



Ionic liquid-based microextraction techniques for trace-element analysis



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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.

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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 (μL 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

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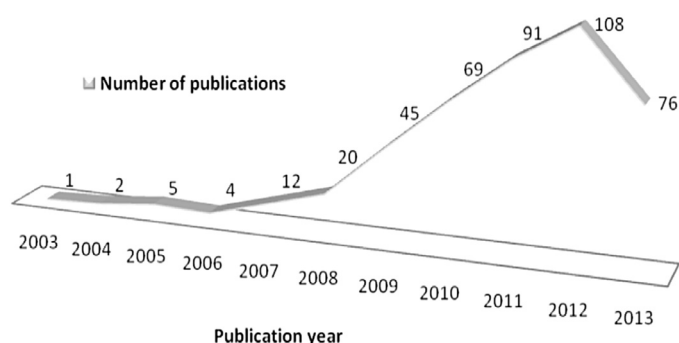


Fig. 1. Number of articles published in the period 2003–13 related to the application of ionic liquids (ILs) in microextraction techniques. Data generated from a search performed in Scopus database (<http://www.scopus.com>) using the terms “ionic liquid” and “microextraction” as search filter.

(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

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