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Dynamic electromembrane extraction: Automated movement of donor and acceptor phases to improve extraction efficiency

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ABSTRACT

In the present research, dynamic electromembrane extraction (DEME) was introduced for the first time for extraction and determination of ionizable species from different biological matrices. The setup proposed for DEME provides an efficient, stable, and reproducible method to increase extraction efficiency. This setup consists of a piece of hollow fiber mounted inside a glass flow cell by means of two plastics connector tubes. In this dynamic system, an organic solvent is impregnated into the pores of hollow fiber as supported liquid membrane (SLM); an aqueous acceptor solution is repeatedly pumped into the lumen of hollow fiber by a syringe pump whereas a peristaltic pump is used to move sample solution around the mounted hollow fiber into the flow cell. Two platinum electrodes connected to a power supply are used during extractions which are located into the lumen of the hollow fiber and glass flow cell, respectively. The method was applied for extraction of amitriptyline (AMI) and nortriptyline (NOR) as model analytes from biological fluids. Effective parameters on DEME of the model analytes were investigated and optimized. Under optimized conditions, the calibration curves were linear in the range of 2.0–100 $\mu g\,L^{-1}$ with coefficient of determination (r^2) more than 0.9902 for both of the analytes. The relative standard deviations (RSD %) were less than 8.4% based on four replicate measurements. LODs less than 1.0 $\mu g\,L^{-1}$ were obtained for both AMI and NOR. The preconcentration factors higher than 83-fold were obtained for the extraction of AMI and NOR in various biological samples.

1. Introduction

Regarding the matrices complexity of the analytes from a biological sample or environmental origin which can disturb the separation and data analysis steps, a sample preparation step is necessary before final analysis. Sample preparation could be explained as the experimental steps need for a sample to make it ready for analysis. Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are well-known sample preparation methods which were associated with many advances in the past few years. However, these techniques have some drawbacks that motivated the analytical chemists to develop new extraction methods.

A good sample preparation method should be as fast as possible, reproducible, involve minimum number of steps, has relatively low cost, be environmentally friendly and offer high recoveries [1]. Down scaling or miniaturization and automation are two key parameters beside the other characteristics which should be considered for a suitable sample preparation technique.

With these considerations kept in mind, a series of new microextraction methods were developed that are generally classified into liquid-, solid- and membrane-based techniques. Among these, the latter case has found a worldwide impact in modern sample preparation due to providing high preconcentration factors and sample cleanup.

Hollow fiber liquid phase microextraction (HF-LPME) and electromembrane extraction (EME) are two important types of miniaturized membrane based extraction techniques introducing by Pedersen-Bjergaard et al. [2,3]. In both techniques, a piece of porous hollow fiber is used as support that is impregnated by a proper water–immiscible organic solvent. The primary EME setup is similar to HF-LPME but utilizes two platinum electrodes which were placed in the sample solution and acceptor phase, respectively providing the electrical field using a power supply. The extraction mechanisms in HF-LPME and EME are based on passive diffusion and electrokinetic migration respectively. Compared to passive diffusion, electrokinetic migration appears to be a much more efficient transport mechanism, providing high analyte recoveries in a short

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period of time. In fact, application of electrical driving force is the current state-of-the-art in miniaturized sample preparation techniques that presents new possibilities for time reducing as well as enhancement of selectivity and extraction efficiency [4]. Since introducing of EME to now, noticeable developments have been presented in this technique to improve its applicability more and more [3,5–27].

An important point concluding from literature is that among various key parameters of a good sample preparation method, automation has scarcely been considered. This may be ascribed to the fact that few research groups have so far worked on automated approaches despite major advantages such as decreasing of sample handling and extraction time as well as improvement of extraction efficiency that can be provided by automation. The design of a dynamic and automated system depends on the particular process and the working conditions under which it is developed. In other words, difficulties in automation of an extraction procedure are dictated by its required working conditions. Among different extraction techniques, dynamic operation and automation of HF-LPME has received major attentions in recent years due to its simplicity and easy operation [28–33]. In dynamic HF-LPME, both acceptor phase and sample solution are mechanically moved using a microsyringe and peristaltic pump, respectively [28,34]. These movements reduce the thickness of double layer and so improve extraction efficiency.

In the present study, a dynamic EME (DEME) system was designed and successfully applied for extraction of nortriptyline (NOR) and amitriptyline (AMI) as model analytes from urine and plasma samples. The effects of various experimental parameters on DEME of NOR and AMI were investigated and optimized. According to the best of our knowledge, there is no report on DEME in the literature.

