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Preconcentration in micro-electromembrane extraction across free liquid membranes

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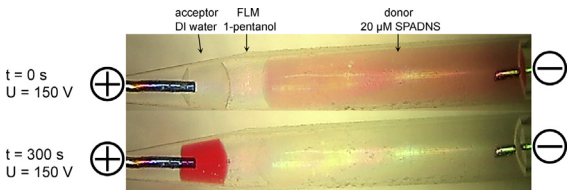
HIGHLIGHTS

- Electrically induced preconcentrations across free liquid membranes (FLMs) are presented.
- Preconcentrations are carried out in conical units with flexible volumes and shapes of FLMs and acceptor/donor solutions.
- Enrichment factors of up to 98 are achieved for preconcentrations of ionic dyes.
- The technique uses sub-μL to μL volumes of FLMs and acceptor solutions (pure water).
- Preconcentrations across FLMs combined with CE are used for analysis of ClO_4^- in drinking waters.

GRAPHICAL ABSTRACT



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ABSTRACT

Preconcentration potential of micro-electromembrane extraction (μ-EME) across free liquid membrane (FLM) was examined with an anionic and a cationic dye, 4,5-dihydroxy-3-(*p*-sulfophenylazo)-2,7-naphthalene disulfonic acid, trisodium salt (SPADNS) and phenosafranine, respectively. For the first time, it was shown that the spatial flexibility of FLMs enabled application of tailored extraction units with mutually different shapes and migration cross-sections for FLMs, donor and acceptor solutions. Thus, e.g. conical units enabled easy and reproducible formation of a three-phase extraction system (donor/FLM/acceptor) with sub-μL volumes of acceptor solutions as well as rapid and highly efficient preconcentration of the two dyes. Quantitative measurements of resulting solutions were carried out by UV–vis spectrophotometry and enrichment factors of up to 98 were achieved for μ-EMEs of 20 μM SPADNS (50 μL) preconcentrated into 0.5 μL of pure water across 1-pentanol at −150 V for 18 min. Visual monitoring of the entire extraction process (with USB microscope camera) was possible across transparent extraction units, moreover, important extraction parameters, such as FLM dimensions and donor-to-acceptor solution volume ratio, which determine the mechanical stability of the membrane and maximum enrichment factor, respectively, were readily adjusted. Combination of μ-EME across FLMs with capillary electrophoresis (CE) was further shown suitable for preconcentration and determination of perchlorate in drinking water samples. Good repeatability of the μ-EME-CE method (RSD values better than 9.5%), linear relationship for the analytical signal vs. concentration (r^2 better than 0.997) and enrichment factors of up to 30 were achieved for μ-EMEs of perchlorate across 1-pentanol and 1-hexanol based FLMs.

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1. Introduction

Despite recent technological advances in the field of analytical chemistry, most samples cannot be injected into modern analytical instruments directly due to their complex matrices and, as a result, sample pretreatment is usually required prior to their analyses. Moreover, real samples are often available in small volumes and concentrations of analytes therein are low. Liquid–liquid extraction (LLE) [1] and solid phase extraction (SPE) [2] are recognised techniques for sample clean-up and preconcentration of trace analytes. As an alternative to LLE and SPE, extractions in micro-scale format have been extensively investigated during the last two decades. The micro-scale extraction techniques focused primarily on improvements of the well-known drawbacks of LLE and SPE, i.e. their high environmental impact, consumption of samples and running costs, and the need for sophisticated external instrumentation.

Solid phase microextraction (SPME) [3] has gained a significant attention as a solvent-free miniaturized extraction technique in the past two decades [4,5], and the unique characteristics of SPME have led into its wide commercial use. In SPME, analytes are adsorbed onto a surface of a porous microextraction fibre during the sample pretreatment. The fibre is then placed into a sampling device of an analytical system for thermal and/or liquid desorption and injection of analytes. SPME has become a simple, easy-to-use and widely accepted extraction technique, nevertheless, the fibres are costly, are reused for several extraction cycles leading to possible sample carry-over, their life-time is limited and their use in analytical methods other than gas chromatography (GC) is less frequent.

