Monitoring Method of Hydroxyl Functionalized Imidazolium Ionic Liquids in Complex Environment Water Samples

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Research Article

Keywords: Environmental water·Hydroxyl functionalized imidazolium ionic liquids, Ion chromatography, Solid-phase extraction, Ultraviolet detection, Ion exchange

Posted Date: June 25th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-593366/v1

Abstract

With the increasing emphasis on the toxicity of ionic liquids, it is imperative to develop detection methods for ionic liquids in complex environments. A new method for the analysis of hydroxyl functionalized imidazolium ionic liquids in complex environmental water samples by using ion chromatography and solid-phase extraction was developed. Under the selected chromatographic conditions, the complete separation of the two analytes was achieved in 14.0 min. The linear and repetitive data of the approach for the analysis of the two cations by ion chromatography meet the requirements of quantitative analysis. The extraction of $[HEMIm]^+$ and $[HPMIm]^+$ in water samples by ion-exchange solid-phase extraction and reversed-phase solid-phase extraction was compared. The results show that the enrichment and purification of two target cations can be better achieved using ion-exchange solid-phase extraction approach, and the enrichment multiple was 50 times. The method was used to determine the target cations in two river waters. The recovery of standard addition was between 82.5% and 96.0%, the detection limit was less than 0.01 mg/L, and inter-assay RSD was less than 2.5%. The method is simple, accurate and reliable. It is suitable for the determination of hydroxyl functionalized imidazolium ionic liquid cations in environmental water samples.

1. Introduction

Ionic liquids (ILs) are special liquid molten salts at room temperature. As new green solvent, ILs have many unique physicochemical properties, such as wide range of liquid temperature, low vapor pressure, strong solubility and recyclable use. At present, ILs have been widely used in organic synthesis, electrochemistry and analytical chemistry etc (Trujillo-Rodriguez et al. 2019; Lei et al. 2017; Berthod et al. 2018; Wu et al. 2018; Zhang et al. 2015; Zhang et al. 2018; Feng et al. 2018; Zhao et al. 2019; Cui et al. 2019; Wen et al. 2019; Hussain et al. 2019). Functionalized ILs, as an important branch of ILs, make full use of the designability of ILs, which are synthesized according to the specific application purpose or actual needs. Because functionalized ILs are more selective and practical than traditional ILs, they have been widely used in chemistry and other fields (Hoogerstraete et al. 2013; Muthyala et al. 2014; Nie et al. 2012; Bian et al. 2017; Pati et al. 2017).

With the expanding application of ILs and the in-depth study of ILs, people are gradually aware of the toxicity of this new solvent. Some literatures reported the results of biological toxicity studies of ILs (Oskarsson and Wright 2019; Pawłowska et al. 2019). ILs have certain toxicity to fish, rice, corn and other organisms, and the toxicity of IL cations increases with the increase of alkyl chain (Shao et al. 2019; Markiewicz et al. 2015; Xia et al. 2018; Jafari et al. 2019; Cheng et al. 2019; Pati and Arnold 2020; Hossain et al. 2013). In addition, ILs are stable, non-volatile and soluble in water, which may lead to environmental pollution. Therefore, the determination of trace IL cations in environmental water samples is very important, which can provide reference for the environmental risk assessment of ILs.

Because the content of IL cations in the environment is very low, it can’t reach the detection limit of the chromatographic instrument. Therefore, the samples should not be directly detected by chromatograph.

In addition, environmental sample systems are complex and may interfere with the analysis of target compounds, so sample pretreatment is needed for the purification and enrichment of the targets. Solid-phase extraction (SPE) is a kind of sample pretreatment technology developed in recent years. It can reduce matrix interference and improve the detection sensitivity of analytes and its operation is simple, time-saving and labor-saving. SPE has been widely used in medicine, food, environment, commodity inspection, chemical industry and other fields (Capriotti et al. 2019; Zhu et al. 2019; Fan and Yu 2018; Liu et al. 2021; Tian et al. 2019; Zhang et al. 2019).

In recent years, the analysis of traditional ILs has been reported in some literatures (Ruiz-Angel and Berthod 2008; Flieger and Czajkowska-Zelazko 2012; Lu et al. 2015; Zhang et al. 2017; Liu et al. 2018; Liu et al. 2020; Onink et al. 2015; Zhang et al. 2017; Rutz et al. 2017). The methods to analyze the traditional ILs mainly include reversed-phase chromatography (Ruiz-Angel and Berthod 2008; Flieger and Czajkowska-Zelazko 2012; Lu et al. 2015), ion-pair chromatography (Zhang et al. 2017; Liu et al. 2018; Liu et al. 2020), ion chromatography (Onink et al. 2015; Zhang et al. 2017; Rutz et al. 2017), hydrophilic interaction chromatography (Fan et al. 2018a; Hawkins et al. 2015; Fan and Yu 2019; Fan et al. 2018b) and capillary electrophoresis (Pyschika et al. 2017). Hydroxyl-functionalized imidazolium ionic liquids is an emerging ionic liquid. They have been widely used in chemical reactions and inorganic nanomaterials. For the analysis of hydroxyl functionalized imidazolium ILs, only our research team has carried out preliminary research (Jin et al. 2019; Liu et al. 2020). The retention and separation behavior of hydroxyl functionalized imidazolium IL cations in reversed-phase ion-pair chromatography and reversed-phase chromatography were investigated. However, how to enrich and purify hydroxyl functionalized imidazolium ILs in environmental water samples has not been studied. In addition, whether other chromatographic methods, such as ion chromatography, can analyze these ionic liquids still need to be explored. On this basis, we will continue to explore a new method for the trace analysis of hydroxyl functionalized imidazolium IL cations in environmental water samples.

The purpose of this work is to develop an analytical method for the determination of hydroxyl functionalized imidazolium ILs in river water samples by combining ion chromatography with SPE. Ion chromatography separation and SPE enrichment of the functionalized ILs in water samples were studied, which provided a new reference method for separation and detection of trace hydroxyl functionalized imidazolium ILs in environmental water samples.

