymers. For example, all the solvents except hexane could be suspended steadily in the PTFE vial cap. While PP vial cap could only hold acetone and methanol steadily. One possible reason may be that PTFE had the smallest solid surface energy among other materials, as shown in Table 1. The solvent drop could be impacted by the biggest adhesion force resulted from the surface tension. The small inner diameter (3 mm) of the cavity offered large contact surface area between the solvent and the wall, result-

Table 1
Physical properties of solvents and polymers being used.

Name	Vapor pressure (mm Hg)[a]			Surface tension[a] or surface energy[b] (mN m^{-1})			Density (g mL^{-1})
	25 °C	−10 °C	−15 °C	20 °C	−10 °C	−15 °C	25 °C
Acetone	231	40.364	30	24.02	27.38	27.94	0.79
Methanol	127	15.503	10.304	22.45	24.773	25.160	0.81
Dichloromethane	435	113.24	67.422	27.842	31.694	32.283	1.33
Hexane	153	34.514	19.187	18.396	21.462	21.973	0.6548
Ethyl acetate	93	17.931	9.234	23.968	27.451	28.032	0.902
Toluene	28.4	4.829	2.837	28.522	32.089	32.684	0.8636
PTFE	–	–	–	20[b]	–	–	–
PP	–	–	–	30.1[b]	–	–	–
PVC	–	–	–	41.5[b]	–	–	–

[a] Values taken and calculated from the 16th edition of Lange's Handbook of Chemistry.
[b] Values from http://www.surface-tension.de/solid-surface-energy.htm.

ing larger volume of extractant to be used. In this device, up to 40 μL solvent, such as acetone, dichloromethane, ethyl acetate and methanol, could be loaded. Another advantage of the PTFE vial cap was that PTFE was one of the most inert materials that could prevent the adsorption of target analytes. Therefore, the PTFE vial cap was used as the extractant carrier in subsequent experiments.

3.2. Optimization of TC-HS-LPME operating conditions

3.2.1. Selection of volatile extractant

Unlike conventional HS-LPME, some solvents with low boiling point could be applied as the extractant in TC-HS-LPME, mainly because of the cooling system that reduced the vapor pressure and volatility of these volatile solvents remarkably. The vapor pressures of some common volatile solvents at subzero temperature are similar with that of toluene at 25 °C, as shown in Table 1. Moreover, the small inner diameter of PTFE vial cap also reduced the evaporation speed of volatile solvents. Both of the factors made the volatile solvents suspended at the headspace of aqueous sample steadily for a certain time. Acetone, ethyl acetate, dichloromethane, hexane and methanol were tested as extractants at −10 °C in this study. The 40-mL aqueous sample were kept at 40 °C and stirred at 900 rpm for 30 min. We found that hexane could not be suspended in PTFE vial cap due to the low surface tension, as can be seen in Table 1. Experimental results showed that both dichloromethane and methanol can be used as extractants, while the former contains impurities which may coeluted with the analytes in GC, and the methanol may result in distorted peaks of analytes in GC chromatogram because of its high polarity. Acetone, on the other hand, showed the best extraction efficiency and separation performance on GC compared with ethyl acetate. Thus, acetone was chosen as the extractant in the following experiments.

3.2.2. Extractant volume

According to the HS-LPME theory, larger volume of extractant should increase the total amount of analytes to be extracted and enhance the extraction efficiency at equilibrium. Much more extractant could be used in TC-HS-LPME than in conventional HS-LPME. For volatile solvents, larger initial volume of extractant can also be sufficient to compensate for the evaporation loss during extraction [25]. Up to 40 μL of acetone can be used in our device. Acetone of 15, 20, 25, 30 and 40 μL were used as extractant respectively at −10 °C, and 10 μL of the extractant was taken and injected into the GC in this study. The solvent was exposed to the headspace of 40 mL aqueous sample, which was spiked with 1 μg/L of CBs, stirred at 900 rpm at temperature of 60 °C for 30 min. As shown in Fig. 2, 20 μL extractant has the maximum peak areas. The peak areas of analytes decreased when the volume of extractant exceeded 20 μL. This is caused by the dilution effect since only 10 μL of extractant is taken for analysis, while the remaining extractant contains more analyts than that injected into GC. Therefore, 20 μL acetone was used in subsequent experiments.

