

Emerging ionic liquid-based techniques for total-metal and metal-speciation analysis

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Ionic liquids (ILs) are generally considered to be more environmentally friendly than common organic solvents and have unique characteristics (e.g., effectively no vapor pressure, adjustable viscosity and miscibility in aqueous phases). They are also considered to be highly efficient extractant phases to improve analyte selectivity and sensitivity, so that they are important tools for chromatographic and spectrometric analysis. We review state-of-the-art applications of ILs in analytical chemistry with special emphasis on metal determination and speciation analysis.

We discuss modern microextraction techniques based on ILs [e.g., dispersive liquid-liquid microextraction (DLLME), single-drop microextraction (SDME), and on-line LLME]. Also, we comment on potential applications and developments of solid-phase extraction (SPE) techniques involving IL-modified surface materials for metal retention and preconcentration. In all cases, we review crucial parameters and practical considerations of method optimization and application. Further, we critically compare IL-based methods in terms of analytical performance and environmental compatibility.

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Abbreviations: See Appendix before References section

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1. Introduction

Separation and preconcentration procedures are considered of great importance in elemental analysis as they eliminate or minimize matrix effects and concomitants, lowering the detection limit and enhancing sensitivity of detection techniques towards metals and their species. One of the most decisive turning points in analytical science has been the introduction of green chemistry into the assessment of analytical methods. Some of the principles of green chemistry (e.g., prevention of waste generation, use of safer solvents, and development of miniaturized methods) are directly related to emerging techniques for total and speciation metal analysis, so utilization of state-of-the-art solvents [e.g., ionic liquids (ILs)] has attracted considerable attention in recent years, as they are very promising in fitting “green chemistry” requirements.

The main potential benefits for the environment come from the negligible

vapor pressure that these solvents show [1]. ILs are liquid salts with melting points close to or below room temperature. They are not made of molecules, but ions, that are present in the liquid with an equal number of positive and negative ions, so that the whole liquid is electrically neutral [2]. Other properties include good thermal stability and tunable viscosity and miscibility with water and organic solvents [1].

ILs can also be designed by combining different anions and cations for task-specific extraction of analytes from various solvent media [3,4]. Furthermore, ILs can incorporate coordinating functional groups for selective extraction of target analytes [5]. Consequently, ILs are considered potential alternatives to conventional organic solvents, which can significantly contribute to environmental contamination with volatile organic compounds (VOCs). ILs can not only be applied on existing methods to enhance analytical sensitivity and selectivity, but also offer

original solutions to analytical challenges based on their singular chemical behavior and properties [6]. The search for new applications of ILs is growing in every area of chemistry, including analytical chemistry.

Different reviews have described ILs and their application to analytical chemistry [2,3,6,7]. However, there are no articles specifically covering IL approaches in the field of metal determination. In this review, we present a full discussion and update of recent applications of ILs for total and speciation metal analysis. We give a brief description of ILs mostly used in analytical chemistry for metal determination, including existing classes and some properties. We fully describe different aspects of IL-based extraction techniques and compare them with regard to their capabilities for elemental preconcentration and species separation. Moreover, we report and evaluate experimental strategies and possible mechanisms involved in metal extraction with ILs. We devote particular to applications from emerging extraction techniques and instrumentation. Finally, we mention future developments and potential application fields of ILs for trace-metal determination and speciation.

2. Ionic liquids used for metal determination

The ILs more frequently used in analytical chemistry are organic salts, composed of organic cations (e.g., imidazolium, phosphonium, pyrrolidinium, pyridinium or quaternary ammonium) and appropriate anions (e.g., hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkylsulfonates, chloride or bromide) [8]. Table 1 shows the main properties of these solvents, including molecular weight, melting point, density and viscosity.

2.1. Imidazolium ionic liquids

ILs derived from imidazole have been frequently utilized in analytical chemistry for elemental determination. Typical characteristics (e.g., low melting points and viscosity, easy and relatively inexpensive synthesis [8,9] and good stability in both oxidative and reductive conditions) led imidazolium-class ILs to attract special interest. They offer greater versatility and scope for the design and the application of metal-separation methods [10]. When alkyl-chain length grows in their structures, solubility in water diminishes and viscosity increases, so both parameters have to be considered in the selection of an appropriated extracting phase, since low solubility allows minimal IL consumption, while high viscosity could cause practical drawbacks during microextraction procedures.

As shown in Table 2, 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_4]$) and 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_4]$) ILs have been widely employed in microextraction techniques. Likewise, 1-alkyl-3-methylimidazolium tetrafluoro-

borate $[C_nmim][BF_4]$ and 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide $[C_nmim][Tf_2N]$ have found different applications [11]. However, there have been reports of some disadvantages of use (e.g., unfavorable transport electrochemical properties and high viscosity) [12].

2.2. Phosphonium ionic liquids

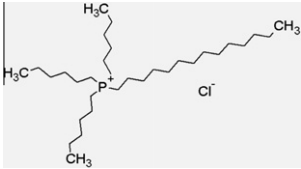
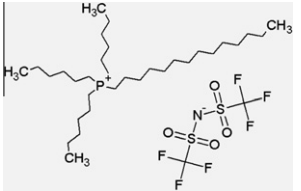
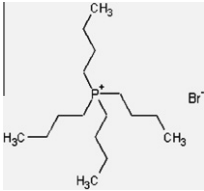
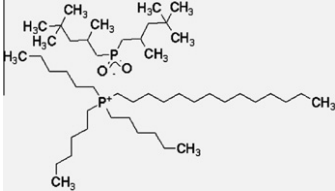
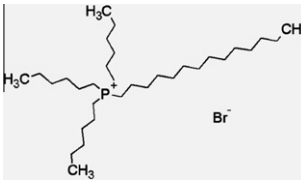
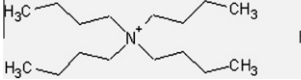
Tetraalkylphosphonium-type ILs have been demonstrated to be thermally and chemically stable, and tend to have viscosities somewhat higher than their ammonium counterparts, especially at or near room temperature. However, at typical industrial reaction temperatures (e.g., 70–100°C), their viscosities generally decrease to less than 1 P [13]. Compared to imidazolium ILs, phosphonium ILs have lower density than water. This property can be beneficial in product work-up steps while decanting aqueous streams containing inorganic salt by-products [13]. Phosphonium ILs have also attracted particular attention due to their capability to extract a variety of metal ions [11,14].

Trihexyl(tetradecyl)phosphonium chloride ($[P_{14.6.6.6}]Cl$) and trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ($[P_{14.6.6.6}][Tf_2N]$) have been employed for Zn extraction [11], while $[P_{14.6.6.6}]Cl$ found application for Fe extraction [15]. Moreover, $[P_{14.6.6.6}]Cl$ has been immobilized on a biopolymeric matrix for solid-phase extraction of Au, Bi, Pd and Hg [14,16–18]. However, Martinis et al. developed a single-drop microextraction (SDME) procedure combining $[P_{14.6.6.6}]Cl$ and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as chelating agent for Pb preconcentration [19]. Mechanisms involved in metal recovery have been generally explained as an ion-exchange phenomenon [16], but we address this point below.

2.3. Quaternary ammonium ionic liquids

This class of ILs has found some unique applications in various fields. Special properties (e.g., low melting points, low viscosity, and chemical and electrochemical stability) facilitate their use as promisingly safe electrolytes for high-energy-density devices [20]. Since nitrogen has lower atomic radius than phosphorous, the charge density of quaternary ammonium cations is higher than that expected for phosphonium analogs, so ammonium-containing ILs generally show lower melting points.