2. Experimental

2.1. Chemicals

1-Hydroxyethyl-3-methyl imidazolium chloride ([HEMIm][Cl]) and 1-hydroxypropyl-3-methyl imidazolium chloride ([HPMIm][Cl]) with purity more than 99.0% were purchased from Lanzhou Yulu Fine Chemical Company Limited (Lanzhou, China). 1-Ethyl-3-methyl imidazolium tetrafluoroborate ([EMIm][BF_4]), 1-propyl-3-methyl imidazolium tetrafluoroborate ([PMIm][BF_4]) and 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIm][BF_4]) with purity more than 99.0% were purchased from Shanghai Chengjie

Chemical Company Limited (Shanghai, China). Oxalic acid, citric acid, tartaric acid, methanesulfonic acid (MSA), phosphoric acid and sodium dihydrogen phosphate with analytical purity were purchased from Beijing Bailingwei Technology Company Limited (Beijing, China). Methanol, acetonitrile (ACN) and sodium decanesulfonate with chromatographic purity were purchased from Tianjin Komeo Chemical Reagent Company Limited (Tianjin, China). Experimental water was ultrapure water with a resistivity of 18.2 MΩ cm.

2.2. Preparation of Solution

The standard stock solutions of hydroxyl functionalized imidazolium IL cations $[HEMIm]^+$ and $[HPMIm]^+$ with mass concentration of 1000.0 mg/L were prepared by using ultrapure water and stored in refrigerator. When in use, the stock solutions were diluted to the standard solutions of the required concentration for the experiment, and then filtered through 0.22 μm filter membrane before chromatographic injection.

According to the experimental requirement, the mobile phase with a certain concentration was prepared by ultrapure water, filtered by 0.22 μm filter membrane, degassed by vacuum for 15 min and then used.

2.3. Instruments

A model LC-20A chromatographic system (Shimadzu, Japan) was used, which was equipped with a model SPD-20A ultraviolet detector, a LC-20AT mobile phase infusion pump, a SIL-20A automatic sampler, a CTO-20A column temperature box and Labsolutions workstation. A model ASE-24 SPE instrument (Tianjin OTSEENS Instrument Company Limited, China) equipped with a model AP-9950 oil-free vacuum pump was used for the SPE of water samples. A model Millipore Milli-Q water purification system (Millipore, USA) was used to produce the ultrapure water with a resistivity of 18.2 MΩ cm. A pH meter with model PHSF-3F (Shanghai Precision Scientific Instrument Company Limited, China) was used for measurement of acidity and basicity. A model Shodex IC YK-421 cation-exchange column with carboxylic acid functional group (125 mm × 4.6 mm i.d., 5 μm; Showa Electrical Engineering Instrument Company Limited, Japan), a Baseline WCX cation-exchange column with carboxylic acid functional group (125 mm × 4.6 mm i.d., 5 μm; Tianjin Bessel Chromatographic Technology Development Center, China), a UF-C18 SPE column (250 mg/3mL; Dalian Medium Spectrum Technology Company Limited, China) and a UF-SCX SPE column (200 mg/6 mL; Dalian Medium Spectrum Technology Company Limited, China) were used.

2.4. Analysis conditions

The optimum ion chromatographic conditions were using the Shodex IC YK-421 cation-exchange column for the separation of the analytes, 2.0 mM MSA aqueous solution/ACN (87/13, *v*/*v*) as mobile phase, ultraviolet detection wavelength at 210 nm, column temperature at 40 °C, flow rate 1.0 mL/min, injection volume 20 μL.

The optimum SPE conditions were as follows. The UF-SCX SPE column was used for the enrichment and purification of the targets in water samples. On the SPE column, 400 mL water samples were enriched at a flow rate of 2.0 mL/min. The rinsing solvent was 3 mL 5% methanol aqueous solution. The eluent was 10 mL 0.17 M H_3PO_4-NaH_2PO_4 buffer solution-55% methanol with the flow rate of 2.0 mL/min.

3. Results And Discussion

3.1. Ion chromatography analysis of hydroxyl functionalized imidazolium IL cations

3.1.1. Effect and selection of chromatographic columns

The Baseline WCX and Shodex IC YK-421 two chromatographic columns were used to determine $[HEMIm]^+$and $[HPMIm]^+$ (Fig. 1). $[HEMIm]^+$ and $[HPMIm]^+$ were both retained on the two columns. Because of the difference of stationary phases in the two columns, the retention times and separation of the two analytes were obviously different. The retention times of $[HEMIm]^+$ and $[HPMIm]^+$ on the Baseline WCX column were relatively short, and their chromatographic peaks overlap completely and the separation was not achieved. When the Shodex IC YK-421 column was used, although the retention times were relatively long, $[HEMIm]^+$ and $[HPMIm]^+$ could be completely separated. It was more advantageous to separate $[HEMIm]^+$ and $[HPMIm]^+$ using the Shodex IC YK-421 column.

In order to further explore the possibility of separating $[HEMIm]^+$ and $[HPMIm]^+$ on the Baseline WCX column, the separation of the two analytes under different concentrations of MSA (3.0, 1.0, 0.5, and 0.1 mM) was investigated. The results showed that the retention times of the two analytes were prolonged with the decrease of MSA concentration, but the chromatographic peaks of the two analytes were overlapped completely. The effects of other acids (tartaric acid, oxalic acid, and citric acid) in mobile phase on the separation of $[HEMIm]^+$ and $[HPMIm]^+$ were also investigated on the Baseline WCX column. The results were that the chromatographic peaks of the two analytes were still completely overlapped. These investigations show that the separation of the two cations cannot be effectively improved on the Baseline WCX column. Therefore, the Shodex IC YK-421 column was selected to continue the investigation.

3.1.2. Effect and selection of acids in mobile phase

The Shodex IC YK-421 column was used to determine $[HEMIm]^+$ and $[HPMIm]^+$ with different acids as mobile phases. The experimental results show that both MSA and tartaric acid as mobile phases can completely separate $[HEMIm]^+$ and $[HPMIm]^+$. The retention times of the two cations were shorter when MSA was used. The reason is that the retention times of $[HEMIm]^+$ and $[HPMIm]^+$ are related to the concentration of hydrogen ion in the eluent. The higher the concentration of hydrogen ion is, the stronger the elution ability of mobile phase is. Compared with the same concentration of tartaric acid aqueous solution, because the concentration of hydrogen ion in MSA aqueous solution is higher, the retention

times of $[HEMIm]^+$ and $[HPMIm]^+$ are shorter. Finally, MSA was selected as the composition of mobile phase.

