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Research Article

Ionic liquid-based dispersive liquid–liquid microextraction with back-extraction coupled with capillary electrophoresis to determine phenolic compounds

Ionic liquid (IL) based dispersive liquid–liquid microextraction (DLLME) with back-extraction coupled with capillary electrophoresis ultraviolet detection was developed to determine four phenolic compounds (bisphenol-A, β-naphthol, α-naphthol, *2, 4*-dichlorophenol) in aqueous cosmetics. The developed method was used to preconcentrate and clean up the four phenolic compounds including two steps. The analytes were transferred into room temperature ionic liquid (1-octyl-3-methylimidazolium hexafluorophosphate, $[C_8MIM][PF_6]$) rich-phase in the first step. In the second step, the analytes were back-extracted into the alkaline aqueous phase. The effects of extraction parameters, such as type and volume of extraction solvent, type and volume of disperser, extraction and centrifugal time, sample pH, salt addition, and concentration and volume of NaOH in back-extraction were investigated. Under the optimal experimental conditions, the preconcentration factors were 60.1 for bisphenol-A, 52.7 for β-naphthol, 49.2 for α-naphthol, and 18.0 for *2, 4*-dichlorophenol. The limits of detection for bisphenol-A, β-naphthol, α-naphthol and *2, 4*-dichlorophenol were 5, 5, 8, and 100 ng mL^{-1}, respectively. Four kinds of aqueous cosmetics including toner, soften lotion, make-up remover, and perfume were analyzed and yielded recoveries ranging from 81.6% to 119.4%. The main advantages of the proposed method are quick, easy, cheap, and effective.

Keywords:
Capillary electrophoresis / Cosmetics / Dispersive liquid–liquid microextraction / Phenolic compounds / Room temperature ionic liquids
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1 Introduction

Phenols are important pollutants because of their wide use in many industrial processes such as the fabrication of dyes, plastics, drugs, and pesticides [1, 2]. They have been receiving considerable attention due to their high toxicity. Moreover, some phenolic compounds have been closely studied in recent years because of their endocrine disruptor function [3]. Bisphenol-A (BPA) is widely used as the monomer for epoxy resins and polycarbonates and shows estrogenic potentials [4]. It is in the priority list of substances for further evaluation of their role in endocrine disruption that is set by the European Union [5]. Chlorophenols, like *2, 4*-dichlorophenol (DCP), are well known pollutants for their toxicity in aquatic life and poor biotreatability. And they are also the exogenous burden of humans and wildlife with hormonally active agents [6]. Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants, and draw a lot of attention owing to their carcinogenesis and teratogenesis [7–11]. Among PAHs, naphthalene shows a significantly higher incidence of tumors even at the lowest level in animal investigation [12]. α-Naphthol (α-NAP) and β-naphthol (β-NAP) are the crucial metabolites of naphthalene. β-NAP is a better biomarker of naphthalene exposure [13]. α-NAP is also an important metabolite of a broad-spectrum insecticide carbaryl [14]. Moreover, α-NAP has a significant correlation with decreased sperm concentration and mobility, found by Meeker et al. [15]. Accordingly, the determination of these phenolic compounds is important because of their

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Abbreviations: BPA, bisphenol-A; **$[C_4MIM][PF_6]$**, 1-butyl-3-methylimidazolium hexafluorophosphate; **$[C_6MIM][PF_6]$**, 1-hexyl-3-methylimidazolium hexafluorophosphate; **$[C_8MIM][PF_6]$**, 1-octyl-3-methylimidazolium hexafluorophosphate; **CPE**, cloud point extraction; **DCP**, 2, 4-dichlorophenol; **DLLME**, dispersive liquid–liquid microextraction; **EF**, enrichment factor; **ER**, extraction recovery; **LPME**, liquid-phase microextraction; **α-NAP**, α-naphthol; **β-NAP**, β-naphthol; **PAHs**, Polycyclic aromatic hydrocarbons; **$[RMIM][PF_6]$**, 1-alkyl-3-methylimidazoliumhexafluorophosphate; **RTILs**, room temperature ionic liquids; **SPME**, solid-phase microextraction

high toxicity. However, these compounds always exist in trace amounts, therefore, it is necessary to establish a method for the determination of these phenolic compounds sensitively, simply, and rapidly.

