Journal of Chromatography A, 1346 (2014) 25–33

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Micro-electromembrane extraction across free liquid membranes. Instrumentation and basic principles☆

Pavel Kubáň*, Petr Boček

Institute of Analytical Chemistry of the Academy of Sciences of the Czech Republic, v. v. i., Veveří 97, CZ-60200 Brno, Czech Republic

ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 14 April 2014
Accepted 15 April 2014
Available online 22 April 2014

Keywords:
Free liquid membranes
Micro-electromembrane extraction
SPADNS, UV–vis spectrophotometry

ABSTRACT

A micro-electromembrane extraction (μ-EME) technique using electrically induced transfer of charged analytes across free liquid membranes (FLMs) was presented. A disposable extraction unit was proposed and it was made of a short segment of transparent perfluoroalkoxy tubing, which was successively filled with three liquid plugs serving as acceptor solution, FLM and donor solution. These plugs formed a three-phase extraction system, which was precisely defined, that was stable and required μL to sub-μL volumes of all respective solutions. Basic instrumental set-up and extraction principles of μ-EME were examined using an anionic and a cationic dye, 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt (SPADNS) and crystal violet, respectively. Transfers of the charged dyes from donor into acceptor solutions across FLMs consisting of 1-pentanol were visualized by a microscope camera and quantitative measurements were performed by UV–vis spectrophotometry. The effects of operational parameters of μ-EME system were comprehensively investigated and experimental measurements were accompanied with theoretical calculations. Extraction recoveries above 60% were achieved for 5 min μ-EME of 1 mM SPADNS at 100 V with repeatability values below 5%. Selectivity of FLMs was additionally examined by capillary electrophoretic analyses of acceptor solutions and the potential of FLMs for μ-EME pretreatment of samples with artificial complex matrices was demonstrated.

1. Introduction

Till the end of the 1980s, sample pretreatment has been performed predominantly using two well-established methods, namely liquid–liquid extraction (LLE) and solid phase extraction (SPE) [1,2]. The fact that LLE and SPE are easy to automate and can be carried out in large batches has predetermined these two extraction techniques to be widely accepted by researchers and practitioners in pharmaceutical, clinical and environmental science. On the other hand, automated and batch-wise sample pretreatment using LLE and SPE is costly, requires use of rather sophisticated instrumentation and consumes large volumes of potentially toxic organic solvents (in LLE method) and real samples (in both LLE and SPE methods).

The fact that the traditional sample pretreatment techniques are burdened by the above mentioned drawbacks resulted into a thorough investigation of alternative sample pretreatment techniques. A special attention has been paid to down-scaling of the new techniques, simplification of their operation, minimizing consumption of samples/reagents and overall costs. Here, the development of microextraction techniques played a very important role. Among the microextraction techniques, single drop microextraction (SDME) [3,4], liquid phase microextraction (LPME) [5] and solid phase microextraction (SPME) [6] have been most frequently reported in scientific literature and progressively accepted by the scientific community.

Special attention has been also paid to selective microextractions of analytes from aqueous donor solutions across water immiscible organic phase layers, i.e., across liquid membranes. Initially, first applications of a thin layer of organic solvent used for separation of two aqueous solutions were described in the mid 1970s [7,8]. Note, however, that these liquid membranes were supported on a glass fibre paper sandwiched between two dialysis papers, were about 1 mm thick and transfer across the membranes was very slow. The potential of supported liquid membranes (SLMs) for sample pretreatment has been recognized about a decade later by employing thin porous polymeric supports where the organic solvent (liquid membrane) was stabilized by capillary forces in micropores of the support, and which made the

☆ Presented at the 20th International Symposium on Electro- and Liquid Phase-Separation Techniques (ITP 2013), 6–9 October 2013, Puerto de la Cruz, Tenerife, Canary Islands, Spain.

* Corresponding author. Tel.: +420 532290140; fax: +420 541212113.
E-mail address: kuban@iach.cz (P. Kubáň).

http://dx.doi.org/10.1016/j.chroma.2014.04.047
0021-9673/

membrane preparation easier and more reproducible [9–11]. A principally different method using a drop of organic solvent as the phase boundary and acceptor solution at the same time, SDME, was reported as another microextraction approach [3,4]. Analytes were extracted into a small drop of an organic solvent, which was immersed into aqueous donor solution, and the drop was then directly used for injection into an analytical system. The major drawbacks of this approach were low stability of the organic drop in an agitated donor solution and limited compatibility of the water immiscible acceptor phase with analytical techniques other than gas chromatography. A three-phase microextraction technique using a small drop of an aqueous acceptor solution covered by a thin layer of an organic phase, which was created on a separation capillary tip, was developed for direct injection of pretreated samples into capillary electrophoresis (CE) [12,13]. This approach has addressed the problem of acceptor phase compatibility with CE. Nevertheless, the drop stability has been reported as an obvious drawback of the extraction method, too. Apparently, stability of the organic drop/phase is a major issue in LPME techniques.