After choosing MSA, the effects of MSA concentrations (1.0, 1.3, 1.5, 1.7, 2.0 and 2.3 mM) on the determination of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. The results show that the retention times of the two analytes decreased with the increase of MSA concentration in the range of investigated concentration. Because the hydrogen ion in mobile phase is one of the elution ions, the concentration of MSA increases, the concentration of hydrogen ion in mobile phase will also increase, the elution ability of mobile phase become stronger, resulting in shorter retention time of each analyte. When the concentration of MSA was 2.0 mM, the retention times of two target cations were relatively short, the detection limits and noise values were the lowest. Considering comprehensively, the concentration of MSA in mobile phase was selected to be 2.0 mM.

3.1.3. Effect and selection of organic solvents in mobile phase

Methanol and ACN are commonly used as organic solvents in ion chromatography (Molíková et al. 2010). 2.0 mM MSA aqueous solution/methanol (95/5, *v*/*v*) and 2.0 mM MSA aqueous solution/ACN (95/5, *v*/*v*) as mobile phase were investigated, respectively. As shown in (Table 1), compared with methanol, when ACN was used, the retention times of $[HEMIm]^+$ and $[HPMIm]^+$ were shorter, the noise values and detection limits were lower. This may be due to the lower viscosity and lower mass transfer resistance of ACN than that of methanol, which is beneficial to improve the column efficiency. Considering the retention times and detection limits of $[HEMIm]^+$ and $[HPMIm]^+$, ACN was selected.

Table 1 The relationship between the organic solvents and the parameters of retention, resolution and detection of $[HEMIm]^+$/$[HPMIm]^+$

Organic solvent	Retention time (min)	Resolution	Baseline noise value (μV)	Limits of detection (mg/L,)
Acetonitrile	14.5/18.8	3.22	48.4	0.13/0.20
Methanol	19.4/28.2	3.53	55.8	0.26/0.33

The effects of volume fraction changes of ACN in mobile phase (5%, 7%, 9%, 11%, 13% and 15%) on the retention of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. According to the relationship between retention factor of analyte and ACN volume fraction(Ruiz-Angel and Berthod 2006), k is the retention factor and φ(ACN) is the ACN concentration, the experimental results as follows: , , the correlation coefficients (r) were 0.9944 and 0.9955, respectively. From the above results, it can be seen that the linear relationship was good, and the retention factor decreases with the increase of ACN concentration. When the volume fraction of ACN was 13%, the retention time was shorter, and the noise values and detection limits were the lowest. Therefore, 13% volume fraction of ACN was selected.

3.1.4. Effect and selection of detection wavelength

In ultraviolet detection, in order to enhance the detection signal, the maximum absorption wavelength of analyte is usually selected as the detection wavelength. The maximum absorption wavelength of imidazolium cations is about 210 nm (Katoh 2007). The influences of wavelengths at 200, 205, 210, 215 and 220 nm on the detection of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated using 2.0 mM MSA aqueous solution/ACN (87/13, *v*/*v*) as mobile phase. When the wavelength was 210 nm, the detection limits of $[HEMIm]^+$ and $[HPMIm]^+$ were the lowest. Therefore, 210 nm was chosen.

3.1.5. Effect and selection of column temperature

The influence of different temperatures (30, 35, 40, 45 and 50 ℃) on the retention of $[HEMIm]^+$ and $[HPMIm]^+$ was further investigated under the previously selected chromatographic conditions. The effect of temperature is usually described by the Van't Hoff curve equation (Yu and Mou 2006), where k is the retention factor, T is the thermodynamic temperature (K), ΔH and ΔS are the change of free enthalpy and the free energy, respectively, R is the molar gas constant, and φ is the ratio of the two phases. The linear regression equation between the $\ln k$ of $[HEMIm]^+$ and the column temperature T is , and the correlation coefficient is 0.9961. The linear regression equation between the $\ln k$ of $[HPMIm]^+$ and the column temperature T is , and the correlation coefficient is 0.9980. It can be seen that both correlation coefficients are good and the slopes are positive, which indicates that the retention was an exothermic process, and retention time of the two cations was shortened with the increase of temperature. Since the retention time of the analytes at 40 ℃ was moderate and the baseline is stable, 40 ℃ was selected.

3.1.6. Verification of interference with common imidazolium IL cations

Common imidazolium cations and hydroxyl functionalized imidazolium cations are structurally similar. In order to verify whether imidazolium cations interfere with the determination of hydroxyl functionalized imidazolium cations, these cations were analyzed and compared under the previously selected chromatographic conditions. (Fig. 2) shows that the retention times of the imidazolium cations were longer and the retention times of hydroxyl functionalized imidazolium cations were shorter, and these cations can be separated from the baseline. Therefore, common imidazolium cations do not interfere with the determination of the target cations.

3.1.7. Quantitative analysis parameters of ion chromatography

Through the above investigations, the optimum chromatographic conditions can be found in the Section 2.4. Under these chromatographic conditions, two target cations $[HEMIm]^+$ and $[HPMIm]^+$ can be completely separated within 14.0 min. The chromatogram is shown in (Fig. 3).

The concentrations of $[HEMIm]^+$ and $[HPMIm]^+$ mixed solutions were diluted to 1.0, 5.0, 10.0, 20.0, 50.0, 80.0 and 100.0 mg/L with ultrapure water, and then were determined under the optimum conditions. The linear regression equation was obtained according to the relationship between peak area (integral) and analyte ion mass concentration (mg/L). Detection limit and quantification limit were calculated according

to and , respectively. Relative standard deviations of peak area and retention time (RSD_s/RSD_t) were obtained by seven repeated measurements of a standard mixture solution of $[HEMIm]^+$ (10.0 mg/L) and $[HPMIm]^+$ (10.0 mg/L). The data of quantitative analysis are listed in (Table 2). The results show that the detection limits are less than 0.20 mg/L and the quantitative limits are less than 0.65 mg/L. Linearity and reproducibility meet the requirements of quantitative analysis.

