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Ionic liquids in microextraction techniques

Review Article

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Abstract: The tremendous potential of room temperature ionic liquids as an alternative to environmentally harmful ordinary organic solvents is well recognized. Due to their unique properties, such as low volatility, tunable viscosity and miscibility, and electrolytic conductivity, ionic liquids have attracted extensive attention and gained popularity in many areas of analytical chemistry including modern sample preparation techniques.

In this review the advantages and limitations of application of ionic liquids as solvents/sorbents for microextraction are critically discussed. Topics covered include solid-phase microextraction, single drop microextraction, dispersive liquid-liquid microextraction and hollow-fiber liquid-phase microextraction. The compatibility of the ionic liquid-based microextraction with different analytical techniques such as gas chromatography, high-performance liquid chromatography, electrothermal or flame atomic absorption spectrometry and some others is also discussed. Finally, the main practical applications on this topic are summarized.

Keywords: *Ionic liquids • Solid-phase microextraction • Single drop microextraction • Hollow fiber-liquid phase microextraction • Dispersive liquid-liquid microextraction*

1. Introduction

Despite the development of highly efficient analytical techniques, most instruments cannot handle complex sample matrices directly and, as a result, a sample preparation step is commonly involved in an analytical procedure. This step gives the ability to isolate the analytes from the matrix, to perform a clean-up of complex samples, as well as to improve the detectability of the analytes. Over the years, it has been realized that, in most cases, the operations associated to sample preparation are the major source of inaccuracy and imprecision on analysis in general, as well as the most time-consuming steps. Ideally, sample preparation techniques should be fast, easy to use, inexpensive, environmentally friendly, compatible with a wide range of analytical instruments, and easy to automate.

Although there are many sample preparation methods that can be used to clean-up and concentrate samples, liquid-liquid extraction and solid-phase extraction remain the most widely used techniques for liquid samples. However, liquid-liquid extraction is time-consuming, tedious, difficult to automate, and uses large amounts of potentially toxic organic solvents that are expensive and cause environmental pollution, health hazards to laboratory personnel and extra operational costs for waste treatment. Although solid-phase extraction uses less solvent than liquid-liquid extraction, the usage can still be considered significant, and usually an extra step of concentrating the extract is required. Another drawback is that the final extract is sometimes incompatible with the analytical technique, so the solvent has to be evaporated and the residue then dissolved in a suitable solvent.

In the past two decades, there has been an increasing and fully justified emphasis on the miniaturization of traditional sample preparation techniques. In this sense, a great effort has been made since the 1990s, when solid-phase microextraction (SPME) appeared as a miniaturized technique directly derived from solid phase extraction [1]. Later on, several liquid-phase microextraction (LPME) techniques such as single drop microextraction (SDME) [2,3], hollow-fiber liquid-phase microextraction (HF-LPME) [4], dispersive liquid-liquid microextraction (DLLME) [5] and some others have been introduced as alternatives to traditional liquid-liquid extraction sample preparation procedures. The main advantages of the miniaturized extraction methods are the high sample throughput, ease of operation, low costs, small sample amounts required and extremely low or even no solvent consumption. However, one of the

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weakest aspects of miniaturized extraction techniques is the limited number of the effective extractants (*i.e.*, fiber coatings for SPME and solvents for LPME).

In recent years, ionic liquids (ILs) have emerged as very attractive alternatives to conventional solvents because of their unique physicochemical properties that depend on the nature and size of their cationic and anionic constituents [6]. These include negligible vapour pressure, high thermal stability, tunable viscosity and hydrophobicity. Furthermore, chemical functionality can be imparted to the IL to promote additional interactions with target compounds. These features of ILs have resulted in a remarkable increase in their use in many academic and industrial fields. In analytical chemistry, ILs are used as alternative solvents in liquid-liquid extraction as well as in spectral and electrochemical analysis, as stationary phases in gas chromatography, as mobile phase additives in liquid chromatography and as carrier electrolytes in capillary electrophoresis. Several reviews on these topics have been published recently [7-10].

The first report on utilization of ILs in microextraction appeared in 2003 [11]. Since then, the potential of ILs as alternative solvents/sorbents for LPME and SPME techniques is intensively investigated. As can be seen in Fig. 1, the number of publications per year on ILs related to microextraction shows an increasing trend, especially during the last four years. Several interesting reviews on ILs in microextraction have appeared recently. In 2010, the utilization of ILs in sorptive microextraction techniques was reviewed by Valcarcel and co-workers [12] and by Sun and co-workers [13]. Later on, Zhao and Anderson [14] provided a brief overview of ILs and highlighted trends in microextraction techniques in terms of performing task-specific extractions using these solvents. Finally, Anderson and co-workers [15] wrote a review focused on the application of ILs and polymeric ILs (PILs) as innovative sorbent materials for SPME.

In this review, we provide a general overview and an update of the last developments of the microextraction techniques in which ILs have been employed as extractants. Topics covered include solid-phase microextraction, single drop microextraction, hollow-fiber liquid-phase microextraction and dispersive liquid-liquid microextraction. In particular, basic principles and modes of each are discussed and a number of selected applications are given to illustrate the merits and drawbacks of each of these.

2. Ionic liquids: a brief overview

ILs are liquids that consist exclusively or almost exclusively of ions. Over the past decade the use of the term “ionic liquids” has generally been limited to the liquids that have melting points below 100ºC. For ILs with melting points at or below room temperature, the term “room temperature ionic liquid” is also often used. Scientific interest in these liquids has started to grow exponentially after discovery of air- and moisture-stable imidazolium salts in 1992 [16]. In most cases, ILs have an organic nitrogen-containing cation (*e.g.* imidazolium, pyridinium, pyrrolidinium) and a halogen-based organic or inorganic anion (*e.g.* chloride, iodide, hexafluorophosphate, methylsulfate, bis(trifluoromethyl) sulfonylimide). The structures of common cations and anions of ILs are shown in Fig. 2. Besides their low melting point, ILs have many other unique physicochemical properties, such as extended liquid-state temperature range, negligible vapour pressure, excellent solvating properties, high electrical conductivity, good thermal stability and low flammability. The physicochemical properties of ILs depend on the nature and size of both their cation and anion constituents. Table 1 lists some data for several ILs most commonly used in microextraction techniques. More detailed information on the properties of ILs can be found in recent review [9] and in references cited therein.

The density of most common ILs is typically greater than that of water but usually declines with increasing

Table 1. Some physicochemical properties of the ILs most commonly used in microextraction (25ºC unless indicated otherwise) [9,17].

IL	Melting point (ºC)	Density (g mL^{-1})	Viscosity (cP)	Water solubility (g per 100 mL)
[C_4MIM][PF_6]	10	1.37	450	1.88
[C_6MIM][PF_6]	-61	1.30	585	0.75
[C_8MIM][PF_6]	-70	1.24	982	0.20
[C_4MIM][NTf_2]	-4	1.43	52	0.80
[C_6MIM][NTf_2]		1.38	71	0.34
[C_8MIM][NTf_2]	-86	1.31	87	0.21
[C_4MIM][BF_4]	-81	1.21	219	Miscible
[C_6MIM][BF_4]	-82	1.20	314 (20ºC)	Miscible

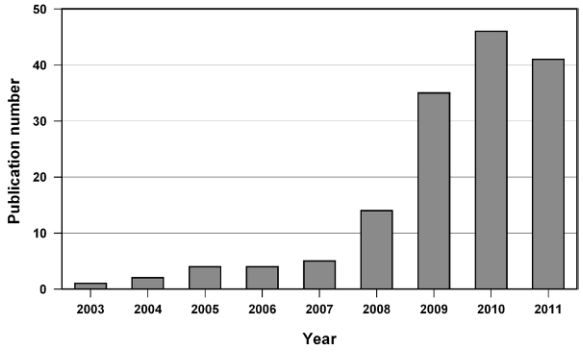

Figure 1. Number of articles published worldwide per year (from 2003 to August 2011) on the subject "ionic liquids and microextraction".

ion size [18]. This property favours rapid settling of the IL phase in phase separation devices used in dispersive liquid-liquid microextraction techniques. Most ILs have relatively high viscosities [19]. This can be of substantial benefit when carrying out single drop microextraction, as the high viscosity facilitates suspending larger drops at the tip of a needle. On the other hand, the precise manipulations with viscous ILs using microsyringes are difficult. Thus, dilution of the IL phase with a miscible solvent before injection into analytical instruments is usually needed, and this has a negative impact to the sensitivity. The water solubility of ILs depends on both the cation and the anion. Therefore, ILs can be designed to be immiscible or miscible with water and a number of organic solvents. Increasing length of alkyl chain on the cation lowers the solubility of ILs containing the same anion. Most of the chloride, bromide, iodide, tetrafluoroborate, trifluoromethanesulfonate ILs are water-soluble. In contrast, hexafluorophosphate, bis(trifluoromethyl)sulfonylimide (NTf_2), tris(pentafluoroethyl)trifluorophosphate (FAP) salts often form two phases with water. Consequently, combinations of different anions and cations make it possible to generate a vast number of different ILs, each with their own specific properties. With all these properties, they are very promising alternatives for traditional organic solvents.

3. Solid-phase microextraction

Solid-phase microextraction developed by Pawliszyn and co-workers in the early 1990s is a miniaturized version of solid-phase extraction [1]. It is a non exhaustive extraction technique based on the partitioning of analytes between the sample matrix and a liquid or solid stationary phase coated on a solid support. The sorption step is followed by desorption of the analytes. This technique is fast, simple and "green", combines sampling and sample preparation into one single step, is portable and thus is especially suitable for field analysis. SPME can be especially easily hyphenated to gas chromatography (GC), however other analytical techniques such as high-performance liquid chromatography (HPLC), supercritical fluid chromatography, capillary electrophoresis (CE), mass spectrometry (MS) and inductively coupled plasma mass spectrometry (ICP-MS) can also be coupled with SPME [20].

A common version of SPME is fiber SPME, where fused-silica fiber or metallic wire is coated with a stationary phase. The fiber can be drawn into a hollow needle by using the plunger on the fiber holder. For extraction, the fiber is pushed out of the hollow needle and immersed into the sample (direct immersion SPME (DI-SPME)) or exposed to its headspace (headspace SPME (HS-SPME)) (Fig. 3). After sorption of the analytes, the fiber is drawn into the needle, the needle is withdrawn from the sample vial and introduced into an analytical instrument for analysis. More recently the other modality of SPME – in-tube SPME, also known as capillary microextraction (CME) was developed [21]. In CME, the retention of the analytes takes place when the sample passes through the capillary column, the inner wall of which is coated with a stationary phase.

The nature of SPME coating plays the main role in the extraction efficiency and selectivity. The coating must be thermally stable in order not to decompose during thermal desorption when SPME is coupled to GC, must be mechanically strong to support agitation of the solution, and must be resistant to chemical media of the sample solution. Currently, only limited number of commercial coatings is available.

In order to enhance extraction selectivity and sensitivity, to expand the applicability of SPME for a wider range of analytes, there is an increasing interest in developing of novel sorbent materials. Since 2005 due to a negligible vapour pressure, good thermal stability and tunable extractability for various compounds, ILs are used as adsorbing coatings for SPME [22]. An extensive review on application of ILs as sorbent materials for SPME is presented by Anderson and co-workers [15]. Table 2 summarizes some representative examples of IL-based SPME technique.

In the simplest version, ILs were used as disposable SPME fiber coatings. Jiang and co-workers [22] were the first to use ILs as disposable SPME fiber coatings in the headspace extraction of benzene, toluene, ethylbenzene and xylenes (BTEXs) from paints. An IL 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) was applied as a SPME coating. The IL was physically adsorbed on a fused silica or stainless steel fiber of a SPME device by dipping the fiber into

Table 2. Representative examples on the use of ILs in SPME.

