Applications of ionic liquids in analytical chemistry with a particular emphasis on their use in solid-phase microextraction

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A B S T R A C T

Nowadays, analytical research is an indispensable factor in the lives of people. Attempts are made to improve quality, speed or safety of analytical procedures. Recently, research on ionic liquids has become a trend. This is due to the possibility of their application in many fields. In this paper, the properties and diversity of ionic liquid application have been described, especially application in advanced analytical techniques such as various electrochemical techniques, chromatography or in sample preparation. From the analytical point of view, the use of ionic liquids in solid phase microextraction is very interesting and important. In the article there are many links to research that led to the creation of a broad summary concerning these unusual chemicals. The relatively large amount of research work on the topic provides only a small peak of the potential of ionic liquids. This provides motivation for further action towards development on the topic.

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1. Ionic liquids

Ionic liquids (ILs) is a term used for chemical compounds belonging to the group of salts, composed of ions, with a melting point under 100°C. They are composed of a large organic cation and a smaller, organic or inorganic anion (Fig. 1). They are characterised by a high thermal stability and a broad range of temperatures in which they have liquid form. Their features make ILs interesting solvents with growing technological importance. One of those features is a negligible vapour pressure, associated with low combustibility and high thermal stability, hence ILs have been broadly proclaimed "environment friendly". A broad selection of ions allows creation of a compound demonstrating certain desired properties (solubility, selectivity, etc.) for a particular application. An appropriate selection of ions is highly important for shaping of physical and chemical properties, including: solubility, melting point, volatility, thermal stability, electric conductivity, viscosity, and flammability, among many others. Due to their various properties and a relatively easy synthesis, the development of ILs is dynamic and they are increasingly used in industry and in numerous fields of science and technology [1].

The onset of ILs dates back to 1914, when Walden obtained the first stable IL: ethylammonium nitrate [3], characterised by a melting point below room temperature. However, high susceptibility of the compound to humidity significantly limited its scientific and industrial application. Further studies on that group of compounds gave results as late as in 1992, with a synthesis of an imidazole salt demonstrating stability in air and absence of susceptibility to humidity [4]. Since that time, the amount of studies and publications associated with ILs has grown rapidly (Fig. 2). At present, ILs are broadly applicable not only in chemistry, but also in nanotechnology, physics and many other fields of science and technology [5,6].

1.1. Physical, chemical and toxic properties

A broad selection of existing ions allows for designing of ILs which demonstrates some desirable properties, which makes them extremely interesting chemical compounds. Their structure and type of building ions directly influence their chemical and physical properties. Thermal stability of ILs depends on the type of both cation and anion.

In reality a cation group has a minor impact on the thermal stability of an IL compared to its anion group. ILs composed of an organic anion is often more thermally stable than ILs composed of inorganic anions [7]. Studies [7,8] demonstrate that the thermal stability of ILs increases depending on the type of anion used, in the

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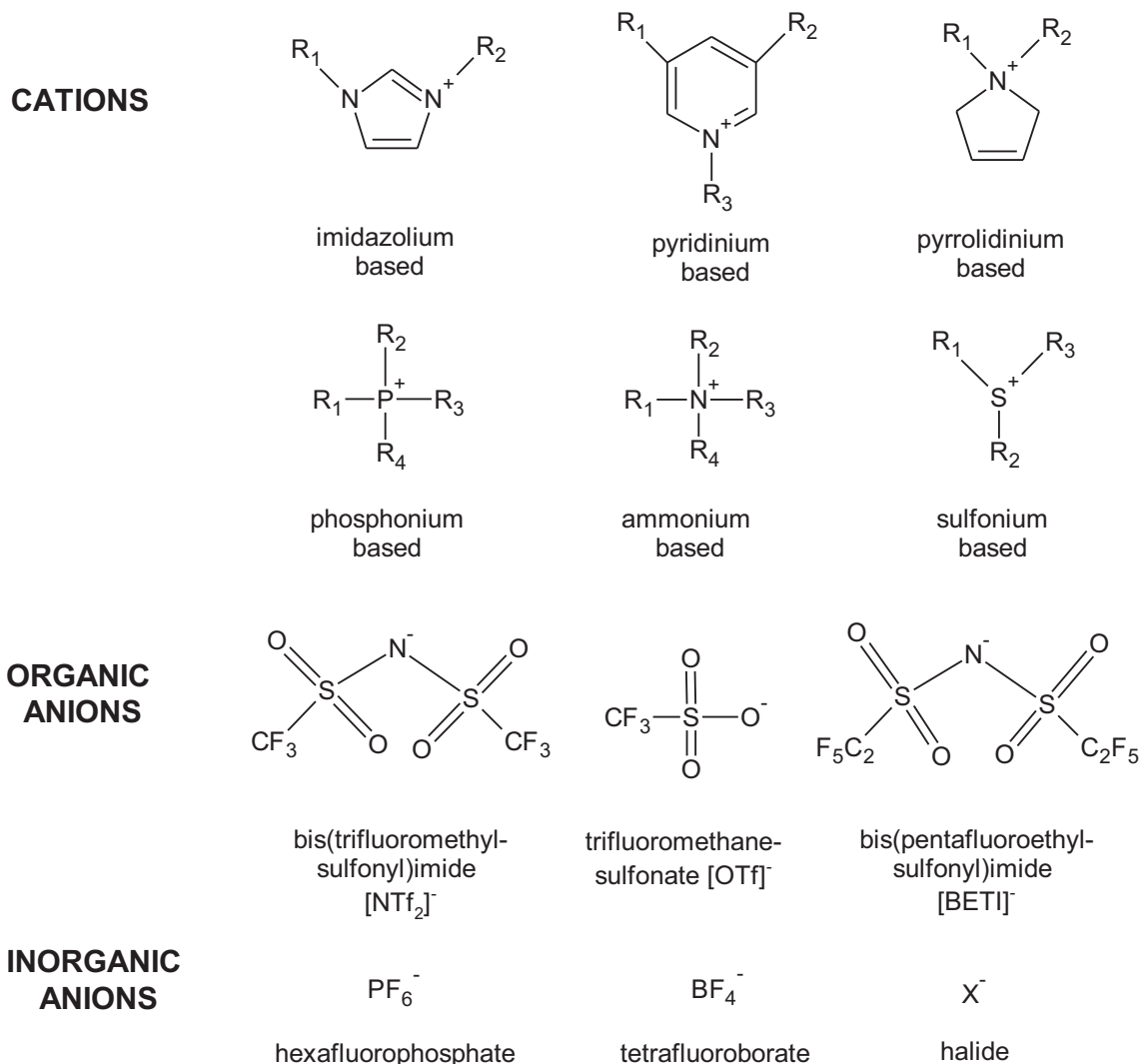 *E-mail address:* stanislaw.popiel@wat.edu.pl (S. Popiel).

CATIONS

imidazolium based

pyridinium based

pyrrolidinium based

phosphonium based

ammonium based

sulfonium based

ORGANIC ANIONS

bis(trifluoromethyl-sulfonyl)imide [NTf$_2$]$^-$

trifluoromethane-sulfonate [OTf]$^-$

bis(pentafluoroethyl-sulfonyl)imide [BETI]$^-$

INORGANIC ANIONS

PF$_6^-$

BF$_4^-$

X$^-$

hexafluorophosphate

tetrafluoroborate

halide

Fig. 1. Cations and anions most commonly used for production of ionic liquids [2].

following order: [Cl]$^-$ < [Br]$^-$ < [I]$^-$ < [BF$_4$]$^-$ < [OTf]$^-$ < [NTf$_2$]$^-$ < [PF$_6$]$^-$. The lower stability of ILs composed of halides is probably a result of their nucleophilic character. The viscosity of ILs is several dozens to several hundred times higher than the viscosity of water at room temperature. The structure of a cation has a great influence on the viscosity of ILs. The introduction of branched and/or longer alkyl groups increases viscosity of the compound [9]. The viscosity of ILs is regulated by changes in intermolecular interactions, including Van der Waals forces and hydrogen bonds. Smaller anions cause reduction of the strength of Van der Waals forces, while simultaneously increasing electrostatic interactions resulting from hydrogen bonds, which leads to decreased viscosity [10]. Besides the structure of an IL, its viscosity depends also on the content of impurities. Seddon et al. presented results indicating that contamination of ILs with chloride ions leads to increased viscosity and that the presence of water and other solvents results in decreased viscosity [11]. ILs may be hydrophobic or hydrophilic. Usually the size of the anion plays a deciding role in the solubility of a particular IL, e.g. 1-butyl-3methylimidazolium tetrafluoroborate ([bmim]BF$_4$) is water soluble, but 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$) [12] is not. The hydrophobic nature of an anion increases in the following order [13]: [Br]$^-$ ~ [Cl]$^-$ < [BF$_4$]$^-$ < [PF$_6$]$^-$ < [NTf$_2$]$^-$ < [BETI]$^-$. The solubility of various substances in ILs may be also modified using various lengths of alkyl substituents in a cation: the longer the alkyl chain in the structure of a cation, the less polar the IL will be [14]. The most commonly used ILs are those that are liquids at or below room temperature (room temperature ionic liquids − RTILs). ILs melting points depends mostly on the level of asymmetry of the cation that builds the IL. A change of length of an alkyl substituent affects the melting point in two ways. Elongation of the chain leads to a reduced melting point as a result of the increasing asymmetry of the cation, destabilisation of molecular packing in the crystalline network, and a tendency for a glassy state. This applies to salts, where the alkyl substituent of the imidazolium cation has 4 to 10 carbon atoms. Further elongation of the chain (8−10 carbon atoms) leads to an increase of the melting point as a result of increasing Van der Waals interactions between alkyl substituents, resulting in a particular arrangement of molecules [15]. In the case of anions, it is hard to define a clear relationship between their structure and melting points. ILs that contain a halide as an anion demonstrate higher melting points than compounds containing [NTf$_2$]$^-$ or [PF$_6$]$^-$, because of the hydrogen bonds that form. It was also observed that fluorine atoms containing anions reduce an IL's melting point [15]. A low vapour pressure is a great advantage of ILs. Rocha et al. scientifically proved that the volatility of
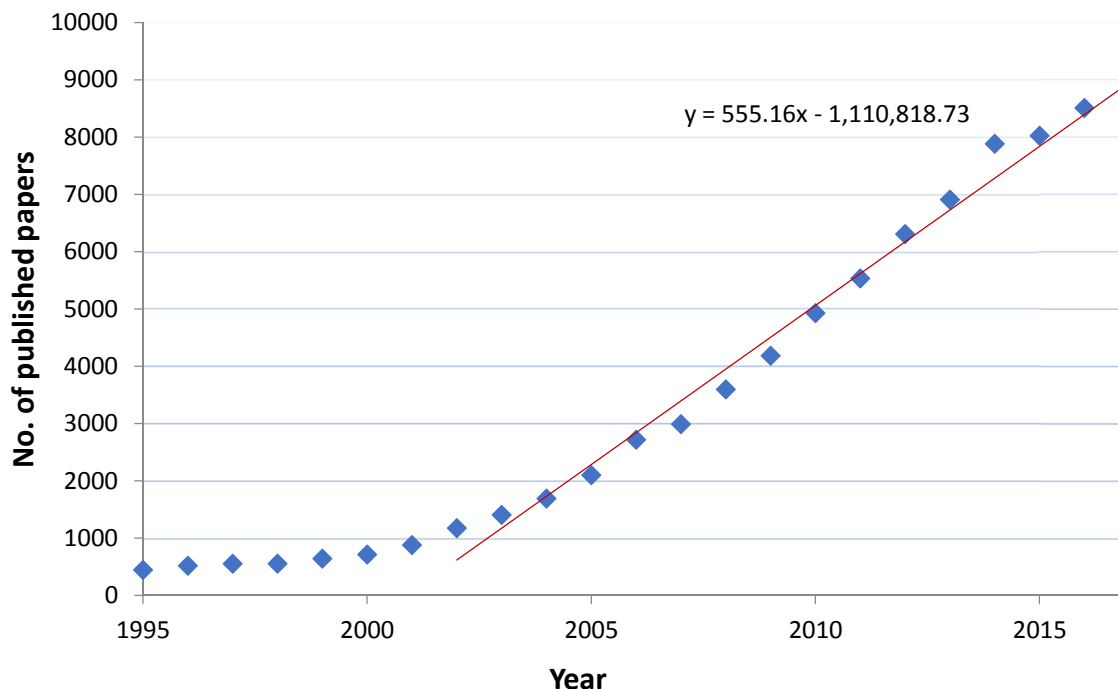
Fig. 2. The number of published scientific papers on obtaining and applicability of ILs as a function of the year of their publication, based on Web of Sciences [the author's own elaboration].

