# Advances in ionic liquids and deep eutectic solvents-based liquid phase microextraction of metals for sample preparation in Environmental Analytical Chemistry

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## ARTICLE INFO

## ABSTRACT

Liquid phase micro-extraction (LPME) of metals has showed its potential for sample preparation in environmental analysis. In particular, the incorporation of ionic liquids to LPME (IL-LPME) has gotten increasing interest due to their unique properties as organic salts liquid at room temperature. In the last years, IL-LPME of metals has evolved to more efficient and selective extraction methods thanks to the development of task specific ionic liquids, and deep eutectic solvents. ILs have been implemented in the main LPME modalities: SDME, DLLME and HFLPME, resulting in new versions of these techniques.

In this review we have analyzed and discussed the latest developments done in IL-LPME of metals, their advantages and limitations, as well as the potential fields of future development.

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## 1. Introduction

Sample preparation is a critical step in the analysis of metals in environmental samples due to their low concentration and the complexity of sample matrix [1]. Liquid phase micro-extraction (LPME) of metals has gained increasing attention since introduced by Chamsaz in 2003 [2], as a more efficient and environmentally friendly alternative to classical liquid-liquid extraction (LLE) [3]. LPME has extensively been investigated in its three main modalities: single drop micro-extraction (SDME), dispersive liquid-liquid micro-extraction (DLLME), and hollow fiber liquid phase micro-extraction (HFLPME) [4].

Ionic liquids (ILs) were incorporated to LPME by Liu et al., in 2005, as co-solvents in the organic solution, with the aim to enhance pre-concentration of metals [5]. ILs are organic salts formed by an organic cation and an organic or inorganic anion, which are liquid at a temperature lower than 100°C [6]. Those ILs liquid at working conditions are called room temperature ionic liquids (RTILs) [7]. Their application in LPME is supported by their thermal stability, negligible vapor pressure, and high hydrophobicity. Based on these properties, they have been considered to be more environmentally friendly than conventional solvents [6].

Additionally, the structure of the cation and the anion in ILs can be finely tuned, adding functional groups for a specific task (TSILs) [8], and the estimated number of possible combination is bigger than $10^{18}$. Reported benefits of using ILs for LPME are a better selectivity and efficiency for metals preconcentration in shorter experimental times, together with a better environmental profile of the organic solution [9]. Despite they have been considered to be greener than molecular solvents due to their low vapor pressure, some ILs present toxicity for aquatic organisms [10]. This aspect must be considered in the selection and design of structures for development of new ILs with application in LPME. In order to overcome this drawback, deep eutectic solvents (DES) have also been tested in the LPME of metals, showing better stability during extraction, more accessible sources to precursors, lower cost, and lower toxicity than ILs [1,11]. DES were discovered by Abbot et al., in 2003, and they are the result of combining various hydrogen bond acceptors and hydrogen bond donors [11,12]. They have been considered by some authors as a sub-class of ILS, due to their similar characteristics and properties [13]. However, they can be considered as different category than ILs due to some unique properties as solvents [11].

Despite recent reviews on the application of ILs to LPME have been published, specific discussion on their application to metals determination has not been carried out since Stanisz et al. (2014) [14]. However, more than 50% of works about IL-LPME of metals for Environmental Analytical Chemistry have been published in the

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period 2015—2020, including the rising development of some sub-classes of ILS as TSILs, or magnetic ILs among others, as well as DES.

## 2. ILs and DES used in LPME of metals: structure and mechanism of extraction

ILs are composed of an organic cation and an anion that can be either organic or inorganic. Cations are based on imidazolium, phosphonium, ammonium, pyrrolidinium and pyridinium; while the common anions are hexafluorophosphate, tetrafluoroborate, halides, alkylsulfates, alkylsulfonate, trifluoromethylsulfonate and bis[(trifluoro-methyl)sulfonyl]amide [15] (Fig. 1). Due to its hydrophobicity, $PF_6^-$ has been the most frequently used anion; however it is highly toxic and leads to the formation of hydrofluoric acid in the presence of moisture, resulting in damage of glassware and steel parts [16]. ILs with this composition have been mainly used as co-solvents, partially substituting a molecular solvent in the organic solutions with good results, but they have been less used in last years.

Hexylmethylimidazolium hexafluorophosphate ([C_6mim][PF_6]) has been applied as solvent for complexing agents as ammonium pyrrolidine dithicarbamate (APDC), di-ethyl-di-thiocarbamate (DDTC), and 2-(6-methylbenzothiazolylazo)-6-nitrophenol [17—19]. Butylmethylimidazolium hexafluorophosphate ([C_4mim][PF_6]) has been applied as a co-solvent of ethanol, using DDTC as complexing agent, and also as a solvent for dilution of L-cysteine [20—22].

However, in the last years the use of ILs not only as co-solvents, but also as extractants has gained relevance. In this regard, ILs can be classified in two groups depending on the characteristics of the anion. First, commercially available ILs as trioctylmethylammonium chloride (Aliquat ® 336) [23,24], and trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) [25]. Second, these ILs have served as precursors for the targeted synthesis of new ILs for LPME, resulting in task specific ionic liquids (TSILs) [8], in which Cl⁻ is substituted by an organic anion through metathesis reaction [24]. The use of TSILs has expanded the possibilities of ILs in LPME, because their structure can be predefined to improve extraction efficiency or selectivity in metal extraction.

In most of cases the organic anion of TSILs is based on an carboxylic acid containing other electron donor atoms, which improve the complexation capability of the IL [6]. These TSILs present irregular behavior at different sample pH due to their zwitterionic nature, and they have showed to be particularly efficient at basic pH (8—10) and highly saline waters [26]. TSILs applied in LPME of metals are shown in Fig. 2.

In order to elucidate the influence of the ILs structure on the extraction capability, TSILs with a common anion have been applied in combination with different cations, mainly changing the length of the linear alkyl group or the central atom [27]. Normally, the cation is considered to control physical properties of the liquid [28]. However, Pirkwieser et al. evaluated the potential of three ILs containing 3-hydroxy-2-naphtoate ([HNA]) anion and three cations: trihexyltetradecylphosphonium ([P_66614]), methyltrioc tylphosphonium ([P_1888]), and methyltrioctylammonium ([N_1888]), observing that extraction with [P_66614] was less sensitive to sample matrix of sea and salt-works water than with [P_1888] and [N_1888], in the extraction of Ag and Cd [27].

The cation [P_1888] has also been combined with salicylate ([Sal]), anthranilate ([Ant]) and hexylsulfanyl acetate ([C_6SAc]) [29,30]. The incorporation of a soft Lewis base as S in the structure of the anion facilitates the extraction of soft acids as Ag and Cd. In the case of TSILs based on the ([N_1888]) cation, anions as methylthiobenzoate ([MTBA]), thiosalicylate ([TS]) have been incorporated. Finally, 1-(4-hydroxy-2-oxybutyl)-3-methylimidazolium salicylate ([HOC_2OC_2-mim][Sal]) and 1-(3-hydroxypropyl)-3-methylimidazolium salicylate ([HOC_3mim][Sal]), were synthesized by Trtić-Petrović et al. from their corresponding chlorides, for the extraction of the free cation of Cd, Cu, Pb and Zn in urine and wastewater [31].

Recently, magnetic ionic liquids (MILs) in which $FeCl_4^-$ or $MnCl_4^{2-}$ are incorporated in substitution of Cl⁻ from the IL precursor have been applied for the mciro-extraction of metals [32—34]. MILs have allowed the recovery of the metal enriched IL from the sample using a magnet, in what can be considered as a rising field of research in IL-LPME.