Capillary electrophoresis (CE) has been acknowledged a powerful separation technique due to its major merit of high resolution, small sample size, short analysis times, extremely low solvent consumption, and low operational costs. While it offers a number of advantages, the main drawback of CE is the low detection limits, due to the small loaded sample volume (nL) and the short path length of detection in most universally used UV detection [16]. Thus, a sample preconcentration method is often required when trace compounds are determined by CE-UV. Several on-line and off-line preconcentration techniques are employed in CE to reduce the detection limits values. In the last few decades, liquid-phase microextraction (LPME) has been proposed as an alternative for sample preconcentration due to its simpleness, inexpensiveness, effectiveness, and mini volume of organic solvents consumed. Different modes of LPME have been developed, such as single-drop LPME [17], hollow fiber-based LPME [18], homogeneous liquid–liquid extraction [19], and solidification of a floating organic drop [20]. However, these methods still have some drawbacks: need to control the stirring speed in case of the organic drop broken up and bubbles formed; need long time but obtain low sensitivity and repeatability. Dispersive liquid–liquid microextraction (DLLME) was first introduced by Rezaee et al. in 2006 [21], which can overcome the above-mentioned issues with the merit of easier and faster operation, lower time and cost, higher preconcentration factor, and repeatability. It has been successfully applied in the extraction of organic and inorganic compounds from water samples and solid matrices [22–26]. Some articles have been reported in the analysis of BPA and other phenolic compounds by DLLME, including high-performance liquid chromatography (HPLC) [27–29] and gas chromatography-mass spectrometry (GC-MS) [30, 31]. However, since many of these compounds are polar, they are usually derivatized with a suitable derivatization reagent before injecting into the GC. On the other hand, CE is a complement technique to HPLC due to its powerful separation capacity and extremely low solvent consumption. Thus, DLLME coupled with CE to determine phenolic compounds has been developed in this work.

In DLLME, chosing an appropriate extraction solvent plays a crucial role for obtaining high enrichment factors (EFs) and good recoveries. Compared with the traditional extracting agent, room temperature ionic liquids (RTILs), which are regarded as green solvents, draw a great interest as the extraction solvent in DLLME due to its interesting property of tunability. The viscosity and surface tension of ILs can be easily tuned and manipulated, which make the ILs have the ability to form larger and more stable droplets compared to traditional organic solvents. Furthermore, ILs can be easily synthesized to be not only hydrophobic or hydrophilic but also miscible or immiscible with the disperser solvent. And their high density is facilitated to the phase separation. Recently, 1-alkyl-3-methylimidazoliumhexafluorophosphate ([RMIM][PF_6]) is the most popular IL used as extraction solvent in DLLME.

There have been several reports about the application of DLLME in combination with CE (DLLME-CE). Zhang et al. [24] and Moreno-González et al. [23] used DLLME coupled with sweeping micellar electrokinetic chromatography (MEKC) to analyze carbamate pesticides in apples and in juice, respectively; Herrera-Herrera et al. [22] studied the determination of fluoroquinolone antibiotics in waters by DLLME combined with nonaqueous capillary electrophoresis (NACE); Zhang et al. [26] established a novel method for the determination of five sulfonylurea herbicides in soil by DLLME coupled with sweeping MEKC; Meng et al. [32] concentrated on the chiral separation and determination of the multiple illicit drugs on forensic samples by DLLME-CE.

In this work, a novel method of IL-DLLME with back-extraction combined with CE-UV is developed to determine four phenolic compounds in aqueous cosmetics. The reasons for using DLLME with back-extraction to determine these phenolic compounds can be shown as follows: [C_8MIM][PF_6] is too viscous to directly inject for CE and has strong UV absorption at detection wavelength; the high concentration of IL injected into CE is possibly attached to the inner surface of separation capillary; the back-extraction plays a role in cleaning up. This is the first application of DLLME with back-extraction coupled to CE. The factors influencing IL-DLLME with back-extraction were optimized and the proposed procedure was successfully applied to analyze the real samples.

