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Development of on-line spectroscopic determination approach of dispersive liquid–liquid microextraction based on an effective device

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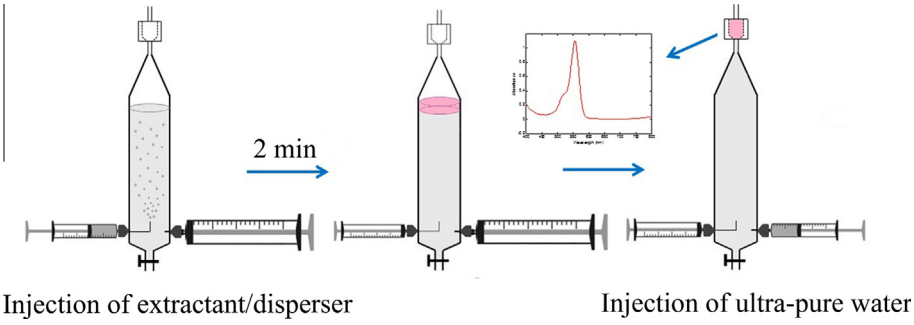
HIGHLIGHTS

- An on-line determination method of DLLME was developed based on an effective device.
- The volume of sample can conveniently change to perform a more effective DLLME.
- The proposed device provided a repeatable and effective injection of the extractant.
- The method was used to quantify a model analyte rhodamine B in three real samples.
- The applicability of the method can be extended to other analytes.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel, rapid, simple, and low-cost on-line determination approach of dispersive liquid–liquid microextraction (DLLME) with low-density solvents was developed with the support of a specially designed effective homemade device. The proposed method surmounted the drawbacks of conventional DLLME of the need of high-density solvents as extractants, and the requirement of centrifugation operation to obtain phase separation, and the difficulties to realize on-line determination. The amount of sample utilized can conveniently change according to practical needs by varying the volume of the extraction tube of the device to perform a more effective DLLME. A case study was carried out to assess this method utilizing the dye rhodamine B as the model analyte. The experiment parameters influencing the extraction were systematically investigated. Under optimum conditions, the linearity was obtained in the range of 0.015–1.000 μg/mL with the correlation coefficient (r^2) of 0.9980. The limit of detection and quantification were 6.1 and 20.4 μg/L, respectively. Good repeatability was achieved with the relative standard deviations (RSD) for five replicate measurements of different concentration samples less than 4.06%, and the presented method was successfully employed to quantify rhodamine B in three real samples.

Introduction

Dispersive liquid–liquid microextraction (DLLME) was introduced as an efficient separation and enrichment technique in 2006 by Rezaee et al. [1]. This method is based on the ternary-component solvent system consisted of extraction solvent, disperser solvent and an aqueous phase containing analytes. In DLLME, the appropriate mixture of extraction solvent and disperser solvent is injected rapidly by syringe into the aqueous sample solution to disperse the extraction solvent as fine droplets. Thereby, cloudy solution is formed and the analytes transfer from the aqueous solution into the extractant droplets promptly. With the help of centrifugation, the dispersion is removed. The major benefits of DLLME method are simplicity of operation, rapidity, low extraction solvent volume, low cost, and high enrichment factor, which make this technique widely adopted in various fields in recent years [2–9]. However, DLLME inevitably has its drawbacks. For the sake of a

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convenient removal of the extractant after centrifugation, a heavier than water, normally chlorinated, highly toxic solvent has to be exploited. In addition, centrifugation, the most time-consuming step, is needed to be utilized in the majority of conventional DLLME processes, which limits, to some extent, the volume of samples and the feasibility of on-line determination of DLLME.

In order to overcome these disadvantages and expand the applicability of DLLME, several researchers made great efforts to attempt to use solvents with low-density as the extractants with the assistance of special extraction devices [10–15]. Hashemi et al. [10] designed a glass tube with a narrow neck inserted inside a centrifuge tube as a simple device to make the use of low-density solvents feasible in DLLME method. The dispersive extractant was accumulated in the narrow neck of the device by the operation of centrifugation, where the extractant can be simply collected by a micro-syringe. Another especial extraction vessel was developed by Farajzadeh et al. [11] for DLLME of three organophosphorus pesticides with low-density solvents. The extraction vessel contained a septum and a narrow portion at the bottom and top of the device, respectively. After centrifugation, the extractant was collected from the supermatant. Then, 1 mL distilled water was injected through the septum to elevate the level of the extractant and transfer it to the narrow portion for easy removal using a microsyringe.