Alkyl ammonium cations have different alkyl chains attached to a central nitrogen atom with a relatively big, asymmetric counter anion [21]. Regarding this point, ammonium-containing ILs incorporating functional groups acting as coordinating sites, namely task-specific ILs (TSILs), have been recently synthesized and used for metal extraction. One of them was trioctylmethylammonium salicylate (TOMAS) [22].

Table 1. Main properties of ionic liquids used for metal extraction and preconcentration						
Ionic Liquid	Molecular weight (g/mol)	Melting point (°C)	Density (g/mL)	Viscosities (mPa.s at 25°C)	Structure	Ref.
Phosphonium Trihexyl(tetradecyl)phosphonium chloride Cyphos IL 101	519.30	-70	0.895 (at 20°C)	1824		[67]
Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide Cyphos IL 109	764.00	-50	1.07 (at 20°C)	N/A		[68]
Tetrabutylphosphonium bromide Cyphos IL 163	339.33	104	N/A	50.34*		[68]
Trihexyl(tetradecyl)phosphonium bis[(2,4,4-trimethyl)pentyl]phosphinate Cyphos IL 104	773.26	N/A	0.885	707		[69]
Trihexyl(tetradecyl)phosphonium bromide Cyphos IL 102	563.76	N/A	0.954 (at 25°C)	2094		[67]
Quaternary ammonium Tetrabutylammonium fluoride	261.46	62-63	N/A	N/A		[20]

Tetraethylammonium [(2,2,2-trifluoro-N-trifluoromethyl)sulfonyl]acetamide	374.34	20	1.37 (at 25°C)	60		[20]
Trimethylethylammonium iodide	332.26	15	1.40 (at 25°C)	51		[20]
Pyridinium 1-Butylpyridinium chloride	171.66	132	N/A	N/A		[70]
1-Octyl-4-methylpyridinium tetrafluoroborate	293.1	N/A	1.08	460		[71]
1-Octyl-4-methylpyridinium bis[(trifluoromethyl)sulfonyl]imide	486.49	7	1.29	105		[71]
1-Octyl-pyridinium [(trifluoromethyl)sulfonate]	341.38	49	N/A	77.1		[71]
3-Methyl-1-propylpyridinium bis[(trifluoromethyl)sulfonyl]imide	416.36	0	N/A	N/A		[70]

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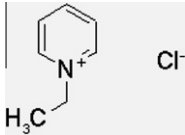
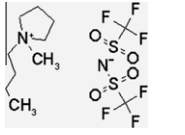
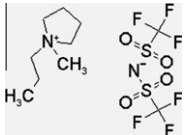
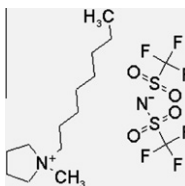
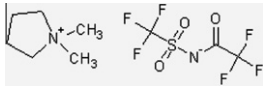
Table 1 (continued)						
Ionic Liquid	Molecular weight (g/mol)	Melting point (°C)	Density (g/mL)	Viscosities (mPa.s at 25°C)	Structure	Ref.
1-Ethylpyridinium chloride	143.61	114	N/A	N/A		[70]
Pyrrolidinium 1-Butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide	422.40	-50	N/A	N/A		[72]
1-Methyl-1-propylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide	408.38	12	1.44	N/A		[73]
1-Methyl-1-octylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide	478.51	N/A	N/A	130		[73]
1,1-Dimethylpyrrolidinium [(2,2,2-trifluoro- N-trifluoromethyl)sulfonyl]acetamide	344.27	24	1.43 (at 25°C)	80		[20]

Table 2. Comparison on analytical performance of IL-based methods for elemental determination										
Technique/purpose	IL class	IL amount	Complexing agent	Sample	Sample volume (ml)	Detection	LOD ($\mu\text{g/L}$)	EF	CI	Ref.
Ag Sensitivity enhancement	[C ₄ py][BF ₄]	-	-	biological and geological reference materials	0.5	AFS	15	2.7	0.19	[58]
Al LLE	[C ₄ tmsim][PF ₆]	7.5 mL	DTBSF	dialysis concentrates	250	Spectrophotometry ETAAS	0.06	N/A	-	[33]
DLLME	[C ₆ py][PF ₆]	0.3 g	Oxine	water fruit juice food samples	25	Spectrofluorometry	0.05	100	0.25	[24]
Au Sensitivity enhancement	[C ₄ py][BF ₄]	-	-	biological and geological reference materials	0.5	AFS	63	3.6	0.14	[58]
Sensitivity enhancement	[C ₄ mim]Br and others	-	-	geological samples	0.5	AFS	1.9	N/A	0.32	[59]
Cd LLE-LLBE	[C ₄ mim][PF ₆]	0.7 g	5-Br-PADAP	water	20	ETAAS	0.003	40	0.50	[28]
On line LLE	[C ₄ mim][PF ₆]	0.7 g	5-Br-PADAP	plastic	20	FAAS	6 ng/g	35	0.57	[38]
Extraction of the iodide complexes	[C ₄ mim][PF ₆]	N/A	N/A	N/A	2	ASV	30000	N/A	-	[31]
USA-DLLME	[C ₆ mim][PF ₆]	73 μL	DDTC	water	10	ETAAS	0.0074	67	0.15	[10]
IL supported	[C ₄ mim][PF ₆]	0.5	Dithizone	water	25	FAAS	0.60	75	0.33	[55]
Co CIAME	[C ₆ mim][PF ₆] [C ₆ mim][Tf ₂ N]	64 mg and 5 mg	PAN	water	10	Linear array detection spectrophotometry	0.14	165	0.06	[9]
Cycle-flow SDME	[C ₄ mim][PF ₆]	1-3 μL	PAN	human hair human serum environmental water	1.5	ETV-ICP-MS	0.0015	350	0.00	[45]
DLLME	[C ₆ mim][PF ₆]	60 mg	1N2N	urine saliva water	6	ETAAS	0.0038	120	0.05	[47]
Cr USA-DLLME	[C ₆ mim][PF ₆]	50 μL	APDC	lake and tap water	8	ETAAS	0.07	300	0.03	[50]
Cu Sensitivity enhancement	[C ₄ py][BF ₄]	-	-	biological and geological reference materials	0.5	AFS	19	4.8	0.10	[58]

