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Electro-driven extraction across a polymer inclusion membrane in a flow-through cell

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ABSTRACT

A flow-through arrangement for electrodriven extraction across a polymer inclusion membrane was developed. Sample introduction into the donor chamber was continuous, while the acceptor solution was stagnant. By adjustment of the total volume of the donor solution pumped through the cell the best compromise between enrichment factor and extraction time can be set. The enriched extract was analyzed by capillary electrophoresis with contactless conductivity detection. Membranes of 20 μm thickness were employed which consisted of 60% cellulose triacetate as base polymer, 20% *o*-nitrophenyl octyl ether as plasticizer, and 20% Aliquat 336. By passing through 10 mL of sample at a flow rate of 1 mL/min the model analytes glyphosate (a common herbicide) and its major metabolite aminomethylphosphonic acid could be transported from the aqueous donor solution to the aqueous acceptor solution with efficiencies >87% in 10 min at an applied voltage of 1500 V. Enrichment factors of 87 and 95 and limits of detection down to 43 and 64 pg/mL were obtained for glyphosate and aminomethylphosphonic acid, respectively. The intra- and interday reproducibilities for the extraction of the two compounds from spiked river water were about 6 and 7% respectively when new membranes were used for each experiment. For consecutive extractions of batches of river water with a single piece of membrane a deterioration of recovery by about 16% (after 20 runs) was noted, an effect not observed with purely aqueous standards.

1. Introduction

The use of electric fields for sample pretreatment in order to achieve pre-concentration of charged analytes or a matrix clean-up has seen considerable recent attention. Compared to conventional extraction techniques the methods are faster as the transport processes are not limited by passive diffusion. Back-extraction (into an aqueous solution) is also not normally needed. An introduction to the methods can be found in several recent review articles [1–4]. Prominent among these techniques has been the method termed electro-membrane extraction (EME) [5–9]. This approach has been based on supported liquid membranes (SLM) usually employing porous hollow fibers made from polypropylene. The material is impregnated with an organic solvent such as 1-heptanol, 1-octanol, *o*-nitrophenyl octyl ether (NPOE) or ethyl nitrobenzene. Extraction of either anionic or cationic species is then achieved by applying a voltage of the appropriate polarity between the sample solution and the acceptor solution behind the membrane.

However, a weakness of the SLMs is the limited mechanical stability of the solvent soaked membranes. Several researchers have indeed reported problems such as leaching of the organic liquid phase into sample and receiving solutions during the electrodriven extraction [10–14]. For this reason, a variation of the EME approach, which is based on a homogeneous, non-porous polymer inclusion membrane (PIM), rather than a supported liquid membrane, was recently developed by us [15]. The plasticized polymer membrane, which consisted of 60% cellulose triacetate as base polymer, 20% NPOE as plasticizer, and 20% Aliquat 336 as cationic carrier and had a thickness of 20 μm, demonstrated a significantly improved mechanical robustness and easier handling compared to our previous experience with the SLMs based on porous polypropylene [8,16]. In this arrangement the solvent is the plasticizer for the polymer rather than being suspended in pores. The membranes are dry and can be stored readily without deterioration. This robust material, which had been reported previously for use in waste water treatment [17,18], was proven to be suitable for extraction of lipophilic organic analytes using an applied voltage as driving force [15]. The strong mechanical structure of the PIM allowed repeated analyses without requiring membrane reconditioning steps.

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The extraction cell used in the previous report consisted of two PTFE compartments clamped together with a flat membrane sandwiched between them [15]. The donor and receiving sections had volumes of 20 mL and 750 μL, respectively. This fixed volume ratio between the two chambers limited the maximum possible enrichment factor to 26. Such a restriction can be removed by employing a flow through cell for continuous extraction from a sample stream. The enrichment factor can then be adjusted by variation of the total volume of sample pumped through the cell. Recently, Petersen et al. indeed demonstrated flow-cell based EME employing SLMs for the determination of selected basic drugs [19–21].

Herein a flow-through cell for electro-driven extraction based on a solid PIM is described. It was designed with a large ratio of membrane surface to sample volume in order to facilitate efficient analyte transport. As model analytes glyphosate (GLYP) and aminomethylphosphonic acid (AMPA) were used. The widely used herbicide glyphosate and its degradation product are of importance in environmental analysis, and were chosen as model analytes in order to allow a comparison with earlier studies on miniature extraction methods conducted in our research groups [15,16]. For quantification of the poorly UV-absorbing species, capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C^4D) was employed. More details on this simple and versatile method for the determination of ionic species can be found in recent review articles [22–28].