Table 2 Linear regression equations, limits of detection (LOD)/limits of quantitation (LOQ), linear ranges and relative standard deviations of retention time (RSD_t) and peak area (RSD_s)

Analyte	Linear regression equation	Correlation Coefficient (*r*)	Linear range (mg/L)	LOD/LOQ (mg/L, ,)	RSD_t/RSD_S (%,)
$[HEMIm]^+$		0.9999	1.0 – 100.0	0.13/0.43	0.2/0.2
$[HPMIm]^+$		0.9999	1.0 – 100.0	0.19/0.64	0.2/0.2

3.2. Reversed-phase SPE of hydroxyl functionalized imidazolium IL cations

The selection of adsorbents in SPE is mainly based on the properties of target compounds. The more similar the polarity of target compound is to that of adsorbent, the better the retention is. For the effective extraction of analytes in water samples, two extraction modes were studied in this work, namely reversed-phase SPE mode and ion-exchange SPE mode. The reversed-phase SPE of hydroxyl functionalized imidazolium IL cations are as follows.

3.2.1. Selection of sample volume for the reversed-phase SPE

The UF-C18 reversed-phase SPE column was used for the enrichment and purification of $[HEMIm]^+$ and $[HPMIm]^+$. Firstly, 5 mL methanol was used for activation of the SPE column. The purpose of activation was to remove impurities in the column and create a certain solvent environment. Secondly, 5 mL ultrapure water was used for equilibrium. Then, the penetration volume was investigated. The flow rate was 2 mL/min and the concentration of analytes was 1.0 mg/L. In this investigation, a small amount of $[HEMIm]^+$ and $[HPMIm]^+$ were detected in the effluent after 1.0 mL water sample was uploaded; while $[HEMIm]^+$ and $[HPMIm]^+$ were not detected in the effluent after 0.5 mM sodium decanesulfonate was added in the water sample. The possible reason is that the retention of analytes in the reversed-phase SPE column is mainly affected by the hydrophobic and hydrophilic force, which increases with the increase of hydrophobicity and decreases with the increase of hydrophilicity. $[HEMIm]^+$ and $[HPMIm]^+$ are hydrophilic compounds, which are difficult to retain on the reversed-phase SPE column, so the reversed-phase ion-pair SPE method is chosen. It is generally understood that in the ion-pair model, the analytes and the ion-pair reagents form neutral ion-pairs, which are then retained on the reversed-phase SPE column. Ion-pair reagents with longer carbon chain have higher hydrophobicity, which enhance the

retention of measured ions on reversed-phase SPE column (Stepnowski and Nichthauser 2008). Therefore, the retention of analyte in the reversed-phase SPE column can be enhanced by adding ion-pair reagent, and the longer the carbon chain of ion-pair reagent is, the stronger the retention of analyte is. Sodium decanesulfonate with a concentration of 0.5 mM was selected as the ion-pair reagent in this experiment.

After selecting the ion-pair SPE mode, then, the sample volume needs to be chosen. In SPE, the penetration volume is equivalent to the maximum allowable sample volume of the target compound through the SPE column without obvious loss. The larger the penetration volume of SPE column is, the larger the sample volume can be treated. In order to investigate the penetration volume of SPE and select the optimum sampling volume, the effects of sample volumes of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 mL on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. The results showed that $[HEMIm]^+$ could be detected in effluent when the sample volume was 55 mL. This shows that the sample loading has exceeded the column capacity at this time. Therefore, a sample volume of 50 mL was selected.

3.2.2. Selection of rinsing solvent for the reversed-phase SPE

In order to reduce the interference of impurities on target compounds, the impurities should be removed as far as possible without affecting the recovery of target compounds (Fan et al. 2018a). The effects of rinsing solvents on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated by using 3 mL water, 3 mL 5% methanol and 3 mL 5% ACN, respectively. The results showed that the target analytes were eluted when the rinsing solvent was 5% methanol or 5% ACN. This affected the enrichment of the targets by the SPE column. When the rinsing solvent was water, no target cations were detected in the effluent. Therefore, water is chosen as rinsing solvent.

3.2.3. Selection of eluent and elution volume for the reversed-phase SPE

In SPE, the eluent should be selected according to the relevant parameters of the target compounds, such as the solubility and structure of the target compounds. Solubility is one of the important factors for selecting eluent. In reversed-phase SPE, the organic solvent with high solubility to the target substance is generally preferred as eluent. According to the structure and functional group of the target compounds and the principle of similar miscibility, the eluent with similar polarity is selected. Owing to the strong polarity of $[HEMIm]^+$ and $[HPMIm]^+$, and the greater polarity of methanol than ACN, methanol was chosen as the organic phase in eluent. The effects of 70%, 80% and 90% methanol aqueous solutions as eluent on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were compared. The results show that the recovery was the highest when the volume fraction of methanol was 90%. The reason may be that the elution capacity of eluent increases with the increase of methanol ratio in the elution solutions. Therefore, the volume fraction of methanol in the elution solution is 90%.

Next, the volume of eluent was selected. More eluents will elute the matrix together and affect the analysis of the targets. So, the eluent should be used as little as possible. The effects of elution volumes

of 1 mL and 2 mL on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. The results showed that the recoveries were higher when the elution volume was 2 mL. Therefore, the elution volume 2 mL was selected.

3.3. Ion-exchange SPE of hydroxyl functionalized imidazolium IL cations

3.3.1. Selection of sample volume for the ion-exchange SPE

The UF-SCX ion-exchange SPE column was used for enrichment and purification. Firstly, 5 mL methanol was used for activation, then ultrapure water of the same volume was used for equilibrium. Secondly, the penetration volume was investigated by sampling. The flow rate of sampling was 2 mL/min, and the concentration of analytes was 0.05 mg/L. The effects of sample volume of 10, 50, 100, 200, 300, 400, 500, and 1000 mL on SPE of two target cations $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. From the adsorption of target cations on UF-SCX SPE column, no penetration was observed. The results show that UF-SCX SPE column has good adsorption properties for $[HEMIm]^+$ and $[HPMIm]^+$. When the sample volume was 4000 mL, a small amount of $[HEMIm]^+$ and $[HPMIm]^+$ targets were detected in the effluent, indicating that the sample volume had exceeded the capacity of the ion-exchange SPE column at this time. When choosing the sample volume, it is also necessary to consider the adsorption of interfering substances in the water samples on the extraction column. In order to achieve good sampling and elution effect, the sample volume 400 mL was selected.

