Journal of Chromatography A, 1324 (2014) 21–28

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Voltage-step pulsed electromembrane as a novel view of electrical field-induced liquid-phase microextraction

Maryam Rezazadeh[a], Yadollah Yamini[a,*], Shahram Seidi[b], Leila Arjomandi-Behzad[a]

[a] Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran
[b] Department of Analytical Chemistry, Faculty of Chemistry, K.N. Toosi University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form
11 November 2013
Accepted 14 November 2013
Available online 22 November 2013

Keywords:
Pulsed electromembrane
Microextraction
Voltage steps
Stability
Low voltage

ABSTRACT

In the present work, the effect of application of voltage steps on extraction efficiency of pulsed electromembrane extraction (PEME) was investigated for the first time. The effects of voltage variations including initial and final voltages, number of steps between the initial and final voltages as well as their time durations were studied on the extraction efficiencies of three different classes of analytes. These classes include amitriptyline (AMI) and nortriptyline (NOR) as more hydrophobic analytes, diclofenac (DIC) and mefenamic acid (MEF) as acidic drugs and salbutamol (SB) and terbutaline (TB) as hydrophilic compounds. It was anticipated that the application of high voltages is not necessary at the beginning of the extraction, since large amounts of target analytes exist around the supported liquid membrane (SLM)/sample solution interface. So, they could be easily transferred into the acceptor phase utilizing lower voltages. Results showed that the benefits of voltage-step PEME (VS-PEME) are more obvious in systems with low electrical resistance (regarding the SLM composition). Efficiencies of VS-PEME for extraction of AMI and NOR (96% and 89% for AMI and NOR, respectively) were comparable with those achieved from applying a constant voltage (95% for AMI and 83% for NOR). However, recoveries from the VS-PEME of DIC and MEF (53% and 44% for DIC and MEF, respectively) were significantly higher than those from the application of a constant voltage (33% for DIC and 31% for MEF). Also, recoveries obtained from the VS-PEME for SB and TB were approximately 3 orders of magnitude greater than those from a constant voltage. Moreover, it was demonstrated that in all cases analytes could effectively be extracted at the beginning of extraction by applying low voltages.

1. Introduction

Electromembrane extraction (EME) is a micro-scaled electrical field-induced liquid-phase extraction technique which was introduced in 2006 [1]. EME is capable of effectively extracting ionizable compounds utilizing an electrical field to make them migrate from an aqueous sample solution into an aqueous acceptor phase through the supported liquid membrane (SLM). Due to the many benefits such as high efficiency, selectivity, sample cleanup and fast kinetics which have been found for this microextraction method, it is associated with rapidly progressing. Up to now, several studies have been performed to figure out the impressive variables and the exact mechanism of this technique [1–6]. Furthermore, a lot of developments have been reported to improve the advantages and overcome the drawbacks of this new microextraction method; such as a new setup for exhaustive EME [7,8], simultaneous extraction of acidic and basic drugs at neutral sample pH [9,10], EME coupling with dispersive liquid–liquid microextraction (DLLME) [11,12] and solid-phase microextraction (SPME) [13] to make it compatible with GC instrument and some EME designs for development of lab-on-chip systems [14–16].

The main trouble with EME is system instability as a result of an increase in the current level when high voltages are applied; especially in analysis of real samples containing large amounts of ionic components. Therefore, Kubáň et al. set an electrical design to control the level of electrical current during the extraction process [17]. To this end, a high voltage power supply was employed to provide stabilized constant DC current down to 1 μA. On the other hand, Yamini et al. presented a simple and inexpensive setup based on the application of pulsed voltages to overcome the problems EME faces in analysis of real samples [18]. They used an electronic device, which created pulsed voltages, in combination with a common constant DC power supply to minimize the thickness of double layer formed by the ambulations of ions on both sides of the SLM.

In each pulse, voltage is applied for a relatively short time which is long enough for the analytes transportation into the acceptor phase. During the outage period, the ions accumulated at the interfaces were dispersed again throughout the stirring sample

* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.
E-mail addresses: yyamini@modares.ac.ir, yyamini2002@yahoo.com (Y. Yamini).

0021-9673/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chroma.2013.11.034

solution and the double layer disappeared. It was shown that pulsed electromembrane extraction (PEME) increases the system stability by decreasing the thickness of double layer at the interfaces and improves extractability by eliminating this mass transfer barrier [18,19]. In addition, two-way PEME has been introduced as a novel approach for highly selective extraction of amino acids utilizing their isoelectric pHs [19].

