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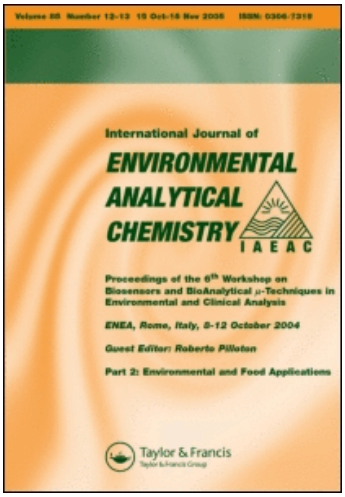

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Determination of chlorophenols in environmental water samples using directly suspended droplet liquid-liquid-liquid phase microextraction prior to high-performance liquid chromatography

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Determination of chlorophenols in environmental water samples using directly suspended droplet liquid-liquid-liquid phase microextraction prior to high-performance liquid chromatography

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A new sample preparation method named directly suspended droplet liquid-liquid-liquid phase microextraction was used in this research for determination of three chlorophenols in environmental water samples. The analytes (2-chlorophenol, 3-chlorophenol and 4-chlorophenol) were extracted from 4.5 mL acidic donor phase, (pH 2, P1) into an organic phase, 350 μL of benzene/1-octanol (90 : 10 *v*/*v*, P2) and then were back-extracted into a 7 μL droplet of an basic (pH 13) aqueous solution (acceptor phase, P3). In this method, contrary to the ordinary single drop liquid-phase microextraction technique, an aqueous large droplet is freely suspended on the surface of the organic solvent, without using a microsyringe as supporting device. This aqueous microdroplet is delivered at the top-centre position of an immiscible organic solvent which is laid over the aqueous donor sample solution while the solution is being agitated. Then, the acceptor phase containing chlorophenols was withdrawn back into a HPLC microsyringe and neutralised by adding of 7 μL HCl 0.1 M. The total amount was eventually injected into the HPLC system with UV detection at 225 nm for further analysis. Parameters such as the organic solvent, phases volumes, extraction and back-extraction times, stirring rate and pH values were optimised. The calibration graphs are linear in the range of 10–2000 μg L^{-1} with $r \geq 0.9973$. The enrichment factors were ranged from 115 to 170, and the limit of detection (LOD, $n = 7$) varied from 5 to 10 μg L^{-1}. The relative standard deviations (RSDs, $n = 5$) were found 6.8 to 7.4 at $S/N = 3$. All experiments were carried out at room temperature, (22 ± 0.5°C).

Keywords: directly suspended droplet; liquid-liquid-liquid microextraction (LLLME); chlorophenols; water analysis

1. Introduction

Chlorophenols (CPs) are one of the most significant pollutants that extensively exist in environmental water and soil samples [1], because of their widespread uses in industrial, chemical and agricultural applications. The main sources of CPs are the effluent discharges of industries such as paper and pesticide industries [2]. These compounds have been used as the intermediates in the production of plastics, dyes, antioxidants and pharmaceutical

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products [3]. On the other hand, the chlorination process of non-chlorinated phenols in water can also generate some chlorophenols.

The negative effect of CPs for human health has led to their categorisation and inclusion by the US Environmental Protection Agency and the Commission of the European Communities in the lists of priority pollutants [4]. The European Economic Community [now European Union (EU)] issued the pollutant list [5] that includes many polychlorophenols and establishes their maximum allowable concentration in drinking water. Therefore, developing the reliable, sensitive and easily operating detection methods are of great interest for determining these compounds in the environmental samples. A wide number of procedures have been used for chlorophenols analysis in the environmental samples such as gas chromatography (GC) [6–8], capillary electrophoresis (CE) [9] and liquid chromatography (LC) [10,11]. High performance liquid chromatography (HPLC) is a popular technique for this purpose and over the past decades has been one of the mainly used methods for the separation and determination of chlorophenols [10–13]. Various detectors such as ultraviolet (UV) [10,11], fluorescence [14], electrochemical [13,15], and mass spectrometry [16] were coupled with HPLC for the determination of CPs.

