Trends in Analytical Chemistry 61 (2014) 54–66

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Liquid-phase microextraction techniques based on ionic liquids for preconcentration and determination of metals

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A R T I C L E I N F O

Keywords:
Dispersive liquid-liquid microextraction
Hollow-fiber liquid-phase microextraction
Inorganic analysis
Ionic liquid
Liquid-phase microextraction
Metal determination
Preconcentration
Sample preparation
Single-drop microextraction
Speciation analysis

A B S T R A C T

Current trends in analytical chemistry are leading to miniaturization and reduction in the cost of chemical analysis. Rapid development of traditional liquid-liquid extraction towards liquid-phase microextraction (LPME) is a direct consequence of these trends. Considerable reduction of solvents and waste has been achieved and the number of applications of LPME is rapidly growing. Different types of LPME have emerged, including single-drop microextraction, hollow-fiber LPME and dispersive liquid-liquid microextraction. However, the past decade brought considerable change to the analytical field with the application of ionic liquids (ILs). Their good thermal stability and low vapor pressure make them relatively non-hazardous for analytical applications in comparison to the solvents used traditionally. This review presents the applications of ILs in LPME of metals. It describes the most widely-used procedures and gives examples of emerging sample-preparation techniques.

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1. Introduction

The properties of hydrophobic ionic liquids (ILs), such as non-volatility, adequate viscosity and thermal stability, make them an attractive alternative to other organic solvents. Nowadays, ILs are increasingly used in sample-preparation techniques, such as liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) [1,2].

LPME emerged from liquid-liquid extraction (LLE), which is probably one of the most popular sample-extraction procedures in organic and inorganic analysis. LPME techniques overcome the main disadvantages of LLE, such as a relatively long time of analysis (especially when evaporation and reconstitution are required), high consumption of solvents, and its tedious application. Also, LPME combines isolation, preconcentration and sample introduction at one stage. It normally takes place in several microliters of a water-insoluble (hydrophobic) solvent (extractant/acceptor) and an aqueous phase (water sample/donor phase) containing the analytes [3].

As a consequence of the evolution of analytical chemistry towards automation, miniaturization and simplification, new miniaturized extraction procedures based on the principles of LPME were recently introduced for inorganic analysis [4]. LPME with ILs as extractants has been carried out under different extraction modes. They can be classified into three main categories:

- IL-based dispersive liquid-liquid microextraction (IL-DLLME);
- IL-based single-drop microextraction (IL-SDME); and,
- IL-hollow-fiber LPME (IL-HF-LPME).

Several variations have also been introduced for each of these categories, which clearly demonstrates the versatility of the method [3]. Fig. 1 shows selected extraction modes.

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http://dx.doi.org/10.1016/j.trac.2014.06.008