SPME mode	Analyte	Sample	IL	IL film thickness (μm)	Desorption temp. (°C)	Analytical method	Recovery (%)	LOD	Ref.
HS-SPME	BTEX	Paints	$[C_8MIM][PF_6]$	-	200	GC-FID	70-114	0.1-0.8 mg L^{-1}	[22]
HS-SPME	Methyl tert-butyl ether	Gasoline	$[C_8MIM][BF_4]$	12.7	180	GC-FID	90-95	0.09 μg L^{-1}	[23]
HS-SPME	PAHs	Water	$[C_8MIM][TfO]$	-	240	GC-MS	80-110	29.7-70.0 ng L^{-1}	[24]
HS-SPME	PAHs	Smoke	$[C_4MIM][PF_6]$	30	220	GC-FID	-	-	[25]
HS-SPME	Methamphetamine, amphetamine	Urine	$[EeMIM][NTf_2]$	50	275	GC-MS	89.0-108.9	0.1-0.5 μg L^{-1}	[27]
HS-SPME	Esters, fatty acid methyl esters	Wine	poly($[ViHIM][NTf_2]$)	12-18	250	GC-FID	60.7-111.0	2.5-50 μg L^{-1}	[26]
HS-SPME	Esters, fatty acid methyl esters	Wine	poly($[ViDDIM][NTf_2]$)	12-18	250	GC-FID	58.9-114.0	2.5-51 μg L^{-1}	[26]
HS-SPME	Esters, fatty acid methyl esters	Wine	poly($[ViHDIM][NTf_2]$)	12-18	250	GC-FID	45.1-138.6	2.5-52 μg L^{-1}	[26]
HS-SPME	Alifatic hydrocarbons, fatty acid methyl esters	Water	Poly($[ViHDIM][NTf_2]$)	20	250	GC-FID	69.9-122	0.1-0.6 mg L^{-1}	[28]
DI-SPME	PAHs, substituted phenols	Water	poly($[ViHDIM][NTf]$)	12-16	250	GC-MS	75.8-119	0.005-4.4 μg L^{-1}	[29]
DI-SPME	PAHs	Water	poly($[VBHDIM][NTf_2]$)	10-15	250	GC-FID	-	0.003-0.07 μg L^{-1}	[30]
DI-SPME	PAHs, alkylphenols, and parabens	Water	poly($[VBHDIM][NTf_2]$)	8	250	GC-FID	78.3-109	0.006-7.0 μg L^{-1}	[31]
HS-SPME	Phenols, volatile fatty acids, alcohols	Water	poly($[ViHIM][Cl]$)	13	200	GC-FID	-	0.02-7.5 μg L^{-1}	[32]
HS-SPME	CO_2	Gas	poly($[VHIM][NTf_2]$)	10	250	GC-TC	-	-	[33]
HS-SPME	CO_2	Gas	poly([VHIM][taurate])	10	180	GC-TC	-	-	[33]
HS-SPME	Alcohols, aromatic hydrocarbons	Water	poly($[ViHIM][NTf_2]$) 50%/poly($[ViHIM][Cl]$) 50%	20	160	GC-FID	-	0.4-129 μg L^{-1}	[35]
HS-SPME	Methyl *tert*-butyl ether	Gasoline	$[MTPIM][NTf_2]$	11	220	GC-FID	91.6-95.8	0.1 μg L^{-1}	[36]
DI-SPME	Phenolic environmental estrogens	Water	$[AMIM][N(SO_2CF_3)_2]$	-	360	GC-FID	83.1-104.1	0.0030-0.1248 μg L^{-1}	[41]

the solution of $[C_8MIM][PF_6]$ in dichloromethane for 1 min. Then the analytes were extracted using HS-SPME mode and desorbed in the injection port of GC at 200°C. Finally, IL-coating was washed out from the fiber with solvents. The coating procedure was repeated before every extraction. This disposable IL-coated fiber showed reproducibility comparable with the commercially available SPME fibers, but its sensitivity was lower because of the relatively thin coating.

Later on, four different ILs including 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4MIM][BF_4]$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[C_8MIM][BF_4]$), $[C_8MIM][PF_6]$ and 1-ethyl-3-methylimidazolium ethylsulphate ($[C_2MIM][ETSO_4]$) were synthesized and examined as disposable coatings for the HS-SPME of methyl tert-butyl ether in gasoline samples [23]. $[C_8MIM][BF_4]$ showed the highest extraction efficiency exceeding that of commercial polydimethylsiloxane (PDMS)-divinylbenzene and PDMS/Carboxen fibers. However, at the desorption temperature higher than 180°C, significant loss of the coating occurred.

In order to increase the amount of IL adsorbed on the fiber and thus to enlarge extraction efficiency, Hsieh and co-workers [24] introduced SPME fiber pre-coated with Nafion membrane prior to IL coating. Nafion is a cation exchange polymer. It enhances the quantity and stability of the IL adsorbed on the fiber surface through the electrostatic interaction between IL and the Nafion-supported membrane. Fused silica fiber was immersed into Nafion solution for 30 s. Then Nafion coated fiber was dried in the air for 30 min and immersed into the IL solution in dichloromethane for 1 min. Due to enhanced surface interactions Nafion support produced an even coating of the IL while ILs coated onto the bare silica resulted in a droplet-like coating. IL and Nafion coatings were removed after every analysis by solvents. Three ILs, namely 1-methyl-3-octylimidazolium trifluoromethanesulfonate ($[C_8MIM][TfO]$), 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([BeMIM][TfO]) and 1-methyl-3-phenylpropylimidazolium trifluoromethanesulfonate ([PhproMIM][TfO]), were applied for the fiber coating. Polycyclic aromatic hydrocarbons (PAHs) were selected as target analytes. They were extracted using HS-SPME mode. Desorption was carried out at 240°C for 1.5 min. The results showed that $[C_8MIM][TfO]$ provided the greatest extraction

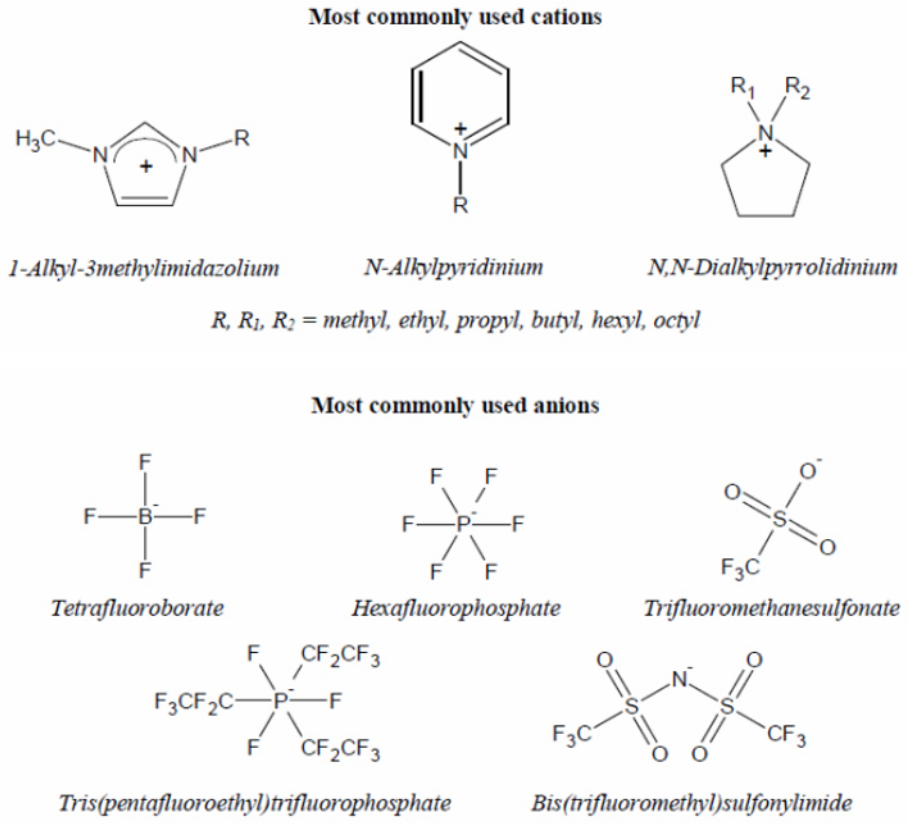

Figure 2. Structures of the cations and anions of the most commonly used ILs.

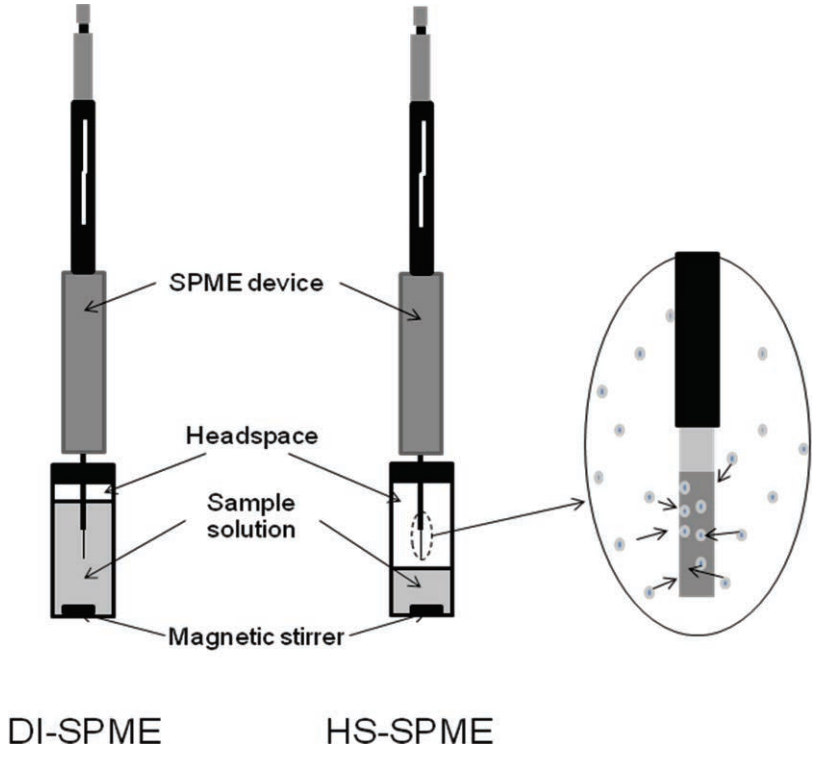

Figure 3. Schematic diagram of SPME.

efficiency. The fibers pre-coated with Nafion could extract two or three times more amount of analytes than those without it.

With the aim to enhance the amount of coated material, Huang and co-authors [25] employed an etched fused-silica capillary for the IL coating. Two ILs, [C_4MIM][PF_6] and [C_8MIM][PF_6], were used as coatings for HS-SPME of PAHs. For comparison, both an untreated fused-silica capillary and one pre-treated with a Nafion were coated with the IL. The etched fibers offered the best extraction efficiencies among the tested fibers.

As the above mentioned SPME coatings are disposable, they have no carryover between the determinations. Due to their liquid nature, the coatings provide high diffusion coefficients and thus fast extraction. The authors also declare much lower cost compared to commercially available SPME fibers due to the small quantities of ILs that were required for coating. On the other hand, the need to recover SPME coating after each extraction is a serious limitation of the practical use of this technique. Moreover, ILs can flow off the fiber easily and even decompose during thermal desorption of the analytes [12,24]. Thus ILs dip into the GC injection port and contaminate the liner, the liner should be constantly cleaned to prevent IL decomposition products to appear as chromatographic ghost peaks [26]. In order to overcome those shortcomings, He *et al.* [27] reported a reusable IL-based SPME fiber prepared by fixing of ILs through cross-linkage of IL-impregnated silicone elastomer on the surface of a fused silica fiber. 1-Ethoxyethyl-3-methylimidazolium bis(trifluoromethyl) sulfonylimide ([EeMIM][NTf_2]) IL was used. IL was trapped and supported by the silicone cross-linkage. The new coating was applied to the headspace GC determination of methamphetamine and amphetamine in human urine samples. The thermal desorption of the analytes was accomplished at 220ºC for 6 min. More than 100 extractions were performed using one single fiber and no decrease in the extraction efficiency was observed.