A common feature of such methods is the requirement for analyte preconcentration because of the low concentration of CPs and the complexity of the environmental samples. Liquid–liquid extraction (LLE) [17] and solid-phase extraction (SPE) [13] are the most commonly used techniques for separation or preconcentration of CPs in environmental samples. However, for extraction or elution, these steps often require a considerable amount of toxic solvents, which are harmful for the operators and also introducing large pollution to the environment. For this purpose in recent years, some different microextraction techniques that use no or small amounts of organic solvents have been developed. Among these techniques, the solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) methods are predominant techniques for analysis of chlorophenols. SPME technique has some drawbacks such as limited lifetime, fragility of fibres and possibility of sample carry-over [18]. Therefore, when the procedure is coupled to high-performance liquid chromatography or gas chromatography, a solvent dissolution or desorption steps for recovering of the analytes from the sorbent are incomplete and carry-over occurs. In addition, it is very difficult to extract some highly polar compounds like chlorophenols without derivatisation using the SPME method. Because of these problems, an alternative miniaturised sample preparation approach, i.e. liquid-phase microextraction (LPME), emerged in the mid-to-late 1990s [19,20]. In LPME, only a small amount of solvent (microlitre) is needed for concentrating the analytes from aqueous samples. This method overcomes many of the disadvantages of LLE and SPME which are mentioned above. In two-phase LPME, extraction takes place between a small amount of a water-immiscible organic solvent and an aqueous phase containing the analytes [21–23]. But, if the analytes are further back-extracted into a third phase (aqueous solution), the procedure is termed liquid-liquid-liquid microextraction (LLLME) or three-phase LPME (extraction/back-extraction) [24], to achieve preconcentration and purification for ioniseable and chargeable compounds (i.e. CPs) from different aqueous samples [10], without the need for both solvent evaporation and analyte desorption. In this method, three liquid phases were used, P1 is the aqueous sample solution where pH is adjusted to deionise the compounds; the organic phase (P2), which is layered over the donor phase as a liquid membrane and the receiving aqueous phase (P3), which is laid over or inside the organic phase and the pH of which is adjusted to

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ionise the sample [25,26]. With the help of stirring, polar compounds are extracted to the organic solvent and then back-extracted to the receiving phase, which can be directly analysed.

In the present work, a very simple, cheap, easy and rapid liquid-liquid-liquid microextraction method utilising a new design was used for preconcentration of three chlorophenols from water samples prior to the liquid chromatography analysis. The effects of some parameters on extraction efficiency have been studied and the optimal preconcentration conditions have been established for HPLC determination of CPs with UV detection.

2. Experimental

2.1 *Chemicals and reagents*

All the target analytes and solvents were HPLC grade. 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP) and sodium hydroxide were purchased from Riedel de Haën (Steinheim, Germany). 1-octanol was obtained from Fluka (Buchs, Switzerland). Methanol, benzene and all other chemicals were purchased from Merck (Darmstadt, Germany) and used without any further purification.

A stock methanolic standard solution ($0.1\,g\,L^{-1}$) of 2-chlorophenol, 3-chlorophenol and 4-chlorophenol was prepared separately and refrigerated at 4°C. The working standard sample solutions were provided daily at different concentrations by diluting the stock standard solutions with deionised water which was purified in a Milli-Q filtering system (Millipore, Bedford, MA, USA).

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2.2 *Instrumentation*

The HPLC system was a Waters 600 E (Millipore, Milford, MA, USA). It consists of a Waters 486 tuneable UV-Vis detector and a Waters 746 integrator. A C1 Cheminert injector valve with a 20 μL loop (Switzerland) and a C18 column (perfectsil, 150 × 4.6 mm I.D., 5 μm particles) were used for injection and separation of the analytes, respectively. The chromatographic separations were performed with a degassed mobile phase which consisted of methanol–pure water (50 : 50, *v*/*v*) and was delivered by a Waters LC-600 HPLC pump. The flow rate of the mobile phase was $1.0\,mL\,min^{-1}$. The column was put at ambient temperature (22 ± 0.5°C).