3.2.3. Extractant temperature

In TC-HS-LPME, the temperature of extractant was an important parameter that influenced the vapor pressure of extractant directly, and determined the feasibility of this technique. The process of extraction of analytes into solvent is exothermic and the partition coefficient is temperature dependent [9]. Decreasing the solvent temperature could increase the partition coefficients of analytes from headspace into extractant, thus enhancing the extraction efficiency. Another important effect of low temperature is to reduce evaporation speed of volatile extractant, then extending the extraction time.

When the temperature of extractant is above 0 °C, the aqueous vapor from sample solution can transfer into the headspace, condensing and mixing with acetone, resulting failure of extraction. The extraction performances at cooling temperature of −5.0, −8.0, −10.0, −13.0, and −15.0 °C were examined, respectively, using 20 μL of acetone as extractant. As expected, the decrease of the acetone temperature from −5 to −10 °C resulted in an increase of peak areas for most analytes. However, further decrease of the temperature from −10 to −15 °C reduces peaks area, as shown in Fig. 3. It was found that after extraction there was only about 12 μL of acetone left at −10 °C, and 15 μL left at −15°C. It indicated that there was still evaporation of acetone during extraction. The possible rea-

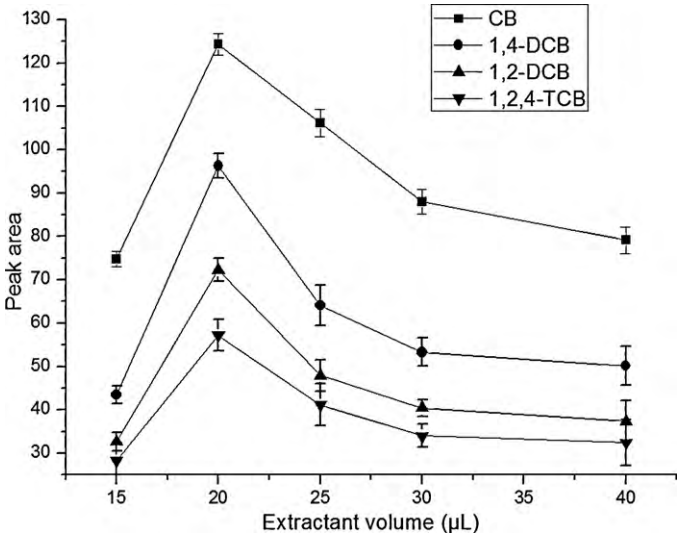

Fig. 2. Effect of extractant volume on extraction efficiency of TC-HS-LPME. Conditions of experiments: acetone at −10 °C; 40 mL standard aqueous sample in 60 mL vial at 60 °C; 900 rpm stirring rate; 30 min extraction time.

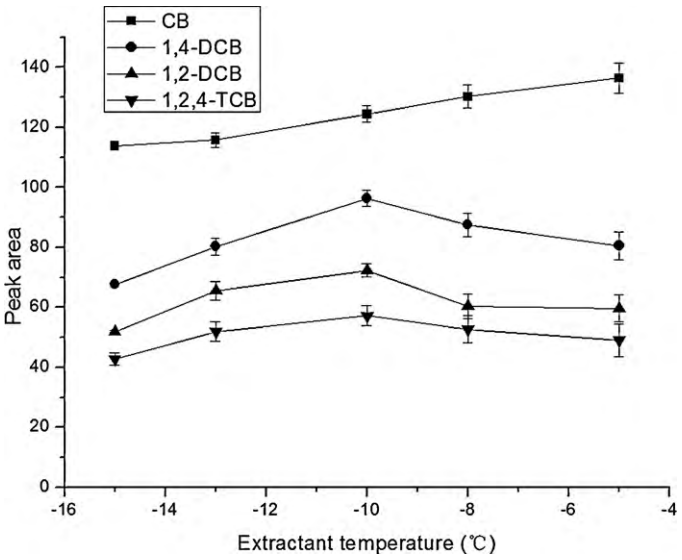

Fig. 3. Effect of extractant temperature on extraction efficiency of TC-HS-LPME. Conditions of experiments are the same as in Fig. 2 except the temperature of extractant.

son was that the total amount of extracted analytes at −15 °C was as the same as that at −10 °C; while the extractant left after taken of 10 μL was 2 μL for −10 °C and 5 μL for −15 °C.The peak areas should decrease as the temperature of extractant decreased. The optimal acetone temperature was −10 °C.