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Table 2 (continued)											
Technique/purpose	IL class	IL amount	Complexing agent	Sample	Sample volume (ml)	Detection	LOD ($\mu\text{g/L}$)	EF	CI	Ref.	
Ge											
LLE	[C ₄ mim][PF ₆]	N/A	MBASF	water	N/A	Spectrophotometry	0.2	N/A	-	[36]	
Hg											
CIAME	[C ₆ mim][PF ₆]	69 mg	TMK	water	10	Spectrophotometry	0.3	30.8	0.32	[8]	
ISFME	[C ₆ mim][Tf ₂ N]	30 mg	TMK	water	5	Spectrophotometry	0.7	37	0.14	[54]	
DLLME	[C ₆ mim][BF ₄]	60 mg	TMK	water	10	Spectrophotometry	3.9	18.8	0.53	[49]	
Cycle-flow SDME	[C ₆ mim][PF ₆]	2.5 μL	PAN	human hair human serum environmental water	1.5	ETV-ICP-MS	0.0098	50	0.03	[45]	
SDME	[C ₆ mim][PF ₆]	4 μL	Dithizone	water	12	HPLC-photodiode array detection	1.0-22.8	40	0.30	[43]	
LLE-LLBE	[C ₄ mim][PF ₆]	0.7 g	5-Br-PADAP	water	20	CV-AAS	0.0023	36	0.56	[29]	
LLE-LLBE	[C ₄ tmsim][PF ₆]	5 mL	CDAA	water	1000	CV-AAS	0.01	N/A	-	[30]	
Lanthanides											
DLLME	[C ₆ mim][PF ₆]	600 μL	HYD	uranium dioxide powder	80	ICP-OES	Sm Eu Gd Dy	1.29 0.66 0.59 0.34	84.04 19.34 86.04 67.92	0.95 4.14 0.93 1.18	[48]
Mn											
SDME	[C ₄ mim][PF ₆]	4 μL	TAN	water	1.8	ETAAS	0.024	30.3	0.06	[42]	
Mo											
LLE-LLBE	[C ₈ mim][PF ₆]	N/A	p-MOPASF	water	N/A	ETAAS	N/A	100	-	[34]	
Ni											
HF-LPME	[C ₆ mim][PF ₆]	8 μL	APDC	environmental and biological samples	3	ETAAS	0.03	60	0.05	[46]	
LLE-LLMBE	[C ₄ mim][PF ₆]	500 μL	PAN	water, rice flour and black tea	10	FAAS	12.5	40.2	0.25	[37]	
Signal Enhanced	[C ₄ mim]Br	-	DDTC	certified biological reference materials	0.5	AFS	0.65	2400	0.00	[60]	
Pb											
LLE-LLBE	[C ₄ tmsim][PF ₆]	N/A	Dithizone	water	1000	ETAAS	0.001	400	2.50	[66]	
Cycle-flow SDME	[C ₄ mim][PF ₆]	1-3 μL	PAN	human hair human serum environmental water	1.5	ETV-ICP-MS	0.0067	60	0.03	[45]	

LLE displace CCl ₄	[C ₄ tmsim][PF ₆]	N/A	N/A	dialysis fluids	1000	ETAAS	N/A	200	5.00	[35]
SDME	[P _{1,4,6,6}]Cl	4 μL	5-Br-PADAP	water	1.5	ETAAS	0.0032	32	0.05	[19]
SDME	[C ₄ mim][PF ₆]	7 μL	APDC	water	1.75	ETAAS	0.015	76	0.02	[44]
LLE	[C ₄ mim][PF ₆]	N/A	N/A	non-fat milk powder	2	ASV	5000	N/A	-	[31]
LLE-LLBE	[C ₈ mim][PF ₆]	5.0 mL	Dithizone	water	1000	ETAAS	100	200	5.00	[32]
CIAME	[C ₆ mim][PF ₆]	50 μL	Dithizone	water	10	FAAS	9.5	NR	-	[51]
HF-LPME	[C ₆ mim][PF ₆]	8 μL	APDC	environmental and biological samples	3	ETAAS	0.02	76	0.04	[46]
V										
CIAME	[C ₄ mim][PF ₆]	45 μL	5-Br-PADAP	water	2	ETAAS	0.0049	40	0.05	[52]
FI-CIAME	[C ₄ mim][PF ₆]	40 μL	5-Br-PADAP	saliva	5	ETAAS	0.0048	N/A	-	[53]
				water						
Zn										
DLLME	[C ₆ py][PF ₆]	0.3 g	Oxine	water	30	FAAS	0.22	71	0.42	[23]
				milk						
N/A: not available.										

2.4. Pyridinium ionic liquids

Among many within this category, 1-alkyl-pyridinium hexafluorophosphate ([C_npy][PF₆]) has been the most widely used IL. This is due to its particular physico-chemical properties, such as high hydrophobicity, water-immiscibility and high viscosity, which make it very attractive for performing biphasic separation and pre-concentration of metals [23]. Despite the potential benefits of its use, only two microextraction methods have been proposed with 1-hexyl-pyridinium hexafluorophosphate [C₆py][PF₆] as an extractant solvent for separation and pre-concentration of trace Zn and Al [23,24]. Also, [C₆py][PF₆] has been a reactant for synthesizing novel TSILs acting as chelating agents for Pd [25].

2.5. Pyrrolidinium ionic liquids

These ILs provide new alternatives to pyridinium and imidazolium ILs. This class of IL has found application in electrochemical development. High thermal stability (decomposition temperatures all above 300°C) increases safety in applications (e.g., rechargeable lithium-ion batteries and other electrochemical devices). They are sparingly soluble in water but hygroscopic [26].

Regarding metal determination and speciation, 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide has been employed for liquid-liquid extraction (LLE) of Cu in the presence of pyridine-based N¹,N¹,N⁴,N⁴-tetrakis(2-(pyridin-2-yl)ethyl)butane-1,4-diamine (C₄N₂Py₄) used as a ionophore to set up the extraction system [27].

3. Ionic liquid-based extraction techniques

Initial reports on utilization of ILs as alternatives to classical organic solvents for LLE techniques started to be published at the end of 1990s. LLE is a versatile classical sample-preparation technique widely employed for sample preparation, with high reproducibility and sample capacity. An improvement in LLE techniques could be achieved if, after LLE is performed, metals are efficiently back-extracted (LLBE) into aqueous phase by modifying the pH of the medium. This approach allows the pre-concentration factor to remain unchanged, as the volume of back-extracting solution could equal that of the original IL phase [28], so, by using ILs as extractant phases for LLE-LLBE, it is possible not only to reduce environmental and safety concern related with high solvent consumption during classical LLEs, but also to recycle the solvent.

Lately, there have been several reports in which ILs were shown to be successfully applied to metal extraction (e.g., Hg, Cd, Pb, Al, Mo, Ge, Ag, Cu, and Zn) in LLE systems [28–36]. However, some shortcomings can be recognized in these procedures (e.g., manual operation, slow extraction, and use of large volumes of sample and reagent, and hence, the generation of significant

amounts of pollutants, leading to more expensive and time-consuming LLE, and environmentally unfriendly practices).

Dafarnia et al. [37] proposed low consumption and recycling of IL. They recently developed a micro-volume back-extraction (LLMBE) procedure. Nickel was extracted from an aqueous solution into 500 μL of $[\text{C}_4\text{mim}][\text{PF}_6]$ (see Table 2).

Generally, IL-based LLE methodologies for metal determination have been developed following only batch procedures. However, Martinis et al. [38] recently showed one of the first attempts at implementing LLE methodologies in a flow-analysis technique. Thus, on-line retention and separation of a $[\text{C}_4\text{mim}][\text{PF}_6]$ -enriched phase was achieved by using a silica-gel-packed micro-column for Cd preconcentration after metal chelation with 5-Br-PADAP. A 99.9% analyte recovery and 35-fold analytical signal enhancement was achieved with 20 mL of sample. High-efficiency extraction with minimal manual operation and contamination risks with on-line separation opens up an attractive alternative in automated extraction and preconcentration methodologies using ILs.

With the aim of reducing costs, consumption of reagents and samples, and time of analysis, while increasing separation efficiency and enabling automation, current research trends involve miniaturization of traditional LLE approaches. Liquid-phase microextraction (LPME), or miniaturized LLE, is a relatively recent concept, whose main advantages are very low consumption of organic solvent, low cost, high selectivity and clean extracts. Moreover, the equipment needed is generally very simple and inexpensive. A wide diversity of novel techniques can be mentioned for LPME, including:

- SDME in different modes [direct-SDME, cycle-flow SDME or headspace-single-drop microextraction (HS-SDME)];
- hollow-fiber liquid-phase microextraction (HF-LPME); and,
- dispersive liquid-liquid microextraction (DLLME).

The latest advances in the development of LPME techniques were fully reviewed by other authors [39,40]. However, and with the exception of this work, no reviews have yet been published specifically addressing applications of ILs in developing extraction techniques for trace-metal determination.