compounds having a symmetrical cation based on imidazolium was significantly higher compared to the volatility of liquids composed of asymmetrical ions [16]. Moreover, the authors found a relationship between volatility and evaporation enthalpy, confirming it with an example of five-times lower volatility of a pyridinium liquid compared to the IL-containing imidazolium rings in its structure [17]. The electric conductivity of ILs strongly depends on the character of the interactions between the anion and the cation. Those interactions are based on Coulomb forces between ionic charges and on Van der Waals forces. The character of those interactions further depends on the structure of the ions, their polarizability and their ability to form hydrogen bonds. On the whole, electric conductivity of a particular anion decreases with increasing length of the substituent in the imidazolium ring. That relationship may be explained by increasing viscosity of the compound and thus by reduced mobility of charge carriers. It is possible to dilute an IL. However, the electric conductivity of the resulting mixture is a result of two antagonistic tendencies: dilution of an IL leads to reduced viscosity, however the molar concentration of the salt is also reduced. For this reason, conductivity increases initially, reaching its top value, and then further dilution leads to a decrease of conductivity [18,19]. Some ILs have a much bigger electrochemical window than water as the basic solvent. Particularly, pyrrolidine and sulphonic groups functionalized with ether [20] have very broad electrochemical windows, which leads to working voltages of over 3.5 V. Kazemiabnavi et al. assessed the effect of cations and anions in imidazolium-based ILs for the size of their electrochemical windows [21]. Their study demonstrated that the reductive potential of cations and the oxidative potential of anions influence this parameter. The authors also demonstrated a minor effect of the length of the alkyl chain connected to the imidazolium cation, resulting in just 2.1% deviation from the mean value. Another important factor determining electrochemical stability of ILs is the structure of the anion. Highly fluorated anions, such as

$[PF_6]^-$ or $[BF_4]^-$, demonstrate a tendency for electrochemical stabilisation. Electrochemical stability of imidazolium-based ILs are as follow: $[C_nMIM]^+[PF_6]^- > [C_nMIM]^+[BF_4]^- >> [C_nMIM]^+[TfO]^- > [C_nMIM]^+[TFSI]^-$ [21]. Surface tension tends to decrease with an increasing size of the anion. This is presented by the following sequence: $[BF_4]^- > [PF_6]^- > [CF_3SO_3]^- > [NTf_2]^-$. Elongation of the alkyl chain leads to reduction of surface tension as a result of dilution of the ionic charge and lower strength of hydrogen bonds between the anion and the cation. Introduction of further alkyl substituents to the cation leads to an increase of surface tension of ILs [22]. Combustibility of ILs is a direct result of the combustibility of their decomposition products, but not of evaporation of the IL itself - as it is in the case of traditionally defined combustible/flammable liquids [23]. Fox et al. demonstrated that combustibility of ILs is similar to combustibility of polymeric aliphatic hydrocarbons, such as polypropylene [24]. Irrespective of whether ILs are defined as "combustible" or "flammable", they pose a significant fire threat and constitute a fuel in the case of fire. It would be therefore appropriate to describe ILs as "possessing low or limited flammability threat", instead of identifying them as "non-combustible". To increase fire safety, ILs, similar to plastics made of aliphatic hydrocarbons, may be supplemented with additives that reduce their combustibility.

ILs are often referred to as "green chemistry". Some scientists do not agree, and instead study the potentially toxic effects associated with ILs. Tsarpali and Dailianis demonstrated that ILs have a strong lethal effect on aquatic organisms, and that their toxicity may be even greater than that of conventional organic solvents [25]. It was also found that due to their low bio-degradability, ILs may cause durable water and soil pollution [26,27]. Toxicity of imidazolium-based ILs is directly correlated to the length of the alkyl substituent in the cation. Presence of alkyl groups intensifies the lipophilic character of ILs, which results in a higher affinity toward viable cells. Elongation of the alkyl chain and an increased number of alkyl

groups substituted in the imidazolium ring increase aquatic toxicity of these compounds. It was additionally demonstrated that the alkyl group attached to the cation has a greater impact on the toxicity of the compound than the main group of the cation [28].

The most important physical and chemical properties of ILs are:

- they are liquid in temperatures below 100°C,
- their physical and chemical properties may vary vastly depending on the structure of their cation and anion,
- they dissolve many organic and inorganic substances,
- they are thermally stable and their boiling points are relatively high,
- they have low vapour pressure at room temperature, they have a hydrophobic and/or hydrophilic nature,
- they conduct electricity, and they have a broad range of electrochemical stability.

2. Application of ionic liquids

A great interest in ILs has grown over the last two decades. The interest has been fuelled by a great number of possible modifications aimed at their greater utility. Scientific papers and reviews bring up numerous characteristics and applications of various ILs [29], [30], [31]. Many organic compounds, including aliphatic and aromatic hydrocarbons, are commonly used as solvent at both laboratory and industrial scales. They are used in large quantities, and considering their volatility, they easily pollute the natural environment. The current tendency is to eliminate this kind of solvents. ILs are a forward-looking reaction medium. They do not contribute to the dissemination of harmful waste products and meet requirements for "green chemistry". The first scientist who published a paper on applicability of ILs was Swain in 1967 [32]. ILs have been applied lately to production of ecological fuels [33], extraction of used paint solvents [34], and as a solvent in other extraction processes [35,36]. Some scientific papers [37], [38], [39] claim that an exchange of a common organic solvent with IL may lead to non-typical chemical reactivity, which means that ILs play the role of both solvent and catalyst. Additionally, the use of ILs leads to reduced costs of the process, because those solvents may often be recovered and re-used. It should be noted that reactions in ILs are not difficult to carry out and usually do not require any special equipment or methodology. Those reactions are often more rapid and easier to carry compared to conventional organic solvents [40]. Another application of ILs is their use as electrolytes in the process of electrolysis [41,42] in lithium cells [43], in lithium-ionic cells [44], electrolytic condensers [45], and in the process of electrochemical polymerisation [46]. This broad range of applications of ILs is possible due to their large electrochemical stability. These compounds may also be used as an alternative for conventional metallurgy processes. Production of pure metallic layers of, among others: zinc [47], cobalt [48], copper [49], silver [50], tin [51], gold [52], or lead [53] is possible with an appropriately selected composition of the electrolytic bath.

3. Ionic liquids in analytical separation methods

Numerous scientific papers demonstrating a great potential of ILs in the chemical analytics have been published since the beginning of the 1990s. ILs have been the most broadly used in the following fields directly associated with analytical chemistry: gas chromatography (GC), liquid chromatography (LC), capillary electrophoresis (CE), mass spectrometry (MS), electrochemistry, sensors and in sample preparation processes (various kinds of extraction, solid phase and liquid phase microextraction, etc) [54], [55], [56].

3.1. Gas chromatography

During the last several decades gas chromatography has become one of the most popular separation methods and combined with an appropriate detector, has also become a valuable method for the detection and identification of volatile and moderately volatile compounds contained in some complex matrixes. Adequate separation of peaks in the shortest possible time is the basic condition for an appropriate chromatogram. Additionally, the produced peaks should be symmetrical and narrow. For that reason, studies on the development of novel stationary phases of capillary columns still continue to develop systems that would offer superior separation compared to conventional commercial stationary phases (e.g. high molecular weight chemically modified polysiloxanes and polyethylene glycols). Due to their unique properties ILs are perfect substances to be used as stationary phases in GC columns. Studies on the application of melted salts as stationary phases in chromatography were started in 1950 by Barber et al. who designed a stationary phase made of melted stearates: Mn, Co, Ni, Cu and Zn for separation of alcohols and amines [57].

Then, studies on stationary phases based on tertiary ammonium and phosphonium salts were published. These salts were used in packed columns or coated on walls of capillary columns [58,59]. However, there is a relatively narrow range of temperatures in which those salts are liquid and their thermal instability greatly limits their practical application in gas chromatography.

Imidazolium-based ILs were another attempt to apply this group of compounds as stationary phases in gas chromatography. In 1999, Armstrong et al. studied properties and interactions of various analytes with 1-butyl-3methylimidazolium hexafluorophosphate ([BMIm][PF$_6$]) and the analogous chloride salt ([BMIm][Cl]) in silicon capillaries, comparing them to polydimethylsiloxane (PDMS) [60]. Based on the obtained results, they concluded that the most important interactions occurring between analytes and RTIL's were: dipolarity, alkalinity of the hydrogen bond and dyspersion forces. Columns with a stationary phase containing ILs demonstrated the same separation properties for non-polar analytes as commercial columns DB-5 [(5%-diphenyl- and 95% dimethyl) polysiloxane]. However, some significant differences were noted in the case of separation of polar compounds and of compounds demonstrating properties of proton donors. These kinds of molecules were strongly retained by stationary ionic phases, and in some cases, they were not eluted at all in the applied conditions of the studies. To solve those problems, in 2003 Armstrong et al. prepared new stationary phases based on two ILs possessing large monocations: 1-benzyl-3-methylimidazolium trifluoromethanosulphonate ([BeMIM] [OTf]) and 1-(4-metoxyphenyl)-3-methylimidazolium trifluoromethanosulphonate ([MPMIM] [OTf]) [61]. Those new stationary phases were characterised by satisfactory thermal stability up to the level of ~250°C and allowed for the production of symmetrical peaks. As a result, this allowed analysis of both polar and non-polar analytes: methylene chloride, methyl caproate, octanal, dodecane, octanol, tridecane, naphthalene, nitrobenzene, tetradecane, pentadecane, and octanoid acid. The application of those columns resulted in satisfactory separation of a mixture composed of alkanes, alcohols, polycyclic aromatic hydrocarbons, and isomers of sulphoxides.