Polymeric ILs (PILs) based SPME coatings were introduced in 2008 by Anderson and co-workers [26]. The selectivity of PIL-based coatings can be modulated by introducing functional groups to the cationic portion of IL or by incorporating different anions to impart desired solvent characteristics. Three homologous polymeric imidazolium-based IL coatings – poly(1-vinyl-3-hexylimidazolium) bis(trifluoromethyl)sulfonylimide (poly[ViHIM][NTf_2]), poly(1-vinyl-3-dodecylimidazolium) bis(trifluoromethyl)sulfonylimide (poly[ViDDIM][NTf_2]), and poly-1-vinyl-3-hexadecylimidazolium bis(trifluoromethyl)sulfonylimide (poly[ViHDIM][NTf_2]) were synthesized [26]. Halogen anions were exchanged with the bis(trifluoromethyl)sulfonylimide anion with the aim of increasing the thermal stability of the PIL. For coating, fused silica fiber was dipped into the PIL solution in acetone for 20 s and then allowed to dry in the air for 10 min. Prior to extraction, the coated fiber was conditioned at 250ºC for 10 min. Fibers coated with PILs were employed for the extraction of esters and fatty acid methyl esters from wine. The same fiber can be utilized in approximately 150 extractions using desorption temperature of 250ºC.

Meng *et al.* [28] applied poly[ViHDIM][NTf_2] to form a SPME coating for the extraction of high molecular weight aliphatic hydrocarbons and fatty acid methyl esters. Later on, the suitability of poly[ViHDIM][NTf_2] PIL for the DI-SPME of PAHs and substituted phenols was demonstrated by Lopez-Darias and co-workers [29]. These coatings exhibited exceptional thermal stability as well as film stability, thereby producing high extraction-to-extraction reproducibility and lifetimes comparable to commercially coated fibers.

A new generation PIL, poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis(trifluoromethyl)sulfonylimide (poly[ViBHDIM][NTf_2]), was synthesized by Meng and Anderson [30]. This PIL was functionalized with benzyl groups capable of imparting π-π interactions. Due to enhanced π-π interactions and high hydrophobicity, poly[ViBHDIM][NTf_2] exhibited high selectivity towards PAHs from aqueous samples when used as a sorbent coating in DI-SPME. It was demonstrated, that the benzyl-functionalized poly[ViBHDIM][NTf_2] PIL exhibited higher extraction efficiency compared to PIL lacking such functionalization as well as to commercial PDMS sorbent coating. In addition, the poly[ViBHDIM][NTf_2] coating exhibited long lifetimes. One fiber was used with no significant loss of extraction efficiency up to 70 extraction/desorption steps when desorption was carried out at 250ºC for 5 min.

Lopez-Darias and co-workers [31] applied poly[ViBHDIM][NTf_2] as a SPME coating to determine a group of 14 endocrine disrupting chemicals, including PAHs, alkylphenols, and parabens in water samples. The PIL fiber (12 μm) was superior to commercial PDMS (30 μm) and polyacrylate (85 μm), in spite of its lower coating thickness.

Meng *et al.* [32] employed poly(1-vinyl-3-hexylimidazolium chloride) (poly[ViHIM][Cl]) as a coating material for SPME of polar compounds including phenols, volatile fatty acids and alcohols. For comparison purposes, a PIL containing the same cation but paired with NTf_2^- anion was also used to extract the same analytes. The results showed that the poly[ViHIM][Cl] PIL coating had higher selectivity towards more polar analytes due to the presence of the Cl^- anion

which provides higher hydrogen bond basicity than the NTf_2^- anion.

Incorporation of functional groups into a PIL can produce task-specific SPME coatings. Zhao *et al.* [33] synthesized and employed two coatings - poly[ViHIM][NTf_2] and poly[ViHIM][taurate] - as sorbents in SPME for the selective extraction of CO_2. Different functional groups in the PILs were responsible for different mechanisms of CO_2 capture, namely, physical sorption by poly[ViHIM][NTf_2] coating and carbamate formation by poly[ViHIM][taurate] coating. The poly[ViHIM][NTf_2] PIL fiber exhibited comparable extraction efficiency to that of the commercial Carboxen-PDMS fiber even though the PIL-based fiber possessed much smaller film thickness (poly[ViHIM][NTf_2] PIL coating 10 µm and Carboxen-PDMS coating 75 µm). Due to the ability to chemically react and sequester CO_2, the poly[ViHIM][taurate] coating exhibited enhanced storage capacity of CO_2 compared to poly[ViHIM][NTf_2] and Carboxen-PDMS coatings.

The effect of humidity and temperature on the extraction efficiency of CO_2 using poly[ViHIM][NTf_2] and poly[ViHIM][taurate] IL coatings and commercial Carboxen-PDMS coating was examined by Zhao and Anderson [34]. It was demonstrated that poly[ViHIM][taurate] coating exhibited the lowest sensitivity drop in the presence of water vapour. Also, poly[ViHIM][NTf_2] coating was found to possess higher CO_2/CH_4 and CO_2/N_2 selectivities compared to Carboxen-PDMS fiber.

Recently, coatings based on mixtures of PILs have been proposed for SPME [35]. Four PILs based on two different cations, poly[ViHIM] and poly[ViHDIM], combined with two different anions, NTf_2^- and Cl^-, were combined in various weight percentages and used as SPME coatings. It was found that the selectivity of the SPME coating for hydrogen-bonding analytes can be varied by adjusting the percentage of the two different anions in the mixture, as with the increase of chloride anion percentage in the mixture, the hydrogen bond basicity of the PIL increases. Thermal stability of PIL-based coatings containing chloride ion was lower due to thermal volatilization of the chloride containing PILs. The most robust coating was observed for the poly[ViHDIM][NTf_2] PIL (over 200 extractions).

Amini and co-workers [36] suggested a chemically bonded IL-coated fiber. The 1-methyl-3-(3-trimetoxysilylpropyl)imidazolium bis(trifluoromethyl) sulfonylimide ([MTPIM][NTf_2]) was synthesized and cross linked to the surface of fused-silica fiber by refluxing the system with fused-silica fiber and 5% [MTPIM][NTf_2] solution for 24 h under nitrogen atmosphere. Methyl *tert*-butyl ether extraction efficiency of the chemically bonded fiber was compared with that of the physically bonded fiber using the same IL. The chemically bonded fiber has better thermal stability and durability than the physically bonded one (220ºC and 180ºC; 16 and 1 extractions, respectively).

Wanigasekara *et al.* [37] suggested to bond dicationic ILs and styrene-based PILs onto silica particles. ILs were previously derivatized to obtain reagents that are able to react with a silica support. The particles with the bonded moieties were used as adsorbents in HS-SPME and DI-SPME of short chain alcohols and amines. All the coatings were declared to be very durable at 220ºC and even when desorption temperature was raised to 250ºC.

Sol-gel technology is a simple and convenient method for the preparation of SPME fibers through *in-situ* synthesis of surface-bonded sol-gel hybrid organic-inorganic coatings. Those coatings for in-tube SPME were introduced in 2002 [38]. The coatings are advantageous because they are chemically anchored to the fused silica fiber, thus are stable to high temperature and harsh solvents. An extensive review on sol-gel microextraction phases for sample preconcentration in chromatographic analysis is presented in [39].

Recently, ILs have been employed in the preparation of sol-gel materials in which ILs serve as solvents, pore templates, drying control chemical additives and catalysts. It was reported, that ILs reduced cracking and shrinking of sol-gel coatings. For the first time, IL-mediated sol-gel materials for CME of nonpolar and moderately polar analytes were suggested in 2009 [20]. The effects of the addition of trihexyltetradecylphosphonium tetrafluoroborate (TTPT) and N-butyl-4-methylpyridinium tetrefluoroborate (BMPT) on the physical characteristics and CME performance of PDMS, poly(ethylene glycol), poly(tetrahydrofuran), and bis[(3-methyldimethoxysilyl) propyl] polypropylene oxide sol-gel coatings were studied. ILs played a role of co-solvents and porogens. However, ILs did not play a role in extractions, since IL-mediated sol-gel coatings were heated to the temperature higher than that of the thermal decomposition of ILs. During thermal conditioning ILs were decomposed and the decomposition products were removed from the capillary with the purging helium flow. Any remaining decomposition products were further removed during the rinsing step. The IL-mediated sol-gel coatings prepared with silanol-terminated polymers provided up to 28 times higher extraction efficiencies compared to analogous sol-gel coatings prepared without any IL in the sol solution. The IL-mediated sol-gel coatings prepared with C-OH terminated polymers provided lower efficiencies compared to their IL-free counterparts. This shows that IL-generated porous morphology alone is not enough to provide effective extraction. Effective chemical bonding

of the organic polymer to the created sol-gel material is also necessary.

The use of two ILs, trihexyltetradecylphosphonium tetrafluoroborate and 1-methyl-3-octylimidazolium chloride to create a surface-bonded organic-inorganic hybrid sol-gel coatings for CME is described by Shearrow *et al.* [40]. Bis[(3-methyldimethoxysilyl) propyl] polypropylene oxide was used to prepare polar sol-gel coatings and poly(dimethyl-co-diphenylsiloxane) was used to prepare nonpolar ones. The IL-mediated sorbents provided more efficient extractions and lower detection limits compared to analogous sol-gel coatings prepared without IL. Individual ILs affected the porosity of sol-gel materials in different degrees. The trihexyltetradecylphosphonium tetrafluoroborate-mediated bis[(3-methyldimethoxysilyl)propyl] polypropylene oxide sol-gel coating was thermally stable up to 330ºC, was solvent resistant and had a high affinity to polar and moderately polar analytes with a fast attainment of extraction equilibrium (10-15 min).

The higher extraction efficiency of above mentioned surface-bonded sol-gel hybrid organic-inorganic coatings is attributed to their higher porosity in comparison with the analogous sol-gel coatings prepared without ILs.

The further attempts to improve the extraction efficiency led to the development of chemically bonded IL-based organic-inorganic hybrid SPME coatings [41,42]. Two allyl-functionalized ILs, 1-allyl-3-methylimidazolium hexafluorophosphate ([AMIM][PF_6]) and 1-allyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ([AMIM] [NTf_2]), were employed as coating materials to prepare chemically bonded ILs-based organic-inorganic hybrid SPME coatings [41]. These fibers were prepared with the aid of γ-methacryloxypropyltrimethoxysilane as bridge using sol-gel method and free radical cross-linking technology. Sol-gel IL-hydroxyterminated silicone oil coatings were created. Thanks to the strong chemical binding between ILs and the formed silica substrate, ILs introduced can be retained in coating during the thermal and solvent desorption, leading to high selectivity and sensitivity towards strong polar phenolic environmental estrogens and aromatic amines. Using thermogravimetric analysis and differential thermal gravimetric curves it was determined that the removal of chemically bonded ILs occurred at 320ºC and 402ºC for coatings with [AMIM][PF_6] and [AMIM] [NTf_2] respectively. Thus, after the thermal conditioning at 280ºC ([AMIM][PF_6]) and 360ºC ([AMIM][NTf_2]), the ILs remained in the coating. These coatings exhibited porous surface structure, high thermal stability, good solvent resistance, a wide pH use range (pH 0-14), good coating preparation repeatability and high selectivity for strongly polar phenolic environmental estrogens and aromatic amines.

As extraction efficiency and selectivity can be strongly influenced by functionalization of ILs with different groups, a novel crown ether functionalized IL, 1-allyl-3-(6'-oxo-benzo-15-crown-5 hexyl) imidazolium hexafluorophosphate was synthesized and used to prepare IL-based SPME fibers by sol-gel method and free radical crosslinking technology [42]. Due to the unique properties of both, IL and benzo-15-crown-5 functional group, this coating exhibited high thermal stability (up to 340ºC), wide pH use range, and good solvent resistance. For polar and medium polar compounds, such as alcohols, phthalate esters, phenolic environmental estrogens, fatty acids and aromatic amines the extraction performance of this coating was superior to that of identically prepared coatings described in [41].