3.3.2. Selection of rinsing solvent for the ion-exchange SPE

The effects of rinsing solvents on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated using 5 mL water, 5 mL 5% methanol and 5 mL 5% ACN, respectively. The results showed that no target cations were detected in the effluent of the three rinsing solvents, which indicated that any of the three rinsing solvents could be used. Considering that the interference impurities in the real samples may be more complex, in order to remove the interference impurities as much as possible, the washing effect of the mixed solution of water and organic solvent will be better. At the same time, compared with ACN, methanol has stronger polarity to wash impurities more effectively. Therefore, 5% methanol is chosen as the rinsing solvent.

3.3.3. Selection of eluent and elution volume for the ion-exchange SPE

In ion-exchange SPE, the eluent must have the ability to resolve the ion-exchange force and non-polar force, and the target should have good solubility in eluent. Because of the low pK_a of the benzenesulfonic acid functional group in the UF-SCX SPE column, it is impossible to neutralize the benzenesulfonic acid by adjusting the pH to release the target compounds. The effects of 0.10, 0.13, 0.15, 0.17 and 0.20 M H_3PO_4-NaH_2PO_4 buffer solution-55% methanol as eluent on SPE of two target cations were investigated. The results showed that the higher the concentration of buffer solution was, the stronger the elution strength was and the better the elution effect was. When the concentration of H_3PO_4-NaH_2PO_4 was 0.20 M, the recovery was the highest, but the separation degrees of $[HEMIm]^+$ and $[HPMIm]^+$ were small and

the peak shapes were poor (Fig. 4). Considering comprehensively, 0.17 M H_3PO_4-NaH_2PO_4 buffer solution was selected.

The effects of 0.17 M H_3PO_4-NaH_2PO_4-40, 45, 50, 55 and 60% methanol as eluent on the elution of $[HEMIm]^+$ and $[HPMIm]^+$ were also investigated. (Table 3) shows that with the increase of methanol concentration, the recovery increases and the elution effect is improved. The possible reason is that methanol has a high enough polarity to weaken the force between the target and the SPE column. When methanol concentration was 60%, partial crystallization occurred in buffer solution. The reason is that phosphate is insoluble in methanol. When a large amount of methanol was added, the buffer property of the solution was affected and phosphate precipitates. Therefore, 0.17 M H_3PO_4-NaH_2PO_4-55% methanol was selected.

Table 3 The recoveries of the target compounds at different content of methanol using 0.17 M H_3PO_4-NaH_2PO_4-methanol as eluent

Content of methanol (%)	Recovery (%)	
	$[HEMIm]^+$	$[HPMIm]^+$
40	76.3	82.1
45	80.4	86.8
50	85.5	90.0
55	91.3	96.1
60	92.8	97.5

After selecting the eluent, the effects of elution volume of 8 mL and 10 mL on SPE of $[HEMIm]^+$ and $[HPMIm]^+$ were investigated. The results showed that when the elution volume was 8 mL, the enrichment factor was 50 times, and the recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ were 81.5% and 88.5% (), respectively. When the elution volume was 10 mL, the enrichment factor was 40 times, and the recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ were 91.3% and 96.1% (), respectively. Although the elution volume of 8 mL had a higher enrichment factor, the recovery was relatively low. In order to obtain a higher recovery, the elution volume of 10 mL was selected.

3.4. Analysis of environmental water samples

Water samples from Songhua River and Hulan River were collected for the analysis. At room temperature, the two water samples were stationary for 48 h, centrifuged and filtered by 0.22 μm filter membrane. River

water samples were treated by two SPE methods, and then filtered by 0.22 μm filter membrane for ion chromatography analysis.

When the reversed-phase UF-C18 SPE column was used, it was found that the recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ in both water samples were lower than 27.5%. The possible reason is that the matrix in environmental water samples is usually complex. In SPE, the adsorbent of reversed-phase SPE not only adsorbed the target compounds, but also adsorbed some impurities. Most of the target compounds can't be adsorbed during the sample loading process, so the recoveries were very low. This indicates that the reversed-phase UF-C18 SPE column can't be applied to the analysis of the environmental water samples.

The UF-SCX ion-exchange SPE column was selected and the recoveries of the standard addition method were tested. The chromatograms of sample analysis are shown in (Fig. 5) and analysis results are shown in (Table 4) (). The recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ were between 82.5% and 96.0%. The detection limits of two kinds of water samples were calculated by 3 times signal-to-noise ratio and 40 times enrichment ratio. The detection limits were less than 0.006 mg/L and RSD was less than 2.5%. The results show that the UF-SCX ion-exchange SPE column can be applied to the analysis of environmental water samples with good extraction effect and recovery. The possible reason is that UF-SCX SPE column can only adsorb cation matrix. And the adsorption capacity of UF-SCX SPE column is very strong when the target cation is adsorbed. Some cation matrix with weak adsorption capacity will be washed by rinsing solvent, which will not affect the determination of targets.

Table 4 Contents and spiked recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ in environmental water samples

Samples	Ion	Sample analysis	Standard added analysis			
		Found (mg/L)	Added (μg/L)	Recovery (%)	Intra-assay RSD (%)	Inter-assay RSD (%)
Songhua River	$[HEMIm]^+$	0.0	20.0	85.0	1.7	2.0
		0.0	50.0	86.0	1.3	1.8
		0.0	80.0	87.5	1.2	1.5
	$[HPMIm]^+$	0.0	20.0	95.0	1.3	2.4
		0.0	50.0	96.0	1.6	1.8
		0.0	80.0	95.0	0.8	1.9
Hulan River	$[HEMIm]^+$	0.0	20.0	85.0	1.6	2.2
		0.0	50.0	84.0	1.8	1.9
		0.0	80.0	82.5	1.5	1.9
	$[HPMIm]^+$	0.0	20.0	90.0	1.7	2.1
		0.0	50.0	92.0	1.7	2.4
		0.0	80.0	91.3	1.4	1.2