As a reaction to the growing interest in ILs and consideration of their high potential, in 2008 Supelco marketed the first column with ILs as the stationary phase. Table 1 presents basic parameters of columns containing ILs (items 10—14) and of classical commercial columns (items 1—9): composition, polarity, range of operating temperatures, dimensions, and possible applications.

Selection of the stationary phase of a chromatographic column is one of initial stages of optimisation of analytical methods. The

Table 1
A list of selected information on commercial and prototypic capillary columns with ionic liquid as a stationary phase.

| No.	Phase	Composition	Polarity	Temperature range		Dimensions [length × diameter × thickness]	Sample analysis	Lit.
				min.	max.			
1	SLB-IL59	1,12-di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide	Polar	−	300°C	30 m × 0.25 mm × 0.20 μm	Complex essential oils, linear hydrocarbons, polycyclic aromatic hydrocarbons (HC, PAH)	[62–65]
2	Watercol™ 1910	1,11-di(3-hydroxyethylimidazolium)3,6,9-trioxaundecane trifluoromethanesulfonate	Extremely polar	30°C	180°C	30 m × 0.25 mm × 0.20 μm	Water	[62,66]
3	SLB-IL60	1,12-di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide	Polar	35°C	300°C	30 m × 0.25 mm × 0.20 μm	Esters, ethers, chlorinated hydrocarbons, fatty acid methyl esters (FAME), industrial solvents	[62,64,67]
4	SLB-IL61	1,12-Di(tripropylphosphonium)dodecane bis(trifluoromethane-sulfonyl)imide trifluoromethanesulfonate	Polar	40°C	290°C	30 m × 0.25 mm × 0.20 μm	Some of polychlorinated dibenzofurans and polychlorinated dibenzodioxins	[62,68]
5	SLB-IL76	Tri(tripropylphosphoniumhexanamido) triethylamine bis(trifluoromethane-sulfonyl)imide	Highly polar	−	270°C	30 m × 0.25 mm × 0.20 μm	Alkenes, alkynes, aromatic hydrocarbons	[62,64]
6	SLB-IL82	1,12-di(2,3-dimethylimidazolium) dodecane bis(trifluoromethane-sulfonyl) imide	Highly polar	50°C	270°C	30 m × 0.25 mm × 0.20 μm	Analytes with cyanopropyl groups	[62,64]
7	SLB-IL100	1,9-di(3-vinyl-imidazolium)nonane bis(trifluoromethane-sulfonyl)imide	Highly polar	−	230°C	30 m × 0.25 mm × 0.20 μm	Compounds containing double and/or triple C−C bonds; benzene, toluene, ethylbenzene and xylene (BTEX)	[62,64,69]
8	SLB-IL111	1,5-di(2,3-dimethyl-imidazolium) pentane bis(trifluoromethane-sulfonyl)imide	Extremely polar	50°C	270°C	30 m × 0.25 mm x 0.20 μm	Compounds containing double and/or triple C−C bonds; BTEX	[62,64,69]
9	SLB-ILPAH	1,12-di(tripropylphosphonium) dodecane bis(trifluoro-methanesulfonyl)imide	Polar	−	300°C	20 m × 0.18 mm × 0.05 μm	PAH	[62]
10	[PSOMIM]⁺[Cl]⁻	Methylimidazolium chloride bonded polysiloxane	Highly polar	−	220°C	8 m × 0.25 mm × 0.30 μm	Aromatic isomers, FAME, polychlorinated biphenyls and aromatic amines	[70]
11	[PSOMIM]⁺[NTf₂]⁻	Methylimidazolium bis(trifluoromethyl-sulfonyl)imide bonded polysiloxane			380°C			
12	IL 7	Trans-1-octenyl-3-(2-hydroxycyclohexyl)-3H-imidazole-1-ium bis(trifluoromethyl-sulfonyl)amide	−	−	300°C	5 m × 0.25 mm × 0.20 μm	Fragrance substances, alcohols, amines, xylene isomers	[71]
13	Phosphonium-based IL	Tetra-butyl phosphonium methanesulfonate	Highly polar	−	220°C	15.8 m × 0.25 mm × −μm	alkanes, PAH, aromatic isomers, alcohols and chlorinated benzene compounds	[72]
14	Poly([C3Im]⁺[NTf₂]⁻)	Poly(propylimidazolium bis(trifluoromethane)sulfonimide	Extremely polar	−	325°C	30 m × 0.25 mm × 0.25 μm	Compounds with an amino, carbonyl and ester group	[73]
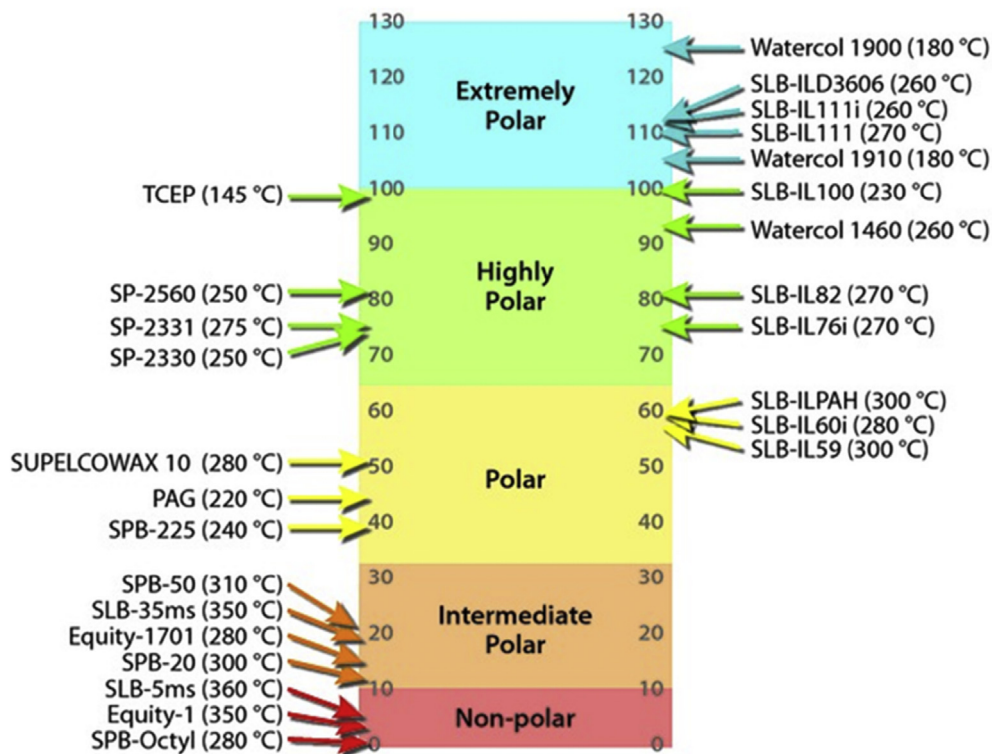
Fig. 3. Types of commercial columns in regard to their polarity. On the left side of the graph there are names of traditional columns, and on the right, there are names of columns containing ILs as stationary phases [62]. Maximum operating temperatures are given in parentheses.

choice of column should depend on its purpose and on the polarity of the separated chemicals. In the case of columns containing ILs, it was necessary to introduce some additional definitions of their polarity: high polarity and extreme polarity. Data presented in the Fig. 3 demonstrate that polarity of commercial columns containing ILs as stationary phases fits within the range between polar and extremely polar. The polarity of parts of ILs columns correspond to other types of columns, such as a GC column filled with 1,2,3-tris(2-aminoethyl) propane (TCEP), or poly(biscyanopropyl-siloxane) (SP-2650), and therefore they may be used interchangeably. In the case where it is necessary that columns demonstrate extreme polarity, only ILs-filled columns are available. They offer an increased selectivity in the case of polarisable compounds.

3.2. Liquid chromatography

Reversed-phase liquid chromatography (RPLC) is one of the most popular techniques for the separation of chemical compounds. However, it is not flawless. Presence of residual silanol groups on the surface of the stationary phase leads to the formation of two adsorption sites, which are different in terms of adsorptive-desorptive interactions between the analyte and the stationary phase. This manifests itself in tailing, asymmetry and broadening of peaks, or by shift of retention times and absence of reproducibility of results of the analysis. Some new stationary phases that are not silica-based need to be developed to avoid those problems, or the mobile phase needs to be enriched with a compound that would interact with silanol residues in traditional HPLC columns. Consequently, the substance dissolved in the mobile phase would ideally pass through the column at the same rate over its whole length. Compounds used for this purpose are, among others, ILs [74]. Poole et al. were the first to study physical and chemical properties of ILs in terms of their applicability as modifiers of the mobile phase in

liquid chromatography [75]. The studied alkylammonium ILs demonstrated a moderate viscosity, but following blending with commonly used chromatographic solvents (acetonitrile, water, methanol), their viscosity was reduced enough to apply them as a mobile phase in LC.

The number of publications on ILs as modifiers of the mobile phase in LC has significantly increased as of late. That is associated with two advantages of ILs [76]:

a) exchange of traditional additives to the mobile phase with ILs leads to improved selectivity,
b) contrary to alkylamines, addition of ILs does not alter pH, which allows their use in columns containing silica as the starting material.

Szymański et al. presented a method of simultaneous determination of diosmine and hesperidin in pharmaceutical products, using high-performance liquid chromatography (HPLC) [77]. For that purpose, the mobile phase was enriched with an IL (Didecyldimethylammonium lactate) which led to reduced time of analysis and improved symmetry of the peak. This was the first attempt to apply ILs in separation and quantitative determination of the above-mentioned analytes. Then, Flieger and Czajkowska-Żelazko demonstrated that ILs used as modifiers of the mobile phase in the analysis of compounds possessing different acidic-alkaline properties improved yield, symmetry and peak separation of the analysis [78]. However, to use them in a proper way, one should be extra careful with choosing elements of the chromatographic system and selecting concentration of the additive. In the case of 1-butyl-3-methylimidazole chloride, just a small addition leads to a significant increase of the separation coefficient of analytes belonging to the group of derivatives of benzodiazepine. Further increase of its concentration leads to a reduction of the

parameter, probably as a consequence of adsorption of lipophilic cations of the IL, which results in pointing the polar part of the molecule towards the flowing eluent [79].