In spite of the potential and applicability of ILs in LPME, there are still some aspects to be improved, mainly derived from their partial dissolution in the sample during extraction [30]. In the last years, the use of deep eutectic solvents (DES) has arisen to overcome this limitation (Fig. 3), improving their properties and environmental profile [1]. They were incorporated in the LPME of
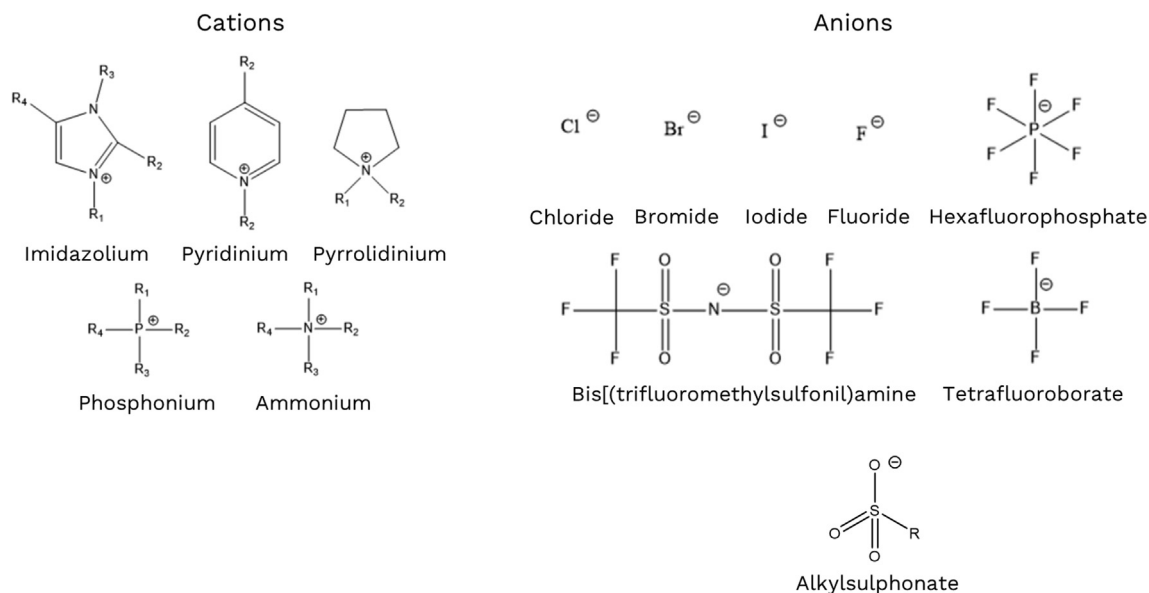


**Fig. 1.** Structure of commercial ionic liquids used in IL-LPME of metals in environmental samples.
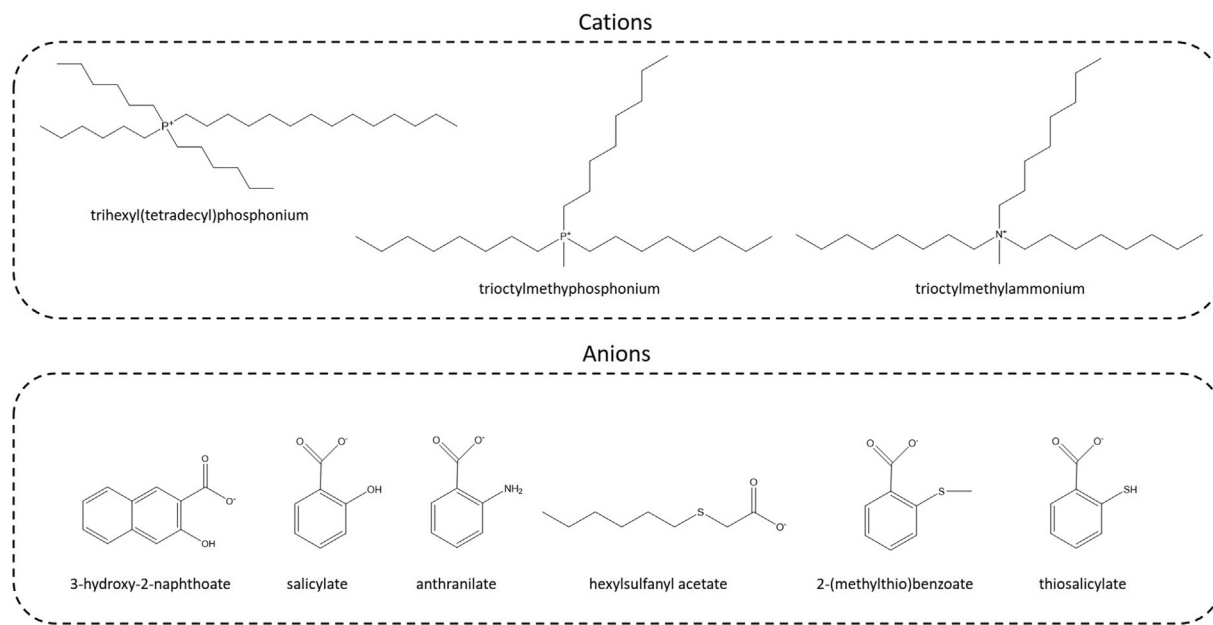
**Fig. 2.** Structure of task specific ionic liquids applied in LPME of metals in environmental samples.

metals in 2016 [35,36]. Since then, they have been applied as solvent media for the microextraction of metals in different environmental samples. The first DES used in LPME of metals was the result of a combination of choline chloride and urea, which was applied as a solvent for magnetic nanoparticles and APDC, in the microextraction of Pb and Cd [35,36]. Phosphonium based ILs as benzyl triphenyl phosphonium bromide and Cyphos® 101 have been used as precursors of DES [37,38]. In combination with salicylate, these DESs act simultaneously as solvents and extractants [38]. This strategy has been also followed combining tetrabutyl ammonium bromide ((TBAB)−H₂O− (NH₄)₂SO₄) and ammonium sulphate, or thiomalic acid and ferric chloride [26,39]. Finally, DESs containing metallic cations as Zn(II) in their structure have been prepared for micro-extraction of V(V) and

Cd(II), combining $ZnCl_2$ with acetamide to dissolve APDC as complexing agent in the presence of Triton X 114 as a dispersing agent [40].

Regarding extraction mechanism of metals in IL-LPME, limited information is available [41]; however, two main mechanisms have been proposed: ionic exchange and ion association. In the first mechanism, metallic anionic species in solution are exchanged by the anion in the IL, as it happens with Ag, Cd, Hg and Pd in saline samples [42], where they appear as the corresponding negatively charged chlorocomplexes. This mechanism prevails when $Cl^-$, $PF_6^-$, or $Br^-$ are used as anions, leading to the loss of ILs into the sample during extraction [41]. This is particularly important in the case of $PF_6^-$, which is among the most commonly used anions in IL-LPME, but it presents some concerns related with the release of
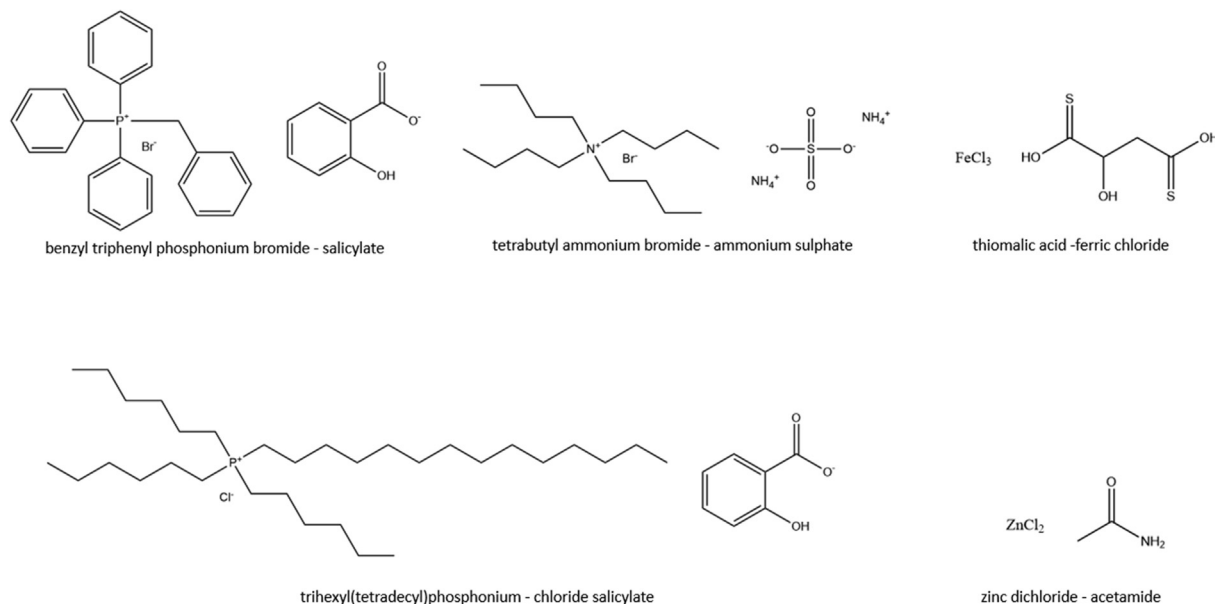


**Fig. 3.** Deep eutectic solvents applied in LPME of metals in environmental samples.

hydrofluoric acid into the samples in slightly acidic media. In ion association, the functional groups of the anion present ability to complex the free ion of metals [6], improving the efficiency and the selectivity of extraction, as well as reducing the loss of IL into the sample [30]. The development of TSILs based on organic anions favors the metallic complexation mechanisms. Despite both mechanisms can be observed when inorganic and organic anions are used, they are highly dependent on the speciation of the metal.

In summary, the application of ILs in LPME of metals in environmental samples has experienced a great evolution in a short period. They were first applied as co-solvents to improve the characteristics of the organic solution, and they have evolved to play the double role of solvent and extractant, thanks to the discovery of new substances as TSILs, MILs and DESs.