2 Materials and methods

2.1 Chemicals and reagents

BPA, β-NAP, α-NAP, and DCP with purities greater than 99.0% were purchased from Shanghai Crystal Pure Industrial Co., Ltd. (Shanghai, China). Stock solutions of 1 mg mL^{-1} were prepared in HPLC grade acetonitrile and stored at 4°C. 1-Butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) (density, 1.32 g mL^{-1}), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) (density, 1.29 g mL^{-1}), and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) (density, 1.20 g mL^{-1}) with purities greater than 99.0% were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). Other reagents were all of analytical reagent grade. Doubly distilled water from a Milli-Q plus system (Millipore Co., USA) was exclusively used in all aqueous and rinsing procedures.

2.2 Apparatus

All CE experiments were performed on a LUMEX CAPEL-105 Capillary Electrophoresis System (LUMEX Ltd. Analytical Equipment R&D and Production Company, RUS), equipped

with an auto sampler, a ± 25 kV high-voltage power supply, and a ultraviolet detector (190 nm−380 nm) working at 214 nm for CE-UV analyses. All of the operations were computer controlled using Chrom & Spec chromatography date system. An uncoated fused–silica capillary (Yongnian Ruifeng Optical Fiber Factory, Hebei, China) of 75 cm (effective length, 65 cm) × 50 μm i.d. was used throughout the experiments. For pH measurements, a pHS-3C digital pHmeter (Shanghai Rex Instruments Factory, China) was used. A TDL-40B centrifuge (ShangHai Anting Scientific Instrument Factory, China) was used for centrifuging.

2.3 Electrophoresis procedure

At the beginning of each day, the capillary was rinsed consecutively with 0.1 mol L^{-1} NaOH, doubly distilled water and background electrolyte (BGE) (5 mmol L^{-1} borax buffer with pH 9.8) for 20 min each. Between consecutive runs, the capillary was rinsed with 0.1 mol L^{-1} NaOH, doubly-distilled water and BGE for 5 min each, successively, in order to obtain good reproducibility. After the experiment, the capillary was rinsed with 0.1 mol L^{-1} NaOH for 30 min and doubly distilled water for 10 min. The above mentioned solutions were filtered through a 0.45 μm micropore membrane before use. Samples were hydrodynamically injected at 25 mbar for 5 s. The experiments were performed at + 25 kV and 20°C.

2.4 Preparation of samples

In the study, four kinds of aqueous cosmetics including toner (sample 1), soften lotion (sample 2), make-up remover (sample 3), and perfume (sample 4) were analyzed. The samples were purchased at the local mall. One milliliter of the sample was taken into a 10-mL centrifugal tube and extracted with 3-mL HPLC grade acetonitrile for 3 min in an ultrasonic bath. No filtration or any further treatment was applied in any of the samples before extraction. Two-hundred microliters of the prepared sample was taken into the 15.0-mL centrifugal tube and then diluted with doubly distilled water to 10.0 mL for analysis.

2.5 DLLME procedure

First step: 10.0 mL doubly distilled water spiked with analytes was put into a 15.0-mL centrifugal tube, and subsequently 10% (*m/v*) sodium chloride was added into the solution to adjust ionic strength; then a mixture of 80 μL (0.0960 g) [C_8MIM][PF_6] (extraction solvent) and 900-μL acetone (disperser solvent) was rapidly injected into the aqueous solution using a transferpette; the cloudy solution was formed immediately and the analytes were quickly extracted into the IL fine droplets; after gentle shaking for a few seconds by hand, the solution was centrifuged for 5 min at 4000 rpm; the upper aqueous solution was removed with a pipette carefully.

Second step: 150 μL of 0.1 mol L^{-1} NaOH solution was added to the IL-rich phase; subsequently, the mixture of IL-rich phase and NaOH solution was shaken acutely and centrifuged for 5 min at 4000 rpm to achieve the back-extraction and the phase-separation; after that, the 150 μL alkaline aqueous phase was removed to a 1.5-mL plastic centrifuge vial and then the vial was placed directly into the CE auto sampler for injection. All the extraction process was taken at room temperature.