The development of SDME techniques using ILs for metal preconcentration was published by Liu et al. in 2005 [41]. In this work, organomercury and organotin were determined among a list of 45 environmental pollutants. A 5- μL drop of 1-alkyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_n\text{MIM}][\text{PF}_6]$, $n = 4, 8$) suspended on the needle of an HPLC microsyringe was employed as extractant medium. Their unique properties (e.g., non-volatility, adequate viscosity and thermal

stability) allow hydrophobic ILs to be easily implemented as extraction solvents in the SDME technique.

Manzoori et al. developed a direct-SDME technique based on ILs for Mn preconcentration. Manganese was extracted from aqueous solution into a drop of $[\text{C}_4\text{mim}][\text{PF}_6]$ after complexation with 1-(2-thiazolylazo)-2-naphthol (TAN). The drop was then directly injected into the graphite furnace of electrothermal atomic absorption spectroscopy (ETAAS) [42].

The IL-based SDME technique was used for Hg species and Pb preconcentration in different works [19,43,44].

A method using an IL-based cycle-flow SDME technique was developed for preconcentration of Co, Hg and Pb from biological and environmental samples [45]. This new conception of the SDME technique proposed capture of analytes by exposing an IL droplet to a flowing stream of sample, thus replacing mechanical agitation by continuous flow. 1-(2-pyridylazo)-2-naphthol (PAN) reagent was used as both extractant and chemical modifier, while $[\text{C}_4\text{mim}][\text{PF}_6]$ IL was the extraction solvent. Since continuous contact between the IL phase and the fresh flowing sample solution was achieved, the extraction efficiency and preconcentration factor were higher than in static conditions.

SDME clearly guarantees simplicity, cost effectiveness and negligible solvent consumption. However, it entails some drawbacks (e.g., instability of the IL microdrop when particles are present in solution, making it difficult to apply with dirty samples) [40]. It is noteworthy that ILs having greater viscosity than common organic solvents could significantly help to attain major stability of a microdrop in the needle tip of a syringe used for SDME, and, consequently, higher reproducibility. Despite this practical contribution of ILs to SDME, the hanging drop could still suffer from limited stability and it could be dislodged into the sample during extraction.

Among LPME techniques, HF-LPME is an option, which has been developed to improve stability of the extractant phase and robustness of the extraction procedure. In HF-LPME, the acceptor organic solvent, where analytes are extracted from an aqueous sample, is immobilized within a supported liquid membrane placed in the inner part of the HF, so the sample can be stirred or shaken vigorously without any loss of extracting liquid, as it is mechanically protected. Another limitation of drop-configuration LPME methodologies is the volume of extractant phase (1–10 μL), and larger volumes are not selected, since they are difficult to handle and can result in loss of the drop. However, different HF lengths have been shown to be suitable for working with different volumes of extractant phase.

HF-LPME based on $[\text{C}_6\text{mim}][\text{PF}_6]$ was developed by Abulhassani et al. [46] for Pb and Ni preconcentration from tap-water and natural-water samples, and NIST SRM 1566b (Oyster Tissue), after complexation with ammonium pyrrolidinedithiocarbamate (APDC). The

[C₆mim][PF₆] was placed, protected and immobilized inside the polypropylene HF. Compared to commercially available solid-phase microextraction (SPME) fibers, disposable IL-coated fibers present lower cost, comparable reproducibility and less chance for cross-contamination between determinations. However, HF-LPME methodologies require greater manual operation than SPME fibers, as several steps are required before extractant-phase exposure to sample solutions (e.g., cleaning, acceptor-solution immersion, and excess-solvent extraction).

Dispersion of IL phase has demonstrated to be an efficient approach to obtain excellent extraction efficiency while keeping the volume of solvents necessary for analysis to a minimum. One of the main advantages of DLLME compared with others LPME methodologies is that shorter microextraction times are required. This observation can be easily explained since equilibrium conditions are not commonly achieved, as a result of the infinitely large surface area formed between extractant and aqueous phase in DLLME. Moreover, the possibility of performing simultaneous extractions of different metals increases sample throughput. Hence, DLLME has been widely performed in combination with an IL as extractant solvent for metal preconcentration. After 8-hydroxyquinoline (oxine) complexation, [HPy][PF₆] IL was employed as an extractant solvent for preconcentration of Zn at trace levels from water and milk samples [23].

The same IL, technique and chelating agent were also used for Al preconcentration from water, fruit juice and food samples [24]. Preconcentration of Co was achieved by a DLLME technique, prior complexation of the metal with 1-nitroso-2-naphthol (1N2N) reagent at pH 4.0, followed by microextraction with [C₆mim][PF₆] IL [47]. The same IL and technique were employed for preconcentrating some lanthanoids complexed with 1-hydroxy-2,5-pyrrolidinedione (HYD) from uranium-dioxide powder [48].

After complexation with 4,4'-bis(dimethylamino)thio-benzophenone (TMK) reagent, Hg was extracted in 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₆mim][Tf₂N]) from water samples [49].

Despite its simplicity, rapidity and cost effectiveness, DLLME still has some drawbacks [i.e. it is difficult to automate the process and it is necessary to use a third component (an organic solvent as disperser) that usually decreases the partition coefficient of analytes into the extractant solvent].

An alternative approach for DLLME, called IL-based ultrasound-assisted dispersive liquid-liquid microextraction (USA-DLLME) [10] combined advantages of IL, ultrasound (to attain extraction equilibrium in a short time) and DLLME. In this way, extraction equilibrium can be reached quickly and there is no need to use VOCs (which tend to volatilize under ultrasonic radiation) as dispersant agents. A known hydrophobic IL, [C₆mim][PF₆], was chosen as extractant for Cd preconcentration.

Recently, Chen et al. [50], employed the same method and IL for Cr(VI) preconcentration from water samples. However, cold-induced aggregation microextraction (CIAME) is another LLME technique that has been developed for trace-metal preconcentration [8]. Basically, a very small amount of hydrophobic IL, used as extractant solvent, is dissolved in the sample solution and the mixture heated in a thermostatted bath at ~60°C. After total dissolution of the IL phase, the solution is cooled in an ice bath, forming a cloudy solution by decreasing solubility of the IL. A fine dispersion is formed by IL microdroplets and metal complexes are extracted. After centrifugation, the condensed IL phase is obtained at the bottom of the glass centrifuge tube. This method is simple, rapid, and robust regarding tolerance to relatively high salt content and water-miscible organic solvents. Moreover, using the CIAME technique, extraction and preconcentration of metal and organic compounds is independent of IL viscosity, as transfer of analytes occurs during the process of microdrop formation. Also, compared to DLLME, it is much safer, since only small amounts of surfactant, as anti-sticking agent, and IL are used.

Several metals (e.g., Hg, V⁴⁺ and V⁵⁺ species, Co and Pb) have been preconcentrated with CIAME with the help of different chelating reagents [8,9,51,52]. In order to automate CIAME and take advantage of benefits added by flow analysis, our research group recently proposed a novel on-line system [53]. The formation of IL dispersion, analyte extraction, and separation of the IL-enriched phase, were performed fully on-line for V preconcentration in biological and environmental samples. The on-line retention of the dispersed IL phase was achieved in a glass microcolumn packed with Florisil material, thus significantly simplifying the microextraction technique, and reducing manual operation and contamination risks, with no need for centrifugation. Moreover, the on-line procedure required lower amounts of IL than a similar technique proposed in batch. The suitability of this on-line system to work with ILs less dense than aqueous media is worth noting, as this factor could be an important limitation with regular LLME techniques for microvolume phase separation using centrifugation.