3.2.4. Sample temperature

Sample temperature is another important parameter for TC-HS-LPME, because it determines not only the solubility of the analytes in water matrix, their corresponding concentrations in the headspace, but also the dynamic process to reach equilibrium. The effect of sample temperature on peak area of analytes was examined from 40 to 80 °C, as shown in Fig. 4. The amount of the analytes increased by raising the temperature up to 70 °C. At a higher temperature level, Henry's constant and the diffusion coefficient of analytes in sample solution became larger, so their vapor pressure and concentrations in the headspace increased [25]. Unfortunately, it was found that when the sample temperature was increased to

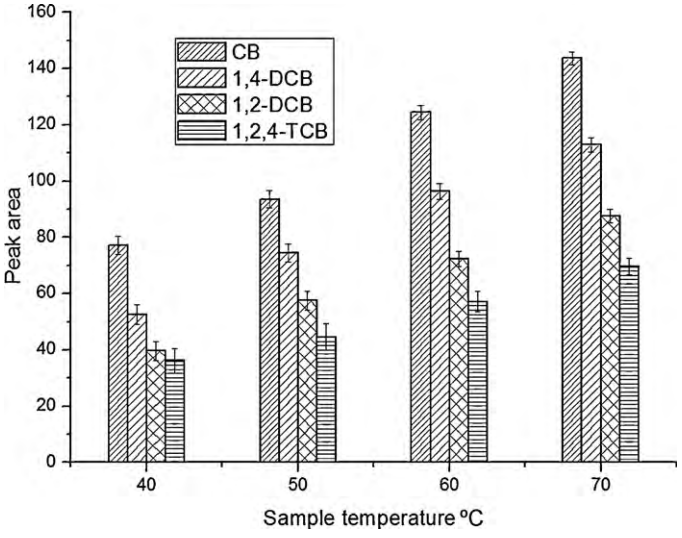

Fig. 4. Effect of sample temperature on extraction efficiency of TC-HS-LPME. Conditions of experiments: 20 μL acetone at −10 °C; Other conditions are the same as in Fig. 2.

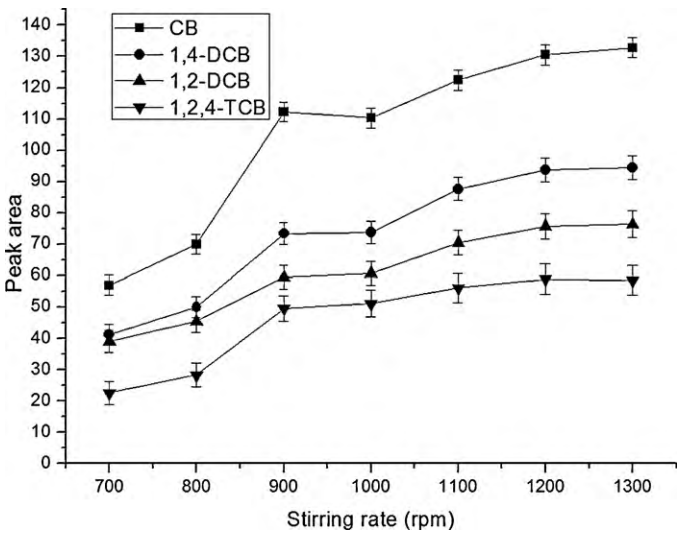

Fig. 5. Effect of stirring rate on extraction efficiency of TC-HS-LPME. Conditions of experiments: 20 μL acetone at −10 °C; 40 mL standard aqueous sample in 60 mL vial with 1 M NaCl at 70 °C; 20 min extraction time.