The extraction performance of the proposed method was described by the EF and extraction recovery (ER). EF is defined as $EF = C_f/C_0$, where C_f and C_0 are the concentration of analytes in the final alkaline aqueous phase and in the sample aqueous phase, respectively. ER is defined as the percentage of total analyte amount extracted to the alkaline aqueous phase and is a function of EF and the phase volume ratio (V_f / V_0), where V_f and V_0 are the volumes of the final alkaline aqueous phase (150 μL) and the sample aqueous phase (10 000 μL), respectively. Thus, another way to express ER is a function of EF and a constant k ($k = V_f / V_0 = 150 / 10\,000$).

3 Results and discussion

3.1 IL-DLLME with back-extraction optimization

To obtain a high ER, various extraction parameters in the IL-DLLME with back-extraction procedure were investigated. 10.0 mL double-distilled water spiked with 2 μg mL^{-1} each of the four phenolic compounds was used to study the extraction performance of the DLLME. The recovery was used to evaluate the extraction efficiency.

3.1.1 Type and volume of the extraction solvent

In DLLME procedure, the choice of an extraction solvent with high density than water (although some applications of lower-density solvents have also been proposed), low solubility in water, and good extraction capability for the target analytes plays an important role. Therefore, three kinds of IL including [C_4MIM][PF_6], [C_6MIM][PF_6], and [C_8MIM][PF_6] which had different alkyl part were compared as extraction solvent, using a volume of 80 μL of extraction solvent with 900 μL of acetone. The alkyl part of the [RMIM][PF_6] has significant effect on its physical characterization, such as density and solubility [33] that might influence the extraction efficiency of target analytes. Among the three ILs, [C_8MIM][PF_6] obtained the highest ER (shown in Fig. 1), therefore, it was selected as the extraction solvent.

The amount of extraction solvent is a critical factor to obtain high ER. In order to evaluate the effect of the amount of extraction solvent on the ER, different volumes of [C_8MIM][PF_6] between 65 and 90 μL in 5 μL intervals were tested, using 900-μL acetone as disperser solvent. By increasing amount of [C_8MIM][PF_6] from 65 to 80 μL, the ER increased remarkably. When we continue to increase the

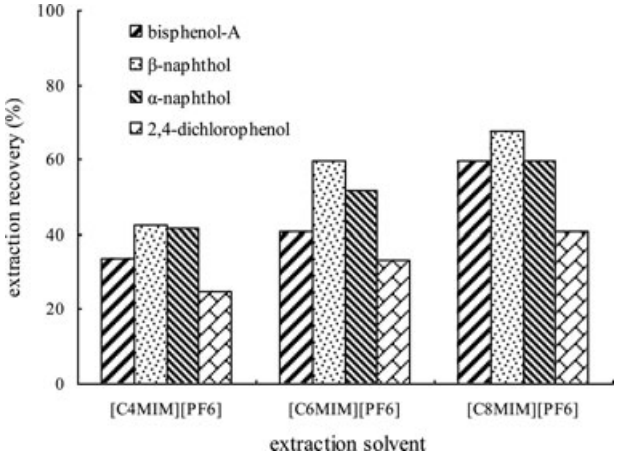

Figure 1. Effect of the type of extraction solvent on extraction recovery (ER). Extraction conditions: spiked concentration, 2 μg mL^{-1}; water sample volume, 10.0 mL; extraction solvent volume, 80 μL; disperser solvent volume (acetone), 900 μL; centrifugal time, 5 min at 4000 rpm back-extraction (0.1 mol L^{-1} NaOH), 150 μL; recentrifuge, 5 min at 4000 rpm. Electrophoresis conditions: +25 kV, 20°C, injection 5 s at 25 mbar, detection at 214 nm; BGE: 5 mmol L^{-1} borax buffer with pH 9.8.

