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Determination of Hexabromocyclododecane Diastereomers in Environmental Water Samples with Ionic Liquid-Dispersive Liquid-Liquid Microextraction

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In this paper, a simple, rapid and sensitive method for the simultaneous enrichment and sensitive determination of hexabromocyclododecane diastereomers (HBCDs) in environmental water samples has been developed. It was based on ionic liquid-dispersive liquid-liquid microextraction (IL-DLLME) and rapid resolution liquid chromatography-electrospray tandem mass spectrometry (RRLC-ESI-MS/MS). Important factors affecting extraction efficiencies were investigated and optimized. Under the optimal conditions, experimental results exhibited excellent linear relationships over the range of 0.1-10 μg L^{-1}. The limits of detection and relative standard deviations were in the range of 0.008-0.035 μg L^{-1} and 1.18-7.58 %, respectively. The proposed method has been successfully applied for the trace analysis of hexabromocyclododecane diastereomers in environmental water samples.

Keywords: Ionic liquid, Dspersive liquid-liquid microextraction, Hexabromocyclododecane diastereomers, RPLC-ESI-MS/MS.

INTRODUCTION

Hexabromocyclododecane diastereomers are widely used in plastics, textiles, electronic circuitry *etc.* to prevent fires. Hexabromocyclododecane diastereomers share the major characteristics of persistent organic pollutants (POPs) *i.e.*, persistency, bioaccumulation, long-range transport and toxicity. Hexabromocyclododecane diastereomers can enter the environment through a number of different pathways, such as emission during production of BFRs or the manufacture of flame-retarded products, by leaching from consumer products, or following disposal[1]. For monitoring and assessing these pollutants in various environmental samples, a suitable enrichment step combined with a matrix separation is often necessary.

The classical liquid-liquid extraction (LLE) often needs time-consuming procedures and large amount of high purity and toxic solvents[2]. Assadi and his colleagues have developed a novel dispersive liquid-liquid microextraction technique[3,4]. The main advantages of the method are simplicity and rapidity of operation, low cost of organic solvent, high extraction recovery and enrichment factor[5]. This method has been successfully applied for extraction of organic pollutants in environmental samples[3,6,7].

Ionic liquids (ILs), one kind of new material, can reduce the use of hazardous and toxic organic solvents, their volatility is negligible and this is the basic property which characterizes them as green solvents[8,9]. The objective of this work was to develop a simple and rapid an analytical method based on ionic liquid-dispersive liquid-liquid microextraction (IL-DLLME) and RRLC-ESI-MS/MS for the simultaneous enrichment and sensitive determination of hexabromocyclododecane diastereomers. Important factors affecting the performance of IL-DLLME procedure were investigated and optimized. Finally, the optimized proposed method was applied for the analysis of hexabromocyclododecane diastereomers in real environmental water samples.

EXPERIMENTAL

Ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$ (99 %), 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$ (99 %) and 1-octyl-3-methylimidazolium hexafluorophosphate $[C_8MIM][PF_6]$ (99 %) were purchased from Chengjie Chemical Company (Shanghai, China) and used as obtained. Hexabromocyclododecane diastereomers standards were obtained from AccuStandard, Inc. (CT, USA).

General procedure: A 5 mL portion deionized water was placed in a 10 mL screw cap glass test tube with conical bottom and spiked with each hexabromocyclododecane diastereomer at concentrations of 5 ng mL^{-1} 400 μL of methanol which was used as disperser solvent containing 40 μL $[C_6MIM][PF_6]$

(as extraction solvent) was rapidly injected into the sample solution with a 1 mL syringe. A cloudy solution (water-methanol-[C_6MIM][PF_6] mixture) was formed in the test tube. The mixture was gently shaken for 7 min for extraction and then centrifuged for 5 min at 5000 rpm, when the dispersed fine droplets of the extraction phase to settle to the bottom of the conical test tube. The upper aqueous phase was removed with a syringe, the residue was dissolved in 50 μL of methanol and 10 μL was injected with an Agilent 1200 series SL autosampler for analysis.

Detection method: An XDB-C18 column (4.6 × 50 mm, 1.8 μm particle size) was used for the analysis. A sample volume of 10 μL was injected with an autosampler using 10 % water and 90 % methanol at a constant flow rate of 0.5 mL/min. The multiple reaction monitoring (MRM) conditions of Agilent 6410 triple quadrupole mass spectrometer fitted with an ESI-MS source were optimized and used.