80 °C, the refrigerating capacity of the PTFE vial could no longer prevent abundant water vapor from going into and condensing in the cavity of vial cap, mixing with acetone and resulting failure of extraction. Thus, sample temperature of 70 °C was selected.

3.2.5. Addition of NaCl

It is known that the addition of salt to an aqueous sample can reduce the solubility of some analytes due to increasing ionic strength in the solution [26]. The impact of ionic strength on extraction efficiency of TC-HS-LPME was studied by adding different concentrations of NaCl (0–4 M). The extraction efficiencies of all analytes were improved with the increase of NaCl concentration, and reached the highest at concentration of 1 M, which was similar as reported in Ref. [7]. The subsequent experiments were all carried out at 1 M NaCl addition in samples.

3.2.6. Stirring rate

Mass transfer in headspace is much faster than the corresponding mass transfer in condensed aqueous phase. So agitation of the sample solution has been universally used to increase the convection, to speed up mass transfer in the aqueous phase. In addition, it can affect convection in the headspace, and also accelerate mass transfer in the headspace phase. Hence, extraction efficiency can be significantly improved by stirring the specimen solution. In this study, 20 μL of acetone at −10 °C was used each time to extract for 20 min, 40 mL water sample spiked at 1 μg/L of all analytes at 70 °C and stirred at different agitation rates (from 700 to 1300 rpm). The influence of stirring rate on extraction efficiency, expressed as peak area, is shown in Fig. 5. The extraction efficiency increased with stirring rate up to 1300 rpm, which was used in the following experiments.

3.2.7. Extraction time

As mentioned above, HS-LPME is an equilibrium process in which analytes partition among sample solution, headspace gas phase, and the extractant, rather than an exhaustive extraction technique [27]. Therefore, the extraction time determines the extraction efficiency. To investigate the effect of extraction time, we extracted the standard sample at above-mentioned conditions for 10–50 min. The results shown in Fig. 6 indicate that the time needed to reach equilibrium was beyond 50 min. Longer extraction time resulted in higher extraction efficiency, while the reproducibility

Table 2
Performance of TC-HS-LPME.

Analyte	Linearity (μg/L)	r^2[a]	RSD (%)[b]	RSD (%)[c]	EF[d]	LODs (μg/L)[e]	LODs (μg/L)[f]	LODs (μg/L)[g]	LODs (μg/L)[h]
CB	0.05–5	0.9997	2.54	3.93	915	0.004	[i]	[i]	0.008
1,4-DCB	0.05–5	0.9996	4.95	4.93	712	0.005	0.890	0.006	0.006
1,2-DCB	0.05–5	0.9993	5.48	5.20	601	0.006	0.270	0.006	0.005
1,2,4-TCB	0.05–5	0.999	4.05	5.27	498	0.008	0.130	0.006	[i]

[a] Number of calibration points = 7.
[b] Spiking level 0.5 μg/L, $n = 5$.
[c] Spiking level 1 μg/L, $n = 5$.
[d] Enrichment factor, the ratio of the concentration of the analyte in acetone after extraction and its concentration in the original water sample.
[e] Limit of detection were calculated as three times of signal to noise ratio(S/N = 3), based on 1 μg/L level (TC-HS-LPME/GC-FID).
[f] Data taken from EPA 8121 [22] (GC-ECD).
[g] Data taken from Ref. [27] (HS-SDME/GC-ECD).
[h] Data taken from Ref. [28] (SDME/GC-ECD).
[i] Not available.

Table 3
Determination of CBs in real water samples.