## 3. Application of ILs and DESs in different modes LPME of metals

ILs have been applied in the three main modalities of LPME for metals: single drop liquid phase micro-extraction (SDME), dispersive liquid-liquid micro-extraction (DLLME), and hollow fiber liquid phase micro-extraction (HFLPME); while DESs have been applied only in DLLME [1]. Different methods based on IL and DES-LPME have been developed to pre-concentrate metals from environmental samples, mainly natural waters (freshwater, seawater, saltwork) and sediment. These applications have focused both on total concentrations of metals and speciation studies, as described below.

### 3.1. Single drop micro-extraction

The first configuration in which ILs were applied to liquid phase micro-extraction was SDME [5]. In SDME a drop of extracting solvent is suspended from a syringe into the aqueous sample containing the analyte. After extraction, the organic drop is retracted back into the

microsyringe and injected into the detector for quantification of the analytes [9]. The droplet can be either disposed to the headspace or directly immersed in the sample, distinguishing two main SDME modalities: headspace SDME (HS-SDME) or direct immersion SDME (D-SDME) (Fig. 4a) [9]. The main advantage of using IL in SDME is an enhancement of stability of the drop during extraction.

In the case of SDME, ILs have been used exclusively as solvents, being in most of cases imidazolium cation ([$C_n$mim], n = 4, 8) based ILs combined with $PF_6^-$ and $BF_4^-$. Cations [$C_4$mim] and [$C_6$mim] have been the most commonly used in this methodology due to a balance between hydrophobicity and viscosity, allowing enough stability of the organic solution without reducing diffusion of the extracted metal [5]. This methodology has been applied to the micro-extraction of Ag, Cu, Hg, Co and Pb in tap and lake water, and human hair and serum [43,44].

Despite, it was the first developed IL-LPME, IL-SDME has had limited interest due to shortcomings related with lower efficiency than DLLME and HFLPME. In fact, new applications of IL-SDME for metals have not been found since the technique was revised by Marcinkowski et al., in 2015 [45].

### 3.2. Dispersive liquid-liquid micro-extraction

DLLME of metals is based on the dispersion of micro-droplets of an organic solution containing the extractant into a sample containing the target metal [9]. This LPME mode uses a ternary solvent system, in which a dispersing solvent is added to the sample to keep the micro-droplets of extractant solution dispersed in the sample, which is placed into a conical tube. Then, a cloudy solution is formed, favoring a fast mass transfer of the analytes to the receiving solution. Centrifugating, the extraction solvent containing the analyte is separated from the sample and then, removed from the tube with a syringe for instrumental determination of the metal (Fig. 4b) [3]. Applications of IL-DLLME can be can be found in Table 1. In comparison with other IL-LPME, IL-DLLME requires
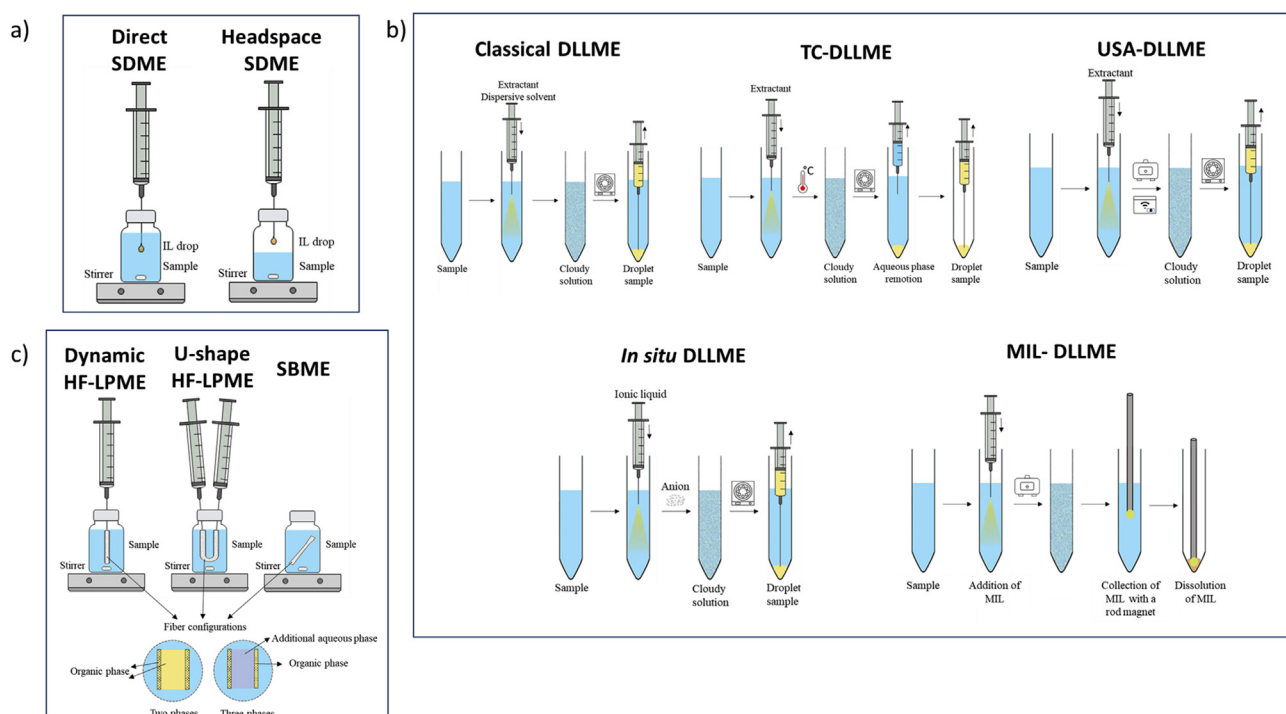


**Fig. 4.** Liquid phase micro-extraction methods in which ILs have been used.

**Table 1**

IL-DLLME of metals in environmental samples.

