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In-line coupling headspace liquid-phase microextraction with capillary electrophoresis

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ABSTRACT

An analytical technique of in-line coupling headspace liquid-phase microextraction (HS-LPME) with capillary electrophoresis (CE) was proposed to determine volatile analytes. A special cover unit of the sample vial was adopted in the coupling method. To evaluate the proposed method, phenols were used as model analytes. The parameters affecting the extraction efficiency were investigated, including the configuration of acceptor phase, kind and concentration of acceptor solution, extraction temperature and time, salt-out effect, sample volume, etc. The optimal enrichment factors of HS-LPME were obtained with the sample volume of about half of sample vials, which were confirmed by both the theoretical prediction and experimental results. The enrichment factors were obtained from 520 to 1270. The limits of detection (LODs, S/N = 3) were in the range from 0.5 to 1 ng/mL each phenol. The recoveries were from 87.2% to 92.7% and the relative standard deviations (RSDs) were lower than 5.7% ($n = 6$). The proposed method was successfully applied to the quantitative analysis of the phenols in tap water, and proved to be a simple, convenient and reliable sample preconcentration and determination method for volatile analytes in water samples.

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1. Introduction

Since single drop microextraction (SDME) was introduced as an effective sample pretreatment technique [1–4], liquid-phase microextraction (LPME) has been developed quickly and applied to chromatographic analysis and capillary electrophoresis (CE) [3]. The pretreatment technique has the advantages of high enrichment factor, fine purification capability, low analysis cost, trace solvent consumption, simple operation setup, etc. In the past ten years, typical LPME techniques were successfully proposed and employed in the sample pretreatment of instrumental analysis, such as SDME [2,3], liquid–liquid–liquid microextraction (LLLME) [4], hollow fiber protected liquid-phase microextraction (HF-LPME) [5] and headspace liquid-phase microextraction (HS-LPME) [6].

HS-LPME can be used to analyze volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), which are evaporated from solid or aqueous samples and enriched by a microlitre solvent drop hanging at the microsyringe tip. As the acceptor phase does not contact with the samples, HS-LPME can concentrate volatile analytes and clean up sample matrices easily and conveniently. It has been applied to the determination of benzyl analytes [7], phenols [8], amines [9], acid preservatives [10], etc. In HS-LPME, organic solvents are frequently used as acceptor phases. When the extraction is carried out with high temperature, solvent loss should be limited. To reduce the solvent loss, external-cooling systems were adopted in the extraction [11,12]. Moreover, electrolyte solutions, buffer solutions and ionic liquids (ILs) were also used as acceptor phases to overcome the deficiency [13–15].

Analytical techniques of coupling sample pretreatment with instrumental analysis are preferable, because of its convenience, speediness, efficiency and reproducibility. Solid-phase extraction (SPE), solid-phase microextraction (SPME) and LPME are suitable for the combination [16,17]. The coupling methods of LPME-CE can transfer the extracted analytes to CE directly and improve the detection sensitivity effectively [18,19]. Choi and Chung reported an on-line SDME-CE method [20], by which the enrichment factor of several hundreds was obtained in 10 min and cross-contamination was eliminated using a fresh solvent drop in each analysis. On the basis of the work, they carried out a LLLME-CE method [21] with a 2-phase acceptor drop formed by the pressure of their CE apparatus, and a 2-phase SDME with a large solvent drop formed by a Teflon sleeve to improve the stability and reliability further. Nozal and Valcárcel reported an in-line LPME-CE method for the selective enrichment of analytes in urine samples [22], in which a microextraction unit was fabricated with a hollow fiber connected with a short capillary and a separation one. We proposed an on-column pretreatment method by combining LLLME

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and pH-mediated stacking as a dual preconcentration method for CE analysis [23].

The purpose of this work is to actualize in-line coupling HS-LPME with CE to determine volatile analytes in water samples. A special cover unit of the sample vial was designed for the combination. As the representative volatile pollutants in environment, phenols were used as the model analytes to evaluate the proposed method. Parameters affecting the extraction efficiency were investigated, including the configuration of acceptor phase, kind and concentration of acceptor solution, extraction temperature and time, salt-out effect, sample volume, etc. The effect of the sample volume on the enrichment factor of HS-LPME was studied by both theoretical and experimental methods. Moreover, the proposed method was applied to the analysis of the phenols in tap water.

