Combination of carbon nanotubes modified filters with microextraction by packed sorbent for the NACE analysis of trace levels of ionic liquids in river water samples

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ABSTRACT

This paper reports for the first time the use of microextraction by packed sorbents in combination with Capillary electrophoresis (CE) for carry out the preconcentration and determination of three characteristics cations of ionic liquids in river water. Before analysis a carbon nanotubes modified filter was used to remove potential organic interferences from the samples. The system was automated by connecting the syringe–microextraction by packed sorbents (MEPS) assembly to a syringe pump and interfacing it to a computer. After preconcentration, analytes were determined by NACE. The limits of quantification of analytes were of 0.02 mg L^{-1} from only 5 mL of sample with an RSD of less than 7%. The values of recovery range between 85 and 97%.

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1. Introduction

Ionic liquids (ILs) are molten salts formed of organic cations and inorganic or organic anions, some of which can be liquid at room temperature. As a rule, any salt with melting point below 100 °C is considered to be IL [1]. Although ILs exist since 1914, they were not exploited at large scale until 2000. The main advantage of ionic liquids is that they are a new class of solvents by their non-molecular nature [2]. Furthermore, ILs have interesting physical and chemical properties like high electrical conductivity, tunable solubility and miscibility, high thermal stability and a wide range of viscosities [3–8].

Ionic liquids have attached more and more attention over the last few years. This is due to the fact that they have been promoted as "green" solvents (although more recent data demonstrate that there are issues with this claim). Due to the increase of the use of ionic liquids, in the future they can be emergent pollutants, for this reason the study of ILs becomes necessary in the environment. If we attend to the ionic liquids properties, such no measurable vapor pressure and easy recycling, we can consider them as green

solvents, therefore their step to the environment is minor that the common organic solvents. However, if we attend to his definition as chemical compound and therefore not native, we cannot to consider them like "green"; since their accidental discharge into the environment is considered like pollution. In addition, the majority of the most useful ionic liquids in chemistry, they have in his structure a cation based on the imidazolium ion, which is an aromatic compound, and therefore very pollutant.

In recent years, several emerging application areas have been described in the literature. These show IL as novel media for electrochemistry, biological studies, as medium for enzyme catalysis and solvents for sample preparation (extraction process) [9,10]. CE has been proved to be a reliable, simple, and with excellent analytical performance parameters in separations of cations such as alkyl and aryl imidazolium IL cations [11]. Stepnowski and Mrozik [12] investigated the chromatographic behavior of eight different ILs with a strong cation exchanger stationary phase.

Stepnowski reports the first published routine SPE method for pre-concentrating room-temperature ionic liquids in environmental water samples [13]. The method is simple and selective and is thought to be applicable to imidazolium ionic liquids. The extraction and isolation of room temperature ionic liquid (RTIL) residues in a number of plants, seeds and soils has been also described [14].

We propose a miniaturized method for pre-concentrating ionic liquids which can be applied to imidazolium and pyridinium ionic liquids. Consequently, the aim of this work is carry out the

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preconcentration of ionic liquids in river water by using MEPS (microextraction by packed sorbents system) and their determination by CE analysis. To best of our knowledge, the use of MEPS to preconcentrate ionic liquids in river water has not been previously reported in the literature.

2. Materials and methods

2.1. Reagents and standards

The analytes studied were HMIMPF$_6$ (1-hexyl 3-methylimidazolium hexafluorophosphate), HMIMIm (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), BMIMPF$_6$ (1-butyl 3-methylimidazolium hexafluorophosphate), BMIMBF$_4$ (1-butyl-3-methylimidazolium tetrafluoroborate) and EMPIm (1-ethyl-3-methyl pyridinium bis(trifluoromethylsulfonyl)imide) >99% were purchased from MERCK (Darmstadt, Germany). The characteristic cation structures of the ionic liquids (target analytes) are shown in Fig. 1. A mixture of five ILs and individual standard stock solutions containing a 1000 mg L^{-1} concentration of each compound was prepared by dissolution in methanol. Working solutions of the ILs were made by using purified water (18 MΩ) from a Milli-Q water purified system (Millipore, Bedford, MA, USA).

Ammonium acetate, formic acid (Sigma–Aldrich) and HPLC-grade methanol (Panreac Química, S.A., Barcelona, Spain) were used to prepare the BGE and eluent. Potassium hydroxide (Merck, Darmstadt, Germany) was used for capillary conditioning.

Multi-walled carbon nanotubes (5–20 nm outer diameter and length 1–10 μm) from Bayer and Triton X-100 (Fluka) were used to prepare the carbon nanotubes modified filters for the sample clean up stage.