Conclusion

A new method for the determination of hydroxyl functionalized IL cations in environmental water samples by ion chromatography combined with SPE was developed. Under the conditions of ion chromatography using a cation-exchange column with carboxylic acid functional group, MSA aqueous solution/ACN mobile phase and ultraviolet detection wavelength 210 nm, $[HEMIm]^+$and $[HPMIm]^+$can be separated and detected within 14.0 min, and the detection limits are less than 0.20 mg/L and the quantitative limits are less than 0.65 mg/L. Ion-exchange SPE is better than reversed-phase SPE for the extraction and enrichment of $[HEMIm]^+$ and $[HPMIm]^+$. A strong acidic cation-exchange SPE column and H_3PO_4-NaH_2PO_4/methanol eluent was used to enrich and purify hydroxyl $[HEMIm]^+$ and $[HPMIm]^+$ in water samples. The recoveries of $[HEMIm]^+$ and $[HPMIm]^+$ in real environmental water samples were between 82.5% and 96.0%. The detection limits were less than 0.01 mg/L and RSD were less than 2.5%. This method is accurate, reliable and simple. Compared with previous studies, this method has lower detection limit, higher anti-interference performance and the experiment without ion-pair reagent is more convenient. It is suitable for monitoring the hydroxyl functionalized imidazolium IL cations in environmental water, and provides a reference for environmental risk assessment of hydroxyl functionalized ILs.

Declarations

Ethical approval and consent to participate

Not applicable

Consent to publish

Not applicable

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors have declared no conflict of interest.

Funding

This work was supported by the Scientific Research Projects on Fundamental Research Expenses of Heilongjiang Provincial Universities (No. 2020-KYYWF-0361).

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by all authors. The first draft of the manuscript was written by [Zhenjie Yin] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript. [Hong Yu] helped with the topic and guide the experiment. [Yajie Ma] provided the funds.

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Figures

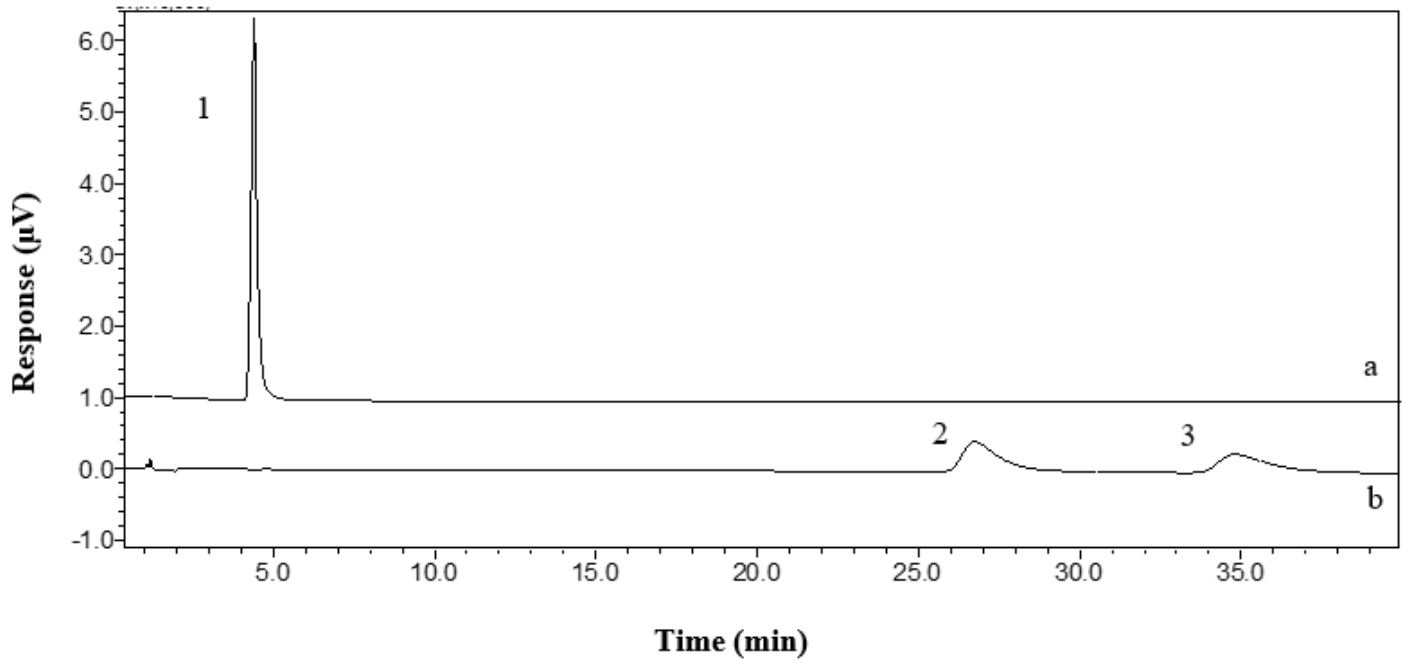

Figure 1

Chromatograms obtained with different cation-exchange columns. a, Baseline WCX column; b, Shodex IC YK-421 column. Chromatographic conditions: mobile phase, 1.0 mM MSA aqueous solution/ACN (95/5, v/v); flow rate, 1.0 mL/min; column temperature, 35 °C; ultraviolet detection, 210 nm; inject volumn, 20 μL. Peaks: 1, [HEMIm]+ and [HPMIm]+; 2, [HEMIm]+; 3, [HPMIm]+. The concentration of each cation is 10.0 mg/L.

