

# Ionic Liquid as Novel Solvent for Extraction and Separation in Analytical Chemistry

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## 1. Introduction

Direct analysis of samples, regardless their origin, is desirable although for the majority of cases unfeasible on account of the complexity of the sample matrix, inadequate concentration of the target analytes, or even incompatibility with the detector. In these cases, a sample pretreatment step is required for interference removal and analytes separation/preconcentration. Despite valuable advances developed in separation science, the traditional solvent extraction is widely used for samples preparation. Main drawback of the solvent extraction is the requirement of large amounts of high-purity solvents that are expensive and toxic and result in the production of hazardous waste. Therefore, the search for new solvent is a key trend in solvent extraction evolution. In this sense, ionic liquid, which is ionic media resulting from the combination of organic cations and various anions, has attracted much attention taking into account their special features like: low-vapor pressure, high viscosity, dual natural polarity, good thermal stability and a wide range of miscibility with water and other organic solvents, hence many environmental and safety problems associated with organic solvents are avoided. As a result of their unique chemical and physical properties, the ionic liquid has aroused increasing interest for their promising role as alternative medium for classical solvent extraction [1-7] and organic synthesis [8-10]. Recently, ionic liquids were rapidly developed as environment-friendly acceptor phase for various microextraction to sample preparation in analytical chemistry such as liquid phase microextraction, single drop liquid phase microextraction, solid phase microextraction, dispersive liquid phase microextraction and cold induced aggregation microextraction. The microextraction with ionic liquid often exhibited better extraction efficiency and enrichment factor than that with conventional solvent extractions. Among the microextractions, dispersive liquid phase microextraction is very rapid and effective. Since the ionic liquid is dispersed completely into aqueous phase and the analytes will more easily migrate into the ionic liquid phase because of the much large contact area, the procedure for dispersive liquid phase microextraction may be complete within several minutes. In recent years, the ionic liquid extraction coupled with different analytical technology has widely been applied to determination of ultra trace analytes in water or other samples such as high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) for organic compounds, and flame atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (ETAAS) for metal ions. In general, the extractions with

ionic liquid have increasingly become the most important samples preparation technologies in analytical chemistry.

## 2. Application of ionic liquids as medium for classical solvent extraction

### 2.1 Metal ion extraction and its application

For metal ion extraction, one needs to find the right combination of ionic liquid and ligand to obtain similar behavior as in organic solvents or one needs to use the differences from organic solvents for achieving more advantageous separations. Although the metal ion extraction in the ionic liquid/aqueous two phase system often indicated high efficiency and selectivity that excelled most of organic solvents, the metal ion partitioning always rely on the species of the ionic liquid, metal ion and ligand seriously. For examples, Bartsch group reported on the influence of structural variations in room temperature ionic liquid on the selectivity and efficiency of competitive alkali metal salt extraction by crown ethers [11]. They showed that extraction efficiency generally diminished as the length of the 1alkyl group on the ionic liquid was increased. It was demonstrated that metal ion affinity for the hydrophobic phase necessitates the presence of an extractant [12]. Professor Rogers has investigated Cyax-923 as an ligand for actinide ions in liquid/liquid separation using the hydrophobic ionic liquid  $[C_{10}mim][Tf_2N]$  as the extracting phase, a mixture of tri-alkyl-phosphine oxides of varying mixture of tri-alkyl-phosphine oxides of varying chain lengths (hexyl- and octyl-) and has been used for actinide extraction into molecular solvents. Distribution ratio measurements for  $Pu^{4+}$  and  $Am^{3+}$  showed little acid dependency for  $Pu^{4+}$ , but strong acid dependency studies seem to support 1:1 metal:ligand binding for  $Pu^{4+}$ , but significantly the notion that ionic liquids can provide different coordination environments [13]. In such application, imidazolium cations were also derived to include the task specific functionalities, such as metal ligating groups that when used as part of the solvent or doped in the less expensive ionic liquids could dramatically enhance the extraction of targeted metal ions [14]. Moreover, the effect of pH on the extraction efficiencies showed a big difference due to its differences in solvent behavior of ionic liquid and conventional organic solvents. After metal ion was extracted to ionic liquid, a strong solution such as nitric acid was applied to stripping metal ion from the ionic liquid. We have investigated the conditions of stripping metal ions from ionic liquid too, the experiments indicated metal ion is easy to be stripped from ionic liquid phase and enter aqueous phase if the neutral complex was formed in a base medium. Otherwise, metal ion stripping required a relatively strong base solution. However, the stripping process is slow very much at room temperature. In order to overcome the problem, a new stripping procedure was developed for stripping metal ion from ionic liquid, in which the equal volume of acetone and the ionic liquid containing metal ion complex mixed before a strong solution was added, whole process can complete within several minutes. At the same, above stripping method may be used to renew of the ionic liquids.

Recently, we attempt that metal ion extraction in the ionic liquid/aqueous two phase system combined with spectrometry technology including AAS and spectrophotometry to determine ultra trace amounts of metal elements in environmental samples. It was found that the extraction procedure can decrease the detect limit and improve the selectivity of analytical method remarkably. For atomic absorption spectrometry, the metal ion extraction must be back-extracted into aqueous solution, then was introduced into atomic absorption spectrometer for determination. For example, a new room temperature ionic liquid

[C<sub>4</sub>tmsim][PF<sub>6</sub>] was developed as a novel medium for liquid/liquid extraction of inorganic mercury with CDAA, the extraction and back-extraction efficiencies were 99.9 and 100.1 % for 5.0 µg.L<sup>-1</sup> standard mercury in 1000 mL of water solution, respectively, the detection limit is 0.01 µg.L<sup>-1</sup> mercury in real water sample, proposed method has been used to the determination of trace inorganic mercury in natural water with satisfactory results [2]. If the ionic liquid phase containing metal complex is transparent, it can be directly used to spectrophotometric determination. So that, metal ion extraction in the ionic liquid/aqueous two phase system in which some excellent chromogenic reagent was selected as ligand to form metal complex is very selective, this may overcome the drawback in sensitivity of conventional spectrophotometric methods. For example, we reported a highly sensitive and selective extraction spectrophotometric method for determination of trace germanium in natural water with a new chromogenic reagent methybenzeneazosalicylfluorone abbreviated as MBASF, in which ionic liquid [C<sub>4</sub>mim][PF<sub>6</sub>] was used as novel medium for liquid/liquid extraction of germanium (IV). In the presence of TritonX-100, MBASF reacted with germanium (IV) to form a red complex rapidly, the complex was then extracted into the [C<sub>4</sub>mim][PF<sub>6</sub>] phase (shown in Fig.1), absorbance of the complex in ionic liquid at 496 nm was recorded and used to determine trace Ge<sup>4+</sup>. The apparent molar absorptivity of the complex and the detection limit for the real sample were found to be 3.12×10<sup>6</sup> L.mol<sup>-1</sup>.cm<sup>-1</sup> and 0.2 ng.mL<sup>-1</sup> respectively. The absorbance of the complex at 496 nm increases linearly with the concentration up to 4mg of Ge<sup>4+</sup> in 250 mL of aqueous solution. The interference study show the determination of germanium is free from the interference of almost all positive and negative ions found in the natural water samples. The determination of Ge<sup>4+</sup> in natural water was carried out by the present method and ETAAS. The results were

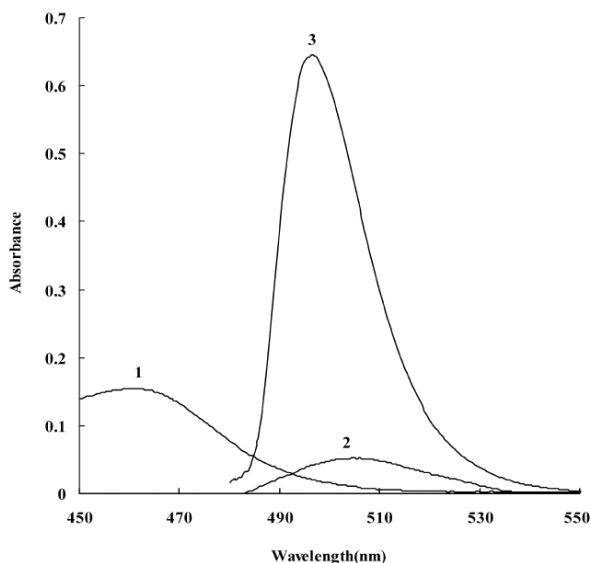


Fig. 1. Absorption spectrum of the reagent against water (1), the complex in the aqueous phase (2), and in the [C<sub>4</sub>mim][PF<sub>6</sub>] (3), germanium (IV): 4.0mg in 250 mL of aqueous solution, [C<sub>4</sub>mim][PF<sub>6</sub>]

satisfactorily comparable so that the applicability of the proposed method was confirmed using the real samples [40]. Metal ion extraction in ionic liquid/aqueous two phase system and their application were listed in Table 1.