4. Single drop microextraction

Single drop microextraction was suggested in 1996 [3]. It is based on the distribution of the analytes between the sample and a microdrop of solvent that is suspended in the tip of a microsyringe needle. The solvent drop can be directly immersed in the aqueous sample (direct immersion SDME (DI-SDME)) or in the headspace (headspace SDME (HS-SDME)) for a determined time. After extraction, the drop is retracted and transferred to the analytical instrument for analysis. SDME requires very small volumes of solvents (1-3 μL), is fast, inexpensive, can be performed with the simplest device, a conventional microsyringe. Schematic diagrams of DI-SDME and HS-SDME systems are presented in Fig. 4. Detailed description of the different SDME approaches can be found in the review articles [43-45].

Since recently, organic solvents have been commonly applied for SDME. However, because of the low viscosity, high vapour pressure, and low surface tension of many organic solvents, the stability of the droplet is often limited. ILs are an attractive alternative to the conventional organic solvents. High viscosity of ILs enables the formation of larger drops. Low vapour pressure prevents the evaporation of the solvent during the extraction from the headspace. Immiscibility of some ILs with water avoids partial dissolution of the solvent in the case of direct immersion SDME. Combining different cations and anions, ILs for task-specific extractions can be easily obtained. ILs-based SDME is compatible with different analytical determinations: HPLC, CE, AAS, GC.

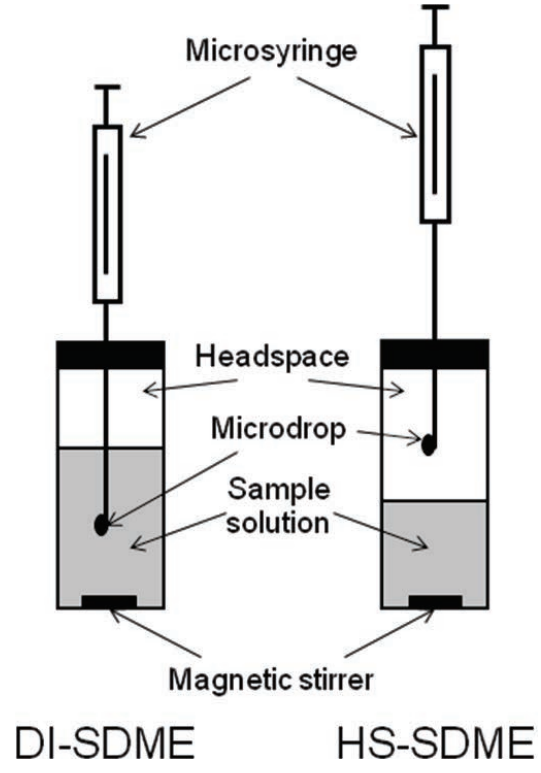

Figure 4. Schematic diagram of SDME.

HPLC is the most used of these detection techniques coupled with IL-based SDME as ILs have short retention times in reversed-phase HPLC, typically elute near the dead volume and thus are easily separated from the analytes peaks. Coupling of IL-based SDME to HPLC does not require any interface or modification of equipment.

For the first time, ILs as extracting solvents in SDME were applied in 2003 [11]. Liu and co-authors for PAHs extraction from water examined three ILs, namely, $[C_4MIM][PF_6]$, 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) and $[C_8MIM][PF_6]$ and suggested $[C_8MIM][PF_6]$ as the best one for both, DI-SDME and HS-SDME extraction modes. For low volatility PAHs, DI-SDME provided higher enrichment factors than HS-SDME. Contrarily, for the most volatile PAH, naphthalene, extraction efficiency was much better using HS-SDME. For all the analytes extraction efficiency was better than that obtained using 1-octanol as extracting solvent. Table 3 summarizes some representative examples of IL-based SDME technique.

A larger solvent drop gives a higher signal response but it is difficult to manipulate with large drops, they can easily detach from the needle tip. In order to maximize the contact area between the needle and the drop and thus to increase the volume of the drop, the tip of the microsyringe needle was sheathed with a 3-mm-long silicon rubber tube [11]. The same principle of the sheathing of the needle was also used in [46-55]. ILs drop volumes were 4-10 µL. Zhou and Ye [56] fitted the microsyringe needle with a small bell-mouthed device which enabled to perform HS-SDME using 20 µL of IL.

Liu and co-workers [46] applied $[C_6MIM][PF_6]$ IL for DI-SDME of 4-nonylphenol and 4-*tert*-octylphenol. The method sensitivity was analyte dependant. Compared to 1-octanol, higher sensitivity was obtained for 4-*tert*-octylphenol and lower for 4-nonylphenol. $[C_4MIM][PF_6]$ IL was employed for HS-SDME of chloroanilines [47] and organochlorine pesticides [48] in environmental water samples. Liu *et al.* [49] demonstrated that two typical ILs, $[C_4MIM][PF_6]$ and $[C_8MIM][PF_6]$ can effectively extract environmental pollutants such as BTEX, PAHs, phthalates, phenols, aromatic amines, herbicides, organotin and organomercury species. 1-Alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM][PF_6]$) IL-based SDME coupled with HPLC was applied for the determination of a wide range of compounds: formaldehyde [50], benzophenone-3 [51], chlorobenzenes [52], tributyltin and triphenyltin [53], UV filters [54], phenols [55], amines [56].

The majority of IL-based SDME-HPLC applications deal with the extraction of organic compounds. However, there are some applications for inorganic analytes. DI-SDME using $[C_6MIM][PF_6]$ IL was applied for the determination of mercury species in water samples [57]. Prior to the extraction mercury species were derivatized to corresponding dithizonates. Derivatization with 2,4-dinitrophenylhydrazine was also required prior to the DI-SDME of carbonyl compounds in environmental water samples [58].

Sarafraz-Yazdi and Mofazzeli [59] modified traditional SDME technique and called it submerged SDME. A 15 µL drop of IL $[C_6MIM][PF_6]$ was injected at the conical bottom of the glass tube under the sample solution. Then, the glass tube was sonicated for 3 min. Finally, the drop of the IL including target compounds was withdrawn by a microsyringe and 7 µL of the drop was injected into HPLC system. The method was applied for the determination of aromatic amines in environmental water samples. Submerged SDME presented lower detection limits, better repeatability and lower extraction time than conventional SDME carried with the same IL.

In all above mentioned publications PF_6-based ILs were used for SDME. However, PF_6-based ILs can partially dissolve in aqueous solutions when long extraction times in DI-SDME are applied. To overcome this shortcoming, more hydrophobic and hydrolytically stable ILs containing tris(pentafluoroethyl) trifluorophosphate (FAP) anion were examined for DI-SDME of PAHs [60]. The anion was paired with

Table 3. Representative examples on the use of ILs in SDME.

SDME mode	Analyte	Sample	IL	IL volume	Analytical method	EF	Recovery (%)	LOD	Ref.
DI-SDME	PAHs	Water	$[C_8MIM][PF_6]$	3 μL	HPLC-VWD-FLD	42-166	-	-	[11]
DI-SDME	Phenols	Water	$[C_6MIM][PF_6]$	10 μL	HPLC-FLD	130-163	90-113	0.3-0.7 μg L^{-1}	[46]
HS-SDME	Chloroanilines	Water	$[C_4MIM][PF_6]$	10 μL	HPLC-PDA	81.9-99.6	81.9-99.6	0.5-1.0 μg L^{-1}	[47]
DI-SDME	Formaldehyde	Mush-room	$[C_4MIM][PF_6]$	10 μL	HPLC-DAD	-	80-102	5 μg L^{-1}	[50]
HS-SDME	Organochlorine pesticides	Water	$[C_4MIM][PF_6]$	10 μL	HPLC-UV	-	86.8-102.6	0.05-0.08 μg L^{-1}	[48]
DI-SDME	Benzophenone	Urine	$[C_6MIM][PF_6]$	5 μL	HPLC-PDA	-	-	1.3 μg L^{-1}	[51]
HS-SDME	Chloroanilines	Water	$[C_4MIM][PF_6]$	5 μL	HPLC-PDA	-	60.8-120.6	0.102-0.203 μg L^{-1}	[52]
HS-SDME	Phenols	Water	$[C_4MIM][PF_6]$	10 μL	HPLC-UV	17.2-160.7	89.4-114.2	0.3-0.5 μg L^{-1}	[55]
HS-SDME	Aromatic amines	Water	$[C_4MIM][PF_6]$	15 μL	HPLC-UV	13.7-150.8	81.9-99.1	0.09-0.38 μg L^{-1}	[56]
HS-SDME	Organotin	Water	$[C_4MIM][PF_6]$	10 μL	HPLC-FLD	-	86.9-92.1	0.62-0.95 μg L^{-1}	[53]
DI-SDME	Hg species	Water	$[C_6MIM][PF_6]$	4 μL	HPLC-PDA	3.0-31	83-123	1.0-22.8 μg L^{-1}	[57]
DI-SDME	Aromatic amines	Water	$[C_6MIM][PF_6]$	15 μL	HPLC-UV	132.4-186.5	81.7-97.9	1.0-2.5 μg L^{-1}	[59]
DI-SDME	Carbonyl compounds	Water	$[C_8MIM][PF_6]$	10 μL	HPLC-UV	70-150	84.2-106.9	0.04-2.03 μg L^{-1}	[58]
DI-SDME	UV filters	Water	$[C_6MIM][PF_6]$	10 μL	HPLC-UV	8-98	92-115	0.06-0.19 μg L^{-1}	[54]
DI-SDME	PAHs	Water	$[C_6MIM][FAP]$	10 μL	HPLC-UV	-	79-114	0.1-0.6 μg L^{-1}	[60]
DI-SDME	Colchicine	Water	$[C_4MIM][PF_6]$	2.40 nL	CE	41	98.8-102.4	0.25 mg L^{-1}	[63]
DI-SDME	Phenols	Water	$[C_4MIM][PF_6]$	2.40 nL	CE	93.5-110.9	107-257	0.005-0.5 mg L^{-1}	[62]
HS-SDME	Trihalomethanes	Water	$[C_8MIM][PF_6]$	2 μL	IMS	-	-	0.1-0.9 μg L^{-1}	[64]
CF-SDME	Co, Hg, Pb	Water	$[C_4MIM][PF_6]$	2.5 μL	ETV-ICP-MS	50-350	98.0-108.7	1.5-9.8 ng L^{-1}	[65]
DI-SDME	Pb	Water	$[C_4MIM][PF_6]$	7 μL	ETAAS	76	-	0.015 μg L^{-1}	[66]
DI-SDME	Mn	Water	$[C_4MIM][PF_6]$	4 μL	ETAAS	30.3	-	0.024 μg L^{-1}	[67]
HS-SDME	Dichloromethane, p-xylene, n-undecane	Water	$[C_4MIM][PF_6]$	2 μL	GC-MS	-	-	5.6-15.6 μg L^{-1}	[69]
HS-SDME	BTEX	Water	$[C_8MIM][PF_6]$	2 μL	GC-MS	-	88.9-103.1	22-91 ng L^{-1}	[70]
HS-SDME	Trihalomethanes	Water	$[C_8MIM][PF_6]$	2 μL	GC-MS	-	91.6-101.7	0.5-0.9 μg L^{-1}	[71]
HS-SDME	Phenols	Water	$[C_8MIM][PF_6]$	1 μL	GC-FID	35-794	81-111	0.1-0.4 μg L^{-1}	[72]
HS-SDME	Organochlorine pesticides	Soil	$[C_4MIM][PF_6]$	1 μL	GC-ECD	-	-	0.1-0.5 μg kg^{-1}	[73]
HS-SDME	Chlorobenzenes	Water	$[C_8MIM][PF_6]$	1 μL	GC-FID	41-127	-	0.1-0.5 μg L^{-1}	[74]
HS-SDME	Chlorobenzenes	Water	$[C_6MIM][PF_6]$	5 μL	GC-MS	-	90-115	1-4 ng L^{-1}	[75]
HS-SDME	Dichlorobenzenes	Soil	$[C_4MIM][PF_6]$	4 μL	GC-FID	-	-	0.001-0.002 mg kg^{-1}	[76]
HS-SDME	Aromatic compounds	Water	$[C_4MIM]$ $[Cl]$-SDS	6.5 μL	HPLC-UV	-	-	0.3-260.3 μg L^{-1}	[61]
HS-SDME	Aromatic compounds	Water	$[C_4MIM]$ $[Cl]$-$[C_{10}MIM]$ $[Br]$	6.5 μL	HPLC-UV	-	-	0.1-260.3 μg L^{-1}	[61]

imidazolium, phosphonium and pyrrolidinium cations. For compounds with high molecular weight and fused rings the highest enrichment factors were obtained with the trihexyl(tetradecyl) phosphonium FAP IL. Better extraction efficiency of smaller, more polar molecules was obtained using $[C_6MIM][FAP]$ IL.

