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On-line coupling of ionic liquid-based single-drop microextraction with capillary electrophoresis for sensitive detection of phenols

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ABSTRACT

An ionic liquid-based single-drop microextraction (IL-SDME) procedure using IL as an extractant on-line coupled to capillary electrophoresis (CE) is proposed. The method is capable of quantifying trace amounts of phenols in environmental water samples. For the SDME of three phenols, a 2.40 nL IL microdrop was exposed for 10 min to the aqueous sample and then was directly injected into the capillary column for analysis. Extraction parameters such as the extraction time, the IL single-drop volume, pH of the sample solution, ionic strength, volume of the sample solution and the extraction temperature were systematically investigated. Detection limits to three phenols were less than 0.05 μg mL^{-1}, and their calibration curves were all linear ($R^2 \geq 0.9994$) in the range from 0.05 to 50 μg mL^{-1}. And enrichment factors for three phenols were 156, 107 and 257 without agitation, respectively. This method was then utilized to analyze two real environmental samples from Yellow River and tap water, obtaining satisfactory results. Compared with the usual SDME for CE, IL-SDME–CE is a simple, low-cost, fast and environmentally friendly preconcentration technique.

1. Introduction

Liquid–liquid extraction (LLE) is a widely used sample preconcentration technique which is extremely time-consuming, costly and labor-intensive. The major disadvantage of LLE is the use of a large amount of toxic, expensive and volatile organic solvent. In the past several years, researchers have developed the liquid-phase microextraction (LPME) to make up the disadvantages of LLE. Single-drop microextraction (SDME), as a kind of extraction form of LPME, has attracted considerable attention due to its low-cost but high sensitivity, rapidity and simplicity and has been off-line coupled with HPLC [1–3], GC [4–7] and CE [8–11]. In these studies, a single drop is suspended on the tip of a microsyringe and the drop is retracted back into the microsyringe after extraction. And then, the drop is injected into HPLC and GC directly or introduced to a CE microvial for subsequent analysis. The whole process is performed manually so that imprecision, irreproducibility and inconvenience are inevitable.

CE is a rapidly growing analytical technique which has been widely used as a fast, powerful, and efficient analytical separation technique with low sample consumption and running cost. However, its applicability for the real sample analysis is limited on account of its low detection sensitivity. Hence, to improve the CE sensitivity, various methods have been developed prior to CE separation, such as solid phase microextraction (SPME) [12], cloud point extraction (CPE) [13], LPME [14]. Arce et al. [15] suggested that using LPME for sample preparation prior to CE analysis was a very important step in the analytical process. Improved on-line sample-preparation methods are very useful with a view to expanding the CE application because they offer low sample consumption, fast analyses and automation. SDME, as its name advises, makes use of only microlitre of solvent for extracting analytes from aqueous samples. As a matter of fact, because of the characteristics of SDME, it is quite suitable to on-line couple with CE. However, there are few of reports about on-line coupling SDME with CE. Up to 2004, Choi et al. [16] developed a simple and efficient on-line sample preconcentraction method prior to a CE run for the first time. They used a layer of octanol to separate a drop of the aqueous acceptor phase hanging at the inlet of a capillary tip from the bulk aqueous donor phase. And analytes were extracted to the acceptor phase through the organic film. In the following study, they performed SDME on commercial CE instruments which made the results more accurate and reliable because of automated instrumental control and drop attachment enhancement with the silane coating [17]. In recent work, they actualized coupling of SDME with sweeping and large volume stacking on CE which perfected this method further and improved the sensitivity of CE greatly [18,19]. Thus, the coupling between SDME and CE

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could be a useful technique for the determination of trace compounds.

In sample preconcentration, organic solvents have been commonly used for extractions. However, organic solvents may result in the environmental contamination and the poor reproducibility associated to their volatilization during the extraction process. Especially, when organic solvents are used as extractants in SDME, a high instability of the drop and poor precision levels have been reported as a result of the organic extractant evaporation and low viscosity [20]. Ionic liquids (ILs), combined by organic cations and various anions with melting point around room temperature, have unique properties of non-volatility, adequate viscosity and good thermal stability to allow ILs to be conveniently adopted as extraction solvents [6,21]. Additionally, ILs are regarded as environmentally benign solvents and are easily synthesized according to need so that ILs can be used as solvent medias widely to replace traditional solvents as extractants. ILs have excellent extractability for a lot of compounds, such as phenols [1,22,23], polycyclic aromatic hydrocarbon [21,24], aromatic hydrocarbons [25–27], dyes [28], metal ions [29–31], aromatic anilines [32,33], pesticides [34], and so on. Also, researchers used ILs in biological field for selective separation of some target analytes from biological sample matrices, like double-stranded DNA [35], proteins [36], lysozyme [37], hemoglobin [38], and amino acids [39,40]. Thus, due to the good extractability of ILs, ILs can be widely applied to extract compounds from aqueous solutions and usually provided good enrichment, reproducibility and limits of detection for analytes. The use of IL as a solvent for SDME–CE is an interesting alternative for the determination of analytes that can be extracted by this environmentally friendly solvent.