Metal ion	Ionic liquid	Ligand	Detection technology /detection limit	Ref.
Ni <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ],	PAN	FI-FAAS/12.5 µg.L <sup>-1</sup>	15
Fe <sup>3+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup>	trioctylmethylammonium salicylate			16
Cd <sup>2+</sup>	ionic liquid functionalized 2-mercaptobenzothiazole	ammonium pyrrolidine dithiocarbamate and diethyldithiocarbamate	AAS	17
Pb <sup>2+</sup> , Cu <sup>2+</sup> , Hg <sup>2+</sup> , Cd <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	2-aminothiophenol		18
Co <sup>2+</sup>	1-hexylpyridinium hexafluorophosphate	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone	AAS/0.70 µg.L <sup>-1</sup>	19
Cd <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	2-mercaptobenzothiazole	AAS/(4.6 ng.L <sup>-1</sup> )	20
La <sup>3+</sup>	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	18-Crown-6 and 2-thenoyltrifluoroacetone		21
Sr <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	DCH-18-C-6		22
Am <sup>3+</sup>	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	tri-n-butylphosphate and n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide		23
UO <sub>2</sub> <sup>+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	tri-n-butyl phosphate		24
Mn <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	[C <sub>n</sub> mim][PF <sub>6</sub> ], [C <sub>n</sub> mim][Tf <sub>2</sub> N]			25
Pb <sup>2+</sup> , Cd <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	tetra-n-propylammonium iodide	differential-pulse anodic stripping voltammetry/0.001 µg.mL <sup>-1</sup>	26
Th <sup>4+</sup>	[C <sub>8</sub> mim][PF <sub>6</sub> ]	primary amine N-1923		27
UO <sub>2</sub> <sup>2+</sup>	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	tri-n-butylphosphate		28
Y <sup>3+</sup>	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Cyanex-923 and EDTA		29
Pu <sup>4+</sup>	[C <sub>8</sub> mim][PF <sub>6</sub> ]	carbamoyl methyl phosphine oxide		30
La <sup>3+</sup>	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	2-thenoyltrifluoroacetone and 18-crown-6		31
Ni <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	2-pyridinealdoxime		32
Sr <sup>2+</sup> , Cs <sup>+</sup>	tri-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide	ionophores dicyclohexano-18-crown-6 and calix[4]arenebis-(tert-octylbenzo-crown-6)		33
Pb <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	dithizone	ETAAS/1.0 ng.L <sup>-1</sup>	5
Al <sup>3+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	3,5-ditertbutylsalicylfluorone	ETAAS/0.06 µg.L <sup>-1</sup>	6
Zn <sup>2+</sup>	Butyl-methyl-pyrrolidinium	2,4-dinitrophenolate		34

	trifluoromethylsulfonate			
Pb <sup>2+</sup>	[C <sub>8</sub> mim][PF <sub>6</sub> ]	dithizone	ETAAS/1.0 ng.L <sup>-1</sup>	7
Sc <sup>3+</sup>	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Cyanex -925		35
M <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	benzoyltrifluoroacetone, 2-naphthoyltrifluoroacetone and trifluoroacetylacetone		36
Pd <sup>2+</sup>	tri-n-octylmethylammonium chloride and tri-n-octylmethylammonium nitrate	Aliquat-336		37
Cu <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	1-methylimidazole		38
La <sup>3+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine		39
Ge <sup>4+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	methylbenzeneazosalicylaldehyde	Spectrophotometry/0.2 ng.mL <sup>-1</sup>	40
UO <sub>2</sub> <sup>2+</sup> , Am <sup>3+</sup> , Nd <sup>3+</sup> , Eu <sup>3+</sup>	[C <sub>9</sub> mim][Tf <sub>2</sub> N]	dialkylphosphoric or dialkylphosphinic acids		41
UO <sub>2</sub> <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	tri-n-butylphosphate		42
Cu <sup>2+</sup>	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	beta-diketonate		43
Cu <sup>2+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	dithizone, 8-hydroxyquinoline, and 1-(2-pyridylazo)-2-naphthol		44

Table 1. Reviews in extraction of metal ions with ionic liquid as medium

## 2. Organic compound/gas extraction and separation

Ionic liquids have been widely applied to organic compound/gas extraction and separation too. Basing on the ionic liquid various unique solvent characteristics and extraction performance, room temperature ionic liquids may be used as liquid membrane materials to separate organic compound and gas. For example, [C<sub>4</sub>mim][PF<sub>6</sub>] as membrane solution can be utilized for hydrocarbon separation by using a supported liquid membrane. Although the permeation rates through the membrane based on the ionic liquids were less than those of water, the selectivity of aromatic hydrocarbons was greatly improved [45]. Ionic liquid as special solution combined with classical separation technologies such as liquid/solid phase microextraction was used to beforehand separation and enrichment of the sample for high performance liquid chromatography, this may improve the separation effect of analytical technology remarkably. Ionic liquid as electrolyte can enhance electric capability to capillary zone electrophoresis. For example, professor Qi reported the ionic liquid used as running electrolyte in capillary zone electrophoresis with cyclodextrin ( $\beta$ -CD) as modifier for the separation of anthraquinones extract of Chinese herb *Paedicalyx attopevensis* Pierre ex Pitard [46]. Ionic liquid as ion pair reagent was applied to reversed-phase high performance liquid chromatography. Moreover, utilization of supercritical carbon dioxide (scCO<sub>2</sub>) in concert with various popular ionic liquids is shown

to have modified and enhanced the overall extraction capabilities and applications of these neoteric solvents [47-50]. Brennecke group have investigated the recovery of organic products from ionic liquids using scCO<sub>2</sub>. The results indicated the recovery rates of various aromatic and aliphatic solutes from [C<sub>4</sub>mim][PF<sub>6</sub>] in the presence of environmentally benign scCO<sub>2</sub> are presented. In a subsequent study, interesting outcomes showing utility of scCO<sub>2</sub> as a separation switch for ionic liquid/organic mixtures were published by the same group [47, 48]. In general, we conjecture ionic liquid will rapidly be applied to many new fields of the extraction and separation with understanding on the extraction performance of room temperature ionic liquid.

### 3. Application of ionic liquids in microextractions

#### 3.1 Liquid phase microextraction

Ionic liquid has been widely applied to various liquid phase microextractions for sample preparation. Commonly, volume of the ionic liquid for liquid phase microextraction is often lower than 25  $\mu$ L in order to obtain high enrichment factor. To fine mix the ionic liquid with aqueous phase, a relatively long extraction time and strong stir process are strongly required. However, so small volume of the ionic liquid is difficult to be precisely collected from aqueous phase due to its dissolution in water and adhere to wall of the vial (Table 2). To overcome the problems, some new types of liquid phase microextraction have been reported in literatures. For examples, single drop microextraction (SDME) (Table 3) and dispersive liquid microextraction (DLME) (Table 4).

