



# Application of a macrocyclic compound, bambus[6]uril, in tailor-made liquid membranes for highly selective electromembrane extractions of inorganic anions



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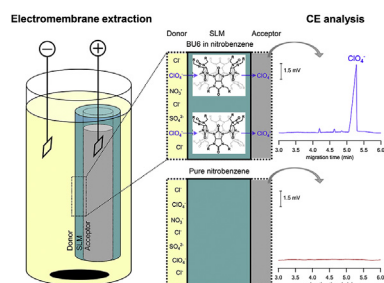
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## HIGHLIGHTS

- Highly selective liquid membrane is proposed for EMEs of specific inorganic anions.
- Selectivity is obtained by modifying liquid membranes with a macrocyclic compound BU6.
- EME selectivity is directly proportional to association constants between BU6 and anions.
- Efficient EMEs of target anions are achieved at up to 100.000-fold excess of matrix anions.
- Sub- $\mu\text{M}$  to  $\mu\text{M}$  concentrations of  $\text{ClO}_4^-$  and  $\text{Br}^-$  are extracted from tap and sea water.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A tailor-made liquid membrane consisting of a resistive organic solvent (nitrobenzene, NB) and a highly selective non-ionic macrocyclic compound (bambus[6]uril, BU6) was employed for electromembrane extraction (EME) of inorganic anions. BU6 facilitates strong host-guest interactions of its internal cavity with selected inorganic anions only and its presence in the liquid membrane ensured excellent selectivity of the EME process. EME transfers were directly related to association constants between BU6 and inorganic anions and nearly absolute selectivity was achieved for EMEs of iodide, bromide and perchlorate. Major inorganic anions (chloride, nitrate, sulphate and carbonate), which exhibit low interactions with BU6 cavity, were efficiently eliminated from the EME transfer. No interferences were observed for EMEs of target analytes from samples containing up to 100.000-fold higher concentrations of the major anions. Addition of species-specific macrocyclic modifiers to free and supported liquid membranes might thus open new directions in fine-tuning of EME selectivity. At optimized EME conditions (polypropylene hollow fiber impregnated with NB + 3% (w/w) BU6, extraction voltage 25 V, extraction time 15 min, deionized water as acceptor solution) perchlorate was selectively extracted from tap water at concentrations below the guideline value recommended by United States Environmental Protection Agency. Excellent selectivity of the tailor-made liquid membrane was further demonstrated by EME of bromide from sea water.

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## 1. Introduction

Microextraction techniques have become increasingly popular for sample treatment during last two decades. The major aspects, which have boosted their popularity, were reduced sample volumes, rapid pretreatment times, low consumption of potentially hazardous chemicals and reduced costs. Several techniques, such as solid phase microextraction [1], single drop microextraction [2,3], stir-bar sorptive extraction [4], hollow-fiber liquid phase microextraction (HF-LPME) [5] and dispersive liquid-liquid microextraction [6] have been introduced and adopted in many research laboratories. One of the most recently developed microextraction techniques is electromembrane extraction (EME) [7]. EME is based on transfer of charged analytes from one aqueous solution (donor) across a thin layer of a water immiscible phase (supported liquid membrane (SLM)) into another aqueous solution (acceptor) by the action of electric potential. Application of the electric potential ensures one obvious advantage of EME over the instrumentally similar HF-LPME since the EME process can be considerably accelerated [8].

The crucial parameters, that determine the overall performance of a microextraction technique, are extraction efficiency and selectivity. Extraction efficiency relates to total transfer of analyte(s) from donor into acceptor solution. Extraction selectivity relates to transfer of particular analyte(s) vs. transfer of matrix components from donor into acceptor solution. In principle, selectivity of a microextraction technique is considered sufficient at conditions, which enable negligible or no transfer of matrix components and considerably higher transfer of analytes into acceptor solution. In EME, efficiency and selectivity are associated mainly with direction and magnitude of electric field, nature of organic solvent used as SLM, presence of modifiers in SLM and composition of donor and acceptor solution [7,9–13].

Various approaches for improvement of EME efficiency and selectivity have been investigated. Extraction efficiency increased after addition of hydrophobic ion-pair reagents, such as alkylated phosphonic acids, to SLMs for EMEs of basic drugs with low log *P* values [9], heavy metal cations [14,15] and amino acids [16]. Addition of ionic modifiers (Aliquat 336 and other quaternary alkylammonium salts) was reported for improved efficiency of EMEs of anionic compounds [17,18]. Enhanced electrically induced transfers of basic and acidic drugs were also achieved after addition of nanoparticles [19–24], ionic liquids [25,26] and graphene oxide [27,28] into SLMs and of ionic [29] or non-ionic surfactants [30–32] into donor solutions. Recently, extraction selectivity was fine-tuned by addition of species-specific modifiers, such as 18-crown-6 ethers, to SLM for EME of potassium from other inorganic cations [33].