2. Experimental

2.1. Reagents and solutions

All the reagents were of analytical grade. Phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP) and other reagents were purchased from Sinopharm Chemistry Reagent (Shanghai, China). Deionized water was obtained from Hefei Lanlan Water (Anhui, China).

The stock solutions of 1000 μg/mL for each phenol were prepared in methanol and stored in 10-mL brown flasks at 4 °C. The calibration solutions of five concentration levels were prepared by diluting the stock solutions with deionized water. The buffer solution for CE separation was 20 mmol/L $Na_2B_4O_7$ and 10 mmol/L Na_2HPO_4, and was adjusted to pH 9.8 using 1.0 mol/L NaOH.

2.2. Instrumentation

A 1229-HPCE Analyzer (Institute of New Technology Application, Beijing, China) detecting at 214 nm was employed throughout the experiment. An N-2000 double-channel chromatography processor (Institute of Information Engineering of Zhejiang University, Zhejiang, China) was used for data acquisition and processing. A 78-1 magnetic stirrer with hotplate (Jintan Experimental Instrument, Jiangsu, China) and a temperature controller (Shanghai Medical Instrument, Shanghai, China) were used to regulate the extraction temperature of sample solutions in a water bath. A 50-μm I.D. fused-silica capillary (Handan Xinnuo Fiber Chromatography, Hebei, China) with its total length of 55 cm and effective length of 40 cm was adopted in the CE separation. The capillary was flushed daily from its outlet by pressure, in the order of 0.1 mol/L HCl for 5 min, 0.1 mol/L NaOH for 10 min, and the running buffer for 10 min. Between the electrophoresis runs, the capillary was flushed with the buffer solution for 2 min. The separation voltage was 20 kV. The sample solution of 6.0 mL was transferred into a 14-mL flat-bottom sample vial. The laboratory-made cover unit of the sample vial consisted of a vial cover and a cover plug, which was made of polytetrafluoroethylene and silicone rubber, respectively. Each of them had a slot from its edge to centre, as depicted in Fig. 1 (1).

2.3. Headspace microextraction procedure

Firstly, the separation capillary with its volume about 1 μL was filled with 0.5 mol/L NaOH solution from its outlet at the pressure of 55 kPa for 20 s. The capillary inlet was placed in the centre of the cover unit through the slots positioned in the same direction, as shown in Fig. 1(2). 6.0 mL sample solution containing 0.10 g/mL sodium chloride was transferred into the sample vial. The silicone plug was turned 180° inside the vial cover and the sample vial was sealed by the cover unit to avoid the phenols escaping from the sample vial during the extraction, as shown in Fig. 1(3). The capillary tip was fixed at 1 cm height above the surface of the sample solution. In the second step, the buffer solution was injected from the capillary outlet using the same pressure and time as the first step to expose an alkaline drop suspending at the capillary tip. Then the capillary outlet was placed into a low potential buffer solution. In the third step, the extraction was carried out at 60 °C for 30 min on the magnetic stirrer. After the extraction, the acceptor solution was hydrodynamically aspirated into the capillary with 10 cm height difference for 20 s. By replacing the capillary inlet to the extraction position, the cover unit was opened, the excessive drop was cleaned by a filter paper and the capillary was removed from the cover unit with the slots in the same direction. Finally, the capillary inlet was placed in a high potential buffer solution to carry out CE separation. A photograph of the HS-LPME setup is shown in Fig. 1(4). The cover unit can be employed in HS-LPME repeatedly.

