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Tutorial

Solvent-terminated dispersive liquid-liquid microextraction: a tutorial

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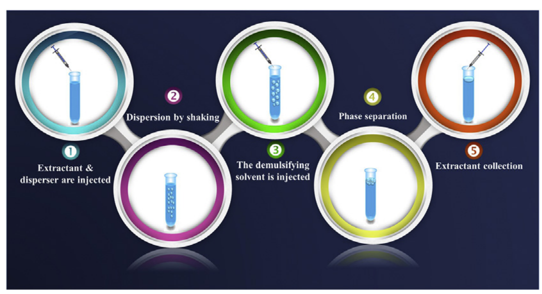
HIGHLIGHTS

- A remarkable progress of ST-DLLME has been observed in the last few years.
- The demulsifier type and volume and the demulsification time control the extraction efficiency in ST-DLLME.
- The different applications of ST-DLLME and the green aspects of this new mode have also been discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Solvent-terminated dispersive liquid-liquid microextraction (ST-DLLME) is a special mode of DLLME in which a demulsifying solvent is injected into the cloudy mixture of sample/extractant to break the emulsion and induce phase separation. The demulsification process starts by flocculation of the dispersed microdroplets by Ostwald ripening or coalescence to form larger droplets. Then, the extractant either floats or sinks depending on its density as compared with that for the aqueous sample. The demulsifier should have high surface activity and low surface tension in order to be capable of inducing phase separation. The extraction efficiency in ST-DLLME is controlled by the same experimental variables of normal DLLME (n-DLLME) such as the type and volume of the extractant as well as the disperser. Other parameters such as pH and the temperature of the sample, the stirring rate, the time of extraction and the addition of salt are also important to consider. Along with these factors, the demulsifier type and volume and the demulsification time have to be optimized. By using solvents to terminate the dispersion step in DLLME, the centrifugation process is not necessary. This in turn improves precision, increases throughput, decreases the risk of contamination through human intervention and minimizes the overall analysis time. ST-DLLME has been successfully applied for determination of both inorganic and organic analytes including pesticides and pharmaceuticals in water and biological fluids. Demulsification via solvent injection rather than centrifugation saves energy and makes ST-DLLME easier to automate. These characteristics in addition to the low solvent consumption, the reduced organic waste and the possibility of using water in demulsification bestow green features on ST-DLLME. This tutorial discusses the principle, the practical aspects and the different applications of ST-DLLME.

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Contents

1. Introduction

Sample preparation is an essential step in most analytical protocols to decrease the matrix effect, pre-concentrate the analytes, derivatize the sample, or protect the instrument [1,2]. The recent trends towards miniaturization of analytical systems inspired scientists to develop new approaches of sample preparation that require smaller amounts of samples and consume minimal quantities of organic solvents. Liquid-phase microextraction (LPME) is one of these recent approaches [3]. In spite of the simplicity and the cost-effectiveness of LPME, the % recovery is small compared with conventional liquid-liquid extraction (LLE). That is because LPME is not exhaustive; the main objective of microextraction is to extract a reproducible representative amount of the analyte from the sample rather than to retrieve all of the analyte.

To increase the extraction efficiency of LPME, Rezaee et al. [4] developed dispersive liquid-liquid microextraction (DLLME) in 2006. In DLLME, the extractant is mixed with an organic disperser and the mixture is injected into the aqueous sample to form a homogenous cloudy solution by manual or mechanical shaking. This induced dispersion leads to a significant increase in the contact surface between the extractant and the sample which markedly increases the extraction efficiency. However, DLLME suffers from three limitations: i) the extractants are heavier than water, which complicates the phase separation step after extraction, ii) two organic solvents, at least are required (the extractant and the disperser) to perform the dispersion-assisted microextraction process and iii) the dispersion is terminated by centrifugation which is time consuming and renders the technique difficult to automate. Automation of the extraction procedures is particularly important in LPME and DLLME due to the dynamic nature of these processes which requires strict control of all the procedures.

In the last decade, a remarkable effort was exerted to overcome the limitations of DLLME. To widen the range of extractants used in DLLME, solvents lighter than water, such as toluene, xylene, and octanol were tried in low density solvent DLLME (LDS-DLLME) [5,6]. To further facilitate the extractant transfer after the microextraction (ME) process, organic solvents with freezing points in the range of 10–25 °C were employed as extractants in DLLME with solidification of floating organic droplets (DLLME-SFOD) [7,8]. After extraction and phase separation, the sample is placed in an icebox to allow the extract to solidify before being transferred by a spatula. Instead of manual shaking, other methods of mechanical agitation were employed to improve the dispersion step using less or no dispersers. These methods include vortexing (as in vortex-assisted DLLME or VA-DLLME) [9,10], ultrasonic waves (as in ultrasound-assisted DLLME or USA-DLLME) [11,12] or repeated aspiration/injection as in air-assisted DLLME (AA-DLLME) [13,14]. A number of review articles has been published about DLLME [15,16] and its different modalities such as LDS-DLLME [6], DLLME-SFOD [7,8], VA-DLLME [9], and ionic liquid based dispersive liquid–liquid microextraction (IL-DLLME) [17]. Their applications in water [18], food [19,20] and biomedical analysis [21] have been characterized.

In order to skip the centrifugation step, Chen et al. introduced solvent-terminated DLLME (ST-DLLME) in 2010 [22]. In ST-DLLME, an amount of the dispersing solvent is added to the cloudy mixture to break the emulsion and induce phase separation. The centrifugation step which is time-consuming and difficult to automate is replaced with a simple fast step of demulsification by solvent injection. This mode has been developed in the last few years to allow for automatic coupling of DLLME with the analytical device. To the best of our knowledge, ST-DLLME has not been reviewed. In this work, the principle, the demulsifying solvents and the factors affecting extraction efficiency in ST-DLLME are discussed. The applications of ST-DLLME in pesticides, water, soil and biological analysis have also been summarized in both the text and a table.

2. Discussion

2.1. Principle of ST-DLLME

In conventional DLLME (also known as normal DLLME (n-DLLME)) [4], the extractant is mixed with an organic disperser before being injected into the aqueous sample. The selected disperser has to be miscible with the aqueous sample and the organic extractant [23]. By manual shaking, the extractant is dispersed as fine droplets in the form of a cloudy solution. The