As mentioned previously, ILs as modifiers of mobile phase in LC allow for better separation of the analysed mixture and improved symmetry of the obtained chromatographic peaks. In the future, this will allow for the development of some more efficient processes of separation in reversed systems of phases. However, it is suspected that these compounds are not applicable as additions to the mobile phase in chromatographic analyses with mass detection (MS), both when ionisation through electro-dispersion is used, and when chemical ionisation under atmospheric pressure is used. In both cases low volatile ILs accumulate and pollute the detector [80]. Other possible application of ILs is their use as stationary phases or their modification in LC. The application of ILs in countercurrent chromatography (CCC) may be the first example. In CCC separation occurs between two non-mixing liquids - one of which is the stationary phase and the other is the mobile one. Berthod et al. studied separation of 38 aromatic compounds containing acidic, alkaline or neutral function groups, using the double-phase system: IL (1-butyl-3-methyloimidazole hexafluorophosphate) and water [81]. They found that viscosity of the pure IL is too high for its direct use in CCC. An addition of a third compound (organic solvent, such as acetonitrile or ethanol) was necessary in order to decrease viscosity. Only with that addition was a double-phase system demonstrating a sufficiently low viscosity obtained. In further studies, the same IL was successfully used for the first time in CCC [82]. Also in this case an addition of acetonitrile was necessary. The best results were obtained for the water-acetonitrile-IL combination at the weight ratio of 40:20:40. That system was used for determination of the division constant of compounds belonging to the same group as those used in previous studies. The discussed paper demonstrated that CCC is a perfect tool for determination of liquid-liquid division constants of dissolved substances in any double-phase system. This may be associated with hydrophobic character of the studied compounds in a particular environment. These pieces of information have a great importance for all studies based on the determination of the quantitative structure—activity relationship — QSAR, or the quantitative structure retention relationship - QSRR.

The use of ILs as stationary phases in CCC still raises a lot of interest. Fan et al. studied the development of this technique in order to apply it to the initial determination of mycotoxins in samples of wine and juice [83]. Modification of the system of solvents with 1-carboxymethyl-3-methylimidazole chloride played a crucial role in the procedure of sample enrichment. Elution of analytes was completed by reversal of the primary stationary phase. The method was characterised by high recovery of mycotoxins, satisfactory reproducibility and low detection limits.

Another example of the use of ILs is high-performance liquid chromatography (HPLC). In this case, the stationary phase is closely bound to the column walls through covalent bonds. Mallik et al. obtained a new stationary phase containing polymerised octadecylimidazole alaninate bound to a silica base. They characterised the system and used it for separation of PAH, steroids and nitrogen bases of nucleotides [84]. The advantage of the newly created column over the commercial column with the octadecyl chain is its increased selectivity for those compounds and also the possibility of using water as a mobile phase for separation of nitrogen bases of nucleotides. Imidazole and carbonyl groups present in the resulting phase allow operation of numerous interaction mechanisms between the column and analytes, including: hydrophobic interactions, π-π, carbonyl-π, electrostatic, hydrogen bonds, and also ion-dipole interactions. The interaction found by Mallik et al. was confirmed by Jiang et al. [85] These authors created a silica-based column with an addition of octylbenzylo imidazole (BeImC8-Sil).

This phase was successfully used for the separation of PAHs, aniline, phenols and inorganic anions. With characteristics of various mechanisms of interaction, stationary phases of this kind offer a great potential in the analysis of composite samples.

3.3. Electrophoresis

Electrophoresis is the separation of a mixture of chemical compounds in an electric field. The separation is based on two phenomena: electrophoretic mobility and electroosmotic flow.

Capillaries most commonly used in electrophoresis are capillaries made of melted silica with silanol groups protruding from its walls (−Si−OH). At pH over 3, the internal wall of a capillary made of melted silica has a negative charge, which is associated with the dissociation of silanol groups (SiOH). With increasing pH, the intensity of ionisation of silanol groups increases, resulting in stronger negative charge. That charge is neutralised with cations from a buffer, forming a stable layer. Other cations, being at a greater distance, form a mobile layer moving from the anode to cathode, which results in the flow of liquid in the whole volume of the capillary.

In order to eliminate most of disadvantages of the discussed method, an attempt was made to use ILs as: an electrolyte, an addition to the buffer, a dynamic coating factor, or as a factor permanently bound to walls of the electrophoretic capillary [59,60]. Unfortunately, a permanent fixation of the IL to the capillary wall is difficult to achieve and expensive, and for those reasons it is seldomly used.

In 2010 Li et al. published the study on the effect of ILs in addition to the basic electrolyte used in the analysis of selected proteins [86]. It was demonstrated that poly(1-vinyl-3-methyloimidazole) bromide generates a strong reverse electroosmotic flow as a result of electrostatic interaction between the cation from the IL and the negatively charged surface of the wall. Repelling interactions between the cations of IL and the studied proteins efficiently eliminated adsorption on the walls. A satisfactory reproducibility and high yield were demonstrated in optimal conditions of the modified electrophoretic system for four enzymes: cytochrome C, lysozyme, ribonuclease A, α-chymotrypsinogen A. One year later, in their experiments, Li et al. used 1-butyl-3-methylimidazole tetrafluoroborate as a basic electrolyte and as a compound forming a dynamic coating on capillary walls [87]. This method was applied to separation and identification of three azo dyes in lipsticks. The experiment led to a complete separation of analysed compounds within 12 min. Also in this case it was found that the use of ILs improves parameters of capillary electrophoresis.

4. Ionic liquids in extraction-based methods of sample preparation

The aim of the analytical process is to determine the chemical composition, a qualitative and quantitative determination, of a studied substance. Considering the type of chemical compounds and information we want to get, various analytical techniques become necessary. Usually a sample received in a laboratory requires additional preparation before it is introduced to analytical equipment. The preparation stage is one of the most important stages of the analytical process. ILs are applied also for this purpose [88,89]. They have contributed to the development of the following sample preparation techniques: solid phase extraction (SPE), stir bar sorptive extraction (SBSE), single drop microextraction (SDME), hollow fibre liquid phase microextraction (HF-LPME), dispersive liquid-liquid microextraction (DLLME), micro extraction by packed sorbent (MEPS), solid phase microextraction (SPME).

4.1. Solid phase extraction

One relatively simple method of sample preparation, which ensures simultaneous enrichment and purification of analytes, is solid phase extraction. Various sources present unclear information regarding the inventor of this method. Nevertheless, its discovery as an alternative for liquid-liquid extraction was in 1970 [90]. This extraction consists of passing of the analysed solution through an extraction column filled with a deposit of a sorbent. Analytes become adsorbed on particles of that deposit. Another stage of the process is washing the column with an appropriately selected solvent in order to remove impurities. Another solvent is used to elute analytes adsorbed on the sorptive deposit. Alternative order of stages of the SPE procedure may be elution of the studied analyte followed by conditioning of the column. The selection of an appropriate filling and solvent for elution is crucial.

In 2016 Songqing et al. coated spherical, hybrid core/shell type nanostructures with a magnetic $Fe_3O_4@SiO_2$ type core with three imidazole-based ILs with different lengths of alkyl chains. Of those three, 1-octyl-3-methylimidazole hexafluorophosphate proved to be the best [91]. This system was then used as a sorbent in SPE for isolation of 2,2-bis(4-hydroxyphenyl)propane (BPA). Carbon chains from the IL covering the carrier provided adsorption sites for the analyte with π-π and hydrophobic interactions. That adsorbent offered superior extraction capacity and a higher enrichment factor compared to commercially available column fillings. The authors demonstrated that the BPA analytical method developed by them was comparable and, in the majority of cases, even superior to alternative analytical methods, e.g. dispersive liquid-liquid micro-extraction combined with HPLC, molecularly imprinted solid phase extraction (MISPE) combined with CE, or cyclic voltammetry. Zhang et al. modified the surface of a polymer with an imidazole-based IL with a different type of substituent in order to separate laminarin and fucidin - compounds commonly found in seaweed. Methyl, amine, and carboxyl substituents were considered, and also non-substituted systems [92]. The IL with the aminoimidazole group was chosen as a selective sorbent that allowed separation of both polysaccharides with a satisfactory linearity, precision on the level of 3.2% and a detection limit of 0.18 mg/mL. The compound additionally demonstrated a satisfactory durability.

4.2. Stir bar sorptive extraction

Extraction with a mobile sorptive element was invented in 1999 by Professor Pat Sandra, as a technique that requires small amounts of solvents or lack thereof [93]. In this method analytes are sorbed in a layer of polymer coated on a mobile sorptive element (similar to a magnetic stir bar). Following the process of sorption and enrichment, the analyte is usually subjected to thermal desorption or elution with a solvent.

In 2014 Fan et al. developed a novel coating layer for the stir bar, resulting in improved extraction performance and adsorption/desorption kinetics of non-steroid anti-inflammatory drugs (NSAIDs) [94]. 1-allylimidazole tetrafluoroborate $[AIM][BF_4]$ was used as the active substance. The compound was bound to the stir bar surface by bridging with γ-(methacryloxypropyl)trimethoxysilane. The newly designed stir bar was successfully used in the analysis of NSAIDs in aqueous environments, human urine and milk samples with high-performance liquid chromatography coupled with UV and visible absorption detectors (HPLC-UV–VIS).

Additionally, a satisfactory mechanical strength, and excellent thermal and chemical strengths of the coating were confirmed. Compared to commercially available stir bars coated with PDMS or C18, the newly developed stir bar offers a superior extraction performance in relation to tested analytes. Studies also determined

precision of the method, with a relative standard deviation of 3.6–9.5%, and a limit of detection on the level of 0.23–0.31 µg/L. Designers of this analytical method foresee its high potential in the determination of NSAIDs in environmental, food and biological samples.

4.3. Single drop microextraction

Single drop microextraction was designed in the early 1990s by Liu and Dasgupta [95]. The isolation of an analyte occurs by the dissolution of sample components in a drop of liquid suspended on the tip of a needle of a syringe, dipped directly into the sample, or in the headspace of the sample. A higher solubility of the analyte in the extracting solvent than that in the sample is a prerequisite of extraction.

In order to develop a novel method of extraction and concentration of flavour and fragrance substances in fruit juices, Jiang et al. used the SDME technique with an innovative application of hydrophilic ILs as an extraction medium, the so called "single drop" [96]. Following the isolation of hexyl acetate, geranyl acetate and limonene from the headspace, their extraction from the IL as a solvent into n-hexane was performed. n-hexane is an appropriate medium for gas chromatography. The substance that demonstrated the most favourable extraction properties in relation to the tested analytes was 1-hexyl-3-methylimidazole tetrafluoroborate. Following optimisation of parameters of the analysis for this solvent, the method was validated. The validation process demonstrated a limit of detection and a limit of quantification of the tested analytes at 4.4–99.0 ng/mL and 15.0–330.0 ng/mL, respectively. Additionally, the tip of the micro-syringe was coated with poly-tetrafluoroethylene, which allowed production of a stable drop with volume of 12.5 µL of the extracting factor and reduced probability of drop separation.

He et al. combined headspace single drop microextraction with high-performance liquid chromatography (IL-HS-SDME-HPLC) with 1-butyl-3-methylimidazole hexafluorophosphate as the extracting substance [97]. This method was used for determination of camphor and *trans*-anethole in licorice tablets. Similar to the earlier example, SDME equipment was modified in order to improve stability and sensitivity of the method. The contact area between the micro-drop and the tip of the PTFE capillary on the syringe was increased, which allowed extension of the duration of the sorption procedure and increased volume of the drop to 12 µL. The method is simple, rapid, selective, precise, accurate and linear for tested analytes. The yield of the described analytical method is similar to that of conventional ultrasound-assisted extraction (UAE). However, separation of substances extracted using the UAE method is difficult, because the method is not selective. On the other hand, SDME allows single step separation, purification and enrichment. This results in reduced noise caused by substances from the matrix and improved signal to noise ratio. Considering the high efficacy of purification achieved with this method, chromatographic separation was very simple and completed within 12 min. Authors expect the method developed by them will be appropriate for common use in the analysis of volatile components of drugs with high boiling points.