Analyte	Tap water		Pond water		River water	
	Found (μg/L)	Recoveries (RSD) (%)[a]	Found (μg/L)	Recoveries (RSD) (%)[a]	Found (μg/L)	Recoveries (RSD) (%)[a]
CB	n.d.	90.97(3.44)	n.d.	99.50(7.90)	n.d.	114.28(5.49)
1,4-DCB	n.d.	89.41(3.87)	n.d.	97.70(9.11)	n.d.	108.52(4.59)
1,2-DCB	n.d.	89.84(4.08)	n.d.	99.95(10.86)	n.d.	88.76(8.06)
1,2,4-TCB	n.d.	83.59(3.12)	n.d.	88.96(7.24)	n.d.	89.48(7.97)

n.d. not detected.
[a] Spiking level 1 μg/L, $n = 5$.

of extraction for 50 min was deteriorated (RSD > 10%). Since it was not necessary to reach equilibrium of extraction, a fixed extraction time was adopted for quantitation in headspace LPME [4]. Considering the extraction efficiency and reproducibility of quantitation, 40 min of extraction time was selected for subsequent experiments.

The optimal extraction conditions were as follows: 20 μL of acetone as extractant, kept at −10 °C; 40 mL aqueous sample containing 1 M NaCl in a 60 mL cylindrical vial, placed in 70 °C water bath and stirred at 1300 rpm; extract time was 40 min.

3.3. Evaluation of TC-HS-LPME performance

To investigate the linearity of TC-HS-LPME, seven spiking levels of CBs in the concentration range of 0.05–5 μg/L for all analytes were extracted under the optimal extraction conditions for five times. The correlation coefficients (r^2) were ranged from 0.999 to 0.9997. The precision, expressed as the relative standard deviation (RSD), of TC-HS-LPME was determined by five replicated measurements from aqueous solution at two concentration levels (0.5 and 1 μg/L) under optimal conditions. The RSDs were between 2.54 and 5.48% for 0.5 μg/L and between 3.93 and 5.27% for 1 μg/L, which were satisfactory in quantitative analysis.

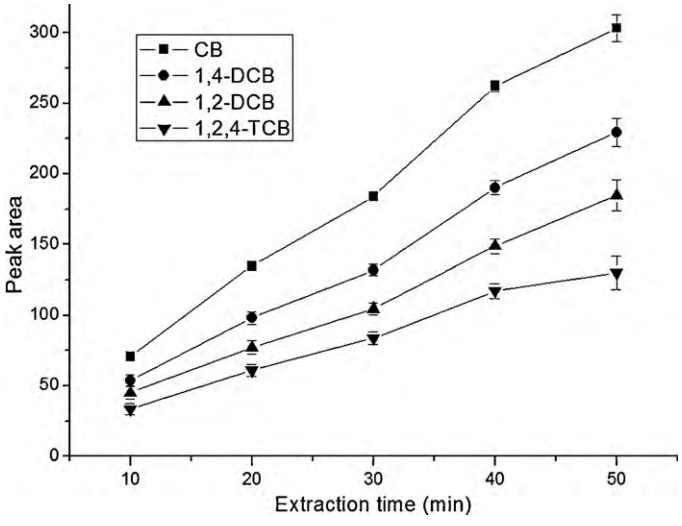

Fig. 6. Effect of extraction time on extraction efficiency of TC-HS-LPME. Conditions of experiments: 20 μL acetone at −10 °C; 40 mL standard aqueous sample in 60 mL vial with 1 M NaCl at 70 °C, stirred at 1300 rpm.

The enrichment factors (EF) defined as the ratio between the final analyte concentration in the extractant and the initial analyte concentration within the sample [27], were between 495 and 915 for all analytes.

The limits of detection (LODs) for all analytes were determined according to published guidelines at a signal to noise ratio (S/N) of 3. The LODs ranged from 0.004 to 0.008 μg/L by using GC-FID, which were two orders of magnitude lower than that of the EPA method 8121 limits [22]. The results were comparable with the LODs reported in Ref. [27] using HS-LPME/GC-ECD and that in Ref. [28] using SDME/GC-ECD. Considering the inferior sensitivity of FID for polychlorobenzenes compared with ECD, lower LODs could be obtained if the ECD was used as the detector of GC.

What should be emphasized was that the extractant used in TC-HS-LPME was acetone, the solvent peak of which did not interference with any target analyte. All the CBs could be determined by this technique in one analysis.

The linear dynamic ranges, correlation coefficients, enrichment factors, reproducibility and limits of detection are summarized in Table 2.