| DLLME | Ionic liquid | Amount of Ionic Liquid | Extractant | Metal | Sample | Amount of sample | Extraction time (min) | LOD ($\mu g\ L^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| AA–DLLME | $[C_6mim][PF_6]$ | – | $[C_6mim][PF_6]$ | Cu | Water | 10 mL | <5 | 0.5 | [19] |
| CP- DLLME | Cetyl pyridinium naphthenate | 2000 µL | Cetyl pyridinium naphthenate | Cu | Water, blood | 20 mL | <20 | 27 | [54] |
| DLLME | $[C_4mim][Br]$ | – | $[C_4mim][Br]$ | Cu | Chia seeds (Salvia hispanica, L.) | 0.05 g | 20 | 0.33 | [50] |
| | $[C_4mim][PF_6]$ | 100 µL | DDTC | Cu | Water | 10 mL | 10 | 3.3 | [48] |
| | $[C_{16}mim][Br]$ | 100 µL | DDTC | Cu | Water | 10 mL | 30 | 5.1 | [48] |
| | $[C_7mim][PF_6]$ | 250 µL | 3-dimethylamino rhodamine | Cu | Lake water, seawater, tap water spiked | 5 mL | – | 830 | [49] |
| | Thiomalic acid/ferric chloride | 200 µL | Thiomalic acid/ferric chloride | Cr | Water fortified | 40 mL | <15 | 1.18 | [39] |
| | $[HOC_2OC_2mim][Sal]$ | 60 µL | $[HOC_2OC_2mim][Sal]$ | Cu | Tap water, wastewater, urine | 2 mL | <15 | – | [31] |
| | $[HOC_3mim][Sal]$ | 60 µL | $[HOC_3mim][Sal]$ | Cu | Tap water, wastewater, urine | 2 mL | <15 | – | [31] |
| | $[C_4mim][Sal]$ | 60 µL | $[C_4mim][Sal]$ | Cu | Tap water, wastewater, urine | 2 mL | <15 | 0.008 | [31] |
| | Aliquat® 336 | 50 µL | Aliquat® 336 | Au | Water, ore | 10 mL | 10 | 0.09 | [51] |
| | ChCl-urea | 200 µL | MNPs | Pb, Cd | River, seawater, soil, hair | 60 mL | 10 | 0.4, 0.1 | [35] |
| | $(TBAB) - H_2O - (NH_4)_2SO_4$ | 1000 µL | $(TBAB) - H_2O - (NH_4)_2SO_4$ | Cd, Co, Cu, Ni, Pb, Zn | Wastewater, surface water, spring water | 20 mL | 15 | 0.012, 0.2, 0.17, 0.11, 0.2, 0.4 | [26] |
| | $[N_{1888}][TS]$ | 150 µL | $[N_{1888}][TS]$ | Cd, Co | Biological samples | 10 mL | <25 | 0.05 | [52] |
| | $ZnCl_2$-acetamide | 200−500 µL | APDC | V | Sea water, waste water, canal water, mineral water, tap | 15 mL | <5 | 0.01 | [36,40] |
| | | | | Cd | Water | 20 mL | <15 | 0.504 | |
| Effervescence-DLLME | DES | 1000 µL | 1,5-diphenyl carbazide | Cu | Water samples | 25 mL | <10 | 2.9 | [37] |
| In situ-DLLME | $[C_4mim][PF_6]$ | 130 mg | DDTC | Ni, Cu, Zn | Wastewater | 10 mL | <10 | 0.93, 0.79, 0.71 | [20] |
| | $[C_6mim][PF_6]$ | 60 mg | DDTC | Cr | Water | 10 mL | 10 | 3.0 | [17] |
| Microfluidic-DLLME | [OPy][BF4] | 3.5 µL | [OPy][BF4] | Hg | Water | 600 µL | – | 0.753 | [65] |
| TC-DLLME | [OPy][BF4] | 125 µL | [OPy][BF4] | Hg | Water | 45 mL | 300 | 0.0342 | [62] |
| | [OPy][TfO] | – | [OPy][TfO] | Hg | Tap, pond, wastewater | 10 g | 150 | 0.05 | [61] |
| USA-DLLME | $[C_4mim][PF_6]$ | 60 µL | $[C_4mim][PF_6]$ | Zn | Environmental water | – | – | – | [21] |
| | $[C_6mim][PF_6]$ | 120 µL | APDC | Cd, Pb | Tap, river, well | 15 mL | <10 | 0.1, 0.15 | [55] |
| | $[C_6mim][PF_6]$ | 200 µL | 2-(6-methylbenzothiazolylazo)-6-nitrophenol | Cd | Real water | 25 mL | <20 | 0.1 | [18] |
| | $[C_4mim][PF_6]$ | 75 µL | APDC | Pb | Biological samples | 10 mL | <20 | 0.19 | [56] |
| | Aliquat® 336 | – | Aliquat® 336 | Te | Surface river water, wastewater | 10 mL | <10 | 0.00042 | [47] |
| | Aliquat® 336 | 700 mg | Aliquat® 336 | Cr, Cd | Water | 3 mL | <15 | 0.45, 0.25 | [58] |
| | Cyphos® 101 | 30 µL | Cyphos® 101 | Pb | Human fluids | 2 mL | 65 | 0.014 | [57] |
| | Cyphos® 104 | 30 µL | Cyphos® 104 | Pb | Human fluids | 2 mL | 65 | 0.018 | [57] |
| | Trihexyl(tetradecyl) phosphonium chloride - thiosalicylic acid | 30 µL | Trihexyl(tetradecyl) phosphonium chloride - thiosalicylic acid | Pb, Cd, Co, Ni | Drinking, rain water | 15 mL | <15 | 0.05, 0.13, 0.06, 0.11 | [38] |
| Vortex-DLLME | $[C_4mim][PF_6]$ | 150 µL | L-cysteine | Cd, Pb | Tap water, groundwater, hair | 25 mL | <20 | 0.13, 0.05 | [21] |
| MIL-DLLME | $[P_{66614}][MnCl4]$ | 150 µL | $[P_{66614}][MnCl4]$ | Pb | Bee products | 8 mL | <10 | 0.030 | [64] |
| | $[P_{66614}][FeCl4]$ | 60 µL | $[P_{66614}][FeCl4]$ | As(III) | Freshwaters | 5 mL | <10 | 0.020 | [33] |
| | $[P_{66614}][FeCl4]$ | 45 µL | $[P_{66614}][FeCl4]$ | Sb(III) | Freshwaters | 6 mL | <5 | 0.02 | [32] |
| | Poly (ethylene glycol) bis (methylimidazolium chloride)- $FeCl_3$ | 75 µL | Poly (ethylene glycol) bis (methylimidazolium chloride)- $FeCl_3$ | K | Oil | 10 mL | <5 | 0.5 | [34] |

shorter extraction times, as it happens when conventional solvents are applied. Sample amount required in this technique ranges from 2 mL to 20 mL, while the amount of IL applied is in the range 30−2000 μL.

Although extensively applied, DLLME suffers from some limitations that need to be overcome, as the use of harmful chlorinated solvents like chloroform, chlorobenzene and carbon tetrachloride to stabilize the dispersion [46]. The use of a dispersant is particularly important in IL-DLLME due to the high viscosity of ILs [47]. According to green solvents assessment, acetone has been the primary choice in IL-DLLME followed by methanol, ethanol, and in less extent acetonitrile. Also surfactants as Triton X-114, Triton X-100 and sodium dodecyl sulphate (SDS), have been applied as dispersants when highly viscous ILs are used in the extraction of saline samples [3]. In this sense, the development of new TSILs has allowed the development of dispersantless DLLME, in which the IL can also substitute the use of the dispersant [41].

As for other LPMEs, the observed trend is to a lesser application of $[C_nmim][PF_6]$ ILs in favor of TSILs. Notwithstanding, $[C_4mim]$ $[PF_6]$, and 1-hexadecyl-3-butylimidazolium bromide ($[C_{16}mim]$ [Br]) have been used in DLLME of Cu, Pb and Cd with DDTC for water samples [48]; 1-heptyl-3-methylimidazolium hexafluorophosphate ($[C_7mim][PF_6]$) solutions of 3-dimethylamino rhodamine have been used for micro-extraction of Cu [49], and butylmethylimidazolium imidazolium bromide ($[C_4mim][Br]$) has been proposed for determination of Cu in Chia seeds [50].

More attention has been paid to ILs acting as carriers, as Aliquat® 336 for the extraction of Au from several water matrices, including mining waters [51]. Additionally, TSILs that incorporate organic anions as methyltrioctylammonium thiosalicylate ($[N_{1888}]$ [TS]) for Co and Cd detection were applied [52,53]. ILs formed by combination of salicylate and the cations $[HOC_2OC_2mim]$ and $[HOC_3mim]$ have been useful for Cu and Cd DLLME [31]. In the case of Cu extraction from blood and serum, the TSIL cetyl pyridinium naphthenate was applied in cloud-point DLLME, using the surfactant Triton X to facilitate the dispersion of IL in the sample, increasing the contact between IL and Cu [54].

A rising field of research in DLLME is the application of deep eutectic solvents, which reduce the use of a dispersant and limit the loss of IL into the sample during extraction. The first DES used in DLLME was choline chloride-urea (ChCl-urea), which was applied for dispersion of magnetic nanoparticles (MNPs) in the micro-extraction of Pb and Cd from river and seawater, as well as from the digested solutions of soil and hair samples [35]. APDC has been incorporated in DES solutions based on $ZnCl_2$-acetamide to extract Cd and V from different types of waters as mining and wastewater [36,40]. The most recent development in DES-DLLME is the use of DES simultaneously as solvents and ligands. For instance tetrabutyl ammonium bromide-ammonium sulphate has been applied in the multi-elemental analysis of Cd, Co, Ni, Pb, and Zn from several environmental water matrices, and thiomalic-ferric chloride has been used in the determination of Cr in water samples [26,39].

Due to their chemical versatility, thermal stability and high viscosity ILs have been incorporated to in-situ, temperature-controlled or ultrasound assisted DLLME. Undoubtedly, ultrasound assisted DLLME (USA-DLLME) has appeared as a rising field of development in IL-LPME. It consists in the application of ultrasound energy to substitute the use of a dispersant, promoting the formation of micro-droplets of the extractant solution, improving the contact between the sample and the organic solution in times even shorter than 1 s [38]. $[C_6mim][PF_6]$ has been used as a medium with APDC and 2-(6-methylbenzothiazolylazo)-6-nitrophenol for the extraction of Cd and Pb from water samples and biological fluids [18,21,55,56]. Playing the double role of solvent and extractant, phosphonium based ILs Cyphos® 101 and Cyphos® 104 have

been applied to the pre-concentration of Pb from human fluids [57], while ammonium based Aliquat® 336 has been used for extraction of Te, Cr, and Cd from several water matrices [47,58]. Also DES have been incorporated to USA-DLLME of Pb, Cd, Co, and Ni from drinking and environmental waters to favor the dispersion of DES, as it is the case of trihexyl(tetradecyl)phosphonium chloride-thiosalicylic acid [38].

In the case of in-situ IL-DLLME, a hydrophilic precursor of the IL is added to the sample to complex the metal and then, an ionic exchanger is added to the sample leading to the metathesis reaction to form the hydrophobic IL, which can be separated from the sample. This methodology was introduced in 2009 by Baghdadi et al. for Hg micro-extraction [59]. In the last year is has gotten renewed attention for pre-concentration of metals. DDTC was added as hydrophilic ligand for Ni, Zn and Cu in wastewaters, and later $[C_4mim][PF_6]$ was incorporated as ion exchanger [20]. Vidal et al. used the same strategy for Cr speciation using $[C_6mim][PF_6]$ as ion exchanger and changing sample pH [17]. This way, they could extract Cr (VI) pH 2, and total Cr at pH 5. Finally, micro-extraction of Cd and Pb from groundwaters has been carried out using L-cysteine as complexing agent and $[C_4mim][PF_6]$ as IL in vortex-assisted DLLME [21]. A main advantage of this methodology is that dispersant agents are rarely needed [60].