Analyte	Ionic liquid	Sample	Remark	Ref.
Steroid and antiinflammatory drugs	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Human urine	Enrichment factors varied between 10.69 for naproxen and 13.93 for fenbufen. HPLC system was employed for analysis. A dynamic liquid-phase microextraction using an ionic liquid as acceptor phase is reported.	51
Aromatic and aliphatic hydrocarbons	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	GC-MS was coupled with determination of analyte; for the first time hollow fiber-protected ionic liquid supported three-phase (liquid-liquid-liquid) microextraction; enrichment factor and extraction time are 210 and 40min.	52
4-Nonylphenol, 4-tert-octylphenol	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; enrichment factors are between 19.5 and 33.8, and extraction time was about at 30 min.	53
Chlorpromazine, promethazine, levomepromazine, prochlorperazine,	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Human urine	HPLC was employed for analysis.	54

trifluoperazine, fluphenazine and thioridazine				
Phorate, parathion and poxim	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; enrichment factors are in the range from 553 to 665.	55
Benzene, toluene, ethylbenzene, and xylene), polycyclic aromatic hydrocarbons, phthalates, phenols, aromatic amines, herbicides, organotin, and organomecury	[C <sub>4</sub> mim][PF <sub>6</sub> ], [C <sub>8</sub> mim][PF <sub>6</sub> ]	Water	HPLC, AAS and or cold-vapor atomic fluorescence spectrometry determination was employed for analysis, respectively; the enrichment factors determined were in the range of 5-168 for 15 min extraction by [C <sub>4</sub> mim][PF <sub>6</sub> ] and 4-178 for 30 min extraction by [C <sub>8</sub> mim][PF <sub>6</sub> ].	56
Chlorpromazine, promethazine, levomepromazine, prochlorperazine, trifluoperazine, fluphenazine and thioridazine	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Human urine	The proposed method is a valuable alternative for the analysis of these drugs in urine within the concentration range 0.07-10µg.mL <sup>-1</sup> . Limits of detection were in the range from 21 ng.mL <sup>-1</sup> for thioridazine to 60ng.mL <sup>-1</sup> for levomepromazine.	102
Cobalt	[C <sub>6</sub> mim][PF <sub>6</sub> ]	Environmental and biological samples	ETAAS was employed for detection of cobalt.	111
Triazines	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC was employed for detection of triazines, the detection limits are for the triazine range from 0.36 to 1.41µg.L <sup>-1</sup> .	116
Palladium	[C <sub>6</sub> mim][PF <sub>6</sub> ]	food additive	The limit of detection was 0.2ng.mL <sup>-1</sup> .	117
Cadmium	[C <sub>4</sub> mim][PF <sub>6</sub> ]	saline	o,o-Diethyldithiophosphate was used as a ligand. FAAS was employed for detection of cadmium, the limit of detection (3s) and the enhancement factor were 0.07 µg.L <sup>-1</sup> and 78, respectively.	127

Table 2. Reviews for common liquid phase microextraction using ionic liquid as acceptor phase

SDME includes direct-immersion liquid phase microextraction and headspace liquid phase microextraction. Because during headspace liquid microextraction the ionic liquid has no loss because it lack effective vapor pressure even at high temperature, headspace liquid phase microextraction often provide a higher enrichment factor for most of analytes than direct-immersion liquid phase microextraction. A typical experimental set-up of headspace liquid phase microextraction is illustrated in Fig.2 [59]. Before each extraction, the microsyringe was rinsed with methanol to avoid analyte carry-over and air bubble

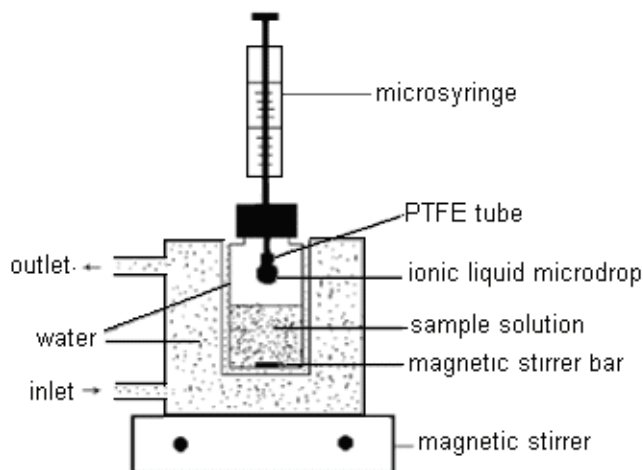


Fig. 2. Schematic diagram of SDME

formation. For the extraction an aliquot of the sample solution was placed in a vial immersed in the recirculating cell. After the uptake of the 10-25  $\mu\text{L}$  of the ionic liquid, the microsyringe needle was inserted through the septum and then tightly fitted with a long polytetrafluoroethylene tube, and the syringe to begin with the extraction process, the syringe plunger was depressed completely to expose an ionic liquid drop and the magnetic stirrer was turned. After extracting, the magnetic stirrer was switched off, and then the microdrop was retracted back into the microsyringe and injected directly into detector for analysis. SDME is based on the equilibrium of the three phases: the condensed aqueous phase, the headspace phase and the microdrop phase. Mass transfer in the headspace is assumed to be a faster process since diffusion coefficients in the gas phase are typically  $10^4$  times greater than corresponding diffusion coefficients in the condensed phase. Thus, both slow mass transfers in the aqueous phase and diffusion of analyte into the microdrop are limiting steps in the overall extraction process was clamped so that the tip of the needle was located in a constant position in the headspace of the vial. The penetration theory indicates the aqueous phase mass transfer coefficient of solute increases with increasing stirring rate, and heating improves the mass transfers in the aqueous phase and induces convection in the headspace. Therefore, consequently the equilibrium between the aqueous and vapor phase can be attained more rapidly. Moreover, an addition of salt (such as  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  etc) to the sample can decrease the solubility of analytes in the aqueous phase and enhance their partitioning into the organic phase, the extraction is often enhanced with increasing salt concentration and polarity of compound. Thus, a salt concentration of about 30 % was used in most SDME.

Analyte	Ionic liquid	Sample	Remark	Ref.
Chlorobenzenes	$[\text{C}_4\text{mim}][\text{PF}_6]$	Water	HPLC was coupled with analysis; extraction time is 37min; an obvious salting-out effect was observed.	57
Formaldehyde	$[\text{C}_8\text{mim}][\text{PF}_6]$	Shiitake mushroom	2,4-Dinitrophenylhydrazine was used as derivative agent; HPLC was coupled	58



Dichlorodiphenyltrichloroethane and its metabolites	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	with analysis; extraction time is 30min HPLC was coupled with analysis; an obvious salting-out effect was observed; extraction time is 30min	59
Phenols	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Water	GC was used for detection of phenols; effect of salting-out is obvious.	60
Phenols	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; enrichment factors were in the range from 17.2-160.7.	61
Chloroform, bromodichloromethane, dibromochloromethane and bromoform	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Water	GC-MS was employed for analysis; extraction time was about 30min; an obvious salting-out effect was observed well.	62
Chlorinated anilines	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; extraction temperature and salting-out have seriously influenced on the extraction efficiencies.	63
Benzophenone-3	[C <sub>6</sub> mim][PF <sub>6</sub> ]	Urine	HPLC was employed for analysis.	64
Dichloromethane, <i>p</i> -xylene, and <i>n</i> -undecane	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	GC-MS was employed for the analysis; a new removable interface that enables the introduction of the extracted analytes into the GC system, while preventing the ionic liquid from entering the column, has been developed	65
Benzene, toluene, ethylbenzene and xylene isomers	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Waters	GC-MS was employed for the analysis; extraction temperature and salting-out effect on the extraction performance.	66
Cobalt, mercury and lead	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Biological and environmental samples	Electrothermal vaporization inductively coupled plasma mass spectrometry was employed for determination; after 10 min of extraction, the enrichment factors were 350 (cobalt), 50 (mercury) and 60 (lead); 1-(2-pyridylazo)-2-naphthol as both extractant and chemical modifier.	67
Chlorobenzenes	[C <sub>6</sub> mim][PF <sub>6</sub> ]	Water	A 20 min of extraction time was required; a microwave was used for assist extraction.	68
Manganese	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	ETAAS was employed for analysis; 1-(2-thiazolylazo)-2-naphthol was used for chelator of manganese; the drop of the ionic liquid was directly injected into the graphite furnace.	69
1-Naphthylamine, N,N-dimethylaniline and diphenylamine	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	Enrichment factors are in the range from 13.7 to 116.3.	93
4-Dichlorophenol, naphthol, 2-nitrophenol and 4-chlorophenol	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	The effect of complex matrices natural water samples could be resolved with addition of sodium ethylene diamine tetracetate into the samples.	71