Micellar systems gain an increasing attention as extraction media as the extraction efficiencies of those systems are often superior to that of commonly used organic solvents. In an effort to increase extraction sensitivity and selectivity, Anderson and co-workers [61] examined micellar IL extraction solvents. Two different micellar solutions were formed by dissolving 1-decyl-3-methylimidazolium bromide ($[C_{10}MIM][Br]$) IL and traditional surfactant sodium dodecyl sulphate (SDS) in $[C_4MIM][Cl]$ IL and applied as extraction solvents for the extraction of 17 aromatic compounds. As the surfactants and $[C_4MIM][Cl]$ are water miscible, HS-SDME extraction mode was applied. Compared to the neat $[C_4MIM][Cl]$ IL, for all the analytes an increase in extraction efficiency was observed using $[C_4MIM][Cl]$-SDS and $[C_4MIM][Cl]$-$[C_{10}MIM][Br]$ micellar systems. For $[C_4MIM][Cl]$-SDS the detection limits decreased 1.3-3.4 times and for $[C_4MIM][Cl]$-$[C_{10}MIM][Br]$ - 1.2-5.0 times compared to the neat $[C_4MIM][Cl]$ IL extraction solvent.

Only two publications deal with IL-based SDME followed by capillary electrophoresis. Wang and co-authors [62] for the first time described IL-based SDME on-line coupled with CE for phenols determination in water samples. A drop of IL was formed at the end of the capillary of CE equipment. For CE very small volume of the sample is needed, thus 2.40 nL microdrop of IL was used. All the manipulations with the drop were accomplished automatically using a pressure. Three ILs including $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ were compared as extraction solvents for DI-SDME of

phenols. [C_4MIM][PF_6] had the best extraction efficiency as its viscosity was the lowest and thus the diffusion of the analytes into the drop was fast. Additionally, [C_6MIM][PF_6] and [C_8MIM][PF_6] dissolved slowly in buffer during CE analysis and thus the separation process was impeded. It was demonstrated that IL suspension at the tip of the capillary is much more stable than that of common organic solvents.

The same group of researchers applied the above mentioned principle of online coupling of IL-based DI-SDME with CE for the determination of alkaloid colchicine in Lanzhou lily sample [63]. Prior to the DI-SDME, colchicine from the lily sample was extracted with distilled water in an ultrasonic bath.

Valcarcel and co-workers [64] for trihalomethane determination suggested a combination of IL-based SDME with an ion-mobility spectrometer (IMS). In order to avoid that IL enters IMS, an injection unit was designed. In it IL was retained in glass wool and the analytes were transferred towards the detector using nitrogen as carrier gas.

The applicability of IL-based SDME coupled to atomic absorption spectrometry (AAS) has focused on the determination of metals. Liu *et al.* [49] applied [C_4MIM][PF_6] and [C_8MIM][PF_6] ILs for DI-SDME of organotin compounds. Before AAS, the ILs were diluted with methanol. In the same publication, for the determination of organomercury compounds, DI-SDME followed by cold-vapour atomic fluorescence spectrometric detection is described [49]. Before detection, IL drop with concentrated organomercury was added to an acidic potassium permanganate and heated to oxidize to inorganic mercury.

Xia and co-workers [65] employed [C_4MIM][PF_6] IL as extraction solvent for cycle-flow-single-drop microextraction of Co, Hg and Pb in biological and environmental samples. In this extraction mode, the sample solution flows around the IL drop in order to increase extraction efficiency. The extractant was analyzed by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) equipped with a modified commercially available graphite furnace as electrothermal vaporizer of the analytes.

The IL [C_4MIM][PF_6] was also employed for SDME of lead after it was complexed with ammonium pyrrolidinedithiocarbamate [66] and of manganese after it was complexed with 1-(2-thiazolylazo)-2-naphthol [67]. Martinis *et al.* [68] for SDME of lead used tetradecyl(trihexyl)phosphonium chloride IL. Before the extraction, lead was chelated with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. The analytes were determined by electrothermal AAS (ETAAS). IL drop with the extracted complex was directly injected into the graphite furnace. In order to increase IL drop volume, the tip of microsyringe needle was inserted into a 3 mm plastic tube and several grooves were created in the inner surface of the tube [66].

Because of the low volatility of ILs, they are incompatible with direct injection in GC as the presence of ILs dirties the chromatograph and even blocks the analytical column. On the other hand, a proper coupling of IL-based SDME with GC is advantageous, since the interference of highly intense organic solvent peaks can be avoided allowing the determination of a wide range of analytes with different polarities and boiling points.

For the first time, IL-based SDME was coupled with GC in 2008 [69]. For this purpose, a removable interface was developed. The interface enabled the introduction of the extracted analytes into the GC system, avoiding the entering of IL in the column. The interface consisted of three main components: an injection zone, a removable unit and a transfer line and is connected to the carrier gas line. The removable unit was packed with clean cotton. After the extraction, the IL containing the extracted analytes was introduced into the interface. The interface was kept at elevated temperature sufficient to achieve complete volatilization of the analytes but too low for IL decomposition. After the injection, IL was retained in the cotton while the volatilized analytes were transferred into the GC inlet. The removable unit was substituted by a clean one every five injections. Three analytes of different nature, *i.e.*, dichloromethane, p-xylene and *n*-undecane, were selected in order to evaluate the applicability of the proposed interface. [C_4MIM][PF_6] IL was applied as an extractant for HS-SDME. It was demonstrated that using the interface the analytes were properly volatilized and efficiently separated in the GC column. The IL did not get into the chromatographic column and thus did not show any peak in the chromatogram. The absence of the solvent peak facilitated the separation of the analytes and shortened the time needed for GC analysis. Thus, the analytes of an extensive range of polarity and volatility could be determined. The same group of researchers demonstrated the applicability of the interface for coupling HS-SDME and GC for determination of BTEX [70] and halogenated hydrocarbons [64,71] in water samples.

Another alternative to make IL-based SDME compatible with GC was suggested by Zhao and co-workers [72]. After extraction they exposed a drop of IL with the dissolved analytes in the injection port of GC. The analytes were desorbed and the involatile IL was withdrawn into the microsyringe. To facilitate the withdrawal of IL the upper diameter of the inlet liner of GC instrument was enlarged. In order to retain the fall-off IL, some glassy wool was placed in the liner. The

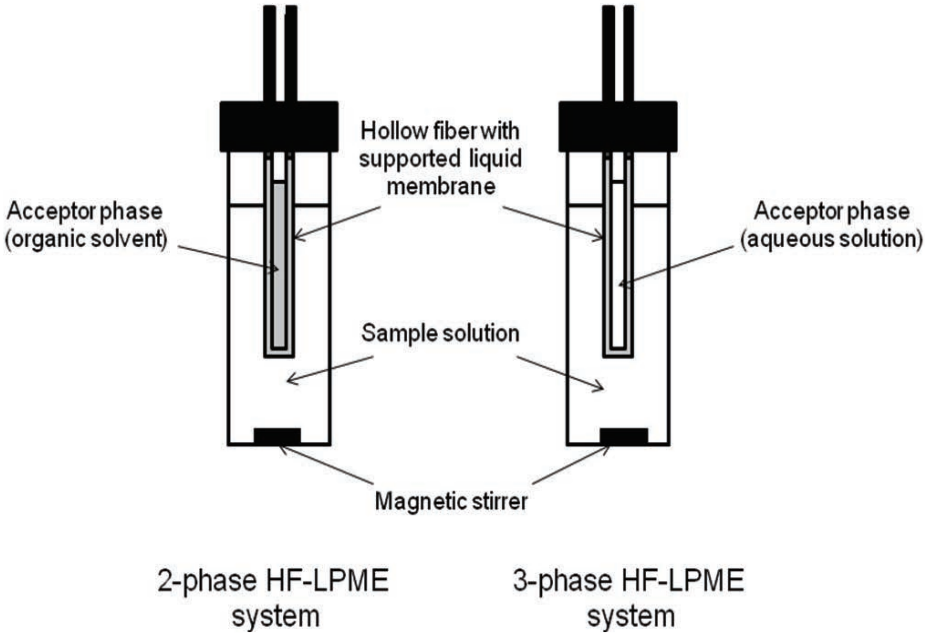

Figure 5. Schematic illustration of HF-LPME.

system using [C_8MIM][PF_6] IL as an extraction solvent was applied for determination of phenols in water samples. A similar approach was also proposed for HS-SDME of organochlorine pesticides in soil samples [73]. Unfortunately, it is not mentioned in the publications how often inlet liner should be cleaned and how often glassy wool should be changed.

In order to avoid IL leaking into the chromatographic column, Zhao *et al.* placed in the injection block a small glass tube [74]. The glass tube incepted the IL drop when it was not successfully retracted. When the glass tube was full, it was replaced or the IL was taken out with a syringe. To evaluate the proposed method five chlorobenzene derivatives were extracted using [C_8MIM][PF_6] IL for HS-SDME.

Chisvert and co-authors [75] for coupling of IL-based SDME and GC determination employed a commercially available thermodesorption unit in which a two-tubes concentrically disposed system made up of outer thermal desorption tube, inner glass Pyrex tube and glass wool was placed. After SDME, an IL drop was injected into the inner tube which was placed inside the outer tube that was fitted with glass wool. The whole device was placed inside a commercial thermodesorption system for thermal desorption of the analytes. After analysis, the outer tube was removed from the thermodesorption system and the glass wool and the Pyrex tube were replaced by the new ones. The proposed approach prevented IL from entering GC system and employed commercially available instrumentation. Additionally, larger volumes of the IL could be injected without a need of disassembling the inlet of GC. The proposed approach was tested for determination of chlorobenzenes in water samples.

Considering the above mentioned efforts to prevent ILs entering into GC column and thereby to avoid serious contamination of GC system, it is surprising that in [76] direct injection of [C_4MIM][PF_6] IL into the GC is described and the contamination of GC system is not noticed.

