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# Multiple functional ionic liquids based dispersive liquid–liquid microextraction combined with high performance chromatography for the determination of phenolic compounds in water samples



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## ABSTRACT

A new mode of ionic liquid based dispersive liquid–liquid microextraction (IL-DLLME) is developed. In this work, [C<sub>6</sub>MIm][PF<sub>6</sub>] was chosen as the extraction solvent, and two kinds of hydrophilic ionic liquids, [EMIm][BF<sub>4</sub>] and [BSO<sub>3</sub>HMIm][OTf], functioned as the dispersive solvent. So in the whole extraction procedure, no organic solvent was used. With the aid of SO<sub>3</sub>H group, the acidic compound was extracted from the sample solution without pH adjustment. Two phenolic compounds, namely, 2-naphthol and 4-nitrophenol were chosen as the target analytes. Important parameters affecting the extraction efficiency, such as the type of hydrophilic ionic liquids, the volume ratio of [EMIm][BF<sub>4</sub>] to [BSO<sub>3</sub>HMIm][OTf], type and volume of extraction solvent, pH value of sample solution, sonication time, extraction time and centrifugation time were investigated and optimized. Under the optimized extraction conditions, the method exhibited good sensitivity with the limits of detection (LODs) at 5.5 μg L<sup>-1</sup> and 10.0 μg L<sup>-1</sup> for 4-nitrophenol and 2-naphthol, respectively. Good linearity over the concentration ranges of 24–384 μg L<sup>-1</sup> for 4-nitrophenol and 28–336 μg L<sup>-1</sup> for 2-naphthol was obtained with correlation coefficients of 0.9998 and 0.9961, respectively. The proposed method can directly extract acidic compound from environmental sample or even more complex sample matrix without any pH adjustment procedure.

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## 1. Introduction

Dispersive liquid–liquid microextraction (DLLME) [1] was introduced by Assadi and co-workers in 2006 based on the homogeneous liquid–liquid extraction (HLL) and cloud point extraction (CPE). In DLLME, the water immiscible extraction solvent is dispersed as fine droplets in sample solution with the effect of water-miscible polar dispersive solvent, and the mass transfer of target analytes is completed in a split second through the infinite large contact area between extraction solvents and sample solution. In the dispersion step, many kinds of external force are used to help the extraction solvent completely disperse into the sample solution including temperature [2], ultrasound [3], and microwave [4]. And most recently, a combination of vortex and ultrasound was first used to enhance the dispersion of extraction solvent [5,6]. All the methods mentioned above increase the extraction efficiency. After

dispersion step, phase separation is achieved by centrifugation and then the enriched analytes in the sedimented phase are determined by analytical instrument. This mode has exhibited excellent extraction capability and has been successfully applied in medicinal [7], environmental [8–10], biological field [11–13] and food samples [14,15].

Recently, many researchers have focused on the application of ILs in DLLME [9,16,17] responding to the growing demand for green, environment-friendly techniques. Room-temperature ionic liquids (RTILs), a category of non-molecular ionic solvent with low melting points, are composed of organic cations and various organic or inorganic anions. Owing to the characteristics of low volatility, low toxicity, high thermal stability and good extraction capacity for most organic compounds, ILs are considered as the appropriate replacement for conventional organic solvent. IL-DLLME was first reported in 2008 by Zhou [18], and has received many attentions in recent years. In an IL-DLLME research, types of extraction solvent and the dispersion degree are the most important parameters influencing the extraction efficiency. According to the former researches, the alkylimidazolium hexafluorophosphate-based ILs were most widely used as extraction solvent, so the researches of

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IL-DLLME have focused on the improvement of dispersion degree of extraction solvent. Until now, three types of dispersive methods have been proposed: The first method is with the aid of external force such as temperature [19,20], ultrasound [21,22] and microwave [4] to help the ILs disperse into sample solution; the second approach is *in situ* IL DLLME [23] involving an *in situ* metathesis reaction. More recently a completely non-organic solvent IL-DLLME was introduced. In this approach, the hydrophilic ionic liquid [EMIm][BF<sub>4</sub>] was used as the dispersive solvent to help the extraction solvent hydrophobic ionic liquid [C<sub>8</sub>MIm][PF<sub>6</sub>] totally disperse into the sample solution, most importantly of all, no traditional organic solvent was utilized [24]. This method provided a potential mode for IL-DLLME, by which the extraction procedure is completely environment-friendly.

But in the above research, the researchers only used the hydrophilic property of ionic liquid, actually the ILs are known as custom-designed solvent for their selectivity and sensitivity for special kinds of organic compounds by introducing functional groups into the structures, which is the most important advantage comparing to organic solvent during extraction. So in this research, two types of ionic liquids including [EMIm][BF<sub>4</sub>] and [BSO<sub>3</sub>HMIm][OTf] with a SO<sub>3</sub>H group covalently linked through an alkyl chain to the cation were introduced serving as dispersive solvent. According to the reported researches [25], [BSO<sub>3</sub>HMIm][OTf] can exhibit acidity in water solution. So [BSO<sub>3</sub>HMIm][OTf] used in this research not only act as the dispersive solvent, but also act as a pH modifier. With the volume change of [BSO<sub>3</sub>HMIm][OTf], the pH of sample solution will be changed at the same time avoiding extra pH adjustment.

