



# Ionic liquid-based microextraction techniques for trace-element analysis



Estefanía M. Martinis<sup>a,b</sup>, Paula Berton<sup>b</sup>, Rodolfo G. Wuilloud<sup>a,b,\*</sup>

<sup>a</sup> Laboratory of Analytical Chemistry for Research and Development (QUIANID), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Padre J. Contreras 1300, 5500 Mendoza, Argentina

<sup>b</sup> Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

## ARTICLE INFO

### Keywords:

Analytical performance  
Complex sample  
Element determination  
Green analytical chemistry  
Ionic liquid  
Liquid-liquid microextraction  
Microextraction  
Preconcentration  
Sample preparation  
Trace-element analysis

## ABSTRACT

Ionic liquid-based liquid-liquid microextraction (IL-LLME) techniques are turning into remarkable tools to develop greener sample-preparation methods in analytical chemistry. The application of ILs in LLME is receiving particular attention due to their unique physico-chemical properties, such as undetectable vapor pressure, versatility arising from high conformational possibilities, variable viscosity and density, and their miscibility with other solvents. ILs can be structurally designed to extract target analytes selectively based on unique molecular interactions, leading to highly efficient extraction procedures. In recent years, a wide range of microextraction techniques implementing ILs as successful extraction phases have been proposed.

The present work outlines the latest applications of IL-LLME for trace-element analysis, focusing on those challenges arisen during the analysis of complex samples. We also discuss environmental and health aspects related to the use of IL-LLME. Finally, we present the outlook for potential applications and further developments of IL-LLME techniques.

© 2014 Elsevier B.V. All rights reserved.

## Contents

1. Introduction .....	54
2. Liquid-liquid microextraction based on ionic liquids .....	55
2.1. Ionic liquids as extraction solvents in liquid-liquid microextraction .....	55
2.2. Ionic liquids as ion-pairing agents in liquid-liquid microextraction .....	61
3. Application of ionic liquid-based liquid-liquid microextraction .....	63
4. Environmental and health aspects .....	66
5. Conclusion and future trends .....	67
Acknowledgements .....	67
References .....	67

## 1. Introduction

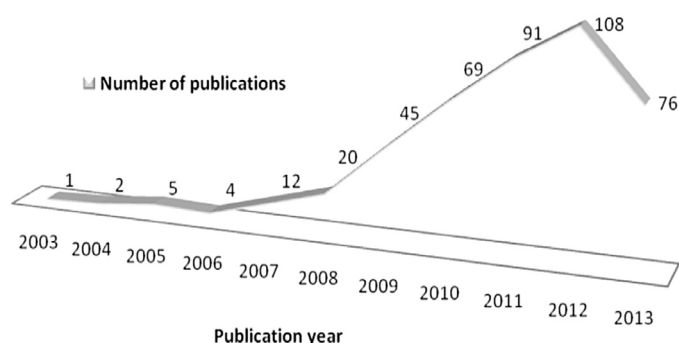
Green analytical chemistry (GAC) is a part of the sustainable development concept. Public interest in protecting the environment has encouraged analytical chemists to look for new sample-preparation techniques that could reduce the adverse environmental impact of chemical approaches [1,2]. Investigation of GAC methodologies covers a number of strategies to diminish the

amounts of reagents consumed and waste generated [1,3]. Miniaturization of sample-preparation procedures in analytical chemistry, automation and the search for alternative solvents are important ways to diminish side environmental effects of analytical methods. These strategies have been the subject of a significant number of research efforts in GAC advances [3,4].

Miniaturization of analytical methods, mainly sample-preparation steps, is considered to be one of the main approaches complying with GAC principles. Microextraction is defined as a non-exhaustive miniaturized sample-preparation method using an insignificant volume of extracting phase ( $\mu\text{L}$  range or smaller) relative to the sample volume [5]. Analytes can be extracted by a small volume of a solid or semi-solid material, as in solid-phase microextraction

\* Corresponding author. Tel.: +54 261 4259738.

E-mail addresses: [rwuilloud@mendoza-conicet.gob.ar](mailto:rwuilloud@mendoza-conicet.gob.ar); [rodolfowuilloud@gmail.com](mailto:rodolfowuilloud@gmail.com) (R.G. Wuilloud).



**Fig. 1.** Number of articles published in the period 2003–13 related to the application of ionic liquids (ILs) in microextraction techniques. Data generated from a search performed in Scopus database (<http://www.scopus.com>) using the terms “ionic liquid” and “microextraction” as search filter.

(SPME), or alternatively by a small volume of a liquid, as in liquid-liquid microextraction (LLME) [5,6]. Microextraction techniques therefore represent an important contribution to improving sample-preparation performance. The main analytical result is related to an increase of analysis reliability, higher precision, and time saving, which is very positively combined with a substantial reduction in waste. Table 1 contains a list of the acronyms used in this review.

In the search for substitute solvents, the main purpose is not just replacement, but the acquisition of advantages originating from different properties of the solvents to improve selectivity, sensitivity and reliability of analysis, while reducing analysis time [4]. The unique properties of ionic liquids (ILs) have given rise to a great number of applications in analytical chemistry. There has particularly been considerable interest in replacing volatile organic solvents in sample preparation [7–10]. ILs had been applied for several types of microextraction techniques due to their chemical and physical characteristics, such as negligible vapor pressure, good extraction efficiency for several organic compounds and metal ions (as neutral or charged complexes), thermal stability, and adjustable viscosity and miscibility with water and organic solvents [8,11]. ILs are valid alternatives to volatile organic solvents normally used in microextraction methods, with high recoveries and enhancement factors (EFs) obtained after their application [11,12].

Development and improvement of new sustainable analytical procedures is considered of great importance for GAC. Thus, application of state-of-the-art solvents, such as ILs, combined with microextraction techniques can be an excellent strategy for sample preparation being greener than classical techniques. Some of the GAC objectives (e.g., minimal or no waste generation, use of safer solvents, and development of miniaturized methods) are fulfilled by the introduction of ILs and microextraction in analytical methods [8]. Also, practical application, safety, and cost effectiveness of using ILs along with microextraction techniques are real advantages for developing environment-friendly and efficient analytical methods, which can find widespread use in routine-analysis laboratories for trace-element determination.

As shown in Fig. 1, the number of publications concerning ILs and microextraction techniques has increased substantially between 2003 and 2012, showing the continually growing interest in this field.

ILs have been proposed as extraction solvents and ion-pairing agents, along with LLME techniques, for metal determination. In order to improve the limit of detection (LOD), the selectivity and the sensitivity in total analysis and speciation analysis of some metals, different IL-based LLME techniques have been proposed, including, dispersive LLME (DLLME), single-drop microextraction (SDME), vortex-assisted liquid-liquid microextraction (VA-LLME) [13–17]. Furthermore, new techniques, such as *in-situ* solvent-formation

microextraction (ISFME) or IL-assisted ion-pairing LLME, may offer original solutions to analytical challenges based on their singular chemical behavior [18,19].

Polymeric ILs bonded onto silica particles have been used as adsorbents for SDME, thus improving the stability of the extractant phase and the robustness of the extraction procedure. In this technique, the acceptor organic solvent, meaning where analytes are extracted from an aqueous sample, is immobilized on an SPME fiber. The sample can be stirred or shaken vigorously without any loss of extracting phase, as it is mechanically protected. This is also an interesting approach to improving the mechanical strength and the durability of commercial SPME fibers [20].

Extraction and preconcentration methods based on IL-LLME techniques have been reviewed by our group in a previous report [12]. In the present work, we describe the latest advances and applications resulted from implementing ILs in LLME techniques. We outline and critically review recent developments involving IL-LLME techniques for metal determination. We also examine modern approaches, such as those reported for sample preparation with magnetic ILs. In Table 2, we summarize applications of microextraction procedures based on ILs in trace-elemental analysis. Finally, we discuss the environmental and health aspects of implementing ILs in LLME techniques.

## 2. Liquid-liquid microextraction based on ionic liquids

### 2.1. Ionic liquids as extraction solvents in liquid-liquid microextraction

LLME is a modified solvent-extraction technique in which acceptor-to-donor phase ratio is greatly reduced compared with other methods. Numerous reports on LLME have been published and ILs were shown to be successfully employed as solvents for extraction of inorganic analytes from different samples [100–102]. The predominant partitioning mechanism that transfers analytes from the aqueous phase to the IL phase is similar to that which occurs in traditional organic solvents. However, larger distribution coefficients for metal-ion extraction have been obtained, even by several orders, than those obtained with volatile organic solvents. Metal-ion extraction in IL/aqueous two-phase systems is often characterized by higher selectivity and extraction efficiency than those reported when regular organic solvents are used [103]. Selectivity and partitioning of the metal ion always depends on the nature of the IL, the metal ion and the ligand [103,104].

Different approaches have been proposed in order to improve metal-ion affinity for the IL phase. Most works reporting on the application of IL-LLME to metal determination used ILs as inert solvents to dilute coordination reagents for metals. These conditions mostly involved the presence of a complexing agent to diminish the polarity of metal ions, so as to result in more extractable chemical forms [21,93,105]. For a series of 1,3-dialkylimidazolium-type ILs, Hawkins et al. showed that the relative importance of cation exchange and neutral complex extraction to the overall ion-transfer process can vary considerably with the hydrophobicity of the IL cation, the concentration of the aqueous acid, and the extracted metal ion [104].

Another strategy to increase metal-ion affinity for the IL phase was proposed as being through chemical functionalization of the cation or the anion of the IL with specific ligands [106]. Thus, several types of functional groups have already been incorporated into ILs. For example, Fang et al. have synthesized a highly selective thiol-functionalized IL (thiol-FIL) for Cd(II) extraction and preconcentration [107]. Furthermore, Nockemann et al. have investigated the coordinating properties of nitrile-functionalized ILs toward Co(II) ions. Coordination was found to depend on the donor abilities of the nitrile group. This work gave an insight into the coordination chemistry

**Table 1**  
Definitions of acronyms used in this review

Acronyms	Definition
<b>Extraction techniques</b>	
ATPS	Aqueous two-phase system
CIAME	Cold-induced aggregation microextraction
DLLME	Dispersive liquid-liquid microextraction
HF-LLME	Hollow-fiber liquid-phase microextraction
HS-SDME	Headspace-single-drop microextraction
ISFME	<i>In-situ</i> solvent-formation microextraction
LLE	Liquid-liquid extraction
LLME	Liquid-liquid microextraction
MA-DLLME	Microwave-assisted dispersive liquid-liquid microextraction
M-CIAME	Modified cold-induced aggregation microextraction
SDME	Single-drop microextraction
SSLME	Single step in-syringe system liquid microextraction
USA-DLLME	Ultrasound-assisted dispersive liquid-liquid microextraction
USA-TILDLLME	Ultrasound-assisted temperature-controlled ionic liquid dispersive liquid-liquid microextraction
TA-DLLME	Temperature-assisted dispersive liquid-liquid microextraction
TS-LLME	Task specific-liquid-liquid microextraction
VA-LLME	Vortex-assisted liquid-liquid microextraction
<b>Ionic liquids</b>	
Aliquat 336	Trioctylmethylammonium chloride
Cyphos IL 101	Trihexyl(tetradecyl)phosphonium chloride
Cyphos IL 104	Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate
Cyphos IL 109	Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide
Cyphos IL 111	Trihexyl(tetradecyl)phosphonium tetrafluoroborate
[C <sub>4</sub> mim][BF <sub>4</sub> ]	1-Butyl-3-methylimidazolium tetrafluoroborate
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C <sub>4</sub> mim][PF <sub>6</sub> ]	1-Butyl-3-methylimidazolium hexafluorophosphate
[C <sub>6</sub> mim][BF <sub>4</sub> ]	1-Hexyl-3-methylimidazolium tetrafluoroborate
[C <sub>6</sub> mim]Cl	1-Hexyl-3-methylimidazolium chloride
[C <sub>6</sub> mim][PF <sub>6</sub> ]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[C <sub>6</sub> mim][Tf <sub>2</sub> N]	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C <sub>8</sub> mim][PF <sub>6</sub> ]	1-Octyl-3-methylimidazolium hexafluorophosphate
[C <sub>8</sub> mim][Tf <sub>2</sub> N]	1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C <sub>4</sub> C <sub>4</sub> mim][PF <sub>6</sub> ]	1,3-dibutylimidazolium hexafluorophosphate
[C <sub>6</sub> py][PF <sub>6</sub> ]	1-Hexylpyridinium hexafluorophosphate
[C <sub>6</sub> mim][FAP]	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[NH <sub>2</sub> C <sub>2</sub> C <sub>4</sub> mim][PF <sub>6</sub> ]	1-(2-Aminoethyl)-3-butylimidazolium hexafluorophosphate
[3C <sub>6</sub> PC <sub>14</sub> ][FeCl <sub>4</sub> ]	Trihexyl(tetradecyl)phosphonium tetrachloroferrate(III)
<b>Complexing agents</b>	
APDC	Ammonium pyrrolidinedithiocarbamate
ABPP	N-(4-{4-[(anilino-carbothioyl)amino]benzyl}phenyl)-N-phenylthiourea
CDAA	O-carboxyphenyldiazoamino-p-azobenzene
DDTC	Diethyldithiocarbamate
DDTP	O,O-diethyldithiophosphate
Disulfiram	Tetraethylthiuram disulfide
Dithizone	Dithizone
DPC	1,5-Diphenylcarbazine
DTBSF	3,5-Ditertbutylsalicylfluorone
HNEO	1-(2-Hydroxynaphtalene-1-yl)ethane oxime
HYD	1-Hydroxy-2,5-pyrrolidinedione
MBASF	Methybenzeneazosalicylfluorone
Oxine	8-Hydroxyquinoline
PAN	1-(2-Pyridylazo)-2-naphthol
PAR	4-(2-Pyridylazo)-resorcinol
PMBP	4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one
PR	Pyrogallol red
p-MOPASF	5-P-methoxyphenylazosalicylfluorone
Quinalizarine	1,2,5,8-Tetrahydroxy anthraquinone
TAN	1-(2-Thiazolylazo)-2-naphthol
TMK	4,4'-Bis(dimethylamino)thiobenzophenone (Michler thioketone)
1N2N	1-Nitroso-2-naphthol
5-Br-PADAP	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol
<b>Detection technique</b>	
AFS	Atomic fluorescence spectrometry
ASV	Anodic stripping voltammetry
CCD spectrophotometry	Handheld charge-coupled device spectrophotometry
CV-AAS	Cold-vapor atomic absorption spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
ETV-ICP-MS	Electrothermal vaporization-inductively-coupled plasma-mass spectrometry
FAAS	Flame atomic absorption spectrometry
FI-HG-AAS	Flow-injection hydride-generation atomic absorption spectrometry
FO-LADS	Fiber optic-linear array detection spectrophotometry.
HPLC	High-performance liquid chromatography
HPLC-DAD	High-performance liquid chromatography with diode-array detection
ICP-OES	Inductively-coupled plasma optical emission spectrometry
SFIS	Stopped-flow injection spectrofluorimetry
W-coil ET-AAS	Electrothermal atomic absorption spectrometry with tungsten coil

