

State-of-the-art analytical methods based on ionic liquids for food and beverage analysis

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ABSTRACT

The use of ionic liquids (ILs) in different fields of analytical chemistry has increased exponentially in recent years, leading to the development of new technologies that try to respect the guidelines proposed by Green Chemistry. ILs are considered relatively ecological compounds due to their thermal stability and non-volatility at room temperature, which prevents their release into the atmosphere. However, recent studies have shown that the growing number of applications that involve them has led to pollution to the aquatic and terrestrial compartments. Despite this, ILs have become environmentally friendlier alternatives to conventional toxic organic solvents for their application in microextraction techniques, both as liquid phases or combined with nanomaterials for solid phase extraction. In addition to this, the use of ILs as mobile and stationary phase additives in chromatographic techniques has introduced substantial improvements in these separation techniques. Likewise, advanced electrodes have been obtained thanks to the functionalization of nanomaterials with ILs for more selective and sensitive electrochemical determinations. In this review, the use of ILs in the development of innovative and efficient analytical methods applied for food and beverage analysis is revised. Special emphasis is made on the environmental impact of the reviewed applications, including their analysis via the AGREE software, which allows the obtention of a numerical estimation of the greenness of an analytical method. In addition, critical issues and future challenges arising from the application of ILs in microextraction, chromatography and electrochemical techniques are discussed.

Abbreviations: [8-HQ-C₂Clmim]Cl, 1-chloroethyl-3-methylimidazolium chloride functionalized with 8-hydroxyquinoline; [8-HQ-C₂mim]Br, 1-ethyl-3-methylimidazolium bromide functionalized with 8-hydroxyquinoline; [APmim]NTf₂, 1-(3-aminopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [CHCA]DEA, α -cyano-4-hydroxycinnamic acid diethylamine; [C₂mim]C₄OSO₃, 1-ethyl-3-methylimidazolium n-butylsulfate; [(C₃)₂im]Br, 1,3-dipropylimidazolium bromide; [C₃im-PTZ]PF₆, 3-(10-H-phenothiazin)propylimidazolium hexafluorophosphate; [C₄(mim)₂]Br₂, Bis-1,4-(3-methylimidazolium)butane bromide; [C₄mim]Cl, 1-butyl-3-methylimidazolium chloride; [C₄mim]C₈SO₄, 1-butyl-3-methylimidazolium octylsulfate; [C₄mim]FeCl₄, 1-butyl-3-methylimidazolium tetrachloroferrate; [C₄mim]HSO₄, 1-butyl-3-methylimidazolium hydrogen sulfate; [C₄mim]PF₆, 1-butyl-3-methylimidazolium hexafluorophosphate; [C₄mim-SH]Br, 1-(4-thiol)-butyl-3-methylimidazolium bromide; [C₄mpi]PF₆, N-butyl-N-methylpiperidinium hexafluorophosphate; [C₆mim]Cl,

1-hexyl-3-methylimidazolium chloride; [C₆mim]NTf₂, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₈mim]NTf₂, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₆mim]PF₆, 1-hexyl-3-methylimidazolium hexafluorophosphate; [C₈mim]PF₆, 1-octyl-3-methylimidazolium hexafluorophosphate; [C₁₂mim]Br, 1-dodecyl-3-methylimidazolium bromide; [C₁₆mim]Br, 1-hexadecyl-3-methylimidazolium bromide; [C₂OHmim]BF₄, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate; [N_{1,8,8,8}]FeCl₄, Trioctylmethylammonium tetrachloroferrate; [P_{6,6,6,14}]Cl, Trihexyl(tetradecyl)phosphonium chloride; [P_{6,6,6,14}]₂CoCl₄, Trihexyl(tetradecyl)phosphonium tetrachlorocobaltate; [P_{6,6,6,14}]FeCl₄, Trihexyl(tetradecyl)phosphonium tetrachloroferrate; [P_{6,6,6,14}]₂MnCl₄, Trihexyl(tetradecyl)phosphonium tetrachloromanganate; [PDC-C₂mim]Br, 1-ethyl-3-methylimidazolium bromide functionalized with pyrrolidinedithiocarbamate; PEG-MDIL, Polyethylene glycol-functionalized magnetic dicationic ionic liquid; [VC₄im]BF₄, 1-vinyl-3-butylimidazolium tetrafluoroborate; [VC₆im]Br, 1-vinyl-3-hexylimidazolium bromide; [VC₆im]PF₆, 1-vinyl-3-hexylimidazolium hexafluorophosphate; CPE, Carbon Paste Electrode; CV-AFS, Cold Vapor Atomic Fluorescence Spectrometry; DAD, Diode Array Detection; DLLME, Dispersive Liquid-Liquid Microextraction; DMC, Defective

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Mesoporous Carbon; ETAAS, Electrothermal Atomic Absorption Spectrometry; FAAS, Flame Atomic Absorption Spectrometry; FID, Flame Ionization Detector; FLD, Fluorescent Detection; GC, Gas Chromatography; GCE, Glassy Carbon Electrode; HG-AAS, Hydride Generation Atomic Absorption Spectrometry; HG-AFS, Hydride Generation Atomic Fluorescence Spectrometry; HPLC, High Performance Liquid Chromatography; HS-SPE, Headspace-Solid Phase Extraction; ICP-MS, Inductively Coupled Plasma-Mass Spectrometry; IL, Ionic Liquid; LLME, Liquid-liquid Microextraction; MIL, Magnetic Ionic Liquid; MMA, Methylmethacrylate; MS, Mass Spectrometry; MSPE, Magnetic Solid Phase Extraction; MWCNT, Multi-Walled Carbon Nanotube; NP, Nanoparticle; PIL, Polymeric Ionic Liquid; PAH, Polycyclic Aromatic Hydrocarbon; RP-HPLC, Reversed-Phase High Performance Liquid Chromatography; RPLC, Reversed-Phase Liquid Chromatography; SPE, Solid Phase Extraction; SWCNT, Single Wall Carbon Nanotube; TSIL, Task-Specific Ionic Liquid; TOMATS, Trioctylmethylammonium thiosalicylate; TUSADMP μ E, Thermal Ultrasound-Assisted Dispersive Multiphasic Microextraction VOC, Volatile Organic Compound

1. Introduction

Food and beverages are composed of a diverse and complex set of substances which are essential for humans (such as proteins, carbohydrates, lipids, vitamins and minerals), along with an extensive number of microconstituents which can either be beneficial (e.g., micronutrients, probiotics) or toxic (e.g. pathogens, toxins) for the human organism. However, the environmental and industrial contamination to which these foods and beverages are exposed during their production and processing causes concerns in the international community, since it affects their composition and quality. In this context, assessing food safety through precise, selective and reliable determinations of toxic substances is demanded by regulatory organisms, thus requiring the constant development of analytical methods which are in turn respectful with the environment [1].

Nevertheless, there is a number of drawbacks that must be considered during the analysis of food and beverages due to the complexity of their matrices and the several challenges observed at different stages of the analytical process. For instance, the presence of interferences can affect sample preparation, chromatographic separation and electrochemical or spectrometric quantifications. In this way, the determination of hazardous chemical substances in foods and beverages is a complex issue which demands time and continuous efforts to develop high-performance analytical methods capable of guaranteeing food and beverage safety [2].

A further challenge in food and beverage analysis is related to the low concentrations at which certain toxic contaminants are usually found. For this reason, modern sample preparation techniques are combined with improved separation and instrumental techniques, for the selective determination of the various contaminants [3]. In this regard, the use of sustainable extraction solvents has become as important as the objective of selectivity, due to the need to reduce contamination from anthropogenic activities related to analytical laboratories. Various ecological extraction agents, including ionic liquids (ILs), have been introduced in recent years, which can also provide shorter extraction times, improved simplicity, lower cost and better selectivity [4].

In the present work, the most recent applications of ILs for the development of analytical methods in food and beverages, with a special emphasis on those published from 2017 to date, are discussed. Advances in microextraction techniques, chromatographic separations and electrochemical detection methods are presented. Moreover, eco-friendly and non-eco-friendly characteristics of the most significant analytical developments reported in the current literature are detailed. A graphical representation of the distribution of the hereby reviewed analytical methods using ILs in food and beverages is presented in Fig. 1.

2. Characteristics of ionic liquids used for the development of analytical methods

Ionic liquids are defined as salts with melting points below 100 °C and are formed by a bulky organic cation and an anion of organic or inorganic nature. The high degree of asymmetry between the ions hinders the formation of a crystalline structure, which makes these salts as liquid at room temperature. Moreover, ILs present a set of characteristic properties that have driven forwards their application in various fields of chemistry, especially in analytical chemistry. Among these, it is worth highlighting their undetectable volatility, high chemical and good thermal stability, good electrical conductivity and wide tuning capacity, a direct consequence of the relationship between their structure and specific functionality. These properties have made ILs attractive alternatives to conventional organic solvents for different analytical purposes, reducing the environmental impact related to the application of the latter [5].