4-Nonylphenol, 4-tert-octylphenol	[C <sub>6</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; the proposed procedure has a detection limit and enrichment factor of 0.3μg.L <sup>-1</sup> and 163 for 4-nonylphenol, and 0.7μg.L <sup>-1</sup> and 130 for 4-tert-octylphenol, respectively.	72
chlorobenzenes	[C <sub>6</sub> mim][PF <sub>6</sub> ]		Limits of detection ranging between 1 and 4ng.L <sup>-1</sup> .	103
mercury species	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	Limits of detection were between 1.0 and 22.8 μg.L <sup>-1</sup> for the four species of mercury.	104
lead	[C <sub>4</sub> mim][PF <sub>6</sub> ]	certified reference materials	Lead was complexed with ammonium pyrrolidinedithiocarbamate; The limit of detection and the enhancement factor were 0.015 and 76μg.L <sup>-1</sup> .	105
Trihalomethanes	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	The limits of the detection range between 0.1 ng/mL (bromoform) and 0.9 ng.mL <sup>-1</sup> (chloroform).	106
Tributyltin and Triphenyltin	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	Detection limits are between 1 and 100 μg.mL <sup>-1</sup> .	108
phenols	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Chinese Medicines	The limit of detection was 0.39μg.L <sup>-1</sup> .	115
carbonyl compounds	[C <sub>8</sub> mim][PF <sub>6</sub> ]	water	capillary electrophoresis was employed for analysis, detection limits to three phenols were less than 0.05μg.L <sup>-1</sup> .	120
cobalt	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	Enrichment factor is up to 150. HPLC was employed for detection of carbonyl compounds, the limit of detection was in the range of 0.04-2.03ng.mL <sup>-1</sup> .	124
2-hydroxy-4-methoxybenzophenone, isoamyl-4-methoxycinnamate, 3-(4'-methylbenzylidene)camphor, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexyl 4-dimethylaminobenzoate and 2-ethylhexyl 4-methoxycinnamate	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	ETAAS was employed for detection of cobalt, the detection limit was 0.04μg.mL <sup>-1</sup> , and the enrichment factor was 120.	131
lead	Tetradecyl(triethyl)phosphonium chloride	water	HPLC was employed for detection, limits of detection were found in the low μg.L <sup>-1</sup> range.	128
			2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was used as ligand. ETAAS was employed for detection of lead, its detection limit is 4.5 μg.L <sup>-1</sup> .	129

Table 3. Reviews for single drop microextraction using ionic liquid as acceptor phase

Recently, a novel liquid phase microextraction technology termed dispersive liquid phase micro-extraction (DLME) was developed and validated (Table 4). From the name, it is obviously that it was based on the temperature change or using organic disperser making ionic liquid completely disperse in the aqueous phase and increase the chance of mass transfer into ionic liquid phase, in which the analytes will more easily migrate into the ionic liquid phase because of the much larger contact area than that of conventional single drop liquid micro-extraction, and the ionic liquid was concentrated into one drop by cooling and centrifugation. Experimental indicated that this system could be tuned to a great extent because ionic liquids can be designable and the method does not suffer from the limitations of that in conventional solvent micro-extraction. DLME has been applied to detect trace organophosphorus pesticides [73], fipronil, chlorfenapyr, buprofezin, hexythiazol [74] and mercury [75] with high extraction efficiencies. In general, DLME is more simple and rapid than SDME.

Analyte	Ionic liquid	Sample	Remark	Ref.
Organophosphorus pesticides	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC was coupled with analysis; a 70 °C of heating and 30min of the centrifugation process were required strongly in order to form a fine dispersive phase and extraction efficiency; serious salting-out effect was also observed.	73
Fipronil, chlorfenapyr, buprofezin, and hexythiazol	[C <sub>4</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; enrichment factors are in the range from 209 to 276.	74
Hg <sup>2+</sup>	[C <sub>6</sub> mim][Ff <sub>2</sub> N]	Water	Spectrophotometry was employed for analysis; 4,4'-bis(dimethylamino)-thiobenzophenone was used as chelator of mercury; enrichment factor is about to 18.8.	75
Sm <sup>3+</sup> , Eu <sup>3+</sup> , Gd <sup>3+</sup> , Dy <sup>3+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	uranium dioxide powder	1-hydroxy-2,5-pyrrolidinedione was used as agent.	90
polycyclic hydrocarbons	[C <sub>8</sub> mim][PF <sub>6</sub> ]	tap, bottled, fountain, well, river, rainwater, treated and raw wastewater	Analysis of extracts was performed by HPLC coupled with fluorescence detection; Quantification limits obtained for all of these considered compounds are between 0.1 and 7 ng.L <sup>-1</sup> .	91
Zn <sup>2+</sup>	1-hexylpyridinium hexafluorophosphate	water and milk	Zinc was complexed with 8-hydroxyquinoline; The ionic liquid was proposed for the	92

non-steroidal inflammatory drugs	anti- [C <sub>4</sub> mim][PF <sub>6</sub> ]	urine	preconcentration of trace levels of zinc as a prior step to determination by flame atomic absorption spectrometry; the limit of detection (3s) and the enhancement factor were 0.22 µg.L <sup>-1</sup> and 71. The suitability of the proposal is evaluated by means of the determination of non-steroidal anti-inflammatory drugs in urine by liquid chromatography/ultraviolet detection; Limits of detection were in the range from 8.3 ng.mL <sup>-1</sup> for indomethacin to 32 ng.mL <sup>-1</sup> for ketoprofen.	93
Cd <sup>2+</sup>	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	Dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry; The enrichment factor of the method is 67. The detection limit was 7.4 ng.L <sup>-1</sup> .	94
Dichlorodiphenyltrichloroethane and its main metabolites	[C <sub>6</sub> mim][PF <sub>6</sub> ]		The experimental results indicated that the detection limits obtained for p,p'-DDD, p,p'-DDT, o,p'-DDT and p,p'-DDE were 0.24, 0.24, 0.45, 0.24 ng.mL <sup>-1</sup> , respectively	95
Thiophanate-methyl, carbofuran, tebuconazole, oxyfluorfen and fenazaquin	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	This paper describes a dispersive liquid-liquid microextraction procedure using room temperature ionic liquids coupled to high-performance liquid chromatography with diode array detection capable of quantifying trace amounts of eight pesticides; Limits of detection are between 0.320-4.66 µg.kg <sup>-1</sup> .	96
phenols	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	The settled phase was injected into HPLC for separation and detection of phenols; The main advantages of the proposed method are high speed, high	97

aromatic compounds	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	recovery, good repeatability and environmental friendliness. The limits of detection for seven polycyclic aromatic hydrocarbons varied from 0.02 to 0.3 µg.L <sup>-1</sup> .	98
dicofol and DDT	1-isooctyl-3-methylimidazolium hexafluorophosphate	water	The enrichment factors were 532 for dicofol and 540 for DDT; Proposed extraction combined with gas chromatography mass spectrometry was a valuable alternative for analysis of dicofol and DDT in environmental water samples within the concentration range 0.005-3.0 µg.L <sup>-1</sup> . The detection limits were 1.3 ng.L <sup>-1</sup> for DDT and 3.2 ng.L <sup>-1</sup> for dicofol.	99
parathion, phoxim, phorate and chlorpyrifos	[C <sub>8</sub> mim][PF <sub>6</sub> ]	water	Enrichment factor of analytes is 200 and the limits of detection calculated at a signal-to-noise ratio of 3 were in the range of 0.1-5.0 µg.L <sup>-1</sup> .	100
thiophanate-methyl, carbofuran, carbaryl, tebuconazole, iprodione, oxyfluorfen, hexythiazox, and fenazaquin	[C <sub>6</sub> mim][PF <sub>6</sub> ]	fruit	Limits of detection were in the range 0.651-5.44 µg/kg for table grapes and 0.902-6.33 µg.kg <sup>-1</sup> for plums.	101
three triazine and two phenylurea herbicides	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC was used for detection of five herbicides, their limit of detections were between 0.46 and 0.89 µg.L <sup>-1</sup> .	109
triclosan and triclocarban	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC-MS was used for detection of triclosan and triclocarban, limits of detection in the range from 0.040 to 0.58 µg.L <sup>-1</sup>	110
Pb <sup>2+</sup> , Cd <sup>2+</sup>	[C <sub>6</sub> mim][PF <sub>6</sub> ]	saline	FAAS was employed for detection of lead and cadmium, detection limits are 0.6 µg/L for lead and 0.03 µg.L <sup>-1</sup> for cadmium	112
triclosan and triclocarban	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC-ESI-MS-MS was employed for triclosan and triclocarb, detection limits are in the range from 0.040 to 0.58 µg.L <sup>-1</sup> .	113

