



## Review article

# Non-conventional solvents in liquid phase microextraction and aqueous biphasic systems



Jiwoo An<sup>a</sup>, María J. Trujillo-Rodríguez<sup>a,b</sup>, Verónica Pino<sup>b</sup>, Jared L. Anderson<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Iowa State University, Ames, IA 50011, USA

<sup>b</sup> Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain

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## ABSTRACT

The development of rapid, convenient, and high throughput sample preparation approaches such as liquid phase microextraction techniques have been continuously developed over the last decade. More recently, significant attention has been given to the replacement of conventional organic solvents used in liquid phase microextraction techniques in order to reduce toxic waste and to improve selectivity and/or extraction efficiency. With these objectives, non-conventional solvents have been explored in liquid phase microextraction and aqueous biphasic systems. The utilized non-conventional solvents include ionic liquids, magnetic ionic liquids, and deep eutectic solvents. They have been widely used as extraction solvents or additives in various liquid phase microextraction modes including dispersive liquid-liquid microextraction, single-drop microextraction, hollow fiber-liquid phase microextraction, as well as in aqueous biphasic systems. This review provides an overview into the use of non-conventional solvents in these microextraction techniques in the past 5 years (2012–2016). Analytical applications of the techniques are also discussed.

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\* Corresponding author at: Department of Chemistry, Iowa State University, 1605 Gilman Hall, Ames, IA, 50011, USA.

E-mail address: [andersoj@iastate.edu](mailto:andersoj@iastate.edu) (J.L. Anderson).

## 1. Introduction

Trends in analytical chemistry have recently focused on the development of safer, environmentally friendlier approaches that are congruent with Green Analytical Chemistry (GAC) [1]. The main objective in GAC is the use of green procedures and the reduction of environmental and human hazards. With this purpose, new sustainable extraction methods are designed not only by replacing the use of toxic reagents but also by the miniaturization and automation of analytical methodologies [2]. In replacing toxic reagents, conventional organic solvents commonly employed during the extraction procedure are gradually substituted by newly designed solvents. These non-conventional solvents include ionic liquids (ILs) and their derivatives [3] and deep eutectic solvents (DESs) [4].

ILs are a class of non-molecular solvents with melting points below 100°C and possess a wide variety of physicochemical properties, including low or negligible vapor pressure at room temperature and high chemical and electrochemical stability [3,5]. ILs that possess melting points below ambient temperature are commonly referred to as room temperature ionic liquids (RTILs). ILs are composed completely of ions, which typically includes asymmetric organic cations containing nitrogen or phosphorus atoms, and both inorganic or organic anions. Fig. 1(A) shows some of the cations and anions of common ILs. Small modifications to the IL structure are accompanied by dramatic modifications to a number of IL properties including water solubility and viscosity [5]. In the same manner, the incorporation of polar or non-polar moieties to the IL structure can promote different interactions with analytes and result in impressive solvation capabilities for different compounds. As a result, ILs can be tailored for specific applications [5].

A large group of IL derivatives have been designed for specific applications, including polymeric ionic liquids (PILs) [6,7] and IL-based surfactants [8,9]. Most recently, magnetic ionic liquids (MILs) and other groups of IL derivatives with interesting properties have been used in GAC [10]. MILs incorporate paramagnetic metals or metal complexes within their chemical structure permitting them to be controlled and manipulated under a magnetic field [11]. Fig. 1(A) represents some of the magnetic anions used in MILs.

DESs, which are IL analogs, are comprised of a mixture of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) [4]. The HBA is often a quaternary salt while HBD can include amines, carboxylic acids, alcohols or carbohydrates, as depicted in Fig. 1(B). It is worth noting that ILs based on quaternary ammonium or phosphonium cations with halide anions can be used as HBAs in designing DESs. DESs can be prepared relatively easily and are generally inexpensive and biodegradable. They also possess freezing points much lower than those of the two components comprising the solution [4]. Thus, they fit under the umbrella of solvents used in GAC.

Liquid phase microextraction (LPME) is a successful extraction and preconcentration technique which is in accordance with the trend of miniaturization and automation of the GAC [2]. The technique reduces the sample and extraction solvent requirements compared to conventional liquid-liquid extraction (LLE). Consequently, higher preconcentration factors are achieved using LPME. Three main modes of LPME are often used and include: dispersive liquid-liquid microextraction (DLLME), single-drop microextraction (SDME), and hollow fiber liquid phase microextraction (HF-LPME).

Aqueous biphasic systems (ABSs) are also effective separation and purification platforms for many types of compounds [12]. They also represent a biocompatible alternative to LLE because of the non-volatile nature of the components of the ABS and the fact that water is the main component of the system [13].

This review provides an overview in the use of non-conventional solvents in LPME and ABSs. A summary over the last 5 years of scientific studies (2012–2016) regarding the use of ILs, MILs, and DES coupled with these liquid microextraction techniques is presented.

## 2. Use of non-conventional solvents in liquid phase microextraction

### 2.1. Dispersive liquid-liquid microextraction

DLLME is based on the formation of a ternary solvent system involving an aqueous solution (the sample containing analytes), a water immiscible solvent acting as extraction solvent, and a dispersive solvent that is miscible with both the sample and the extraction solvent [14,15]. The contact of the three components forms a cloudy solution containing many microdroplets that maximize the interface between the phases and promotes a rapid partitioning of the analytes into the extraction solvent. The analyte-enriched extraction solvent can then be separated from the remaining components of the system by centrifugation.

DLLME was initially developed by Rezaee et al. in 2006 [16]. To date, many laboratories have utilized this technique. The success of the method is related to its simplicity of operation, low requirements of extraction solvent (volume on the order of microliters) and dispersive solvent (volume on the order of milliliters), and short extraction times. In addition, the technique provides high preconcentration factors due to the high phase ratio of the sample and the extraction solvent, as well as high extraction efficiency.

Adaptations and improvements have been performed to enhance the extraction efficiency of the classical DLLME method while also reducing the extraction time. The main modifications include the application of high temperatures and/or the use of microwaves [17], ultrasound [17,18], vortex [18,19] or any other stirring methods [20]. The main aim of these modifications is to promote a high surface contact area between the sample and the extraction phase. Further modifications involve the use of new extraction devices that facilitate the extraction [15] or the development of *on line* processes [21].

Current trends are devoted to replace conventional organic solvents that are highly toxic and to expand the applicability of DLLME to a wide number of analytes. Many studies that focus on this topic use ILs as new solvents [20]. However, other non-conventional solvents such as MILs and DESs have also been explored. The use of these solvents in the various DLLME modes will be discussed in the subsequent sections.

#### 2.1.1. Ionic liquids in dispersive liquid-liquid microextraction

Within non-conventional solvents, ILs are among the most studied in DLLME. They have been widely applied in all DLLME modes, including classical DLLME, temperature-controlled DLLME, microwave-, ultrasound- or vortex-assisted DLLME, as well as the *in-situ* mode [20]. Fig. 2 shows the percentage of publications of each IL-DLLME mode within the last 5 years.

The classical DLLME method is based on the simple mixture of the three system components, namely, the aqueous sample, extraction solvent, and dispersive solvent. The mixture is gently shaken by hand to form a cloudy solution, followed by centrifugation. Thus, it is the simplest DLLME mode because it does not require any additional step. Liu et al. were the first to report a classical IL-DLLME method for the determination of heterocyclic insecticides in water samples [22].

In the temperature-controlled DLLME mode, the ternary solvent mixture is heated to between 50 and 90°C in the IL-DLLME procedure. The solubility of the extraction solvent in the sample increases which ensures contact between both phases. In some cases, an

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