However, it is important to understand that, based on the expansion in the range of applications of ILs, their release into the environment has systematically increased, which has led to the need to determine their toxic influence. This has casted considerable doubts on their characterization as "green" solvents, for being harmful to organisms at various trophic levels. ILs have been shown to be cytotoxic in human cells and contaminants for aqueous and terrestrial environmental compartments, where the relationship between their structures and their toxicity has been tested [6]. Hence, although the properties of ILs can be tuned to achieve high separation efficiencies, their applications are not completely free of potentially pollutant effects. On the one hand, certain ILs have high viscosities, which demands the use of organic solvents to dilute them and improve their dispersibility. On the other hand, the potential dissolution of hydrophilic ILs in water implies a degree of contamination to be considered, especially when the disposal of aqueous phases is performed ignoring this fact [4].

However, and despite the characteristics that reduce the supposed greenness of ILs, the possibility of using them in miniaturized analytical methods still stands as the main factor that most defines their reduced environmental impact. This adds to the fact that several studies confirm that, although they are relatively toxic, the environmental impact of ILs is reduced when compared to that of traditional solvents [4]. Additionally, applications of immobilized ILs on solid supports have also been developed for SPE-based sample preparation methods, avoiding some of the aforementioned drawbacks and adding a new dimension to the possibilities afforded by ILs, as is discussed further on [7].

Concerning their structures, the diversification and exponential increase in the number of known ILs has made it necessary to classify them into different groups based on specific properties and structures. The structures of cations and anions most widely used for the preparation of those ILs applied in food and beverage analysis and reviewed in this work are shown in Fig. 2. Conventional ILs comprise an organic cation such as dialkylimidazolium, tetraalkylphosphonium, tetralkylammonium, pyridinium or pyrrolidinium type, while the most common anions are based on halides, tetrafluoroborate, hexafluorophosphate and trifluoromethanesulfonimide. The vast number of cation-anion combinations has been key for the marked increase in analytical applications in recent years, since the properties of the resulting ILs depend strongly on these. For example, the use of conventional ILs in microextraction techniques has been notable due to their low volatility compared to conventional organic solvents, being less harmful to the environment in terms of their release into the atmosphere, and safer for the operator for the same reason.

As an additional benefit, the ionic nature of ILs, along with the presence of alkyl chains in some of them, has allowed the suppression of silanol groups in chromatographic separations, leading to improvements in resolution and avoiding the addition of toxic reagents. Also, ILs have proven their effectiveness as electrolytes and electrode modifiers in electrochemical applications thanks to their conductivity, avoiding the

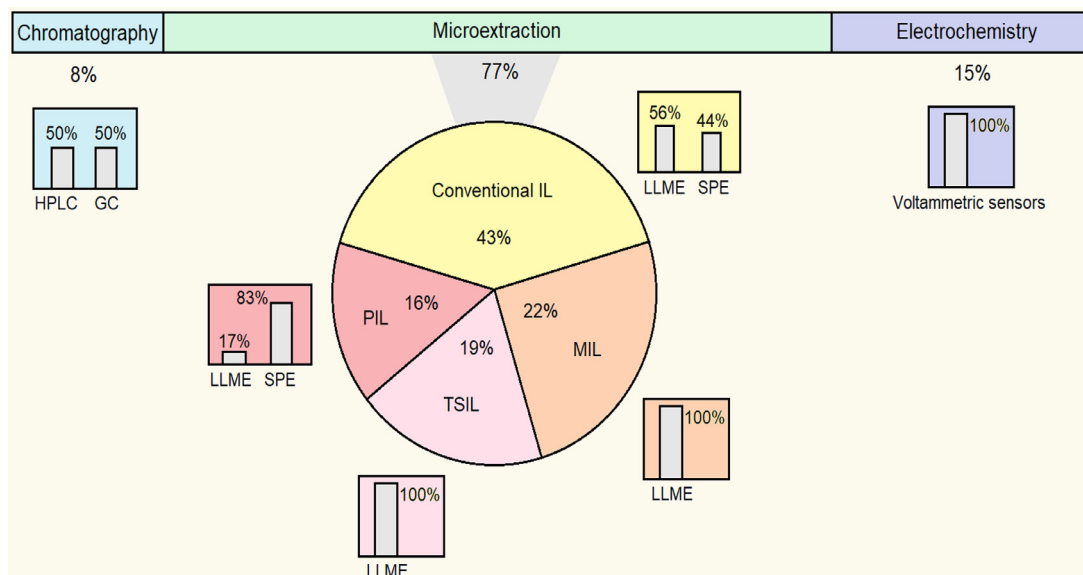


Fig. 1. Distribution of the hereby reviewed IL-based analytical methodologies applied in food and beverage analysis from 2017 to the present.

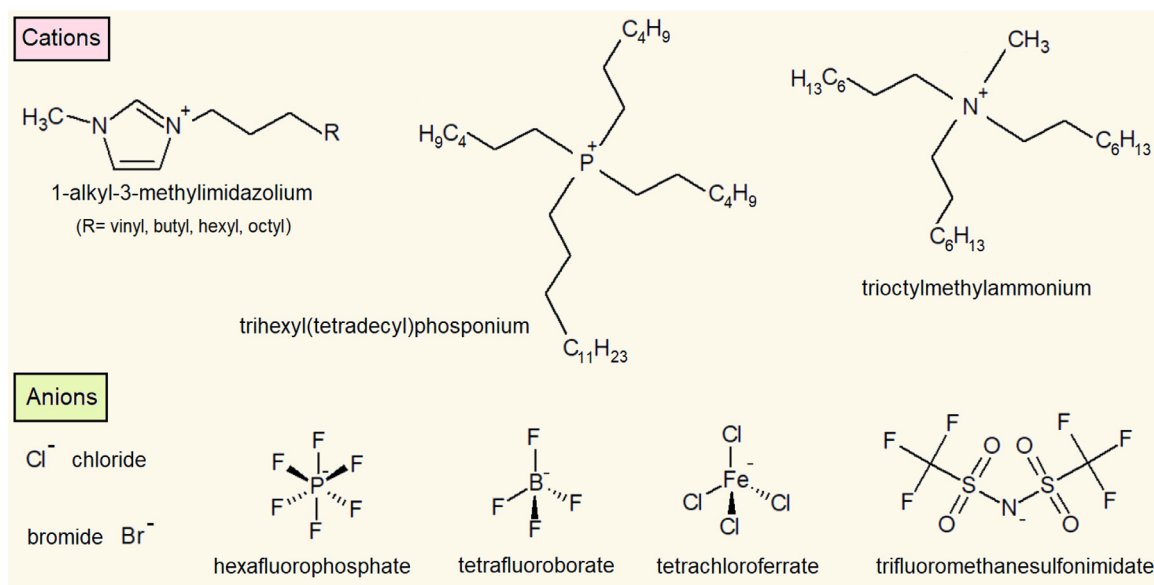


Fig. 2. Most common ions present in ILs used for food and beverages analysis.

excessive use of polluting ions [8]. However, at present, the use of non-conventional ILs is increasing, thus leading to simpler and more cost-effective, sensitive and selective methods.

Various microextractions techniques based on conventional ILs require the use of a time- and energy-consuming centrifugation step to separate the IL phase in contact with an aqueous solution. This drawback was initially solved with the addition of a magnetic sorbent (usually Fe_3O_4) that, after being functionalized with an IL, could be swiftly retrieved by means of an external magnetic field [9]. However, in recent years a surpassing option has emerged in the form of magnetic ILs (MILs), whose intrinsic magnetic properties avoid the use of these additives and exhibit a strong response to external magnetic fields. This family of ILs has captured the interest of the scientific community, resulting in a significant increase in the number of reports using MILs instead of conventional ILs. The presence of a paramagnetic component in the cation or anion of the MIL is responsible for the magnetic susceptibility of these solvents. Among these, transition metal ions (Mn, Fe, Co and Ni) or rare earth metal ions (mainly Gd and Dy) are the most usual

choices [10], with their toxicity increasing with the atomic number of the metallic atom of the anion and with the alkyl chain length of the cation. This leads to say that MILs with anions comprising Co are more toxic than Fe and Mn analogs, but less toxic than those with rare earth metals. However, the toxicological effect of MILs depends not only on their structure, but also on the biological system under study. Therefore, it is necessary to extend the toxicity studies of MILs to various organisms at different trophic levels in order to accurately conclude on the relative toxicity of MILs [11]. However, the use of MILs has not been restricted to the field of microextractions, since MILs have been investigated as electrochemical sensors whose response depends on a switchable magnetic behavior and as stationary phases in gas chromatography (GC), with satisfactory results [10].