In liquid phase microextraction (LPME), analytes are extracted from aqueous samples across [6,7] or into [8] μL volumes of water immiscible organic solvents. Supported liquid membranes (SLMs) were introduced as the first truly miniaturized sample pretreatment tools in LPMEs [9]. An SLM is usually made of a thin inert porous polymeric material (usually polypropylene (PP) or polytetrafluoroethylene (PTFE)), which is impregnated with a water immiscible solvent, and acts as a selective phase interface between aqueous donor and acceptor solution. Analytes, which are present in the donor solution, are transferred across the SLM into the acceptor solution based on diffusion [10] or on application of electric field [11]. Acceptor solutions can then be directly injected into various analytical systems. Single drop microextraction (SDME) is based on extraction of analytes from an aqueous sample into a small drop of a water immiscible solvent, which is directly immersed into the sample or sample headspace and acts simultaneously as a phase interface and an acceptor solution [12,13]. The solvent drop is usually formed at the tip of a liquid handling device (syringe, micropipette, etc.) and analytes diffuse into the drop rapidly due to its high surface area-to-volume ratio. After extraction, the drop is withdrawn into the device, which is transferred to an analytical system (GC or reversed-phase HPLC), and the drop is then injected for analysis. A novel concept of a three-phase SDME, which can be coupled directly to capillary electrophoresis (CE), was reported recently [14,15].

SDME and LPME across SLMs are characterized by excellent sample clean-up and preconcentration capabilities. Additionally, they require no sophisticated instrumentation, reduce consumption of organic solvents to low μL volumes, are cheap, and can be directly coupled to various analytical systems. On the other hand, inferior mechanical stability of the hanging drop system [8] and of the solvent layer immobilized in the pores of a thin SLM made of volatile solvents [16] or used with proteinaceous samples [17,18] were often reported as serious drawbacks of the micro-scale extraction techniques.

Several approaches, which addressed the stability issues of the organic phase in LPME, were presented in the past. Ulmeanu et al. [19] have described a set-up suitable for stabilisation of volatile organic solvents, which normally evaporate from SLMs and result in the SLM failure. Instead of immobilizing 1,2-dichloroethane into the porous support, 200 μL of the solvent was dispensed between two dialysis membranes held by a PTFE cylinder and formed an organic layer with defined dimensions. The device was placed between two glass compartments filled with aqueous solutions, which prevented the organic solvent from evaporation, and the system was used for voltammetric measurements of hydrophilic ions. Guo et al. [16] used principally similar arrangement and formed a layer of trichloromethane between two PVC membranes, which was encompassed by two aqueous solutions and was used for extractions of alkaloids from natural products. The solvent layer between the two PVC membranes was stable for up to 24 h extractions with minimum solvent evaporation. Raterink et al. [20] reported an electrically induced extraction of charged carnitines across a layer of an organic solvent formed in a 500 μL Eppendorf tube. In their set-up, 50 μL of a sample was pipetted into the tube and was topped-up with 150 μL of an organic solvent. A small aqueous drop (~2 μL) was dispensed into the organic layer from a conductive micropipette tip, which held the drop and acted as one electrode. Second electrode, a PTFE-isolated platinum wire, was inserted directly into the sample and charged ions were transferred from the sample across the organic phase into the small acceptor drop at the micropipette tip. Recently, a novel concept called micro-electromembrane extraction (μ-EME) across free liquid membranes (FLMs) was presented [21,22]. FLM is formed in a narrow bore (internal diameter (ID) ≤1 mm) transparent polymeric tubing and is typically applied as a plug of a water immiscible organic solvent sandwiched between two plugs of aqueous solutions (donor and acceptor). FLM is not anchored in any supporting material, its dimensions are precisely defined by the tubing ID and solvent volume, and the extraction process can be monitored visually. Analytes from donor solution are transferred across the FLM due to the action of electric field and are gathered in acceptor solution during μ-EME. μ-EMEs across FLMs are characterized by simple instrumentation, disposability of extraction units, high mechanical stability of the system, short extraction times, excellent sample clean-up, and minimum consumption (~1 μL) of organic solvents and real samples. On the other hand, preconcentration capability of the sample pretreatment technique was not reported previously. This contribution brings experimental study of the basic aspects of preconcentration in μ-EME across FLMs, which are investigated with optically active organic dyes and enable visual monitoring of the preconcentration process. Furthermore, μ-EME across FLMs is shown suitable for preconcentration of perchlorate from drinking water samples.

2. Materials and methods

2.1. Reagents, background electrolyte solutions, standards and samples

All chemicals (reagent grade) were purchased from Pliva–Lachema (Brno, Czech Republic), 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 SPADNS and phenosafranine (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 solutions of Cl^- (1 M) and ClO_4^- (10 mM) were prepared from NaCl and $KClO_4$ (Pliva–Lachema), respectively, and 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

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