**Table 2**  
Analytical performance of ionic liquid liquid-liquid microextraction (IL-LLME) methods

Analyte	Sample	Sample volume (mL)	Microextraction technique	IL	IL amount	Complexing agent	EF <sup>b</sup>	LOD <sup>c</sup> ( $\mu\text{g L}^{-1}$ )	Detection technique	Ref.
Ag	Water	6	CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	50 $\mu\text{L}$	Disulfiram	120	$5.2 \times 10^{-3}$	ETAAS	[21]
Ag	Hair	10	DLLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	250 mg	DDTC	22	3	FAAS	[22]
Ag	Water	10	M-CIAME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	60 $\mu\text{L}$	TMK	95.5	0.4	UV-Vis spectrophotometry	[23]
	X-ray photographic films solution									
	Photographic waste									
Ag	Water	20	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	250 $\mu\text{L}$	ABPP	48.3 Ag	$2.6 \times 10^{-3}$ Ag	ETAAS	[24]
Au	Hair						48.7 Au	$4.8 \times 10^{-3}$ Au		
Al	Water	25	DLLME	[C <sub>6</sub> py][PF <sub>6</sub> ]	300 mg	Oxine	100	0.05	SFS	[25]
	Fruit juice									
	Wheat flour									
	Milk									
Al	Water	10	USA-DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	75 $\mu\text{L}$	Quinalizarine	n.r.	1.70 Al	UV-Vis spectrophotometry	[26]
Ga								2.02 Ga		
In								2.06 In		
As <sup>e</sup>	Urine	15	DLLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	200 g	APDC	10	$5 \times 10^{-3}$	FI-HGAAS	[27]
	Whole blood									
As <sup>e</sup>	Water	10	VA-LLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	60 mg	APDC	135	0.010	ETAAS	[28]
	Urine									
	Waste water									
As <sup>e</sup>	Wine	4	DLLME	[C <sub>8</sub> mim][PF <sub>6</sub> ]	40 mg	DDTC	46	$5 \times 10^{-3}$	ETAAS	[29]
As <sup>e</sup>	Water	10	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	30 mg	APDC	198	$6 \times 10^{-3}$	ETAAS	[30]
	Food salts									
	Nail									
	Hair									
	Rice									
As <sup>e</sup>	Water	5	DLLME	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	50 $\mu\text{L}$	APDC	255	0.013	ETAAS	[14]
As <sup>e</sup>	Water	5	LLME	CYPHOS IL 101 (IPA <sup>a</sup> )	10 $\mu\text{L}$	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	125	2	ETAAS	[31]
Au	Water	9	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	140 mg	–	40	3.4	FAAS	[32]
	Soil									
	Ore									
Au	Water	10	USA-TILDLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	75 mg	–	170	0.59	FAAS	[33]
	Geological samples									
Au	Seawater	10	M-CIAME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	50 $\mu\text{L}$	TMK	28	0.7	UV-Vis spectrophotometry	[34]
Au	Ore	100	HF-LLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	n.r.	Ditizona	130	0.9	FAAS	[35]
Cd	Water	7	VA-LLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	60 $\mu\text{L}$	APDC	14	0.01	ETAAS	[36]
	Apple									
Cd	Water	10	DLLME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	50 mg	5-Br-PADAP	100	0.06	FAAS	[37]
Cd	Rice	10	SDME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	20 $\mu\text{L}$	APDC	42	0.015	W-coil ETAAS	[38]
	Water									
Cd	Water	7	VA-LLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	500 $\mu\text{L}$	Oxine	35	2.9	FAAS	[15]
	Rice									
	Apple									
Cd	Water	10	VA-LLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	60 $\mu\text{L}$	APDC	31	1.1	FAAS	[39]
	Spinach leaves									
Cd	Water	100	HF-LLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	30 $\mu\text{L}$	APDC	90	$9 \times 10^{-3}$	Thermospray flame furnace AAS	[40]

Table (continued)

Analyte	Sample	Sample volume (mL)	Microextraction technique	IL	IL amount	Complexing agent	EF <sup>b</sup>	LOD <sup>c</sup> (µg L <sup>-1</sup> )	Detection technique	Ref.
Cd	Water	15	TS-DLLME	TOMATS	40 mg	–	48.1	1.16	FAAS	[41]
Cd	Milk									
Cd	Water	5	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	30 mg	DDTP	78	0.07	FAAS	[42]
Cd	Food grade salts									
Cd	Biological samples	10	DLLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	100 µL	Dithizone	75	0.05	FAAS	[43]
Cu								0.08		
Cd	Water	10	ISFME	[C <sub>8</sub> mim][Tf <sub>2</sub> N]	30 µL	APDC	280	0.2 × 10 <sup>-3</sup> Cd	ETAAS	[44]
Pb	Children toys lixivates							3 × 10 <sup>-3</sup> Pb		
Cd	Water	10	CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	75 mg	DDTP	70 Cd	0.12 Cd	FAAS	[45]
Pb							67 Pb	1.61Pb		
Co	Nutritional supplements	5	USA-TILDLM	[C <sub>6</sub> mim][PF <sub>6</sub> ]	80 mg	1N2N	60	5.4 × 10 <sup>-3</sup>	ETAAS	[46]
Co	Water	50	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	150 µL	5-Br-PADAP	50	0.97	FAAS	[47]
Co	Water	10	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	75 mg	PAN	118	0.1	FAAS	[48]
	Saline samples									
Co	Water	2	DLLME	CYPHOS IL 101	35 mg	PAR	20	8 × 10 <sup>-3</sup>	ETAAS	[49]
	Pharmaceutical formulations									
Co	Water	1.7	SDME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	9 µL	APDC	120	0.04	ETAAS	[50]
Co	Water	6	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	60 mg	1N2N	120	3.8 × 10 <sup>-3</sup>	ETAAS	[51]
	Saliva									
	Urine									
Co	Water	10	DLLME	[C <sub>6</sub> mim][FAP]	80 µL	APDC	78 Co	0.3 Co	HPLC	[52]
Cu							68 Cu	2 Cu		
Cr							75 Cr	0.5 Cr		
Ni							71 Ni	1.5 Ni		
Co	Water	30	DLLME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	210 µL	TTA	79 Co	0.10 Co	ICP-OES	[53]
Cu							91 Cu	0.10 Cu		
Mn							102 Mn	0.10 Mn		
Ni							100 Ni	0.2 Ni		
Zn							86 Zn	0.10 Zn		
Co	Water	10	M-CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	60 µL	PAR	74 Co	5.9 × 10 <sup>-3</sup> Co	UV-Vis spectrophotometry	[54]
Ni	Hair						79.5 Ni	5.87 × 10 <sup>-3</sup> Ni		
Co	Water	10	DLLME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	65 mg	PAN	26 Co	0.65 Co	UV-Vis spectrophotometry	[55]
Ni	Food						27 Ni	0.32 Ni		
	Geological samples									
Cr	Water (high levels of salts)	10	ATPS	[C <sub>4</sub> mim][BF <sub>4</sub> ]	150 µL	DPC	100	1.25	FAAS	[56]
Cr <sup>e</sup>	Water	100	HF-LLME	[C <sub>4</sub> mim][BF <sub>4</sub> ]	n.r.	DDTC	175	0.7	FAAS	[57]
Cr	Water	1.4	HF-LLME	Aliquat 336	n.r.	DPC	10.9	4.6	CCD spectrophotometry	[58]
	Soil leachates									
Cr <sup>e</sup>	Water	5	DLLME	[C <sub>8</sub> mim][PF <sub>6</sub> ]	40 µL	DDTC	16.5	1.00 Cr(III)	FAAS	[59]
								0.41 Cr(VI)		
Cr <sup>e</sup>	Water	30	M-CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	90 mg	MBED	60	0.7	FAAS	[60]
	Food samples									

(continued on next page)

Table (continued)

Analyte	Sample	Sample volume (mL)	Microextraction technique	IL	IL amount	Complexing agent	EF <sup>b</sup>	LOD <sup>c</sup> (μg L <sup>-1</sup> )	Detection technique	Ref.
Cr <sup>e</sup>	Water	5	CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	25 μL	APDC	42	5.40 × 10 <sup>-3</sup> Cr(III)	ETAAS	[61]
Cr <sup>e</sup>	Urine							2.45 × 10 <sup>-3</sup> Cr(VI)		
Cr <sup>e</sup>	Water	10	ISFME	[C <sub>8</sub> mim] [Tf <sub>2</sub> N]	100 μL	APDC	300	2 × 10 <sup>-3</sup>	ETAAS	[62]
	Lixiviates of plastic toys									
Cr	Water	8	USA-DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	50 μL	APDC	300	0.07	ETAAS	[63]
Cu	Food	10	CIAME	[C <sub>6</sub> mim] [PF <sub>6</sub> ]	48 mg	DDTC	75	0.42	FAAS	[64]
	Water									
Cu	Water	10	ISFME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	5 mg					
Cu	Water	10	ISFME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	8 μL	–	200	4 × 10 <sup>-3</sup>	ETAAS	[65]
Cu	Water	3	TS-LLME	[NH <sub>2</sub> C <sub>2</sub> C <sub>4</sub> im][PF <sub>6</sub> ]	0.3	–	n.r.	29	UV-Vis spectrophotometry	[66]
Cu	Water	5	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	35 mg	Thiamine	25	0.024	SFIS	[67]
	Food (tomato, rice, tea)									
Cu	Water	10	SDME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	20 μL	DDTC	33	0.15	UV-Vis spectrophotometry	[68]
	Milk									
	Tea									
Cu	Water	10	DLLME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	65 mg	TMK	136.6	0.45	FAAS	[69]
Hg <sup>e</sup>	Water	5	DLLME	[C <sub>8</sub> mim][PF <sub>6</sub> ]	0.05 g	Dithionate	25	0.031 Hg(II)	HPLC-AFS	[13]
								0.016 MeHg <sup>+</sup>		
								0.024 EtHg <sup>+</sup>		
								0.092 PhHg <sup>+</sup>		
Hg <sup>e</sup>	Water	10	USA-DLLME	TOMAS	30 μL	–	310	0.03 Hg(II)	CV AAS	[70]
	Fish tissue							0.4 CH <sub>3</sub> Hg <sup>+</sup>		
Hg <sup>e</sup>	Liquid cosmetic	5	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	52 mg	APDC	760 Hg <sup>2+</sup>	1.3 × 10 <sup>-3</sup> Hg(II)	HPLC-ICP-MS	[71]
							115 MeHg <sup>+</sup>	7.2 × 10 <sup>-3</sup> MeHg <sup>+</sup>		
							235 EtHg <sup>+</sup>	5.4 × 10 <sup>-3</sup> EtHg <sup>+</sup>		
Hg <sup>e</sup>	Water	5	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	70 μL	Dithizone	107	0.32 Hg(II)	HPLC-DAD	[72]
							114	0.96 MeHg <sup>+</sup>		
							106	1.91 PhHg <sup>+</sup>		
Hg <sup>e</sup>	Water	10	HS-SDME	CYPHOS IL 101	6 μL	–	75	0.01	ETAAS	[73]
	Fish									
	Hair									
Mn <sup>e</sup>	Tea	8	DLLME	[C <sub>4</sub> C <sub>4</sub> Bim][PF <sub>6</sub> ]	100 μL	PMBP	20	0.26 Mn(II)	FAAS	[74]
Mo	Water	10	DLLME	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	60 mg	PR	72.6	1.86 Mn(VII)	FO-LADS	[75]
	mint, Pepper black									
	Fenugreek leaves									
Ni	Water	5	DLLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	40 μL	PAN	67	0.018	ETAAS	[76]
Ni	Food	8	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	30 mg	PAN	153	0.6 × 10 <sup>-3</sup>	FAAS	[77]
Ni	Serum	20	DLLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	0.1 g	NaDDC	100	5 × 10 <sup>-3</sup>	ETAAS	[78]
	Urine									
	water									
Ni	Water	3	HF-LLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	8 μL	APDC	60 Ni	0.03 Ni	ETAAS	[79]
Pb	Oyster Tissue						76 Pb	0.02 Pb		

Table (continued)

Analyte	Sample	Sample volume (mL)	Microextraction technique	IL	IL amount	Complexing agent	EF <sup>b</sup>	LOD <sup>c</sup> (μg L <sup>-1</sup> )	Detection technique	Ref.
Pd	Water Alloy Jewels Pd catalysts	6.8	ISFME	[C <sub>6</sub> mim]Cl	n.r.	PAN	460	3 × 10 <sup>-3</sup>	ETAAS	[80]
Pd	Seawater Geological samples	10	M-CIAME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	30 mg	PAN	164	0.4	FO-LADS	[81]
Pd	Food additive Water Tea Blood	10	M-CIAME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	60 μL	TMK	97	0.2	UV-Vis spectrophotometry	[82]
Pb	Hair	10	CIAME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	150 μL	–	30	5.8	FAAS	[83]
Pb	Apple leaves	10	VA-LLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	200 μL	PAN	54.2	0.307	FAAS	[84]
Pb	Blood	10	CIAME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	45 μL	APDC	93	0.13	FAAS	[85]
Pb	Water	10	SSLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	100 μL	Dithizone	82.6	0.281	FAAS	[86]
Pb	Water	5	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	20 mg	PBHA	70	0.1	FAAS	[87]
Pb	Water	10	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	500 μL	APDC	40	1.5	FAAS	[88]
Pb	Water	1.5	SDME	CYPHOS IL 101	4 μL	5-Br-PADAP	32	3.2 × 10 <sup>-3</sup>	ETAAS	[89]
Pb	Water	10	CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	50 μL	Dithizone	nr	9.5	FAAS	[90]
Pb	Water	10	LLME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	200 μL	APDC Pb	38	0.25 Pb	Portable	[91]
Cu	Milk Tea					Dithizone Cu	26	0.10 Cu	W-coil ETAAS	
Rh	Platinum–iridium Alloy Water	10	USA-DLLME	[C <sub>8</sub> mim][Tf <sub>2</sub> N]	30 mg	5-Br-PADAP	29.1	0.37	FAAS	[92]
Se <sup>e</sup>	Water Garlic	4	DLLME	CYPHOS IL 101	50 mg	APDC	20	0.015	ETAAS	[93]
Sn	Canned food	30	USA-DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	250 μL	APDC	52.7	42	FAAS	[94]
Tl	Water Urine Mussel tissue	15	DLLME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	n.r.	Bromine	290	0.86	FAAS	[95]
Tl <sup>e</sup>	Water	5	DLLME	CYPHOS IL 101 (IPA <sup>a</sup> )	n.r.	–	nr	0.4 × 10 <sup>-3</sup>	ICP-MS	[19]
Tl <sup>e</sup>	Water	5	DLLME	CYPHOS IL 101 (IPA <sup>a</sup> ) [C <sub>6</sub> mim][PF <sub>6</sub> ]	60 mg	–	100	3.3 × 10 <sup>-3</sup>	ETAAS	[96]
V	Water Saliva	5	CIAME	[C <sub>4</sub> mim][PF <sub>6</sub> ]	40 μL	5-Br-PADAP	n.r.	4.8 × 10 <sup>-3</sup>	ETAAS	[97]
Zn	Water	5	ISFME	[C <sub>6</sub> mim][BF <sub>4</sub> ]	30 mg	HNEO	81	0.05	FAAS	[98]
Zn	Water Food	30	M-CIAME	[C <sub>6</sub> mim][PF <sub>6</sub> ]	95 mg	Oxine	60	0.18	FAAS	[99]

<sup>a</sup> IPA, Ion-pairing agent.

