

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

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

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

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Abbreviations: See Appendix before References section

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1. Introduction

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

The main potential benefits for the environment come from the negligible

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

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

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

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

2. Ionic liquids used for metal determination

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

2.1. Imidazolium ionic liquids

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

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

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

2.2. Phosphonium ionic liquids

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

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

2.3. Quaternary ammonium ionic liquids

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

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

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