To improve the mass transfer of the metal between the sample and the organic phase, air assisted DLLME (AA-DLLME) of Cu was introduced by Du et al. minimizing the need of dispersant in a system composed of $[C_6mim][PF_6]$ and $Fe_3O_4$ nanoparticles, in the presence of Triton 100 X as emulsifier [19]. Similarly effervescence-assisted DLLME (EA-DLLME) using a ChlCl-phenol DES as extraction medium for Cu by 1,5-diphenyl carbazide has been reported [37]. These methodologies are simpler than USA-DLLME, and in the case of EA-DLLME, external sample agitation is avoided, facilitating the portability of the microextraction systems.

Temperature-controlled DLLME (TC-DLLME) in which the IL is formed in the sample at a temperature of approximately 80°C [61], has showed to be effective in the pre-concentration of Hg(II) from tap, pond and wastewater with ILs N-octylpyridinium tetrafluoroborate ($[OPy][BF_4]$) and N-octylpyridinium trifluoromethylsulfonate ($[OPy]$ [TfO]) [61,62]. However, the need of excessive heating may limit the applicability for a bigger number of samples.

Magnetic nanoparticles of $Fe_2O_3$ were incorporated to the ILs applied in DLLME by Soylak and Yilmaz (2015), to avoid the need of centrifugation of the metal enriched IL and the sample [63]. Magnetic nanoparticles allowed the separation APDC after extraction of Cd using a magnet, simplifying DLLME. This idea has evolved to the recent application of magnetic ionic liquids to the extraction of metals, described in section 2. MIL trihexyl(tetradecyl)phosphonium tetrachloromanganate ($[P_{66614}][MnCl_4]$) has been applied in the pre-concentration of Pb from organic matrices as bee products i.e.: honey, vinegar or beer [64]. $FeCl_4^-$ has been used as anion in poly (ethylene glycol) bis (methylimidazolium) $2FeCl_4^-$ for the microextraction of K from oil [34], and for speciation of As(V) and As(III). In the last case, a TSIL trihexyl(tetradecyl)phosphonium hexachlorodisprosiate was applied to extract As(III) and total As was extracted using trihexyl(tetradecyl)phosphonium $FeCl_4$ [33]. This strategy was also used for speciation of Sb(III)/Sb(V), using ammonium diethyldithiophosphate for selective extraction of Sb(III) [32].

Finally, an approach to automation of IL-DLLME of metals has been recently proposed by Hui et al. (2019), based on the use of a centrifugal microfluidic disk to enrich and detect Hg in water samples [65]. In this case, IL and the sample are separated, after extraction, by means of centrifugal forces of the spinning disk and capillary valves, that allow separating the supernatant. Automation can be consider as one of the challenges for IL-DLLME that can lead

also to the development of portable sampling devices based on the use of ILs.

### 3.3. Hollow fiber liquid phase micro-extraction

In hollow fiber liquid phase micro-extraction (HFLPME), analytes are transported from the sample to an acceptor phase placed inside the lumen of the hollow fiber, through an organic solution immobilized in the pores of the fiber walls [6] (Fig. 4c). HFLPME can be used in a two-phase (2-HFLPME) mode when the acceptor solution in the lumen is the same organic solution in the fiber pores, or in a three-phase mode (3-HFLPME), in which the organic solution impregnates the pores, separating an aqueous acceptor phase from the sample, acting as a liquid membrane (Fig. 4c) [66]. Common HFLPME setups are: U-shape, dynamic, and solvent bar micro-extraction (SBME). Among them, SBME has gotten increasing interest in IL-HFLPME due to its simplicity, as the fiber ends are sealed and the solvent bar can be left freely tumbling in the sample [67]. Table 2, summarizes the application of IL-HFLPME to the micro-extraction of metals. While extraction times are longer than for IL-DLLME, several experiments can be carried out simultaneously, without intervention of the analyst. The amount of ionic liquid as acceptor phase in 2-HFLPME is between 70 mg and 220 mg, while in the case of 3-HFLPME has not been defined, but it is smaller, as it is exclusively impregnating the pores of the fiber wall. Sample volume for this methodology ranges from 30 to 50 mL.

As for the rest of LPME techniques, the first use of ILs in HFLPME was the partial substitution of the molecular solvent by imidazolium based ILs, mainly $[C_nmim][PF_6]$, to improve metal extraction by a ligand [3,6]. However, in the reviewed period the trend has been the application of commercial and synthesized TSILs, which can act as solvents as well as extractants. One of the advantages of using a HF to support the IL, is that it offers a better control of partial dissolution of the IL into the sample during extraction [29]. In fact, this phenomenon, so-called "leaching" is generalized for IL-LPME, and should be taken into account when deciding the type of IL, the LPME modality, and during optimization of the micro-extraction [6].

The commercial IL Aliquat® 336 has been applied in HFLPME of Ag ultra-traces in seawater samples, using a 2 phases mode, showing the capacity of ILs for the extraction of metals in the presence of a highly saline matrix, that limits the applicability of most of conventional ligands [24]. For this metal, Cyphos® 101 has showed to be selective for the extraction of $AgCl_n^{(n-1)-}$ complexes at the natural pH of seawater [25]. This way, the speciation of silver associated to dissolved organic matter could be estimated. This IL has been useful also for the micro-extraction of priority and emerging pollutants as

Cd, and Pd from saline and hypersaline waters [42]. The success of Aliquat® 336 and Cyphos® 101 for micro-extraction of metals, forming chloro-complexes in marine waters, is based on its capacity to exchange the Cl⁻ of the IL by the negatively charged chloro-complexes of Ag and Cd from the sample [68].

The main development in IL-HFLPME has been the implementation of tailored ILs based on ammonium and phosphonium precursors, substituting the inorganic anion by an organic one. Derivatives of Aliquat® 336 in which Cl⁻ has been substituted by methyl thiobenzoate ([MTBA]) or thyosalicylate ([TS]) have showed to be effective in the HFLPME of Cd, Cr, Cu, Ni, and Pb from tap and river water samples. Additionally, trihexyl(tetradecyl)phosphonium anthranilate ($[P_{66614}][Ant]$) and trihexyl(tetradecyl)phosphonium salicylate ($[P_{66614}][Sal]$) have been applied to Ag and Pt microextraction in the same matrices [29].

Some new TSILs have been proposed specifically for the HFLPME of metals from saline and hypersaline samples, including saltworks. Pb, Cu, Cd, and Ag were selectively extracted with ILs based on 3-hydroxy-2-naphtoate anion. In this case, ILs containing methyltrioctylphosphonium and methyltrioctylammonium cations showed to be sensitive to the saline matrix, offering poor results in seawater, while trihexyltetradecylphosphonium based IL kept the same efficiency as in non-saline samples [27]. Recently, methyltrioctilphosphonium hexylsulfanyl acetate ($[P_{1888}][C_6SAc]$) and methyltrioctylammonium hexylsulfanyl acetate ($[N_{1888}][C_6SAc]$) have been used for the selective microextraction of Ag, Ni, Cd, Cu and Zn species in the form of chloro-complexes from saltworks [30].

In general, for IL-HFLPME the use of 2 phases configuration is preferred over 3-HFLPME, because ILs present high affinity for metallic species; and the release of metal from the organic solution to the acceptor phase is limited.

## 4. Instrumental determination of metals

Several instrumental techniques have been applied for metal determination after pre-concentration by IL-LPME. Selection of the instrumental technique is driven by the nature of the acceptor solution. In the case of two phases systems, it is an ionic liquid solution, and some adaptions have to be made in the instrumental technique for metal quantification.