<sup>b</sup> EF, Enhancement factor.

<sup>c</sup> LOD, Limit of detection.

<sup>e</sup> Speciation study.

of functionalized ILs [108]. However, applications of coordinating ILs in LLME techniques have not been fully explored.

Mass transfer of analytes between aqueous and IL phases in LLME depends, among other factors, on the interfacial area created between the two phases. In order to improve the aqueous/IL interfacial area, and thus the extraction efficiency in LLME methods, a wide diversity of novel techniques has been developed and applied for preconcentration and determination of inorganic analytes. Among them, DLLME is the most applied for metal determination due to the infinitely large surface area formed between the IL phase and the sample [29,44,53,59]. Thus, high recoveries and high EFs could be obtained. Also, it is a powerful, efficient separation/preconcentration technique, which offers simplicity, rapidity and low cost. In DLLME, hydrophobic ILs containing alkyl-imidazolium cations 1-hexyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_6\text{mim}][\text{PF}_6]$ ), 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ ), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ ) are those most used for extracting trace elements.

However, the main drawback and shortcoming of DLLME is the need for a third component to be the disperser solvent. In that case, highly polluting organic solvents (e.g., acetone, methanol, acetonitrile and tetrahydrofuran) are used as dispersants. The volume of the disperser solvent is a critical factor directly affecting the formation of a cloudy solution, thus controlling the degree to which IL is dispersed in the aqueous phase, and, ultimately, the extraction efficiency. A reduced volume of disperser solvent could not disperse the IL properly, so a cloudy solution could not be formed completely. However, the solubility of analytes in the aqueous phase becomes higher by increasing the volume of disperser solvent, so the extraction process is not complete [109].

In order to avoid the use of a third component in LLME, other techniques have emerged to increase the interfacial area between the IL and aqueous phases. These new approaches are based on alternative sources of energy, such as temperature, microwaves, and ultrasonic radiation. These techniques are termed temperature-assisted DLLME (TA-DLLME) or cold-induced aggregation microextraction (CIAME), ultrasound-assisted DLLME (USA-DLLME) and IL-based microwave-assisted dispersive LLME (IL-MA-DLLME), respectively. The use of vortex stirring is a simple alternative to avoid the need for a third component or solvent (vortex-assisted DLLME) [15,39,84]. Temperature in TA-DLLME increases solubility of the IL phase, so full contact between the two phases is obtained. Even though high EFs were achieved with this approach [21,46,85,90], this is a time-consuming LLME technique due to the time invested in heating and cooling steps. Furthermore, application of the TA-DLLME technique is limited mainly to extraction of thermally-stable compounds.

Since ILs absorb microwave radiation extremely well and transfer energy quickly by ionic conduction, this energy source can be an interesting alternative to classical heating methods. This strategy may improve extraction efficiency and speed up the analysis. Even when there are several publications regarding MA-DLLME application for organic compound determination [110–114], this technique has not yet been applied for inorganic analytes.

However, ultrasound has been widely used in LLME for metal preconcentration [46,92,115]. Thus, the main advantages of this technique are short analysis time and high analytical recovery.

Other interesting techniques have been proposed for determination of inorganic analytes [e.g., homogeneous LLME (HLLME), which involves phase-separation phenomenon from a homogeneous solution (aqueous and hydrophilic ILs) to extract target solutes simultaneously into the separated phase]. We can therefore consider that initial surface area at the interface between the two phases is infinitely large. Consequently, vigorous shaking or mixing is not required [23]. Two approaches have been developed based on this

principle. One of them is the IL-based aqueous two-phase system (ATPS). In this technique, analyte extraction is performed with low viscous and hydrophilic ILs. Separation of phases is induced by salt addition (generally inorganic) to the homogeneous aqueous solution [116]. In the second HLLME method, called *in-situ* solvent formation microextraction (ISFME), sodium hexafluorophosphate ( $\text{NaPF}_6$ ) was used as ion-pairing agent. A small amount of the salt was added to the sample solution containing very small amounts of 1-alkyl-3-methylimidazolium tetrafluoroborate. A cloudy solution was observed as a result of the fine droplets formed by the hydrophobic IL. Then, the IL-enriched phase was separated by centrifugation [30,80,98]. ISFME can therefore be considered a fast, simple, suitable method for extracting and preconcentrating analytes from sample solutions containing high concentrations of salts (see Section 3).

Other techniques such as SDME and hollow-fiber LLME (HF-LLME) have scarcely been applied to the determination of metals in recent years – probably because these techniques are impractical since the frequency of analysis is much lower than that of other LLME techniques described above.

Fig. 2 shows the trend in applications of IL-LLME techniques in trace-element analysis. Other strategies, such as the synthesis of ILs with magnetic properties (MILs), were recently reported. MILs are primarily based on high-spin d5 Fe(III) in the form of tetrachloroferrate(III) or tetrabromoferrate(III) combined with different counter cations. Other MILs containing transition metal ions, such as Gd, Mn, Co, and Dy, were also reported [117,118]. MILs not only have tunable properties but also exhibit an unexpectedly strong response to an external magnetic field [119]. Thus, formation of an undesirable emulsion may be overcome with extraction by MILs.

Despite this obvious advantage, only Deng et al. have proposed the application of an MIL as an extraction solvent for the separation of various phenolic compounds from aqueous solution. Pentachlorophenol, a major component in a contaminated soil sample from a superfund site, was successfully extracted and removed by using trihexyltetradecylphosphonium tetrachloroferrate(III) ( $[\text{3C}_6\text{PC}_{14}][\text{FeCl}_4]$ ) with high extraction efficiency: its concentration was dramatically reduced from  $7.8 \mu\text{g mL}^{-1}$  to  $0.2 \mu\text{g mL}^{-1}$  after magnetic extraction [120]. The microextraction set-up is shown in Fig. 3.

## 2.2. Ionic liquids as ion-pairing agents in liquid-liquid microextraction

Besides their role as extraction solvent, some ILs bearing phosphonium or ammonium groups have attracted attention as potential novel ion-pair reagents to increase the extraction efficiency of elemental species from aqueous phase. Also, trihexyl(tetradecyl)phosphonium chloride (CyphosIL 101) and trioctylmethylammonium chloride (Aliquat 336), which are the ILs mostly used as ion-pair reagents, are produced in tons, so they are fairly inexpensive choices [121].

In hydrochloric acid media, some metal ions, such as Fe(III), Zn(II), or Pd(II), form anionic or neutral stable chlorocomplexes, which are supposed to be exchanged by the chloride/sulfate anion of the IL, extracted by an ion-association mechanism with the anion of the IL, or a combination of both processes [122]. However, positively charged species are not expected to show ion-association or ion-exchange behaviors with ILs. Chloroanionic complexes formed between Cyphos ILs and Pd(II), Zn(II), Fe(III), or Co(II) were then extracted with different organic solvents (such as toluene, chloroform, carbon tetrachloride or butylene carbonate) proposed as extractant phases [19,122–132]. Furthermore, Aliquat 336 (generally dissolved in an appropriate organic solvent) was proposed as ion-pair reagent for several metals in hydrochloric acid solutions [e.g., Cd(II), Fe(III), Pt(II), U, Th, lanthanides, and Hg(II)] [121]. Aliquat



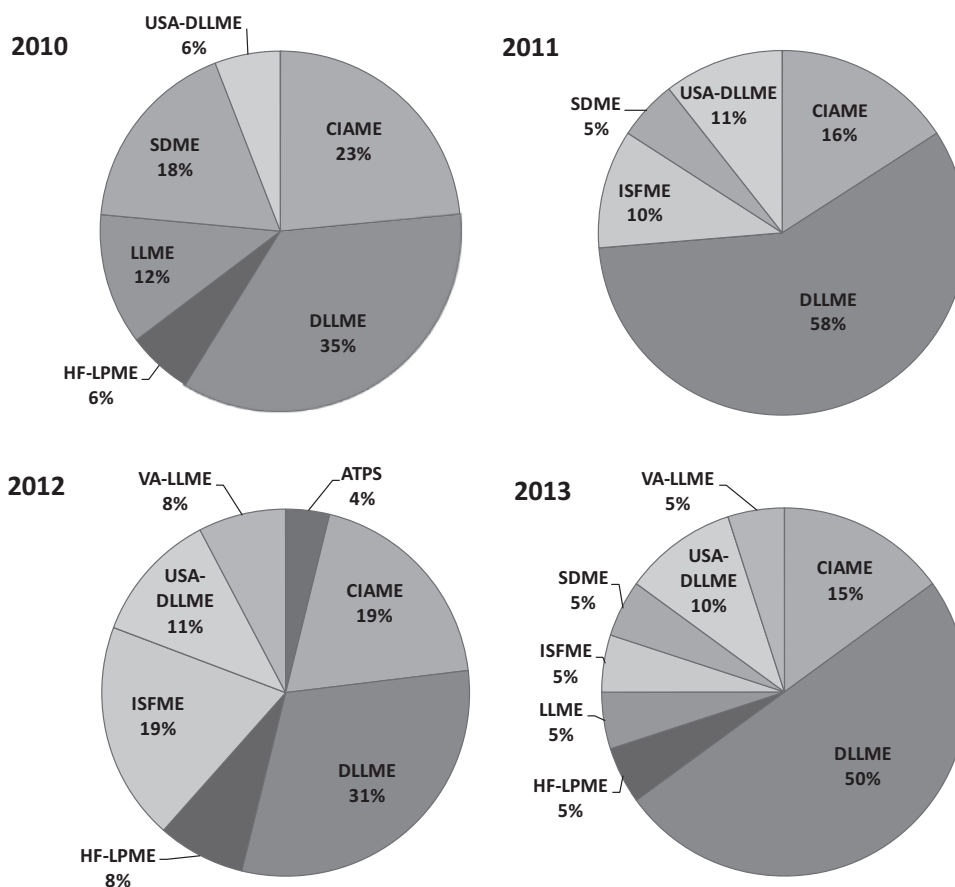


Fig. 2. Percentage distribution of published works reporting ionic liquid liquid-liquid microextraction (IL-LLME) methods applied to trace-element analysis in the period 2010–13.

336 dissolved in kerosene was successfully used for selective separation of Co(II) and Ni(II) from sulfuric acid solutions, while Pt(IV) and Rh(III) were extracted from hydrochloric acid solutions [133,134].

The efficiency of quaternary phosphonium salts for extracting metals from hydrochloric acid solutions depends on the hydrophobic character of the anion in phosphonium salts. Mixtures of toluene with Cyphos IL 101, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104), (trihexyl) tetradecylphosphonium bis(trifluoromethylsulfonyl)imide (Cyphos IL 109) and trihexyl(tetradecyl)phosphonium tetrafluoroborate (Cyphos IL 111) were assayed for Zn(II) and Fe(III) extraction [125,126]. It was observed that the extraction efficiency increased when the hydrophobicity of the IL decreased. As a consequence, higher extraction efficiency was observed for phosphonium salts with chloride anion (hydrophilic) than those having  $\text{BF}_4^-$  and  $\text{NTf}_2^-$  anions (highly hydrophobic). However, the results obtained for Cyphos IL 104 indicated that not only hydrophobicity of the anion is responsible for efficient extraction of Zn(II), but, for this extractant it is likely that another unclear mechanism is also involved [126]. This could be one of the reasons why Cyphos IL 101 is employed most as an ion-pairing reagent, while a few methods were reported as using Cyphos IL 104.

Aqueous phase composition strongly alters the formation of metal species, thus influencing extraction yield. As mentioned above, one of the main advantages of using ILs as extracting agents is that extraction efficiency is poorly influenced by metal ions that do not form anionic species with anions occurring in the aqueous medium.

Among metals forming chlorocomplexes, selectivity can be regulated upon selection of proper pH and HCl concentration in aqueous solution or varying the stripping agent during a retro-extraction step. For example, Pd(II) from Pt(IV) has been successfully separated in a hydrochloric aqueous media by selective stripping of Pd(II) from the loaded organic phase [129,135]. For back-extraction, several acidic and basic solutions have been used as stripping medium based on the formation of stronger complexes or ion pairs with metals extracted into the organic phase. In the case of Aliquat 336, effective metal stripping was easily achieved by changing the pH, or via an efficient complexing agent, such as thiourea.