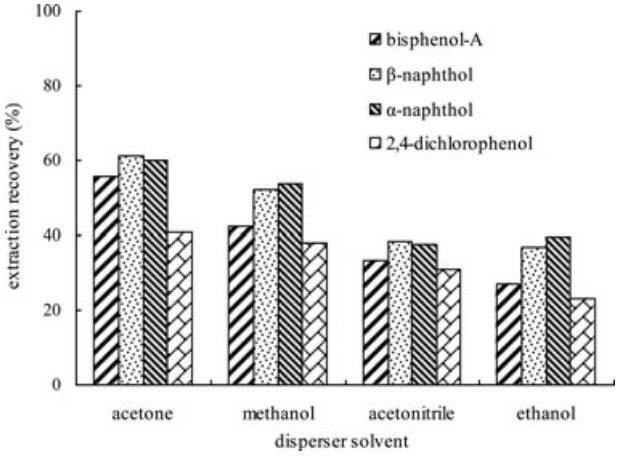

Figure 2. Effect of the type of disperser solvent on extraction recovery (ER). Extraction conditions: spiked concentration, 2 μg mL^{-1}; water sample volume, 10.0 mL; extraction solvent volume ($[C_8MIM][PF_6]$), 80 μL; other conditions are the same as in Fig. 1.

amount of $[C_8MIM][PF_6]$ more than 80 μL, there was no distinct changes on the ERs for higher IL amounts. So, in terms of attaining the highest ER and minimizing IL usage, 80 μL was selected as optimum.

3.1.2 Type and volume of the disperser solvent

In DLLME, the disperser solvent must be a water miscible, polar solvent, and should be soluble in the extraction solvent [34]. Under the function of disperser solvent, the extraction solvent is formed into fine droplets in the aqueous phase [34]. Therefore, the type of the disperser solvent is an important parameter affecting the ER. Four candidate solvents including methanol, ethanol, acetonitrile, and acetone were tested. It could be seen from Fig. 2 that acetone obtained the best recoveries for the analytes among above-mentioned solvents. Thus, acetone was chosen as the disperser solvent for subsequent study.

The dispersive solvent volume directly affects the solubility of extraction solvent in water solution, the formation of cloudy solution, and the dispersion degree of extraction solvent in aqueous phase, which has influence on ER. For acquiring the optimal volume, volumes of acetone between 400 μL and 1200 μL containing 80-μL $[C_8MIM][PF_6]$ were tested. With increasing volume of acetone, the ERs increased first and then decreased. The reason could be as follows: at low volumes of acetone, the cloudy state was formed not well, so the ERs were low; yet, at high volumes of acetone, the solubility of both analytes and extraction solvent $[C_8MIM][PF_6]$ in aqueous solution was increased, leading to a decrease in ER. Therefore, the volume of 900 μL was chosen as the optimum disperser solvent amount.

3.1.3 Effect of shaking time and centrifugal time

The shaking time is after the mixture of extraction solvent and disperser solvent injected into the aqueous solution and before centrifugation. The influence of shaking time was tested from a few seconds to 20 min. The results showed that there were no significant differences in recovery values by increasing the extraction time. Apparently, it was indicated that the proposed IL-DLLME method was time-independent. The reason for this is that the surface area between the extraction solvent droplets and the aqueous phase is infinitely large after the formation of cloudy solution. Therefore, the mass transfer of analyte molecules from aqueous phase to extraction phase is very quick and the equilibration time is extremely short [35]. So, gentle shaking a few seconds by hand was adopted in the subsequent experiment.

Centrifugation is an important step in DLLME for phase separation. The effect of centrifugal time was studied for the range of 2–14 min, finding that in general, the ERs of all the analytes were higher at 5 min or more than 5 min. A centrifugal time of 5 min at 4000 rpm was selected, since this time was enough for complete phase separation and longer periods of times did not have appreciable improvements on analyte extraction.

3.1.4 Effect of sample solution pH

The pH of the sample solution plays a crucial role in the extraction, because it can influence the form of the phenolic compounds and then influence the ER. For finding the best value, the pH values were changed between 3.0 and 8.0 by adding an appropriate amount of HCl or NaOH. The results were shown in Fig. 3. As could be seen, the ERs of analytes all reached a higher level at pH 5.0 to 7.0, which approached to the pH of the spiked sample solution. It seems