Polymeric ILs (PILs) represent another modern alternative to conventional ILs, originally designed to be used as sorptive coatings for solid phase extraction (SPE). PILs are polyelectrolytes obtained by the combination of monomers containing IL moieties which can be classified as polycations, polyanions or polyzwitterions, depending on the repeating

unit within their backbone. They present the special properties of conventional ILs, albeit with enhanced mechanical and thermal stabilities and higher viscosities [12]. It was precisely these characteristics that made PILs attractive sorption materials for SPE, avoiding their leaching from the SPE fibers. Moreover, these properties have pushed their application as coatings for other materials, especially magnetic nanomaterials applied for magnetic solid phase extraction (MSPE). The chemical characteristics of PILs can be easily designed by modifying both the polymer backbone and counterions; hence, their chemical and mechanical properties can be tuned not only post-polymerization, but also by in situ ion-exchange reactions [13]. In turn, based on the above-mentioned characteristics, PILs have also been useful as modifiers in electrochemical sensors, in the same way as conventional ILs and MILs [14].

Another interesting family is that of task-specific ILs (TSILs). These consist in ILs with covalently-bound functional groups (e.g. amines, ethers, alcohols, alkyl chains, amino acids) which impart them with specific properties or reactivities, represent an interesting alternative to improve the selectivity of analytical methods. This subclass of ILs have been designed for uses in a wide range of applications, including synthesis, catalysis, electrochemistry and sample preparation methods [15]. The functional substituents in the structure of TSILs contribute to obtaining a high selectivity to interact with target organic or inorganic analytes, both as an extraction agent or as part of an electrochemical sensor. Furthermore, the addition of metal-chelating groups (e.g. urea, thiourea, and thioether as part of the cation, thiosalicylate and thioglycolate as part of the anion) increases the affinity of the TSIL towards specific metal ions, thus achieving high extraction efficiencies without the use of complexing agents [16]. Despite the selectivity provided by TSILs, their application as stationary or mobile phase modifiers in chromatographic techniques has not yet been exploited.

3. Ionic liquids in sample preparation

It is well known that sample preparation is a crucial aspect for the successful application of several analytical methods, especially with the aim of enriching analytes to achieve high sensitivities and separating potential interfering species for accurate determination. In this sense, the characteristic properties of ILs make them the right choice for the efficient and selective microextraction of different types of analytes [3]. In the following subsections, different analytical methods where ILs have had a main role in the preparation of food and beverage samples are discussed, highlighting their strengths and weaknesses in terms of Green Chemistry guidelines. The main characteristics of the extraction methodologies exposed in this section are summarized in Tables 1 and 2, which include an evaluation of the degree of greenness performed with the AGREE software, including the processes applied for the synthesis of the ILs, the sample preparation stage *per se* and the final determination [17]. This software assigns a numerical penalty value to factors regarding the entire analytical process, such as the amounts and toxicity of reagents, generated waste, energy requirements, the number of procedural steps, miniaturization and automatization, and assigns a value in the scale from 0 to 1 to the method, with 1 being the highest possible greenness mark. In addition, diagrams of the extraction procedures used in this section are presented in Fig. 3.

3.1. Application of conventional ionic liquids in microextraction techniques

3.1.1. Liquid-liquid microextraction

Different green alternatives have been studied in the last decade to replace volatile organic solvents by non-volatile alternatives for liquid-liquid microextraction (LLME), including ILs, surfactants, deep eutectic solvents and switchable hydrophilicity solvents, among others. Among these, ILs have found numerous applications in food and beverage analysis for the determination of organic and inorganic analytes. These methods reveal the extraction capacity of ILs even in highly complex matrices through different mechanisms [2].

Among LLME techniques, dispersive liquid-liquid microextraction (DLLME) has become the most popular. The rise of DLLME-based methods has been a consequence of their simplicity, speed and low cost. The technique is based on a three-component system: aqueous phase, non-polar extraction phase and a dispersant agent which is miscible in both phases and favors the dispersion of the extractant and, thus, increases the extraction efficiency [18].

Different DLLME-based methods using UV-Vis detection can be found in the literature (Table 1). Among them, an interesting work applied in fish and meat products for the determination of histamine (an imidazole amine with functions in the immune, digestive and nervous systems) at trace concentration levels can be mentioned [19]. The method was based on the formation of a charged complex between the analyte and a phenothiazine group dye followed by the subsequent ion pair formation with the IL $[C_4mim]C_8SO_4$. The greenness of the methodology was affected by the use of a significant volume of trichloroacetic acid during sample treatment; therefore, a future improvement of this development should focus on opting for the use of a less harmful reagent during sample preparation. A similar strategy was developed for the determination of 4-methylimidazolium (a carcinogenic dye) in caramel-colored foods (brown sugar, honey and ice cream) and beverages (beer, brewed coffee, caramel syrup, cola, red wine and tea) [20]. In this case, the analyte formed an anionic complex which was subsequently extracted by the IL $[P_{6,6,6,14}]Cl$ via ion pair formation. Said methodology did not require the use of significant amounts of organic solvents (less than 2 mL of chloroform), which represents a positive aspect concerning its environmental impact.


















In the same line, different IL-DLLME-based methods with atomic spectrometry detection have been developed for the determination of trace metals. For example, a work focused on the determination of Sn(IV) by electrothermal atomic absorption spectrometry (ETAAS) in fruit juice samples (apple, cherry and lemon) has been reported [21]. The method required the use of pyrocatechol violet as a complexing agent and $[C_6mim]NTF_2$ as an extraction agent and was superior to previous reports regarding limits of detection (LODs) and enrichment factors. It is also noteworthy to mention that the determination of Cd(II) and Mn(II) have been performed in vegetable (broccoli, lettuce and spinach), grains (beans, chickpeas and lentils) and nut (walnut and peanut) samples with flame atomic absorption spectrometry (FAAS) [22]. The analytes were complexed with resorcinol and extracted in the IL $[C_4mim]Cl$. The authors presented this methodology as a more inexpensive alternative to already reported methods. Finally, an extraction method for inorganic Se species using the IL $[C_8mim]NTF_2$ with determination by hydride generation atomic absorption spectrometry (HG-AAS) was recently published [23]. This methodology was applied to various beverage (iced tea, beer, red wine, orange juice and sheep milk) and food samples (tomato, mushroom, black pepper, garlic, walnut and rice). The authors highlighted that the proposed method presented a lower LOD and a wider linear range than other extraction methods with more expensive detection systems. However, these three IL-DLLME-based methods involved digestion processes with significant volumes of oxidizing acids, severely affecting their greenness. In this way, these methodologies avoided the excessive use of organic solvents throughout the extraction process, but generated acid residues during sample preparation.

Different techniques have emerged as alternatives to DLLME, pursuing the elimination of dispersants solvents. To achieve this goal, novel techniques must ensure an adequate dispersion of the extractant without the use of a third component or mechanical agitation, or else produce the extraction without the requirement of the extractant dispersion [2]. For example, the IL $[C_8mim]PF_6$ has been used in LLME supported onto a hollow fiber for the determination of polycyclic aromatic hydrocarbons (PAHs) in milk samples, followed by high-performance liquid chromatography (HPLC) with spectrophotometric detection [24]. The use of the hollow fiber made it possible to mechanically stabilize the extraction phase, which was favored by the high surface tension of the

IL, thus minimizing the risk of leaching. It must be noted though, that the developed methodology eliminated the use of acetonitrile as a dispersant, but required it during the sample preconditioning (2 mL) and the chromatographic separation stages (more than 10 mL). A possible improvement of this development could be based on the minimization of the use of acetonitrile in the mobile phase, with the aim of reducing the volume of residue of this solvent.

Another interesting approach to avoid the use of dispersants is air-assisted IL-LLME, which has been applied for the quantification of herbicides in tomato and onion samples [25]. In this case, the IL $[C_6\text{mim}]PF_6$ was repeatedly aspirated into the sample solution through a syringe needle to cause turbulence, thus avoiding the use of a dispersant solvent. The separation and quantification of the analytes was then performed by HPLC with diode array detection (DAD). In this case, the sample

Table 1
Recent ILs-based LLME methods for food and beverage analysis.