3.4. Application of TC-HS-LPME/GC-FID methods to real samples

Three kinds of real water samples (filtered with 0.45 μm cellulose acetate membrane filters before experiments) were used in this study. Target analytes could not be detected in tap water, pond water and river water. The relative recoveries and RSDs of CBs for three kinds of water samples were evaluated at 1 μg/L spiked concentration level and under the optimal extraction conditions. The relative recoveries ranged from 83.59 to 90.97% for tap water and from 88.96 to 99.5% for pond water, and from 88.76 to 114.28% for

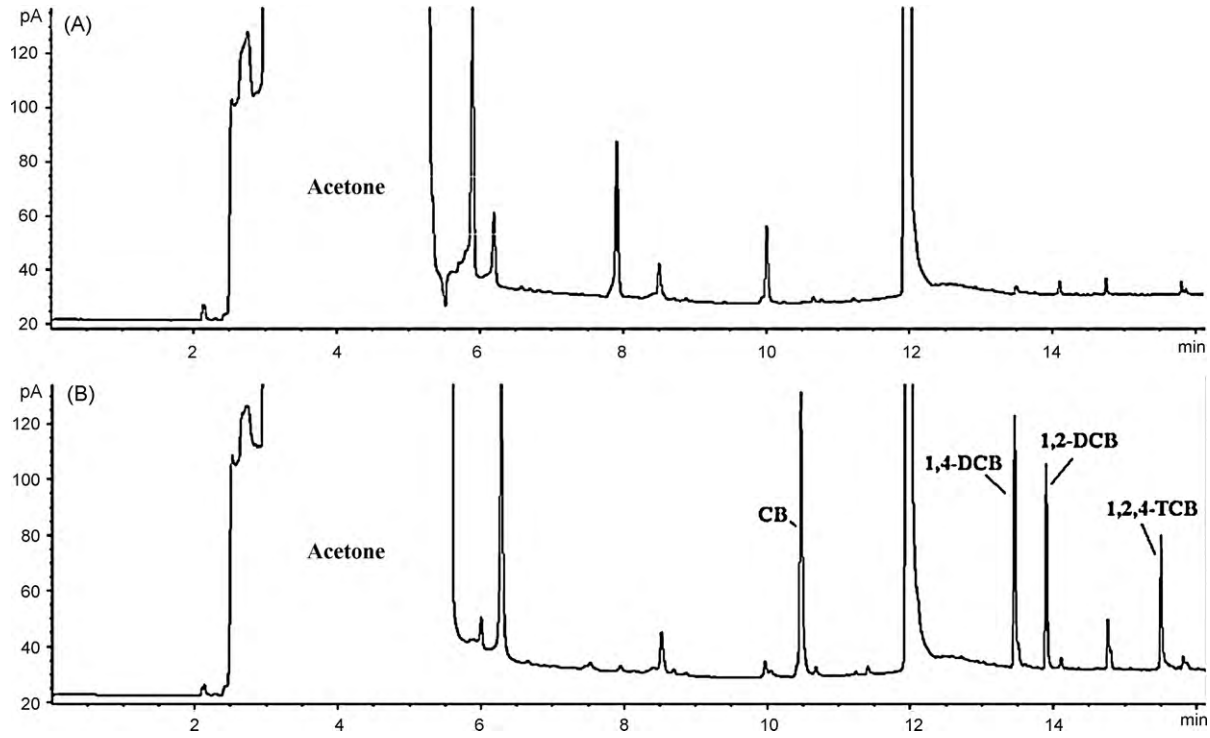

Fig. 7. Chromatogram of CBs obtained by TC-HS-LPME under optimum extraction conditions: (A) unspiked river water, (B) river water spiked with 1 μg/L of CBs. Conditions of experiments: 20 μL acetone at −10 °C; 40 mL standard aqueous sample in 60 mL vial with 1 M NaCl at 70 °C, stirred at 1300 rpm; extraction time 40 min.

river water. The RSDs were from 3.12 to 4.08% for tap water, from 7.24 to 10.86% for pond water and from 4.59 to 8.06% for river water. The performance and results of TC-HS-LPME are summarized in Table 3. The chromatograms are shown in Fig. 7.