4.4. Hollow fibre liquid phase microextraction

Liquid phase microextraction (LPME) with Hollow fibre microporous membranes is a sister method to SDME. Both methods operate on the principle of liquid-liquid microextraction, but the HF-LPME method uses an acceptor phase placed in a thin capillary with walls playing the role of a membrane permeable for analytes
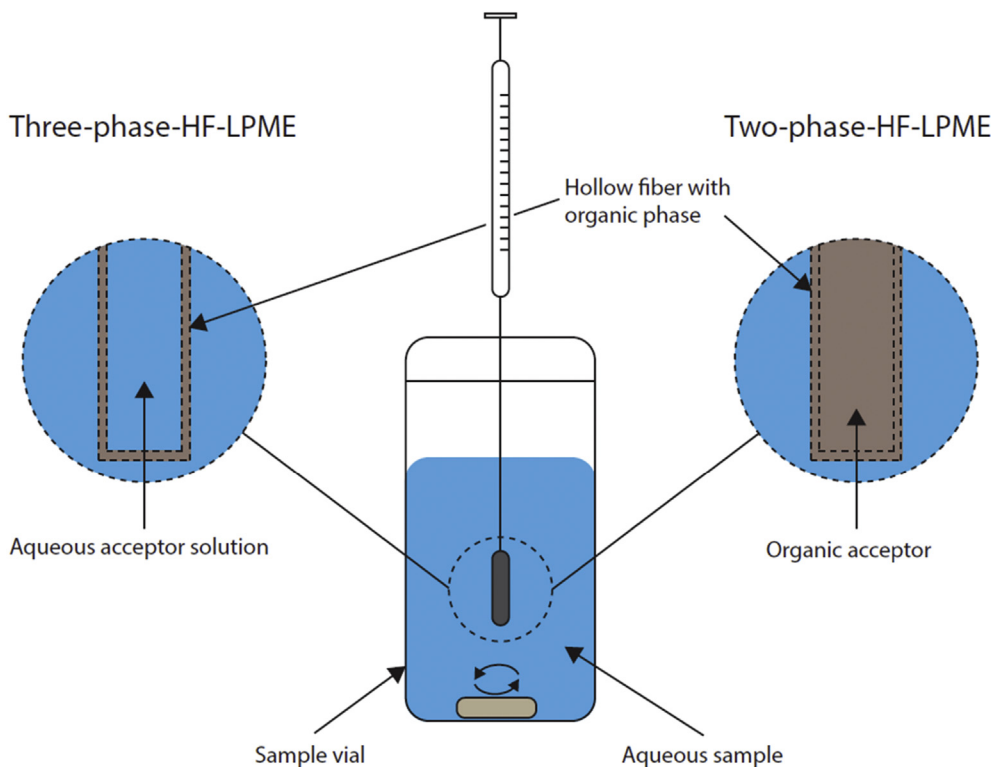
Fig. 4. Classification of LPME in respect to the number of phases [own elaboration].

instead of a single drop. Depending on the number of phases, there are double-phase and triple-phase HF-LPME (Fig. 4).

In 1999 Pedersen-Bjergaard and Rasmussen introduced the HF-LPME method as a modification of SDME. The purpose of the modification was to eliminate instability of a single drop of solvent [98]. The technique was based on double-stage extraction:

1) the first stage involved extraction of analytes into a membrane usually made of polypropylene and saturated with an organic compound,
2) then analytes migrate from the membrane into the acceptor solution contained in the capillary lumen.

The method allowed separation of analytes from the components of the matrix. Also, a greater concentration of solution was obtained.

One of the most important procedures to be completed in HF-LPME is the appropriate selection of an organic solvent contained in the porous membrane. Toluene and 1-octanol are currently most commonly used for that purpose. ILs may constitute an alternative for those compounds because they are less harmful for both the analyst and the natural environment. Chen et al. used 1-butyl-3-methylimidazole hexafluorophosphate ([C_4MIM]PF_6) to fill pores of fibres used for extraction and for increasing Cd^{2+} cation concentration in environmental and food samples [99]. Besides extraction of heavy metals, IL-HF-LPME was also applied for the extraction and enrichment of, among others:

- malachite green from aqueous samples [100] — the authors compared the developed method of sample preparation with MISPE, SPE, MSPE (magnetic solid phase microextraction); they concluded that compared to other methods IL-HF-LPME was relatively simple, offered the lowest limit of detection (0.01 μg/L), a satisfactory linearity range (0.20–100 μg/L), a good

reproducibility (relative SD of 8.9% for N = 5), and a high recovery (84.0–106.2%),
- kanamycin sulphate [101] — also in this case the authors compared IL-HF-LPME with other methods; the observed limit of detection of 0.00067 μg/mL proved to be one of the lowest among all and close to the LOD of capillary zone electrophoresis with UV detection (CZE-UV),
- bisphenol A and diethylstilboestrol [102] — in that case the LOD on the level of 0.05–0.20 μg/L was not that impressive compared to other methods but the newly developed method offered the best enrichment factor (624–850).

ILs belonging to the group of 1-alkyl-3-methylimidazole hexafluorophosphate were used in all the above-mentioned cases. ILs differed only in length of the alkyl chain at the imidazolium cation.

4.5. Dispersive liquid-liquid microextraction

The youngest variety of the LPME technique is dispersive liquid-liquid microextraction (DLLME) developed by Rezaee at al. For the purpose of determination of PAH in water samples [103]. The technique is based on the extraction of analytes from a few millilitres of aqueous sample to several dozen of microlitres of the extracting solvent. Solvents most commonly used in this technique are: chlorobenzene, dichloromethane, carbon tetrachloride, chloroform, tetrachloroethane and 1-octanol. Extracting solvents are used as a mixture with a small volume of a dispersing solvent, such as: acetone, acetonitrile, methanol, or ethanol. Presence of the dispersing solvent improves dispersion of the extracting solvent assuming form of microscopic droplets suspended in the whole volume of the solution, which significantly increases the extraction rate. Additionally, the dispersing solvent prevents the adsorption of analytes on the walls of a laboratory vessel. Following extraction,

the sample is centrifuged and the separated liquid phase containing the extracting solvent and the analyte is analysed.

One of the first papers on the application of ILs as extracting solvents was published by Fan et al. [104] The authors described a method of isolation of four phenols (4-nitrophenol, 2,4-dimethylphenol, bisphenol A, 2-naphthol) from aqueous solution using the IL-DLLME technique with 1-butyl-3-methyloimidazole hexafluorophosphate as the extracting substance. The use of a dispersing solvent was not necessary in the case of this kind of substance. Following optimisation, the method was validated. The validation demonstrated the limit of detection of 0.68−10 µg/L (depending on the determined substance), and the relative standard deviation of not more than 4.8%. Summing up their study, the authors compared the newly developed technique with other extraction methods, namely with LPME and SPME, in terms of time required for extraction and volume of the solvent consumed. In terms of both, the IL-DLLME method proved superior, offering 20-times shorter extraction time and approximately 13-times lower volume of required solvent. Wang et al. studied the analysis of bisphenols A, AF and AP with the IL-DLLME method and confirmed the reported advantages. They also underlined a similar value of the LOD in comparison to other analytic methods [105]. Studies are continued on the expansion of the applicability of the method, improvement of extraction parameters, and on miniaturisation of the technique [106].

4.6. Solid phase microextraction

Solid phase microextraction is a modern isolation technique applicable mostly to organic compounds. It was developed in 1990 at the Waterloo University by the group coordinated by Prof. Pawliszyn [107]. It is a simple, rapid and relatively cheap technique which requires small amounts of solvents or lack thereof. At present, SPME is the most commonly used method of isolation of volatile and medium volatile substances in both simple and complex matrices.

SPME is a double-stage process:

- sorption − division of analytes between the sample and the sorptive layer of a fibre, or adsorption of analytes on the sorptive surface of a fibre,
- desorption − release of the analyte from the surface of the fibre into the analytical equipment.

For the SMPE analysis a sample is placed in a vial. The vial is then tightly closed with cap equipped with a silicon membrane. A fibre placed in a syringe is introduced through the membrane. The fibre

is exposed in the headspace or directly in a solution. During a predefined time, analytes from the closed vial are sorbed from the sample matrix into the stationary phase of the fibre. When the extraction process is over, the fibre, with a coating containing analytes, is retracted into the needle. Then, the fibre, along with its coating soaked in analytes, is introduced into the dosing chamber of a chromatograph. Analytes are desorbed in the dosing chamber of a gas or liquid chromatograph, and the sample is analysed (Fig. 5).

5. Ionic liquids used in solid phase microextraction

Just like any other extraction method, despite some excellent advantages, SPME is burdened with some disadvantages. The most important of them are: low chemical and thermal strength of the SPME fibre, low selectivity of analytes, fragility, and limited operating time.

Therefore, some new sorptive coatings have been sought out that would allow elimination, or at least partial reduction, of those disadvantages. Considering a vast variety of ILs and also possible manipulation with their physical and chemical properties by selection of appropriate ions, they seem to be an excellent alternative for the currently used SPME fibre sorptive materials [108,109].

5.1. Ionic liquids as sorptive coatings in SPME

The application of the unique properties of ILs as extraction coatings in SPME is a broadly discussed topic [110]. The first attempt of this kind was made by Liu et al., in 2005 [111]. The authors developed a disposable sorptive coating based on 1-octyl-3-methylimidazolium hexafluorophosphate. A stainless-steel fibre was coated with an IL before each analysis. With a prepared fibre, the analyte was extracted (BTEX in paint samples) followed by desorption in a dosing chamber of a chromatograph. After the whole process, the coating was washed away from the fibre with solvents. Compared to commercially available fibres, the fibre coated with the disposable IL layer demonstrated a comparable reproducibility and much lower costs (even if counted per a single determination). At the same time, the fibre memory effect was eliminated. However, besides some obvious advantages, the fibre also had a serious disadvantage: an inferior sensitivity resulting from a relatively thin coat. The potential demonstrated in this paper encouraged other scientists to study properties of ILs in terms of their possible applicability as SPME stationary phases.

Long studies on the application of ILs as stationary phases in SPME resulted in the development of several methods of preparing coats for SPME fibres. Those methods resulted in various parameters of the produced coatings, including a number for/to describe
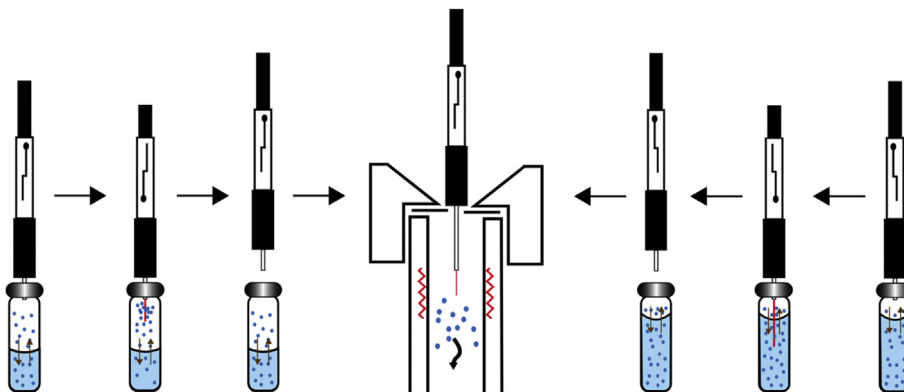
Fig. 5. Flowchart of a chromatographic analysis with SPME. J.-S. Aulakh, A.-K. Malik, V. Kaur, P. Schmitt-Kopplin, A Review on solid phase micro extraction—high performance liquid chromatography (SPME-HPLC) analysis of pesticides, Crit. Rev. Anal. Chem., 2005 (35) 71−85.

the sensitivity associated with thickness of the coat and for the stability of the produced layer.