2.3 *Directly suspended droplet LLLME*

The experimental microextraction setup is shown in Figure 1. The extraction was performed according to the following procedure. Sample solution (4.5 mL, adjusted to pH 2 with HCl) was added to the glass vial (6 mL cylindrical sample cell) and stirring bar (7 × 3 mm) was placed on the bottom of the vial. A heating-magnetic stirrer (0–1200 rpm) was used for stirring the extraction mixture. Organic solvent (350 μL, benzene/1-octanol 90 : 10 *v*/*v*) was then added to the sample solution by a 1000 μL syringe (Knauer, USA). Then the mixture was agitated vigorously for 120 s at 1200 rpm which was led to form a cloudy mixture of the sample solution and the tiny droplets of the organic solvent. Thereafter, the mixture was allowed to be quiescent for few seconds to gather the drops of the organic solvent together up to the aqueous sample solution and therefore, the organic

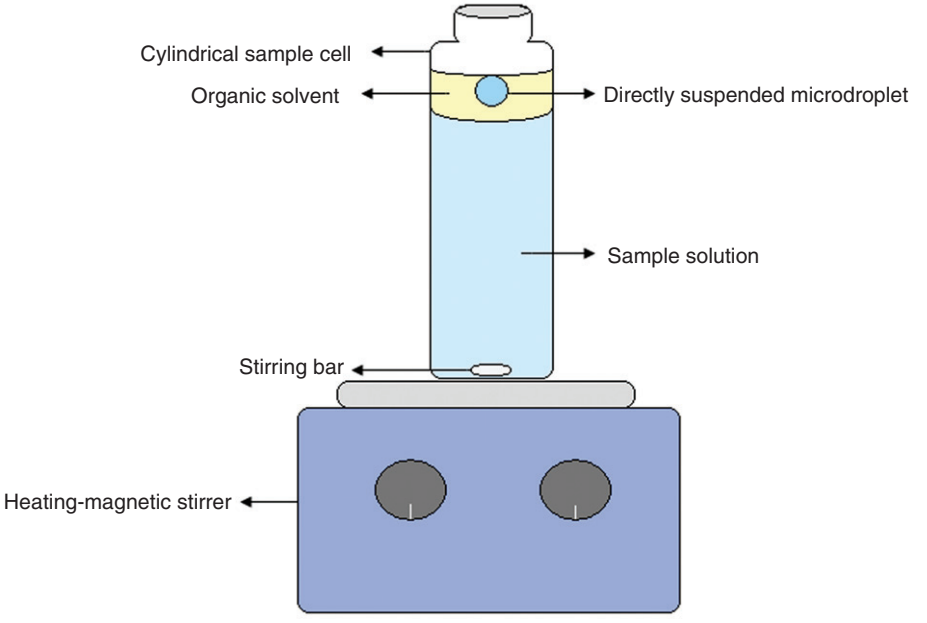

Figure 1. Schematic illustration of the used apparatus for directly suspended droplet three liquid phase microextraction.

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layer which was enriched by the analytes created again above the donor phase. After this time, the acceptor phase (7 μL 0.1 M NaOH, pH 13) was delivered at the top-centre position of the immiscible organic solvent by a 25 μL flat-cut HPLC microsyringe (Hamilton, Reno, Nevada, USA) which was used to introduce the acceptor phase and also acts as an injection device. After agitating at 720 rpm for 5 min, the microdroplet was withdrawn back by the HPLC microsyringe and neutralised by adding 7 μL of 0.1 M HCl. Finally, the total amount was injected into the HPLC system with UV detection at 225 nm. The photographs of this extraction method are in our last published work [26].

3. Results and discussion

Three liquid-phase microextraction consists of two steps, extraction and back-extraction. At the first step, the analytes are extracted from the donor phase into an organic solvent and in the second step they are back-extracted from the organic solvent into an aqueous acceptor phase. For extraction of the analytes, the pH of the sample solution is adjusted to change the analytes into neutral forms so that they become extractable into the organic solvent. In the second step, the analytes are back-extracted into aqueous phase as ionic forms by changing the pH of the acceptor phase. The theory of the method has been well described [27,28].

3.1 *Optimisation method*

In order to obtain the optimal conditions, the effects of different factors such as organic solvent, phases volumes, extraction and back-extraction times, stirring rate and pH of the donor and acceptor phases on the extraction efficiency have been investigated.