Baghdadi et al. [54] developed a novel microextraction technique based on ILs, termed in situ solvent-formation microextraction (ISFME). In this method, a small amount of sodium hexafluorophosphate (as an ion-pairing agent) was added to the sample solution containing very small amounts of 1-hexyl-3-methylimidazolium tetrafluoroborate ([C₆mim][BF₄]) IL. A cloudy solution was observed as a result of formation of fine droplets of hydrophobic [C₆mim][PF₆] IL. After centrifugation, the fine droplets of the extractant phase settled to the bottom of the glass centrifuge tube. ISFME was applied to determining Hg in several real-water samples previously complexed with TMK. This novel method was demonstrated to be simple and robust against high salt

content (up to 40%). However, it was necessary to add reagents to synthesize the extractant phase *in situ*.

An on-line procedure based on ILs was proposed by Liang et al., who immobilized [C₄mim][PF₆] IL on modified silica as sorbent for Cd preconcentration [55].

Supported IL solid phases combine the advantages of ILs with those of heterogeneous supporting materials. Although IL-impregnated resins were prepared for solid-liquid extraction of rare-earth elements and noble-metal ions [56,57], this was the first report of an application of a supported IL phase for preconcentrating trace-metal ions. Furthermore, a new method using a microcolumn packed with IL-modified silica as sorbent was developed for preconcentration of trace amounts of Cd after forming a complex with dithizone. The proposed method was applied to the determination of Cd in lake-water and tap-water samples. The column can be reused after regeneration and was stable up to at least 20 adsorption-elution cycles without significant decrease in Cd recovery.

Most works related to IL applications for metal determination had dealt with their use as extractant solvents. However, a few investigations on additional effects of ILs for metal detection have been reported. For example, ILs were used in chemical-vapor generation (CVG) of transition and noble metals with KBH₄ as reducing agent [58–60] (Table 2). The efficiency of CVG in the presence of IL was evaluated with flow-injection atomic fluorescence spectrometry (FI-AFS). The role of the IL was supposed to be inhibition of the coalescence of metal nanoparticles comprising volatile metal species released from the reactant solution. Transportation of metal vapor to the elemental detector was improved, and hence so was analytical sensitivity (Table 2). Certainly, ILs open up another attractive area to be explored for expanding the CVG technique towards sensitive determination of elements other than Hg.

4. Mechanisms and strategies for metal extraction with ILs

The extraction process is a complex result of several parameters (e.g., partition coefficient, diffusion coefficient of solute, solubility of extraction solvent, liquid viscosity, and complex hydrophobicity).

Data on partition coefficients of species between ILs and water are very limited, not only in terms of the number of analytes assayed, but also with regard to the number of ILs investigated. Nevertheless, that represents essential information to understand the mechanisms of partitioning, separation and enrichment of analytes from aqueous phase to IL phase. It is generally believed that the partitioning mechanism that transfers analytes from aqueous into IL phase is similar to that occurring in traditional organic solvents. Although metal-ion extraction in IL/aqueous biphasic systems often indicates better selectivity

and extraction efficiency than that observed with common organic solvents, the metal-ion partitioning always relies on the nature of the IL, metal ion and ligand. For example, IL structural variations (e.g., the lengths of alkyl groups) could greatly influence selectivity and efficiency of competitive alkali-metal salt extraction by crown ethers [61]. In order to improve affinity of metal ions for the IL phase, two different strategies have been investigated:

- using ILs as extractant solvents only in combination with appropriate chelating reagents; or,
- using an IL itself as a complexing reagent, due to the presence of coordinating functional groups in the cation or in the anion.

At present, combination of chelating reagents and ILs has been the most usual approach for metal extraction and preconcentration (Table 2) [2,6,10,29,43,50]. This option is certainly useful to expand application of several ILs in metal-ion extraction. However, some limitations (e.g., an increase in process complexity and great difficulty in removing the chelating reagent from the IL phase after extraction) should be considered.

The vast majority of the studies so far reported in the literature (Table 2) have focused on extraction properties displayed by various imidazolium or pyridinium ILs. The high chemical affinity of imidazolium-based ILs to compounds with one or more aromatic rings in their structures (e.g., many complexing reagents) could be explained through CH– π hydrogen interactions between C₂-H bonds of the imidazolium ring and the aromatic parts [62]. The extraction capacity of aromatic compounds with 1-alkyl-3-methylimidazolium ILs increases with anion volume, and decreases with hydrogen-bond strength between the anion and the imidazolium cation. Moreover, concentration of aromatics in the IL phase increases with length of the imidazolium alkyl side, but it reduces selectivity. Different types of hydrogen bonds may be operative, depending on structural and electronic properties of both the IL and the aromatic compound.

In the case of nitrogen heterocycles, the interaction occurs preferentially through N(heteroaromatic)-H(imidazolium) hydrogen bonds and the extraction process is largely controlled by the pK_a value of the nitrogen heterocycle [62]. However, the second strategy involved cation or anion derivatization to add task-specific functionalities to ILs (i.e. disulfide, urea, thiourea, thioether, phosphoryl groups or other complexing functional groups) (e.g., metal-coordinating groups), so TSILs have been synthesized for specific applications. When used, with organic solvents, or doped in less expensive ILs, TSILs could dramatically enhance extraction of targeted metal ions.

Separations with ILs as extractant phases are more complex than those with simple molecular organic solvents. The behavior of ILs was observed to parallel that of conventional solvents, except that ILs played a more

active role in ion-exchange processes. Both partition and ion-exchange mechanisms play important roles in the extraction process. These two processes may generally work together to expand further application opportunities and selectivity of ILs for metal extraction. However, understanding the IL systems, it is possible to choose appropriate conditions to design targeted extractions. One can either take advantage of the different extraction mechanisms that ILs afford, or find those separations, ligands, and ILs having identical behavior to molecular solvents. A complete review on multiple mechanisms happening during metal separation with ILs was made by Cocalia et al. [63].

5. Instrumental techniques for IL-based methods

Several instrumental techniques have been applied for metal detection in IL-enriched phases, including ETAAS, flame absorption spectroscopy (FAAS), cold vapor-generation atomic absorption spectroscopy (CV-AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS), chromatography [high-performance liquid chromatography (HPLC)] and the widespread UV-Vis spectrophotometry.

The high viscosity of most ILs is an important aspect in method development. From this point of view, ETAAS has been the technique that more easily solved this problem, as it allows elemental determination in organic solvents and manual injection of the IL phase into the graphite furnace. However, in order to inject the IL phase directly into the graphite furnace in a reproducible manner, it must be previously dissolved in an appropriate solvent, due to the high viscosity of the IL phase. It is widely known that trace-element detection by ETAAS in an organic-rich phase can entail some drawbacks if sufficient matrix elimination is not performed. An increase in background signal during the atomization step has been observed in the presence of IL, due to its organic nature. High accuracy of background correction can be obtained when background absorbance is minimal with respect to the atomic absorption signal of the analyte. The main work with elemental determinations in the IL phase has therefore focused on matrix elimination before the atomization step. The development of diverse temperature ramps in the pyrolysis-step graphite-furnace program (drying, pyrolysis and atomization temperatures) as well as the time required during each step must be carefully studied to obtain the highest ratio of absorbance-to-background signal. To improve these conditions, the addition of chemical modifiers was investigated to reduce chemical interferences and increase accuracy [19,45,46,50]. In addition to background reduction, a decrease in analytical signal was

also observed for increasing amounts of IL phase injected into the graphite furnace, which was attributed to metal loss occurring during the pyrolysis step. Moreover, direct formation of metal-fluoride volatile species, with HF occurring from $[\text{C}_4\text{mim}][\text{PF}_6]$ thermal decomposition, could explain this phenomenon.

Similarly to ETAAS, and due to its high viscosity, the IL-rich phase had to be conditioned by an appropriate diluting agent (generally organic solvents) before introducing it into the nebulizer of FAAS technique [23,38,51].