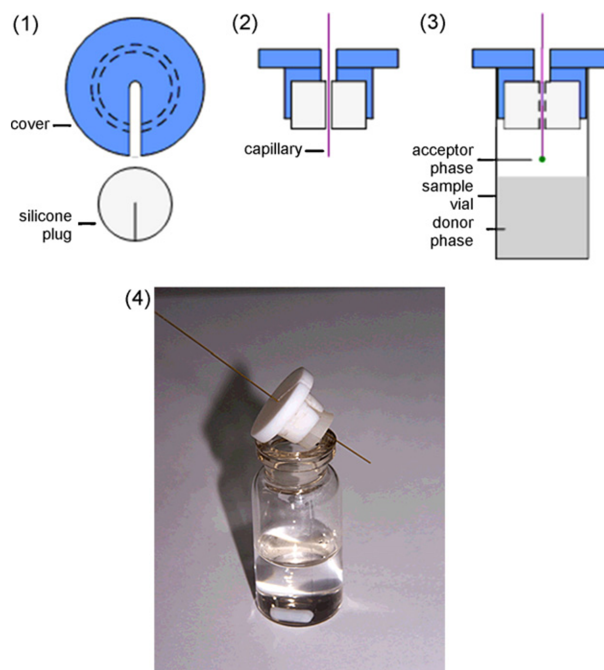

Fig. 1. Schematic of cover unit for sample vial and a setup of headspace liquid-phase microextraction. (1) A planform view of the slotted cover and plug; (2) a sectional view of the cover unit by aligning the slots of the cover and plug, and inserting the separation capillary into the cover center; (3) a sectional view of the HS-LPME setup by rotating the silicone plug to 180° and sealing the sample vial with the cover unit; (4) a photograph of the HS-LPME setup.

3. Results and discussion

3.1. Headspace liquid-phase microextraction

The static and dynamic theory of HS-LPME has been demonstrated [6,7,24,25], and water-based (WB) HS-LPME [13] was also studied, in which the distribution constant K_{ah} is expressed as

$$K_{ah} = \frac{C_a}{C_h} = \frac{[\mathrm{HA}]}{C_h}\left(\frac{K_a}{[\mathrm{H}^+]} + 1\right) \quad (1)$$

The equilibrium concentration of an analyte in acceptor phase of HS-LPME is given by [26]

$$C_a = \frac{K_{as}V_sC_o}{K_{as}V_a + K_{hs}V_h + V_s} \quad (2)$$

where K_{ah}, K_{hs} and K_{as} are the distribution constants of acceptor phase-headspace, headspace-sample solution and acceptor phase-

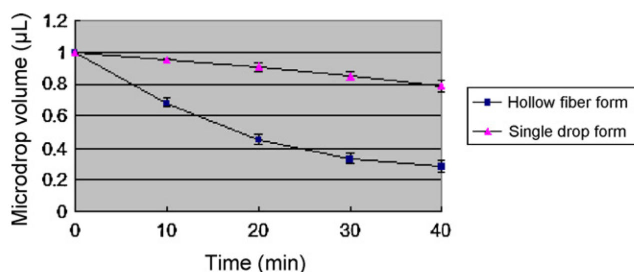

Fig. 2. Effect of extraction time on acceptor volume in headspace liquid-phase microextraction. Temperature, 60 °C; stirring rate, 1000 rpm; concentration of sodium hydroxide, 0.5 mol/L; sample concentration, 0.10 μg/mL each phenol; sample volume, 6.0 mL; concentration of sodium chloride, 0.10 g/mL.

sample solution, respectively. K_a is the ionization constant of an analyte. C_a and C_h are the equilibrium concentrations of the analyte in acceptor phase and headspace, and C_o is the original concentration of the analyte in sample solution. [HA] and [H^+] are corresponding to the concentrations of the analyte molecule and H^+ in acceptor phase. V_a, V_h and V_s are the volumes of acceptor phase, headspace and sample solution, respectively.

The enrichment factor of HS-LPME can be expressed as

$$E = \frac{C_a}{C_o} = \frac{K_{as}V_s}{K_{as}V_a + K_{hs}V_h + V_s} \tag{3}$$

After the numerator and denominator of Eq. (3) are divided by K_{as}, we found that Eq. (3) can be simplified to Eq. (4), on condition that K_{as} is very large and V_a is small enough.

$$E \approx \frac{K_{ah}V_s}{1 - V_s} \tag{4}$$

where the volume of the sample vial is supposed to be a unit volume. To obtain the optimal value of E, an equation is obtained from the derivative of Eq. (4),

$$V_s^2 \frac{dK_{ah}}{dV_s} - V_s \frac{dK_{ah}}{dV_s} - K_{ah} = 0 \tag{5}$$

where dK_{ah}/dV_s and K_{ah} are the functions of V_s, but weakly influenced by V_s. The solutions of Eq. (5) can be expressed as

$$V_s = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 + 4K_{ah}/\frac{dK_{ah}}{dV_s}} \tag{6}$$

In accordance with Eq. (4) and the definition of K_{ah}, C_h can be approximately expressed as,

$$C_h \approx \frac{C_oV_s}{1 - V_s} \tag{7}$$

From Eqs. (1) and (7), K_{ah} is obtained approximately, and dK_{ah}/dV_s can be expressed by the derivative of K_{ah}. By introducing K_{ah} and dK_{ah}/dV_s into Eq. (6), a valid solution of V_s is 1/2. It manifests that the optimal enrichment factor of HS-LPME can be obtained when half of sample vial is filled with sample solutions. However, the conclusion is based on equilibrium conditions.