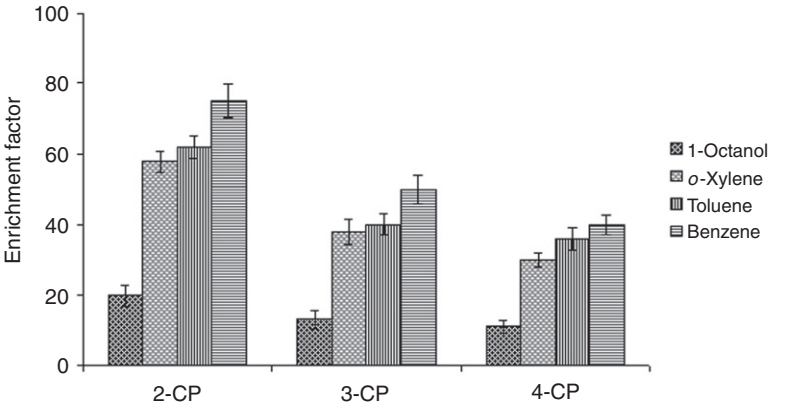

Figure 2. Relative extraction efficiencies of target analytes using different types of extracting solvents ($n = 3$): The analytes concentrations were 1 μg mL^{-1}.

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3.1.1 *Selection of the organic solvents*

In the three liquid-phase microextraction, the selection of organic solvent is a vital step to obtain the maximum extraction efficiency and the analyte preconcentration. High partition coefficient of analyte between donor phase and organic solvent should be met.

The appropriate organic solvent which was used in this work should have lower density than that of water to lay over the aqueous sample solution. In addition, it should have low solubility in water to minimise dissolution in the aqueous phase and also have high viscosity to hold the aqueous microdroplet. Several kinds of organic solvents such as benzene, toluene, 1-octanol, *o*-xylene and *n*-heptane have been examined in this work. Among them, benzene showed the highest analytes enrichment (Figure 2). But, we were faced with a practically problem due to the instability of microdroplet inside it, which was solved by mixing a small amount of benzene with 1-octanol. 1-Octanol (viscosity = 6.49) helped to increase the lifetime of the microdroplet inside the organic phase (two binary mixture of benzene/1-octanol). Therefore, benzene (having high enrichment factor) and 1-octanol (having high viscosity for holding the microdroplet) were selected as the extractants.

The effects of different amounts of benzene in the binary mixtures of organic solvent were studied (Figure 3). It is plausible to say that the best extraction efficiency has been obtained in the binary mixture of benzene/1-octanol, 90 : 10 (*v*/*v*). Hence, this mixture was chosen as our organic solvent for our subsequent studied.

3.1.2 *Volume of the organic and acceptor phases*

In LLLME method, the enrichment factor can be improved by increasing the volume ratio of donor and acceptor phases [29,30]. The volume of the acceptor solution may also be adjusted to the analytical technique which is coupled to LLLME. For example, the injected sample volume in GC is less than HPLC which may be in the range of 10–25 μL. In this manner, the use of a larger drop results in the increase of the analytical response. However, these large drops are not very stable; especially, at high stirring speeds. Therefore, the volume of the drop (acceptor phase) should be optimised. The various

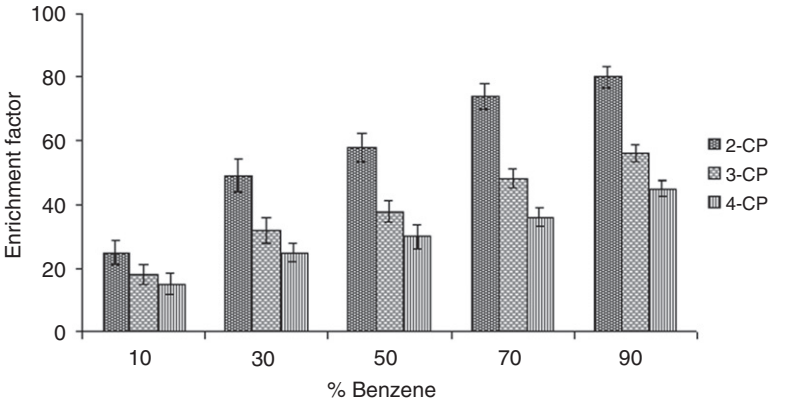

Figure 3. Effect of different amounts of benzene in the binary mixtures of the organic solvent on extraction efficiency ($n = 3$): The analytes concentrations were 1 μg mL^{-1} and the sample volume was 4.5 mL.

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volumes of aqueous microdroplets were examined and finally a 7 μL droplet was chosen as the optimised acceptor phase (see Figure 4).