The use of special extraction devices enables the application of low-density solvents in DLLME procedures. However, each of these devices is usually based on a similar principle that the extractant is always removed from the narrow upper parts of the devices for further analysis. Furthermore, in these approaches, centrifugation is still needed to achieve phase separation. Currently, Several researches have been reported, which present different solutions of avoiding the use of centrifugation [16–21]. Chen et al. [16] suggested a low-density based DLLME method employing a volumetric flask as the extraction device to conveniently collect the extractant at the neck of the volumetric flask. The developed procedure did not need centrifugation to achieve phase separation, but by introducing a chemical demulsifier into the cloudy solution. Recently, Farajzadeh et al. [17] presented a simple DLLME method which was performed in a narrow-bore tube with one end blocked by a septum. The extractant was injected through the septum into the tube filled with aqueous solution of analytes. After phase separation by droplet floatation, the extracant was easily sucked and transferred by a capillary tube at the top of the tube for further analysis.

The cancellation of centrifugation enables the realization of on-line determination DLLME. Very recently, automated on-line determination DLLME technique has been developed based on the accomplishment of multisyringe flow injection analysis system and the extraction "in-syringe", in which syringes were used as the container for DLLME [22–28].

In Suarez et al.'s study [23], the flow technique was coupled with DLLME to realize automated DLLME and on-line determination. The sequential injection analysis system comprised a 5000-step syringe pump equipped with a 5 mL syringe, a rotary 8-port multiposition valve (MPV) used for handling solutions required for DLLME and cleaning procedures, and a homemade fluorescence detector. The central port of the MPV was connected to a three-way solenoid head valve to control the load and dispensation of a fluid to perform the DLLME process. 1-hexanol and 2-propanol which can provide a full phase separation by floatation were selected as extractant and disperser solvent, respectively. The separated extractant droplets were collected at the head of the syringe and automatically injected into the specially made flow channel detection cell for determination.

A similar technique was presented by Maya et al. [24], in which an automatic multisyringe burette employed for the liquid handling was equipped with a 5 mL glass syringe, and the extraction syringe was combined with a three-way solenoid head valve. By changing the position of the solenoid valve, a fluid can be loaded into the syringe or dispensed towards the flow network or a reservoir to perform the DLLME process. A homemade fiber-adapter was specially made for in-syringe spectrophotometric measurement. 1-octanol and 1-propanol were used as extractant and disperser solvent, respectively, to DLLME of rhodamine B in aqueous samples. After phase separation obtained by floatation, the separated extractant droplets were collected at the head of the syringe, and the spectra of the extractant containing the analyte was measured directly out of the syringe. In this method at least 1 mL organic phase was needed to obtain a reliable spectrum. Meanwhile, at most 4 mL sample can be analysed on account of the maximum volume of the extraction syringe, which limits the enrichment factor of DLLME.

Notwithstanding, these approaches mentioned above, solve the current challenges of DLLME, like automation and on-line determination, regrettably, in these strategies, sequential injection analysis system and multiway solenoid head valves are absolutely necessary, which make the device extremely complex and not commodious to realize field determination. Moreover, the enrichment factor of DLLME was limited result from the maximum volume of the extraction syringe.

In this work, a very simple effective homemade device composed of an extraction tube and a detection cell was specially designed for on-line determination of DLLME with low-density solvents. The volume of the extraction tube can optionally change according to practical needs. Thus, the volume ratio of sample to the extractant can be facilely improved, which will make a more effective extraction to some extent. The volume and optical path of the detection cell can also be modified with the help of designing a suitable cell holder to place the detection cell. For simplicity, fixed volume and optical path were used to make the device. The spectra of the extractant containing analyte can be measured directly in the detection cell without removal. When cooperated with a portable instrument, this method can easily accomplish field determination. During this method, no centrifugation operation was needed since phase separation was achieved by floatation when appropriate extraction and disperser solvent were utilized. Rodamine B was extracted as the model analyte to evaluate the effectiveness of the presented method. Several parameters, which may influence the performance of DLLME were investigated.

Experimental

Chemicals and reagents

All chemical reagents used were of analytical purity grade and used without further purification. Rodamine B was purchased from Shanghai Yuanye biology and Science Co., Ltd.

A standard stock solution of rodamine B with the concentration of 1000 μg/mL was prepared by dissolving the powder rodamine B with ultra-pure water and stored in a refrigerator. All sample solutions were obtained by stepwise diluting the stock solution with ultra-pure water obtained from an ultra-pure water purification system (SARTORIUS arium 611DI, Germany, 18.2 MΩ cm).

Apparatus

The extraction and spectra acquiring were performed in a homemade device constituted by an polypropylene extraction tube which contains 3 ports and a detection cell (Fig. 1). As shown in Fig. 1, the extraction tube with a conic top is about 12 cm in height and 15 mm in diameter, and its volume is ca. 14 mL. Port 1 is a stainless steel syringe needle located in the bottom of the tube wall