2.2. Instrumentation

Capillary electrophoresis was performed on a Beckman Coulter (Palo Alto, CA, USA) P/ACE 5500 instrument equipped with an on-column diode array detector (DAD). The instrumental setup was controlled, and data acquired and processed using a 32 Karat software.

2.3. Instrumental operation conditions

The uncoated fused-silica capillaries used (50 mm I.D., 375 mm O.D.) were supplied by Beckman (Fullerton, CA). Each new capillary was initially conditioned with 1 M HCl (5 min), 0.1 mol L^{-1} NaOH (10 min) and Milli-Q water (5 min), in this sequence. Each day, the capillary in use was conditioned with 0.05 mol L^{-1} potassium hydroxide (5 min), methanol (5 min) and running buffer (10 min). Between runs, the capillary was rinsed with potassium hydroxide (5 min), methanol (5 min) and BGE (5 min). All conditioning steps were performed at 20 psi.

The optimum BGE was found to consist of 100 mmol L^{-1} ammonium acetate in methanol. The capillary cartridge was kept at 20 °C. Samples were kept at ambient temperature in the autosampler and injected in the hydrodynamic mode at 0.5 psi for 15 s. Tests were carried out in the positive polarity mode, using a detection wavelength of 210 nm, a constant voltage of 10 kV and an over imposed pressure of 50 psi in both vials in order to avoid the current interruption due to the evaporation of the organic solvent during analysis due to Joule effect. The current was around 20 μA in all analysis.

2.4. Analytical procedure

Automatic setup was performed with a microextraction by packed sorbents system (MEPS) (SGE Analytical Science); each cartridge contain ~4 mg of silica, the cartridge volume is 8 μL, the particle size is 45 μm and a pore size of 60 Å. The system was automated by connecting the syringe–MEPS assembly to a syringe pump (Cavro) that was controlled via a computer running the software Sagittarius 3.0, which was obtained from the working group on Chemical Analysis and Vibrational Spectroscopy of the Vienna University of Technology, Austria. 5 mL of sample was passed through the MEPS in 8 min. Finally, analyte elution was performed by passing through the MEPS a volume of 250 μL methanol containing 5 mmol L^{-1} ammonium acetate and a 0.2% formic acid. Elution flow rate was 0.25 mL min^{-1}.

The MEPS system was conditioned with methanol first and then water prior to first use. In addition, it was washed with sodium hydroxide 0.1 mol L^{-1} and water after each run in order to regenerate the sorbents and to improve the precision.

The sample treatment was carried out following the above described procedure. To improve the preconcentration and to prevent possible matrix effects, a previous clean up stage was carried out by filtering the river water before carrying out the preconcentration process. River water samples come from different effluents of river Guadalquivir. For this purpose the use of a carbon nanotubes modified filters was recommended. Modified filters were obtained from commercially available nylon filters (25 mm, 0.45 μm). For modification, 5 mL of a solution – containing 1.34 mg mL^{-1} MWC-NTs dispersed with 0.5% Triton X-100 and ultrasonication (50 W, 60 Hz, 20 min) – were passed through the filters by vacuum suction. Finally, the excess of surfactant was removed from the filters with 10 mL methanol and 5 mL water with the aim of removing the surfactant.

3. Results and discussion

The study of variables affecting the preconcentration and determination of analytes as well as the analytical features of the analysis of spiked samples are discussed in this section.

