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Study on electrical current variations in electromembrane extraction process: Relation between extraction recovery and magnitude of electrical current

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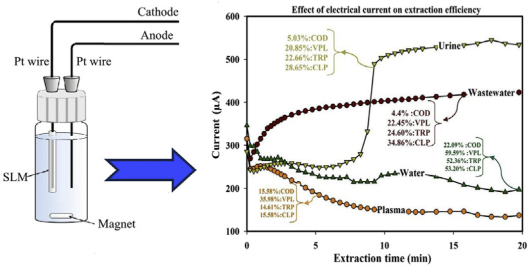
HIGHLIGHTS

- Study on electrical current variation in electromembrane extraction.
- Prediction of successful extraction using current pattern.
- High currents (>500 μA) result low extraction efficiencies.
- Complex matrices can increase electrical current in duration of extraction.

GRAPHICAL ABSTRACT



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ABSTRACT

This contribution presents an experimental approach to improve analytical performance of electromembrane extraction (EME) procedure, which is based on the scrutiny of current pattern under different extraction conditions such as using different organic solvents as supported liquid membrane, electrical potentials, pH values of donor and acceptor phases, variable extraction times, temperatures, stirring rates, different hollow fiber lengths and the addition of salts or organic solvents to the sample matrix. In this study, four basic drugs with different polarities were extracted under different conditions with the corresponding electrical current patterns compared against extraction recoveries. The extraction process was demonstrated in terms of EME-HPLC analyses of selected basic drugs. Comparing the obtained extraction recoveries with the electrical current patterns, most cases exhibited minimum recovery and repeatability at the highest investigated magnitude of electrical current. . It was further found that identical current patterns are associated with repeated extraction efficiencies. In other words, the pattern should be repeated for a successful extraction. The results showed completely different electrical currents under different extraction conditions, so that all variable parameters have contributions into the electrical current pattern. Finally, the current patterns of extractions from wastewater, plasma and urine samples were demonstrated. The results indicated an increase in the electrical current when extracting from complex matrices; this was seen to decrease the extraction efficiency.

Abbreviations: EME, electromembrane extraction; SLM, supported liquid membrane; COD, Codeine; VPL, Verapamil; TRP, Trimipramine; CLP, Clomipramine; NPOE, 2-Nitrophenyl octyl ether; ETH, 2-ethyl hexanol; TEHP, tris-(2-ethylhexyl) phosphate; DEHP, di-(2-ethylhexyl) phosphate.

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1. Introduction

The concept of electromembrane extraction (EME) was initially suggested by Pedersen-Bjergaard and Rasmussen in 2006 [1]. EME is based on electrically-driven transfer of charged species from aqueous solutions (donor) across a supported liquid membrane (SLM), formed as a thin layer of a water immiscible organic solvent on a supporting material, into another aqueous solution (acceptor) [2]. Thereafter, application of an electrical potential to generate the driving force shortened the extraction time [3,4]. A number of papers have reported the extraction of both basic and acidic substances from water, plasma, urine, whole blood, breast milk, and tap water [5–8]. Peptides have also been extracted successfully with EME [8,9]. There are several reviews where EME has been described, either partially or completely, by the originators and experts [10–16].

Today, EME is normally performed at constant voltage in almost all of its applications. At constant voltage, electrical current variations with different extraction conditions found in the EME system, follow Ohm's law, because the EME system's total resistivity is determined by the low-conductive SLM. Even small differences in extraction conditions will therefore induce measurable alterations in the resulting electrical current. Total electric charge (Q in Coulombs) passed through the system will be different for different extraction conditions; consequently, total charged species transferred through SLMs will be governed by Faraday's law [17]. In addition to applying constant voltage, electromembrane extractions were performed at stabilized constant d.c. current. The current-controlled transfer of analytes from donor to acceptor solutions, across SLMs, has significantly enhanced repeatability of the extraction process. Furthermore, extraction process repeatability was significantly improved when undertaking EME at constant electrical current rather than constant voltage. EME at constant electrical current does not suffer from SLM instabilities frequently reported in experiments with constant voltage [2,3,17].

Some reports are released on the evaluation of the electrical current in the course of extraction process [6,17–23]. However, various literatures have reported different values for electrical current at which analytes have been successfully extracted. For example, Pedersen-Bjergaard et al. checked the stability of SLM in the course of the extraction of basic drugs, including pethidine, haloperidol, nortriptyline, methadone and loperamide, and observed a stable current magnitude within the range of 4–7 μA [18]. In another work, they studied electromembrane extraction of peptides, where they monitored the current throughout the SLM during extraction experiments; the measured magnitude of current ranged from 1 to 500 μA [20]. Also, Kuban et al. electro-extracted 17 essential amino acids and the related compounds from human body fluids; they observed electrical current values above 100 μA [2].