Extraction solvent	Analyte	Extraction technique	Detection technique	Sample	LOD ^a ($\mu\text{g L}^{-1}$)	EF ^b	Greenness degree ^c	Reference
Conventional ILs								
$[C_4\text{mim}]C_8SO_4$	Histamine	DLLME	UV-Vis	Fish and meat	1.35	95	0.38 	[19]
$[P_{6,6,6,14}]Cl$	4-methyl imidazolium	DLLME	UV-Vis	Beer, coffee, cola, honey, ice cream, wine and tea	1.27 – 1.42	115	0.43 	[20]
$[C_6\text{mim}]NTf_2$	Sn(IV)	DLLME	ETAAS	Apple, cherry and lemon juice	3.40	200	0.41 	[21]
$[C_4\text{mim}]Cl$	Cd(II) Mn(II)	DLLME	FAAS	Vegetables, grains and nuts	0.25 0.15	150 110	0.36 	[22]
$[C_8\text{mim}]NTf_2$	Se(IV) and Se(VI)	DLLME	HG-AAS	Beverages, vegetables and grains	1.5 ng L ⁻¹	120	0.44 	[23]
$[C_8\text{mim}]PF_6$	PAHs	HF-LPME ^c	HPLC-UV	Milk	0.14 – 0.71	N.R. ^d	0.46 	[24]
$[C_6\text{mim}]PF_6$	Herbicides	AA-LLME ^e	HPLC-DAD	Onion and tomato	0.16 – 0.31	380 – 415	0.46 	[25]
$[C_6\text{mim}]PF_6$	Cd(II)	TC-LPME ^f	ETAAS	Bread and biscuit	0.002	24	0.50 	[26]
$[C_6\text{mim}]PF_6$	Bisphenols	DLLME	HPLC-FLD	Milk, orange and tangerine juice	0.13 – 0.82	28.1 – 31.6	0.42 	[58]
Magnetic ILs								
$[P_{6,6,6,14}]FeCl_4$	Cd(II)	DLLME	ETAAS	Honey	0.40 ng L ⁻¹	112	0.43 	[35]
$[P_{6,6,6,14}]FeCl_4$	As(III)	DLLME	ETAAS	Honey	0.012	110	0.41 	[36]
$[P_{6,6,6,14}]FeCl_4$	Cr(III)	DLLME	ETAAS	Honey	0.005	105	0.40 	[37]
$[P_{6,6,6,14}]_2MnCl_4$	Pb(II)	DLLME	ETAAS	Honey and its derivatives	0.003	107	0.42 	[38]
$[C_4\text{mim}]FeCl_4$	Se(IV) and Se(VI)	DLLME	ETAAS	Rice	0.018	100	0.43 	[39]
$[C_4\text{mim}]FeCl_4$	As(III) and As(V)	ETA-LLME	ETAAS	Celery, coriander, lettuce and spinach	0.007	50	0.49 	[40]
$[P_{6,6,6,14}]_2CoCl_4$	Estrogens	DLLME	HPLC-UV	Milk	5.0 – 15	N.R.	0.50 	[41]
$[N_{1,8,8,8}]FeCl_4$	Parabens	DLLME	HPLC-UV	Beer and peach juice	0.9 – 1.5	90 – 125	0.45 	[42]

(continued on next page)

Table 1 (continued)

Task-specific ILs								
TOMATS	Co(II)	DLLME	ETAAS	Tea beverage and vitamin supplements	0.011	24	0.42	[52]
[CHCA]DEA and [C ₂ OHmim]BF ₄	Cd(II) and Ni(II)	TUSADMPμE	FAAS	Olive oils	0.60–2.20	13.7–19.6	0.38	[51]
[8-HQ-C ₂ lim]Cl	Cd(II)	DLLME	FAAS	Lettuce, mineral water, potato and rice	0.55	500	0.42	[53]
[8-HQ-C ₂ im]Br	Fe(III)	DLLME	FAAS	Apple and tomato juice and tea	6.90	210	0.48	[54]
PEG-MDIL	K(I)	DLLME	FAES ^g	Oils	0.50	128	0.53	[55]
[PDC-C ₂ mim]Br	As(III) and As(V)	DLLME	ETAAS	Rice	0.01	200	0.48	[56]
[C ₄ mim]HSO ₄	Triazine herbicides	EA-DLLME ^h	HPLC-UV	Tea beverages	0.08	N.R.	0.47	[57]

LOD^a: Limit of detection; ^bEF: Enhancement factor; ^cHF-LPME: Hollow Fiber Liquid-Phase Microextraction; ^dN.R.: Not Reported; ^eAA-LLME: Air-Assisted Liquid-Liquid Microextraction; ^fTC-LPME: Temperature-Controlled Liquid-Phase Microextraction; ^gFAES: Flame Atomic Emission Spectrometry; ^hEA-DLLME: Effervescence-Assisted Dispersive Liquid-Liquid Microextraction.

*The proposed color scale, according to the AGREE software, is the following:

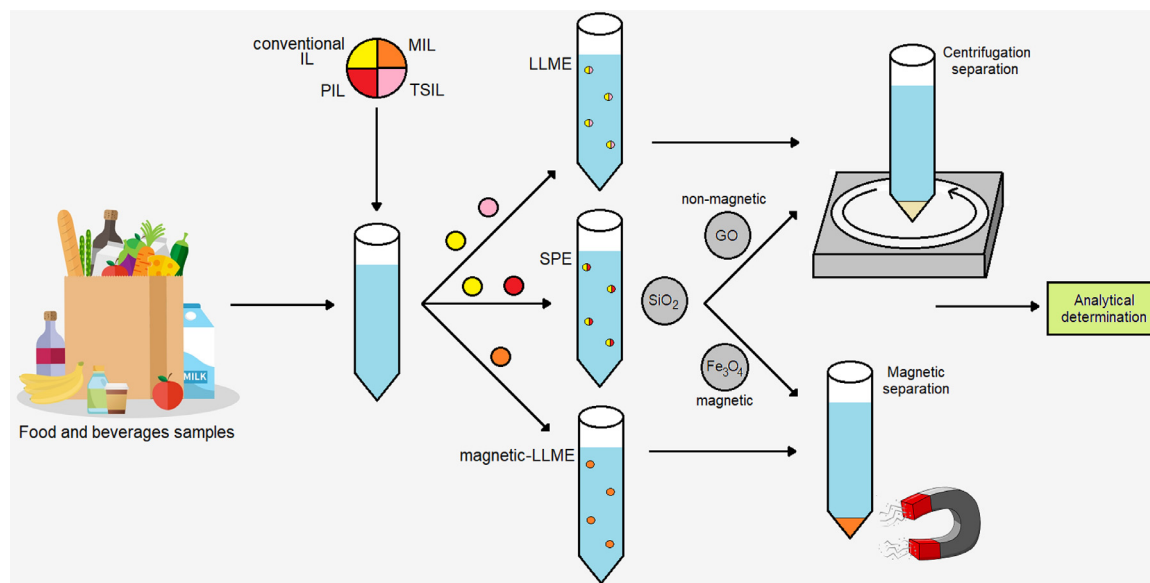
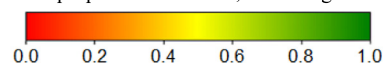


Fig. 3. General extraction procedures depending on different types of ILs and extraction techniques.















preparation was exempt from the use of toxic reagents, while the chromatographic separation required the use of over 10 mL of methanol per run, which could be reduced to ensure a lower residual flow of this solvent, given that methanol is considered a toxic solvent, although less harmful than other traditional organic substances such as chlorinated solvents. Finally, the same IL was used for the extraction of Cd(II) from bread and biscuit samples with temperature-assisted dispersion [26]. The technique consisted on the mixing of the sample solution with a complexing agent and the IL, followed by its heating in an ultrasonic bath, favoring the dispersion of the IL due to the increase in its solubility. The mixture was then cooled in an ice bath to separate the analyte-

enriched IL phase, which was finally used for the determination of the analyte by ETAAS. The authors reported the use of only 2 mL of HNO₃, used for sample digestion, which represents an advantage, considering that the usual volumes of oxidizing acids used in these treatment stages are much higher than this.

3.1.2. Solid phase extraction

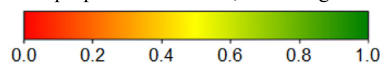
SPE comprises a set of analytical techniques used for sample treatment which are based on the selective extraction of analytes from a sample (usually aqueous) using a solid sorbent. ILs are not suitable for SPE due to their aggregation state, but their incorporation into novel

Table 2
Recent ILs-based SPE methods for food and beverage analysis.