Atomic absorption is the most frequent option, with flame (FAAS) and with electro-thermal (ETAAS) atomization. In the case of FAAS, the volume of sample required is sometimes bigger than the IL used in microextraction. In this particular case the IL solution is diluted in an organic solvent as ethanol, methanol, or acetonitrile, reducing the viscosity of the sample and easing its injection [20,58]. To avoid dilution of the metal enriched IL solution, Yan et al. have

**Table 2**
ILs-HFLPME of metals in environmental samples.

| HF-LPME | Ionic liquid | Metal | Sample | Amount of sample | Amount of IL | Extraction time (min) | LOD (ng L$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 3-HFLPME | Aliquat® 336 | Cd | Seawater | 35 mL | — | 60 | 0.04 | [68] |
| 2-HFLPME | $[N_{1888}][MTBA]$ | Cr, Cu | River water, tap water | 50 mL | 150 mg | 360 | — | [29] |
| | $[N_{1888}][TS]$ | Pb, Cd, Cr, Cu, Ni | River water, tap water | | | 300, 180, 360, 240, 240 | — | |
| | $[P_{66614}][Ant]$ | Ag | River water, tap water | | | 600 | — | |
| | $[P_{66614}][Sal]$ | Ag, Pt | River water, tap water | | | 600, 180 | — | |
| | Aliquat® 336 | Cd, Ag | Saline, hypersaline water | 35 mL | 220 mg | 30 | — | [23] |
| | Aliquat® 336 | Ag | Seawater | 37 mL | 90 mg | 60 | 0.09 | [24] |
| | Cyphos® 101 | Ag, Cd, Pd | Seawater, hypersaline water, saltworks | 50 mL | 145 mg | 30 | 21, 12, 7 | [42] |
| | Cyphos® 101 | Ag | Seawater | 50 mL | 70 mg | 30 | 0.4 | [25] |
| | $[N_{1888}][C_6SAc]$ | Ag, Cd, Ni, Cu, Zn | Saline, hypersaline, saltwork | 50 mL | 95 mg | 60 | — | [30] |
| | $[P_{1888}][C_6SAc]$ | Ag, Cd, Ni, Cu, Zn | Saline, hypersaline, saltwork | 50 mL | 95 mg | 60 | — | [30] |
| | $[N_{1888}][HNA]$ | Cu, Pb, Cd, Ag | Seawater, hypersaline water, saltworks | 50 mL | — | 120 | — | [27] |
| | $[P_{1888}][HNA]$ | Cu, Pb, Cd, Ag | Seawater, hypersaline water, saltworks | 50 mL | — | 120 | — | [27] |
| | $[P_{66614}][HNA]$ | Cu, Pb, Cd, Ag | Seawater, hypersaline water, saltworks | 50 mL | — | 120 | — | [27] |

proposed the use of micro-injection of the sample in thermospray flame furnace [69]. Using ETAAS, adaption of atomization programs can be enough in some cases [24]; however, molecular solvents can be added also in this case to reduce sample viscosity and to minimized background signal, or potential loss of the analyte together with IL during pyrolysis step prior atomization [57].

The strategy of diluting the IL phase prior injection has been extended to other instrumental techniques, as tungsten coil atomic emission spectrometry for Cr detection [17], or HPLC-UV determination of Pb, Cd, Co and Ni after extraction in DES trihexyl(tetradecyl)phosphonium chloride and thiosalicylic acid [38]. In both cases acetonitrile was used as a diluent.

Fluorescence has been used for the determination of Hg in TC-DLLME, adding p-tetraphenylethene—rhodamine to the concentrated solution of [OPy][BF4]-Hg [62]. For Hg, a photomicrograph fluorescence device was incorporated to a micro-fluidic disc, in which the metal was enriched, automatizing pre-concentration and detection [62].

Electrochemical methods as differential pulse anodic stripping voltammetry were used for Cu determination in enriched imidazolium IL, using hanging drop Hg electrode [31]. In the case of Hg detection by stripping voltammetry, the IL loaded with the metal was diluted in acetonitrile before instrumental determination.

Last, when the metal is eluted from the IL phase or when 3-phase LPME is used, it is stripped in an aqueous solution with better compatibility for elemental analysis techniques. For instance, inductively coupled plasma combined with mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES) have been used for detection of Cd, Co, Cu, Te, or Zn [26,47].

## 5. Conclusion and future perspectives

The application of ILs in LPME of metals in environmental samples has experienced an important evolution during the last year, from their application as co-solvents to their simultaneous role as solvents and reagents. The design of new structures has led to a wide variety of task specific ionic liquids that have resulted in more selective methods, with application to complex matrices as seawater, improving the performance of conventional extractants. Additionally, the incorporation of DESs establishes a new category of LPME for metallic species, that overcomes the limitations of ILs associated with partial dissolution in the sample, accessibility to precursors, and toxicity.

These solvents have been incorporated to all the LPME techniques; however, the most important progress has been done for DLLME and HFLPME. New modes of operation in DLLME of metals as in-situ, TC-DLLME, USA-DLLME, AA-DLLME, EA-DLLME haven been developed thanks to the use of ILs. The use of TSILs in HFLPME has arisen as a reliable tool in the speciation of metals in complex matrices as seawater or saltwork. Finally, advances on the optimization of instrumental techniques have been done to adapt instrumental determination to the IL matrix, including de development of lab-on-a-disk determination of metals.

In summary, future trends in their application to LPME are the targeted development of TSILs with improved selectivity for metallic species, and the take-off of DES-LPME. Last but not least, research on the optimization of instrumental determination and the incorporation of microfluidic systems can be an opportunity for broader application of IL-LPME of metals.

## Declaration of competing interest

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.

## References

[1] V. Jalili, A. Barkhordari, A. Ghiasvand, New extraction media in micro-extraction techniques. A review of reviews, Microchem. J. 153 (2020) 104386. https://doi.org/10.1016/j.microc.2019.104386.

[2] M. Chamsaz, M.H. Arbab-Zavar, S. Nazari, Determination of arsenic by electrothermal atomic absorption spectrometry using headspace liquid phase microextraction after in situ hydride generation, J. Anal. At. Spectrom. 18 (2003) 1279—1282. https://doi.org/10.1039/b303169a.

[3] M.Á. Aguirre, P. Baile, L. Vidal, A. Canals, Metal applications of liquid-phase microextraction, TrAC Trends Anal. Chem. (Reference Ed.) 112 (2019) 241—247. https://doi.org/10.1016/j.trac.2018.11.032.

[4] J. Płotka-Wasylka, K. Owczarek, J. Namiesnik, Modern solutions in the field of microextraction using liquid as a medium of extraction, TrAC Trends Anal. Chem. (Reference Ed.) 85 (2016) 46—64. https://doi.org/10.1016/j.trac.2016.08.010.

[5] J. Liu, Y. Chi, G. Jiang, Screening the extractability of some typical environmental pollutants by ionic liquids in liquid-phase microextraction, J. Separ. Sci. 28 (2005) 87—91. https://doi.org/10.1002/jssc.200401805.

[6] M.J. Trujillo-Rodríguez, H. Nan, M. Varona, M.N. Emaus, I.D. Souza, J.L. Anderson, Advances of ionic liquids in analytical Chemistry, Anal. Chem. 91 (2019) 505—531. https://doi.org/10.1021/acs.analchem.8b04710.

[7] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Room temperature ionic liquids and their mixtures - a review, Fluid Phase Equil. 219 (2004) 93—98. https://doi.org/10.1016/j.fluid.2004.02.003.

[8] J.H. Davis, Task-specific ionic liquids, Chem. Lett. 33 (2004) 1072—1077. https://doi.org/10.1246/cl.2004.1072.

[9] J. Soares da Silva Burato, D.A. Vargas Medina, A.L. de Toffoli, E. Vasconcelos Soares Maciel, F. Mauro Lanças, Recent advances and trends in miniaturized sample preparation techniques, J. Separ. Sci. 43 (2020) 202—225. https://doi.org/10.1002/jssc.201900776.

[10] P. Pirkwieser, J.A. López-López, M. Schagerl, W. Kandioller, B.K. Keppler, C. Moreno, F. Jirsa, Heavy metal extraction under environmentally relevant conditions using 3-hydroxy-2-naphthoate-based ionic liquids: extraction capabilities vs. acute algal toxicity, Appl. Sci. 10 (2020) 1—15. https://doi.org/10.3390/app10093157.

[11] J. Płotka-Wasylka, M. de la Guardia, V. Andruch, M. Vilková, Deep eutectic solvents vs ionic liquids: similarities and differences, Microchem. J. 159 (2020) 105539. https://doi.org/10.1016/j.microc.2020.105539.

[12] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. (2003) 70—71. https://doi.org/10.1039/b210714g.

[13] K. Oliveira, F. Jerome, Synthesis and properties, in: D.J. Ramón, G. Guillena (Editors), Deep Eutectic Solvents: Synthesis, Properties and Applications, Wiley-VCH, Weinheim, 2020, pp. 1—23.

[14] E. Stanisz, J. Werner, A. Zgoła-Grześkowiak, Liquid-phase microextraction techniques based on ionic liquids for preconcentration and determination of metals, TrAC Trends Anal. Chem. (Reference Ed.) 61 (2014) 54—66. https://doi.org/10.1016/j.trac.2014.06.008.

[15] I. Rykowska, J. Ziemblińska, I. Nowak, Modern approaches in dispersive liquid-liquid microextraction (DLLME) based on ionic liquids: a review, J. Mol. Liq. 259 (2018) 319—339. https://doi.org/10.1016/j.molliq.2018.03.043.

[16] P. Zhang, L. Hu, R. Lu, W. Zhou, H. Gao, Application of ionic liquids for liquid—liquid microextraction, Anal. Method 5 (2013) 5376—5385. https://doi.org/10.1039/c3ay40597d.