Even when the use of phosphonium-based ILs as ion-pairing reagents is a promising strategy to extract metal ions from aqueous solutions, an important point to consider is that organic solvents are still unavoidable in LLME techniques. The reason for this limitation is that high viscosity of these ILs could make manipulation of extractant phase and analysis difficult. This issue definitely compromises both price and “greenness” of the whole analytical procedure. An alternative to overcome this drawback is the immobilization of ILs onto different solid materials or embedding ILs into different matrices, such as membranes, which increases their stability. For example, Cyphos IL 101 has been immobilized in composite biopolymer capsules and conventional resins for the sorption of Zn(II), Pd(II), Pt(IV), Hg(II), Au(III), Cd(II), Fe(III) and Bi(III) from hydrochloric acid solutions [136–146]. Other interesting approaches that have received significant attention for extraction of several metals from an aqueous feeding phase to an adequate stripping phase were:

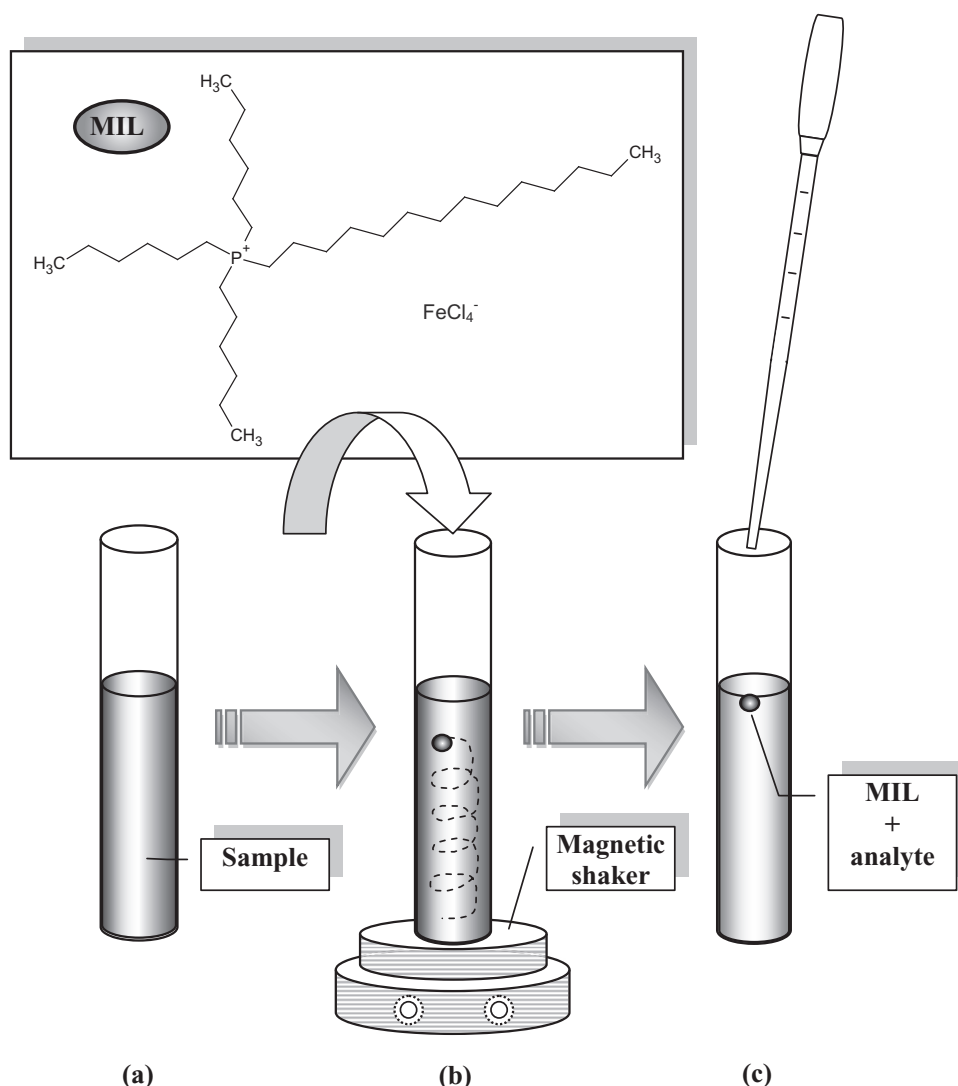


Fig. 3. A microextraction set-up based on magnetic ionic liquids (MILs): (a) sample containing the analyte; (b) MIL addition; and, (c) magnetic phase separation.

- (1) liquid membranes (either bulk or supported liquid membranes), with Cyphos IL 101 or Aliquat 336 as ionic carriers; and,
- (2) the immobilization of ILs by encapsulation of liquid extractants in polystyrene microcapsules.

Since this topic exceeds the current overview, it is recommendable to follow the complete, extensive review recently published by Stojanovic et al [121]. Also, a novel strategy has been proposed for Cr(III) and Cr(VI) extraction, using phosphonium and ammonium ILs to functionalize resins, membranes, and polymers, without the addition of chloride [147–149].

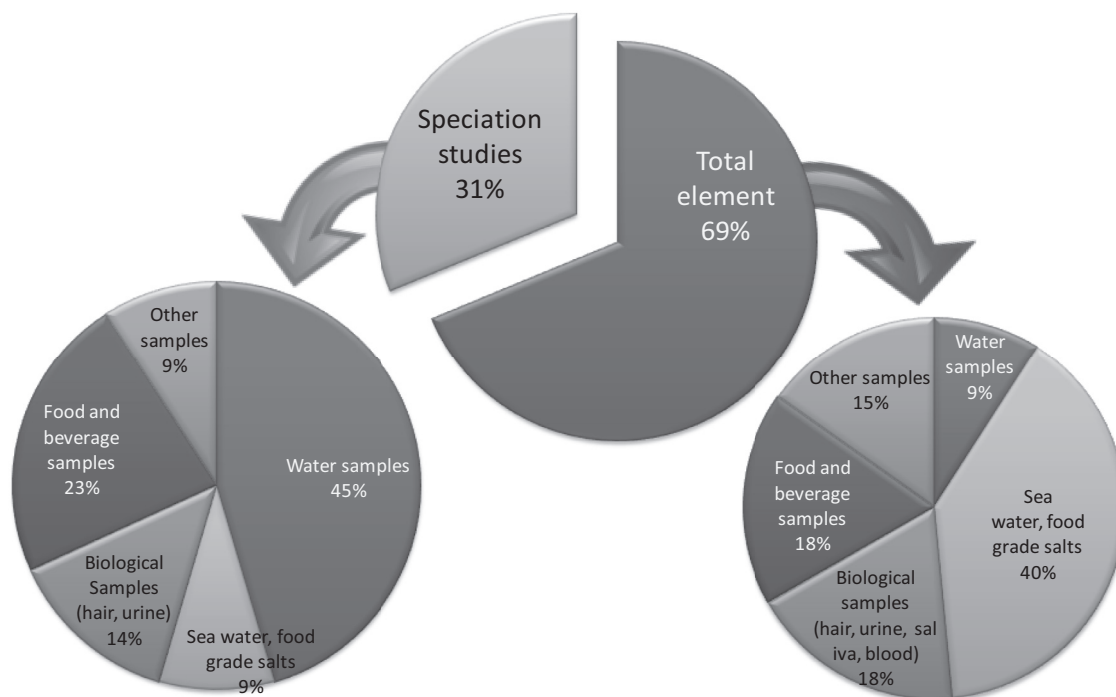
A different approach to overcome the aforementioned drawbacks occurring with phosphonium-ILs in LLEs has been proposed by Escudero et al. IL-LLME techniques were developed using Cyphos IL 101 as ion-pairing reagent for fast separation of Tl species at ultratrace levels in real water samples [19,96]. Initially, an ion pair was formed between the anionic complex tetraiodothallate (III) ( $[\text{TlI}_4]^-$ ) and Cyphos IL 101. Once formed, the ion pair was extracted into  $[\text{C}_6\text{mim}][\text{PF}_6]$  using the DLLME procedure. Finally, the IL phase was solubilized in methanol and directly injected into the graphite furnace of in electrothermal atomic absorption spectrometry (ETAAS). An extraction efficiency of 77% and a sensitivity EF

of 100 were obtained with only 5.00 mL of sample [96]. In a second method, an ion pair was formed between Cyphos IL 101 and the anionic complex tetrachlorothallate (III) ( $[\text{TlCl}_4]^-$ ). After DLLME, and using carbon tetrachloride as extractant phase, the upper aqueous phase containing Tl(I) was analyzed by inductively-coupled plasma mass spectrometry (ICP-MS). Total Tl concentration was obtained by direct sample introduction into an ICP-MS instrument. Under optimal conditions, the LOD of the Tl species was  $0.4 \text{ ng L}^{-1}$ . The relative standard deviation (RSD) was 1.3% for Tl(I) and 1.5% for Tl(III) ( $n = 10, 1 \text{ ng mL}^{-1} \text{ Tl}$ ) [19].

Finally, we can be assured that one of the main advantages of using ILs as ion-pair reagents lies in these extracting phases being recyclable. Organic solvents or solid phases enriched with ILs can be used for many extraction-stripping cycles. Regeneration of IL-enriched wastes and their reuse for several extraction cycles must be a GAC and ecological demand (see Section 4) in modern sample-preparation methods for analytical chemistry.

### 3. Application of ionic liquid-based liquid-liquid microextraction

In our previous review, published back on 2010, it was observed that most IL-LLME methods were applied for water-sample



**Fig. 4.** Application distribution of ionic liquid liquid-liquid microextraction (IL-LLME) techniques depending on the type of sample analyzed in total trace-element determination and speciation studies.

analysis, water being a simple matrix [12]. Since then, only a few IL-LLME methods have been proposed for metal determination (Pb and Cd) exclusively in water samples [40,88,89]. Thus, most of the recently developed techniques were proposed for metal determination in more complex samples, such as those with high salt concentration, biological samples, food and beverage samples, among others. Fig. 4 shows the application scenario of IL-LLME methods depending on the sample being analyzed.

Direct determination of trace amounts of metals in seawater is difficult due to their low concentration, strong interference from the sample matrix and high salt concentrations, so many of the developments made in microextraction techniques have involved some modifications of the regular approaches in order to overcome these drawbacks. The addition of  $\text{NaPF}_6$  as a common ion decreases the solubility of the  $[\text{Hmim}][\text{PF}_6]$ -phase in saline solutions and, due to the common ion effect, the robustness of the technique can be substantially increased, even for samples with high salt concentrations (up to 40%). For example, IL-DLLME with the addition of  $\text{NaPF}_6$  has been proposed for Pb and Cd determination in tap water, table salt and food-grade  $\text{NaNO}_3$  with EFs of 273 and 311, and LODs of  $0.6 \mu\text{g L}^{-1}$  and  $0.03 \mu\text{g L}^{-1}$  for Pb and Cd, respectively [150].

The same strategy of adding a common ion of the imidazolium-based IL into the sample solution has been proposed for Co determination in saline samples using DLLME [48]. Moreover, trace amounts of Cu(II) and Mo(VI) have been successfully determined in seawater samples using the IL  $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$  in a DLLME procedure. Under optimal conditions, LODs were  $0.45 \mu\text{g L}^{-1}$  and  $1.43 \mu\text{g L}^{-1}$  and RSDs were 3.3% and 2.8% ( $n = 5$ ), for Cu(II) and Mo(VI), respectively [69,75].

Another microextraction technique widely used for trace-metal determination in highly saline samples has been ISFME. In these cases,  $\text{NaPF}_6$  has been used as ion-pairing agent. This technique was proposed for Cd, Co and Ni in natural water samples, including seawater and food-grade salts [42,47,77]. Stanisław and Zgoła-Grzeškowiak recently proposed an *in-situ* DLLME technique for Cu(II) extraction in water samples using  $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$  as extraction

solvent. Under optimal conditions, a  $0.004 \text{ mg L}^{-1}$  LOD, an EF of 200 and a 4% RSD ( $n = 7$ ) were obtained [18].

The same extraction technique was proposed for B extraction in synthetic seawater. In the proposed methodology, Joshi et al. used  $\text{LiNTf}_2$  and potassium tris-(pentafluoroethyl)trifluorophosphate (KFAP) as metathesis salts to synthesize *in situ* two B-selective glucaminium-based ILs [151]. This is one of the few microextraction methods reported in the literature where task-specific ILs (TSILs) have been used for metal extraction.

Following the same principles of ISFME, modified CIAME (M-CIAME) using 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_6\text{mim}][\text{BF}_4]$ ) as extractant phase and  $\text{NaPF}_6$  added to the solution, was applied for determination of Pd(II) and Au in blood, tea, seawater and sodium nitrate food-grade samples with recoveries higher than 90% [34,81,152]. Ultratrace levels of Au(III) from aqueous hydrochloric acid solutions were extracted using  $[\text{C}_6\text{mim}][\text{PF}_6]$  and stripped from the IL phase with  $\text{NaPF}_6$ . Recycle tests indicated that IL loss could be avoided by adding  $[\text{C}_6\text{mim}]^+$  to the initial  $\text{AuCl}_4$  solutions before extraction and/or using  $\text{NaPF}_6$  solutions for stripping. This method was validated by recovery and determination of trace amounts of Au in river water, seawater and mine samples [33].

Microextractions based on ILs have also been proposed for metal determination in biological samples. For example, IL-DLLME and TA-DLLME were proposed for separation and preconcentration of ultratrace amounts of Au(III) and Ag(I) in natural water and hair samples. Under optimal conditions, EFs of 48.7 and 48.3, RSDs of  $\pm 4.1$  and  $\pm 3.7\%$  and LODs of  $4.8 \text{ ng L}^{-1}$  and  $15.9 \text{ ng L}^{-1}$  were obtained for Au and Ag, respectively [21,24]. Lead was also extracted with imidazolium-based ILs in hair and urine samples with recoveries higher than 95% [84,86], and in acid-digested blood samples of children with different respiratory disorders [85]. Among these procedures, Shah et al. proposed a new IL-LLME experimental setup based on a single step with an in-syringe system for determination of Pb in hair samples. The system required only conventional plastic syringes: a 10-mL syringe as extraction unit and a 1–3-mL

syringe for addition and recovery of extractant, thus avoiding a centrifugation step [86].

An IL-DLLME method has been developed for selective determination of Co in saliva and urine samples with an EF of 120 and an LOD of  $3.8 \text{ ng L}^{-1}$  [51]. We need to mention that one important advantage of the techniques here described for elemental determination in biological samples is that almost all of them were developed for non-invasive samples, such as urine, hair or saliva. These samples are easy to collect, which is very useful to screen large populations [153]. However, a major challenge for detection of chemical contaminants in these samples is that concentrations are often several orders of magnitude lower than those normally found in blood [153]. This drawback can be easily overcome by using simple, rapid IL-LLME techniques, thus achieving the low LODs required for elemental determination in biological samples with complex matrices.