On the other hand, in this work the especial design of extraction device was used. In this setup, the organic solvent in addition to be an extractant, it acts as the holder of the acceptor phase and its volume affects the life time of the droplet. Therefore, the volume of the organic phase is a very important factor and should be optimised carefully. The best volume of the organic solvent was found to be 350 μL. Smaller volumes of the organic solvent (i.e. less than 300 μL) tend to cause instability of the aqueous drop during agitation; whereas, the extraction efficiency will be reduced if larger volumes of the organic phase are used. Consequently, a 350 μL volume of the organic solvent was chosen for the subsequent works.

3.1.3 *Extraction time*

Extraction time is one of the most important factors which is influences the extraction efficiency. In the liquid-phase microextraction technique, transition of the analytes from the aqueous sample into the organic phase is a slow equilibrium process and mass transfer is a time-dependent procedure. The reason is that, the solute molecules need enough time to pass through the interface between the donor and organic phases. Therefore, the recovery percentage depends on the time that the analytes are in contact with the organic phase.

In this work, we used the organic solvents which are insoluble in water and have lower density than that of water. Thus, before addition of the suspended microdrop, the aqueous sample solution and the organic phase (benzene/1-octanol, 90 : 10 *v*/*v*) was agitated at 1200 rpm and mixed together vigorously for 120 s. Afterwards, a cloudy mixture of the sample solution and the tiny droplets of the organic solvent was obtained. Due to the high intersections between the donor solution and these tiny droplets of the organic solvent, the mass transfer occurred very fast. The changes of the HPLC signals became steady after 120 s, thus, the extraction time for further experiments was chosen as 120 s.

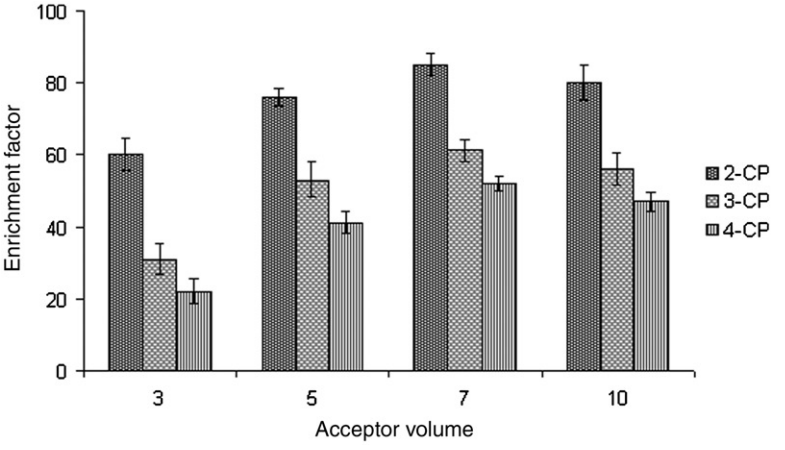

Figure 4. Effect of volume of the microdroplet on enrichment factor ($n = 3$): The analytes concentrations were 1 μg mL^{-1}, the sample volume was 4.5 mL and the organic phase was 350 μL of benzene/1-octanol (90 : 10, *v*/*v*).

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3.1.4 *Back-extraction time*

As a common rule, raising the extraction time increases the extraction efficiency until equilibrium is attained. Thus, longer extraction times will produce higher extraction efficiency. However, this is not a general rule for all experiments. Directly suspended droplet LLLME is not an exhaustive extraction technique. Although, maximum efficiency is attained at equilibrium, but, the droplet life time can not be too long due to the drop dissolution, loss or fall. Therefore, the back-extraction time from the organic solvent (benzene/1-octanol 90 : 10 *v*/*v*) into the aqueous acceptor phase (7 μL, 0.1 M NaOH) should not be too long. The experiment results, which were shown in Figure 5, indicate that for all of the three analytes, the enrichment factors reach the highest at the extraction time of 5 min and then, there is no significant increase with further increasing of the back-extraction time.

3.1.5 *The alkalinity and acidity of acceptor and donor phases*

In liquid-liquid-liquid microextraction technique, the compositions of both donor and acceptor phases are important parameters that affect the extraction efficiency and should be optimized carefully. Since a three-phase extraction process was used in this experiment and according to the basic principle of extraction/back-extraction, the acidity of the sample solution can influence the extraction efficiency, due to form of de-ionised analytes with high tendencies for the organic phase. A suitable alkalinity of the acceptor solution is also necessary, which causes the chlorophenols to be ionised. It ensures that the ionised analytes are irreversibly trapped by the aqueous acceptor phase and thereby concentrated. Therefore, the difference between pH of the donor and acceptor phases is also one of the major parameters that promotes the transfer of analytes from the donor phase into the acceptor phase and should be optimised. The results show that the high enrichment factor is obtained with increasing the alkalinity of the microdrop up to 13, but there is no significant increase in higher pH of the acceptor solution. Therefore, 0.1 M NaOH was chosen for acceptor solution for our next studies.