IL-based sorptive coatings for SPME may be produced using the following methods: physical coating of a fibre with ILs, chemical binding of ILs with a fibre, production of hybrid materials, and modification with ILs.

5.1.1. Sorptive coatings for SPME made by physical coating with ionic liquid

Phases not directly bound to a fibre — that is, physically fixed — were the first attempts of applications of ILs as stationary phases in SPME. These coatings do not contain any crosslinking substances, and moreover, they are not resistant to organic solvents. They also demonstrate a tendency toward swelling. They also demonstrate inferior thermal stability compared to coatings chemically bound to the carrier. These types of coatings are used for single analysis. Afterwards it is necessary to remove the sorptive layer and apply it again before the next extraction. The most commonly used technique is coating by immersion of the carrier in an IL solution in methylene chloride, followed by spontaneous evaporation of the solvent. That process may be repeated several times to achieve an expected thickness of the phase.

Kang et al. developed the method of determination of phosphorus flame retardants (PFR) in water samples by stationary phase microextraction with physically fixed ionic ILs as sorptive coatings [112]. Among the tested ILs, the coating based on 1-octyl-3-methyloimidazole hexafluorophosphate proved the most effective. In optimal conditions of extraction, the linear range of the suggested method was 10—50000 ng/L. Reproducibility of the SPME fibre described by a relative standard deviation was 3.9—8.2%, and the limit of detection was 0.8—9.3 ng/L. The new fibre was also compared to commercially available ones: PDMS, CAR/PDMS and PDMS/DVB. Results clearly indicated that the IL-coated fibre offered a higher PRF extraction efficiency than aqueous samples.

Amini eta al. prepared a fused silica SPME fibre coated with 1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis (trifluoromethylsulfonyl) imide for determination of methyl *tert*-butyl ether (MTBE) in a gasoline sample by HS-SPME-GC-FID [113]. The optimum conditions for the sorption of MTBE were as follow:

temperature at $40 \pm 1°C$, time 12 min, desorption time 30s and string rate at 200 rpm. The data obtained during these studies show that prepared SPME fibres have high operating temperatures, are easy to prepare, and have high stability and durability. The chemically bonded IL film on the surface of the fibre was durable over 16 headspace extractions without any significant loss of the film. Compared to commercially available SPME fibres, these proposed IL-coated fibres have a much lower cost, comparable reproducibility, and no carryover between determinations. The calibration graph was linear in the range from 2 to 240 μg/L, with $R^2 = 0.996$. The detection limit of MTBE in gasoline was 0.1 μg/L. The reproducibility (RSD %, n = 6) of the new IL bonded fused-silica fibre was 8.9% and it was better than the physically coated fibre (12%). This suggests that the new chemically IL-modified fibre is more robust than the physically IL-modified fibre. The proposed IL-modified fibres showed improved thermal stability at temperatures up to 220°C relative to the physically modified fibres (180°C).

Amini et al. synthesized four different ILs and used them for the determination of MTBE by HS-SPME-GC-FID in gasoline samples [114]. SPME fibres were coated with: $[C_8C_1IM][PF_6]$, $[C_8C_1IM][BF_4]$, $[C_4C_1IM][BF_4]$ and $[C_2C_1IM][EtSO_4]$. The large viscosity, involatility and good thermal stability of the IL kept the IL film remaining on the fibre while the analyte was thermally desorbed in the GC injection. The best temperature for analysis of MTBE was 45°C with sorption time of 18 min. The optimum value for solution stirring was obtained as 300 rpm. The desorption time was at least 10s for an injector temperature of 180°C. Compared to widely used, commercially available SPME fibres, these proposed IL-coated fibres have a much lower cost, comparable reproducibility (RSD = 8.3% for IL fibres versus 6.3% and 7.7% for commercial fibre), and no carryover between determinations. The calibration graph was linear in the range of 1—120 μg/L with an $R^2 > 0.994$. The detection limit of MTBE was 0.09 μg/L for IL fibres and it was lower than LOD for commercial fibres (0.45 μg/L for PDMS/DVB and 0.27 μg/L for PDMS/Carboxen).

Table 2 lists examples of applications of SPME fibres with sorptive layers physically covered with IL. The table also lists analytical methods, methods of desorption and the active substance of each coating, along with its thickness.

Table 2
List of physically fixed ionic liquids used as coatings for SPME fibres.

No.	SPME film		Method of analysis	Desorption	Analyte	Lit.
	Active compound	Abbreviation/thickness				
1	1-octyl-3-methylimidazolium hexafluorophosphate	$[C_8MIM][PF_6]$/—	HS-IL-SPME-GC	Thermal desorption/max. 200°C	BTEX	[111]
2	1-ethyl-3-methylimidazolium hexafluorophosphate	$[C_2MIM][PF_6]$/—	HS-IL-SPME-GC	Thermal desorption/—	triphenyl phosphate (TPHP), tri-n-butyl phosphate (TNBP),	[112]
3	1-butyl-3-methylimidazolium hexafluorophosphate	$[C_4MIM][PF_6]$/—			tri(2-chloroethyl) phosphate (TCEP), tri(2-chloroisopropyl)	
4	1-hexyl-3-methylimidazolium hexafluorophosphate	$[C_6MIM][PF_6]$/—			phosphate (TCIPP), tri(dichloropropyl) phosphate	
5	1-octyl-3-methylimidazolium hexafluorophosphate	$[C_8MIM][PF_6]$/—			(TDCIPP), tri(2-ethylhexyl) phosphate (TEHP), tripropyl phosphate (TPP)	
6	1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis(trifluoromethyl sulfonyl) imide	—/~11 μm	HS-IL-SPME-GC	Thermal desorption/max. 180°C	MTBE	[113]
7	1-butyl-3-methylimidazolium tetraflouroborate	$[C_4C_1IM] [BF_4]$/—	HS-IL-SPME-GC	Thermal desorption/max. 180°C	*tert* MTBE	[114]
8	1-octyl-3-methylimidazolium tetraflouroborate	$[C_8C_1IM] [BF_4]$/—				
9	1-octyl-3-methylimidazolium hexafluorophosphate	$[C_8C_1IM] [PF_6]$/~12,7 μm				
10	1-ethyl-3-methylimidazolium ethylsulphate	$[C_2C_1IM] [ETSO_4]$/—				

Table 3
Characteristics and applications of chemically bound ionic liquids as coatings for SPME fibres.

No.	SPME film		Method of analysis	Desorption	Lifetime	Analyte	Lit.
	Active compound	Abbreviation/thickness					
1	Poly(1-vinyl-3-butylimidazolium) chloride	−/~20 μm	DI-IL-SPME-GC	Thermal desorption/max. 280°C	~40	Nap, Acenaphthylene (Acpy), Acenaphthene (Acp, Ace), Fluorine (Flu), Anthracene (Ant), Phenanthrene (Pa, Phe), Fluoranthene (Fl, Flt), Pyrene (Pyr), Benz [a] anthracene (Baa), Chrysene (Chr), Benzo [b] fluoranthene (Bbf), Benzo [k] fluoranthene (Bkf), Benzo [a] pyrene (Bap), Benzo [ghi] perylene (Bjhip), Dibenzo [a,h] anthracene (Dba), Indeno [1,2,3-cd] pyrene (Ind)	[115]
2	Poly(1-vinylbenzyl-3-hexadecylimidazolium) bis [(trifluoromethyl)sulfonyl]imide	PIL−benzyl/~1 μm	HS−IL-SPME−GC	Thermal desorption/max. 250°C	−	Nap, Acp, Flu, Phe, Ant, Flt, Pyr	[116]
3	Poly(1-vinylbenzyl-3-hexadecylimidazolium) bis [(trifluoromethyl)sulfonyl]imide	poly(ViBC$_{16}$Im$^+$ NTf$_2^-$)/~14 μm	DI-IL-SPME-HPLC	Solvent desorption/ Metanol	>100	carbamazepine (Cmz), benzaldehyde (Bnzal), bisphenol A (BPA), 2-nitrophenol (NP), α,α,α,6-tetrafluoro-m-toluidine (tfTol), 3-tert-butylphenol (t-BuP), ethyl benzoate (EB), naphthalene (Nap), gemfibrozil(Gfz), irgasan (Irg)	[117]
4	Poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide	poly(ViC$_{16}$Im$^+$ NTf$_2^-$)/~13 μm					
5	Poly(1-vinyl-3-hexadecylimidazolium) bromide	poly(ViC$_{16}$Im$^+$ Br$^-$)/~14 μm					
6	Poly(1-vinylbenzyl-3-hexadecylimidazolium) bis [(trifluoromethyl)sulfonyl]imide	poly(ViBC$_{16}$Im$^+$ NTf$_2^-$)/~35 μm				BPA, 4-cumylphenol (CuP), 4-tert-octylphenol (t-OP), and 4-octylphenol (OP), 4-n-nonylphenol (n-NP)	
7	Poly(1-vinyl-3-hexylimidazolium) chloride	poly(ViC$_6$Im$^+$ Cl$^-$)/~35 μm					
8	Poly(1-vinyl-3-octylimidzaolium p-styrenesulfonate)	poly(VOIm$^+$ SS$^-$)/~5−7 μm	DI-IL-SPME-GC HS-IL-SPME-GC	Thermal desorption/max. 250°C	~90	Aniline (A), 4-methylaniline (4-MA), 2-chloroaniline (2-CA), 4-chloroaniline (4-CA), dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dicyclohexyl phthalate (DCHP), di-2-ethylhexyl phthalate (DEHP), 2-Methylphenol (2-MP), 4-methylphenol (4-MP), 2-ethylphenol (2-EP), 4- ethylphenol (4-EP)	[118]
9	Poly(1-vinyl-3-octylimidzaolium benzenesulfonate)	poly(VOIm$^+$ BS$^-$)/−	DI-IL-SPME-GC		−		
10	1-methyl-3-(3-trimethoxysilyl propyl) imidazolium bis(trifluoromethylsulfonyl)imide	−/~11 μm	HS-IL-SPME-GC	Thermal desorption/max. 220°C	>16	MTBE	[113]
11	Bis-hydroxyethyl imidazolium trioxyethylene bis-(trifluoromethylsulfonyl)imide	(HeIM)$_2$PEG$_3$, 2NTf$_2^-$/~50 μm	HS-IL-SPME-GC	Thermal desorption/max. 200°C	−	HS-IL-SPME-GC: Ethyl acetate, n-butanol, acetonitrile (ACN), i-propanol (IPA), n-propanol, ethanol, methanol, acetone	[119]
12	Bis-hydroxyethyl imidazolium trioxyethylene bis-trifluoromethanesulfonate	(HeIM)$_2$PEG$_3$, 2TfO$^-$/~50 μm			−		
13	Poly(bis-styrene 1,1′-(1,6-hexanediyl) bis-imidazole) bis-(trifluoromethylsulfonyl)imide	poly[(StyrIM)$_2$C$_6$, 2NTf$_2^-$]/~50 μm	HS-IL-SPME-GC DI-IL-SPME-GC	Thermal desorption/max. 250°C	−	DI-IL-SPME-GC: Ethyl acetate, n-butanol, acetonitrile (ACN), i-propanol (IPA), n-propanol, ethanol, methanol, acetone, methylamine, dimethylamine, trimethylamine	
14	Poly(bis-styrene 1,1′-(1,6-hexanediyl) bis-imidazole) trifluoromethanesulfonate	poly[(StyrIM)$_2$C$_6$, 2TfO$^-$]/~50 μm	HS-IL-SPME-GC DI-IL-SPME-GC		>50		
15	1-allyl-3-methylimidazolium hexafluorophosphate	[AMIM][PF$_6$]−OH-TSO/~77 μm	DI-IL-SPME-GC	Thermal desorption/max. 280°C	−	4-tert-butylphenol (4-TBP), 4-tert-octylphenol (4-TOP), BPA, 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), A, o-toluidine (OT), 2,4-dimethylaniline (2,4-DMA), 3,4-dimethylaniline (3,4-DMA), N,N-diethyl-aniline (2-EA)	[120]
16	1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[AMIM][N(SO$_2$ CF$_3$)$_2$]−OH-TSO/~67 μm					

