Use of ionic liquids in analytical sample preparation of organic compounds from food and environmental samples

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This review highlights relevant advances in the use of ionic liquids (ILs) for analytical extraction and purification of organic compounds from food and environmental matrices.

Following a technique-based structure, we discuss advantages and shortcomings of ILs compared to conventional volatile organic solvents. We focus on the use of ILs in modern miniaturized extraction techniques, highlighting recent trends. However, when relevant, we also consider more classical approaches to sample preparation.

We discuss remaining limitations, gaps detected and possible future developments in this research area.

Finally, we illustrate the feasibility of the several analytical procedures for the analysis of relevant organic and biomolecules in foodstuffs and environmental samples of different natures on the basis of representative studies of applications.

Keywords: Biomolecule; Environmental analysis; Extraction; Food analysis; Ionic liquid; Miniaturization; Organic compound; Purification; Sample preparation; Volatile organic solvent

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1. Introduction

The many efforts in recent decades to develop more environmentally friendly and cost-effective sample-preparation methods have yielded a number of achievements. Novel enhanced-solvent and solvent-less extraction techniques are now available [1–3]. These techniques represent valuable analytical alternatives to more conventional approaches based on (essentially) shaking the sample with volatile organic solvents, and have contributed to solving the most pressing demands arising from solvent-based approaches, namely safety and human health and environmental protection. More recent concerns regarding the use of volatile organic solvents also include an economic-orientated perspective deriving from the costs of waste generation and disposal, legal liabilities and increasing regulatory constraints. In this context, the use of neoteric solvents, a category that includes supercritical CO_2, aqueous biphasic systems and ionic liquids [4], is attracting increasing interest as a valuable way to green chemical processes and technologies. Among the neoteric solvents, room-temperature ILs RTILS or simply ILs are nowadays considered promising alternatives to traditional volatile organic solvents. As a consequence, ILs have become the subject of intensive studies in many areas of fundamental and applied chemistry [5,6].

ILs are a group of non-molecular solvents that are liquid at or near room temperatures (generally defined as less than 150°C) due to poor coordination of the ions [1]. ILs are defined as green solvents due to their negligible volatility over wide temperature ranges, low flammability and high thermal stability. However, the toxicity of many of these solvents has not yet been evaluated and their capability to spread in the environment looks to be largely determined by their solubility in water. Other IL properties include high electrical conductivity, enlarged electrochemical window, miscibility with a wide

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range of organic solvents, good extractability for many different organic, inorganic and organometallic materials, and high viscosity. These features explain their increasing use in different fields of research and application, including electrochemical analysis, catalysis and synthetic experiments, and extraction processes [4,5,7].

ILs are salts usually composed of organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium or quaternary ammonium), and organic or inorganic anions (e.g., acetate, trifluoroacetate, tetrafluoroborate, hexafluorophosphate or bromide). The overall physicochemical properties of ILs result from the composite properties of both cation and anion. In principle, this characteristic can be used to fine-tune the properties of the resulting IL [4,8]. ILs can be superacidic, basic, hydrophilic, water-miscible, water-immiscible and hydrophobic. In general, the anion is used to control the water miscibility of the IL, but the cation can also influence the hydrophobicity or hydrogen-bonding ability of the solvent [4]. Although ILs have been known since the early nineteenth century, they started to attract scientists' attention when the first RTIL with the 1-alkyl-3-methylimidazolium cation was reported in 1982 [9]. However, it was not until 1992 that the first air-stable and water-stable 1-ethyl-3-methylimidazolium-based IL was synthesized [10]. Table 1 summarizes relevant physicochemical properties of ILs used for analytical preparation of samples of different types.

Unfortunately, systematic studies on characterization and comparison of the physicochemical properties of ILs are still scarce in the literature, which limits the present possibilities of predicting IL properties on the basis of the cation-anion combination selected [4,7]. As a consequence, in most published studies, IL selection has relied on trial and error, involving a limited number of accessible or commercially-available solvents. Despite the constantly increasing number of ILs synthesized and commercialized, applications reported so far usually involve a relatively small sub-set of these solvents, among which 1-alkyl-3-methylimidazolium salts predominate.

Although they have extensive use as solvents in organic synthesis, investigation of IL feasibility for analytical determinations started in the late 1990s [23]. Since then, a plethora of papers has demonstrated the benefits of using ILs primarily in construction of electrodes and sensors, in some electrochemical processes, and as extractants and complexing agents for anions and cations.

In the analytical field, ILs have been used to synthesize solid-phase microextraction (SPME) coatings and stationary phases for liquid chromatography (LC) and gas chromatography (GC), although, in these applications, they do not remain as liquids. ILs have also been used as additives to running buffers for LC and thin-layer chromatography (TLC) and capillary electrophoretic (CE) separations. Several detection techniques [e.g., matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS) and other spectroscopic techniques] have also profited from their ability to dissolve compounds of divergent nature. Most of these applications were summarized in recent reviews of a general [1,23] or technique-orientated [18,24–28] nature, in which the potential of these non-molecular solvents for the intended determinations were discussed on the basis of selected applications in different research areas. The use of ILs as ''green'' solvents for analytical [6,7,29] and process [5,30] extraction of metals and organic molecules has also been discussed in a number of reviews. Meanwhile, biomolecules have received only limited (if any) attention.

This article reviews current use of ILs in analytical sample preparation for the determination of relevant organic matrix components and trace-level analytes in food and environmental samples. It is divided into two parts. In the first part, we discuss the potential benefits associated with the use of ILs, compared to conventional volatile organic solvents in different modern, but widely accepted and employed, extraction and preconcentration techniques. We also highlight recent trends in the field. The second part reviews the more successful and more frequently-used IL-based sample-treatment procedures for the analysis of selected relevant organic and biomolecules in food and environmental matrices in an analyte-orientated section. In all instances, we give preference to those approaches and developments that have already demonstrated their practicality for the analysis of real-life samples.

2. Use of ILs in analytical sample preparation

Sample preparation plays a crucial role in the analytical process. However, it is still considered the limiting step of many modern analytical approaches [2]. Sample preparation includes a number of treatments to extract the target analyte from the matrix in which it is entrapped, to isolate analyte from co-extracted material that could interfere during its instrumental determination and, when required, to preconcentrate analyte.

2.1. Treatment of liquid samples

2.1.1. Liquid-based extraction techniques. As in many other research areas, the main (initial) application of ILs in analytical sample preparation of organic compounds was as extractant [7,23,29]. The immiscibility of ILs in water and their capability to solubilize organic species made them particularly suited to isolation and preconcentration of compounds from aqueous solutions, and so they were a valuable alternative to the volatile organic solvents used in conventional liquid-based extraction processes.