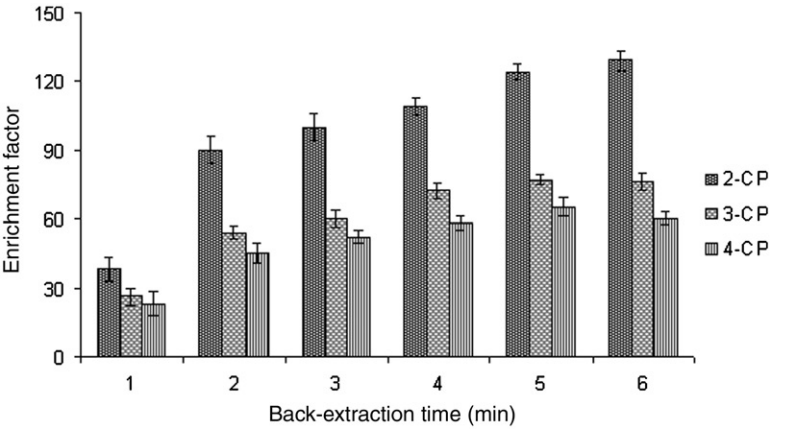

Figure 5. Effect of back-extraction time on extraction efficiency ($n = 3$). Experimental conditions: analytes concentrations, 1 μg mL^{-1}; sample volume, 4.5 mL; organic phase, 350 μL of benzene/1-octanol (90 : 10, *v*/*v*), acceptor phase volume, 7 μL; extraction time, 120 s.

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The sample solution acidity can also influence the extraction efficiency of a weak organic base or acid. In our experiment, the effect of the sample solution acidity was studied by adding different amounts of 12 M HCl into the donor phase. No significant change of extraction efficiency was obtained in the range of pH 1–4. This result is reasonable, since the pK_a values of the three chlorophenols are 8.50 for 2-CP, 9.12 for 3-CP and 9.41 for 4-CP [31] and most of the CPs exist in molecule form in this range of pH. From the theoretical point of view, pH 2.0 is enough to keep CPs in molecule form in all procedures since the lowest pK_a value is 8.50.

3.1.6 *Stirring rate*

In extraction methods, higher stirring rate can accelerate the diffusion of the analytes and abbreviate the extraction dynamic equilibrium time. In this method, a large volume of the acceptor phase was used (7 μL microdrop) which was unstable in high speed. Therefore, the stirring speed was also optimised to obtain the better extraction efficiency. The range of the stirring speed which was used in this study was between 360 and 720 rpm. The extraction efficiency increases by increasing the stirring rate, but the aqueous microdroplet became unstable at high speed (above 720 rpm) of the magnetic stirrer. Consequently, the stirring speed was selected as 600 rpm for the following investigations.

3.2 *Quantitative analysis*

Some characteristics of the proposed method such as linear range, correlation coefficients, limit of detections (LODs) and repeatability were all investigated by enriching 4.5 mL of CPs standard solutions. In the optimum conditions, the calibration graphs were constructed for eight working aqueous standards prepared in pure deionised water which was spiked with the three chlorophenols at different concentrations. Each analyte exhibited the good linearity with the correlation coefficient $r \geq 0.9973$ in the working range. The limit of detections which were calculated on the basis of signal-to-noise ratio of

Table 1. Some analytical performance data of the proposed method.

Analytes	RSD% ($n=5$)[a]	Correlation coefficient (r)	Linear range ($\mu g\,L^{-1}$)	Limit of detection (LOD, $\mu g\,L^{-1}$)	Enrichment factor (EF)
2-CP	7.4	0.9973	50–2000	10	170
4-CP	6.8	0.9989	10–2000	5	115
3-CP	7.2	0.9985	50–2000	10	123

Note: [a]Determined at a concentration of $100\,\mu g\,L^{-1}$ for each analytes.

Table 2. The relative recoveries of three chlorophenols in real environmental water samples at $100\,\mu g\,L^{-1}$ spiking level ($n=3$).