(continued on next page)

Table 3 (*continued*)

No.	SPME film		Method of analysis	Desorption	Lifetime	Analyte	Lit.
	Active compound	Abbreviation/thickness					
17	1-(3-triethoxysilyl propyl)-3-methyl imidazolium hexafluorophosphate	TESPMIM[PF$_6$]/~82 μm	DI-IL-SPME-GC HS-IL-SPME-GC	Thermal desorption/max. 280°C	–	DI-IL-SPME-GC: 4-MP, 2,4-dimethylphenol (2,4-DMP), 4-TBP, 2,4,6-TCP, 2,6-di-*tert*-butylphenol (2,6-DTBP), 4-TOP, PCP, BPA, A, OT, 2,4-DMA, 3,4-DMA, diphenylamine (DPA), N,N-diethylaniline (N,N-DEA), DMP, DEP, DBP, diamyl phthalate (DAP), din-octyl phthalate (DnOP), diisooctyl phthalate (DiOP), dinonyl phthalate (DNP), didecyl phthalate (DDP), indene (Ind), Nap, Ace, Phe, fluorene (Flu), n-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol, n-pentanol, n-hexanol, n-octanol, isobutyric acid, valeric acid, hexanoic acid, heptanoic acid, n-octanoic acid HS-IL-SPME-GC: n-propanol, isobutyl alcohol, n-butanol, n-pentanol, n-hexanol, n-octanol	[121]
18	1-(3-triethoxysilyl propyl)-3-methylimidazolium tetrafluoroborate	TESPMIM[BF$_4$]/~82 μm	DI-IL-SPME-GC HS-IL-SPME-GC				
19	1-(3-triethoxysilylpropyl)-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide	TESPMIM[N(SO$_2$CF$_3$)$_2$]/~81 μm	DI-IL-SPME-GC HS-IL-SPME-GC				
20	1-hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C$_{16}$MIM][NTf$_2$]/~35 μm	HS-IL-SPME-GC	Thermal desorption/max. 250°C	>40	tris(2-chloroethyl)phosphate (TCEP), tris(chloroisopropyl) phosphate (TCPP), tris(dichloropropyl)phosphate(TDCP), tris(2-butoxyethyl)phosphate (TBEP), tributylphosphate (TnBP), triphenyl phosphate (TPhP), tricresyl phosphate (TCrP)	[122]
21	Poly(1-Vinylbenzyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide	poly[VBHDIM][NTf$_2$]/~37 μm	DI-IL-SPME-GC	Thermal desorption/max. 220°C	>100	acrylamide	[123]
22	Poly(1-vinyl-3-(10-hydroxydecyl) imidazolium) bis[(trifluoromethyl) sulfonyl]imide	poly[VC$_{10}$OHIM] [NTf$_2$]/~53 μm			>100		
23	1-vinyl-3-(9-carboxynonyl) imidazolium bis[(trifluoromethyl) sulfonyl]imide	poly[VC$_9$COOHIM] [NTf$_2$]/~51 μm			–		
24	Poly(1-vinylbenzyl-3-hexadecylimidazolium) bis[(trifluoromethyl) sulfonyl]imide	Fibre 1/~21 μm	HS—IL-SPME—GC DI—IL-SPME—GC HS-DI—IL-SPME—GC	Thermal desorption/max. 250°C	–	ethyl benzene, m-xylene, Nap, Acpy, Ace, Flu, Phe, Ant, Fl, Pyr, α -benzene hexachloride, β-benzene hexachloride, δ-benzene hexachloride, γ-benzene hexachloride, aldrin, heptachlor, heptachlor epoxide, dieldrin, di-iso-propyl phthalate, di-iso-butyl phthalate, di-heptyl phthalate	[124]
25	1-vinyl-3-hexylimidazolium chloride	Fibre 2/~36 μm	HS-DI—IL-SPME—GC	Thermal desorption/max. 175°C			
26	1-vinylbenzyl-3-hexadecylimidazolium chloride	Fibre 3/~40 μm					
27	1-butyl-3-methylpyridinium bis(trifluoromethane-sulfonyl)imide	[C$_4$C$_1$Py][TFSI]/~23—30 μm	HS—IL-SPME—GC	Thermal desorption/max. 220°C	–	Hexachloroethane (HCE), hexachlorobutadiene (HCBD), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 2-chloronaphthalene(2-CN)	[125]
28	1-butyl-1-methylpyrrolidinium bis(trifluoromethane-sulfonyl)imide	[C$_4$C$_1$Pyrr] [TFSI]/~23—30 μm			>100		
29	1-butyl-1-methylpiperidinium bis(trifluoromethane-sulfonyl)imide	[C$_4$C$_1$Pip][TFSI]/~23—30 μm			–		
30	1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide	[C$_4$MIM][TFSI]/~65—70 μm	HS—IL-SPME—GC	Thermal desorption/max. 220°C	~60	benzene, bromobenzene, n-butylbenzene, ethylbenzene, p-isopropyltoluene, Nap, styrene, toluene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m-xylene	[126]

5.1.2. Sorptive coatings for SPME made by chemical coating with ionic liquid

The phase chemically bound to the surface of a SPME fibre contains crosslinking substances that ensure formation of bonds between IL molecules and the surface of the carrier. Coatings of this type are stable in most popular organic solvents. Swelling may occur only in the case of use of some non-polar solvents. This type of coating of a SPME fibre is also characterised by a high thermal stability.

In the analysis of PAH, the SPME fibre coated with a covalently bound polymerised 1-vinyl-3-butyloimidazole chloride developed by Pang et al. had a comparable operating time to those of commercially available fibres [115]. After analyte extraction was repeated 40 times, the analytical signal was reduced by 20—58% for the IL-coated fibre, and by 23—52% for a commercial PDMS fibre. Additionally, the IL-coated fibre demonstrated superior extraction capacity and a lower LOD value for PAH with a low number of aromatic rings (<4) compared to the PDMS fibre.

A benzyl-functionalized crosslinked polymeric ionic liquid (PIL) was successfully used as a sorbent coating in headspace solid-phase microextraction coupled to gas chromatography with flame-ionisation detection to determine seven volatile polycyclic aromatic hydrocarbons (in environmental water samples [116]. The optimum extraction conditions for the PAHs were as follow: an extraction temperature of 50°C, ionic strength content adjusted with 30% (w/v) NaCl in the aqueous sample, and an extraction time of 60 min. In all cases, higher log K_{fs} values for the crosslinked PIL fibre coating were obtained compared to the PDMS fibre coating for the PAHs, indicating the superior affinity of the PIL fibre. For all tested PAHs, higher log K_{fs} values for the crosslinked PIL fibre coating were obtained compared to the PDMS fibre coating, indicating the superior affinity of the PIL fibre. The linearity of the PIL—benzyl fibre and PDMS were tested up to 20 µg/L of PAHs concentration. The linear ranges were between 0.02 and 20 µg/L for the PIL—benzyl fibre with correlation coefficients higher than 0.997 and between 0.03 and 20 µg/L for the PDMS fibre with an R [2] higher than 0.996. The obtained LODs for the PIL—benzyl fibre were lower than for the PDMS fibre, so the method was better. LODs ranged from 0.01 to 0.04 µg/L for the PIL—benzyl and from 0.01 to 0.07 µg/L for the PDMS. The RSD values for the PIL—benzyl fibre varied from 2.8% to 7.9% and for the PDMS fibre from 1.0% to 9.0%. Relative recoveries ranged from 97.8% to 111% for river water and from 67.2% to 130% for seawater using the PIL—benzyl fibre. In the case of the PDMS fibre, relative recoveries range from 74.7% to 116% for river water and from 77.0% to 110% for seawater. RSD values were lower than 9.4% in all cases, which highlights the reproducibility of the method. No damage to the fibre coating was observed during the whole analysis, which can be indicative of a long lifetime of the thinness coating.

Pacheco-Fernandez et al. prepared several crosslinked polymeric ionic liquid (PIL)-based sorbent coatings of different natures for determination of polar organic pollutants in water [117]. The PIL coatings contained either vinylalkyl or vinylbenzyl imidazolium-based (V_iC_nIm- orV_iBC_nIm-) IL monomers with different anions, as well as different dicationic IL crosslinkers. These PIL-based SPME fibres were tested for the extraction of 10 different model analytes, including hydrocarbons and phenols. The extraction efficiencies for these fibres were compared to the extraction efficiencies of commercial fibres (PDMS, PA and PDMS/DVB) during an analysis by DI-SPME-HPLC-DAD. Based on the results obtained in the preliminary study, several PIL-based fibres were selected for the determination of alkylphenols (BPA, CuP, t-OP, OP and n-NP). The selected fibres were PIL—1b (with thicker coating, ~35 mm) and PIL—4 (which contains a chloride anion to ensure higher affinity towards polar compounds and with a thicker coating of ~35 mm). The result showed that the PIL—1b fibre gave recoveries of 108% and precision values lower than 19%. Correlation coefficients for the overall method with the PIL—1b fibre ranged between 0.990 and 0.999, and limits of detection were down to 1 µg/L for the fibre PIL—4. Partition coefficients for the alkylphenols to the specific SPME coating varied from 1.69 to 2.45 for PIL—1, and from 1.58 to 2.30 for PA, pointing out the high affinity of the PIL—1 for the studied analytes, while the PIL—4 fibre presented the highest value for BPA (1.73).