5. Hollow-fiber liquid-phase microextraction

In conventional SDME, a small organic solvent drop held at the needle tip can be unstable, and may dislodge during extraction. In order to eliminate this problem, hollow-fiber liquid-phase microextraction technique was proposed in 1999 by Pedersen-Bjergaard and Rasmussen [4]. In this technique, a piece of a polypropylene hollow fiber, containing an acceptor solution in its lumen, is immersed in a vigorously stirred aqueous sample solution for the extraction of target analytes. After extraction, the acceptor solution is removed by a microsyringe and further analyzed by appropriate analytical technique. The schematic illustration of HF-LPME device is shown in Fig. 5. HF-LPME can be performed both in a two-phase and three-phase modes. In the two-phase mode, the water immiscible organic solvent is used to fill both the wall pores and the hollow fiber lumen. This mode suites for the extraction of hydrophobic analytes. In

the three-phase mode, analytes are extracted from the aqueous sample solution through the water immiscible organic solvent immobilized in the pores of the hollow fiber into aqueous acceptor phase present inside the lumen of the hollow fiber. In this case the analytes must be able to exist in two forms: in a nonionic form on the sample side to be extracted into the membrane and in an ionic form on the acceptor side in order to be irreversibly trapped. This is usually achieved by pH adjustments in the two aqueous phases. The method is, therefore, particularly well suited for ionizable analytes such as weak acids and bases. The volume of sample in HF-LPME ranges between several hundred µL and more than 1 L, whereas the volume of acceptor solution in most cases is in the range 2-25 µL. Compared with SDME, HF-LPME enables the use of larger extractant volumes and provides higher enrichment factors. In addition, it is also less prone to matrix effects because high molecular mass compounds cannot pass through the membrane. Finally, HF-LPME may easily be on-line coupled to chromatography and other analytical techniques. One of the main drawbacks of this technique is relatively long extraction time. Extraction time required to reach equilibrium ranges between 15 and 45 min for sample volumes below 2 mL, whereas for 1 L samples even 2 h may be required. For excellent reviews on HF-LPME and its applications, the reader should consult references [77,78].

The requirements for the organic solvent are low volatility and immiscibility with water as well as good extraction efficiency and suitable mass transfer properties for the analytes. Rather few organic solvents (*e.g.* toluene, 1-octanol, *n*-dodecane and some others) are currently used as solvent barriers (supporting solvents)/acceptor phases and this restricts the range of possible applications for this technique.

The first application of ILs in HF-LPME was described by Peng and co-workers in 2007 [79]. They developed IL supported three-phase HF-LPME mode coupled with HPLC-UV to determine four chlorophenols in environmental water samples. $[C_8MIM][PF_6]$ ionic liquid was immobilized in the pores of a polypropylene hollow fiber and an alkaline aqueous solution was used as acceptor phase. The analytes were extracted with recoveries ranging from 70.0 to 95.7% using 60 min extraction time and 15 mL of sample solution containing 5 µg L^{-1} of each analyte. The LODs obtained were in the range 0.5-1.0 µg L^{-1}.

Basheer and co-workers published a related study [80] on the use of IL supported three-phase HF-LPME for the determination of aliphatic and aromatic hydrocarbons by GC-MS. Toluene was used as acceptor solution, thus, allowing the direct injection of the extract into the GC-MS system without further sample treatment. $[C_4MIM][PF_6]$ ionic liquid was selected as the intermediate solvent due to its immiscibility with both the aqueous sample and the organic acceptor phase. Under the optimized conditions, analytes were extracted from a 10 mL sample solution to 5 µL of acceptor solution, and enrichment factors in the range of 53-210 were achieved after 40 min of extraction. With analyte recoveries of 77-102% (RSDs ≤ 11%), the LODs were 1-7 ng L^{-1}. However, a similar setup utilized in the two-phase HF-LPME mode (*i.e.*, without IL as intermediate solvent) using 30 min extraction time gave only slightly lower extraction recoveries (70-99%) with comparable precision (RSDs ≤ 13%).

IL supported three-phase HF-LPME (aqueous sample - $[C_8MIM][PF_6]$ support – aqueous (pH 13) acceptor phase) combined with HPLC-UV was also applied to determine sulfonamides in environmental water samples [81]. In order to enhance diffusion of relatively polar analytes through IL membrane, the IL phase was doped with 14% (w/v) trioctylphosphine oxide, a strong H-bonding agent. Analytical performance was fully satisfactory with analyte recoveries of 82.2-103.2% (RSDs ≤ 5%) and LODs of 0.1-0.4 µg L^{-1}. However, quite long extraction time (8 h) required to reach equilibrium makes the proposed system hardly suitable for real applications.

In the recent research [82], the IL based HF-LPME procedure was extended to inorganic analytes - lead and nickel cations. Two-phase HF-LPME was combined with ETAAS. Ammonium pyrrolidinedithiocarbamate was employed as a chelating agent to form neutral metal-ammonium pyrrolidinedithiocarbamate complexes. The metal complexes were extracted from 3.0 mL of sample solution through a polypropylene hollow fiber impregnated with $[C_6MIM][PF_6]$ into 8 µL of $[C_6MIM][PF_6]$ as acceptor solution inside the fiber. The extracts were directly injected into graphite furnace. LODs of 0.02 and 0.03 µg L^{-1} were obtained for Pb and Ni, respectively. The method was successfully applied to natural water samples with recoveries ranging from 95 to 105%. Surprisingly, despite relatively high viscosity of the IL acceptor phase and thus slow mass transfer between phases, only 15 min were required to reach extraction equilibrium.

6. Dispersive liquid-liquid microextraction

The most recent microextraction technique, dispersive liquid-liquid microextraction was introduced in 2006 by Rezae and co-workers [5] and is based on a ternary solvent component system involving an aqueous phase,

Table 4. Representative examples on the use of ILs in DLLME.

DLLME mode	Analyte	Sample	IL (amount)	Disperser	Analytical method	EF	Recovery (%)	LOD	Ref.
IL-DLLME	Heterocyclic insecticides	Water	$[C_6MIM][PF_6]$ (0.052 g)	Methanol	HPLC-DAD	209-276	79-110	0.53-1.28 $\mu g\ L^{-1}$	[87]
IL-DLLME	PAHs	Water	$[C_8MIM][PF_6]$ (50 μL)	Acetone	HPLC-FLD	301-346	90.3-103.8	0.03-2.0 ng L^{-1}	[88]
IL-DLLME	Non-steroidal drugs	Urine	$[C_4MIM][PF_6]$ (280 μL)	Methanol	HPLC-UV	36.8-42.3	99.6-107	9.2-32 $\mu g\ L^{-1}$	[106]
IL-DLLME	Pb, Cd	Saline Water	$[C_6MIM][PF_6]$ (0.075 g)	Ethanol	FAAS	273 (Pb) 311 (Cd)	95-105	0.6 $\mu g\ L^{-1}$ (Pb) 0.03 $\mu g\ L^{-1}$ (Cd)	[89]
IL-DLLME	Pyrethroid pesticides	Water	$[C_8MIM][PF_6]$ (50 μL)	$[C_4MIM][BF_4]$	HPLC-UV	-	84.1-113.5	0.28-0.83 $\mu g\ L^{-1}$	[91]
IL-DLLME	Mo(VI)	Water, Plant leaves	$[C_6MIM][Tf_2N]$ (0.060 g)	Acetone	FO-LADS	72.6	98.7-104.3	1.43 $\mu g\ L^{-1}$	[92]
IL-DLLME	NO_2^-	Water, Saliva	$[C_8MIM][Tf_2N]$ (0.0315 g)	Methanol	HPLC-Vis	430	96.5-107.3	0.05 $\mu g\ L^{-1}$	[107]
IL-DLLME	Aromatic amines	Water	$[C_4MIM][PF_6]$ (50 μL)	-	HPLC-UV	31-269	93.4-106.4	0.45-2.6 $\mu g\ L^{-1}$	[92]
TCIL-DLLME	Pyrethroid pesticides	Water	$[C_6MIM][PF_6]$ (45 μL)	-	HPLC-UV	-	76.7-135.6	0.28-0.6 $\mu g\ L^{-1}$	[78]
TCIL-DLLME	V(V)	Water Saliva	$[C_4MIM][PF_6]$ (40 μL)	-	ETAAS	-	96.5-103	4.8 ng L^{-1}	[93]
TCIL-DLLME	Triclosan, Triclocarban	Water	$[C_6MIM][PF_6]$ (80 μL)	-	HPLC-MS/MS	-	81.7-109.4	0.04-0.3 $\mu g\ L^{-1}$	[94]
TCIL-DLLME	Pesticides	Water	$[C_6MIM][PF_6]$ (50 μL)		HPLC-UV	50	88.2-103.6	0.17-0.29 $\mu g\ L^{-1}$	[95]
CIAME	Hg(II)	Water	$[C_6MIM][PF_6]$ (64 mg) $[C_6MIM][Tf_2N]$ (5 mg)	-	SF	30.8	97.5-100.4	0.3 $\mu g\ L^{-1}$	[96]
CIAME	Co(II)	Water	$[C_6MIM][PF_6]$ (64 mg) $[C_6MIM][Tf_2N]$ (5 mg)	-	FO-LADS	165	96-103	0.14 $\mu g\ L^{-1}$	[97]
IL-DLLME/ TCIL-DLLME	Phthalate esters	Water	$[C_8MIM][PF_6]$ (32 μL)	Acetonitrile	HPLC-UV	174-212	90.1-99.2	0.68-1.36 $\mu g\ L^{-1}$	[98]
IL-USA-DLLME	Aromatic amines	Water	$[C_6MIM][PF_6]$ (60 μL)	-	HPLC-UV	-	92.2-119.3	0.17-0.49 $\mu g\ L^{-1}$	[99]
IL-USA-DLLME	Cd	Water	$[C_6MIM][PF_6]$ (73 μL)	-	ETAAS	67	87.2-106	7.4 ng L^{-1}	[100]
IL-USA-DLLME	Cr(VI)	Water	$[C_6MIM][PF_6]$ (50 μL)	-	ETAAS	300	96-102	0.07 $\mu g\ L^{-1}$	[101]
IL-USA-DLLME	Biogenic amines	Beer	$[C_4MIM][PF_6]$ (30 μL)	-	HPLC-FLD	-	90.2-116	0.25-50 $\mu g\ L^{-1}$	[102]
ISFME	Hg(II)	Water	$[C_6MIM][BF_4]$ (30 mg) $NaPF_6$ (72 mg)	-	SF	37	97.3-104.0	0.7 $\mu g\ L$	[103]
ISFME	Cd	Water	$[C_6MIM][BF_4]$ (30 mg) $NaPF_6$ (120 mg)	-	FAAS	78	97.5-104.2	0.07 $\mu g\ L^{-1}$	[104]
ISFME	PAHs	Water	$[C_4MIM][Cl]$ (38 μL) $LiTf_2N$ (94 mg)	-	HPLC-UV	184-935	84-115	0.02-0.3 $\mu g\ L^{-1}$	[105]

a non-polar water immiscible solvent (extraction solvent) and a polar water miscible solvent (disperser solvent). Schematic diagram of DLLME procedure is shown in Fig. 6. In this technique, the appropriate mixture of extraction and disperser solvents is rapidly injected by syringe into an aqueous sample solution containing the analytes. The extraction solvent is dispersed into the aqueous sample as very fine droplets. Owing to the large surface area between extraction solvent and aqueous sample, the equilibrium is reached quickly and the extraction is almost independent of time. In fact, this is the principal advantage of DLLME. The cloudy solution is then centrifuged and the extraction solvent settles at the bottom of the conical tube. The sedimented phase is used for the determination of analytes of interest by appropriate analytical technique. Compared to other microextraction techniques, this method results in significantly reduced extraction times, is more convenient and simple, and, in most cases, provides higher extraction efficiencies and recoveries. More details on the theoretical aspects and general applications of DLLME technique can be found in recent review [83].