Metal atomization by hydride generation or CVG has not been widely studied in hydrophobic ILs. However, water-soluble ILs {e.g., 4-butylpyridinium tetrafluoroborate ($[\text{C}_4\text{py}][\text{BF}_4]$) and 1-butyl-3-methylimidazolium bromide ($[\text{C}_4\text{mim}]\text{Br}$)} have been used to improve CVG synergistically in the presence of KBH_4 , in combination with AFS, with good results [58–60]. Zhang et al. studied the effect of several ILs on CVG of Au^0 . It was found that ILs improved CVG, probably by electrostatic interaction between metal species and ILs, providing a protective micro-environment [59].

The impossibility of directly injecting solutions containing high concentrations of organic solvents into ICP-based detectors makes it difficult to apply of these instrumental techniques. In order to overcome this difficulty, some authors published methodologies in which an acid back-extraction step was performed with nitric acid. The effects of viscosity and organic matter were then diminished [21]. Nevertheless, Au determination in 50% (w/v) IL-aqueous solutions with ICP-OES detection was reported by Whitehead et al. [64].

For methods using UV-Vis detection, sample introduction does not bring further problems. The IL-rich phase is usually dissolved in organic solvents or directly measured. However, some known drawbacks of UV-Vis (e.g., spectral interferences, low sensitivity and the need of derivatization for metal determination) also apply to analysis in IL media. Moreover, these methods could require greater amounts of IL phase to perform the measurements than that injected in ETAAS. However, dissolving the IL phase with organic solvents does not avoid use of potentially more toxic or volatile organic solvents [8].

As shown in Table 2, ILs have also been used in combination with HPLC. Thus, ILs have been assayed as modifiers for mobile and stationary phases, as well as being used in LLE procedures prior to HPLC analysis [6]. Certainly, this combination is feasible, thanks to the possibility of adding organic solvents to mobile phases [43].

6. Ionic liquids in total-metal determination

The first analytical methods developed for metal determination using IL-based techniques were for Pb, Hg, Cd and Ni (Fig. 1). However, recent developments on pre-concentration of different elements also include Co, V,

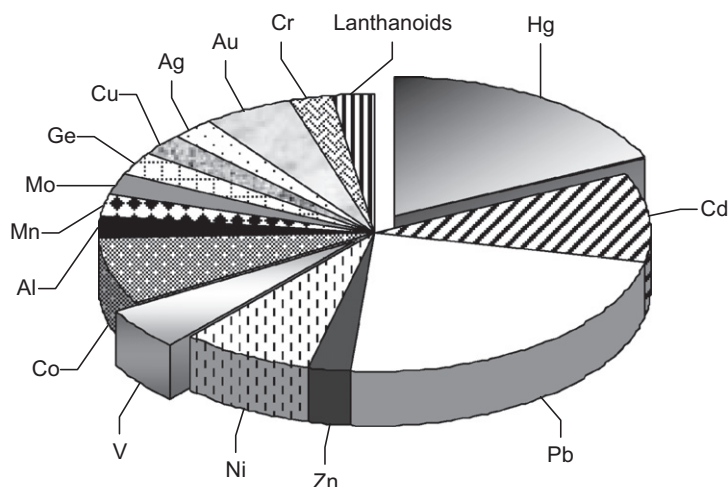


Figure 1. Application of ionic liquid-based techniques utilized for elemental studies. Exploded wedge represent elements included in speciation analysis.

Al, Mo, Mn, Ge, Cu, Ag, Au and some lanthanides (Sm, Du, Gd, Dy). Table 2 compares analytical performance of methods, based on common analytical parameters {e.g., enhancement factor (EF) (Fig. 2) and limit of detection (LOD) (Fig. 3)}. In addition, the consumptive index (CI) is also important. CI can be defined for practical purposes as:

$$CI = \frac{V_s}{EF}$$

where V_s is the volume of sample (in mL) consumed to achieve the EF value [65], so CI reflects the efficiency of sample utilization by the analytical method, and it can be very useful for selecting a preconcentration method where the sample amount is limited (e.g., some body fluids or biological tissues).

ILs in LLE-LLBE, on-line LLE, MP and USA-DLLME have been proposed for Cd preconcentration and determination [10,28,31,38,55]. An interesting approach proposed by Li et al. [10], using $[C_6mim][PF_6]$ IL, yielded a low LOD and a high EF to determine Cd in different samples, including tap, well, river and lake waters. A low CI was also obtained. In this work, USA-DLLME technique was used in combination with ETAAS detection.

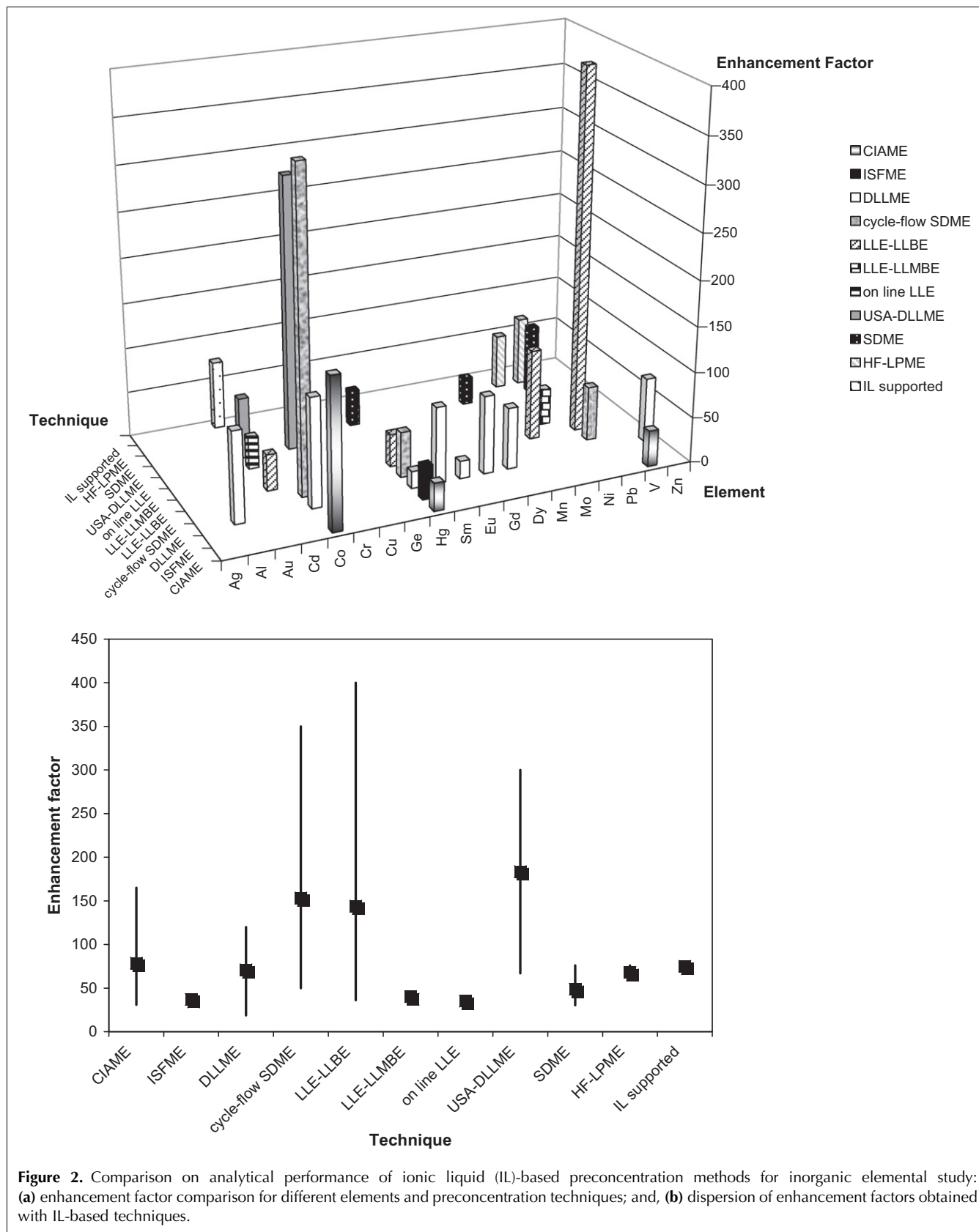
The possibility of using ILs for Cd extraction from complex matrices was demonstrated by our group [38]. The metal-chelation strategy was applied for Cd determination in plastics food-packaging materials. The method was based on the complexation of Cd with 5-Br-PADAP reagent after sample digestion, followed by extraction of the complex with $[C_4mim][PF_6]$ and FAAS detection.