In food and beverage samples, an ISFME combined with stopped-flow injection spectrofluorimetry (SFIS) was proposed for Cu(II) determination in tomato, tea, and rice samples with recoveries higher than 90%, an LOD of  $0.024 \mu\text{g L}^{-1}$  and an RSD of 2.1% [67]. This was the first time that SFIS was used along with IL-LLME for elemental determination, thus extending the number of detectors that can be used after IL-LLME. Furthermore, ultra-trace Cu(II) was accurately detected in natural waters, tea, and defatted milk-powder samples using 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_4\text{mim}][\text{PF}_6]$ ) as extractant in SDME. Under optimal conditions, an LOD of  $0.15 \mu\text{g L}^{-1}$  and an EF of 33 were achieved [68].

Using the VA-LLME technique, Chamsaz et al. developed analytical methods for Pb and Cd determination in samples of spinach leaves, apple and rice. In addition to the simplicity of this microextraction technique, TX-100 was used as dispersant solvent, which avoided the application of volatile organic solvents [15,39]. Another method aimed to determine trace amounts of Mo(VI) in three plant samples (mint, black pepper and fenugreek leaves) was developed using the IL  $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$  in a DLLME procedure. An LOD of  $1.43 \text{ ng mL}^{-1}$ , an RSD of 2.8%, and an EF of 72.6 were obtained with this method [75]. Moreover, using an ISFME technique coupled to flame atomic absorption spectrometry (FAAS), Ni was determined in lettuce with an LOD and an RSD ( $n = 6$ ) of  $0.6 \text{ ng mL}^{-1}$  and 2%, respectively. In addition to the advantages previously mentioned for ISFME, such as its robustness with highly saline samples (up to 40%), optimization of ISFME variables has been carried out with the aid of design of experiments (DOE) [77]. An optimization method based on DOE was applied by Khani et al. for Cu extraction and preconcentration by the DLLME technique [69]. Likewise, Shah et al. developed a Plackett–Burman design, followed by a central  $2^3 + \text{star}$  orthogonal composite design, to optimize the recovery of Pb extracted by TA-DLLME [85]. Although a limited number of examples combining IL-LLME and chemometrics was reported for trace-element determination, this approach should be strongly encouraged as it significantly simplifies sample processing and also addresses problems related to improvement in detectability and method validation [154].

Other samples, such as alloys, lixiviates from plastics, coal, and ophthalmic and nutritional solutions, have been analyzed for metal determination using microextraction techniques based on ILs. An *in-situ* IL-DLLME procedure was proposed for determination of Pb, Pd and Cd in waters, lixiviates obtained from plastic toys, alloy samples, jewels, and palladium catalysts [44,80]. Likewise, Co was determined in water samples and in ophthalmic and parenteral solutions, yielding recoveries of 97.9–103% using CYPHOS IL 101 for IL-DLLME implemented in an original flow-injection system for on-line microextraction and preconcentration. An on-line IL-DLLME approach, like the one proposed in that work, makes it feasible to use ILs with lower density than aqueous media, which is usually a significant drawback in regular LLME procedures. The LOD obtained

after preconcentration of 2 mL of sample solution was  $8 \text{ ng L}^{-1}$ , while the RSD ( $n = 10$ ) was 5.1% [49].

Elements such as Al (III), Ga(III), and In(III) have been extracted from water and coal samples using  $[\text{C}_6\text{mim}][\text{PF}_6]$  IL as extractant phase in an USA-DLLME method prior to their simultaneous spectrophotometric determination using least squares support vector machines (LS-SVM) regression. This work is another example of how chemometrics, specifically numerical analytical methods, such as LS-SVM, can be used to solve linear and non-linear multivariate calibration problems in a relatively fast way, so allowing simultaneous elemental determination without previous separation. The LODs for Al(III), Ga(III), and In(III) were  $1.70 \text{ ng mL}^{-1}$ ,  $2.02 \text{ ng mL}^{-1}$  and  $2.06 \text{ ng mL}^{-1}$ , respectively, with RSDs below 3.2% for most of these elements [155]. Trace amounts of Rh(III) were determined in a platinum–iridium alloy with a 95% recovery. The IL  $[\text{C}_8\text{mim}][\text{NTf}_2]$  was used to develop a USA-DLLME method followed by FAAS analysis. With the assistance of ultrasound, the IL-USA-DLLME/FAAS method showed a relatively low LOD ( $0.37 \text{ ng mL}^{-1}$ ) and a short extraction time (2 min) [92].

Depending on their oxidation state and chemical association to organic molecules, metal species show different toxicity levels or, by contrast, essentiality towards living organisms. Metal-speciation analysis has therefore attracted great interest in not only analytical chemistry but also other fields of science (e.g., toxicology, biology and ecology). However, in our previous review [12], microextraction techniques based on ILs were proposed only for V and Hg speciation. Although speciation studies are still a difficult analytical task, the number of applications using IL-based microextraction techniques for such studies increased remarkably in the past few years. For example, inorganic Tl species (see sub-section 2.2) and speciation of elements, such as Se, Hg, Cr, As, and Co, in different complex samples have been studied using IL-based LLME techniques. Moreover, selenium inorganic species  $[\text{Se(IV)}]$  and  $[\text{Se(VI)}]$  were determined using CYPHOS IL 101 as extractant solvent with IL-DLLME-ETAAS [93]. In that work, retention and separation of the IL phase containing the enriched analytes was achieved using a Florisil-packed microcolumn. The LOD was  $15 \text{ ng L}^{-1}$  and the RSD ( $n = 10$ ) was 5.1%. The method was successfully employed for Se-speciation studies in garlic extracts and natural water samples [93]. On-line IL-DLLME methods, such as that proposed by the authors, show some advantages over on-line preconcentration procedures using retention microcolumns. Thus, the use of retention materials with specific surface functionalization and specially-designed commercial columns was avoided with the proposed on-line IL-DLLME method [93].

In the case of Hg, an innovative method has been proposed for Hg-species separation and preconcentration based on headspace capture of Hg cold vapor into a CYPHOS IL 101 microdrop, followed by direct injection into ETAAS for elemental detection. The application of CYPHOS IL 101 as a sequestration phase for an atomic vapor provides a novel, simple approach for extraction and preconcentration of metal species. This new method, termed cold-vapor IL-assisted headspace single-drop microextraction (CV-IL-AHS-SDME), was used to determine inorganic and organic Hg species at trace levels in seawater, fish tissues, hair and wine with satisfactory analytical figures of merits (EF of 75, LOD of  $10 \text{ ng L}^{-1}$  and RSD of 4.6% at  $0.25 \mu\text{g L}^{-1}$  Hg and  $n = 10$ ) [73].

Also, Hg species have been determined in lake-water and river-water samples by Song et al. using IL-DLLME coupled to high-performance liquid chromatography-atomic fluorescence spectrometry (HPLC-AFS), with average recoveries for spiked samples of 96.9% for  $\text{Hg}^{2+}$ , 90.9% for  $\text{MeHg}^+$ , 90.5% for  $\text{EtHg}^+$ , and 92.3% for  $\text{PhHg}^+$  [13].

Jia et al. proposed a methodology for extraction of Hg species ( $\text{Hg}^{2+}$ ,  $\text{MeHg}^+$  and  $\text{EtHg}^+$ ) from liquid cosmetic samples with  $[\text{C}_6\text{mim}][\text{PF}_6]$  as extracting phase in DLLME. The final IL-enriched

phase was dissolved in methanol and finally injected into the HPLC-ICP-MS system for separation and detection. Recoveries for spiked analytes in real samples were in the range 86.7–101.2% [71].

In a different approach, Stanisz et al. proposed a TSIL-USA-DLLME method combined with cold vapor atomic absorption spectrometry (CV-AAS) to determine Hg species ( $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$ ) in lake water, seawater and tap water, and fish tissue. Coordination agents commonly used for Hg extraction, such as DTZ, DDTC, APDC, 5-Br-PADAP or TMK, were avoided using a TSIL [methyltrioctylammonium thiosalicylate (TOMAS)] as disperser and extraction solvent [156].

Determination of Cr inorganic species is one of the most reported practices using IL-LLME coupled to different detectors. Due to the toxicological interest in Cr species determination in natural water, these samples are the most commonly analyzed with IL-LLME.

Lopez-García et al. proposed a methodology based on ISFME with  $[\text{C}_8\text{mim}][\text{NTf}_2]$  IL, obtaining an EF and an LOD of 300 and  $2 \text{ ng L}^{-1}$ , respectively. The method was applied for analysis of water samples and lixiviates obtained from plastic toys with recoveries within 95–104% [62]. Moreover, the same IL was used in DLLME to determine Cr species in real water samples (laboratory water, purification water and lake water). Under optimized conditions, the LODs for Cr(III) and Cr(VI) were  $1.00 \mu\text{g L}^{-1}$  and  $0.41 \mu\text{g L}^{-1}$ , with RSDs for Cr(III) and Cr(VI) of 3.3% and 4.0% ( $n = 5$ ), respectively [59].

A salt-assisted LLME of cationic complexes of Cr(VI) ion was also proposed using the hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate  $[\text{C}_4\text{mim}][\text{BF}_4]$  and potassium hydrogen phosphate. The method was successfully applied to Cr species determination in environmental water samples containing high levels of dissolved salts or food-grade salts [56]. Another technique recently proposed for Cr species determination in aqueous solution with high salt content has been TA-DLLME, using  $[\text{C}_6\text{mim}][\text{PF}_6]$  as extractant. Under the optimal conditions, LODs of  $5.40 \text{ ng L}^{-1}$  and  $2.45 \text{ ng L}^{-1}$  for Cr(III) and Cr(VI) ions, respectively, and an EF of 42 were obtained. The method was successfully applied for the determination of Cr species in tap and underground water and urine samples [61].

Finally, an alternative method for the speciation of Cr(VI) and Cr(III) with the IL-HF-LLME technique has been developed. The addition of ILs led to a 3.5-fold enhancement in FAAS sensitivity in the determination of Cr(VI). Under optimal conditions, an LOD of  $0.7 \text{ ng mL}^{-1}$  and an EF of 175 were achieved. The proposed method was successfully applied for speciation of Cr in natural water samples [57].

Inorganic As species have been extracted by IL-DLLME using 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  $[\text{C}_4\text{mim}][\text{NTf}_2]$  IL as extractant. The highest EF obtained with this method was 255. Application of the method was successful in tap-water and river-water samples with relative analytical recoveries in the range 93.3–102% [14]. Also, As species have been determined in mono-varietal wines with on-line IL-DLLME using 1-octyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_8\text{mim}][\text{PF}_6]$ ) IL. The extraction efficiency for As(III) species was 100% and a sensitivity EF of 46 was obtained with only 4.0 mL of sample [29].

Finally, Co is widely known as an essential trace element in nature, with an important role in many body functions, as a component of vitamin B<sub>12</sub>. However, unnecessary administration of Co(II) salts causes adverse side effects, since their accumulation promotes organ damage and dysfunction due to enhanced oxidative stress [157]. Since Co determination is therefore an important toxicological assay, different IL-LLME techniques were recently proposed for Co speciation. Inorganic Co(II) species was extracted in a variety of nutrient supplements using  $[\text{C}_6\text{mim}][\text{PF}_6]$  as extractant phase with the USA-TILDLLME technique. The main difficulty in these samples was caused by high concentrations of potential

interfering ions. The LOD was  $5.4 \text{ ng L}^{-1}$ , while the RSD was 4.7% ( $n = 10$ ). Selective microextraction of inorganic Co species was achieved simply by controlling the pH during the procedure [46].

In a different study, an organic Co species (vitamin B<sub>12</sub>) was extracted from urine samples using the ATPS technique. The proposed ATPS-based method involved the application of the hydrophilic  $[\text{C}_6\text{mim}]\text{Cl}$  IL and  $\text{K}_2\text{HPO}_4$  salt to cause formation of a biphasic system. The average extraction efficiency was 97% under optimal conditions, with an LOD of  $0.09 \mu\text{g mL}^{-1}$  and an RSD of 4.50% ( $n = 10$ ) [116].

#### 4. Environmental and health aspects

Due to the unique properties of ILs, such as high thermal stability and low volatility, there is significant interest in incorporating them into technological processes with small scale to industrial applications. However, such increased usage implies the need for cautious procedures to avoid the release of ILs into the environment. Although ILs minimize the risk of air pollution due to negligible vapor pressure, the threat of discharging these solvents into wastewaters and, by accident, directly into soils, surface water or groundwater, is higher.

Recent efforts leading to better assessments of ILs in terms of their potential effects on the environment indicate that their structure strongly conditions their “greenness” and biodegradability [158]. In 2010, Thuy Pam et al. published a comprehensive review about fate, removal options, and (eco)toxicological assessment strategies of ILs [159]. After a systematic gathering and analysis of existing information, the authors concluded that ILs commonly used to date cannot be classified as non-toxic and “readily biodegradable”, and that their toxicities vary considerably across organisms and trophic levels [159]. Nevertheless, an aspect to consider is that the large number of existing and potential ILs provide large opportunities to design and to develop environmentally benign ILs with specific physical, chemical and biological properties. Structural design of ILs with substantially improved biodegradability has been found feasible using IL cations, such as cholinium or pyridinium compounds substituted with alkyl chains containing an ester group in position 1 or 3 or a terminal hydroxyl group, and anions, such as octylsulfate or cholate, acetate, propionate or benzoate [160]. Despite these alternatives, ILs with better biodegradability or lower toxicity have not yet been used radically to develop microextraction techniques.

Another aspect to consider is the improvements in stability, regeneration and recyclability of the used ILs [161]. For treatment of ILs, the waste hierarchy expressed as “Re-duce, Re-use, Re-cycle” proposed by the European Union (EU) Directive 2008/98/EC should be followed [162]. Methods of regeneration, recovery and removal of ILs, along with their biodegradability, toxicity and sorption in the environment have been extensively discussed by Siedlecka et al. and Fernandez et al [163,164].