Extraction solvent	Analyte	Extraction technique	Detection technique	Sample	LOD ^a ($\mu\text{g L}^{-1}$)	EF ^b	Greenness degree	Reference
Conventional ILs								
[C ₁₂ mim]Br@ATP ^c	Pyrethroid insecticides	DSPE ^d	HPLC-DAD	Tea	0.30 – 0.60	N.R. ^e	0.48 	[28]
[C ₁₆ mim]Br@AL ^f	Benzoylurea insecticides	DSPE	HPLC-UV	Tea	0.19 – 0.23	29 – 36	0.50 	[29]
[C ₄ mim]Cl@MIL-100(Fe) ^g	PAHs	D- μ -SPE ^h	GC-FID	Vegetables and fruit juice	0.002 – 0.005	187 – 196	0.44 	[30]
[APmim]NTf ₂ @GO	Polyphenols	SPE	GC-MS	Wines	0.02 – 0.10	N.R.	0.50 	[31]
Aminoimidazolium-ILs @montmorillonite	Phenolic compounds	SPE	GC-MS and HPLD-DAD	Fruit juice	2.5	N.R.	0.43 	[32]
[C ₄ (mim) ₂]Br ₂ @ NiFe ₂ O ₄	PAHs	MSPE	HPLC-FLD	Beef and pork	0.01 – 0.07	N.R.	0.42 	[33]
[C ₆ mim]Cl@Fe ₃ O ₄ @mSiO ₂	Parabens	MSPE	GC-MS	Cola and green tea	0.05	N.R.	0.43 	[34]
Polymeric ILs								
Poly([VC ₆ im]PF ₆)@GO@SiO ₂	VOCs	HS-SPE	GC-MS	Wines	N.R.	N.R.	0.54 	[43]
Poly([VC ₆ im]PF ₆)@GO@SiO ₂	Phenolic acids	SPE	HPLC-UV	Wolfberry yogurt	0.20 – 0.50	N.R.	0.49 	[44]
Poly([VC ₄ im]BF ₄)@Fe ₃ O ₄ @SiO ₂	Parabens	MSPE	GC-MS	Milk	0.10	N.R.	0.31 	[46]
Poly([Vim]Cl)@Fe ₃ O ₄ @SiO ₂	Pyrethroid residues	MSPE	GC-MS	Apples	0.24 – 1.99 ($\mu\text{g kg}^{-1}$)	N.R.	0.25 	[47]
Poly(calixarene IL)@Fe ₃ O ₄	Flavonoids	MSPE	HPLC-DAD	Fruit juice and green tea	0.15 – 0.75	N.R.	0.39 	[48]
Poly([VC ₄ im]BF ₄)@Fe ₃ O ₄ @SiO ₂	PAHs	DLLME	GC-FID	Tea, rice, tapioca and corn flours	0.02 – 0.07	N.R.	0.41 	[49]
Poly([VC ₆ im]Br-MMA) membrane	Sulfathiazole	SPE	FLD	Milk and honey	70	N.R.	0.43 	[50]

^aLOD: Limit of detection; ^bEF: Enhancement factor; ^cATP: Attapulgit; ^dDSPE: Dispersive Solid-Phase Extraction; ^eN.R.: Not reported; ^fAL: Alkalinized luffa sponge fibers; ^gMIL-100(Fe): Metal-organic Framework; ^hD- μ -SPE: Dispersive Solid-Phase Microextraction.

*The proposed color scale, according to the AGREE software, is the following:



hybrid materials as sorbent coatings has made their application in SPE feasible. Among the used solid supports, nanomaterials such as carbon nanotubes, graphene and graphene oxide, and magnetic Fe₃O₄ nanoparticles (NPs), among others, have proven to be the preferred choice, given their high surface-to-mass ratio, which favors the miniaturization of the methodologies [27]. This, along with the extraction ability provided by the IL, gives place to highly efficient hybrid nanomaterials, as is discussed next.

Several current SPE methods based on the use of hybrid materials with ILs can be found in the literature (Fig. 1). For example, two SPE-HPLC methods applied to tea samples have been recently reported. One of them was based on the determination of pyrethroid-type insecticides with the use of attapulgit (a mineral from the group of phyllosilicates) modified with [C₁₂mim]Br [28]. The second one was suitable for the determination of benzoylurea insecticides using alkalinized luffa sponge fibers modified with [C₁₆mim]Br [29]. The authors mentioned that the

proposed methods could be considered as alternatives to the currently available methods for the determination of this type of insecticides [29]. However, it should be mentioned that the sorbent materials activation required high volumes of HCl or NaOH solution (greater than 100 mL), while the chromatographic separation used considerable volumes of organic solvents (between 18 and 24 mL of methanol). In this way, both methodologies generated an excessive volume of waste, which should be reduced before considering them as green alternatives.

It is noteworthy to mention that vortex-assisted SPE has been used in vegetables (carrot, lettuce and potato) and fruit juices (apple and grape) sample treatment followed by GC with flame ionization detector (FID) for the determination of PAHs [30]. A metal-organic framework modified with the IL $[C_4\text{mim}]\text{Cl}$ was used as sorbent in this case and the retention of the analytes on its surface was achieved by hydrophobic and π - π interactions. It should be mentioned that the greenness of the methodology was affected by a digestion that used 15 mL of oxidizing acids, which should be reduced. On the other hand, a SPE methodology was applied for the extraction of polyphenols in wine samples using a homemade fiber coated with graphene oxide modified with the IL $[\text{APmim}]\text{NTf}_2$ [31]. The analytes were separated and quantified by GC-MS and the authors emphasized that the extraction efficiency of the homemade fiber was higher than that of commercial fibers, due to the high intermolecular and electrostatic attractions it allowed with the analytes. Although the fiber preparation required 5 mL of methanol, the rest of the methodology was exempt from the use of toxic reagents. Finally, novel montmorillonite (clay) compounds containing amino-functionalized imidazolium-type ILs were recently used as coating materials for SPE fibers [32]. SPE with these materials was coupled to GC-MS and HPLC-DAD, allowing the determination of 16 phenolic compounds in fresh fruit juices (orange, quince, grape, tangerine, apple and pear). The authors commented that the use of inexpensive and readily available clay ensured an economical veneering material. In this case, the greenness of the methodology was affected by the use of aqua regia during the synthesis of the fibers (the volume is not reported by the authors), while methanol and acetonitrile (6 mL per chromatographic run) were used in the mobile phase for HPLC.

Magnetic NPs have also been used together with ILs for the development of MSPE methods. For example, NiFe_2O_4 -based magnetic effervescent tablets containing the dicationic IL $[C_4(\text{mim})_2]\text{Br}_2$ have been used for the extraction of PAHs from beef and pork meat, followed by HPLC with fluorescent detection (FLD) [33]. In this case, the introduction of the effervescent tablet and the magnetic retrieval agent avoided tedious and time-consuming stirring, ultrasonication and centrifugation steps. As a further advantage, said methodology presented a green sample preparation (only ultrapure water and micromolar concentrations of KOH were required) and the use of organic solvents in the extraction was minimized, since only microliters of acetonitrile and toluene were used. A different strategy that included a hydrophilic magnetic ball composed of nano- Fe_3O_4 , mesoporous silica (mSiO_2) and the IL $[C_6\text{mim}]\text{Cl}$ has been applied for the determination of parabens (preservatives that affect the human endocrine system) [34]. Here, the material counted with active sites for the extraction of analytes through π - π interactions, allowing its application in samples of cola drink and green tea with GC-MS. However, the degree of greenness of the methodology decreased due to the use of 80 mL of methylbenzene and 75 mL of hexanediol in the synthesis of the sorbent material.

3.2. Magnetic ionic liquid-based liquid-liquid extraction

MILs have captured the interest of the scientific community due to their intrinsic magnetism and high extraction efficiency, aside from the fact that they avoid drawbacks related to the use of IL-functionalized magnetic nanomaterials, such as IL leaching. Therefore, the development of LLME-based methods using MILs has been increasingly reported (Fig. 1).

Recently, several MIL-DLLME-ETAAS methods can be found in the literature for the determination of trace metals. Phosphonium-type MILs have been employed, such as $[\text{P}_{6,6,6,14}]\text{FeCl}_4$ for the preconcentration of Cd(II) [35], As(III) [36] and Cr(III) in honey [37], and $[\text{P}_{6,6,6,14}]\text{MnCl}_4$ for the preconcentration of Pb(II) [38] in honey and its derivatives. These methods required the prior complexation of the analytes in the sample solution or the adjustment of the acidity to promote the formation of ionic pairs, with subsequent collection of the extraction phase with a magnetic bar or rod. Interestingly, matrix interferences of the samples and the MIL phase could be overcome through different strategies that included a careful evaluation of ETAAS conditions. These methodologies managed to minimize the use of solvents used throughout the extraction process but, however, the proposed sample pretreatments (dilution in an acid medium, clean-up with chloroform, calcination in H_2SO_4 and acid digestion, respectively) deteriorated the degree of greenness. Based on these weaknesses in the methodologies, the authors sought throughout their development to minimize the environmental impact of the proposed sample preparations. Therefore, low concentration acid dilutions were used in the article based on Cd(II) determination. Only microliters of organic solvents were used in the proposed clean-up for As(III) determination, while only 2 mL of H_2SO_4 were required for calcinations prior to Cr(III) microextraction. On the other hand, a total of 8 mL of oxidizing acids were required for sample digestion prior to Pb(II) microextraction, a volume that could be reduced.