A significant improvement was achieved by rediscovering the SLMs and by anchoring the organic solvents into thin walls of tubular porous polymeric materials – hollow fibres (HF) – in the late 1990s [5]. In HF-LPME, the fibre is impregnated with appropriate organic solvent, aqueous acceptor solution is filled into the fibre lumen and the fibre is finally placed into agitated aqueous donor solution. The SLM acts as a selective barrier between donor and acceptor solution and analytes are diffusively transferred across the SLM based on their distribution coefficients between the organic and the aqueous phase. Apart from higher stability of the organic phase, acceptor solutions are aqueous in HF-LPME and may be used for injections into analytical techniques that are compatible with aqueous samples, such as HPLC, IC and CE. Although HF-LPME has successfully resolved the problem of the low stability of organic phase and compatibility of acceptor solutions with all main-stream analytical techniques, long times were required to achieve steady-state of the extractions as the analytes were transferred across SLMs by diffusion [14,15].

In order to speed-up the HF-LPME process, analyte transfer was accelerated by application of electric field in a technique called electromembrane extraction (EME) [16–20]. The instrumental set-up in EME is identical to that in HF-LPME with the exception that electrodes are inserted into donor and acceptor solution and d.c. electric voltage is applied across the SLM during EME. The principles of the analyte transfer across SLMs are therefore fundamentally different and have been described in recent publications [21,22]. Application of the electric field has improved extraction rates of EMEs and excellent results were reported for pretreatment of samples with various matrices [17–20].

An increasing number of fundamental studies and applied research on extractions across SLMs have proved that SLMs are an efficient extraction tool in various fields of preparative analytical chemistry [14,15,17–20,23,24]. Nevertheless, despite their excellent characteristics, SLMs also encounter several common drawbacks. Exact dimensions of the membranes, which are necessary for fundamental studies of extraction processes, are difficult to measure. Variability of the membrane dimensions is restricted by the limited range of commercially available supporting polymeric materials and visual monitoring of the extraction process is not possible as the membranes are not transparent. Moreover, application of electric field across SLMs results into distortions of the organic phase in SLMs and the EME technique collapses, sometimes.

In this contribution a new approach to EME is presented, which eliminates the need for stabilization of liquid membranes in porous supporting materials and demonstrates the possibility of using free liquid membranes (FLMs). The proposed instrumental set-up enables rapid manipulation with precisely defined (and easily measurable) volumes of FLMs as well as of working (donor and acceptor) solutions. Application of transparent materials enables optical visualization of the extraction process and the presented work offers a comprehensive evaluation of selected parameters on the performance of a micro-electromembrane extraction (μ-EME) technique. During the submission process of this manuscript a principally similar extraction technique, called three-phase electroextraction, was described by Raterink et al. [25].

2. Experimental

2.1. Reagents, background electrolyte solutions and standards

All chemicals (reagent grade) were purchased from Pliva-Lachema (Brno, Czech Republic), Sigma (Steinheim, Germany) and Fluka (Buchs, Switzerland). Deionized (DI) water with resistivity higher than 18 MΩ cm was prepared by exchange of ions in a mixed-bed ion exchanger water purification system G 7749 (Miele, Gütersloh, Germany). Stock solutions of crystal violet (10 mM, Sigma) and SPADNS (10 mM, Pliva-Lachema) were prepared in DI water from pure chemicals. Standard sample solutions were freshly prepared from these stock solutions and were diluted with DI water. Stock solution of Na^+ and Cl^- (1.5 M) was prepared from NaCl (Pliva-Lachema) and stock solution of phosphate (1 M) was prepared from Na_2HPO_4 (Fluka). Stock solutions of choline and creatinine (10 mM, Sigma) were prepared from pure chemicals. Human serum albumin (HSA) was purchased from Sigma and was prepared at a concentration of 20 g L^{-1} using DI water. All stock solutions were refrigerated at 4 °C. Background electrolyte (BGE) solutions for CE measurements were prepared from concentrated (99.8%) acetic acid (Fluka) and were stored for one week at room temperature. The optimum CE separation of inorganic cations and biochemical species in cationic mode as well as separation of chloride and phosphate in anionic mode was achieved in BGE solution consisting of 30% (5.2 M, pH 2.0) acetic acid. 1-Pentanol, 1-hexanol, 1-octanol, 1-ethyl-2-nitrobenzene (ENB) and 2-nitrophenyloctyl ether (NPOE), all Fluka, were used as FLMs in μ-EME experiments. Extraction recoveries were determined according to Ref. [16].

2.2. Instrumentation

2.2.1. Micro-electromembrane extraction across free liquid membranes

A photograph of a μ-EME unit is depicted in Fig. 1. The unit is made of a chemically inert perfluoroalkoxy (PFA, Vici-Jour, Schenkon, Switzerland) tubing, which is filled successively with aqueous acceptor solution, organic solvent acting as the FLM and

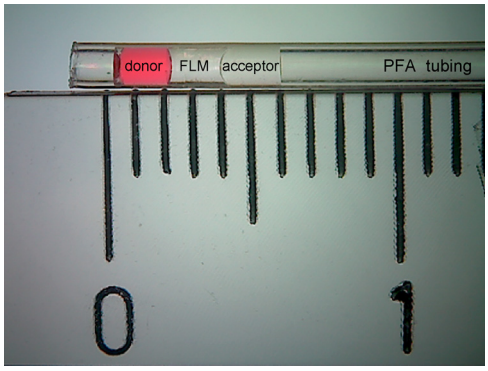

Fig. 1. A photograph of the PFA microextraction unit (1.0/1.6 mm ID/OD) filled subsequently with 1.5 μL acceptor solution (acceptor, DI water), 1.5 μL free liquid membrane (FLM, 1-pentanol), 1.5 μL donor solution (donor, 1 mM SPANDS) and 1.5 μL air. Scale is in cm.