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REVIEW

The recent developments in dispersive liquid–liquid microextraction for preconcentration and determination of inorganic analytes



H.M. Al-Saidi *, Adel A.A. Emara

Department of Chemistry, University College in Makkah, Umm Al-Qura University, Makkah 21955, Saudi Arabia

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Complex formation;
Preconcentration;
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Abstract Recently, increasing interest on the use of dispersive liquid–liquid microextraction (DLLME) developed in 2006 by Rezaee has been found in the field of separation science. DLLME is miniaturized format of liquid–liquid extraction in which acceptor-to-donor phase ratio is greatly reduced compared with other methods. In the present review, the combination of DLLME with different analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), gas chromatography (GC), and high-performance liquid chromatography (HPLC) for preconcentration and determination of inorganic analytes in different types of samples will be discussed. Recent developments in DLLME, e.g., displacement-DLLME, the use of an auxiliary solvent for adjustment of density of extraction mixture, and the application of ionic liquid-based DLLME in determination of inorganic species even in the presence of high content of salts are presented in the present review. Finally, comparison of DLLME with the other liquid-phase microextraction approaches and limitations of this technique are provided.

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* Corresponding author. Tel.: +966 5 04512320; fax: +966 2 5566401.

E-mail addresses: alsaidihm@yahoo.com, hmh1973@hotmail.com (H.M. Al-Saidi).

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1. Introduction

Although the significance of sample preparation is often overlooked, it is arguably the most important step in the analytical process because the precision and accuracy of the analytical method is largely based upon this step. Current trends in analytical chemistry are highly focused on improving the quality of analytical results, and introduction of new technological developments involving miniaturization, simplification and automation of the whole analytical procedure (Rios et al., 2009). On the way to achieving that final objective, important advances have been made in miniaturization and simplification of sample-preparation procedures. These advances have focused on minimizing samples and reagents consumption (and thus the cost of the analysis), maintaining high selectivity and recoveries, using environmental friendly methods, and speeding up the sample treatment process, which is currently considered the rate determining step of the analytical process. Traditional methods for sample preparation including liquid–liquid extraction (LLE), Soxhlet extraction, chromatography, distillation, and absorption (Xiao-Huan et al., 2009), usually suffer from the disadvantages of time-consuming and tedious, large amounts of toxic organic solvent to be used, and difficulty in automation to some extent. Therefore, analytical chemists have focused on the development of new sample-preparation techniques, which are less time-consuming, more effective, fast, low cost, and require smaller amounts of organic solvents, yet provide accurate and precise data with reasonable quantization limits.

One of the techniques attracting special attention is dispersive liquid–liquid microextraction (DLLME), which was introduced in 2006 by Rezaee for the preconcentration of organic and inorganic analytes from aqueous matrices (Rezaee et al., 2006). Although, several reviews on microextraction in general and DLLME in particular have been published in the last years (Stalikas and Flamengos, 2008; Sarafraz-Yazdi and Amizi, 2010; Pena-Pereira et al., 2009, 2010; Herrera-Herrera

et al., 2010; Nerin et al., 2009; Anthemidis and Miró, 2009; Dadfarnia and Mohammad, 2010), some of these reviews are general and they did not independently discuss DLLME technique (Stalikas and Flamengos, 2008; Sarafraz-Yazdi and Amizi, 2010; Nerin et al., 2009; Dadfarnia and Mohammad, 2010). While, some others include applications of DLLME for preconcentration and determination of both organic and inorganic analytes (Xiao-Huan et al., 2009; Pena-Pereira et al., 2010). Also, the recent developments in DLLME technique like the use of auxiliary solvent for the adjustment of density of extraction mixture and displacement – DLLME did not describe in these reviews. On the other hand, the number of papers devoted for the application of DLLME to the analysis of metal ions has rapidly grown in the last three years. Therefore, the present review is focused on the recent developments and applications of DLLME for the preconcentration and sequential determination of total metal and metal speciation in variety of samples. The abbreviations of the compounds and techniques used in this review are listed in Table 1.

2. Principle of DLLME

Dispersive liquid–liquid microextraction is a miniaturized kind of (liquid–liquid extraction) LLE in which microliter volumes of extraction solvent are used. An appropriate mixture of the extraction solvent and the disperser solvent with high miscibility in both organic and aqueous phases is rapidly injected into the aqueous solution of sample and a cloudy solution is then formed as a result of the formation of fine droplets of the extraction solvent which disperse in the sample solution. The cloudy solution is centrifuged and the fine droplets are settled at the bottom of the conical test tube. The analytes are extracted from the initial solution and concentrated to a small volume of the sedimented phase, and the determination of the analytes in the settled phase can then be performed by the conventional analytical techniques. In fact, the surface area between the extracting solvent and the aqueous sample

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