3.1. Electrophoretic conditions

Ionic liquids have a high affinity to be adsorbed on the capillary wall surface. In relation with this fact several publications exist, where ionic liquids are used as modifiers of the wall of the capillary to improve the electrophoretic separation of some analytes [15,16]. For this reason we selected a silica MEPS to carry out the pre-concentration of ionic liquids. Moreover NACE analysis was chosen in order to compatibilize the pre-concentration step with electrophoretic separation. In order to avoid problems due to analyte adsorption, methanol was selected as a media to carry out the CE separation. Using methanol as a solvent, several acid and basic buffers (citric acid and ammonium acetate) were investigated to check the non-aqueous electrophoretic separation of the analytes. We selected these buffers in order to obtain an appropriate electroosmotic flow and appropriate electrophoretic resolution. When citric acid was used as BGE, in general, a poor sensitivity and resolution was observed. Controversy, when the BGE was based in ammonium acetate at basic pH the sensitivity was satisfactory. It became crucial to determine the influence of the BGE's conditions like type of dissolvent, ionic strength and pH on ionic liquid migration times. The BGE composition is known to affect CE analyses, so we studied the effect of the addition of acetonitrile and water to the BGE. Based on the results, a 100% volume of methanol provided the best CE system in terms of CE-current stability and sensitivity.
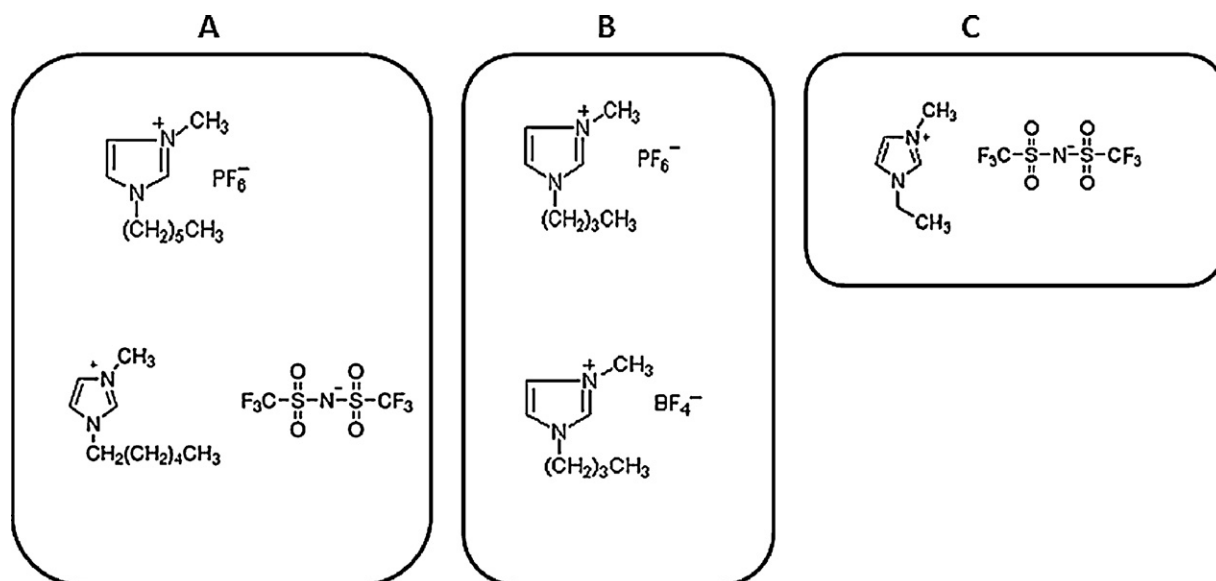
Fig. 1. Structures of 5 ionic liquids. (A) Ionic liquids with HMIM cations, (B) ionic liquids with BMIM cations and (C) ionic liquid with EMP cation.

The effect of the concentration of ammonium acetate was studied in the range from 50 to 150 mmol L^{-1}. As the concentration of the buffer increased from 50 to 100 mmol L^{-1}, the resolution of separated peaks of the analyzed compounds increased, so, considering these results, the concentration of 100 mmol L^{-1} was finally recommended. In addition, we studied the effect of the pH on peak shape and migration times of analytes. pH$_a$ was studied in the range 6.5–9.0. The best resolution was obtained at pH$_a$ 7.7. Therefore such value was chosen as the optimal one for separating the mixture of ionic liquids under study.

The dependence of the migration velocities of the analytes on the applied electrical field strength was also examined. As expected, the migration time decreased with increasing separation voltage. Owing to the Joule heat generation effect in the BGE (100% methanol), which is a function of the applied field strength, molar conductivity of electrolyte and its concentration, the highest applied voltage which provide an acceptable current (22 μA) was 10 kV.

In order to improve sensitivity, volume sample injection was also studied. The compounds were hydrodynamically introduced into the capillary for 5–15 s at 0.5 psi. Working in the recommended CE conditions, it was possible to introduce 15 s of sample without lose of resolution or peak symmetry. Fig. 2 presents an
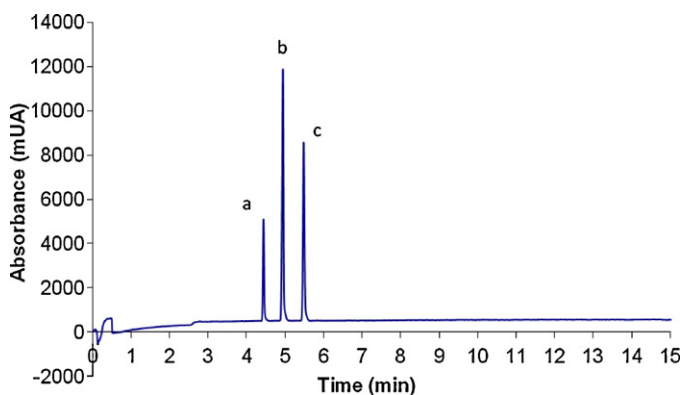