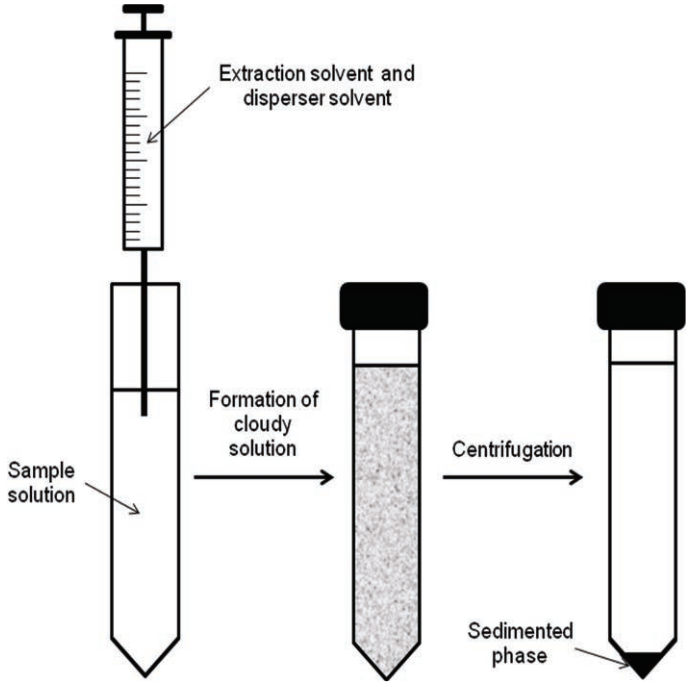

Figure 6. Schematic diagram of DLLME procedure.

One of the weakest aspects of DLLME technique is the limited number of the effective and environmentally friendly extraction solvents. Generally, extraction solvent used in DLLME should have a higher density than water, a low solubility in water and high extraction capability of the target analytes. Of all the requirements listed, the most restrictive is the necessity of using an extraction solvent having a density higher than that of water, since the number of organic solvents meeting this requirement is relatively small, and hazardous solvents such as chlorinated hydrocarbons were commonly used in the initial version of DLLME. In the last few years, efforts have been made to replace chlorinated solvents with more environmentally friendly ones. There were two types of solvents employed: lighter than water solvents (*e.g.* long-chain alcohols or hydrocarbons) and ILs. However, in order to employ lighter than water solvents, special devices [84] or tedious procedures [85] are required to collect the extractant phase from the surface of an aqueous sample. Thus, the replacement of chlorinated solvents with ILs can be considered as the best choice. The unique properties of ILs such as tunable hydrophobicity, higher density than water, as well as good extractability for various organic compounds and metal complexes make them ideal candidates as extraction solvents for DLLME.

Since the first application of IL in DLLME by Zhou and co-workers in 2008 [86] about 50 papers on IL-based DLLME sample preparation combined with different analytical techniques have been reported. Table 4 summarizes some representative examples of IL-based DLLME technique. Some of them are briefly discussed below.

Conventional IL-DLLME is based on a ternary solvent component system (aqueous sample, water immiscible IL and polar disperser solvent). Liu *et al.* [87] proposed IL-DLLME combined with HPLC-DAD for the determination of four heterocyclic insecticides in water samples. A mixture of 0.052 g $[C_6MIM][PF_6]$ and 0.5 mL methanol (disperser solvent) was quickly injected into the sample (5.0 mL). Then, the mixture was centrifuged for 10.0 min, sedimented phase was diluted with methanol to reduce its viscosity and analyzed by HPLC-UV. Under the optimized conditions, good enrichment factors (209-276) and acceptable recoveries (79-110%) were obtained. The LODs for the four insecticides ranged from 0.53 to 1.28 μg L^{-1}. Using a similar protocol, IL-DLLME combined with various analytical techniques was applied to determine PAHs in water samples [88], Pb(II) and Cd(II) cations in saline water after complexation with sodium diethyldithiocarbamate [89], Mo(VI) in water and plant leaves after derivatization with pyrogallol red [90], *etc*.

One of the disadvantages associated with conventional DLLME, however, is that it uses relatively high volumes of a polar solvent such as methanol or acetonitrile to disperse the extraction solvent into the aqueous sample. This may result in lower extraction efficiency due to increased solubility of the analytes in aqueous sample solution. Thus, significant efforts have

been made to disperse the IL phase effectively using less hazardous disperser solvent or even without the use of disperser solvent. For instance, ionic liquid/ionic liquid DLLME was developed by Zhao and co-workers [91] for the determination of two pyrethroid pesticides (permethrin and biphenthrin) in water samples. In this approach, hydrophobic [C_8MIM][PF_6] was used as the extraction solvent and hydrophilic [C_4MIM][BF_4] as the disperser. This procedure avoided the use of volatile and toxic organic disperser solvents.

In order to avoid the use of disperser solvent, a binary solvent component system was developed by Fan *et al.* [92] for the determination of aromatic amines. Briefly, a 1.8 mL portion of sample solution and 50 µL of [C_4MIM][PF_6] as extraction solvent were placed in a test tube. Then, a 1 mL of the mixture was aspirated in a 1 mL syringe and rapidly injected back into the remaining solution. The above procedure was repeated twice in order to entirely disperse IL into the aqueous phase, thus inducing the formation of a cloudy solution. The mixture was subsequently centrifuged and the sedimented IL phase directly injected into the HPLC system. Enrichment factors in the range of 31 to 269 were obtained with LODs ranged from 0.45 to 2.6 µg L^{-1}.

Another technique, so-called temperature-controlled IL-DLLME (TCIL-DLLME), utilizes an increase in temperature to fully dissolve the IL in the sample solution followed by cooling and centrifugation to recover the IL phase. This approach was initially applied by Zhou *et al.* [86] to extract pyrethroid pesticides in different types of natural water samples. Briefly, 45 µL of [C_6MIM][PF_6] was added to the sample (10 mL) and the mixture was heated in a thermostated bath at 70ºC to completely dissolve the IL phase. The solution was subsequently cooled with ice-water for a certain time. During the cooling process, the solubility of IL decreased and a cloudy solution appeared in the sample vial. The cloudy solution was then centrifuged and the IL phase injected into the HPLC. In this study acceptable recoveries (76.7-135.6%) were obtained and LODs of five pesticides ranged from 0.28 to 0.6 µg L^{-1}. TCIL-DLLME was also applied for the determination of V(V) [93], triclosan and triclocarban [94], organophosphorus pesticides [95].

Baghdadi and Shemirani [96] developed a similar approach called "cold-induced aggregation microextraction" (CIAME). In this method, small amounts of two hydrophobic ILs ([C_6MIM][PF_6] and [C_6MIM][NTf_2]) were added to the sample solution containing Triton X-114. Triton X-114 prevents IL sticking onto the surface of the centrifuge tube wall. The subsequent procedure is similar to that for TCIL-DLLME but lower temperature (35ºC) was used in the dissolving step. Two different ILs were needed to decrease IL solubility (common ion effect) in samples with high ionic strength. The performance of CIAME was evaluated with the spectrophotometric determination of mercury [96] and cobalt [97] in water samples.

In a more recent study by Zhang *et al.* [98], both IL-DLLME and TCIL-DLLME approaches have been employed simultaneously. In this method, the sample was heated in a water bath to 50ºC before the injection of a mixture of IL (32 µL of [C_8MIM][PF_6]) and disperser solvent (0.75 mL of acetonitrile). The solution was subsequently cooled with ice-water and centrifuged. The method was successfully applied to the determination of phthalate esters in water samples. Also, the analytical performance was compared to that of a conventional IL-DLLME method which uses acetonitrile as disperser solvent. The analytical performance data of the two techniques were found to be closely similar, the only difference being that the conventional IL-DLLME technique required slightly higher amounts of IL (36 µL against 32 µL).

Another addition to the list of IL-based DLLME techniques is ultrasound-assisted dispersive liquid-liquid microextraction (IL-USA-DLLME) [99-102]. The technique is rather similar to TCIL-DLLME, the only difference being that instead of the initial heating step, ultrasound was applied to disperse or even dissolve the IL phase. However, a cooling process is still needed to obtain a turbid solution. For example, Zhou and co-workers [99] determined aromatic amines in water by means of IL-USA-DLLME combined with HPLC-UV. Briefly, 60 µL of [C_6MIM][PF_6] was added to 10 mL of the water sample and the mixture was then sonicated for 5 min. The solution was subsequently cooled with ice-water and centrifuged. In other related studies, Cr(VI) was determined in waters by ETAAS [101] and biogenic amines were determined in beer samples by HPLC-FLD [102].

In comparison with conventional IL-DLLME, in TCIL-DLLME, CIAME and IL-USA-DLLME techniques an additional heating/ultrasonification and cooling steps are required. Those steps are relatively time (up to 20-30 min) and energy consuming.

In one more interesting approach, Baghdadi and Shemirani [103] introduced a modified IL-DLLME method that involved an in situ solvent formation. In this approach, termed in situ solvent formation microextraction (ISFME), a small amount (30 mg) of hydrophilic [C_6MIM][BF_4] was dissolved completely in the aqueous sample solution. An ion-pairing reagent ($NaPF_6$) was then added to carry out the in situ metathesis reaction. As a result, a cloudy solution with fine droplets of the water-immiscible [C_6MIM][PF_6] was

formed and was recovered by centrifugation. Hg^{2+} ions were extracted by employing Michler's thioketone as a chelator, and then determined by UV/Vis spectrometry. Later on, the same methodology has been applied for the determination of cadmium in saline samples by AAS [104].

Yao and Anderson published a related study [105] on the use of ISFME for the preconcentration of PAHs from waters. In this case, the $[C_4MIM][Cl]$ and $LiNTf_2$ salts were employed for in situ solvent formation. With analyte recoveries of 84-115%, the LODs (HPLC-UV) were 0.02-0.3 μg L^{-1}. In comparison to conventional IL-DLLME approach using the same IL, a 1.1- to 2.4-fold increase in analyte enrichment factors was observed. The authors attributed enhanced extraction efficiencies to a larger surface area between the extraction solvent and aqueous sample solution obtained in the ISFME mode.

One remarkable advantage of ISFME technique is that it does not require the use of a heating/cooling step or a disperser solvent. In addition, this approach is robust against highly saline water samples. In such samples, the solubility of the IL considerably increases and its recovery after extraction by conventional IL-DLLME is complicated or even impossible. In contrast, under ISFME conditions due to the common ion effect (excess of an ion-pairing reagent) the solubility of the IL formed does not increase even in the presence of high concentration of electrolytes.

In all above described DLLME approaches, phase separation is performed by centrifugation, which is a typical off-line process. In an effort to eliminate the centrifugation step, Valcarcel and co-workers [106] developed so-called in-syringe IL-DLLME. In this approach, a specific volume (typically 10 mL) of sample solution was introduced into a plastic syringe, which acts as extraction vessel. Then, the extraction mixture (280 μL of $[C_4MIM][PF_6]$ and 720 μL of methanol) was sprayed and a cloudy solution immediately formed. Later on, the plunger of the syringe was slowly moved to the initial point allowing the recovery of the IL from the wall and the lower part of the syringe while the sample was removed from the unit. Finally, the IL phase was recovered from the syringe tip, diluted with the mobile phase and analyzed by HPLC-UV. This configuration not only avoids the centrifugation step, thus reducing the extraction time but also offers the possibility to employ extraction solvents with lower density than water simply by changing the orientation of the syringe during the phase separation step. However, the efficiency in the recovery of IL phase should be increased, since it has an evident influence on the precision of the procedure.

Later on, Berton and co-workers [91] developed a flow-injection system for on-line TCIL-DLLME coupled with ETAAS detection for the determination of V(V) in water and saliva samples. Vanadium was complexed with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and extracted on-line into the dispersed (by heating and subsequent cooling) $[C_4MIM][PF_6]$ phase. Then the IL phase was on-line retained on the Florisil-packed microcolumn, analyte was eluted from the microcolumn with a 10% (*v/v*) nitric acid (in acetone) solution, and measured by ETAAS.

As in SDME and HF-LPME, the vast majority of the applications related to IL-based DLLME involve the use of 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM][PF_6]$, n = 4, 6, 8) as extraction solvents (Table 4). Such popularity of the ILs may be attributed to their relatively simple synthesis, commercial availability, relatively low price, and easily tailored properties such as miscibility with water, density, etc. Some authors used 1-alkyl-3-methylimidazolium ILs containing the NTf_2^- anion [90,107]. Other ILs employed include 1-hexylpyridinium hexafluorophosphate $[C_6Py][PF_6]$ [108], 1,3-diisooctylimidazolium hexafluorophosphate $[D(i\text{-}C_8)IM][PF_6]$ [109], and functionalized pyrrolidinium-based ILs containing the tris-(pentafluoroethyl)-trifluorophosphate anion (FAP) [110].