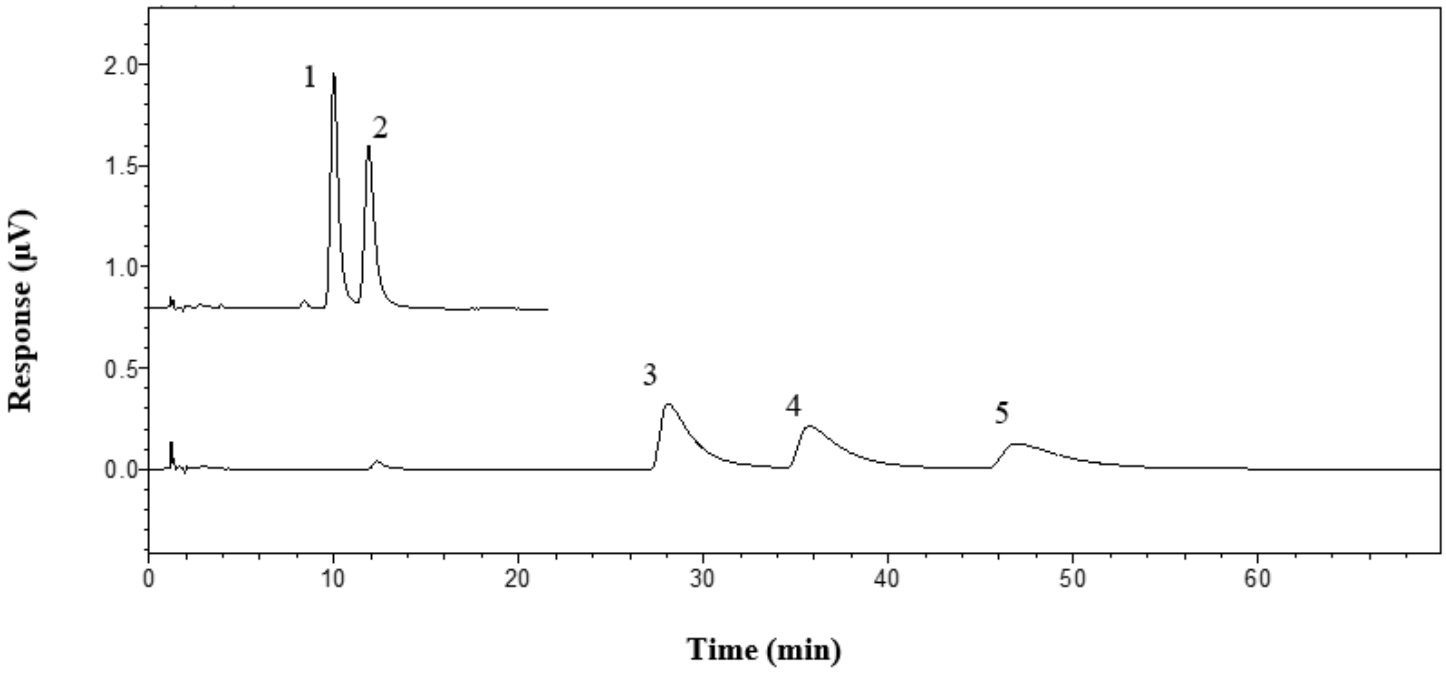

Figure 2

Comparative chromatograms of hydroxyl functionalized imidazolium cations and imidazolium cations. Chromatographic conditions are listed in the Section 2.4. Peaks: 1, [HEMIm]+; 2, [HPMIm]+; 3, [EMIm]+; 4, [PMIm]+; 5, [BMIm]+. The concentration of each cation is 10.0 mg/L.

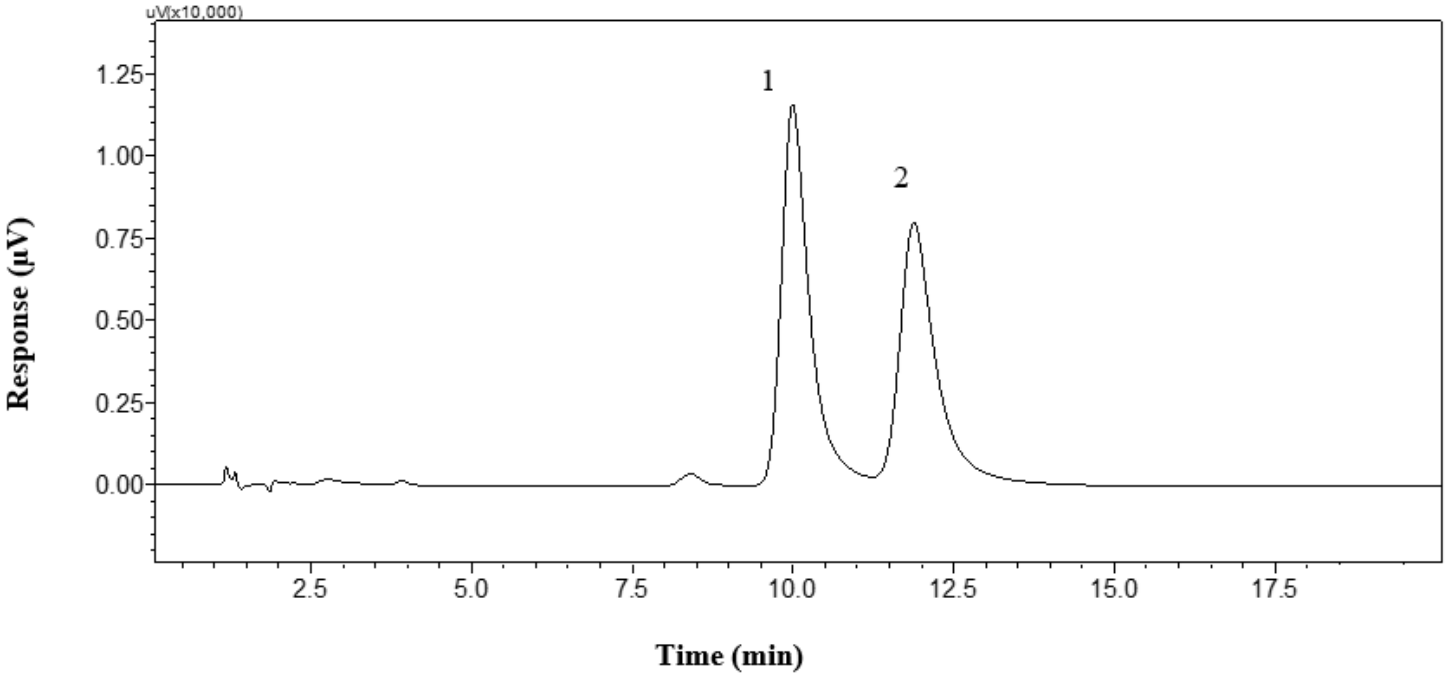

Figure 3

Chromatogram of a mixed standard solution of [HEMIm]+and [HPMIm]+. Chromatographic conditions are listed in the Section 2.4. Peaks: 1, [HEMIm]+; 2, [HPMIm]+. The concentration of each cation is 10.0 mg/L.

