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Original article

Combination of ionic liquid dispersive liquid-phase microextraction and high performance liquid chromatography for the determination of triazine herbicides in water samples

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ABSTRACT

A temperature-controlled ionic liquid dispersive liquid-phase microextraction in combination with high performance liquid chromatography was developed for the enrichment and determination of triazine herbicides such as cyanazine, simazine, and atrazine in water samples. 1-Octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) was selected as the extraction solvent. Several experimental parameters were optimized. Under the optimal conditions, the linear range for cyanazine was in the concentration range of 0.5–80 μg/L and the linear range for simazine and atrazine was in the range of 1.0–100 μg/L. The limit of detection (LOD, S/N = 3) was in the ranges of 0.05–0.06 μg/L, and the intra day and inter day precision (RSDs, *n* = 6) was in the ranges of 3.2%–6.6% and 4.8%–8.9%, respectively. Four real water samples were analyzed with the developed method, and the experimental results showed that the spiked recoveries were satisfactory. All these exhibited that the developed method was a valuable tool for monitoring such pollutants.

1. Introduction

Triazines have been widely used in agricultural domain due to their high power for weed control for many years. The wide use of these herbicides at large scale has resulted in serious pollution of the environment [1]. Triazine herbicides and their degradation products are highly toxic, mobile and soluble in water and can also be strongly adsorbed onto soil, hence have been an environmental safety concern [2,3]. In the United States, a joint project of the Environmental Protection Agency's Office of Drinking Water (ODW) and the Office of Pesticide Programs carried out a national pesticide survey [4,5], and the results showed that atrazine and simazine existed in the drinking water samples. In the EU, the maximum allowed limit for each individual herbicide has been set at 0.1 μg/L [6]. Hence it is necessary to develop simple, sensitive and low cost monitoring techniques for the analysis of the residual level of these pollutants.

Generally, a sample pretreatment step is used before an effective method is developed, and up to now, many methods have been established for the enrichment of triazines residues from complex matrices. Liquid–liquid extraction often needed a large volume of the sample of interest and toxic organic solvents and also was labor intensive, expensive, and time-consuming. Single-drop microextraction is established based on the principle of liquid–liquid extraction and the enrichment is finished in a single drop of solvent. However, the shortcomings of this method are the instability of the drop when fast stirring or volatile organic solvents are used [7]. This method is also time-consuming and the equilibrium requires a long time to achieve in most cases. Dispersive liquid–liquid microextraction [8] is a recently constructed method and has many applications for the determination of pesticides, pharmaceuticals, PCBs, PBDEs and PAHs, *etc.* However, chlorobenzene, chloroform and carbon disulfide were often used as the extraction solvent and methanol, acetonitrile and acetone *etc.* were used as the disperser solvents, which will result in secondary pollution. In order to resolve such problems, ionic liquid (IL) was an ideal selection because ionic liquids have many interesting properties including wide liquid ranges, low volatility, good stability, reusability, *etc.* Due to these useful properties, ILs have been widely used in organic chemistry and analytical chemistry. In dispersive liquid–liquid microextraction processes, ILs also have some applications for the analysis of hexabromocyclododecane diastereomers [9], polar herbicides [10], pesticides and heavy metals, *etc.* [11–13]. In this work, 1-octyl-3-methylimidazolium hexafluorophosphate $[C_8MIM][PF_6]$ was chosen as the extraction solvent and triazine herbicides were selected as the

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model analytes. A new temperature controlled ionic liquid dispersive liquid phase microextraction was developed for the sensitive determination of triazine herbicides. The possible factors were optimized.

2. Experimental

Cyanazine, simazine, and atrazine were purchased from AccuStandard, Inc. (New Haven, USA). The stock solutions with a concentration of 1000 mg/L were prepared by dissolving the solid bulk triazine herbicides in methanol and were stored at 4 °C in a refrigerator. The working solutions were obtained by diluting the stock solutions with methanol. 1-Octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) was synthesized in our own laboratory [14]. HPLC grade methanol and acetonitrile were purchased from Jiangsu Guoda Chemical Reagent Co., Ltd. (Huaian, China). Ultrapure water used in the experiments was prepared on a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glass used in the experiments was washed with pure water, then soaked in 6 mol/L nitric acid for 24 h and cleaned with ultrapure water before use.

The analysis and separation was carried out on a high performance liquid chromatography system including two LC-10 ATvp pumps and an SPD-10 Avp ultraviolet detector (Shimadzu, Kyoto, Japan). The analytical column was a reversed-phase SunFire C18 column (150 mm × 4.6 mm, particle size 5 μm) and the software of Chromato Solution Light Chemstation for LC system was used to acquire and process chromatographic data. The mobile phase was a mixture of methanol and ultrapure water (40/60, v/v). The mobile phase flow rate was set at 1.2 mL/min, the injection volume was set at 20 μL, and the detection wavelength was set at 275 nm. An Anke 80-2 (Shanghai, China) centrifuge was utilized to centrifuge the cloudy water solutions.