In several papers the influence of alkyl chain length of 1-alkyl-3-methylimidazolium-based ILs on the extraction performance was evaluated [88,91,98,102,111]. For example, Zhou and co-workers [111] compared four different alkyl chain length ILs ($[C_nMIM][PF_6]$, n = 4, 6, 7, 8) for the extraction of pyrethroid insecticides. The obtained results indicated that the longer alkyl chain resulted in better extraction efficiency. In the work by Huang *et al.* [102] the opposite trend was observed for derivatized biogenic amines. Most likely, this behaviour may be attributed to the lower hydrophobicity of the analytes: partitioning of more polar analytes may be preferred by less hydrophobic IL with shorter alkyl chain.

The majority of work on IL-based DLLME has so far been applied to extract and preconcentrate non-polar to medium polarity organic compounds (see Table 4). For more hydrophilic analytes such as biogenic amines, a derivatization step is required prior to extraction [102]. Extraction of metal ions from environmental waters is another main use of IL-DLLME. The conventional procedure for the extraction of metals involves use of a chelating reagent to convert the charged metal species into neutral chelates before extraction. Chelating agents typically are the same as used in classical liquid-liquid extraction procedures: sodium diethyldithiocarbamate

[89], 1-(2-pyridylazo)-2-naphtol [97], Michler's thioketone [96,103], ammonium pyrrolidinedithiocarbamate [101], 8-hydroxyquinoline [108] and some others.

To date, the majority of the applications related to IL-DLLME deal with various types of water samples. Nonetheless, some authors have applied this technique for liquid and semi-liquid biological samples such as urine [112], bananas [113], table grapes and plums [114] or plant leaves [90]. In such cases, an additional pretreatment of the sample (*e.g.* UV digestion, mineralization with subsequent dissolution or traditional liquid-liquid extraction) is usually required in order to obtain an aqueous solution before microextraction.

For the determination of the analytes after their extraction, HPLC is the method used most frequently (Table 4). In contrast to halogenated hydrocarbons usually used in conventional DLLME, ILs are compatible with reversed-phase HPLC mobile phases, therefore, an extra step of solvent exchange is not required before analysis. However, the direct injection of the IL phase into the HPLC system is difficult due to its high viscosity. Thus, dilution of the extract with acetonitrile or methanol is usually carried out before injection. Among the detectors used by the combination of IL-DLLME with HPLC, UV/Vis and DAD are by far the most popular. Other HPLC detectors have also been employed but with less frequency. For example, Pena *et al.* [88] determined PAHs in water by means of IL-DLLME combined with HPLC-FLD and the LODs achieved (0.03-2.0 ng L^{-1}) were considerably lower than for UV detection. Zhao *et al.* [94] used TCIL-DLLME in combination with HPLC-ESI-MS/MS for the determination of two bactericides (triclosan and triclocarban) in environmental water samples. The high resolution capacity of HPLC and the high sensitivity of ICP-MS make their combination very attractive for speciation analysis. The combination of IL-DLLME with HPLC-ICP-MS for the extraction and determination of mercury species (Hg^{2+}, methylmercury and ethylmercury) in liquid cosmetic samples was proposed recently by Jia *et al.* [115]. The analytes were complexed with ammonium pyrrolidinedithiocarbamate, and then the complexes were extracted into [C_6MIM][PF_6]. Under optimized conditions, LODs with ICP-MS detection were in the range of 1.3-7.2 ng L^{-1}.

As discussed in the section on SDME, direct combination of IL-based microextraction techniques with GC is a real challenge due to low volatility of ILs. There are only two reports in which IL-based DLLME has been combined with GC-MS [109,116]. To avoid IL entering into GC capillary column, analytes were desorbed from the ionic liquid in the injection port of gas chromatograph, and the ionic liquid was then drawn back into the microsyringe.

Following IL-based DLLME, metal ions are typically detected by the spectrometric techniques. Electrothermal and flame AAS are the most common methods combined with IL-based DLLME [89,93,100,101,104]. Other techniques such as UV/Vis spectrophotometry (SF) [96,103], stopped-flow spectrofluorometry (SFS) [108] and ICP-OAS [117] have also been employed.

ETAAS is advantageous over FAAS in terms of sensitivity and sample consumption. The latter characteristic makes them especially suitable for combination with microextraction techniques. For example, IL-based DLLME-ETAAS has been successfully applied to the determination of V(V) [93] in water and saliva samples, Co [112] in water, saliva and urine samples, Cd [100] and Cr(VI) [101] in water samples. The ETAAS analysis was carried out by injecting the IL phase without dilution [101] or after dilution with appropriate solvent to reduce the viscosity [93,100,112]. The LODs obtained with the ETAAS technique were in the ng L^{-1} to a sub-ng L^{-1} range.

In general, sample volume required to perform a single analysis by FAAS is significantly bigger than that obtained after microextraction procedure. In order to overcome this problem, a microsample introduction system for microvolume nebulization was employed for the determination of lead and cadmium [89]. Using this system, injection of low volume (20-50 µL) of the extract can be used without loss of sensitivity and precision. As another example, Mahpishanian and Shemirani [104] used ISFME-FAAS technique for the determination of cadmium in saline samples. In both cases, obtained extracts were diluted to decrease their viscosity and increase nebulization efficiency.

Gharehbaghi and co-workers proposed IL-based DLLME combined with fiber optic-linear array detection spectrophotometer (FO-LADS) for the determination of cobalt [97] and molybdenum (VI) [90]. After centrifugation, the IL phase was diluted to decrease its viscosity and injected into a 50 µL quartz cylindrical micro-cell located in a spectrophotometer. However, compared to electrothermal and flame AAS techniques, the sensitivity of the spectrophotometric techniques is considerably lower.

IL-DLLME followed by stopped-flow spectrofluorometric (SFS) determination has been proposed for the determination of aluminium [108]. 8-Hydroxyquinoline, which forms a highly fluorescent complex with Al^{3+}, was chosen as the chelating agent. After extraction, the diluted IL phase was introduced into a micro-cell (16 µL capacity) by the peristaltic sipper.

Finally, the combination of IL-DLLME with ICP-OAS for the extraction and determination of some lanthanoids (samarium, europium, gadolinium and dysprosium) in

uranium dioxide powder was employed by Mallah *et al.* [117]. In this case, the extractant phase was dried by a furnace at 160ºC, then diluted to 0.5 mL with 1 mol L^{-1} HNO_3 and analyzed by ICP-OAS.

Overall, the performance of IL-based DLLME is comparable to, or even better than that of conventional DLLME, as clearly evaluated in some published studies [107,118].

All the IL-based DLLME approaches considered are well established and can be applied to a wide spectrum of analytes. However, it should be highlighted that the direct comparison of their performance is difficult, because there are no comprehensive studies in which different IL-based DLLME techniques have been applied for the same samples and analytes for comparative purposes.

In summary, the main advantages of IL-based DLLME are high extraction rates, ease of operation, low costs, relatively high recovery, high enrichment factors, and environmental safety. The main drawback of this technique is related to the high viscosity of the ILs used. The extract is commonly diluted with a miscible solvent before analysis thus decreasing to some extent the enrichment factors achieved.

7. Conclusions

The developments described in this review clearly demonstrate that in the field of IL-based microextraction techniques, a variety of approaches is continually being opened, optimized and applied to a wide spectrum of analytes and samples. Generally, by replacing traditional solvents with ILs the main merits of microextraction techniques such as ease of operation, low cost, and environmental safety are achieved. Moreover, in most cases the performance of IL-based techniques is better than that of traditional microextraction methods.

While this field continues to progress, some specific problems should be noted. For example, direct combination of IL-based LPME techniques with GC is difficult due to the low volatility of ILs. In addition, most of the IL phases are too viscous to be injected directly into an analytical instrument. Finally, compared to traditional solvents, commercially available ILs are relatively expensive and their purity keeps below what would be typically specified for laboratory solvents.

Although ILs offer selectivity advantages compared to commercial SPME coatings, only few IL- or PIL-based coatings have been examined. Similarly, relatively few ILs have been employed in LPME techniques. Considering the vast number of ILs that can be obtained by combinations of different anions and cations, further research should focus on synthesis and employing new ILs with more tailored properties (*e.g.* viscosity, hydrophobicity, thermal stability, purity, *etc.*). For example, with the development of functionalized task-specific ILs acting as extractants and selective binding (*e.g.* chelating) agents, it should be possible to further improve selectivity and efficiency of microextraction techniques.

Acknowledgements

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Abbreviations

AAS: atomic absorption spectrometry;
AMIM: 1-allyl-3-methylimidazolium;
BeMIM: 1-benzyl-3-methylimidazolium;
BMPO: bis[(3-methyldimethoxysilyl)propyl] polypropylene oxide;
BMPT: n-butyl-4-methylpyridinium tetrefluoroborate;
BTEX: benzene, toluene, ethylbenzene, xylene;
C_2MIM: 1-ethyl-3-methylimidazolium;
C_4MIM: 1-butyl-3-methylimidazolium;
C_6MIM: 1-hexyl-3-methylimidazolium;
C_6Py: 1-hexylpyridinium;
C_8MIM: 1-octyl-3-methylimidazolium;
C_{10}MIM: 1-decyl-3-methylimidazolium;
C_nMIM: 1-alkyl-3-methylimidazolium;
CE: capillary electrophoresis:
CME: capillary microextraction;

D(i-C_8)IM: 1,3-diisooctylimidazolium;
CIAME: cold-induced aggregation microextraction;
DAD: diode array detector;
DI: direct immersion;
DLLME: dispersive liquid-liquid microextraction;
ESI: electrospray ionization;
ETAAS: electrothermal atomic absorption spectrometry;
EeMIM: 1-ethoxyethyl-3-methylimidazolium;
$ETSO_4$; ethylsulphate;
ETV-ICP-MS: electrothermal vaporization-ICP-MS;
FAAS: flame AAS;
FAP: tris(pentafluoroethyl)trifluorophosphate;
FID: flame ionization detector;
FLD: fluorescence detector;
FO-LADS: fiber optic-linear array detection spectrophotometer;
GC: gas chromatography;
HF-LPME: hollow-fiber LPME;
HPLC: high performance liquid chromatography;
ICP-MS: inductively coupled plasma MS;
ICP-OAS: inductively coupled plasma optical emission spectrometry;
IL: ionic liquid;
IL-USA-DLLME: IL ultrasound-assisted DLLME;
IMS: ion-mobility spectrometry;
ISFME: in situ solvent formation microextraction;
LPME: liquid-phase microextraction;
MS: mass spectrometry;
MTPIM: 1-methyl-3-(3-trimetoxysilyl propyl)imidazolium;
NTf_2: bis(trifluoromethyl)sulfonylimide;
PAH: polycyclic aromatic hydrocarbon;
PDA: photodiode array detector;
PDMS: polydimethylsiloxane;
PhproMIM: 1-methyl-3-phenylpropylimidazolium;
PIL: polymeric ionic liquid;
Poly[ViHIM]: poly(1-vinyl-3-hexylimidazolium);
Poly[ViDDIM]: poly(1-vinyl-3-dodecylimidazolium);
Poly[ViHDIM]: poly-1-vinyl-3-hexadecylimidazolium;
Poly[ViBHDIM]: poly(1-4-vinylbenzyl)-3-hexadecylimidazolium;
SDME: single drop microextraction;
SDS: sodium dodecyl sulphate;
SF: spectrophotometry;
SFS: stopped-flow spectrofluorometry;
SPME: solid-phase microextraction;
TC: thermal conductivity detector;
TCIL-DLLME: temperature-controlled IL-DLLME;
TfO: trifluoromethanesulfonate;
TTPT: trihexyltetradecylphosphonium tetrafluoroborate.

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