A SPME fibre with immobilized ionic liquids can be obtained by sol-gel technology. Pang et al. developed a high loading 1-hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide confined within a hybrid network based on the condensation reaction of methyltrimethoxysilane in the presence of TFA [122]. The designed fibre possesses a coating thickness of 35 µm with good thermal stability and a long lifetime. This fibre was for the analysis of six organophosphate esters (OP). The LODs of the developed analytical method ranged between 0.04 and 0.95 µg/L with precision in the range 9—13%. This method was successfully applied for the determination of the OPs in real water samples with a recovery in the range 64.8—125.4%.

Nine crosslinked PIL based fibres were developed for the trace level determination of acrylamide in brewed coffee and coffee powder using GC-MS [123]. The LOQ was 0.5 µg/L for 50% [(VBBIM)$_2$C$_{12}$]2[NTf$_2$] in [VC10OHIM][NTf$_2$] coating. The developed fibres showed good repeatability with RDS below 10%. They were obtained from real coffee samples and the structure of the coatings appeared intact after coffee sampling, thus proving the matrix compatibility of the PIL sorbent coatings.

Pena-Pereira et al. developed inogels derived from three different ILs based on anionbis(trifluoromethanesulfonyl)imide (TFSI), namely 1-butyl-3methylpyridiniumbis(trifluoromethanesulfonyl)imide ([C$_4$C$_1$Py][TFSI]), 1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([C$_4$C$_1$Pyrr][TFSI]) and 1-butyl-1methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([C4C1Pip] [TFSI]), were obtained on optical fibres by sol-gel technology [125]. These SPME fibres were used in the analysis of volatile chlorinated organic compounds. The best sorbet for extraction of the target substances was [C$_4$C$_1$Pyrr][TFSI]. LODs and LOQs ranged from 0.011 to 0.151 and from 0.037 to 0.503 µg/L, respectively. The recoveries for the seven chlorinated compounds were in the range 96—106%. The best SPME fibre exhibited high extraction efficiency for the tested chlorinated organic compounds and a long lifetime of approximately 100 consecutive extraction/desorption cycles.

Ionogels 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_4$MIM][TFSI]) confined within the hybrid network were used for the analysis of aromatic volatile compounds [126]. The proposed ionogel fibre showed excellent enrichment factors up to 7400. The LODs for the tested compounds were in the range of 0.03—1.27 µg/L, whereas the repeatability and fibre-to-fibre reproducibility were 5.6% and 12.0% respectively. The recovery of the selected aromatic volatile substances from water samples were in the range of 88.7—113.9%. Based on these results, it can be confirmed that ionogel fibres are an excellent option for the preparation of advanced SPME coatings.

Table 3 lists examples of applications of SPME fibres with sorptive layers chemically covered with IL. The table also lists analytical methods, methods of desorption and the active substance of each coating, along with its thickness.

5.1.3. The SPME sorptive coat with a modified ionic liquid

Another kind of coating is hybrid coating. These coatings are composed of two or more active substances. One of them is an IL and the other is a substance that improves sorption capacity, thermal and mechanical stability, or ensures a higher selectivity of the coating in relation to particular analytes. Table 4 presents some

Table 4
Characteristics and applications of modified ILs as coatings for SPME fibres.

No.	SPME film		Method of analysis	Desorption	Lifetime	Analyte	Lit.
	Active compound	Abbreviation/thickness					
1	Poly(1-vinyl-3-hexylimidazolium) bis(trifluoromethanesulfonyl) imide, graphene oxide	poly(VHIm$^+$NTf$_2^-$)-GO/ ~15 μm	HS-IL —SPME-GC	Thermal desorption/max. 260°C	~50	Nap, biphenyl (Bp), Flu, symmetric diphenylethylene (Sde), Ant, Flt, DBP, dioctyl phthalate (DOP), DCHP	[127]
2	Poly(1-vinyl-3-hexylimidazolium) bromide, graphene oxide	poly(VHIm$^+$Br$^-$)-GO/ ~15 μm			–		
3	1-aminoethyl-3-methylimidazolium bromide, graphene oxide	(C$_2$NH$_2$MIm$^+$Br$^-$)-GO/ ~13 μm					
4	1-aminoethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide, graphene oxide	(C$_2$NH$_2$MIm$^+$NTf$_2^-$)-GO/ ~13 μm					
5	1-hydroxyethyl-3-methylimidazolium bis[(tri-fluoromethyl)-sulfonyl]imide, polycarbazole	PCz-[HOEMIm][NTf$_2$]/ ~84 μm	HS-IL —SPME-GC	Thermal desorption/max. 260°	>200	environmental pollutants: o-Chlorotoluene (o-CT), p-bromotoluene (p-BT), o-nitrotoluene (o-NT), m-nitrotoluene (m-NT), p-nitrotoluene (p-NT)	[128]
6	1-hydroxyethyl-3-methylimidazolium hexafluoro-phosphate, polycarbazole	PCz-[HOEMIm][PF$_6$]/ ~84 μm			–		
7	1-methyl-3-octylimidazolium hexafluoro-phosphate, polycarbazole	PCz-[OMIm][PF$_6$]/~84 μm			–		
8	1-hydroxyethyl-3-methylimidazolium tetrafluoroborate, carboxyl multiwall carbon nanotubes, reduced graphene oxide, polyaniline	PANI-MWCNTs-rGO-[HOEMIm] BF$_4$/~40 μm	HS-IL —SPME-GC	Thermal desorption/max. 250°C	>200	1,4-dimethylbenzene, 1,2-dimethylbenzene, 1,3,5-trimethylbenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, ANI, N-methylaniline, 3-methylbenzenamine, 2-chlorobenzenamine, 3-chlorobenzenamine, methyl benzoate, methyl salicylate, methyl laurate, ethyl anthranilate, methyl anthranilate, trans-2-hexenal, benzaldehyde, benzeneacetaldehyde, decyl aldehyde, octanol, nonanol, geraniol, decanol, undecanol, dodecanol	[129]
9	1-(triethoxy silyl)-propyl-3-aminopropyl imidazole hexafluoro-phosphate, porous aromatic frameworks	PAF-IL/~30 μm	HS-IL —SPME-GC	Thermal desorption/max. 250°C	>100	organochlorine pesticides (OCPs)	[130]

of possible combinations developed by various scientists all over the world.

An example of a hybrid coating is the one developed by Hou et al., who besides IL, also used nanotubes and reduced graphene oxide and/or polyaniline in order to improve the properties of a SPME fibre [127]. The resulting composite coating was porous and highly thermally stable, which proved beneficial in the analysis of some alcohols from headspace with SPME. The developed fibre was compared to some commercially available ones: 100 μm thick PDMS and PDMS/DVB 65 μm. The PDMS fibre demonstrated higher effectiveness in relation to the selected WWA and phthalate esters (PAE) compared to the PDMS/DVB fibre. The newly produced fibre demonstrated to 24 times higher productivity compared to the better of the two commercially available fibres − PDMS.

To stress the importance of the role of a modifier incorporated into the IL-coated fibre, Feng at al [128]. compared fibres with a sorptive coating in the following forms: IL, polycarbazole (PCz), a composite of IL and polycarbazole (PCz + IL), PA and PDMS. Sorption effectiveness demonstrated by the PCz-IL fibre was much higher than the one presented by the IL fibre, and 2 to 5 times higher than the effectiveness of the PCz fibre. The composite fibre was also superior to PDMS and PA, although its layer thickness was lower compared to both commercially available fibres. Its long operating life was an additional advantage (>200 repetitions of sorption-desorption cycles). The study of this parameter demonstrated an 8%–30% difference between the area under the peak. Mian et al. proposed the use of an ionic liquid (IL, i.e. 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate), carboxyl multiwall carbon nanotubes (MWCNTs) and reduced graphene oxide (rGO) to prepare a three dimensional porous material (MWCNTs-rGO-IL) by one-step self-assembly which was then co-electrodeposited with polyaniline (PANI) on stainless steel wires by cyclic voltammetry [129]. The resulting fibre (PANI-MWCNTs-rGO-IL) was used for the HS-SPME analysis of alcohols. The LODs of the analysed compounds were in the range of 2.2–28.3 ng/L. The developed analytical method was applied for the determination of the alcohols in green and black tea. Octaniol and geraniol were detected in the two samples while nonanol was also detected in green tea. The recoveries of alcohols from tea were in the range of 86.6–114.2%.

A novel hybrid material incorporating porous aromatic frameworks and an ionic liquid, 1-(triethoxy silyl)-propyl-3-aminopropyl imidazole hexafluorophosphate, was developed [130]. This novel fibre was used for the analysis of organochlorine pesticides. Under optimized conditions, the linear range was 1–500 μg/L with an R^2 from 0.9932 to 0.9995. The LODs and LOQs for the target chemicals were in the ranges of 0.11–0.29 μg/L and 0.35–0.93 μg/L respectively, while precision ranged from 4.4% to 7.2% and fibre-to-fibre RSD ranged from 5.7% to 10.1%. The high extraction efficiency of the tested fibre was mainly due to hydrophobic interactions, π-π interactions, and electrostatic interactions between the coating and analysed compound.

6. Conclusion

Rapid increase in the interest in ILs and their potential applications in many fields of science and industry has been observed as of late. This success was contributed by a specific character of these compounds which is a completely free design of their structure. That freedom allows production of substances demonstrating desirable physical and chemical properties. Considering the vast number of already existing ions and of ions that may be constructed, the complete potential of IL remains unknown.

One of the first applications of this group of compounds was their use as solvents. Due to their low vapour pressure and less toxic character compared to commonly used organic solvents, they have become a valuable alternative. Besides being a reaction medium, they also favour some reactions acting as catalysts. Other fields where ILs have been applied included: electrochemistry, chromatography, electrophoresis and microextraction-based methods of sample preparation.

One of the techniques in which a particularly rapid development of studies on the application of ILs was noted is stationary phase microextraction. Novel methods of fibre coating with layers composed of ILs and of their modifications resulted in improved stability of SPME fibres compared to commercially available ones. However, further studies aim at improving their thermal and chemical stabilities. The obtained refinements of coatings composed of ILs allow their application within complex analyses which require both broad and selective analytical properties of SPME fibres. It is very important that new materials composed of ILs, as well as new methods of production of composite hybrid materials, allow modification of properties of SMPE fibres leading to a possible development of a set of SPME fibres offering the opportunity of analysing various components of a complex matrix with simultaneous selectivity of the analysis. The application of ILs to the SPME technique has resulted in improved selectivity and effectiveness, and the lowering of the limit of detection for particular analytes. The introduction of functional changes of ILs by the use of various substituents forming hydrogen bonds or π-π bonds has allowed for the achievement of a difficult goal of selective separation of polar analytes from aqueous matrices. This is particularly important in the case of determination of polar analytes with SPME because currently available commercial coatings demonstrate only limited affinity to highly polar analytes. Moreover, the use of polymeric and crosslinked ILs will play a significant role in DI-SPME of these kind of analytes, possibly leading to the elimination of the problem of excessive swelling of sorbents. Besides the synthesis of coatings for SPME fibres composed of ILs presenting high resistance to aggressive components of a matrix, we should expect a wave of future scientific studies aimed at production of fibres coated with composite materials involving a vast variety of ILs.

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