Fig. 2. Electropherogram of the standard mixture of ionic liquids obtained under selected optimum conditions. Running BGE, 100 mmol L^{-1} ammonium acetate buffer, pH$_a$ 7.7; temperature, 20 °C; separation voltage, 10 kV; injection, 15 s. (a) EMP$^+$, (b) BMIM$^+$, (c) HMIM$^+$.

electropherogram of the mixture of 3 ionic liquid cations under optimized conditions. In the electropherogram we only observe three picks corresponding to three cations studied, since we selected 2 ILs with the cation BMIM$^+$, two with HMIM$^+$ and one with EMP$^+$. From the reported results it must be conclude that anions do not affect the CE separation of the cations even in the case of the most insoluble salts.

3.2. IL preconcentration with MEPS

The variables studied in the MEPS preconcentration step included type and volume of eluent, flow rate of preconcentration and volume of sample. These variables were evaluated by using an aqueous standard solution containing the five ionic liquids at a final concentration of 5 mg L^{-1}.

Two different organic solvents were evaluated as eluent, namely: methanol and acetonitrile. These eluents were selected on the base of the solubility of ionic liquids and in order to avoid the interaction between the ionic liquids and the silanol groups of the stationary phase. In this way, it is important to remark that preconcentration was higher than C$_{18}$ when using silica as sorbent. Elution yield was better with methanol than acetonitrile. However, it was not quantitative. In order to improve the elution the effect to add a salt such as ammonium acetate in the methanol as eluent was tested. The salt concentrations were evaluated within the interval 0–15 mmol L^{-1}. In general, elution yield increases when increase the concentration of the salt. However, higher concentration of salt in the sample results in non-symmetrical peaks in the CE separation (Fig. 3). Based on the results a concentration of 5 mmol L^{-1} was fixed as the optimum concentration, and the effect of adding an acid such as formic acid which has a low effect on the ionic strength of the system was studied. The effect of formic acid was evaluated in the range from 0 to 1% (v/v). Finally, 0.2% formic acid was recommended to ensure quantitative elution of the analytes and to assure the analyses by CE. Considering these studies, we selected 5 mmol L^{-1} AcNH$_4$ and 0.2% formic acid in methanol as eluent. The volume of eluent was studied in the interval 0.1–0.5 mL and it was concluded that quantitative elution can be carried out in only 250 μL. The sample volume was optimized within the interval 1–10 mL of aqueous standards containing in all cases 5 mg L^{-1} of each ionic liquid. It was observed that volumes higher than 5 mL produced a decrease in the peak areas, and therefore, it was fixed as the breakthrough
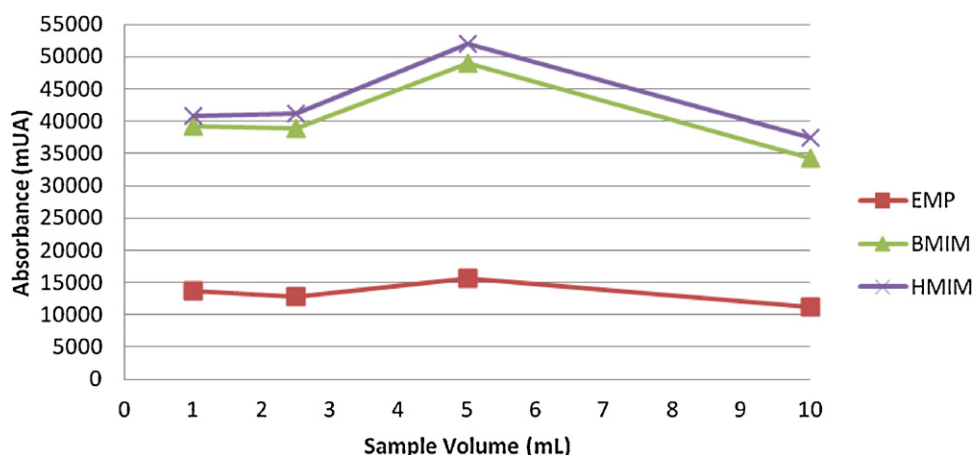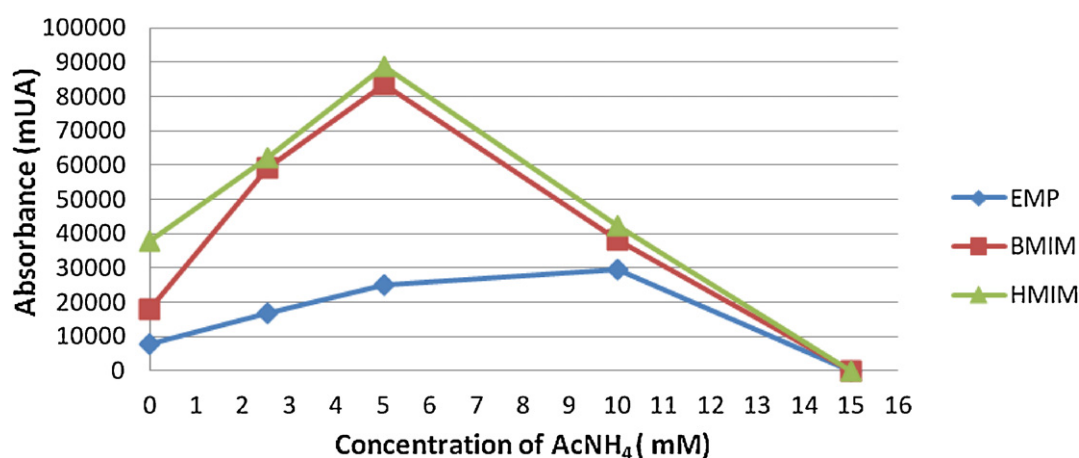
Fig. 3. Optimization of the sample volume.