4. Conclusions

In this study, a new temperature-controlled headspace liquid-phase microextraction (TC-HS-LPME) device was developed in which 20 μL of volatile solvent could be used as extractant based on the effects of low solid surface energy of PTFE vial cap and low temperature offered by TEC. At subzero temperature, the PTFE vial cap with a cylindrical cavity could suspend volatile solvents at the headspace of sample. The extractant cooling system based on TEC can lower the temperature of extractant, reducing the evaporation speed of extractant and leaving enough volume of extractant to be used in subsequent analysis. The method (TC-HS-LPME) can not only expand the selection of extractant to volatile solvents for HS-LPME, but also enhance the compatibility of HS-LPME with GC. TC-HS-LPME has been applied successfully to determine the CBs in aqueous sample. With this new HS-LPME device and retention gap technique, we could inject 10 μL extractant into GC-FID, resulting a two orders of magnitude lower detection limits than those in the EPA method 8121 [22] and comparable results reported in Ref. [27] in which HS-SDME/GC-ECD was used. It should be noted that, by employing more sensitive detectors, such as ECD or mass spectrometry instead of FID, much lower LODs could be expected.

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References

[1] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[2] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 938 (2001) 113.
[3] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[4] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651.
[5] L. Xu, C. Basheer, H.K. Lee, J. Chromatogr. A 1152 (2007) 184.
[6] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[7] M. Khajeh, Y. Yamini, M. Hassan, Talanta 69 (2006) 1088.
[8] M. Kaykhaii, M.R. Mirbaloochzahi, Environ. Monit. Assess. 147 (2008) 211.
[9] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.
[10] E. Aguilera-Heirador, R. Lucena, S. Cardenas, M. Valcarcel, Anal. Chem. 80 (2008) 793.
[11] G. Shen, H.K. Lee, Anal. Chem. 75 (2003) 98.
[12] S.P. Huang, S.D. Huang, J. Chromatogr. A 1176 (2007) 19.
[13] S.-P. Huang, P.-S. Chen, S.-D. Huang, J. Chromatogr. A 1216 (2009) 4347.
[14] Y.A. Shi, M.Z. Chen, S. Muniraj, J.F. Jen, J. Chromatogr. A 1207 (2008) 130.
[15] H. Xu, Y. Liao, J.R. Yao, J. Chromatogr. A 1167 (2007) 1.
[16] C.L. Ye, Q.X. Zhou, X.M. Wang, J. Chromatogr. A 1139 (2007) 7.
[17] X.M. Jiang, C. Basheer, J. Zhang, H.K. Lee, J. Chromatogr. A 1087 (2004) 289.
[18] M. Holdren, S. Danhof, M. Grassi, J. Stets, B. Keigley, V. Woodruff, A. Scrugli, Anal. Chem. 70 (1998) 4836.
[19] S.H. Haddadi, J. Pawliszyn, J. Chromatogr. A 1216 (2008) 2783.
[20] J.M. Liu, G.B. Jiang, J.F. Liu, Q.F. Zhou, Z.W. Yao, J. Chromatogr. Sci. 26 (2003) 629.
[21] A.E. Sgro, P.B. Allen, D.T. Chiu, Anal. Chem. 79 (2007) 4845.
[22] EPA method 8121, SW-846, Chlorinated Hydrocarbons by Gas Chromatography:Capillary Column Technique, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1994.
[23] K. Grob, D. Frohlich, B. Schilling, H.P. Neukom, P. Nageli, J. Chromatogr. 295 (1984) 55.
[24] T. Jiang, Y.F. Guan, J. Sep. Sci. 37 (1999) 255.
[25] P.S. Chen, S.P. Huang, M.R. Fuh, S.D. Huang, Anal. Chim. Acta 647 (2009) 177.
[26] W.N. Guan, F. Xu, W.M. Liu, J.H. Zhao, Y.F. Guan, J. Chromatogr. A 1147 (2007) 59.
[27] L. Vidal, A. Canals, N. Kalogerakis, E. Psillakis, J. Chromatogr. A 1089 (2005) 25.
[28] A. Tor, J. Chromatogr. A 1125 (2006) 129.