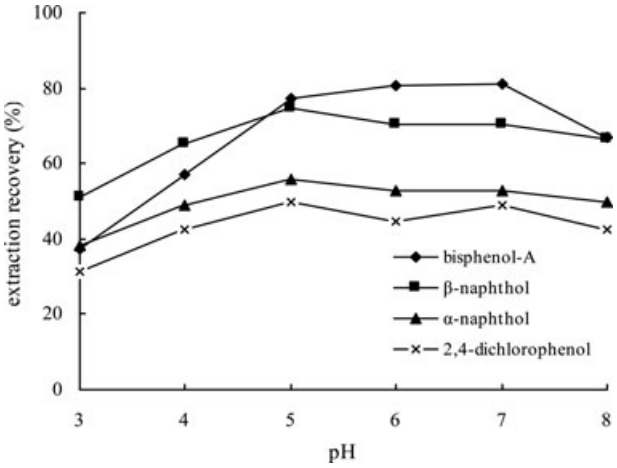

Figure 3. Effect of sample pH on extraction recovery (ER). Extraction conditions: spiked concentration, 2 μg mL^{-1}; water sample volume, 10.0 mL; extraction solvent volume ($[C_8MIM][PF_6]$), 80 μL; other conditions are the same as in Fig. 1.

that both neutral and ionized phonelic compounds are efficiently extracted to the IL sediment phase at these pH values. So, the subsequent study was operated without pH adjustment.

3.1.5 Effect of ionic strength

The influence of the ionic strength on the performance of DLLME was evaluated by adding different amounts of NaCl (0–20%, *m*/*v*) into the sample solution under the previous optimum conditions. Increasing the ionic strength generally causes a decrease in solubility of the organic compounds in water, especially for high polarity compounds, so it has been widely used to improve the ERs of analytes. The results demonstrated an increase of the amount of NaCl up to 10% (*m*/*v*) provided greater recovery values, particularly for BPA. When it was more than 10%, the ERs remained constant in general. Therefore, 10% (*m*/*v*) NaCl was used in the following experiments.

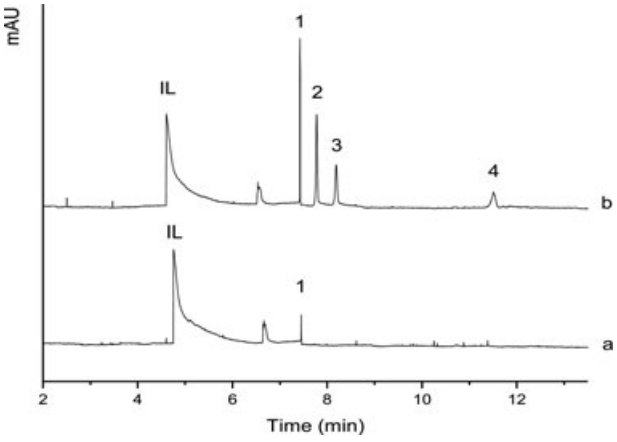

Figure 4. Electropherogram of a perfume sample applying the proposed method: (A) unspiked sample; (B) sample spiked with 1 μg mL^{-1} for BPA and DCP and 0.5 μg mL^{-1} for β-NAP and α-NAP; peaks: (1) BPA, (2) β-NAP, (3) α-NAP, and (4) DCP. Electrophoresis conditions: +25 kV, 20°C, injection 5 s at 25 mbar, detection at 214 nm; BGE: 5 mmol L^{-1} borax buffer with pH 9.8.

Table 1. Standard calibration curves without extraction

Analyte	Linear range (μg mL^{-1})	Regression equation ($n = 5$)	Correlation coefficient (R^2)
BPA	5–500	$y = (0.050 \pm 0.002)$ $x - (0.097 \pm 0.148)$	0.998
β-NAP	1–300	$y = (0.282 \pm 0.005)$ $x - (1.640 \pm 0.957)$	0.999
α-NAP	1–300	$y = (0.192 \pm 0.004)$ $x - (1.357 \pm 2.253)$	0.999
DCP	5–500	$y = (0.098 \pm 0.003)$ $x - (0.051 \pm 0.037)$	0.994

3.1.6 Concentration and volume of NaOH in back-extraction

Under the alkaline condition, the phenolic compounds present in hydrophilic salt forms [36, 37]. So, the phenolic compounds can be extracted to the alkaline aqueous phase from the IL-rich phase in the back-extraction. The NaOH concentrations of 0.05−1 mol L^{-1} were investigated. When the NaOH concentrations were more than 0.1 mol L^{-1}, these phenolic compounds were not separated well and the baseline was unstable. The possible reason was that the conductivity of the injection sample and BGE was much different. Thus, 0.1 mol L^{-1} NaOH was used in back-extraction.