LLME techniques follow the first concept (Re-duce) established by the EU Directive, since only minimal amounts of substances are used in the process. If possible, the extractant phase should then be reused and eventually recovered from the waste stream. Also, regeneration is often necessary if their direct reutilization is not possible. However, the majority of microextraction techniques based on ILs for metal determination involves the complete injection of the IL phase into atomic spectrometers, where the high temperatures decompose the organic phase. Only a few IL-LPME techniques reported in the period 2010–13 evaluated the possibility of recovery, regeneration and recycling of ILs. As remarked by Wu et al., even when a key property responsible for the increasing popularity of ILs has been their easy recyclability, it has not yet been extensively studied [165]. This is the case of a method proposed for B extraction and determination: TSIL regeneration after extraction was achieved by treating the IL complex with an acidic aqueous

solution (HCl) for only 60 s. The extraction efficiency achieved using the same TSIL after multiple extraction and regeneration cycles (a maximum of three cycles) was very stable, indicating that the TSIL can be effectively re-used after stripping the borate ion from the IL complex during regeneration [151]. Another approach has been proposed by Majidi and Shemirani, who suggested an easy stripping of  $\text{Au}^{3+}$  from the IL  $[\text{C}_6\text{mim}]\text{PF}_6$  using a dilute, low-acidity solution. Furthermore, to avoid IL loss during the extraction process, the authors proposed the addition of  $[\text{C}_6\text{mim}^+]$  to the initial  $\text{Au}^{3+}$  solutions and/or the use of a  $\text{KPF}_6$  solution as stripping agent. Since  $[\text{C}_6\text{mim}]\text{PF}_6$  acted as an anion exchanger during the extraction process of  $\text{Au}^{3+}$  in an acidic medium, the anion was recovered during the stripping process. Therefore,  $[\text{C}_6\text{mim}][\text{PF}_6]$  could be reused for at least 10 cycles of the extraction-stripping process [33].

Due to the usually high costs of ILs and the environmental and financial policy of the EU Waste Framework Directive legislation, companies strive to extend the lifetime of ILs as long as possible. Thus, microextraction techniques might contribute to IL applications in industrial extraction processes, which require high extraction efficiency and low extractant consumption. Furthermore, recycling after regeneration or recovery is of critical importance, not only to define the economic convenience of using IL-based microextraction processes in industry, but also because of the environmental concerns regarding IL disposal, biodegradation and toxicity. These are indeed regularly issues to be considered during the daily work of analytical laboratories.

## 5. Conclusion and future trends

There is an increasing demand for novel sample-preparation techniques in analytical chemistry to achieve efficient extraction and preconcentration of several analytes, including trace elements. In recent years, many efforts have been oriented to reduce the scale of liquid-liquid extraction techniques and explore new options to replace traditional volatile organic solvents. Thus, the synergy obtained by combining ILs with LLME techniques is increasingly being accepted in sample preparation. Different microextraction techniques, such as DLLME, ISFME, TA-DLLME, and IL-assisted ion-pairing LLME, have emerged as viable sample-preparation approaches due to their simplicity, rapidity and adaptability to a wide variety of samples and analytes. The use of ILs as solvents for LLME has allowed sensitivity and selectivity enhancement of methods for extraction and preconcentration of metal species, and application to analysis of different matrix samples. Furthermore, methods with excellent analytical performance have resulted from coupling IL-LLME to major instrumental analytical techniques. However, although some progress has been made to automate IL-LLME, further research is still needed to exploit its capabilities in chemical analysis. Also, the attachment of functional groups to chemical structures of ILs is a convenient strategy to provide highly selective, direct extraction of trace elements, but needs to be further developed.

ILs are better choices than volatile organic solvents due to their negligible vapor pressure, the possibilities to tune their chemical structure and their versatility compared to conventional organic solvents. Thus, higher EFs and analytical recoveries could be obtained after application of ILs in LLME, making possible sensitive and accurate determinations. However, future application of ILs in sample preparation strongly depends on overcoming some issues, such as toxicity, and reducing the biodegradability of some ILs. More efforts still are needed to solve these problems, so a real contribution to promote the progress of sample preparation in analytical chemistry would be that future developments in LLME progressively incorporate recycling and reutilization of IL wastes.

## Acknowledgements

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (FONCYT) (PICT-BID) and Universidad Nacional de Cuyo (Argentina).

## References

- [1] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the significance mnemonic of green analytical practices, *TrAC, Trends Anal. Chem.* 50 (2013) 78–84.
- [2] M. Koel, M. Kaljurand, Application of the principles of green chemistry in analytical chemistry, *Pure Appl. Chem.* 78 (2006) 1993–2002.
- [3] S. Armenta, S. Garrigues, M. de la Guardia, Green analytical chemistry, *TrAC, Trends Anal. Chem.* 27 (2008) 497–511.
- [4] M.D.L. Guardia, S. Garrigues, Challenges in Green Analytical Chemistry, RSC Publishing, Cambridge, 2011.
- [5] J. Pawliszyn, S. Pedersen-Bjergaard, Analytical microextraction: current status and future trends, *J. Chromatogr. Sci.* 44 (2006) 291–307.
- [6] D. Han, K.H. Row, Trends in liquid-phase microextraction, and its application to environmental and biological samples, *Microchim. Acta* 176 (2012) 1–22.
- [7] J.F. Liu, G.B. Jiang, J.A. Jönsson, Application of ionic liquids in analytical chemistry, *TrAC, Trends Anal. Chem.* 24 (2005) 20–27.
- [8] E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, The roles of ionic liquids in sorptive microextraction techniques, *TrAC, Trends Anal. Chem.* 27 (2010) 602–616.
- [9] P. Sun, D.W. Armstrong, Ionic liquids in analytical chemistry, *Anal. Chim. Acta* 661 (2010) 1–16.
- [10] X. Han, D.W. Armstrong, Ionic liquids in separations, *Acc. Chem. Res.* 40 (2007) 1079–1086.
- [11] V. Vičkačkaite, A. Padaruskas, Ionic liquids in microextraction techniques, *Cent. Eur. J. Chem.* 10 (2012) 652–674.
- [12] E.M. Martinis, P. Berton, R.P. Monasterio, R.G. Wuilloud, Emerging ionic liquid-based techniques for total-metal and metal-speciation analysis, *TrAC, Trends Anal. Chem.* 29 (2010) 1184–1201.
- [13] X. Song, M. Ye, X. Tang, C. Wang, Ionic liquids dispersive liquid-liquid microextraction and HPLC-atomic fluorescence spectrometric determination of mercury species in environmental waters, *J. Sep. Sci.* 36 (2013) 414–420.
- [14] S. Babieh, M. Bagheri, B. Planer-Friedrich, Speciation of arsenite and arsenate by electrothermal AAS following ionic liquid dispersive liquid-liquid microextraction, *Microchim. Acta* 180 (2013) 415–421.
- [15] M. Chamsaz, A. Atarodi, M. Eftekhari, S. Asadpour, M. Adibi, Vortex-assisted ionic liquid microextraction coupled to flame atomic absorption spectrometry for determination of trace levels of cadmium in real samples, *J. Adv. Res.* 4 (2013) 35–41.
- [16] B. Hu, M. He, B. Chen, L. Xia, Liquid phase microextraction for the analysis of trace elements and their speciation, *Spectrochim. Acta B* 86 (2013) 14–30.
- [17] M.S. El-Shahawi, H.M. Al-Saidi, Dispersive liquid-liquid microextraction for chemical speciation and determination of ultra-trace concentrations of metal ions, *TrAC, Trends Anal. Chem.* 44 (2013) 12–24.
- [18] E. Stanis, A. Zgoła-Grzeškowiak, In situ metathesis ionic liquid formation dispersive liquid-liquid microextraction for copper determination in water samples by electrothermal atomic absorption spectrometry, *Talanta* 115 (2013) 178–183.
- [19] L.B. Escudero, R.G. Wuilloud, R.A. Olsina, Sensitive determination of thallium species in drinking and natural water by ionic liquid-assisted ion-pairing liquid-liquid microextraction and inductively coupled plasma mass spectrometry, *J. Hazard. Mater.* 244–245 (2013) 380–386.
- [20] E. Wanigasekara, S. Perera, J. Crank, L. Sidisky, R. Shirey, A. Berthod, et al., Bonded ionic liquid polymeric material for solid-phase microextraction GC analysis, *Anal. Bioanal. Chem.* 396 (2010) 511–524.
- [21] G. Absalan, M. Akhond, L. Sheikhan, D.M. Goltz, Temperature-controlled ionic liquid-based dispersive liquid-phase microextraction, preconcentration and quantification of nano-amounts of silver ion by using disulfiram as complexing agent, *Anal. Methods* 3 (2011) 2354–2359.
- [22] M.D.M. Abadi, M. Chamsaz, M.H. Arbab-Zavar, Ionic liquid-based dispersive liquid-liquid microextraction combined with flame atomic absorption spectrometry for determination of silver in water samples, *Asia J. Chem.* 25 (2013) 3984–3988.
- [23] M. Vaezzadeh, F. Shemirani, B. Majidi, Determination of silver in real samples using homogeneous liquid-liquid microextraction based on ionic liquid, *J. Anal. Chem.* 67 (2012) 28–34.
- [24] H. Ashkenani, M.A. Taher, Use of ionic liquid in simultaneous microextraction procedure for determination of gold and silver by ETAAS, *Microchem. J.* 103 (2012) 185–190.
- [25] H. Abdolmohammad-Zadeh, G.H. Sadeghi, Combination of ionic liquid-based dispersive liquid-liquid micro-extraction with stopped-flow spectrofluorometry for the pre-concentration and determination of aluminum in natural waters, fruit juice and food samples, *Talanta* 81 (2010) 778–785.
- [26] J.B. Ghasemi, E. Zolfounoun, Ultrasound-assisted ionic liquid-based microextraction combined with least squares support vector machines regression for the simultaneous determination of aluminum, gallium, and