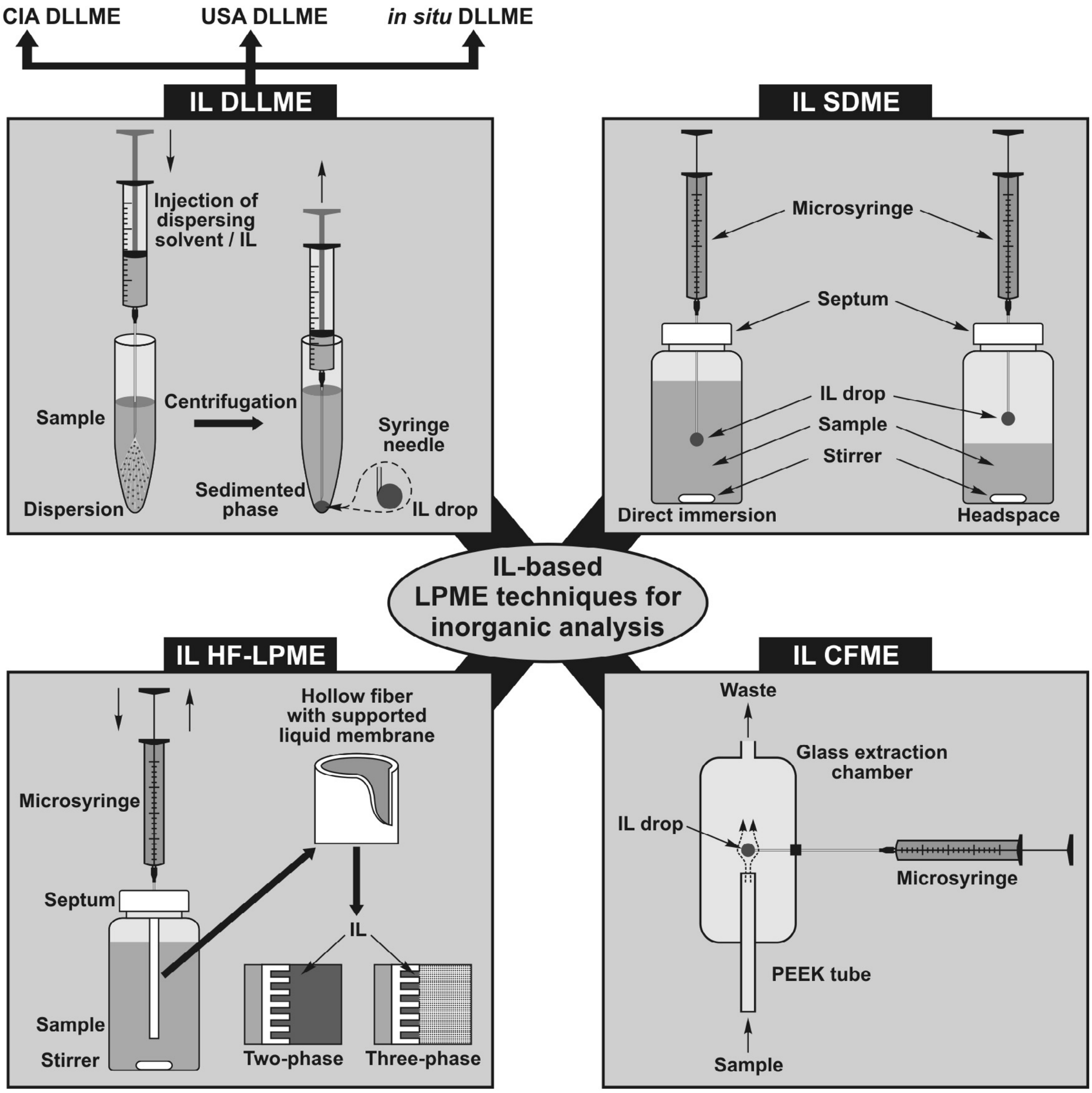

Fig. 1. Ionic liquid-based liquid-phase microextraction modes for inorganic analysis.

IL-based microextraction is usually combined with different spectroscopic techniques, including atomic absorption (AAS), fluorescence (AFS) and emission (ICP), and spectrophotometry, in order to determine ultra-trace amounts of analytes in environmental, biological and food samples. For many cases of AAS, the extracted analyte must be back-extracted into aqueous solution, and then introduced into a spectrometer for determination [1]. However, in a growing number of recently published new approaches, a back-extraction step was not required and that further reduced the number of sample-preparation steps [5,6]. In these studies, the IL phase (with metal ions) was analyzed directly or after dissolving in a small amount (10–50 µL) of an organic solvent (methanol or ethanol).

Although metal extraction using ILs is often indicative of high efficiency and selectivity, metal-ion partitioning always heavily relies upon the species of the IL, the metal ion and the ligand [1], so different procedures have been applied for the isolation of analytes from aqueous samples [4]:

- the extraction of metals using crown ethers, with the resulting crown-ether complexes exhibiting high hydrophobicity while retaining a residual electric charge [7,8];
- the extraction of metals as neutral complexes using anionic ligands [9,10], as extensively applied for the extraction of different metals, such as mercury [11], aluminum [12] or nickel [13]; and,
- the extraction of metals using task-specific ILs (TSILs), which contain a cationic interchangeable group in their structure [14–16].

2. Ionic liquid single-drop microextraction

In 1995, Dasgupta's group first developed methods involving a liquid droplet as a gas-sampling interface to extract substances, such as ammonia and sulfur dioxide, from the air [17,18]. Solvent microextraction into a single drop for organic analysis was suggested by Jeannot and Cantwell in 1996 [19]. The authors used an 8-µL drop of n-octane held at the hollowed out end of a Teflon rod immersed in the aqueous sample for the extraction of 4-methylacetophenone. In later work [20], the authors, as well as He and Lee [21], proposed the use of a conventional microsyringe as an extraction manifold for this technique.