The volume of NaOH in back-extraction directly influences the detection limit and EF. The larger is the volume; the lower is EF, which results in higher detection limits (according to the definition of EF in section 2.5). However, if the volume of NaOH is too small, alkaline aqueous phase and IL sediment phase cannot be evenly mixed. So, 150 μL was chosen as the back-extraction volume.

3.2 Evaluation of the method performance

To investigate the feasibility of this method, four types of aqueous cosmetic samples including toner (sample 1), soften lotion (sample 2), make-up remover (sample 3), and perfume (sample 4) were examined. The typical electropherograms of unspiked and spiked sample are shown in Fig. 4. The four target analytes can be separated very well within less than 12 min using common buffer (5 mmol L^{-1} borax buffer with pH 9.8). The results indicate that this sample contains BPA. For evaluating the analytical performance of the proposed method, calibration linearity, standard deviation of the

Table 2. Standard calibration curves after extraction

Analyte	Linear range (μg mL^{-1})	Regression equation ($n = 5$)	Correlation coefficient (R^2)	Detection limit (μg mL^{-1})	Preconcentration factor
BPA	0.05–10	$y = (3.006 \pm 0.084)$ $x + (0.043 \pm 0.128)$	0.994	0.005	60.1
β-NAP	0.025–5	$y = (14.884 \pm 0.028)$ $x + (0.222 \pm 0.106)$	0.998	0.005	52.7
α-NAP	0.05–5	$y = (9.455 \pm 0.033)$ $x + (0.678 \pm 0.569)$	0.991	0.008	49.2
DCP	0.25–8	$y = (1.768 \pm 0.039)$ $x + (0.218 \pm 0.478)$	0.997	0.1	18.0

Table 3. Results of assays to check the recovery, precision, and accuracy of the proposed method for the analyte in four samples ($n = 5$).

Analyte	Spiked level (μg mL^{-1})	Sample 1			Sample 2			Sample 3			Sample 4		
		Recovery (%)	RSD (%)	$t^{a)}$	Recovery (%)	RSD (%)	$t^{a)}$	Recovery (%)	RSD (%)	$t^{a)}$	Recovery (%)	RSD (%)	$t^{a)}$ (%)
BPA	0.2	106.6	12.5	0.002	108.9	9.8	0.004	102.7	7.0	0.002	107.6	12.8	0.003
	2	92.7	7.6	−0.044	97.5	3.8	−0.029	112.9	4.1	0.141	109.1	6.6	0.062
	5	91.6	5.1	−0.184	93.1	1.6	−0.482	105.7	2.5	0.255	96.3	4.4	−0.094
β-NAP	0.05	122.6	8.4	0.003	118.3	4.1	0.005	108.7	4.2	0.002	104.6	4.7	0.001
	0.5	111.3	3.8	0.033	106.8	3.5	0.022	114.8	5.8	0.029	100.7	3.9	0.005
	5	115.2	4.3	1.435	102.2	1.7	0.145	104.1	1.1	0.417	101.4	1.8	0.087
A-NAP	0.05	117.1	8.8	0.002	119.4	7.7	0.003	114.2	7.4	0.002	108.9	3.8	0.003
	0.5	107.6	5.9	0.014	100.9	9.1	0.001	113.0	1.8	0.081	87.6	3.9	−0.036
	5	105.8	7.7	0.084	107.1	2.4	0.331	112.7	1.3	1.092	105.1	2.4	0.238
DCP	0.5	81.6	11.1	−0.018	99.5	7.3	−0.001	82.1	11.4	-0.018	83.9	10.0	−0.018
	2	106.5	5.6	0.052	111.7	7.2	0.073	104.6	4.0	0.051	106.0	5.9	0.045
	5	116.8	3.1	0.606	108.8	6.3	0.156	99.8	6.84	−0.018	111.1	4.6	0.270

a)The values of *t*-test (95% confidence level, $n = 5$).

regression, limit of detection (LOD), and reproducibility were studied. The standard calibration curves without extraction were obtained by plotting the peak areas versus the concentrations of analytes in working solutions (prepared by diluting the mixed standard solutions with acetonitrile) and were listed in Table 1. The standard calibration curves after extraction were listed in Table 2. As shown in Table 2, good linearity was exhibited with correlation coefficient (R^2) of 0.991–0.998. The detection limits were 5, 5, 8, and 100 ng mL^{-1} for BPA, β-NAP, α-NAP, and DCP, respectively and determined based on the signal-to-noise (S/N) ratio of 3. The preconcentration factors were 60.1 for BPA, 52.7 for β-NAP, 49.2 for α-NAP, and 18.0 for DCP.