These reports clearly demonstrate that modification of SLM composition may considerably alter EME performance. However, addition of ionic modifiers to SLM leads to lower resistance of the organic phase interface between donor and acceptor solution, electric currents increase significantly and most importantly, enhanced EME efficiencies of target analytes are accompanied by considerable increase in transfer of interfering matrix components [34]. Modification of SLMs with nanoparticles or sorbents and feeding donor solutions with surfactants might eliminate the problem of excessive electric currents in the EME systems. Nevertheless, these modifiers are rather non-selective and enhanced transfer of large groups of species with similar properties is usually achieved. In addition to the increased electric currents and relatively low selectivity, the reported procedures were mainly adopted for EMEs of cationic species and optimization of EME efficiency/selectivity of anionic analytes was substantially less frequent [17,18,20,22–24,26,28,31,32]. Thus, although in its infancy, addition

of species-specific non-ionic modifiers to SLM might be highly attractive for fine-tuning of EME selectivity. Resistivity of such tailor-made SLM remains nearly unchanged compared to that consisting of pure organic solvent and only particular analyte(s) is/are transferred across the SLM. Transfer of even structurally similar species is efficiently eliminated by the tailor-made SLMs and application of species-specific modifiers in SLMs may open new directions in selective EMEs of ionic analytes.

Although EMEs were mainly adopted for extractions of small drugs, EMEs were recently applied to pretreatment of inorganic anions from various complex samples. Perchlorate [35–38], bromate [39], chromate [17,40] and major inorganic anions [41,42] were the analytes of interest and SLMs formed by pure aliphatic alcohols were exclusively used for their EMEs. Aliphatic alcohols are, however, rather non-selective and apart from the target analytes, considerable transfers of matrix anions with similar physico-chemical properties were reported [17,36,37]. Transfer of matrix anions may impair the overall extraction performance especially for saline samples, which contain matrix anions at much higher concentration levels compared to target analytes.

In this manuscript a novel approach for species-selective EME is presented on an example of EMEs of inorganic anions. EMEs are carried out across SLM formed by nitrobenzene (NB) with addition of a non-ionic macrocyclic compound bambus[6]juril (BU6) [43,44]. NB is a highly resistive solvent and SLMs formed by pure NB facilitate no EME transfer of inorganic anions. On the other hand, BU6 can selectively host specific inorganic anions in its cavity, whereas host-guest interactions with other anions do not take place. After addition of BU6 into NB, selective EMEs of bromide, iodide and perchlorate were achieved, while common inorganic anions (chloride, nitrate, sulphate and carbonate) exhibited no EME transfer across the tailor-made SLMs. Due to the non-ionic character of BU6 and fact that only target analytes were transferred across the tailor-made SLM, low and stable electric currents and efficient EMEs of target anions were achieved with donor solutions containing up to 100.000-fold excess of matrix vs. target anions. The nearly absolute selectivity of the tailor-made SLM was further evidenced by efficient EMEs of perchlorate and bromide from tap and sea water samples.

## 2. Materials and methods

### 2.1. Reagents, standard solutions and samples

All chemicals were of reagent grade and deionized (DI) water with resistivity higher than 18 M $\Omega$  cm was used throughout. Stock solutions of inorganic anions (100 mM) were prepared in DI water from sodium chloride, sodium nitrate, magnesium sulphate, sodium carbonate, potassium iodide, potassium bromide and potassium perchlorate (Sigma, Steinheim, Germany and Fluka, Buchs, Switzerland). Standard solutions for capillary electrophoresis (CE) and donor solutions for EME and micro-electromembrane extraction ( $\mu$ -EME) were prepared from the stock solutions and were diluted with DI water. All solutions were stored at the temperature of 4 °C.

Background electrolyte (BGE) solutions for CE of inorganic anions were prepared from L-histidine (His, Sigma), acetic acid (Fluka) and NaOH (Lach: Ner, Neratovice, Czech Republic). SLMs and free liquid membranes (FLMs) were made of NB (Sigma), 1-ethyl-2-nitrobenzene (ENB, Fluka) and nitrophenyl octyl ether (NPOE, Sigma) with highest available purity ( $\geq 98\%$ ). The solvents were used without any further purification and a non-ionic modifier, BU6, was added to the organic solvents for selective EMEs of species-specific inorganic anions. BU6 was synthesized according to the previously described procedure [45] and its structure is shown in Fig. 1.

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