- indium in water and coal samples, *Environ. Monit. Assess.* 184 (2012) 3971–3981.
- [27] H. Shirkanloo, A. Rouhollahi, H.Z. Mousavi, Ultra-trace arsenic determination in urine and whole blood samples by flow injection-hydride generation atomic absorption spectrometry after preconcentration and speciation based on dispersive liquid-liquid microextraction, *Bull. Korean Chem. Soc.* 32 (2011) 3923–3927.
- [28] H. Shirkanloo, H.Z. Mousavi, A. Rouhollahi, Speciation and determination of trace amount of inorganic arsenic in water, environmental and biological samples, *J. Chin. Chem. Soc.* 58 (2011) 623–628.
- [29] L.B. Escudero, E.M. Martinis, R.A. Olsina, R.G. Wuilloud, Arsenic speciation analysis in mono-varietal wines by on-line ionic liquid-based dispersive liquid-liquid microextraction, *Food Chem.* 138 (2013) 484–490.
- [30] B. Majidi, F. Shemirani, In situ solvent formation microextraction in the presence of ionic liquid for preconcentration and speciation of arsenic in saline samples and total arsenic in biological samples by electrothermal atomic absorption spectrometry, *Biol. Trace Elem. Res.* 143 (2011) 579–590.
- [31] R.P. Monasterio, R.G. Wuilloud, Ionic liquid as ion-pairing reagent for liquid-liquid microextraction and preconcentration of arsenic species in natural waters followed by ETAAS, *J. Anal. At. Spectrom.* 25 (2010) 1485–1490.
- [32] M. Soylak, E. Yilmaz, Ionic liquid-based method for microextraction/enrichment of gold from real samples and determination by flame atomic absorption spectrometry, *At. Spectrosc.* 34 (2013) 15–19.
- [33] B. Majidi, F. Shemirani, Separation and determination of trace level of gold from hydrochloric acid solutions using ultrasound-assisted cold-induced aggregation microextraction, *Anal. Methods* 4 (2012) 1072–1077.
- [34] S. Mahpishanian, F. Shemirani, Ionic liquid-based modified cold-induced aggregation microextraction (M-CIAME) as a novel solvent extraction method for determination of gold in saline solutions, *Miner. Eng.* 23 (2010) 823–825.
- [35] C. Zeng, L. Tang, Determination of gold by flame atomic absorption spectrometry with hollow fiber liquid phase microextraction using room temperature ionic liquids, *Anal. Lett.* 46 (2013) 1442–1453.
- [36] M. Chamsaz, A. Sarafraz, F. Yazdi, Dousti, Vortex-assisted ionic liquid microextraction coupled to graphite furnace atomic absorption spectrometry for preconcentration and determination of trace levels of cadmium in real samples, *Asian J. Chem.* 25 (2013) 7543–7547.
- [37] M. Rajabi, M. Kamalabadi, M.R. Jamali, J. Zolgharnein, N. Asanjarani, Application of response surface methodology for optimization of ionic liquid-based dispersive liquid-liquid microextraction of cadmium from water samples, *Hum. Exp. Toxicol.* 32 (2013) 620–631.
- [38] X. Wen, Q. Deng, J. Wang, S. Yang, X. Zhao, A new coupling of ionic liquid based-single drop microextraction with tungsten coil electrothermal atomic absorption spectrometry, *Spectrochim. Acta A* 105 (2013) 320–325.
- [39] M. Chamsaz, M. Eftekhari, A. Atarodi, S. Asadpour, M. Ariani, Preconcentration procedure using vortex agitator system for determination of trace levels of cadmium by flame atomic absorption spectrometry, *J. Brazil. Chem. Soc.* 23 (2012) 1630–1635.
- [40] C. Zeng, Y. Hu, J. Luo, Ionic liquid-based hollow fiber supported liquid membrane extraction combined with thermospray flame furnace AAS for the determination of cadmium, *Microchim. Acta* 177 (2012) 53–58.
- [41] M. Mohamadi, A. Mostafavi, Flame atomic absorption determination of trace amounts of cadmium after preconcentration using a thiol-containing task-specific ionic liquid, *J. AOAC Int.* 94 (2011) 959–967.
- [42] S. Mahpishanian, F. Shemirani, Preconcentration procedure using in situ solvent formation microextraction in the presence of ionic liquid for cadmium determination in saline samples by flame atomic absorption spectrometry, *Talanta* 82 (2010) 471–476.
- [43] G.A. Kandhro, M. Soylak, T.G. Kazi, E. Yilmaz, H.I. Afridi, Room temperature ionic liquid-based microextraction for pre-concentration of cadmium and copper from biological samples and determination by FAAS, *At. Spectrosc.* 33 (2012) 166–172.
- [44] I. Lopez-Garcia, Y. Vicente-Martinez, M. Hernandez-Cordoba, Determination of lead and cadmium using an ionic liquid and dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry, *Talanta* 110 (2013) 46–52.
- [45] M. Shamsipur, M. Ramezani, A.A.M. Beigi, T. Poursaberi, Cold induced aggregation microextraction with an ionic liquid for trace determination of cadmium and lead in water samples, *Indian J. Chem., Sect. A* 51 (2012) 825–829.
- [46] P. Berton, E.M. Martinis, L.D. Martinez, R.G. Wuilloud, Selective determination of inorganic cobalt in nutritional supplements by ultrasound-assisted temperature-controlled ionic liquid dispersive liquid phase microextraction and electrothermal atomic absorption spectrometry, *Anal. Chim. Acta* 713 (2012) 56–62.
- [47] M.R. Jamali, B. Soleimani, R. Rahnama, S.H.A. Rahimi, Development of an in situ solvent formation microextraction and preconcentration method based on ionic liquids for the determination of trace cobalt (II) in water samples by flame atomic absorption spectrometry, *Arab. J. Chem.* (2012) in press.
- [48] S. Yousefi, S. Ahmadi, Development a robust ionic liquid-based dispersive liquid-liquid microextraction against high concentration of salt combined with flame atomic absorption spectrometry using microsample introduction system for preconcentration and determination of cobalt in water and saline samples, *Microchim. Acta* 172 (2011) 75–82.
- [49] P. Berton, R.G. Wuilloud, An online ionic liquid-based microextraction system coupled to electrothermal atomic absorption spectrometry for cobalt determination in environmental samples and pharmaceutical formulations, *Anal. Methods* 3 (2011) 664–672.
- [50] M. Amjadi, J.L. Manzoori, J. Abulhassani, Ionic liquid-based, single-drop microextraction for preconcentration of cobalt before its determination by electrothermal atomic absorption spectrometry, *J. AOAC Int.* 93 (2010) 985–991.
- [51] P. Berton, R.G. Wuilloud, Highly selective ionic liquid-based microextraction method for sensitive trace cobalt determination in environmental and biological samples, *Anal. Chim. Acta* 662 (2010) 155–162.
- [52] I. Razmislevičiene, V. Olšauskaite, A. Padarauskas, Ionic liquid-based dispersive liquid-liquid microextraction combined with ultra performance liquid chromatography for the determination of metal ions, *Chemija* 22 (2011) 197–203.
- [53] L. Ranjbar, Y. Yamini, A. Saleh, S. Seidi, M. Faraji, Ionic liquid based dispersive liquid-liquid microextraction combined with ICP-OES for the determination of trace quantities of cobalt, copper, manganese, nickel and zinc in environmental water samples, *Microchim. Acta* 177 (2012) 119–127.
- [54] F. Tadayon, M. Hanasaei, Determination of cobalt and nickel after modified-cold-induced aggregation microextraction based on ionic liquid in hair and water samples, *Stud. Univ. Babeş-Bolyai Chem.* 2013 (2013) 115–125.
- [55] R. Khani, F. Shemirani, Simultaneous determination of trace amounts of cobalt and nickel in water and food samples using a combination of partial least squares method and dispersive liquid-liquid microextraction based on ionic liquid, *Food Anal. Method* 6 (2013) 386–394.
- [56] B. Majidi, F. Shemirani, Salt-assisted liquid-liquid microextraction of Cr(VI) ion using an ionic liquid for preconcentration prior to its determination by flame atomic absorption spectrometry, *Microchim. Acta* 176 (2012) 143–151.
- [57] C. Zeng, Y. Lin, N. Zhou, J. Zheng, W. Zhang, Room temperature ionic liquids enhanced the speciation of Cr(VI) and Cr(III) by hollow fiber liquid phase microextraction combined with flame atomic absorption spectrometry, *J. Hazard. Mater.* 237–238 (2012) 365–370.
- [58] S. Nitiyanontakit, P. Varanusupakul, M. Miró, Hybrid flow analyzer for automatic hollow-fiber-assisted ionic liquid-based liquid-phase microextraction with in-line membrane regeneration, *Anal. Bioanal. Chem.* 405 (2013) 3279–3288.
- [59] S. Wen, J. Wu, X. Zhu, Room temperature ionic liquid-based dispersive liquid-liquid microextraction combined with flame atomic absorption spectrometry for the speciation of chromium(III) and chromium(VI), *J. Mol. Liq.* 180 (2013) 59–64.
- [60] M. Zeeb, M.R. Ganjali, P. Norouzi, Preconcentration and trace determination of chromium using modified ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction: application to different water and food samples, *Food Anal. Method* (2012) 1–9.
- [61] S. Sadeghi, A. Zeraatkar Moghaddam, Preconcentration and speciation of trace amounts of chromium in saline samples using temperature-controlled microextraction based on ionic liquid as extraction solvent and determination by electrothermal atomic absorption spectrometry, *Talanta* 99 (2012) 758–766.
- [62] I. Lopez-Garcia, Y. Vicente-Martinez, M. Hernandez-Cordoba, Determination of very low amounts of chromium(III) and (VI) using dispersive liquid-liquid microextraction by in situ formation of an ionic liquid followed by electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 27 (2012) 874–880.
- [63] H. Chen, P. Du, J. Chen, S. Hu, S. Li, H. Liu, Separation and preconcentration system based on ultrasonic probe-assisted ionic liquid dispersive liquid-liquid microextraction for determination trace amount of chromium(VI) by electrothermal atomic absorption spectrometry, *Talanta* 81 (2010) 176–179.
- [64] N.S. Amiri, F. Shemirani, R. Khani, Combination of cold-induced aggregation microextraction and central composite design for preconcentration and determination of copper in food and water samples, *Desalin. Water Treat.* 51 (2013) 4622–4629.
- [65] E. Stanisz, A. Grzeškowiak, In situ metathesis ionic liquid formation dispersive liquid-liquid microextraction for copper determination in water samples by electrothermal atomic absorption spectrometry, *Talanta* 115 (2013) 178–183.
- [66] Y. Fan, S. Zhang, F. Yang, H. Niu, J. Shi, Extraction behavior of copper(II) ion with a hydrophobic amino-functionalized ionic liquid, *Microchim. Acta* 177 (2012) 237–243.
- [67] M. Zeeb, M.R. Ganjali, P. Norouzi, M.R. Kalaei, Separation and preconcentration system based on microextraction with ionic liquid for determination of copper in water and food samples by stopped-flow injection spectrofluorimetry, *Food Chem. Toxicol.* 49 (2011) 1086–1091.
- [68] 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 A* 79 (2011) 1941–1945.
- [69] R. Khani, F. Shemirani, B. Majidi, Combination of dispersive liquid-liquid microextraction and flame atomic absorption spectrometry for preconcentration and determination of copper in water samples, *Desalination* 266 (2011) 238–243.
- [70] E. Stanisz, J. Werner, H. Matusiewicz, Mercury species determination by task specific ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction combined with cold vapor generation atomic absorption spectrometry, *Microchem. J.* 110 (2013) 28–35.
- [71] X. Jia, Y. Han, C. Wei, T. Duan, H. Chen, Speciation of mercury in liquid cosmetic samples by ionic liquid based dispersive liquid-liquid microextraction combined with high-performance liquid chromatography-inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 26 (2011) 1380–1386.

- [72] Z. Gao, X. Ma, Speciation analysis of mercury in water samples using dispersive liquid-liquid microextraction combined with high-performance liquid chromatography, *Anal. Chim. Acta* 702 (2011) 50–55.
- [73] E.M. Martinis, R.G. Wuilloud, Cold vapor ionic liquid-assisted headspace single-drop microextraction: a novel preconcentration technique for mercury species determination in complex matrix samples, *J. Anal. At. Spectrom.* 25 (2010) 1432–1439.
- [74] S. Wen, X. Zhu, Speciation Analysis of Mn(II)/Mn(VII) in Tea Samples Using Flame Atomic Absorption Spectrometry After Room Temperature Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction, *Food Anal. Method* (2013) 1–7.
- [75] M. Gharehbaghi, F. Shemirani, Ionic liquid-based dispersive liquid-liquid microextraction and enhanced spectrophotometric determination of molybdenum (VI) in water and plant leaves samples by FO-LADS, *Food Chem. Toxicol.* 49 (2011) 423–428.
- [76] P. Liang, L. Peng, Determination of nickel in water samples by graphite furnace atomic absorption spectrometry after ionic liquid-based dispersive liquid-liquid microextraction preconcentration, *At. Spectrosc.* 33 (2012) 53–58.
- [77] Z. Zarei, F. Shemirani, Determination of Nickel in Food Samples by Flame Atomic Absorption Spectroscopy after Preconcentration and Microextraction Based Ionic Liquids Using Full Factorial and Central Composite Design, *J. Food Sci.* 77 (2012) C1242–C1248.
- [78] H. Shirkhanloo, A. Rouhollahi, H.Z. Mousavi, Preconcentration and determination of trace amount of nickel in water and biological samples by dispersive liquid-liquid microextraction, *J. Chin. Chem. Soc.* 57 (2010) 1035–1041.
- [79] J. Abulhassani, J.L. Manzoori, M. Amjadi, Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry, *J. Hazard. Mater.* 176 (2010) 481–486.
- [80] H. Eskandari, In situ formed 1-hexyl-3-methylimidazolium hexafluorophosphate for dispersive liquid-liquid microextraction of Pd(II) prior to electrothermal AAS and spectrophotometry, *Turk. J. Chem.* 36 (2012) 631–643.
- [81] Z. Zarei, F. Shemirani, Modified-cold induced aggregation microextraction based on ionic liquid and fibre optic-linear array detection spectrophotometric determination of palladium in saline solutions, *Int. J. Environ. Anal. Chem.* 91 (2011) 1436–1446.
- [82] M. Vaezzadeh, F. Shemirani, B. Majidi, Microextraction technique based on ionic liquid for preconcentration and determination of palladium in food additive, sea water, tea and biological samples, *Food Chem. Toxicol.* 48 (2010) 1455–1460.
- [83] Z.A. Allothman, E. Yilmaz, M. Habila, A. Shabaka, M. Soy lak, Ligandless temperature-controlled ionic liquid-phase microextraction of lead(II) ion prior to its determination by FAAS, *Microchim. Acta* 180 (2013) 669–674.
- [84] F. Shah, E. Yilmaz, T.G. Kazi, H.I. Afridi, M. Soy lak, Vortex-assisted liquid-liquid microextraction coupled to flame atomic absorption spectrometry for lead determination: ionic liquid based microextraction using Triton X-100 as dispersant, *Anal. Methods* 4 (2012) 4091–4095.
- [85] F. Shah, T.G. Kazi, Naeemullah, H.I. Afridi, M. Soy lak, Temperature controlled ionic liquid-dispersive liquid phase microextraction for determination of trace lead level in blood samples prior to analysis by flame atomic absorption spectrometry with multivariate optimization, *Microchem. J.* 101 (2012) 5–10.
- [86] F. Shah, M. Soy lak, T.G. Kazi, H.I. Afridi, Single step in-syringe system for ionic liquid based liquid microextraction combined with flame atomic absorption spectrometry for lead determination, *J. Anal. At. Spectrom.* 27 (2012) 1960–1965.
- [87] M. Hosseini, N. Dalali, S.M. Nejad, A new mode of homogeneous liquid-liquid microextraction (HLLME) based on ionic liquids: in situ solvent formation microextraction (ISFME) for determination of lead, *J. Chin. Chem. Soc.* 59 (2012) 872–878.
- [88] M. Soy lak, E. Yilmaz, Ionic liquid dispersive liquid-liquid microextraction of lead as pyrrolidinedithiocarbamate chelate prior to its flame atomic absorption spectrometric determination, *Desalination* 275 (2011) 297–301.
- [89] E.M. Martinis, P. Bertón, J.C. Altamirano, U. Hakala, R.G. Wuilloud, Tetradecyl(trihexyl)phosphonium chloride ionic liquid single-drop microextraction for electrothermal atomic absorption spectrometric determination of lead in water samples, *Talanta* 80 (2010) 2034–2040.
- [90] H. Bai, Q. Zhou, G. Xie, J. Xiao, Temperature-controlled ionic liquid-liquid-phase microextraction for the pre-concentration of lead from environmental samples prior to flame atomic absorption spectrometry, *Talanta* 80 (2010) 1638–1642.
- [91] X. Wen, Q. Deng, J. Wang, X. Zhao, Application of portable spectrometer for ultra trace metal analysis after ionic liquid based microextraction, *Anal. Methods* 5 (2013) 2978–2983.
- [92] E. Molaakbari, A. Mostafavi, D. Afzali, Ionic liquid ultrasound assisted dispersive liquid-liquid microextraction method for preconcentration of trace amounts of rhodium prior to flame atomic absorption spectrometry determination, *J. Hazard. Mater.* 185 (2011) 647–652.
- [93] E.M. Martinis, L.B. Escudero, P. Berton, R.P. Monasterio, M.F. Filippini, R.G. Wuilloud, Determination of inorganic selenium species in water and garlic samples with on-line ionic liquid dispersive microextraction and electrothermal atomic absorption spectrometry, *Talanta* 85 (2011) 2182–2188.
- [94] M. Amjadi, J.L. Manzoori, V. Hamedpour, Optimized ultrasound-assisted temperature-controlled ionic liquid microextraction coupled with FAAS for determination of tin in canned foods, *Food Anal. Method* (2013) 1–8.
- [95] A.N. Anthemidis, K.I.G. Ioannou, Sequential injection ionic liquid dispersive liquid-liquid microextraction for thallium preconcentration and determination with flame atomic absorption spectrometry, *Anal. Bioanal. Chem.* 404 (2012) 685–691.
- [96] L.B. Escudero, P. Berton, E.M. Martinis, R.A. Olsina, R.G. Wuilloud, Dispersive liquid-liquid microextraction and preconcentration of thallium species in water samples by two ionic liquids applied as ion-pairing reagent and extractant phase, *Talanta* 88 (2012) 277–283.
- [97] P. Berton, E.M. Martinis, R.G. Wuilloud, Development of an on-line temperature-assisted ionic liquid dispersive microextraction system for sensitive determination of vanadium in environmental and biological samples, *J. Hazard. Mater.* 176 (2010) 721–728.
- [98] M. Hosseini, N. Dalali, S.M. Nejad, R. Jamali, In situ solvent formation microextraction based on ionic liquids and 1-(2-Hydroxynaphtalene-1-yl)ethane oxime for determination of zinc, *J. Brazil. Chem. Soc.* 23 (2012) 78–84.
- [99] M. Zeeb, M. Sadeghi, Modified ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction followed by atomic absorption spectrometry for trace determination of zinc in water and food samples, *Microchim. Acta* 175 (2011) 159–165.
- [100] M. Cruz-Vera, R. Lucena, S. Cárdenas, M. Valcárcel, One-step in-syringe ionic liquid-based dispersive liquid-liquid microextraction, *J. Chromatogr. A* 1216 (2009) 6459–6465.
- [101] M.C. Breadmore, Ionic liquid-based liquid phase microextraction with direct injection for capillary electrophoresis, *J. Chromatogr. A* 1218 (2011) 1347–1352.
- [102] H. Shirkhanloo, A. Rouhollahi, H.Z. Mousavi, Ultra-trace arsenic determination in urine and whole blood samples by flow injection-hydride generation atomic absorption spectrometry after preconcentration and speciation based on dispersive liquid-liquid microextraction, *B. Korean Chem. Soc.* 32 (2010) 3923–3927.
- [103] S. Chun, S.V. Dzyuba, R.A. Bartsch, Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether, *Anal. Chem.* 73 (2001) 3737–3741.
- [104] C.A. Hawkins, S.L. Garvey, M.L. Dietz, Structural variations in room-temperature ionic liquids: influence on metal ion partitioning modes and extraction selectivity, *Sep. Purif. Technol.* 89 (2012) 31–38.
- [105] M. Regel-Rosocka, M. Wisniewski, P.S. Handy (Editor), Applications of Ionic Liquids in Science and Technology, *InTech*, 2011, pp. 375–398.
- [106] A.E. Visser, R.P. Swatoski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, et al., Task-specific ionic liquids for the extraction of metal ions from aqueous solutions, *Chem. Commun.* 135–136 (2001).
- [107] G. Fang, J. Zhang, J. Lu, L. Ma, S. Wang, Preparation, characterization, and application of a new thiol-functionalized ionic liquid for highly selective extraction of Cd(II), *Microchim. Acta* 171 (2010) 305–311.
- [108] P. Nockemann, M. Pellens, K. Van Hecke, L. Van Meervelt, J. Wouters, B. Thijs, et al., Cobalt(II) complexes of nitrile-functionalized ionic liquids, *Chem. Eur. J.* 16 (2010) 1849–1858.
- [109] A. Sarafraz-Yazdi, A. Amiri, Liquid-phase microextraction, *TrAC, Trends Anal. Chem.* 29 (2010) 1–14.
- [110] X. Xu, R. Su, X. Zhao, Z. Liu, Y. Zhang, D. Li, et al., Ionic liquid-based microwave-assisted dispersive liquid-liquid microextraction and derivatization of sulfonamides in river water, honey, milk, and animal plasma, *Anal. Chim. Acta* 707 (2011) 92–99.
- [111] X. Xu, R. Su, X. Zhao, Z. Liu, D. Li, X. Li, et al., Determination of formaldehyde in beverages using microwave-assisted derivatization and ionic liquid-based dispersive liquid-liquid microextraction followed by high-performance liquid chromatography, *Talanta* 85 (2011) 2632–2638.
- [112] X. Xu, Z. Liu, X. Zhao, R. Su, Y. Zhang, J. Shi, et al., Ionic liquid-based microwave-assisted surfactant-improved dispersive liquid-liquid microextraction and derivatization of aminoglycosides in milk samples, *J. Sep. Sci.* 36 (2013) 585–592.
- [113] R. Wang, P. Su, Y. Yang, Optimization of ionic liquid-based microwave-assisted dispersive liquid-liquid microextraction for the determination of plasticizers in water by response surface methodology, *Anal. Methods* 5 (2013) 1033–1039.
- [114] L.B. Agudelo Mesa, J.M. Padró, M. Reta, Analysis of non-polar heterocyclic aromatic amines in beefburguers by using microwave-assisted extraction and dispersive liquid-ionic liquid microextraction, *Food Chem.* 141 (2013) 1694–1701.
- [115] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, *Spectrochim. Acta B* 64 (2009) 666–671.
- [116] P. Berton, R.P. Monasterio, R.G. Wuilloud, Selective extraction and determination of vitamin B12 in urine by ionic liquid-based aqueous two-phase system prior to high-performance liquid chromatography, *Talanta* 97 (2012) 521–526.
- [117] R. Giernoth, *Angewandte Chemie International Edition*, WILEY-VCH Verlag, 2010, pp. 2834–2839.
- [118] C. Biao, L. Quan, Z. Baozhong, Application of magnetic ionic liquids, *Progr. Chem.* 24 (2012) 225–234.
- [119] S. Lee, S. Ha, C.-Y. You, Y.-M. Koo, Recovery of magnetic ionic liquid [bmim]FeCl<sub>4</sub> using a supermagnet, *Korean J. Chem. Eng.* 24 (2007) 436–437.
- [120] N. Deng, M. Li, L. Zhao, C. Lu, S.L. de Rooy, I.M. Warner, Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic