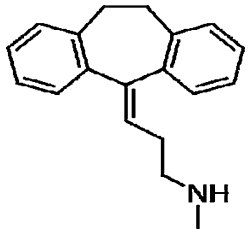
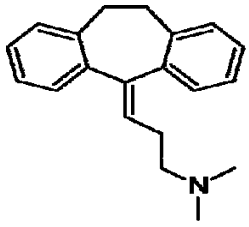
2. Experimental

2.1. Chemicals and reagents

AMI and NOR were purchased from Razi Pharmaceutical Company (Tehran, Iran). The chemical structures and physicochemical properties of the drugs are provided in Table 1. 2-Nitrophenyl octyl ether (NPOE), tris-(2-ethylhexyl) phosphate (TEHP), and di-(2-ethylhexyl) phosphate (DEHP) were purchased from Fluka (Buchs, Switzerland). 1-Octanol and 1-undecanol were obtained from Merck (Darmstadt, Germany). All chemicals used were of analytical reagent grade. The porous hollow fiber (HF) used for the SLM was a PPQ3/2 polypropylene HF from Membrana (Wuppertal, Germany) with inner diameter of 0.6 mm, wall thickness of 200 μm and pore size of 0.2 μm. Ultrapure water was prepared by a Younglin 370 series aquaMAX purification instrument (Kyounggido, Korea).

A stock solution containing 1.0 mg mL^{-1} of AMI and NOR was prepared in methanol. All standard solutions were stored at 4 °C protected from light. Working standard solutions were prepared daily by dilution of the stock solutions with ultrapure water.

Table 1
Chemical structure, pK_a and log P of the analytes.

Name	Chemical structure	pK_a[a]	Log P[a]
Nortriptyline		10.47	4.43
Amitriptyline		9.76	4.81

[a] Ref. [38].

2.2. Apparatus

Separation and detection of the target analytes were performed by a Varian HPLC (Walnut Creek, CA, USA) comprising a 9012 HPLC pump, a six-port Cheminert HPLC valve from Valco Instruments (Houston, TX, USA) with a 20 μL sample loop and a Varian 9050 UV–Vis detector. Chromatographic data were recorded and analyzed using Chromana software (version 3.6.4), developed by Marjaan Khatam (Tehran, Iran). The separations were run on an ODS-3 column (150 mm × 4.6 mm, with particle size of 5 μm) from MZ-Analysentechnik (Mainz, Germany) under isocratic elution conditions at a flow rate of 1.0 mL min^{-1}. The mobile phase consisted of 25 mM phosphate buffer (pH 4.0) and acetonitrile (60:40). The detector wavelength was set at 210 nm.

GPFA1-380 peristaltic pump from Ultra-Voltammetry Company (Tehran, Iran) was applied to pass the solutions through the DEME extraction cell. A syringe pump form Fanavaran Nano Meghyas model SP1000HPM (Tehran, Iran) was used for movement of acceptor phase into and out of the lumen of the hollow fiber.

2.3. Equipment for DEME

Schematic diagram of homemade DEME extraction glass cell is shown in Fig. 1. The extraction cell contains a main glass tube with the length of 100 mm and inner diameter of 8 mm and two glass tee (T) connectors with the length of 40 mm and inner diameter of 1.5 mm embedded at both ends of main glass tube. Two plastic screw caps were used to seal both ends of the main glass

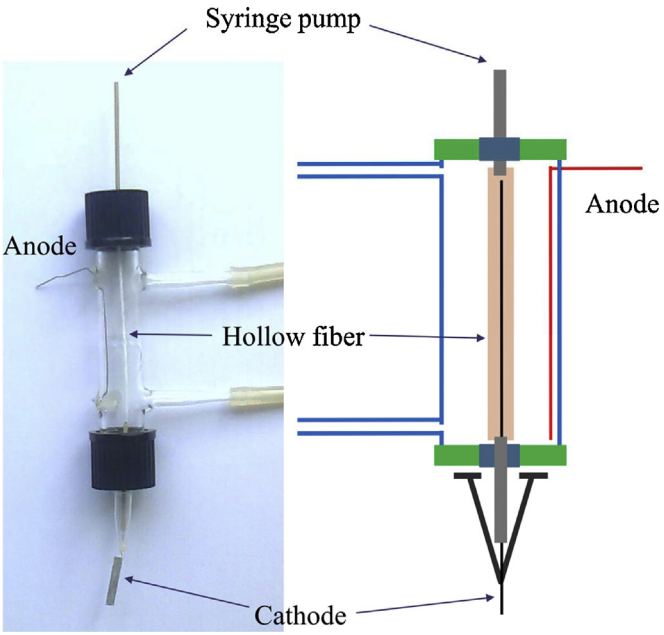


Fig. 1. Schematic illustration of DEME extraction glass cell.