organophosphorus pesticides	1,3-dibutylimidazolium hexafluorophosphate	water and fruit	Enrichment factors are more than 300 times. HPLC was employed for detection of pesticides, Limits of detection were 0.01-0.05 $\mu\text{g.L}^{-1}$ for four analytes.	121
V <sup>5+</sup>	[C <sub>4</sub> mim][PF <sub>6</sub> ]	environmental and biological samples	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was used as ligand. ETAAS was employed for detection of vanadium. The detection limit achieved after preconcentration of 5 mL of sample solution, was 4.8 $\text{ng.L}^{-1}$	122
triclosan and triclocarban	[C <sub>6</sub> mim][PF <sub>6</sub> ]	water	HPLC-ESI-MS/MS was employed for detection of triclosan and triclocarban, detection limit is 0.04 and 0.3 $\mu\text{g.L}^{-1}$	125
anthraquinones	[C <sub>6</sub> mim][PF <sub>6</sub> ]	Radix	HPLC was employed for detection of anthraquinones, the limits of detection for all target analytes were ranged from 0.50 to 2.02 $\mu\text{g.L}^{-1}$ .	126
Cr <sup>6+</sup>	[C <sub>6</sub> mim][PF <sub>6</sub> ]	lake and tap water	ETAAS was employed for detection of chromium, the limit of detection of the proposed method was 0.07 $\text{ng.mL}^{-1}$ .	130

Table 4. Reviews for dispersive liquid phase microextraction using ionic liquid as acceptor phase

### 3.2 Solid phase microextraction

Solid-phase microextraction (SPME) has developed rapidly and it has been widely applied in sample analysis. This is because this simple and solvent-free sample preparation technique, which combines extraction, concentration and sample introduction in one step, is portable, sensitive and convenient to couple with various analytical instruments, especially GC. Almost a dozen different fiber coatings have been commercialized. Among them, the polydimethylsiloxane shows excellent selectivity for non-polar compounds while the polyacrylate coating facilitates the extraction of relatively polar analytes. To date, most of these fiber coatings suffered from limited life span, relatively low operating temperatures in GC applications, and incompatibility with the organic solvents in HPLC mobile phases. In recent years, ionic liquid was widely applied to coating for SPME (Table 4). A typical experimental set-up of headspace SPME mode was illustrated in Fig.3 [79]. The SPME fiber was coated with IL prior to every extraction, the analytes were then extracted and desorbed on the injection port of gas chromatography, and finally the ionic liquid coating on the fiber was washed out with solvents. The coating and washing out of the ionic liquid from the fiber can be finished in a few minutes. Experimental demonstrated that the relatively large

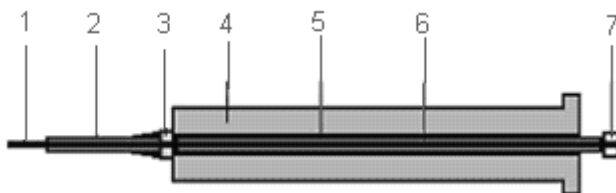


Fig. 3. Schematic diagram of the home-made SPME device: (1) ionic liquid-coated fiber tip; (2) stainless steel needle; (3) silicone rubber O-ring; (4) glass syringe body; (5) moveable stainless steel tubing; (6) stainless steel fiber or polyimide coated fused-silica fiber; (7) localizer.

viscosity of ionic liquid aided its coating on the SPME fiber and permitted easy washing out after sample injection. On the other hand, the involatility and good thermal stability of the ionic liquid will keep it staying on the fiber when the analytes were thermally desorbed in the injection port of GC, though loss of some of the ionic liquid film occurred due to the simple coating procedure. This proposed disposable ionic liquid-coated fibers show reproducibility comparable with the widely used commercially available SPME fibers, but its sensitivity is lower due to the relatively thin coating. The major advantage of the disposable ionic liquid-coated fiber is the very low cost because only a very low amount of ionic liquid is consumed for each determination. Another advantage of this disposable coating is the carryover was avoided as new fiber coating is used for every determination. However, the detection limits were higher than those obtained using commercially available SPME fibers due to the relative thin film of ionic liquid that can be coated on the fiber. Therefore, this proposed method is only applicable to samples with relatively high levels of analytes. Considering that ionic liquid possess good extractability for various organic compounds and metals ions, and task-specific ionic liquid can be designed and synthesized for selective extraction of target analytes, disposable SPME/LPME coating ionic liquid might has great potential in sample preparation.

Baghdadi group reported a new microextraction with ionic liquid termed cold-induced aggregation microextraction procedure (CIAME) [85]. In this method, very small amounts of 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (as extractant solvents) were dissolved in a sample solution containing Triton X-114 (as an anti-sticking agent). Afterwards, the solution was cooled in the ice bath and a cloudy solution was formed. After centrifuging, the fine droplets of extractant phase were settled to the bottom of the conical-bottom glass centrifuge tube. CIAME is a simple and rapid method for extraction and preconcentration of metal ions from water samples and can be applied for the sample solutions containing high concentration of salt and water miscible organic solvents. Furthermore, this technique is much safer in comparison with the organic solvent extraction. Performance of the technique was evaluated by determination of the trace amounts of mercury as a test analyte in several real water samples. Michler thioketone was chosen as a complexing agent. Analysis was carried out using spectrophotometric detection method. Type and amount of IL and the surfactant, temperature and the other parameters were optimized. Under the optimum conditions, the limit of detection of the method was  $0.3 \text{ ng mL}^{-1}$  and the relative standard deviation was 1.32% for  $30 \text{ ng mL}^{-1}$  mercury.

Analyte	Ionic liquid	Sample	Remark	Ref.
	trihexyltetradecylphosphonium, N-butyl-4-methylpyridinium tetrafluoroborate		Ionic liquid-mediated sol-gel hybrid organic-inorganic materials present enormous potential for effective use in analytical microextraction; Detection limits ranging from 4.9 to 487ng.L <sup>-1</sup> .	76
Polycyclic aromatic hydrocarbons	[C <sub>6</sub> mim]Br, 1-hexadecyl-3-butylimidazolium bromide and 1,3-didodecylimidazolium bromide	sediment BCR-535	GC-MS was employed for the analysis; an aqueous ionic liquid aggregate was used as acceptor; the extraction tube was introduced into the microwave cavity.	77
Esters	polymeric ionic liquids	Water	For the first time polymeric ionic liquids was used as fiber coatings for extraction; GC was employed for analysis; long lifetime and high thermal stability of the polymeric ionic liquid solid phase microextraction coatings may provide them particular advantages in GC-MS applications involving highly selective ester and FAME extractions from complex matrices.	78
benzene, toluene, ethylbenzene, and xylenes	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Paint	GC was employed for analysis; the SPME fiber was coated with ionic liquid prior to every extraction; an extraction time of 30min was selected; an obvious salting-out effect was observed well.	79
ethanol	[C <sub>4</sub> mim]Cl and [C <sub>2</sub> mim]acetate		The application of ionic liquids as nonderivatizing solvents for the pretreatment and regeneration of cellulose is a growing area of research; GC was employed for analysis.	80
nonane, methyl caproate, <i>o</i> -cresol, <i>sec</i> -phenethyl alcohol	six dicationic ionic liquids	Water	GC was employed for analysis; the partitioning behavior of six imidazolium-based ionic liquid aggregates in water has been studied for the first time. Monocationic and dicationic ionic liquids-aggregates behave as traditional surfactant systems; the obtained partition coefficients show that hydrophobic analytes are preferably extracted with ionic liquids-aggregates compared to more polar analytes.	81
4-Chlorophenol, 3-	[C <sub>8</sub> mim][PF <sub>6</sub> ]	Water	HPLC was employed for analysis; a 60 min of extraction time was required; an obvious salting-out effect was observed.	82