3.2. Configuration of acceptor phase

In this work, the separation capillary was used as the holder of acceptor solution, and its inner volume was equal to the volume of acceptor phase. Two types of acceptor configuration were studied, SDME and HF-LPME. In the HF-LPME, a porous polypropylene hollow fiber of 400 μm I.D. and 2 mm effective length connected with the capillary inlet, which had the same acceptor volume as that of single drop one. The volume of the acceptor phase varying with the extraction time at 60 °C was investigated, as shown in Fig. 2. It was found that the acceptor solution in the hollow fiber was evaporated more than that of the single drop, and caused the analyte adsorption on the hollow fiber of large surface area. To obtain favorable recovery and reproducibility, SDME was adopted in this work.

3.3. Acceptor phase

In headspace WB-LPME, buffer or NaOH solutions can be adopted as acceptor phases to extract the phenols. It is convenient to use the buffer solutions directly as the acceptor phase in HS-LPME. By optimizing the separation conditions, borate, phosphate and their mixture solutions could be adopted as the running buffer, among which the best one was the mixed buffer solution. To obtain high enrichment factors, phenols should be changed to their ionic forms in alkaline solutions. As the pH values of the buffer solutions were lower than 12, their extraction efficiency was lower than that of NaOH solution. Therefore, NaOH solution was used as the acceptor phase in this work.

The effect of NaOH concentration on peak area of the phenols was investigated. According to the experimental results, the equilibrium concentration of the phenols in the acceptor phase was enhanced by increasing NaOH concentration from 0.05 to 0.5 mol/L, owing to the enhancement of the distribution constants of acceptor phase-headspace (K_{ah}), as indicated by Eq. (1). However, it kept almost constant with the concentrations higher than 0.5 mol/L. It implied that the phenols were totally ionized in the acceptor phase. Moreover, the peak broadening and reduced resolution were observed with 0.75 mol/L NaOH. To form an acceptor drop, the NaOH solution filled in the capillary was pushed out with the fresh buffer solution by pressure. When NaOH concentration was higher than 0.75 mol/L, the NaOH amount remaining in the capillary could influence the pH value and the concentration of the buffer solution, and thus increase the peak broadening and reduce the separation resolution. With 0.75 mol/L NaOH, the peak broadening increased to about 1.2-fold of normal one, and 4-nitrophenol and 2-nitrophenol could not be separated completely. Therefore, 0.5 mol/L NaOH was selected as the acceptor phase in this work.

3.4. Headspace and donor phase

In HS-LPME, mass transfer coefficient, evaporation rate, Henry's law constant and distribution constant of headspace-sample solution (K_{hs}) are enhanced by increasing the extraction temperature [27]. The peak area of the phenols varying with the extraction temperature was investigated from 40 to 70 °C. It was found that the peak area of the phenols was enhanced by increasing the extraction temperature up to 60 °C, especially for 2-chlorophenol with higher Henry's law constant. However, the peak area changed slowly and the recovery of the phenols was unsatisfactory with the extraction temperature higher than 60 °C. The possible exothermic processes for transferring the phenols into the acceptor phase and the loss of acceptor phase might have negative effects on the extraction with high temperature. In this work, the extraction temperature was chosen at 60 °C.

To evaporate the phenols from sample solutions, the pH value of sample solutions should keep the phenols in their neutral forms. The pH value of sample solutions was investigated from 2.0 to 6.5. According to the experimental results, it did not influence the extraction in this pH range. Considering the possibility of other phenols with low pK_a values, the pH value of sample solution was selected at 5.0.

The mass transfer of the analytes from sample solutions is one of the limitation steps in the extraction [28]. To increase the mass transfer speed and keep a uniform temperature in sample solutions, an agitating step should be adopted in LPME. The stirring rate was investigated from 400 to 1200 rpm, as shown in Fig. 3. It was found that the peak area of the phenols was enhanced by increasing the

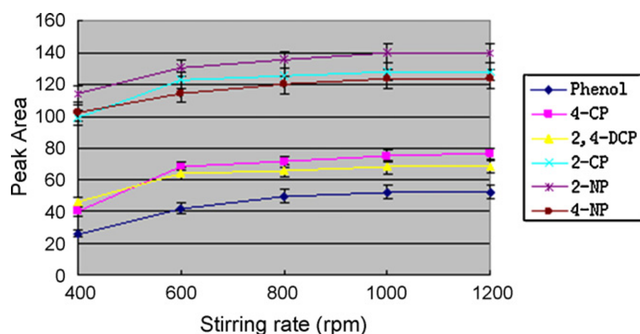

Fig. 3. Effect of stirring rate on extraction efficiency. The extraction time is 30 min. Other conditions are the same as in Fig. 2, except the stirring rate.

stirring rate from 400 to 1000 rpm. With the stirring rate higher than 1000 rpm, the analytical signals kept almost constant.