The application of ILs in Co determination was mainly focused on development of preconcentration and separation procedures [9,45,47]. For example, Xia et al. [45] reported a high EF for Co determination (350) using

$[C_4mim][PF_6]$ IL as extractant solvent in a cycle-flow SDME technique with prior chelation of the metal with PAN reagent. The method was also suitable for evaluating trace levels of Hg and Pb in human serum and environmental water samples. PAN was also used as chemical modifier for subsequent ETV-ICP-MS determination of Hg and Pb, as it remarkably changed the vaporization behaviors of these elements. The method yielded a low LOD (0.0015 $\mu\text{g/L}$) thanks to ICP-MS detection. In a different approach, a highly selective separation and preconcentration method for Co at trace levels was proposed by Berton et al. [47]. Co was complexed with 1N2N reagent, followed by extraction into dispersed $[C_6mim][PF_6]$ IL phase with DLLME technique. The reagent, 1N2N, can selectively react with Co under specific conditions, so the method was successfully applied for evaluating Co in water, urine and saliva samples.

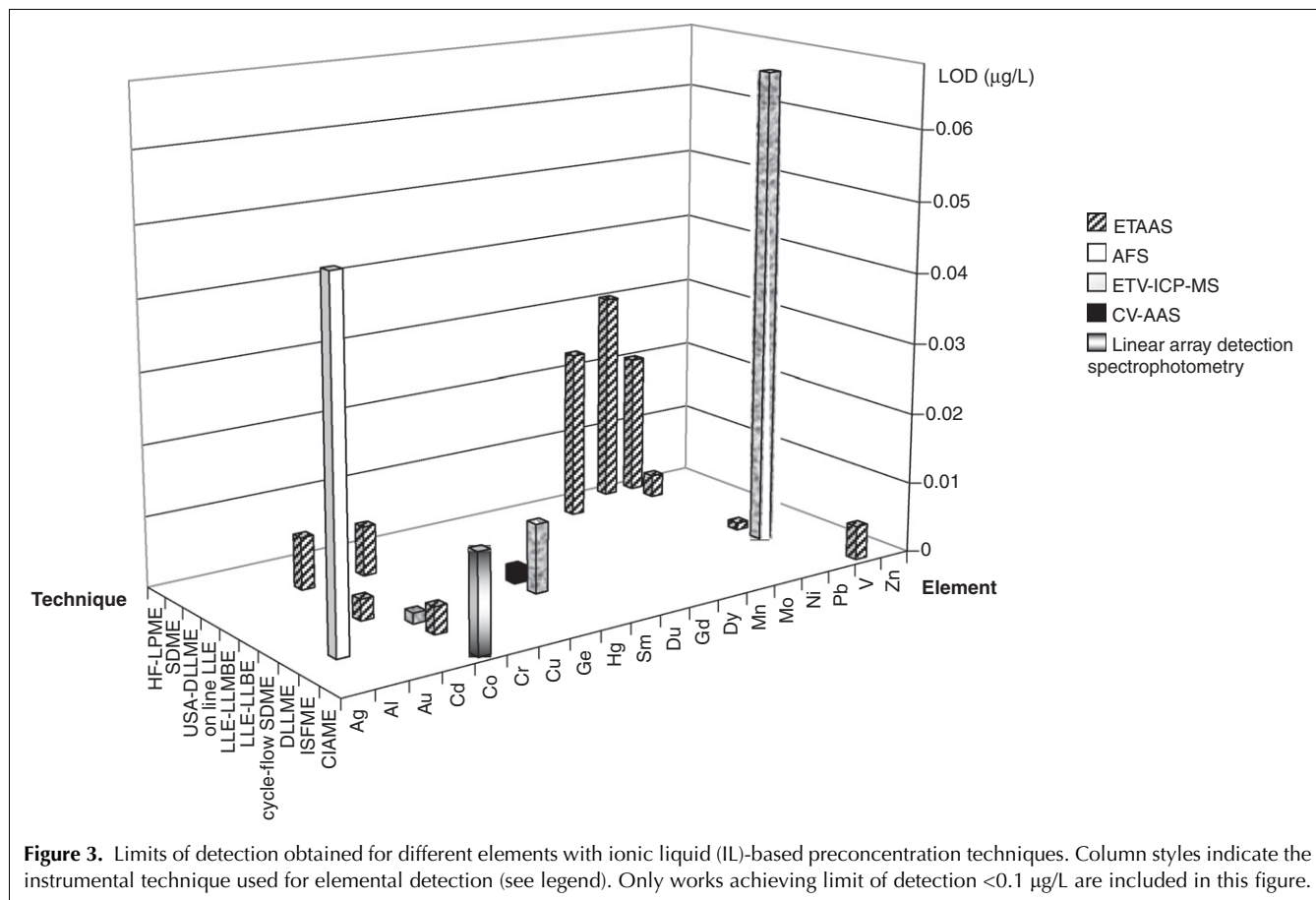
Lead has been one of the most determined elements using IL-based techniques (Fig. 1). Different types of samples including, environmental, biological and food have been analyzed [19,31,32,35,44–46,51,66]. LLE-LLBE and SDME coupled to ETAAS detector were the main analytical approaches for determining Pb in human hair, human serum, dialysis fluids, non-fat milk and water samples. Zaijun et al. [66] proposed *l*-butyl-3-trimethylsilylimidazolium hexafluorophosphate ($[C_4tmsim][PF_6]$) IL as a medium for LLE of Pb(II) in water, using dithizone as metal chelator to form a neutral complex. Determination of Pb was performed by ETAAS after back-extraction of Pb into a nitric-acid solution obtaining an EF of 400. However, the CI value was very high due to excessive sample consumption, which could limit the suitability of this method for analysis of biological samples.

Different IL-based preconcentration techniques (e.g., CIAME, ISFME, DLLME, SDME and LLE-LLBE) were



developed for Hg determination [8,29,30,43,45,49,54] (Table 2). The highest EF was obtained with SDME of

different variants. For example, Xia et al. [45] reported an EF of 50 and a low LOD (0.0098 µg/L).



The combination of IL-based techniques with CV-AAS is an attractive option for obtaining lower LODs for Hg determination [29]. Mercury has been studied almost exclusively in water samples (i.e. tap, river and sea waters) and there is only one work reporting Hg determination in human hair and serum [45]. Considering the toxicological implications of this element, it would be interesting to develop further studies on IL applications for Hg determination in biological and food samples.