2. Experimental

2.1. Chemicals and reagents

Aminomethylphosphonic acid (AMPA), Aliquat-336 (a commercial product mainly consisting of the lipophilic quaternary amine salt methyltrioctylammonium chloride) and sodium perchlorate ($NaClO_4$) were obtained from Aldrich (Buchs, Switzerland). Glyphosate (GLYP), 3-(*N*-morpholino)propanesulfonic acid (MOPS), histidine (His), hexadecyltrimethylammonium bromide (CTAB), cellulose triacetate (CTA), *o*-nitrophenyl octyl ether (NPOE) and dichloromethane were purchased from Fluka (Buchs, Switzerland). Ultrapure deionized water was produced on a Nano-Pure water purification system (Barnstead, IA, USA). All other reagents were of analytical grade and used without any further purification.

2.2. Membrane preparation

The polymer inclusion membranes (PIMs) were prepared by casting a solution of CTA (15 mg) as base polymer, NPOE (5 mg) as plasticizer and Aliquat-336 (5 mg) as cationic carrier in 4 mL dichloromethane. The solution was spread evenly into an 8 cm diameter glass petri-dish and the solvent was allowed to gradually evaporate overnight. All membranes tested were modified by replacing chloride by perchlorate as counter-ion by immersing the membrane for 24 h in 20 mL of a stirred 2.0 M $NaClO_4$ solution. The membrane thickness was measured with a digital micrometer (MDC-1, Mitutoyo Corporation, Kawasaki, Japan) and was determined to be approximately 20 μm.

2.3. Solutions

Stock solutions of GLYP and AMPA at a concentration of 1 mg/mL were prepared in deionized water and stored in the refrigerator. River water was collected from the Rhine in Basel, Switzerland. An analysis of this sample did not show the presence of GLYP and AMPA before adding these compounds to validate the method. Donor test solutions and spiked river water samples were obtained by appropriate dilution of the stock solution and $NaClO_4$ was added to these to obtain a final concentration of 1 mM $NaClO_4$ in order to assure a constant background conductivity. All samples had a pH in the range between 6 and 7. The acceptor solution also contained 1 mM $NaClO_4$ in all cases.

2.4. Electro-driven extraction system

A high voltage DC power supply with negative voltage output in the range from 0 to 1500 V was obtained from Advance Hivolt (GM12-1K5N, Woburn, MA, USA). The peristaltic pump was obtained from Gilson (Minipuls 3, Villiers le Bel, France). The operational amplifier used for recording the current was a TL071 (Texas Instruments, Austin, TX, USA) and the data acquisition system an e-corder (eDAQ, Denistone East, NSW, Australia).

2.5. CE-C^4D analysis

The CE experiments were performed on a PrinCE 500 2-lift system (Prince Technologies, Emmen, The Netherlands) equipped with a contactless conductivity detector system (eDAQ). The excitation frequency of the detector was set to 300 kHz and the amplitude was fixed at 100%. A bare fused silica capillary of 50 μm I.D. and 365 μm O.D. (Polymicro Technologies, Phoenix, AZ, USA) with total and effective lengths of 55 and 45 cm respectively was employed. The new capillary was conditioned by flushing with 1 M sodium hydroxide (NaOH) for 15 min and water for 5 min. The pretreated capillary was then rinsed with the running buffer for 30 min. After each analysis run, the capillary was rinsed for 3 min with the running buffer to maintain the reproducibility of the analysis. The running buffer consisted of 12 mM His, 8 mM MOPS and 50 μM CTAB (pH 6.3). Large volume sample stacking (LVSS) was performed using hydrodynamic injection for 100 s at 50 mbar [29]. The separation voltage was −30 kV.

2.6. Calculations

The extraction recovery (R) and enrichment factor (EF) were calculated according to the following equations:

$$R = \frac{n_a}{n_d} = \frac{V_a \cdot C_{a,\text{final}}}{V_d \cdot C_{d,\text{initial}}} \quad (1)$$

$$\text{EF} = \frac{C_{a,\text{final}}}{C_{d,\text{initial}}} = R \times \frac{V_d}{V_a} \quad (2)$$

The recovery is the ratio between the number of moles of the analyte collected in the acceptor solution (n_a) and the number of moles initially present in the donor solution (n_d), which can be obtained from the acceptor and donor volumes (V_a and V_d) and the final and initial concentrations ($C_{a,\text{final}}$ and $C_{d,\text{initial}}$) of the two solutions. The enrichment factor is the ratio of the concentrations in the two solutions (and can also be obtained from the recovery and the volume ratio).

3. Results and discussion

3.1. Cell design

The continuous electro-driven extraction setup is shown schematically in Fig. 1. The extraction cell was based on two polytetrafluoroethylene (PTFE) blocks each having the dimensions of 1 cm × 3.5 cm × 3.5 cm (width × height × depth). The donor and receiving compartments had a round cross-section of 2 cm diameter with depths of 1.6 mm and 0.3 mm and volumes of 500 μL and 100 μL respectively (Fig. 1). Appropriate holes allowed access for tubings and electrodes. The membrane used was cut in a square with each dimension being 2.5 cm. To assemble the extraction