3.5. Salt-out effect

Salt-out effect is widely used in LPME to increase the extraction efficiency. The concentration of NaCl up to 0.20 g/mL in sample solutions was examined. It was found that the peak area of the phenols achieved a maximal value with 0.10 g/mL NaCl, resulting from the interaction of water molecules with analytes and salt ions [27]. Hydration spheres around the salt ions formed by water molecules could reduce the water concentration to dissolve the phenols and be beneficial to remove the phenols into the headspace. However, the interactions between salt ions and analyte molecules were also accelerated with the NaCl concentration higher than 0.10 g/mL, which reduced the phenol evaporation into the headspace.

3.6. Sample volume and extraction time

The volume of sample solutions can influence the equilibrium concentration of analytes in acceptor phase and the enrichment factor of analytes in HS-LPME, as indicated by Eq. (3). With a fixed concentration of 0.10 μg/mL for each phenol and the vial volume of 14 mL, the sample volume was investigated from 3.0 to 12 mL. It was found that the peak area of the phenols achieved the optimal value with the sample volume about 6.0 mL. The experimental results of this work and most of the analytes in reported works [8,10,14,29–31] were close to the prediction of Section 3.1, in which the optimized volume ratio of sample solution to sample vial ranged from 40% to 65%. Under the equilibrium conditions, the analytes extracted into acceptor phases were enhanced by increasing the sample volume, viz., increasing the analyte amount in sample solutions, but reduced by decreasing the headspace volume further, viz., limiting the analyte vapor into headspace. Only a few analytes were in the range of 65–75% and different from the prediction [32,33]. This resulted from non-equilibrium conditions with lower extraction temperature and shorter extraction time. In this situation, the volume ratio may be higher than the prediction.

HS-LPME is dependent on equilibrium processes rather than exhaustive ones, and should take a period of time to achieve the equilibrium concentration in acceptor phase. When the extraction equilibrium is achieved, the increase of extraction time cannot improve the extraction efficiency further. In addition, more acceptor solution can be lost with long extraction time. The peak area varying with extraction time from 10 to 40 min was investigated, as shown in Fig. 4. The responses of the phenols were enhanced by increasing the extraction time from 10 to 30 min. When the extraction time was longer than 40 min, more than 20% acceptor solution was lost, as illustrated in Fig. 2, which made the peak area

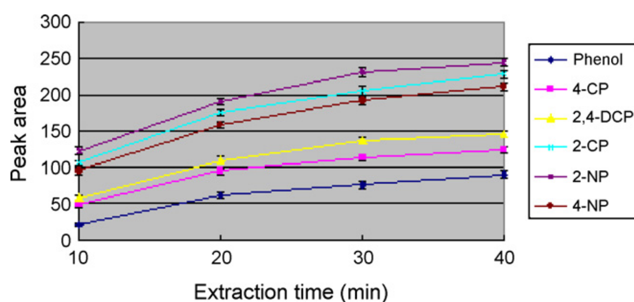

Fig. 4. Effect of extraction time on extraction efficiency. Other conditions are the same as in Fig. 2, except the extraction time.

increase slowly. Therefore, the extraction time was set at 30 min in this method.

3.7. Analytical characteristic and real sample analysis

The proposed method was applied to the analysis of the phenols in tap water, and the electropherograms are illustrated in Fig. 5. To