Likewise, MIL-LLME-ETAAS methods have been developed for the speciation analysis of inorganic Se in rice samples [39] and inorganic As in vegetable samples (celery, coriander, lettuce and spinach) [40], through the use of MIL $[C_4\text{mim}]\text{FeCl}_4$. In the first method, an up-and-down-shaker vortex agitator was used and Se(IV) was complexed with 2,3-diaminonaphthalene. On the other hand, the second method involved the use of an effervescent tablet containing the MIL for the extraction of As(V) after its complexation with ammonium molybdate. In both methods, the selective extraction and separation of the inorganic species was achieved without chromatographic separation in highly complex food samples, which avoided an excessive usage of organic solvents (only microliters of ethanol to reduce the viscosity of the MILs prior to their injection into the graphite furnace). Both methodologies sought to minimize the use of oxidizing acids, although 6 mL were required for sample digestion before their analysis.

Similarly, MIL-DLLME-HPLC-UV has been applied for the preconcentration, separation and determination of organic compounds. For example, $[\text{P}_{6,6,6,14}]\text{CoCl}_4$ has been used as extraction phase of estrogens in milk samples, where the MIL led to an extraction efficiency greater than 96% and a low chromatographic background that allowed the direct analysis [41]. In a similar fashion, $[\text{N}_{1,8,8,8}]\text{FeCl}_4$ was used for the extraction of parabens in beer and peach juice samples [42]. The main advantages of this method included its simplicity, adequate sensitivity and short analysis time (only 9 min). In both cases, green sample preparations and green extractions were achieved due to the use of organic solvents being reduced to only microliters, while the rest of the extraction required only ultrapure water and salts to adjust the ionic strength. Nevertheless, the chromatographic separations did require significant volumes of acetonitrile, of about 6 mL and 16 mL, respectively.

3.3. Polymeric ionic liquid-based solid phase extraction

PILs arose as alternatives to conventional ILs for micro-SPE fiber coatings due to their increased thermal and mechanical stability, thus avoiding the leaching of the extractant phase. In fact, a recent report comparing the performance of PILs with conventional micro-SPE sorbent phases for the extraction of volatile organic compounds (VOCs) from wines found that a PIL-coated fiber was more efficient and allowed for the extraction of more analytes than conventional poly(acrylate) and divinylbenzene/carboxen/poly(dimethylsiloxane) coatings [43]. Nevertheless, advances in material science have driven the evolution of PILs towards more modern and efficient applications, being their coupling

with nanomaterials the most relevant. For example, a poly-[VC₆im]PF₆-coated graphene oxide@SiO₂ hybrid nanomaterial has been developed for the SPE of phenolic acids in wolfberry yogurt prior to HPLC-UV-Vis detection [44]. A total of 15 extraction cycles could be performed without efficiency losses due to the stability of the hybrid, which represented a positive aspect in terms of waste generation, but a mobile phase with around 10 mL of methanol was used for each chromatographic separation, negatively affecting the overall greenness of the process.

In this context, the combination of PILs with magnetic nanomaterials has been the most exploited strategy in recent years, because it takes advantage of the high extraction capacity obtained with PILs with the possibility offered by magnetic nanomaterials to serve as excellent supporting materials, thus facilitating phase separation (Fig. 3). Fe₃O₄ NPs are the most usual choice as core material for the development of these sorbents [45], with a first coating that acts both as protection and as anchoring surface for functionalization. Nanosilica is the preferred material in these cases, yielding Fe₃O₄@SiO₂, which can then be coated with a PIL. This type of NP has been functionalized with a combination of [VC₄im]BF₄ as monomer and 1,4-butanediyl-3,3'-bis-L-vinylimidazolium dibromide as crosslinker for the MSPE of parabens from milk samples [46] and with poly-[Vim]⁺ modified with phenyl and cyano groups for the extraction of pyrethroid residues in apples [47]. In the former, 35 mL of trifluoroacetic acid were used for preparing the samples, while in the latter 10 mL of acetonitrile were required for pre-treating the sample, making both methods quite environmentally unfriendly. Nevertheless, in both cases, the authors highlighted the synergistic effect obtained from the presence of abundant binding sites on the nanostructured silica surface and the extractant capacity of the PIL, added to the magnetic properties for phase separation.

Furthermore, magnetic nanomaterials with mixed coatings involving PILs and a second component to improve selectivity have become a modern trend in the field of microextractions. For example, magnetic NPs coated with a poly(calixarene IL) have been applied for the preconcentration of five flavonoids from fruit juice and green tea prior to determination by HPLC-DAD [48]. 9 mL of methanol were used as part of the mobile phase for this analysis, resulting in a significant environmental impact. Similarly, a poly(β -cyclodextrin-IL)-based magnetic nanomaterial coupled with octanol as a ferrofluid system was successfully applied for the extraction of PAHs with minimal sample pre-treatment from tapioca, corn flours, tea and white rice. This method required only 300 μ L of dichloromethane for elution and 1.5 mL of acetonitrile for sample pre-treatment, making it one of the best reviewed methods in term of greenness [49].

Finally, a method for the determination of sulfathiazole in milk and honey that did not require a chromatographic separation was recently developed [50]. The analyte was extracted by SPE with a membrane obtained via the copolymerization of [VC₆im]Br and methylmethacrylate (MMA), and its quenching effect on copper nanoclusters was taken advantage of for its quantification by fluorescence spectrometry. Although fairly simple, the process involved the use of an unstated volume of trichloroacetic acid for pre-treating the milk samples, which raised its environmental impact when applied to these samples. On the other hand, honey samples required only a dilution step with ultrapure water, making the application of the method to these fairly clean.

3.4. Task-specific ionic liquid-based liquid phase extraction

TSILs have been widely applied in several DLLME methods for the preconcentration of metal ions, since they can act simultaneously as complexing agents and extractants (Fig. 3). The improved selectivity provided by TSILs in liquid microextractions is notable and it is generally achieved by introducing a specific functional group into the structure of an IL. Based on this aspect, a higher number of stages and reagents are necessary for their synthesis, which in many cases affects

the degree of greenness of the methodologies due to the use of different toxic compounds [51]. For example, an ultrasound-assisted DLLME was performed with the use of triethylmethylammonium thiosalicylate (TOMATS) as extraction solvent and complexing agent for the preconcentration of Co(II) in vitamin supplements and tea samples followed by ETAAS detection [52]. In this case ultrasonication was used to disperse the extraction phase, while a back-extraction step was not required, thus eliminating the need of volatile and flammable organic solvents. However, 5 mL of concentrated HNO₃ along with 1 mL of H₂O₂ and HF, was required to digest the samples, reducing the greenness of the methodology. In addition, two hydrophilic TSILs: [CHCA]DEA and [C₂OHmim]BF₄, were applied simultaneously as chelating agents and extracting phases for the separation and preconcentration of Cd(II) and Ni(II) in olive oil samples by thermal ultrasound-assisted dispersive multiphasic microextraction (TUSADMP μ E) [51]. The authors highlighted that the microextraction of the analytes with the proposed TSILs mixture achieved extraction percentages close to 100%. Nevertheless, 20 mL of n-hexane were required, which significantly increased the environmental impact and which should be reduced to avoid this negative aspect.

The simultaneous chelation and extraction of Cd(II) has also been performed using the hydrophilic TSIL [8-HQ-C₂Clmim]Cl by DLLME in lettuce, potato and rice samples [53]. Although a reduced volume of the extraction solvent (600 μ L) was used without the need of complexing agent or dispersing solvent, a high volume of concentrated HNO₃ (10 mL) was required for sample digestion. In another work, the TSIL [8-HQ-C₂mim]Br was used for the complexation and microextraction of Fe(III) in apple and tomato juice, and tea samples by in situ DLLME coupled to FAAS analysis [54]. The phase separation was performed with the use of KPF₆ as an ion exchanger salt to decrease the water solubility of the TSIL phase, providing high mass transfer rates between both phases and leading to a more efficient and fast extraction of Fe. It is important to mention that the sample preparation, the TSIL synthesis and the extraction process were free of appreciable amounts of toxic reagents, in such a way that this can be considered an environmentally friendly method. Also, a magnetic-polymeric TSIL was applied for chelation and extraction of K(I) from oil samples by DLLME without the need of a centrifugation step [55]. This method offered some advantages, including simplicity and ease of operation. In addition, this work avoided the use of toxic compounds throughout the development of the entire method, so it could be considered a more ecological alternative. In another report, the speciation analysis of As in rice samples was performed using the TSIL [PDC-C₂mim]Br and ETAAS determination. According to the authors, this method was fast, low cost, highly efficient and avoided the use of reagents that could be harmful to the environment both during the synthesis of the TSIL and during sample preparation [56].