The findings show that such extraction conditions as the applied voltage, donor and acceptor volumes, organic solvents (SLM) and differences among samples can change the optimal electrical current range. However, to the best of our knowledge, as of this research, a comprehensive study on electrical current measurement under different extraction conditions, and with various matrices as well as electrical current magnitude – extraction recovery relationship is yet to be reported.

This study is an attempt to address electrical current magnitude – extraction recovery relationship. For this purpose, electrical current variations were monitored during extraction experiments under different conditions, and extraction efficiencies were obtained for analytes. In other words, this study looks for the electrical current variation pattern via which a successful extraction is to be achieved. Several experiments were conducted under wide ranges of different conditions (different SLMs, carriers, voltages, pH values of acceptor and donor solutions, ionic strengths, hollow fiber lengths, temperatures, extraction times and sample matrices) to extract some model compounds (codeine, verapamil, trimipramine and clomipramine). The main criterion by which these model compounds were chosen was their polarities (log P 1.34–5.04). To the best of our knowledge, this is the first research on the effect of extraction conditions on EME membrane current; the results can serve as important contributions toward a better understanding of the extraction process.

2. Experimental

2.1. Chemicals and materials

Codeine (COD) and Verapamil (VPL) were obtained from Parand Darou (Tehran, Iran). Trimipramine (TRP) and Clomipramine (CLP) were obtained from Tofigh Darou Pharmaceutical Company (Tehran, Iran). 2-Nitrophenyl octyl ether (NPOE), 2-ethyl hexanol (ETH), 1-octanol, undecanol, tris-(2-ethylhexyl) phosphate (TEHP), di-(2-ethylhexyl) phosphate (DEHP) and KH_2PO_4 were purchased from Fluka (Buchs, Switzerland). All used chemicals were of analytical reagent grades. A wastewater sample was obtained from Tofigh Daru Pharmaceutical Company (Tehran, Iran). Drug-free human plasma and urine samples were obtained from Taleghani Hospital (Tehran, Iran).The porous hollow fiber used for SLM was a PPQ3/2 polypropylene hollow fiber from Membrana (Wuppertal, Germany) with the inner diameter of 1.2 mm, wall thickness of 300 μm and pore size of 0.2 μm. HPLC grade water was obtained through a Millipore water purification system (Milford, MA, USA).

2.2. Preparation of standard solutions and real samples

Stock solutions containing 0.1 mg mL^{-1} of each model drug were prepared in HPLC grade water and stored at 4 °C. Then, the required working standard solutions were freshly prepared by diluting appropriate amount of stock solution with HCl solution (10 and 100 mM) to achieve the desired concentration of 100 ng mL^{-1} of each drug substances before extraction. Urine, plasma and wastewater samples were diluted at 1:3, 1:6 and 1:1 ratios using HPLC grade water, respectively. Spiked samples were prepared by addition of stock standard solution of the analytes into the samples.

2.3. Electromembrane extraction setup and procedure

The equipment used for EME included an EPS-600Z power supply (Paya Pajohesh Pars, Tehran, Iran) with constant voltage in the range of 0–600 V. Two Platinum wires with a diameter of 0.25 mm were used as electrodes in the sample and acceptor solutions (Fig. 1). A 6.9 mL glass vial was used as the sample compartment, with a height of 4.5 cm and an internal diameter of 14 mm. The porous hollow fiber was used for the immobilization of SLM and for housing the acceptor solution. The fiber was cut into 31 mm pieces. The SLM was constituted of a hollow fiber dipped in the organic solution for 10s to impregnate the pores with the organic solvent. The excess organic solvent was gently wiped away with a medical wipe. Thirty microliters of the acceptor solution (10 mM HCl) was then entered into the lumen of the hollow fiber via a micropipette. The excess of acceptor solution was removed from the end of fiber and then the lower end of the hollow fiber was closed by mechanical pressure. The hollow fiber containing the SLM and acceptor solution was then inserted, through a hole in the lid of the sample reservoir, into 5.0 mL of the sample solution. Cathode and anode electrodes were placed into the acceptor and sample solution, respectively. The extraction device was then placed on a