To the best of our knowledge, the on-line coupling of IL-SDME and CE, which could be a useful tool for some analytical purposes, has not been described before. In this study, IL is used as the extracting media for the on-line coupling SDME with CE in order to establish a novel, green, sensitive and simple method for determination of trace compounds. Three phenols were used as model compounds in order to evaluate the potential of the proposed method. In this SDME, a drop of hydrophobic IL was formed at the tip of the capillary column and immersed in the aqueous sample for the extraction. Parameters, such as the extraction time, the IL single-drop volume, pH of the sample solution, ionic strength, volume of sample solution and the extraction temperature were optimized. To fulfill this method would help expand the application of CE as a routine technique for the real sample analysis.

2. Experimental

2.1. Chemicals

4-Chlorophenol (4-CP) was obtained from the Beijing Chemical Corporation (China). 3-Nitrophenol (3-NP) was purchased from the Shanghai Chemical Reagent Corporation (China). 2-Nitrophenol (2-NP) was obtained from Sinopharm Chemical Reagent Co. Ltd. (China). 1-Butyl-3-methylimidazoium hexafluorophosphate ([BMIM][PF_6]), 1-hexyl-3-methylimidazoium hexafluorophosphate ([HMIM][PF_6]) and 1-octyl-3-methylimidazoium hexafluorophosphate ([OMIM][PF_6]) were supplied by Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (Lanzhou, China). All reagents were of analytical reagent grade unless otherwise stated.

Each phenol was dissolved in the distilled water to obtain a standard stock solution with the concentration of 1000 $\mu g\,mL^{-1}$ and then stored at 4 °C. Working solutions were prepared daily by rigorous dilution of the stock solutions with the distilled water.

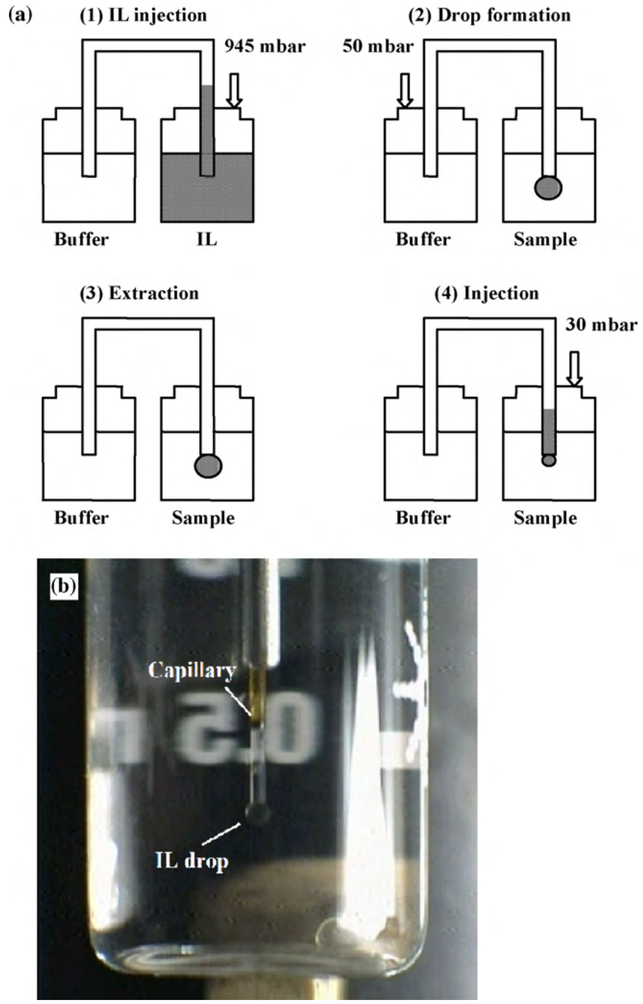

Fig. 1. (a) Scheme of the IL-SDME-CE. (1) Injection of the IL, (2) IL single drop formation, (3) extraction of the target analytes in the aqueous solution into the IL phase, and (4) injection of the enriched IL phase into the capillary. (b) Image of an IL single drop hanging at the capillary tip.

2.2. Apparatus

Experiments were carried out using a HP^{3D}CE CE system (Agilent Technologies, Germany) with a diode array UV–vis detector. The detector was set at 254 nm which is not absorbed by the [BMIM][PF_6] [41]. A new fused silica capillary of 75 μm ID and 365 μm OD and effective/total length of 40/48.5 cm (Hebei Ruifeng Instrumental Co., China) was flushed with methanol for 5 min, water for 5 min, 1 $mol\,L^{-1}$ NaOH in water for 30 min, water for 10 min, and finally a flush buffer for 10 min in succession. Between runs, the capillary was treated by rinsing with methanol for 2 min and the flush buffer for 2 min. The temperature was maintained at 25 °C. A small CCD camera was placed in the apparatus which was used to monitor the IL single drop handling processes.

2.3. IL-SDME–CE procedure

We demonstrated a method which on-line coupled SDME and CE with IL as an extraction solvent without any alteration on instrument. Based on Ref. [17], the procedures of IL-SDME–CE were proposed which were shown in Fig. 1(a). Firstly, capillary was flushed with 20 $mmol\,L^{-1}$ borate (pH 10.0) including 66.7% methanol (v/v) for 2 min. Then, IL was pressed into the capillary inlet under 945 mbar for 3 s followed by applying afterward pres-