chorop henol, 2,4- dichlor opheno l and 2,4,6- trichlor opheno l				
Aromat ic compo unds	[C <sub>16</sub> mim]Br, 1-hexadecyl-3- butylimidazolium bromide, 1,3-didodecylimidazolium bromide	water	HPLC was employed for analysis.	83
Polycyc lic aromati c hydroc arbons short- chain alcohol s, polar and basic amines	[C <sub>8</sub> mim][PF <sub>6</sub> ], 1-benzyl-3- methylimidazolium trifluoromethanesulfonate:and 1-methyl-3- phenylpropylimidazolium trifluoromethanesulfonate	Water	nafion membrane was used to support the ionic liquid; GC-MS was employed for analysis.	84
	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	two ionic liquids contained styrene units that allowed for polymerization and higher carbon content of the bonded silica particles; The sensitivities of the two ionic liquid fibers differing by the anion were similar. Their efficacy compares favorably to that of commercial fibers for polar analytes. The mechanical strength and durability of the polymeric ionic liquid fibers were excellent.	87
Metha mpheta mine and amphet amine	1-Ethoxyethyl-3- methylimidazolium bis(trifluoromethane)sulfonyli mide	human urine	combined with gas chromatography/mass spectrometry working in selected ion monitoring mode, the new method showed good linearity in the range of 20-1500µg/ L and low detection limits (0.1µg.L <sup>-1</sup> for MAP and 0.5 µg.L <sup>-1</sup> for AP.	88
polycyc lic aromati c hydroc arbons	[C <sub>4</sub> mim][PF <sub>6</sub> ]	mosquito coil incense	A simple and cost effective solid-phase microextraction device has been developed	89
Sulfadi azine, sulfame razine sulfame thazine, sulfadi methox	[C <sub>4</sub> mim][PF <sub>6</sub> ]	water	By using ionic liquid as membrane liquid and tri-n-octylphosphine oxide as additive, hollow fiber supported liquid phase microextraction was developed for the determination of five sulfon-amides in environmental water samples by high performance liquid chromatography with ultraviolet	107

ine and sulfame thoxazole	detection; Detection limits are between 0.1 and 0.4 $\mu\text{g}\cdot\text{L}^{-1}$ .	
Acetone bonded ionic liquid polymeric material	GC was employed for detection.	114
$\text{CO}_2$ poly(1-vinyl-3-hexylimidazolium)-bis[(trifluoromethyl)sulfonyl]imide and poly(1-vinyl-3-hexylimidazolium) taurate	GC was employed for detection of $\text{CO}_2$ .	118
polycyclic aromatic hydrocarbons and substituted phenols	GC-MS was employed for analysis, detection limits oscillate from 0.005 $\text{ng}\cdot\text{mL}^{-1}$ for fluoranthene to 4.4 $\text{ng}/\text{mL}$ for 4-chloro-3-methylphenol.	119
lead and nickel [C <sub>8</sub> mim][PF <sub>6</sub> ]	Ammonium pyrrolidinedithiocarbamate was used as ligand. ETAAS was employed for detection lead and nickel, the detection limits of the method were 0.03 and 0.02 $\mu\text{g}\cdot\text{mL}^{-1}$ , for Ni and Pb, respectively	123

Table 5. Reviews for solid phase microextraction using ionic liquid as acceptor phase

#### 4. The combination of analytical technologies with the extraction

Many modern analytical technologies have been applied to couple with microextraction using ionic liquid as extracting media for different analytical purpose such as AAS for metal ions, HPLC, GC and GC-MS for organic compounds. When ionic liquids are employed as medium in various LPME and SPME, HPLC is preferred to GC as separation technique since this ionic liquid is incompatible with GC due to the non-volatility of the ionic liquid. Consequently, the utilizations of ionic liquid in GC are limited to their use as stationary phases, as coaters of the surface of fibers in solid-phase microextraction or as solvents in various liquid phase microextraction including SDME and DLME etc. In order to overcome the problem, some effective attempts have been reported recently in the literatures. For example, Miguel Valcarcel group has successfully developed a new interface for the direct coupling between ionic liquid-SDME and GC-MS<sup>[65]</sup> (shown in Fig.4). Using this interface, no ionic liquid can reach the GC system dirtying the chromatographic column and a proper volatilization and subsequent transference of the substances to the GC is achieved. Therefore, the advantages of the use of ionic liquids with SDME, avoiding the irreproducibility associated with the use of organic solvents to form the drop, are added to the analytical possibilities of GC-MS. Furthermore, using the interface analytes of an extensive range of polarity/volatility can be determined on account of the fact that no solvent delay is necessary in the detection step. Moreover, Zeng Baizhao group also

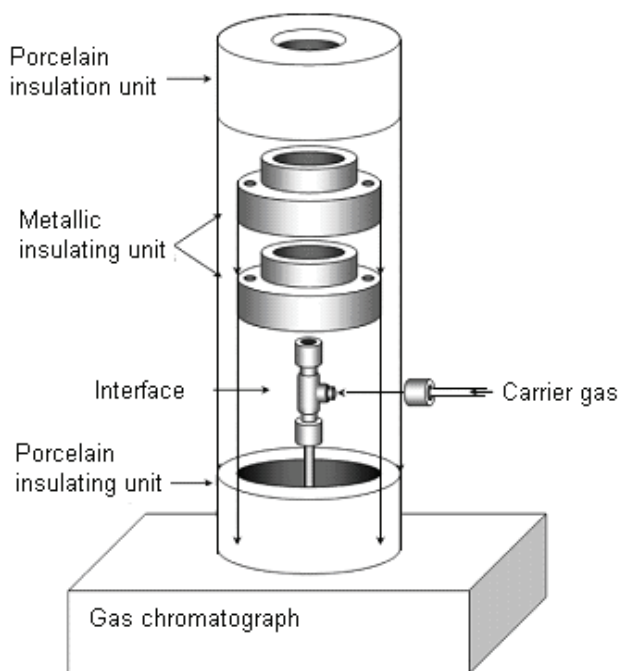


Fig. 4. Scheme of the household unit of the interface for the direct introduction of analytes extracted in a drop of ionic liquid into a gas chromatograph

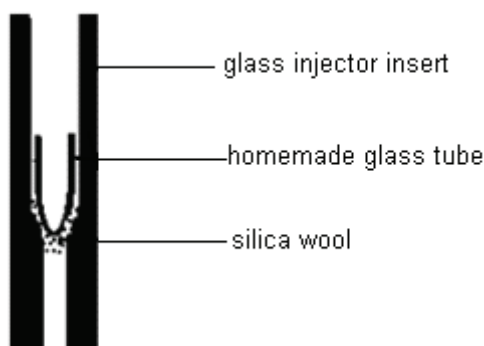


Fig. 5. The modified sample injection part of GC instrument. The dimension of the homemade tube: outer diameter, 2.0 mm; length, about 15 mm

provided another scheme to avoid ionic liquid leaking into the chromatographic column (shown in Fig.5). In the scheme through placing a small glassy tube in the sample injection part, ionic liquid no longer enters into the chromatographic column, thus ionic liquid based microextraction technique can be coupled with GC. To evaluate the proposed method, five chlorobenzene derivatives are used as model. Results show that the chlorobenzenes can be extracted effectively by the ionic liquid and the extractant exhibits good chromatographic

behavior. The linear ranges are up to  $1.5\text{mg}\cdot\text{L}^{-1}$  and the detection limits range from 0.1 to  $0.5\ \mu\text{g}\cdot\text{L}^{-1}$ . As ionic liquids have many unique properties, ionic liquid based microextraction technique coupled with GC has potential application in the detection of pollutants etc [86]. In our laboratory, above two schemes have been investigated too, the results exhibited above two schemes can not avoid the ionic liquid entering into chromatographic column.