- liquids for environmental remediation, *J. Hazard. Mater.* 192 (2011) 1350–1357.
- [121] A. Stojanovic, C. Morgenbesser, D. Kogelnig, R. Krachler, B.K. Keppler, A. Kokorin (Editor), *Ionic Liquids: Theory, Properties, New Approaches*, Intech, 2011, pp. 657–680.
- [122] D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler, B.K. Keppler, Transport and separation of iron(III) from nickel(II) with the ionic liquid trihexyl(tetradecyl)phosphonium chloride, *Sep. Purif. Technol.* 72 (2010) 56–60.
- [123] A. Cieszyńska, M. Wiśniewski, Extractive recovery of palladium(II) from hydrochloric acid solutions with CyphosIL 104, *Hydrometallurgy* 113–114 (2012) 79–85.
- [124] A. Cieszyńska, M. Wisniewski, Extraction of palladium(II) from chloride solutions with CyphosIL 101/toluene mixtures as novel extractant, *Sep. Purif. Technol.* 73 (2010) 202–207.
- [125] M. Regel-Rosocka, Extractive removal of zinc(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants, *Sep. Purif. Technol.* 66 (2009) 19–24.
- [126] B. Marszałkowska, M. Regel-Rosocka, Ł. Nowak, M. Wiśniewski, Quaternary phosphonium salts as effective extractants of zinc(II) and iron(III) ions from acidic pickling solutions, *Pol. J. Chem. Technol.* 12 (2010) 1–5.
- [127] M. Regel-Rosocka, M. Wisniewski, Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101, *Hydrometallurgy* 110 (2011) 85–90.
- [128] M. Regel-Rosocka, Ł. Nowak, M. Wiśniewski, Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids, *Sep. Purif. Technol.* 97 (2012) 158–163.
- [129] A. Cieszyńska, M. Wisniewski, Selective extraction of palladium(II) from hydrochloric acid solutions with phosphonium extractants, *Sep. Purif. Technol.* 80 (2011) 385–389.
- [130] M. Regel-Rosocka, A. Cieszyńska, M. Wiśniewski, Methods of regeneration of spent pickling solutions from steel treatment plants, *Pol. J. Chem. Technol.* 9 (2007) 42–45.
- [131] A. Cieszyńska, M. Regel-Rosocka, M. Wiśniewski, Extraction of Palladium(II) ions from chloride solutions with phosphonium ionic liquid CyphosIL101, *Pol. J. Chem. Technol.* 9 (2007) 99–101.
- [132] P. Rybka, M. Regel-Rosocka, Nickel(II) and Cobalt(II) extraction from chloride solutions with quaternary phosphonium salts, *Sep. Sci. Technol.* 47 (2012) 1296–1302.
- [133] A.A. Nayl, Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336, *J. Hazard. Mater.* 173 (2010) 223–230.
- [134] J.-Y. Lee, J.R. Kumar, J.-S. Kim, D.-J. Kim, H.-S. Yoon, Extraction and separation of Pt(IV)/Rh(III) from acidic chloride solutions using Aliquat 336, *J. Ind. Eng. Chem.* 15 (2009) 359–364.
- [135] S. Katsuta, Y. Yoshimoto, M. Okai, Y. Takeda, K. Bessho, Selective extraction of palladium and platinum from hydrochloric acid solutions by trioctylammonium-based mixed ionic liquids, *Ind. Eng. Chem. Res.* 50 (2011) 12735–12740.
- [136] E. Guibal, K.C. Gavilan, P. Bunio, T. Vincent, A. Trochimczuk, CYPHOS IL 101 (Tetradecyl(Trihexyl)Phosphonium Chloride) immobilized in biopolymer capsules for Hg(II) recovery from HCl solutions, *Sep. Sci. Technol.* 43 (2008) 2406–2433.
- [137] K. Campos, T. Vincent, P. Bunio, A. Trochimczuk, E. Guibal, Gold recovery from HCl solutions using cyphos IL-101 (a Quaternary phosphonium ionic liquid) immobilized in biopolymer capsules, *Solvent Extr. Ion Exch.* 26 (2008) 570–601.
- [138] T. Vincent, A. Parodi, E. Guibal, Pt recovery using Cyphos IL-101 immobilized in biopolymer capsules, *Sep. Purif. Technol.* 62 (2008) 470–479.
- [139] T. Vincent, A. Parodi, E. Guibal, Immobilization of Cyphos IL-101 in biopolymer capsules for the synthesis of Pd sorbents, *React. Funct. Polym.* 68 (2008) 1159–1169.
- [140] E. Guibal, A.F. Piñol, M. Ruiz, T. Vincent, C. Jouannin, A.M. Sastre, Immobilization of cyphos ionic liquids in alginate capsules for Cd(II) sorption, *Sep. Sci. Technol.* 45 (2010) 1935–1949.
- [141] K. Campos, R. Domingo, T. Vincent, M. Ruiz, A.M. Sastre, E. Guibal, Bismuth recovery from acidic solutions using Cyphos IL-101 immobilized in a composite biopolymer matrix, *Water Res.* 42 (2008) 4019–4031.
- [142] V. Gallardo, R. Navarro, I. Saucedo, M. Ávila, E. Guibal, Zinc(II) extraction from hydrochloric acid solutions using amberlite XAD-7 impregnated with cyphos IL 101 (Tetradecyl(Trihexyl)Phosphonium Chloride), *Sep. Sci. Technol.* 43 (2008) 2434–2459.
- [143] R. Navarro, I. Saucedo, M.A. Lira, E. Guibal, Gold(III) recovery from HCl solutions using amberlite XAD-7 impregnated with an ionic liquid (Cyphos IL-101), *Sep. Sci. Technol.* 45 (2010) 1950–1962.
- [144] R. Navarro, I. Saucedo, C. Gonzalez, E. Guibal, Amberlite XAD-7 impregnated with Cyphos IL-101 (tetraalkylphosphonium ionic liquid) for Pd(II) recovery from HCl solutions, *Chem. Eng. J.* 185–186 (2012) 226–235.
- [145] A. Arias, I. Saucedo, R. Navarro, V. Gallardo, M. Martínez, E. Guibal, Cadmium(II) recovery from hydrochloric acid solutions using Amberlite XAD-7 impregnated with a tetraalkyl phosphonium ionic liquid, *React. Funct. Polym.* 71 (2011) 1059–1070.
- [146] R. Navarro, V. Gallardo, I. Saucedo, E. Guibal, Extraction of Fe(III) from hydrochloric acid solutions using Amberlite XAD-7 resin impregnated with trioctylphosphine oxide (Cyanex 921), *Hydrometallurgy* 98 (2009) 257–266.
- [147] Y. Liu, L. Guo, L. Zhu, X. Sun, J. Chen, Removal of Cr(III, VI) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials, *Chem. Eng. J.* 158 (2010) 108–114.
- [148] L. Guo, Y. Liu, C. Zhang, J. Chen, Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr(VI) transport, *J. Membrane Sci.* 372 (2011) 314–321.
- [149] S. Kalidhasan, A. Santhana Krishna Kumar, V. Rajesh, N. Rajesh, Enhanced adsorption of hexavalent chromium arising out of an admirable interaction between a synthetic polymer and an ionic liquid, *Chem. Eng. J.* 222 (2013) 454–463.
- [150] S.R. Yousefi, F. Shemirani, Development of a robust ionic liquid-based dispersive liquid-liquid microextraction against high concentration of salt for preconcentration of trace metals in saline aqueous samples: application to the determination of Pb and Cd, *Anal. Chim. Acta* 669 (2010) 25–31.
- [151] M.D. Joshi, D.J. Steyer, J.L. Anderson, Evaluating the complexation behavior and regeneration of boron selective glucamine-based ionic liquids when used as extraction solvents, *Anal. Chim. Acta* 740 (2012) 66–73.
- [152] V. Meysam, F. Shemirani, B. Majidi, Microextraction technique based on ionic liquid for preconcentration and determination of palladium in food additive, sea water, tea and biological samples, *Food Chem. Toxicol.* 48 (2010) 1455–1460.
- [153] M. Esteban, A. Castaño, Non-invasive matrices in human biomonitoring: a review, *Environ. Int.* 35 (2009) 438–449.
- [154] C. Stalikos, Y. Fiamegos, V. Sakkas, T. Albanis, Developments on chemometric approaches to optimize and evaluate microextraction, *J. Chromatogr. A* 1216 (2009) 175–189.
- [155] J. Ghasemi, E. Zolfonoun, Ultrasound-assisted ionic liquid-based microextraction combined with least squares support vector machines regression for the simultaneous determination of aluminum, gallium, and indium in water and coal samples, *Environ. Monit. Assess.* 184 (2012) 3971–3981.
- [156] E. Stanisz, J. Werner, H. Matusiewicz, Mercury species determination by task specific ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction combined with cold vapor generation atomic absorption spectrometry, *Microchem. J.* 110 (2013) 28–35.
- [157] D.G. Barceloux, Cobalt, *Clin. Toxicol.* 37 (1999) 201–216.
- [158] B. Peric, E. Marti, J. Sierra, R. Cruaños Terradas, M.A. Garau, Green chemistry: ecotoxicity and biodegradability of ionic liquids, in: D. Muñoz-Torrero, D. Haro, J. Vallès (Editors), *Recent Advances in Pharmaceutical Sciences II*, Transworld Research Network, 2012, pp. 89–113.
- [159] T.P. Thuy Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: a review, *Water Res.* 44 (2010) 352–372.
- [160] N. Gathergood, P.J. Scammells, M.T. Garcia, Biodegradable ionic liquids Part III. The first readily biodegradable ionic liquids, *Green Chem.* 8 (2006) 156–160.
- [161] Y. Zhang, B.R. Bakshi, E.S. Demessie, Life cycle assessment of an ionic liquid versus molecular solvents and their applications, *Am. Chem. Soc.* 42 (2008) 1724–1730.
- [162] E. Union, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives, *Official Journal of the European Communities* (2008).
- [163] E.M. Siedlecka, M. Czerwicka, J. Neumann, P. Stepnowski, J.F. Fernández, J. Thöming, A. Kokorin (Editor), *Ionic Liquids: Theory, Properties, New Approaches*, Intech, 2011, pp. 701–722.
- [164] J.F. Fernandez, J. Neumann, J. Thoming, Regeneration, recovery and removal of ionic liquids, *Curr. Org. Chem.* 15 (2011) 1992–2014.
- [165] B. Wu, W. Liu, Y. Zhang, H. Wang, Do we understand the recyclability of ionic liquids?, *Chem. Eur. J.* 15 (2009) 1804–1810.