RESULTS AND DISCUSSION

In this work, three ionic liquids, [C_4MIM][PF_6], [C_6MIM] [PF_6] and [C_8MIM][PF_6], were compared for the extraction of hexabromocyclododecane diastereomers. From experimental results, it can be observed that [C_6MIM][PF_6] as extraction solvent could achieve the highest extraction efficiency (70.5-82.9 %) when compared with [C_4MIM][PF_6] (48.1-60.7 %) and [C_8MIM][PF_6] (66.2-78.4 %). Therefore, [C_6MIM][PF_6] was selected as the extraction solvent in further experiments. The [C_6MIM][PF_6] volume was investigated over the range of 40-80 μL. Fig. 1 shows that the extraction efficiency reached a maximum for three hexabromocyclododecane diastereomers when 40 μL [C_6MIM][PF_6] was used. Therefore, in order to achieve a good enrichment factor, 40 μL of [C_6MIM][PF_6] was chosen in the following experiments.

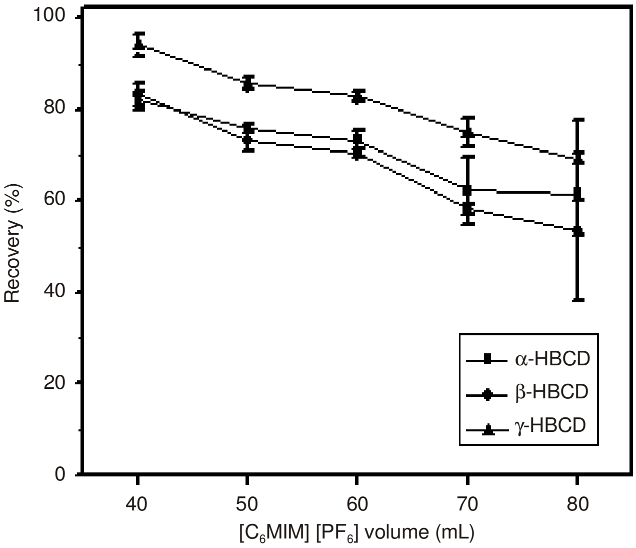

Fig. 1. Influence of [C_6MIM][PF_6] volume on the recoveries of hexabromocyclododecane diastereomers. Conditions: IL, [C_6MIM][PF_6]; acetone volume, 500 μL; sample volume, 5 mL; sample concentration, 5 μg L^{-1}; extraction time, 5 min; pH, 7

For IL-DLLME process, disperser solvent is an important parameter affecting the enrichment efficiency of hexabromocyclododecane diastereomers. In this experiment, three disperser solvents, methanol, acetonitrile and acetone, were tested. Experimental results indicated that using methanol as a disperser solvent can achieve the highest extraction efficiency (85.6-92.1 %) for three hexabromocyclododecane diastereomers. Thus, methanol was selected as disperser solvent. In this experiment, the volume of methanol was investigated over the range 300-700 μL. Fig. 2 demonstrates the extraction efficiencies of hexabromocyclododecane diastereomers *versus* the volume of methanol. According to Fig. 2, 400 μL of methanol was chosen as the optimum volume.

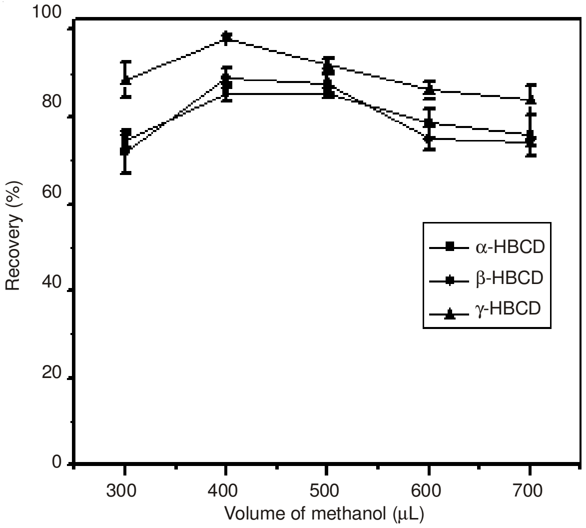

Fig. 2. Influence of methanol volume on the recoveries of hexabromocyclododecane diastereomers. Conditions: [C_6MIM] [PF_6] volume, 40 μL; disperser solvent, methanol; sample volume, 5 mL; sample concentration, 5 μg L^{-1}; extraction time, 5 min; pH, 7)

The pH of the sample determines the existing state of target compounds in water samples and thus affects extraction efficiencies of target compounds. The influence of sample pH was investigated over the pH range 3-11. The experimental results indicated that the extraction efficiency reach a maximum (93-98.6 %) when the sample pH was equal to 7. Therefore, a sample pH of 7 was selected for further experiments.