With the aim of evaluation, the repeatability, precision, and accuracy of the whole method, a study was carried out at three concentrations levels (level selection is based on the linear range) for the four types of aqueous cosmetics. Table 3 showed the results of this study. As it could be seen in this table, mean recovery values were in the range of 81.6–119.4% and relative standard deviation (RSD) values were in the range of 1.1–12.8%. A one-sample test (Student's *t*-test) was used to compare the concentration found for each phenol with the spiked concentration. As also shown in Table 3, *t* values were all in the range of −2.770 to +2.770 (tabulated *t* value is 2.770 for 95% confidence level and $n = 5$ [38]) and thus, there were no significant differences between the real sample and the experimental values.

Comparison of the proposed method with other preconcentration CE methods was shown in Table 4. In comparison with other reported methods, the main advantages of this extraction method were quick, simple, and cheap. And this extraction method had relatively higher preconcentration factor. The extraction time was just a few seconds at room temperature, which was much shorter than some other extraction methods. For example, 10 min at 30°C was needed when cloud point extraction (CPE) was used as the preconcentration method and combined with CZE-UV determinations of BPA, α-NAP, and β-NAP [39]. Furthermore, solid-phase microextraction (SPME), like hybrid silica polymeric monolith-based in-tube microextraction [44], always needed complicated and difficult synthesis process. Compared with these methods, the present strategy was much simpler and cheaper. This methodology was a fast, simple, reproducible, and low cost technique. Thus, the proposed method could be of great interest, especially for phenolic compounds determination in routine analytical laboratories.

Table 4. Comparison of the proposed method with other preconcentration CE methods.

Analyte	Method	Application	LOD[a)] (ng mL^{-1})	Extraction time (min)	Sample volume (mL)	Enrichment factor	RSD (%)
BPA, α-NAP and β-NAP	CPE-CZE-UV [39]	River water	1.67	10 (at 30°C)	10	50	5.7
BPA, DCP	SPE-RAMs-CE-MS [40]	Honey	7.5 ng g^{-1}	>20	16	-	15.0–23.0
BPA, DCP	SPE-MEKC-AD [41]	Sewage	3500	>2	200	-	1.8–4.8
BPA, DCP	MSPDE-pCEC-AD [42]	Eggs and milk powder	5	>5	-	-	3.1–7.1
BPA	SPE-RM-MEKC-UV [43]	Ground water	9.1	>23	100	71	2.0–9.6
BPA	SPME-Sample stacking-MEKC-UV [44]	Beverages	1.8	>10	-	-	<6
BPA	SPE-FASI-MECC-UV [45]	Canned soft drinks	3	-	25	50	<12.5
BPA	MISPE-CE-UV [46]	Water and urine	1.8	-	50	-	<7.2
BPA, β-NAP, α-NAP and DCP	This method	Aqueous cosmetics	5	A few seconds	10	60.1	1.1–12.8

RAMs: restricted access materials; MSPDE: matrix solid phase dispersion extraction; RM: reverse-migration; FASI: field-amplified sample injection; MISPE: molecularly imprinted solid-phase extraction.
a)The LOD of BPA.

4 Concluding remarks

In the present study, with a combination of IL-DLLME with back-extraction and CE-UV, a novel method was developed for the determination of phenolic compounds in aqueous cosmetics. Through the second extraction, some substances that did not dissolve in alkaline aqueous phase would be removed and the interferences from the sample matrix could also be decreased to a certain extent. The main advantages of the proposed method were quick, easy, cheap, and effective. High enrichment factors and acceptable recoveries were achieved. The results indicated that the IL-DLLME with back-extraction was a preconcentration and clean-up technique for CE determination of the four phenolic compounds.

The authors have declared no conflict of interest.

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