In this research, we aimed to explore the extraction performance and application of the [BSO<sub>3</sub>HMIm][OTf] involved multiple functional ionic liquids in dispersive liquid–liquid microextraction. So the target analytes should be acidic to meet the research aim.

Industrial wastewater has been the most urgent problem for environmental protection. The phenolic compounds are the major contaminants presented in environmental water, among which 4-nitrophenol and 2-naphthol, as the intermediates or precursors for the production of insecticides, pharmaceuticals and dyes, have been regarded as the very important ones. Due to the high toxicity and carcinogenicity, 4-nitrophenol is even included in the list of priority pollutants in many countries. According to the present Environmental Quality Standards for Surface Water in China [26], the content of phenolic compounds in surface water should be below 100 µg L<sup>-1</sup>. So considering low concentration of phenolic compound in aqueous samples, the sample preparation process is necessary before instrumental analysis. Solid-phase extraction (SPE) [27], liquid–liquid extraction (LLE) [28], solid-phase microextraction (SPME) [29,30] and liquid-phase microextraction (LPME) [31,32] have been successively developed for the enrichment of phenolic compounds.

In this research, a new mode of IL-DLLME based on hydrophilic and hydrophobic ionic liquids are developed for the determination of two acidic phenolic compounds, 2-naphthol and 4-nitrophenol, in environmental water. The possible factors affecting extraction efficiency, such as the type of hydrophilic ionic liquids, the ratio of [EMIm][BF<sub>4</sub>] to [BSO<sub>3</sub>HMIm][OTf], type and volume of extraction solvent, pH value of sample solution, sonication time, extraction time and centrifugation time, were investigated and optimized.

## 2. Experimental

### 2.1. Chemicals and reagents

2-naphthol (2-NA) and 4-nitrophenol (4-NP) were obtained from Alfa Aesar (Tianjin, China) and their purities were > 99%. Chromatographic-grade methanol and acetonitrile were purchased from Merck Co. (Darmstadt, Germany). Ionic liquids of

1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>MIm][PF<sub>6</sub>]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C<sub>6</sub>MIm][PF<sub>6</sub>]), 1-octyl-3-methylimidazolium hexafluorophosphate ([C<sub>8</sub>MIm][PF<sub>6</sub>]), 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIm][BF<sub>4</sub>] and 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfate [BSO<sub>3</sub>H-MIm][OTf] were obtained from Lanzhou Institute of Chemical Physics of CAS (Lanzhou, China). Other chemicals are of analytical grade and purchased from Tianjin Chemical Reagent Co. (Tianjin, China). Ultrapure water (18.20 MΩ cm, 25 °C) obtained from a OKP-S210 purification system (Shanghai Laikie Instrument Co., Ltd, Shanghai, China) was used for the preparation of mobile phase and sample solution.

### 2.2. Apparatus

An Agilent 1200 HPLC system comprising a G1312A binary pump, a G1315D diode-array detector and a G1328B manual injector was used for chromatographic analysis. Chromatographic separation of the analytes was performed on a Kromasil C<sub>18</sub> column (5 µm, 4.6 mm × 250 mm i.d.) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China). Agilent ChemStation was employed to acquire and process chromatographic data. The mobile phase was consisted of methanol–water (75:25, v/v) at a flow rate of 1.0 mL min<sup>-1</sup>. The column temperature was maintained at 25 °C. The detection wavelengths were set at 313 nm for 4-nitrophenol and 274.5 nm for 2-naphthol.

### 2.3. Preparation of stock solution and environmental water samples

The stock standard solution of 2-naphthol and 4-nitrophenol were prepared in methanol of HPLC grade with concentration of 0.35 and 0.10 mg mL<sup>-1</sup>, respectively, and stored at 4 °C before use. Then the working solutions were prepared freshly by diluting the stock solution with ultrapure water and used immediately for the optimization of IL/IL DLLME procedure and the method validation. Calibration standard solutions containing 2-naphthol and 4-nitrophenol were prepared by ultrapure water over the concentration range of 28–336 and 24–384 µg L<sup>-1</sup>.

Three local environmental water samples, including tap water, snow water and river water, were collected. The tap water was obtained from our lab, and the snow water was collected in Lanzhou, China. The river water was collected from the Yellow River (Lanzhou, China). These samples were all filtered through a 0.45 µm filter and stocked in amber glass at 4 °C avoiding light.

### 2.4. Ultrasound-assisted IL/IL-DLLME procedure

First, 5 mL aqueous sample was placed in a 10 mL screwcap glass conical tube without pH adjustment. Then the mixture of 65 µL [C<sub>6</sub>MIm][PF<sub>6</sub>], 120 µL [EMIm][BF<sub>4</sub>], and 30 µL [BSO<sub>3</sub>HMIm][OTf] were rapidly injected into the tube and the cloudy solution was formed. Subsequently, the tube was immersed in an ultrasonic water bath (KQ500DB, Kunshan, China), and sonicated at 200 W power for 5 min at room temperature. Then the cooling step was carried out for 20 min, and the phase separation was achieved by 8 min centrifugation. Finally, the upper aqueous phase was disposed by a pipette and the sedimented phase was diluted to 60 µL with methanol. 10 µL filtrates was injected into the HPLC system for analysis.

## 3. Results and discussion

### 3.1. Optimization of ultrasound assisted IL/IL-DLLME

The present work focused on finding the optimum extraction conditions for the phenols in environmental water samples using

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