[17] L. Vidal, S.G. Silva, A. Canals, J.A. Nóbrega, Tungsten coil atomic emission spectrometry combined with dispersive liquid-liquid microextraction: a synergistic association for chromium determination in water samples, Talanta 148 (2016) 602—608. https://doi.org/10.1016/j.talanta.2015.04.023.

[18] E.M. Hafez, R. El Sheikh, A.A. Sayqal, N. AlMasoud, A.A. Gouda, Ultrasound-assisted ionic liquid microextraction for preconcentration of cadmium in water, vegetables and hair samples prior to FAAS determination, Curr. Anal. Chem. 16 (2020) 1022—1031. https://doi.org/10.2174/1573411015666191205104244.

[19] W. Du, L. Yao, J. Bian, Y. Liu, X. Wang, J. Zhang, L. Pang, Ionic liquid-based air-assisted liquid-liquid microextraction combined with dispersive micro-solid phase extraction for the preconcentration of copper in water samples, Anal. Method 10 (2018) 3032—3038. https://doi.org/10.1039/c8ay00800k.

[20] V. Zare-Shahabadi, P. Asaadi, F. Abbasitabar, A. Shirmardi, Determination of traces of Ni, Cu, and Zn in wastewater and alloy samples by flame-AAS after ionic liquid-based dispersive liquid phase microextraction, J. Braz. Chem. Soc. 28 (2017) 887—894. https://doi.org/10.21577/0103-5053.20160241.

[21] R. Shaikh, T.G. Kazi, H.I. Afridi, A. Akhtar, J.A. Baig, An environmental friendly enrichment method for microextraction of cadmium and lead in groundwater

samples: impact on biological sample of children, Chemosphere 237 (2019). https://doi.org/10.1016/j.chemosphere.2019.124444.

[22] A. Preethi, R. Vijayalakshmi, A. Brinda Lakshmi, Dispersive liquid-liquid microextraction of zinc from environmental water samples using ionic liquid, Chem. Eng. Commun. 1 (2021) 1–10. https://doi.org/10.1080/00986445.2020.1865935.

[23] B. Herce-Sesa, J.A. López-López, J.J. Pinto, C. Moreno, Ionic liquid based solvent micro-extraction of Ag and Cd from saline and hyper-saline waters, Chem. Eng. J. 308 (2017) 649–655. https://doi.org/10.1016/j.cej.2016.09.095.

[24] J.A. López-López, B. Herce-Sesa, C. Moreno, Solvent bar micro-extraction with graphite atomic absorption spectrometry for the determination of silver in ocean water, Talanta 159 (2016) 117–121. https://doi.org/10.1016/j.talanta.2016.06.018.

[25] B. Herce-Sesa, J.A. López-López, C. Moreno, Selective ionic liquid solvent bar micro-extraction for estimation of ultra-trace silver fractions in marine waters, Sci. Total Environ. 650 (2019) 27–33. https://doi.org/10.1016/j.scitotenv.2018.08.438.

[26] S.V. Smirnova, D.V. Ilin, I.V. Pletnev, Extraction and ICP-OES determination of heavy metals using tetrabutylammonium bromide aqueous biphasic system and oleophilic collector, Talanta 221 (2021) 121485. https://doi.org/10.1016/j.talanta.2020.121485.

[27] P. Pirkwieser, J.A. López-López, W. Kandioller, B.K. Keppler, C. Moreno, F. Jirsa, Solvent bar micro-extraction of heavy metals from natural water samples using 3-hydroxy-2-naphthoate-based ionic liquids, Molecules 23 (2018). https://doi.org/10.3390/molecules23113011.

[28] M.Q. Farooq, D. Chand, G.A. Odugbesi, M. Varona, Y. Mudryk, J.L. Anderson, Investigating the effect of ligand and cation on the properties of metal fluorinated acetylacetonate based magnetic ionic liquids, New J. Chem. 43 (2019) 11334–11341. https://doi.org/10.1039/c9nj02595b.

[29] J.A. López-López, P. Pirkwieser, R. Leyma, W. Kandioller, R. Krachler, B.K. Keppler, F. Jirsa, C. Moreno, Solvent bar micro-extraction for greener application of task specific ionic liquids in multi-elemental extraction, J. Clean. Prod. 201 (2018) 22–27. https://doi.org/10.1016/j.jclepro.2018.08.008.

[30] B. Herce-Sesa, P. Pirkwieser, J.A. López-López, F. Jirsa, C. Moreno, Selective liquid phase micro-extraction of metal chloro-complexes from saline waters using ionic liquids, J. Clean. Prod. 262 (2020). https://doi.org/10.1016/j.jclepro.2020.121415.

[31] T. Trtić-Petrović, A. Dimitrijević, N. Zdolšek, J. Đorđević, A. Tot, M. Vraneš, S. Gadžurić, New sample preparation method based on task-specific ionic liquids for extraction and determination of copper in urine and wastewater, Anal. Bioanal. Chem. 410 (2018) 155–166. https://doi.org/10.1007/s00216-017-0705-z.

[32] M. Oviedo, E. Fiorentini, A. Lemos, R. Wuilloud, Ultra-sensitive Sb speciation analysis in water samples by magnetic ionic liquid dispersive liquid-liquid microextraction and multivariate optimization, Anal. Method 13 (2021) 1033–1042.

[33] M. Oviedo, E. Fiorentini, A. Lemos, M. Botella, R. Wuilloud, Two-step separation and determination of inorganic as species in water, soil and sediment samples by implementing two ionic liquids in dispersive liquid-liquid microextraction with electrothermal atomic absorption spectrometry detection, Microchem. J. 159 (2020) 105386. https://doi.org/10.1016/j.microc.2020.105386.

[34] A. Beiraghi, M. Shokri, A novel task specific magnetic polymeric ionic liquid for selective preconcentration of potassium in oil samples using centrifuge-less dispersive liquid-liquid microextraction technique and its determination by flame atomic emission spectroscopy, Talanta 178 (2018) 616–621. https://doi.org/10.1016/j.talanta.2017.08.080.

[35] M. Karimi, A.M.H. Shabani, S. Dadfarnia, Deep eutectic solvent-mediated extraction for ligand-less preconcentration of lead and cadmium from environmental samples using magnetic nanoparticles, Microchim. Acta. 183 (2016) 563–571. https://doi.org/10.1007/s00604-015-1671-9.

[36] Naeemullah, M. Tuzen, T.G. Kazi, J. Ali, Green and deep eutectic solvent microextraction method for faas determination of trace level cadmium in water samples using multivariate strategic approach, At. Spectrosc. 37 (2016) 244–251. https://doi.org/10.46770/as.2016.06.005.

[37] Ç. Arpa, S. Albayati, M. Yahya, Effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent for preconcentration and FAAS determination of copper in aqueous samples, Int. J. Environ. Anal. Chem. 98 (2018) 938–953. https://doi.org/10.1080/03067319.2018.1517872.

[38] J. Werner, Ligandless, deep eutectic solvent-based ultrasound-assisted dispersive liquid-liquid microextraction with solidification of the aqueous phase for preconcentration of lead, cadmium, cobalt and nickel in water samples, J. Separ. Sci. 43 (2020) 1297–1305. https://doi.org/10.1002/jssc.201901184.

[39] M.A. Habila, E.A. Alabdullkarem, Z.A. ALOthman, E. Yilmaz, M. Soylak, Thiomalic acid/ferric chloride-based deep eutectic solvent for microextraction of chromium in natural water samples prior to FAAS analysis, Int. J. Environ. Anal. Chem. 1 (2020) 1–9. https://doi.org/10.1080/03067319.2020.1743831.

[40] J. Ali, M. Tuzen, T.G. Kazi, Green and innovative technique develop for the determination of vanadium in different types of water and food samples by eutectic solvent extraction method, Food Chem. 306 (2020) 125638. https://doi.org/10.1016/j.foodchem.2019.125638.

[41] S.V. Smirnova, I.V. Pletnev, New ionic liquids for extraction preconcentration, J. Anal. Chem. 74 (2019) 1–11. https://doi.org/10.1134/S106193481901009X.

[42] B. Herce-Sesa, J.A. López-López, C. Moreno, Multi-elemental ionic liquid-based solvent bar micro-extraction of priority and emerging trace metallic

pollutants (Cd, Ag, Pd) in natural waters, J. Hazard Mater. 370 (2019) 63–69. https://doi.org/10.1016/j.jhazmat.2018.02.024.

[43] X. Wen, Q. Deng, J. Guo, Ionic liquid-based single drop microextraction of ultra-trace copper in food and water samples before spectrophotometric determination, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 79 (2011) 1941–1945. https://doi.org/10.1016/j.saa.2011.05.095.