Recently, TSILs have also been applied for preconcentration and extraction of organic analytes. For instance, the acidic TSIL [C₄mim]HSO₄ was applied for separation and microextraction of triazine herbicides by effervescence-assisted DLLME in tea beverage samples [57]. The TSIL was implemented as an extraction phase and Brønsted acid to generate carbon dioxide, which produced bubbles that generated the turbulence and improved the mass transfer between the extractant solvent and target analytes. As a negative aspect, each chromatographic run required around 27 mL of acetonitrile, generating an important residue of this organic solvent. TSILs have also been used as dispersing reagents avoiding the use of organic solvents commonly applied in classical DLLME techniques. For instance, the IL [C₆mim]PF₆ (extraction phase) and the TSIL [C₄mim-SH]Br (dispersing agent) were applied for preconcentration of bisphenols in milk and juice samples [58]. According to the authors, the use of a TSIL as a dispersant reagent avoided the pH adjustment step and produced a clear stratification phenomenon, leading to a more efficient separation. Nevertheless, over 8 mL of acetonitrile were used as a mobile phase in each HPLC run, compromising the overall greenness of the method.

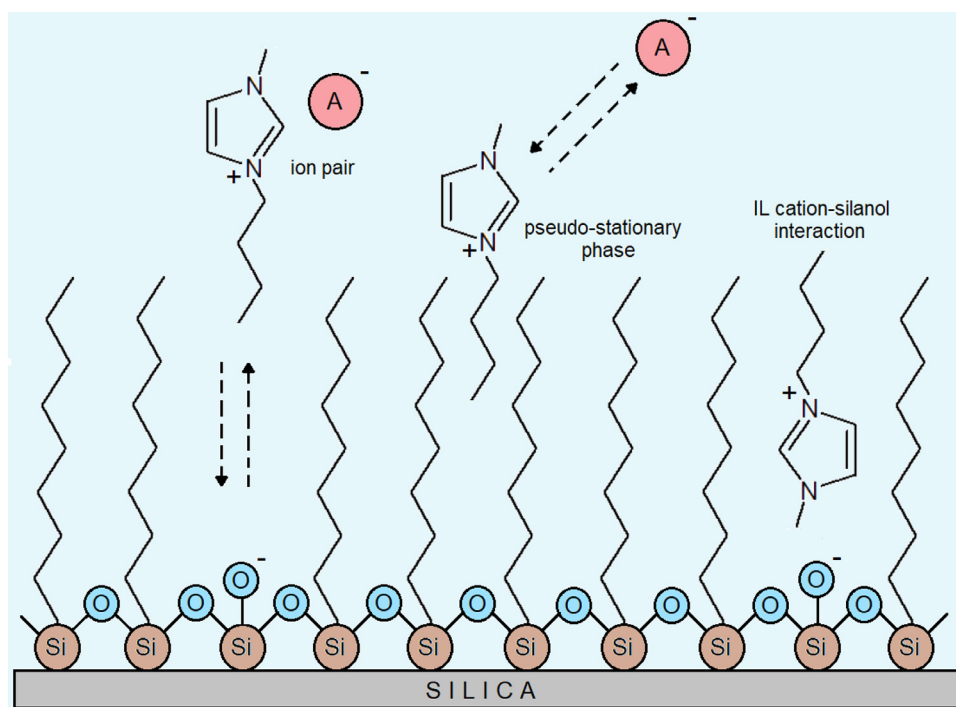


Fig. 4. Proposed interactions of ILs with analytes and the stationary phase when used as mobile phase additives in liquid chromatography.

4. Ionic liquids in chromatographic techniques

The remarkable properties of ILs have also been exploited in HPLC and GC, especially to improve the resolution and separation efficiency. Thus, ILs have been used both as additives of the mobile phase in HPLC and as components of GC stationary phases.

4.1. High-performance liquid chromatography

Reversed-phase liquid chromatography (RPLC) is one of the most used techniques for the separation of complex mixtures of analytes. However, it is not possible to functionalize all the silanol groups on the silica support used in most RPLC columns and some free silanol groups can still remain accessible to both analytes and mobile phase components [59]. These residual silanol groups can be ionized easily within the working pH range of classic RPLC columns and, therefore, stationary phases are negatively charged between pH values of 2.5 and 7.5 and present additional ion-exchange interactions with cationic compounds. These interactions cause broad peaks, tailing and poor separation selectivity [60]. A new alternative to reduce or suppress the effect of free silanol groups is the use of low concentrations of ILs as mobile phase additives. It is important to mention that when ILs are used as mobile phase additives, their main function is related to their ionic nature, such that both cations and anions may contribute to improve the performance of the separation [61].

The main advantage obtained with the addition of IL to a mobile phase is that it is possible to separate basic, acidic and neutral analytes due to the multiple interactions taking place (Fig. 4). ILs can produce a pseudo-stationary phase by interacting with the components in the mobile phase and with the surface of the stationary phase [61]. In this way, IL cations can interact through electrostatic interactions with free silanols on the alkyl-bonded silica surface and compete with the basic groups of the analytes. Simultaneously, the non-polar alkyl groups of the stationary phase can interact through hydrophobic and other unspecific interactions with both the cationic and anionic components of the ILs [62]. Besides this, ILs can act as ion-pairing reagents with cationic solutes due to the chaotropic character of their

anions and can also develop ionic interactions with analytes. Therefore, the retention mechanisms observed with ILs are quite complex and involve different combinations of hydrophobic partitioning, ion exchange and ion pairing, and the extension of these interactions depends on the properties of analytes and the ILs chosen in the experiments [61].

Recently, several ILs were applied as additives to mobile phases for elemental speciation analysis by RP-HPLC. For example, ILs containing imidazolium or phosphonium cations have been successfully applied for Se speciation analysis [63]. Selenite [Se(IV)], selenate [Se(VI)], selenomethionine and Se-methylselenocysteine in wine, beer, yeast and garlic samples were separated by RP-HPLC coupled to hydride generation atomic fluorescence spectrometry (HG-AFS) detection. The result demonstrated that ILs caused a significant improvement of the separation performance, which was evidenced by a resolution higher than 0.98 in 12 min. The authors declared that the obtained LODs were comparable with those reported in other studies where RP-HPLC was coupled to sensitive detectors such as inductively coupled plasma-mass spectrometry (ICP-MS). Finally, the minimum use of organic solvent applied in this separative process was highlighted, given that only 375 μL of methanol was generated as a residue, which determines a score of 0.66 (among the highest determined in this review) according to the AGREE software. On the other hand, the same authors studied the potential of some alkyl-methyl-imidazolium ILs and a phosphonium IL used as mobile phase additives for the separation and determination of Hg(II), methylmercury (CH_3Hg^+) and ethylmercury ($\text{C}_2\text{H}_5\text{Hg}^+$) species in fish samples by RP-HPLC coupled to UV-cold vapor atomic fluorescence spectrometry (CV-AFS) [64]. Under optimal conditions, the separation and determination of Hg species was obtained within 12 min. In this work, the use of a low-cost detector such as AFS was a highlight, along with the possibility of applying the developed method in routine laboratories. Nevertheless, the last 5 min of the chromatographic run involved the use of methanol as mobile phase, generating more than 5 mL of organic waste in each run, resulting in an AGREE score of 0.56, being this value greater than those obtained by the sample preparation methods presented in previous sections. In both articles, the use of ILs as mobile phase modifiers allowed for the separation of both organic and inorganic species by

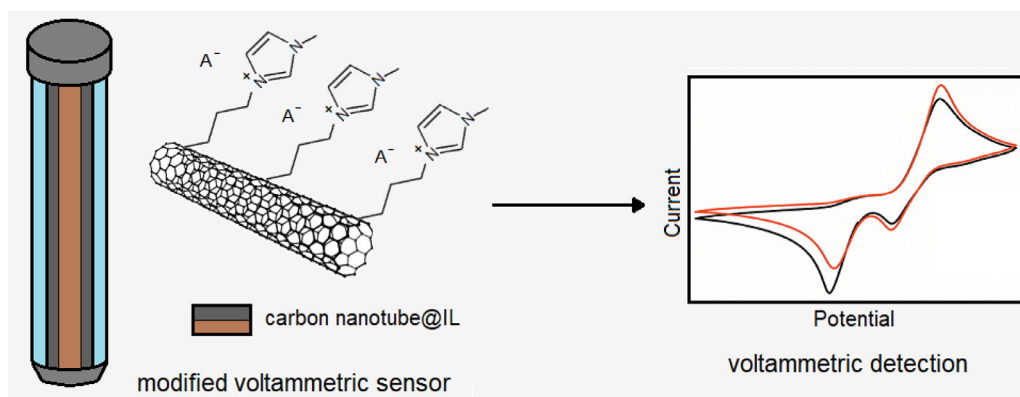


Fig. 5. IL-nanomaterial for the fabrication of voltammetric sensors applied in food and beverages analysis.