Samples	2-CP	4-CP	3-CP
Groundwater	97.2	93.8	96.7
River water	94.6	89.2	95.8
Tap water	82.9	85.4	83.5

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3 ($S/N=3$) were in the range of 5–10 $\mu g\,L^{-1}$. The repeatability of the analytical performance was studied for five replicate experiments of the working standard at an intermediate concentration of the calibration curve, which is expressed as relative standard deviation (RSD). The values are lower than 7.4%. The results are shown in Table 1.

3.3 *Real sample analysis*

In order to check the validity of the proposed method, three real environmental water samples including groundwater, river water and tap water were analysed. The real water samples were collected from Mashhad (Iran). The results show that the contents of CPs in the three samples are all under the detection limits; therefore, the relative recoveries were determined by spiking the samples with $100\,\mu g\,L^{-1}$ of each CPs. As the results were shown in Table 2, the relative recoveries are higher than 83% for all of the three target compounds which are reasonable for the method.

Figure 6 shows the chromatograms obtained after enriching 4.5 mL of groundwater without and with spiking of $100\,\mu g\,L^{-1}$ CPs, respectively, using our proposed method.

3.4 *Comparison with other LPME methods*

There is a comparison between the figures of merit generated by the proposed method and the other LPME methods like, single drop microextraction (SDME) and dispersive liquid microextraction (DLME) for the extraction of 4-chlorophenol from water samples (Table 3). A study of the data shows that the linear range of the proposed method is comparable with conventional SDME and shows a wider value in comparison with another method. Although the developed method has less sensitivity (higher LOD) than other methods, our proposed method is very fast; especially, in comparison with the conventional SDME. The extraction time of DLME is a few seconds, but there is an extra step for centrifuging the sample solution which takes a few minutes.

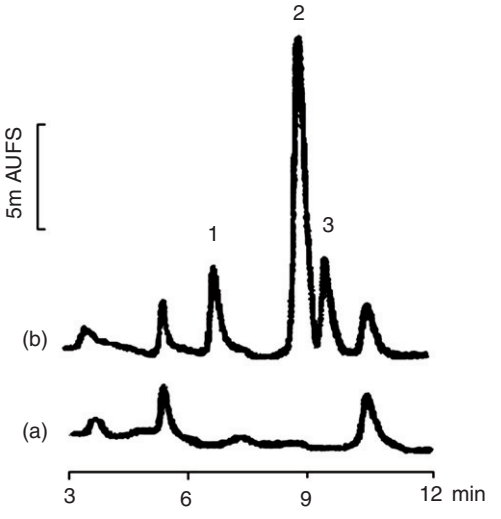

Figure 6. Typical chromatograms of groundwater and groundwater spiked with 100 μg L^{-1} of 2-CP, 4-CP, 3-CP standard solutions. (a) Groundwater; (b) Groundwater spiked with 100 μg L^{-1} of the standards; peaks identified as: (1), 2-CP; (2), 4-CP; (3), 3-CP. The experimental conditions are indicated in the text.

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Table 3. The comparison of figures of merit of the proposed method with other methods applied for the analysis of 4-chlorophenol.

Method	Extraction solvent	LOD[a] (μg L^{-1})	LR[b] (μg L^{-1})	r[c]	Extraction time (min)	Ref.
Proposed	Benzene/1-Octanol	5	10–2000	0.9989	7	–
SDME	Toluene/Heptane	0.23	1–1000	0.9920	31	[10]
DLLME	Chlorobenzene	2	4–400	0.9994	Few seconds + 2	[8]

Notes: [a]Limit of detection for S/N = 3.
[b]Linear range.
[c]Correlation coefficient.

4. Conclusions

In this research, we have developed a new, simple, rapid and cheap method of liquid phase microextraction named directly suspended droplet liquid-liquid-liquid phase microextraction. It has been used in extraction of three chlorophenols in water samples. In this method an aqueous large droplet is freely suspended on the surface of the organic solvent without using a microsyringe as supporting device which is led to form a self-stable single microdrop system, easy to operate and control. Furthermore, the rotation of the microdroplet around a symmetrical axis may cause internal recycling and intensify the mass transfer inside the droplet along with decreasing in the extraction time. Using this technique, the high enrichment factors and excellent clean up of the samples are attainable and the analytes can be extracted from real water samples quantitatively. The reasonable relative recoveries have also been obtained.

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