## 5. Effect of solvent properties on the extraction performances

Although several 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids, abbreviated as  $[\text{C}_n\text{mim}][\text{PF}_6]$ , have been widely developed as friendly acceptor phase for various extractions in literatures, their application also suffers from many drawbacks. Firstly, these ionic liquids are difficult to be dispersed into aqueous phase and tend to tightly adhere on vessel wall due to high viscosity. The special property results that a long heating process (or mechanical agitation) and extract operation were required strongly in order to obtain good extraction efficiency. Secondly, most of the ionic liquids have relatively high water-solubility, the aqueous phase in the extraction system contains large amounts of imidazolium and hexafluorophosphate. The salting-out will effect on the extraction performance and following analysis in present of high ionic strength for complex samples. Moreover, the imidazolium dissolved in water is of good surface activity, the property may result in producing serious emulsification phenomenon during extraction and prolong phase separation time. In order to resolve above problems, some new ionic liquids have been designed, synthesized and applied to microextraction in the laboratory. For examples, 1,3-diisooctylimidazolium hexafluorophosphate (shown in Fig.6) was developed as a novel solvent for DLPME. In this study, dicofol and its three degradation products were selected as model compounds to optimize the factors relevant to the extraction and evaluate the applicability of the method. Experimental showed the proposed method offers the advantage of simplicity of operation, rapidity, high extraction efficiency and enrichment factor. The temperature-controlled ionic liquid 1-isooctyl-3-methylimidazolium hexafluorophosphate has been developed as novel medium for DLPME. This new mode of LPME with temperature-controlled ionic liquid increases the rapidity due to good hydrophobic property and relatively high melting point of the ionic liquid, the stability of extraction because of the larger volume of extraction solvent that may be used, enhances the sensitivity because of the much larger contact area than that of conventional LPME and SPME. Comparing with room temperature ionic liquid, proposed method has all performance during liquid/liquid and co-precipitation extraction, it can extract various polar or non-polar analyte from aqueous phase into the ionic liquid with high extraction efficiency. Moreover, new extraction can easily avoid the degradation of the pesticide during enrichment step due to no use a long heating time. Thirdly, the incompatibility between the extraction with ionic liquid and GC or GC-MS has become a problem in analytical chemistry due to ionic liquid's decomposition and leakage. Recently, Zhao group carried out a beneficial attempt to resolve above difficulty [78]. In this study, a new class of stationary phase coatings for SPME based on polymeric ionic liquids is presented. Proposed SPME coatings exhibit exceptional film stability, high thermal stability, reproducible extraction efficiencies, and long lifetimes. Moreover, the fiber coatings were used to extract esters and fatty acid methyl esters from aqueous solution followed by gas chromatographic separation and flame ionization detection. To examine the effect of the matrix on the coatings, extractions were carried out in a synthetic wine solution followed by recovery experiments in two real wine samples.

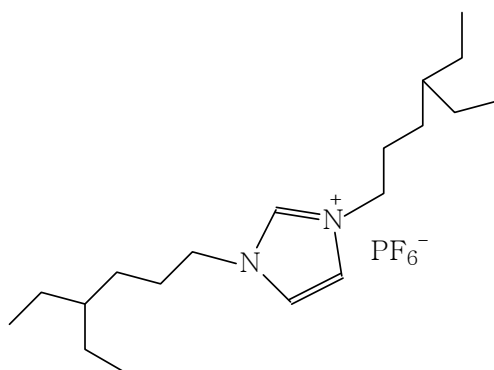


Fig. 6. Molecular structure of 1,3-diisooctylimidazolium hexafluorophosphate

When carrying out the extractions in aqueous solution, the detection limits for most analytes ranged from 2.5 to 50  $\mu\text{g}\cdot\text{L}^{-1}$  whereas lower detection limits were obtained for larger fatty acid methyl esters. Recovery experiments carried out in red and white wines ranged from 70.2 to 115.1% using the poly(ionic liquid) fibers compared to 61.9 to 102.9% using a commercial polydimethylsiloxane fiber of similar film thickness. The structural tuning capability of these new coating materials makes them widely amendable to performing task-specific microextractions.

In selection of solvents for extraction and extractive distillation processes knowledge of the activity coefficients at infinite dilution ( $\gamma^\infty$ ) is very important and useful. A large number of works concerns measurements of activity coefficients at infinite dilution of organic solvents in ionic liquids. In separation processes both properties of extractant are important, namely selectivity  $S$  and capacity  $k$  which can be directly calculated from activity coefficients at infinite dilution for different separation problems. Activity coefficients at infinite dilution are also very helpful for characterizing the behaviour of liquid mixtures, estimation of mutual solubilities, fitting the excess molar energy (GE) model parameters, predicting the existence of an azeotrope, analytical chromatography, calculation of Henry constant and partition coefficients, development of thermodynamic models based on the group contribution methods such as mod. Typical solvents used in separation of aromatic hydrocarbons from aliphatic hydrocarbons are polar components such as sulfolane and *N*-methylpyrrolidone (NMP). Replacement of these volatile solvents in the separation processes by the nonvolatile ionic liquids can offer advantages such as less complex processes, more simple regeneration of the extractant using techniques as simple as flash distillation or stripping and the environmental protection. Extraction of aromatics from aromatic/aliphatic mixture with ionic liquids is expected to require less process steps and less energy consumption than extraction with conventional solvents due to negligible vapor pressure of ionic liquids. Andrzej Marciniak has made the analysis of cation and anion structure of the ionic liquid and effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and *n*-hexane/hex-1-ene separation problems [132]. It was found the highest values of selectivity show ionic liquids with less aliphatic character of the anion and the cation, e.g. based on following cations 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-ethylpyridinium, triethylsulfonium and with  $-\text{C}\equiv\text{N}$  group in the structure, like [C<sub>3</sub>mim]CN. Unfortunately always when the ionic liquid reveals high values

of the selectivity, the capacity takes low values. Therefore a selection of proper anion and cation is required. The highest values of capacity have  $\text{Tf}_2\text{N}^-$  and  $\text{FeCl}_4^-$  anions. As was shown most of ionic liquids with high values of both selectivity and capacity is based on  $\text{Tf}_2\text{N}^-$  anion. 1-Butyl-4-methyl-pyridinium bis(trifluoromethylsulfonyl)amide have higher values of selectivity than sulfolane and NMP and much higher value of capacity than these two mentioned entrainers for the n-hexane/benzene separation. The highest selectivity for the n-hexane/benzene separation has  $[\text{C}_4\text{mim}][\text{SCN}]$  above 4 times higher than for sulfolane with a slightly better capacity. There are a large number of ionic liquids with selectivity and capacity better than sulfolane. A large number of ionic liquids have comparable or better both of selectivity and capacity values than NMP, e.g.: [1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide, triethyl-sulfonium bis(trifluoromethylsulfonyl)-amide, 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide, hexyl-trimethyl-ammonium bis(trifluoromethylsulfonyl)amide, tributylmethylphosphonium methylsulfate, 1-hexyl-oxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide and  $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ . For n-hexane/hex-1-ene the 3-(3-(Acryloyloxy)propyl)-1-methyl-imidazolium bromide has the highest selectivity of 15.2. For this separation process majority of ionic liquids have selectivity on the level of 2. To improve selectivity and capacity lower temperature is favourable.

From the values of selectivities and capacities, obtained for the large number of ionic liquids, it can be concluded that majority of ionic liquids may replace conventional entrainers applied for the separation processes of aliphatic/aromatic hydrocarbons and alkanes/alkenes.