The aim of this work is to explore the effect of applied voltage in detail during the extraction using VS-PEME. To this end, pulsed voltages were exploited for extraction of different classes of analytes while the applied voltage was raised staircase-like in each pulse. In all EME works, until now, constant voltages have been applied for extraction of target analytes. Nevertheless, it is anticipated that at the beginning of the extraction process, when relatively high amounts of the analytes exist in the sample solution, EME could be performed by applying low voltages. Employing low electrical potential has many advantages such as decreasing the thickness of double layer at the interfaces, avoiding the extraction of interferences (to some extent), reducing the energy requirements, diminishing the level of electrical current in the system and increasing the system stability. Nonetheless, as the concentrations of analytes in the sample solution decline, more effective driving force is necessary to make them transfer across the SLM. Therefore, it is expected that by prolonging the extraction time, higher voltages are required to reach admissible extraction efficiencies. Thus, even for extraction of analytes which need high electrical potential (such as very hydrophilic compounds or species with low affinities for the organic phase), the prevalence of the applied voltage may enhance system stability and extraction efficiency.

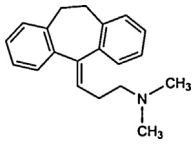
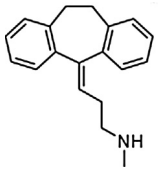
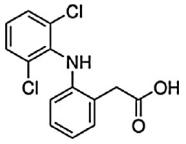
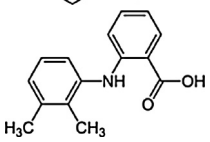
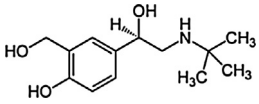
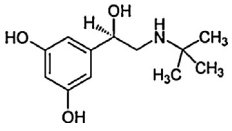
In this paper, PEME was exploited using the prevalence of applied voltage. Each extraction process began with the lowest possible voltage and the applied electrical potential was raised staircase-like up to the highest possible amount over a fixed extraction time. To examine the behaviors of various compounds, AMI and NOR were chosen as more hydrophobic analytes which require average applied voltage and extraction time in EME [12,13,16,20]. On the other hand, DIC and MEF were selected as acidic drugs, which need relatively low extraction time and applied voltage for extraction by EME [9,21]. Finally, SB and TB were scrutinized as candidates requiring high extraction time and applied voltage during the EME process [22]. Then, the VS-PEME was conducted for extraction of these three different classes of analytes. Impressive variables, such as the initial and final voltages, number of ON/OFF steps between the initial and final voltages as well as their time durations, were optimized. Ultimately, the results were compared with those attained by conventional EME to gain detailed information about the role of the applied voltage during the extraction.

2. Experimental

2.1. PEME equipment

The equipment for PEME procedure is shown in Fig. 1A. A glass vial with an internal diameter of 10 mm and a height of 8 cm was used. The electrodes utilized in this work were platinum wires with diameters of 0.2 and 0.5 mm for cathode and anode, respectively, which were obtained from Pars Platin (Tehran, Iran). The electrodes were coupled to a power supply model 8760T3 with programmable voltages in the range of 0–600 V and output currents in the range of 0–500 mA from Paya Pajoohesh Pars (Tehran, Iran). A homemade pulse generator equipped with a timer in the range from 1 s to 10 min was employed to set the pulse duration and outage period. During the extraction, the PEME unit was stirred using a magnetic bar (5 mm × 2 mm) at a pre-adjusted speed by a heater-magnetic stirrer model 3001 from Heidolph (Kelheim, Germany).

Table 1
Chemical structures, pK_a and $\log K_{o/w}$ of the analytes.

Chemical structure	Name	pK_a [a]	$\log K_{o/w}$ [a]
	Amitriptyline	9.4	4.94
	Nortriptyline	9.7	1.7
	Diclofenac	4.2	4.5
	Mefenamic acid	4.2	6.0
	Salbutamol	9.22, 9.83	0.01
	Terbutaline	9.12, 9.33, 10.77	0.48

[a] Ref. [23].

2.2. Chemicals and materials

AMI and NOR were purchased from Razi Pharmaceutical Company (Tehran, Iran). SB was obtained from Sigma (St. Louis, MO, USA). DIC, MEF and TB were gifts given by the Department of Pharmaceutics of Tehran University (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 was obtained from Merck (Darmstadt, Germany). All of the 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 (Kyounggi-do, Korea).

A stock solution containing 1 mg mL^{-1} of AMI and NOR was prepared in methanol. The stock solution of SB and TB with concentration of 0.2 mg mL^{-1} of each analyte was prepared in methanol, as well. Also, a 1 mg mL^{-1} solution of MEF and DIC was prepared in acetonitrile. All standard solutions were stored at −4 °C protected from light. Working standard solutions were prepared by dilution of the stock solutions in methanol.

2.3. HPLC conditions

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