Fig. 4. Effect of the concentration of ammonium acetate in the methanol as eluent.

Table 1
Figures of merit of the analytes following the recommended procedure.

Analyte	Slope $\pm S$	$S_{y/x}$	R^2	LOQ ($\mu g\,L^{-1}$)	RSD (%)
EMP$^+$	$38{,}517 \pm 1887$	571	0.9905	20	3.5
BMIM$^+$	$32{,}051 \pm 1909$	1727	0.986	30	2.0
HMIM$^+$	$35{,}323 \pm 1128$	828	0.997	25	3.8

volume (Fig. 4). We also examined the influence of the flow rate of sample which was studied over the range 5–1000 $\mu L\,s^{-1}$; based on the results, the best sensitivity was achieved with 100 $\mu L\,s^{-1}$.

As it has been indicated, ILs were preconcentrated on MEPS of silica. MEPS containing C$_{18}$ were not efficient to preconcentrate the ILs. ILs present a high tendency to interact with carbon nanotubes, therefore the use of carbon nanotubes modified filters to preconcentrate the ILs was also tested. Using the carbon nanotubes provided by Bayer, it was observed that ILs were not retained in the filter. Contrary, other organic compounds were preconcentrated as it is well described in the literature [17,18]. Therefore, the use of modified filters was proposed to remove potential interference from the matrix before preconcentration. It must be point out that microextraction techniques, such as MEPS, are limited for the rapid saturation of the sorbents. The effect of the filters to remove organic compounds in part was observed in terms of a higher stability of the

Table 2
Precision and recovery values of the analysis of spiked samples. Samples 1–5 means that they come from different effluents of river Guadalquivir.

Samples	Analyte	Added concentration ($\mu g\,L^{-1}$)	Found concentration ($\mu g\,L^{-1}$)	Recovery (%)	RSD (%)
1	EMP$^+$	40	35	88	5.3
2	BMIM$^+$	54	42–48	85–88	7
3	BMIM$^+$	320	305–310	95–97	4
4	HMIM$^+$	320	300–304	94–95	4.5
	EMP$^+$	110	99–102	90–92	–
5	BMIM$^+$	350	330–340	94–97	–
	HMIM$^+$	280	250–270	89–96	–

background line of the electropherogram of real samples. Syringe and support of the filters was of polyethylene in order to avoid the non-desired adsorption of the analytes.

3.3. Analytical figures of merit

Table 1 shows the analytical figures of merit of the proposed method. The studies were made for individual cations and a mixture of the three cations. No effect of the presence of anions was observed. The RSD values for migration times were under 2% in method. The RSD values for peak areas were under 7% in method and samples. The values of recovery range between 85 and 97% (see Table 2).

4. Concluding remarks

The usefulness of silica-MEPS to preconcentrate ionic liquids has been demonstrated. In addition it has been proposed the use of a carbon nanotubes modified filter to remove potential organic interference from the sample. The method, which is rapid and simple can be used to monitor the presence of ILs in environmental water samples as well as to perform environmental and toxicological studies in order to establish the real effect of IL on environment.

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