Under the optimal conditions, important parameters were carefully investigated to evaluate whether the performance of proposed method could be reliable for the determination of hexabromocyclododecane diastereomers in environmental samples. The experimental results are given in Table-1. All the analytes exhibited good linearity over the range of 0.1-10 μg L^{-1}. The repeatability of the IL-DLLME system was performed by deionized water sample spiked at 0.5 μg L^{-1} of each hexabromocyclododecane diastereomer (six replicates) and their relative standard deviations (RSDs) were in the range of 1.84-7.58 %. The limits of detection (LODs), based on signal-to-noise ratio (S/N) of 3, were in the range of 0.008-0.035 μg L^{-1}.

The novel method was applied to analyze three real water samples including lake water, river water and snow water samples. The experimental results indicated that these real water samples were free of hexabromocyclododecane diastereomers contamination (*i.e.*, hexabromocyclododecane diastereomers

TABLE-1
PARAMETERS OF ANALYTICAL PERFORMANCE

Analyte	Linear range (μg L^{-1})	R	RSD (%)	LOD (μg L^{-1})
α-HBCD	0.1-10	0.9954	1.18	0.035
β-HBCD	0.1-10	0.9985	7.10	0.008
γ-HBCD	0.1-10	0.9990	7.58	0.020

were undetectable). These real water samples were spiked with hexabromocyclododecane diastereomers standard at the concentration of 0.25 and 0.50 μg L^{-1} to assess matix effects. Fig. 3 shows the typical chromatograms of hexabromocyclododecane diastereomers obtained for blank lake water sample and spiked with different concentrations of hexabromocyclododecane diastereomers standard. The relative recovery data revealed that satisfactory recoveries over the range of 86.4-98.2 % were achieved for these three real samples, thus confirming the accuracy of the IL-DLLME procedure and its independence from matrix effects.

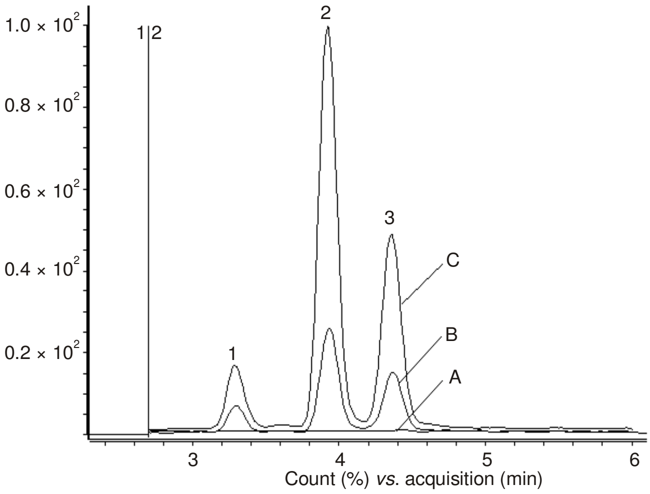

Fig. 3. Typical chromatograms of lake water sample (a) Lake water sample; (b) Lake water sample spiked with 0.25 μg L^{-1} hexabromocyclododecane diastereomers; (c) Lake water sample spiked with 0.50 μg L^{-1} hexabromocyclododecane diastereomers (1) α-HBCD (2) β-HBCD (3) γ-HBCD

Conclusion

In this study, ionic liquid-dispersive liquid-liquid microextraction approach was successfully developed for the rapid preconcentration and determination of hexabromocyclododecane diastereomers in water samples prior to RRLC-ESI-MS/MS analysis. The proposed method has higher extraction recovery, lower sample volume and better linear range for the determination of hexabromocyclododecane diastereomers in water samples. In a word, the novel method possesses great potential in enrichment and analysis of trace organic pollutants in real water samples.

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