[44] L. Xia, X. Li, Y. Wu, B. Hu, R. Chen, Ionic liquids based single drop micro-extraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for determination of Co, Hg and Pb in biological and environmental samples, Spectrochim. Acta Part B At. Spectrosc. 63 (2008) 1290–1296. https://doi.org/10.1016/j.sab.2008.09.018.

[45] Ł. Marcinkowski, F. Pena-Pereira, A. Kloskowski, J. Namieśnik, Opportunities and shortcomings of ionic liquids in single-drop microextraction, TrAC Trends Anal. Chem. (Reference Ed.) 72 (2015) 153–168. https://doi.org/10.1016/j.trac.2015.03.024.

[46] P. Biparva, A.A. Matin, Microextraction techniques as a sample preparation step for metal analysis, in: At. Absorpt. Spectrosc, 2012, pp. 61–88.

[47] L. Nyaba, N.R. Biata, J.C. Ngila, P.N. Nomngongo, Ultrasound assisted-ionic liquid-dispersive liquid-liquid microextraction for preconcentration of inorganic tellurium in environmental water samples prior to inductively coupled plasma − optical emission spectrometry detection, J. Mol. Liq. 231 (2017) 154–159. https://doi.org/10.1016/j.molliq.2017.02.012.

[48] J.F. Ayala-Cabrera, M.J. Trujillo-Rodríguez, V. Pino, Ó.M. Hernández-Torres, A.M. Afonso, J. Sirieix-Plénet, Ionic liquids versus ionic liquid-based surfactants in dispersive liquid−liquid microextraction for determining copper in water by flame atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 96 (2016) 101–118. https://doi.org/10.1080/03067319.2015.1128538.

[49] Ç. Yasemin, E.T. Saka, Ionic liquid based dispersive liquid e liquid micro-extraction procedure for the spectrophotometric determination of copper using 3-dimethylamino rhodanine as a chelating agent in natural waters, Karbala Int. J. Mod. Sci. 3 (2017) 185–190. https://doi.org/10.1016/j.kijoms.2017.09.002.

[50] J. Wojcieszek, D. Popowski, L. Ruzik, Ionic liquids as a key medium for efficient extraction of copper complexes from chia seeds (Salvia hispanica L.), Talanta 152 (2016) 482–488. https://doi.org/10.1016/j.talanta.2016.02.051.

[51] N. Zari, J. Hassan, K. Tabar-heydar, S.H. Ahmadi, Ion-association dispersive liquid−liquid microextraction of trace amount of gold in water samples and ore using Aliquat 336 prior to inductivity coupled plasma atomic emission spectrometry determination, J. Ind. Eng. Chem. (2019). https://doi.org/10.1016/j.jiec.2017.01.038.

[52] N. Khan, T.G. Kazi, H.I. Afridi, M.B. Arain, Determination of cadmium in human serum and blood samples after dispersive liquid-liquid microextraction using a task-specific ionic liquid, Anal. Lett. 51 (2018) 673–685. https://doi.org/10.1080/00032719.2017.1354868.

[53] E. Stanisz, J. Werner, Ligandless, task-specific ionic liquid-based ultrasound-assisted dispersive liquid−liquid microextraction for the determination of cobalt ions by electrothermal atomic absorption spectrometry, Anal. Lett. 50 (2017) 2884–2899. https://doi.org/10.1080/00032719.2017.1322095.

[54] M. Aswathi, S. Mathai, S.C. Joseph, V.M. Biju, Room temperature ionic liquid, cetyl pyridinium naphthenate, supported cloud point extractive separation and ultra trace determination of copper in blood and environmental samples, Separ. Sci. Technol. 52 (2017) 2540–2546. https://doi.org/10.1080/01496395.2017.1324491.

[55] L. Yao, X. Wang, H. Liu, C. Lin, L. Pang, J. Yang, Q. Zeng, Optimization of ultrasound-assisted magnetic retrieval-linked ionic liquid dispersive liquid − liquid microextraction for the determination of cadmium and lead in water samples by graphite furnace atomic absortion spectrometry, J. Ind. Eng. Chem. 56 (2017) 321–326. https://doi.org/10.1016/j.jiec.2017.07.027.

[56] S. Talpur, T.G. Kazi, H.I. Afridi, F.N. Talpur, S. Nizamani, A. Lashari, A. Akhtar, M. Khan, Ultrasonically dispersed ionic liquid-based microextraction of lead in biological samples of malnourished children prior to analysis by flame atomic absorption spectrometry, J. AOAC Int. 101 (2018) 883–890. https://doi.org/10.5740/jaoacint.17-0269.

[57] Y. Zheng, X. Huang, Y. Ling, W. Huang, J. Wang, Z. Zheng, X. Wang, H. Wang, Ultrasonic-enhanced preconcentration of trace Pb(II)using hydrophobic, lighter-than-water ionic liquid microextraction combined with solidification of the aqueous solution prior to detection by graphite furnace atomic absorption spectrometry in human flui, Spectrochim. Acta Part B At. Spectrosc. 157 (2019) 27–36. https://doi.org/10.1016/j.sab.2019.05.009.

[58] A. Elik, T. Karakoy, Y. Çilesiz, N. Altunay, Flame atomic absorption spectrometric determination of total chromium and cadmium in bean samples after ultrasonic-assisted microextraction using ionic liquid Aliquat-336, J. Iran. Chem. Soc. 18 (2021) 117–127. https://doi.org/10.1007/s13738-020-02009-7.

[59] M. Baghdadi, F. Shemirani, In situ solvent formation microextraction based on ionic liquids: a novel sample preparation technique for determination of inorganic species in saline solutions, Anal. Chim. Acta 634 (2009) 186–191. https://doi.org/10.1016/j.aca.2008.12.017.

[60] M.J. Trujillo-Rodríguez, P. Rocío-Bautista, V. Pino, A.M. Afonso, Ionic liquids in dispersive liquid-liquid microextraction, TrAC Trends Anal. Chem. (Reference Ed.) 51 (2013) 87–106. https://doi.org/10.1016/j.trac.2013.06.008.

[61] Z. Li, S. Xia, J. Wang, C. Bian, J. Tong, Determination of trace mercury in water based on N-octylpyridinium ionic liquids preconcentration and stripping voltammetry, J. Hazard Mater. 301 (2016) 206–213. https://doi.org/10.1016/j.jhazmat.2015.08.061.

[62] Y. Hui, C. Xiong, C. Bian, S. Gui, J. Tong, Y. Li, C. Gao, Y. Huang, W.C. Tang, S. Xia, Temperature-controlled ionic liquid dispersive liquid-liquid microextraction combined with fluorescence detection of ultra-trace Hg2+ in water, Anal. Method 11 (2019) 2669−2676. https://doi.org/10.1039/c9ay00029a.

[63] M. Soylak, E. Yilmaz, Determination of cadmium in fruit and vegetables by ionic liquid magnetic microextraction and flame atomic absorption spectrometry, Anal. Lett. 48 (2015) 464−476. https://doi.org/10.1080/00032719.2014.949732.

[64] E. Fiorentini, M. Botella, R. Wuilloud, A simple preconcentration method for highly sensitive determination of Pb in bee products by magnetic ionic liquid dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry, J. Food Compos. Anal. 95 (2021) 103661. https://doi.org/10.1016/j.jfca.2020.103661.

[65] Y. Hui, Y. Liu, W.C. Tang, D. Song, M. Madou, S. Xia, T. Wu, Determination of mercury(II) on a centrifugal microfluidic device using ionic liquid dispersive liquid-liquid microextraction, Micromachines 10 (2019). https://doi.org/10.3390/mi10080523.

[66] E. Carasek, L. Morés, J. Merib, Basic principles, recent trends and future directions of microextraction techniques for the analysis of aqueous environmental samples, Trends Environ. Anal. Chem. 19 (2018). https://doi.org/10.1016/j.teac.2018.e00060.

[67] J.A. López-López, C. Mendiguchía, J.J. Pinto, C. Moreno, Application of solvent-bar micro-extraction for the determination of organic and inorganic compounds, TrAC Trends Anal. Chem. (Reference Ed.) 110 (2019) 57−65. https://doi.org/10.1016/j.trac.2018.10.034.

[68] B. Herce-Sesa, J.A. López-López, C. Moreno, Ionic liquid solvent bar microextraction of CdCln(n−2)- species for ultra-trace Cd determination in seawater, Chemosphere 193 (2018) 306−312. https://doi.org/10.1016/j.chemosphere.2017.11.004.

[69] S. Yang, H. Liu, K. Hu, Q. Deng, X. Wen, Investigation of thermospray flame furnace atomic absorption spectrometric determination of cadmium combined with ultrasound-assisted dispersive liquid-liquid microextraction, Int. J. Environ. Anal. Chem. 1 (2020) 1−13. https://doi.org/10.1080/03067319.2020.1723566.