There are few publications about Ni determination using ILs [37,46,60]. The synergetic effect of [C₄mim]Br and DDTC to enhance CVG of Ni in acidic aqueous solution with NaBH₄ as a reductant was demonstrated by Zhang et al. [60]. The combination of [C₄mim]Br and DDTC showed a 2400-fold enhancement in sensitivity. Another interesting work developed by Abulhassani et al. proposed Ni preconcentration using an HF membrane for supporting [C₆mim][PF₆] IL, thus eliminating the problem of drop instability observed with the SDME technique [46]. This was the first attempt to apply ILs in an HF-LPME technique with direct injection of eluent into the graphite furnace of the ETAAS instrument. An EF of 60 was obtained.

There are also few publications involving application of IL-based techniques for determination of V, Al, Mo, Mn,

Ge, Cu, Ag and Au. Thus, only Zhang's group has studied the enhancement of IL on CVG of Cu, Ag and Au and analytical sensitivity obtained with AFS detection [58]. Relatively low EFs were obtained in this method (i.e. 2.7, 3.6 and 4.8 for Ag, Au and Cu, respectively). However, different preconcentration techniques (e.g., LLE, USA-DLLME, SDME and CIAME) were developed for Al, Cr, Ge, Mn, Mo, and V, obtaining good extraction efficiencies and EF values [24,33,34,36,42,50,52,53] (e.g., for Cr and Mo, EFs were 300 and 100, respectively).

7. Ionic liquids in metal-speciation analysis

Metal-speciation analysis has attracted great interest not only within analytical chemistry but also in other fields of science (e.g., toxicology, biology and ecology). Thus, depending on their oxidation state and chemical association to organic molecules, metal species can show different toxicity levels or, by contrast, essentiality towards living organisms. Metal-speciation analysis is a very useful and recognized tool for environmental, geological, biological and clinical studies. However, the number of works aiming at metal speciation with the aid of ILs is still small, considering the environmental and

toxicological importance of speciation. Our group has been one of the pioneers at investigating the potential that ILs have in metal-speciation studies. Initial efforts were invested in developing a sensitive method to separate V^{4+} and V^{5+} species with additional preconcentration effect for determination of V species in tap-water and river-water samples [52]. The preconcentration of V species was performed by extracting the V-5-Br-PADAP complex with only 45 μ L of $[C_4mim][PF_6]$ using the CIAME technique. Selectivity among V species was achieved using 1,2-cyclohexanediaminetetracetic acid (CDTA) as masking agent for V^{4+} . Total V was determined by prior oxidation of V^{4+} to V^{5+} with hydrogen peroxide. Concentration of V^{4+} species was calculated by difference between total V and V^{5+} concentrations. The final IL-enriched phase containing the analyte was directly injected into ETAAS.

As an alternative, an analytical method based on an IL-SDME technique was used for separation and preconcentration of inorganic and organic Hg species ($MeHg^+$, $EtHg^+$, $PhHg^+$ and Hg^{2+}) in different water samples (e.g., tap and river waters, and wastewater) [43]. The principle of this work was formation of neutral Hg-dithizonate chelates with the different species, which were then extracted into an $[C_6mim][PF_6]$ microdrop. Afterwards, separation and determination of Hg species were carried out by HPLC with photodiode-array detection.

8. Future developments and applications

At present, ILs have shown certain benefits when they were employed as extractant solvents for trace-metal determination. However, in contrast with the growing information regarding the properties of ILs, the total potential of these unique solvents for separation, preconcentration and speciation studies is still not fully explored. To date, ILs have been used mainly as conventional solvents. Nevertheless, they offer many particular properties that need deeper understanding. It is necessary to profit from their differences from organic solvents to achieve more advantageous methods. In fact, the number of works explaining the mechanisms involved during metal extraction is very limited.

ILs have been utilized effectively for metal extraction from various relatively simple matrix samples, so future methods should focus on the application of ILs to analyze complex matrix samples (e.g., food, biological or pharmaceutical), expanding the capabilities of ILs for routine analysis. Certainly, they will replace harmful organic solvents in analytical-chemistry laboratories. Moreover, we expect that ILs will continue to replace common organic solvents in extraction processes, so the typical properties of these solvents (e.g., non-volatility, high viscosity, distinct density compared to aqueous systems) will be more and more exploited in LPME techniques.

9. Conclusions

ILs have been demonstrated to be attractive, efficient tools for improving LODs, selectivity and sensitivity in total and speciation analysis of some metals. They are, without doubt, valid alternatives to organic solvents normally used in analytical chemistry, due to their high recoveries and sensitivity EFs obtained after their application. Furthermore, the practicality, the safety, and the cost effectiveness of implementing ILs along with microextraction techniques are real advantages for developing environmentally-friendly, efficient analytical methods, which can find widespread use in routine-analysis laboratories undertaking trace-metal determination.

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Appendix. Abbreviations

Extraction technique

CIAME	Cold-induced aggregation microextraction
ISFME	In situ solvent formation microextraction
DLLME	Dispersive liquid-liquid microextraction
cycle-flow SDME	Cycle-flow single drop microextraction
HS-SDME	Head space-single drop microextraction
LLE-LLBE	Liquid-liquid extraction back extraction
LLE-LLMBE	Liquid-liquid extraction micro-back extraction
on line LLE	On line liquid-liquid extraction
USA-DLLME	Ultrasound assisted dispersive liquid-liquid microextraction
SDME	Single drop microextraction
HF-LPME	Hollow fiber-liquid phase microextraction
SPME	Solid phase microextraction

Detection technique

ETV-ICP-MS	Electrothermal vaporization - Inductively coupled plasma-mass spectrometry
HPLC	High performance liquid chromatography
CV-AAS	Cold vapor atomic absorption spectrometry

Appendix (continued)

ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
ASV	Anodic stripping voltammetry
AFS	Atomic fluorescence spectrometry
FO-LADS	Fiber optic-linear array detection spectrophotometry.
ICP-OES	Inductively coupled plasma optical emission spectrometry
Ionic liquid	
[C ₆ mim][Tf ₂ N]	1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide
[C ₆ mim][BF ₄]	1-Hexyl-3-methylimidazolium tetrafluoroborate
[C ₄ mim][PF ₆]	1-Butyl-3-methylimidazolium hexafluorophosphate
[C ₆ mim][PF ₆]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[C ₈ mim][PF ₆]	1-Octyl-3-methylimidazolium hexafluorophosphate
[C ₄ tmsim][PF ₆]	1-Butyl-3-trimethylsilylimidazolium hexafluorophosphate
[P _{14,6,6,6} Cl]	Trihexyl(tetradecyl)phosphonium chloride
[C ₆ py][PF ₆]	1-Hexylpyridinium hexafluorophosphate
[C ₄ mim]Br	1-Butyl-3-methylimidazolium bromide
[C ₄ py][BF ₄]	4-Butylpyridinium tetrafluoroborate
TOMAS	Trioctylmethylammonium salicylate
TSIL	Task-specific ionic liquid
Complexing agent	
TMK	4,4'-Bis(dimethylamino)-thiobenzophenone (Michler thio ketone)
PAN	1-(2-Pyridylazo)-2-naphthol
Dithizone	Dithizone
5-Br-PADAP	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol
CDA	o-Carboxyphenyldiazoamino-p-azobenzene
APDC	Ammonium pyrrolidinedithiocarbamate
Oxine	8-Hydroxyquinoline
DDTC	Sodium diethyldithiocarbamate
DTBSF	3,5-Ditertbutylsalicylfluorone
p-MOPASF	5-p-methoxyphenylazosalicylfluorone
TAN	1-(2-Thiazolylazo)-2-naphthol
MBASF	Methylbenzeneazosalicylfluorone
1N2N	1-Nitroso-2-naphthol
HYD	1-Hydroxy-2,5-pyrrolidinedione

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