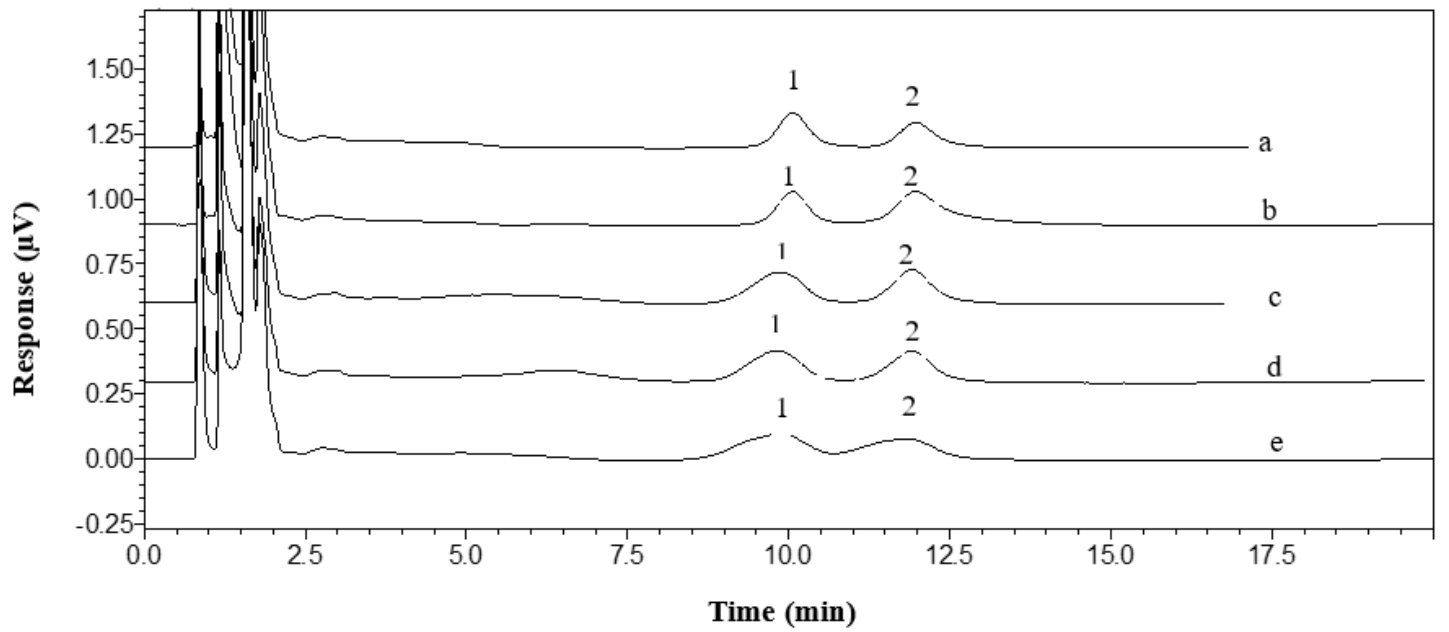

Figure 4

Chromatograms of the effluent obtained with different eluent. a, 0.10 M H3PO4-NaH2PO4-55% methanol; b, 0.13 M H3PO4-NaH2PO4-55% methanol; c, 0.15 M H3PO4-NaH2PO4-55% methanol; d, 0.17 M H3PO4-NaH2PO4-55% methanol; e, 0.20 M H3PO4-NaH2PO4-55% methanol. Chromatographic conditions are listed in the Section 2.4. Peaks: 1, [HEMIm]+; 2, [HPMIm]+.

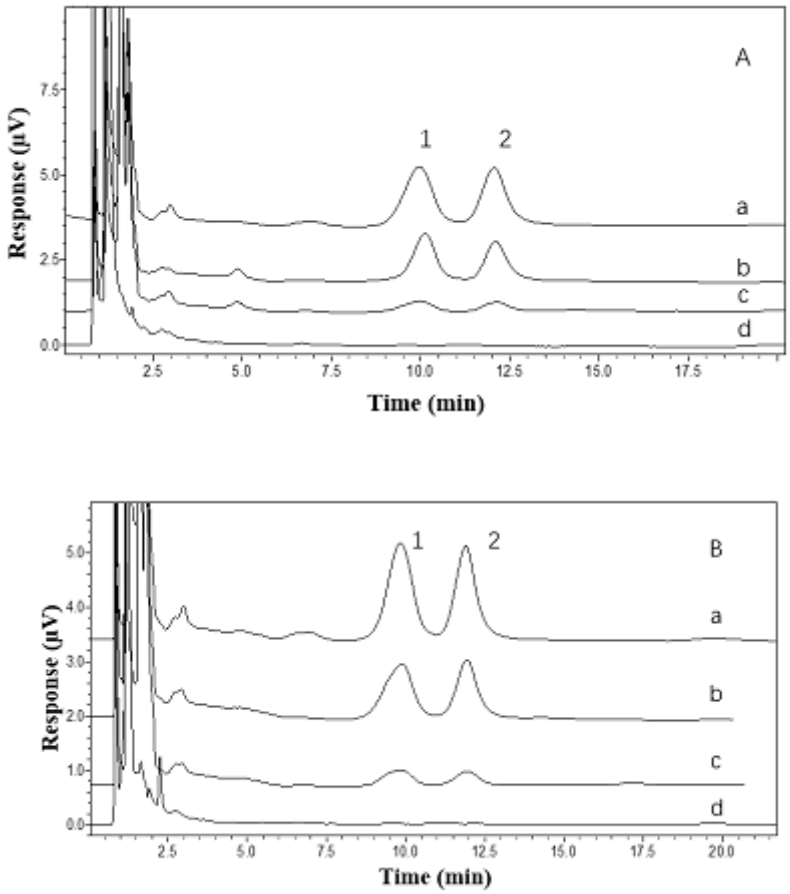

Figure 5

Chromatograms of environmental water samples. A, Songhua River; B, Hulan River. Spiked concentration: a, 80.0 μg/L; b, 50.0 μg/L; c, 20.0 μg/L; d, 0.0 μg/L; Chromatographic conditions are listed in the Section 2.4. Peaks: 1, [HEMIm]+; 2, [HPMIm]+.