The enrichment procedure was as follows: 10 mL of ultra-pure water was put in a 10 mL conical tube, the cyanazine, simazine and atrazine were spiked with a concentration of 10 μg/L, 20 μg/L and 20 μg/L, respectively. Then sodium chloride was added at a concentration of 20% (w/v). After 50 μL of $[C_8MIM][PF_6]$ was added, the tube was heated in a water bath with the temperature controlled at 80 °C. When $[C_8MIM][PF_6]$ was completely dissolved in the aqueous solution and a nearly homogenous solution was obtained, the tube was cooled with ice water. The tube was kept for 30 min to enhance the extraction of triazine herbicides from the sample solution into the tiny droplets of $[C_8MIM][PF_6]$. Thereafter the mixture was centrifuged for 20 min at 4000 rpm. The upper aqueous phase was removed, and the residue was dissolved in 200 μL of methanol and 20 μL of the resulting solution was injected into the HPLC system for analysis. Each experiment was done in triplicate to ensure the accuracy of the experimental data.

Four water samples were collected for use. River water was taken from Baihe, Nanyang City, Henan Province, China. Underground water was obtained from Henan Normal University in Xinxiang City, Henan Province, China. Drainage water was collected from Gongchanzhuyi drainage, Xinxiang City, Henan Province, China. Wastewater was obtained from the outlet of Luotuowan sewage treatment plant, Xinxiang City, Henan Province, China. Before use, all the environmental water samples were filtered with 0.45 μm micro-pore membranes and then stored in brown glass containers at a low temperature of 4 °C.

3. Results and discussion

3.1. Effect of ionic strength

The salting-out effect is often present in many cases, and it is often utilized to enhance the enrichment or preconcentration performance. In theory, addition of salt will decrease the solubility of analytes in the aqueous sample and enhances their partitioning into the adsorbent or organic phase. On the other hand, the addition of salt increased the solubility of the ionic liquid in water, which played a dominant role in the decrease of the volume of the sediment phase. A series of experiments were designed to investigate the salting-out effect (Fig. 1). The results demonstrated that a significant increase of the peak area occurred as the ionic strength of the solution increased from 0% to 20% (w/v), but the peak area decreased when the ionic strength of the solution was further increased to the range of 20%–25%. So 20% (w/v) NaCl was added in the following experiments.

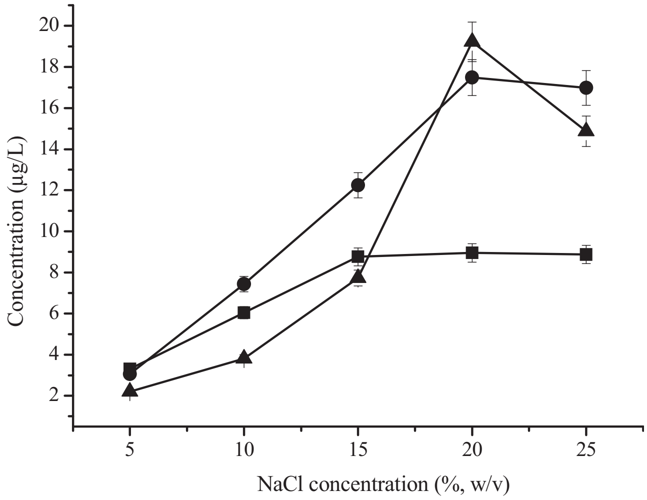

Fig. 1. Effect of sodium chloride content. Conditions: $[C_8MIM][PF_6]$ volume, 50 μL; sample volume, 10 mL; spiked concentration, 10 μg/L for cyanazine, 20 μg/L for simazine and atrazine; temperature, 70 °C; extraction time, 30 min; centrifuging time, 20 min; (■) cyanazine, (●) simazine, (▲) atrazine.

3.2. Effect of the volume of ionic liquid

The volume of extraction solvent was a key factor in the newly developed procedure, which determines the enrichment performance to a certain extent. In order to achieve the maximum enrichment performance possible, the volume of extraction solvent was optimized in the range of 40–60 μL (Fig. 2). From Fig. 2, we can see that the largest peak area of the targeted analytes

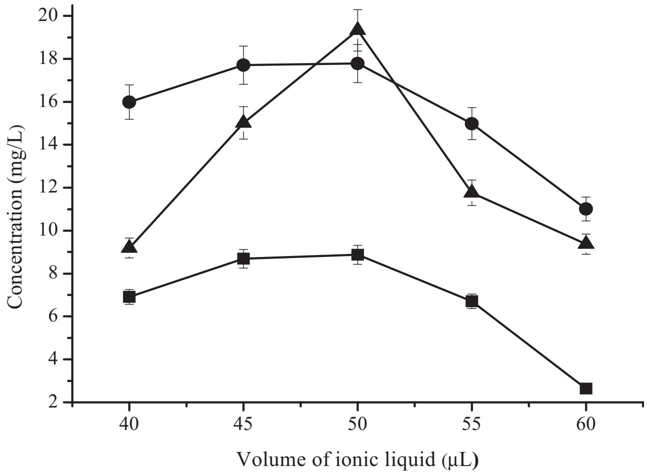

Fig. 2. Effect of ionic liquid volume. Conditions: ionic liquid, $[C_8MIM][PF_6]$; sample volume, 10 mL; spiked concentration, 10 μg/L for cyanazine, 20 μg/L for simazine and atrazine; sodium chloride content, 20% (w/v); temperature, 70 °C; extraction time, 30 min; centrifuging time, 20 min. (■) cyanazine, (●) simazine, (▲) atrazine.