## 6. Extraction mechanism

There are many investigations concerning extraction mechanism, these mainly are solvent ion pair extraction, ion exchange, and simultaneous combination of these. Among these, ion exchange mode was widely applied to understand the separation performance. In general, the ion exchange mode think metal ions will replace imidazolium cation or the anion combined with the ionic liquid in ionic liquid phase. For example, Dietz's group has suggested that high distributions in ionic liquid/aqueous system were due to a change in extraction equilibria in comparison to the octanol/aqueous system. In octanol,  $\text{Sr}^{2+}$  is extracted as a strontium nitratocrown ether complex, whereas in ionic liquids, the two axial bound nitrates are substituted with two water molecules bound to the metal ion, and the charged  $\text{Sr}(\text{CE})(\text{H}_2\text{O})_2^{2+}$  species, where CE is dicyclohexano-18-crown-6-ether, is transferred to the ionic liquid phase, the neutrality of the system is maintained through the migration of two imidazolium cations to the aqueous phase for each extracted metal ion. Therefore, the loss of the ionic liquid components in the aqueous phase would be a major limitation for practical applications of ionic liquids in separations and enrichments<sup>[143]</sup>. However, the nature of the ionic liquid is not the only factor which determines the metal extraction pathway, ligand type also has a very important contribution. Professor Jensen has suggested  $\text{La}^{3+}$  was shown to follow an anion exchange mechanism when extracted in an ionic liquid/aqueous system, in contrast to the cation exchange observed in molecular solvents. Here, changing the lipophilicity of the ionic liquid did not change the partitioning mechanism<sup>[144]</sup>. Recently, the ion exchange theory was also applied to explain the extraction performance of amino acids using a room temperature ionic liquid 1butyl3methylimidazolium hexafluorophosphate with dicyclohexano-18-crown-6 system

[145]. The indication of an ion exchange mechanism is the significant leakage of the dialkylimidazolium cation into the aqueous phase on extraction of amino acids—confirmed by monitoring the corresponding UV band. After extraction of amino acids the clear absorption peak of the dialkylimidazolium cation appeared in the spectrum of the aqueous phase at ca. 300 nm. Increasing the initial amino acid concentration in the aqueous phase from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  mol L<sup>-1</sup> results in an increase of the dialkylimidazolium concentration in water after extraction. Clearly this is caused by ion exchange of the dialkylimidazolium cation with the amino acid cation. Thus, the absence of any appreciable anion effect and distribution of dialkylimidazolium cation into water, which accompanies extraction, strongly suggest that extraction of amino acids with DC<sub>18</sub>C<sub>6</sub> into the ionic liquid is an ion exchange process. However, above all extraction mechanism mode did not consider the extraction functions of the surface charge on the ionic liquid phase and the ionic liquid dissolved in water. In our previous work, the surface tension and Zeta potential of the ionic liquid solution were investigated in detail in order to understand the extraction performance in the room temperature ionic liquid [C<sub>4</sub>tmsim][PF<sub>6</sub>] with CDAA system. It was found the surface tension of the solution decreased with increase of the concentration of [C<sub>4</sub>tmsim][PF<sub>6</sub>] solution, its critical micelle concentration and surface tension of saturated [C<sub>4</sub>tmsim][PF<sub>6</sub>] solution are  $1.59 \times 10^{-3}$  mol L<sup>-1</sup> and 65.95 Nm/m, respectively. The data showed ionic liquid has surface activity, this property allow the ionic liquid to fully interact with the complex or CDAA in aqueous phase and easy to extract the complex into the ionic liquid phase due to micelle extraction function, which is unique property of surfactant. On the other hand, the Zeta potential value of saturated [C<sub>4</sub>tmsim][PF<sub>6</sub>] solution was found to be +2.1mV. The result showed the double electron layer at the [C<sub>4</sub>tmsim][PF<sub>6</sub>] water interface existed the positive charge. The positive charge will produce strong interaction between Hg-CDAA complex or CDAA species and ionic liquid surface. Above two factors allow ionic liquid has a higher the extraction efficiency than ordinary organic solvent. It should be stated that Zeta potential may be positive or negative value for different ionic liquid, that decide various ionic liquid has different extraction performance. In order to test suggested extraction mechanism, the extraction efficiencies of CDAA in different acidity was researched in detail. The result is very interesting that the order of the extraction efficiency of CDAA is in base > neutral > acid medium. Because CDAA is a weak organic acid, its dissociation product three reagent species in water, these are RH<sub>2</sub>, RH<sup>-</sup> and R<sup>2-</sup> respectively, in which CDAA was replaced by RH<sub>2</sub> in order to simple. In strong base solution, reagent specie is R<sub>2</sub> mainly, it is easy to extract into ionic liquid due to its strong negative electric charge, the order accord with suggested extraction mechanism [2]. Recently, professor Yan Yongsheng suggested a new extraction mechanism by use of ionic liquid-salt aqueous two phase system (shown in Fig.7). Aqueous two-phase system consisting of a hydrophilic ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [C<sub>4</sub>mim][BF<sub>4</sub>]) and Na<sub>2</sub>CO<sub>3</sub>, which is a novel, simple, non-toxic and effective sample pretreatment technique coupled with molecular fluorescence spectrophotometry, was developed for the simultaneous separation, enrichment and rapid analysis of roxithromycin. The extraction yield of roxithromycin (ROX) in [C<sub>4</sub>mim][BF<sub>4</sub>]-Na<sub>2</sub>CO<sub>3</sub> is influenced by the types of salts, concentrations of Na<sub>2</sub>CO<sub>3</sub> and [C<sub>4</sub>mim][BF<sub>4</sub>], as well as the extracting temperature. The mechanism of ionic liquid-salt aqueous two-phase system formation was discussed by hydration theory, and the extraction mechanism of the [C<sub>4</sub>mim][BF<sub>4</sub>]-salt was investigated by FT-IR spectroscopy and UV-vis spectroscopy. The results demonstrate that no chemical (bonding) interactions are observed between ionic liquid and roxithromycin (ROX), while the nature properties of the ROX are not altered [146].

It should be pointed the extraction performance of the ionic liquids are very complex due to its complex solvent characteristics, the theory modes concerning extraction mechanism need improve and confirmed by reliable experiments technologies in the future.

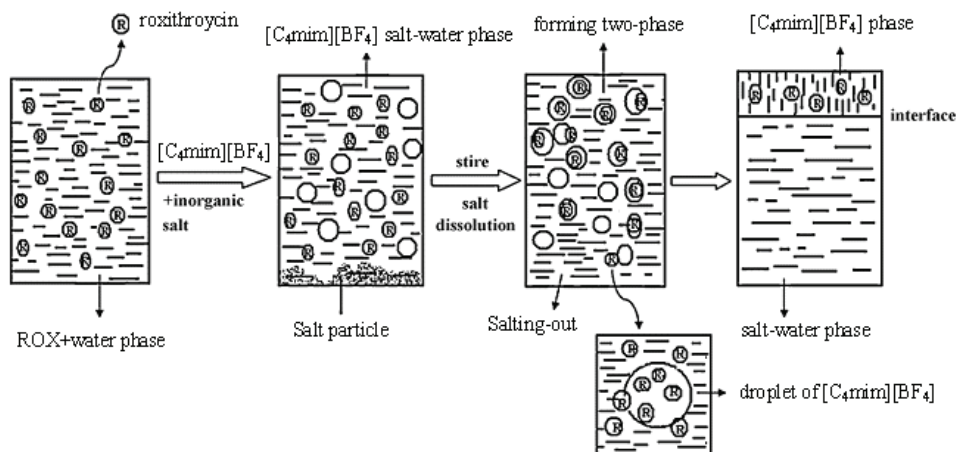


Fig. 7. The schematic diagram of separating ROX in ionic liquid-salt aqueous two phase system

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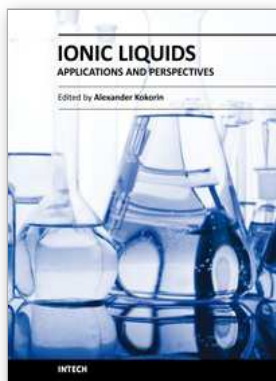


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