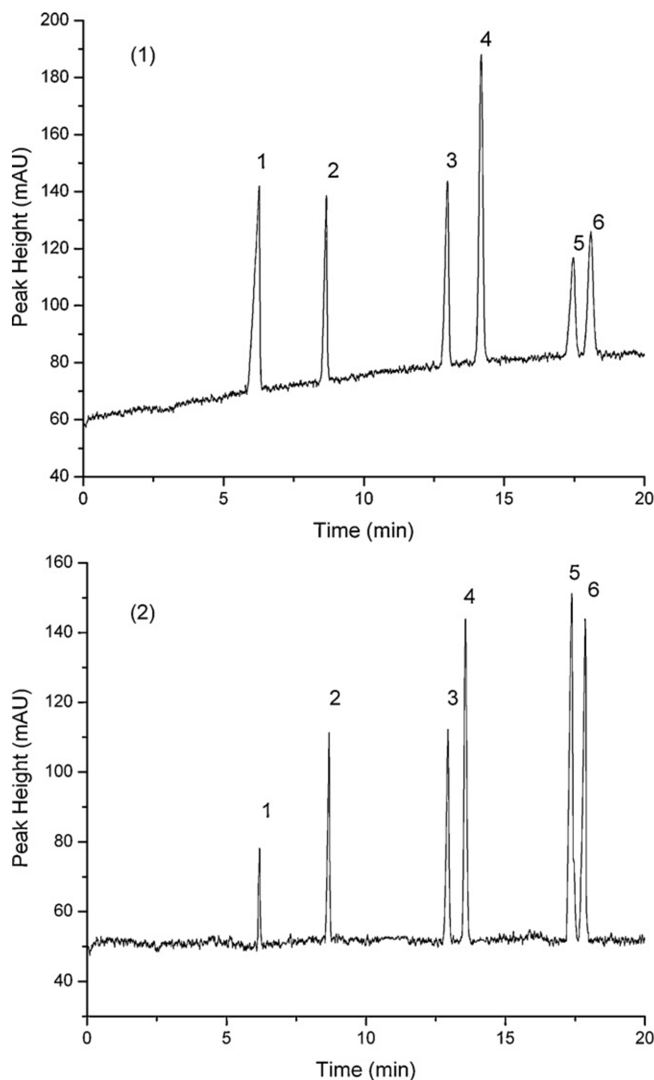

Fig. 5. Electropherograms of phenols in standard and sample solution: (1) 100 μg/mL of each phenol in deionized water without the extraction; and (2) tap water spiked with 0.10 μg/mL of each phenol by HS-LPME-CE. The extraction time is 30 min and other conditions are the same as in Fig. 2. Peaks identification: (1) phenol, (2) 2,4-dichlorophenol (2,4-DCP), (3) 4-chlorophenol (4-CP), (4) 2-chlorophenol (2-CP), (5) 4-nitrophenol (4-NP) and (6) 2-nitrophenol (2-NP).

Table 1
Performance of in-line headspace LPME method.

Compound	Enrichment factor	RSD (%)	Linear range (ng/mL)	LOD (ng/mL)	Recovery (%)
Phenol	520	5.7	3–300	1	87.2
2-Nitrophenol	1020	4.2	1.5–300	0.6	90.1
4-Nitrophenol	1150	3.9	1.5–300	0.5	92.7
2-Chlorophenol	1270	4.1	1.5–300	0.5	91.4
4-Chlorophenol	820	4.9	3–300	0.75	89.2
2,4-Dichlorophenol	630	4.2	3–300	1	90.1

evaluate the accuracy of the proposed method, the recovery of the phenols was examined, which was defined as the ratio of analytical signals of phenols spiked into tap water to those in deionized water. With the concentration of 20, 50 and 100 ng/mL each phenol spiked into the tap water samples, the recoveries of the proposed method were in the range of 87.2–92.7%. The enrichment factors of the proposed method were from 520 to 1270, which were defined as the ratio of the analyte concentration after the extraction to those before. The LODs of the proposed method were in the range from 0.5 to 1 ng/mL each phenol (S/N = 3) in the tap water, and comparable with 1–10 ng/mL in on-line LPME methods [34,35], but much lower than those of 0.1–0.25 μg/mL in CE-UV [36]. The linear calibration concentration was in the range from 3.0 to 300 ng/mL. The relative standard deviations (RSDs) of the peak area were less than 5.7% ($n = 6$). The analytical characteristics are listed in Table 1. Each phenol in tap water samples was lower than its limit of quantification (<3.0 ng/mL).

4. Conclusion

The analytical method of in-line coupling HS-LPME with CE was proposed by using the special cover unit of sample vial. Single drop of acceptor phase was adopted in the HS-LPME, in order to reduce the loss of acceptor phase. The optimal enrichment factor was obtained with the sample volume about half of sample vials, which were confirmed by the theoretical prediction and experiment results in this work. The proposed method was successfully applied to the quantitative analysis of the phenols in tap water, and the HS-LPME technique proved to be a simple, convenient and reliable sample pretreatment method for CE analysis.

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