RP-HPLC, at a pH where the stationary phases were highly stable. This is difficult with conventional ion-pairing agents in non-polar stationary phases, especially concerning the separation of inorganic species. In addition, another disadvantage is based on the fact that some ion-pairing agents (such as perfluorocarboxylic acid) must be used at low working pHs (between 2.0 and 2.5), which can affect the stability of the stationary phases [62].

4.2. Gas chromatography

The low volatility, high thermal stability and tunable selectivity of ILs make them interesting alternatives to be applied as GC stationary phases. IL-based stationary phases provide exceptional selectivities towards a large range of analytes due to the numerous interactions in which ILs can be involved, including hydrogen-bonding, coulombic and dispersive forces [65]. In fact, their unique properties make them very useful in the food analysis field, where selectivity plays a vital role due to the complexity of the samples. However, despite all of these advantages there are not many applications reported in the literature of recent years that have included the use of GC columns based on ILs for food and beverage analysis [66]. This is perhaps due to the decomposition temperatures of most ILs being below 300 °C. In this way, the thermal stability of IL-based stationary phases can hinder applications that require a higher operating temperature. For example, stationary phases based on imidazolium-type ILs have been reported whose stability is up to 270 °C and with phosphonium-type ILs at 290 °C, while conventional stationary phases of polydimethylsiloxane reach thermal stability above 320 °C [67].

Nevertheless, the chromatographic performance of several commercial IL stationary phases was studied for the analysis of volatile compounds in coffees [68]. The results showed that a column composed by 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide had a comparable resolution and efficiency to that obtained with a regular column. Additionally, an interesting study was developed where a GC column based on monocationic imidazolium with a terminal iodine atom was synthesized by a quaternization-anion exchange chemical sequence [69]. The researchers showed that this column exhibited good thermal stability (290 °C), as well as good efficiency (2000 plates/m) for the successful separation of volatile compounds in cider apple juices. Finally, it is important to mention that in both works, green extractions based on a headspace solid phase extraction (HS-SPE) and green separations (reduced use of organic solvents) were achieved with practically no residues. As a consequence, an average value of 0.65 after the application of the AGREE software was obtained, being this value higher than that obtained for most of the sample preparation methods presented in previous sections.

5. Ionic liquids in electrochemical sensors

Some properties of ILs (e.g., high chemical and good thermal stability, high conductivity and wide electrochemical window) make them suitable for uses in electroanalytical methods, especially in electrochemical sensors where ILs have been applied as fabricated materials onto the electrode surface. In this context, their high viscosity allows their application as binders to immobilize sensitive molecules onto the electrodes. In this sense, several electrochemical sensors based on the application of ILs have been efficiently fabricated, including gas sensors, voltammetric sensors and ion-selective electrodes, where ILs have been used as electrolytes or combined with other molecules as modifiers [70]. Additionally, nanomaterials have also been applied for the modification of electrochemical sensors since they have a high surface area and low charge transfer resistance. Therefore, the implementation of ILs and nanomaterials as combined electrode modifiers enhance the sensitivity and selectivity of electrochemical sensors. However, recently reported methods for the determination of target organic or inorganic analytes mainly involve the use of ILs and nanomaterials in voltammetric sensors due to their fast response and easy operation (Fig. 5) [71].

For example, a composite film made of multi-walled carbon nanotubes (MWCNTs) and $[C_4mip]PF_6$ was used to modify a glassy carbon electrode (GCE) for electrochemical sensing of riboflavin [72]. This electrochemical method showed a wide linear range, an LOD in the $nmol L^{-1}$ level and selectivity for the determination of the analyte in milk and soymilk powder samples. In addition, during the analysis stage, the use of toxic organic solvents was avoided, thus decreasing the environmental impact. Moreover, defective mesoporous carbon (DMC) and the IL $[C_4mim]PF_6$ were used for the modification of a carbon paste electrode (CPE) for the detection of rutin in orange juice sample [73]. According to the authors, the efficiency of the electroactive surface of the IL-modified electrode was improved when compared to the unmodified electrode. However, the greenness of the methodology was affected by the use of 100 mL of ethanol, generating a significant volume of organic waste per sample although with a solvent with not such a high environmental impact. In another work, the simultaneous determination of vanillin and folic acid was performed by square wave voltammetry using a CPE modified with CdO nanoparticles loaded onto single wall carbon nanotubes (SWCNTs) and the IL $[(C_3)_2im]Br$ as a binder [74]. This method was applied to chocolate, biscuit and coffee milk samples, and the authors reported that the modified electrode improved the electrical conductivity and resolved the overlapped voltammetric peaks of both analytes by ~ 320 mV. Nevertheless, the use of a 10 mL of ethanol in the sample preparation stage could be a negative aspect of the methodology. In another report, a modified electrode with a Pt-decorated SWCNTs nanocomposite and the IL $[C_2mim]C_4OSO_3$ as a highly conductive binder was fabricated for the determination of bisphenol A in stew and

canned tuna samples by a voltammetric technique [75]. This electrode was highly sensitive and selective towards the analyte, although sample treatment involved the consumption of 10 mL of ethanol per sample, affecting the greenness of the methodology.

Furthermore, an electroanalytical sensor was developed based on the IL [C₃im-PTZ]PF₆ immobilized onto MWCNT on a GCE for the efficient detection of sulfite in vinegar and pickle samples [76]. The authors highlighted that the fabricated electrode was highly selective, sensitive, stable and allowed for the reproducible determination of the analyte without the use of enzymes and expensive metals. Additionally, a CPE modified with reduced graphene oxide and the IL [C₆mim]PF₆ was applied for determination of the antioxidant additive tertbutylhydroquinone in the presence of folic acid [77]. According to the results, the high selectivity and conductivity of the modified electrode turned it suitable for determination of the analyte and folic acid in oil, apple juice and drinking water samples. Moreover, the voltammetric performance of a CPE modified with RuO₂ nanorods (RuO₂/NR) and the IL [(C₃)₂im]Br was evaluated for the determination of amaranth in soft drink and juice samples [71]. In this case, a decrease of the amaranth over-potential was achieved, along with a 9.64-fold increase in the sensitivity using CPE/RuO₂/NR/IL as an electrochemical sensor compared to the unmodified CPE. It is important to mention that the electrochemical measurements involved in these three methodologies were performed without the use of toxic organic solvents, improving their greenness and thus allowing to reduce the level of waste generated.

The greenness degree of the methodologies belonging to this section resulted in a range between 0.47 and 0.61 according to the AGREE software. This slight improvement with respect to other methods analyzed in this review could be explained by the fact that, in general terms, the toxic organic solvents consumption was minimized, added to the fact that the reported methods required fewer steps and demanded equipment with lower energy requirements.

6. Conclusions and future trends

ILs can be considered useful tools for the development of novel methods in foods and beverages analysis. Their unique properties have made them interesting alternatives to improve pre-existing methodologies, thanks to the possible structural tuning based on the virtually infinite potential combinations between cations and anions. Thus, this work highlights the high capacity of ILs for the efficient extraction of different analytes and their contributions to modify classical LLME methods by replacing common volatile organic solvents. Likewise, the combination of ILs with nanomaterials has resulted into remarkable improvements on the performance of SPE methods. In fact, the high surface area of nanomaterials and the properties of ILs to disperse, functionalize and expand the chemical interactions of these sorbents with different analytes can be considered responsible for these benefits. However, although the majority of the microextraction methodologies that use ILs have managed to reduce their use during their application, the consumption of solvents during their synthesis is still intensive. This makes the latter stage an important -albeit barely discussed- stage in which efforts to reduce the use of substances harmful to the environment should be focused.

The use of ILs has allowed the suppression of silanol groups in chromatographic columns, improving the resolution and separation efficiency, both as mobile phase additives in HPLC and as components of stationary phases in GC. These improvements have been possible based on the ability of ILs to promote different types of interactions, which has led to an expansion of the possible separation mechanisms and the ability to separate analytes of different nature. It should be noted that the use of large volumes of organic solvents in liquid chromatography continues to be a weakness that must be improved in the future to meet the requirements proposed by Green Chemistry.

Furthermore, thanks to the unique properties of ILs, their use in electrochemical sensors has been possible, especially when consider-

ing their combination with nanomaterials. These hybrid materials have resulted in a marked improvement in the sensitivity and selectivity of electrodes, in addition to increased response times and ease of operation, while reducing solvent consumption. Finally, the advances in synthesis and chemical functionalization will continue to push the combination of ILs and nanomaterials to develop novel analytical methods having improved specificity, reproducibility and simplicity, thus providing more efficient tools for food and beverage analysis. Still, as it stands, efforts should focus on developing even more environmentally friendly methodologies, through the use of new, more ecological, biodegradable and less toxic ILs, synthesized from renewable sources, which will be reflected in the increase in their degree of greenness.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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