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Integration of the free liquid membrane into electrokinetic supercharging – capillary electrophoresis for the determination of cationic herbicides in environmental water samples

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ABSTRACT

A new approach based on the integration of the free liquid membrane (FLM) into electrokinetic supercharging (EKS) was demonstrated to be a new powerful tool used in order to enhance online preconcentration efficiency in capillary electrophoresis (CE). A small plug of water immiscible organic solvent was used as a membrane interface during the electrokinetic sample injection step in EKS in order to significantly enhance the analyte stacking efficiency. The new online preconcentration strategy was evaluated for the determination of paraquat and diquat present in the environmental water samples. The optimised FLM-EKS conditions employed were as follows: hydrodynamic injection (HI) of 20 mM potassium chloride as leading electrolyte at 50 mbar for 75 s (3% of the total capillary volume) followed by the HI of tris(2-ethylhexyl) phosphate (TEHP) as FLM at a 1 mm length (0.1% of the capillary volume). The sample was injected at 10 kV for 360 s, followed by the HI of 20 mM cetyl trimethylammonium bromide (CTAB) as terminating electrolyte at 50 mbar for 50 s (2% of the total capillary volume). The separation was performed in 12 mM ammonium acetate and 30 mM NaCl containing 20% MeOH at +25 kV with UV detection at 205 nm. Under optimised conditions, the sensitivity was enhanced between 1500- and 1866-fold when compared with the typical HI at 50 mbar for 50 s. The detection limit of the method for paraquat and diquat was 0.15–0.20 ng/mL, with RSDs below 5.5%. Relative recoveries in spiked river water were in the range of 95.4–97.5%. A comparison was also made between the proposed approach with sole preconcentration of the field-enhanced sample injection (FASI) and EKS in the absence of the FLM.

1. Introduction

Capillary electrophoresis (CE) has emerged as a versatile and robust separation tool in various applications including pharmaceutical, environmental, biomedical and food analyses [1]. However, the detection sensitivity in CE has posed significant limitations in terms of extending the wide range of applications thereof due to the low sample injection volume (in nanoliter range) and short optical path length for absorbance detection. Much effort has been devoted in order to address this problem, such as the coupling with highly sensitive detectors (e.g. laser-induced fluorescence and mass spectrometer), integration with online and/or offline preconcentration methods. Among these approaches, online preconcentration is currently the most facile proposition to increase the detection sensitivity in CE due to its advantages in terms of low cost, high throughput and automated analysis. The details on the development and applications of online sample preconcentration in the past ten years have been extensively reviewed [2–6].

In recent years, the combinations of two or more online preconcentration methods have been substantially implemented in various CE applications. The synergistic effect of two or more online preconcentration methods showed significant enhancement in terms of detection sensitivity compared to sole online preconcentration. Quirino's group reported the combination of two online preconcentration methods, namely field-enhanced sample injection (FESI) and micelle to solvent stacking (MSS) with thousand-fold enhancements for the analysis of antibiotics in seawater [7], herbicides in milk [8] and antipsychotic drugs in urine samples [9]. In their latest attempt, a significant 6500-fold enhancement was reported for the determination of cationic and anionic drugs in plasma samples combining the three-step

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online preconcentration of FESI, sweeping and micelle to solvent stacking (MSS) [10,11]. In addition, Hirokawa et al. [12] introduced the powerful and noteworthy online preconcentration method featuring the combination of field-amplified sample injection (FASI) and transient isotachophoresis (t-ITP), termed electrokinetic supercharging (EKS). In the EKS, analytes are introduced electrokinetically between the leading electrolyte (LE) and the terminating electrolyte (TE) prior to the capillary zone electrophoresis (CZE). EKS displayed several thousand-fold enhancements in the peptide analysis [13], non-steroidal anti-inflammatory drugs in water samples [14,15], inorganic cations in heat exchanger fluids from nuclear power plants [16] and phenolic acids in river water [17,18]. Recently, our group also reported on the identification of anti-estrogen drugs in human plasma with the combination of two online preconcentration methods in nonaqueous CE, namely the EKS [19] and FESI-MSS [20].

The introduction of a solvent plug prior to the sample injection is an ordinary practice in CE analyses. Zhang and Thormann [21] demonstrated the head-column field-amplified sample stacking (HC-FASS) in which the low conductivity solvent plug was introduced prior to the electrokinetic injection (EKI) of the analytes. This method yielded an improved sensitivity enhancement with reproducible results as the analytes introduced into the capillary under the amplified electric field showed rapid stacking at the boundary between the low conductivity solvent plug and the running buffer. Thousand-fold enhancements were successfully reported in environmental and biological origins [22–25]. Later, Kubáň and Boček [26,27] reported an interesting integration of the immiscible organic solvent plug, termed as free liquid membrane (FLM), into a micro-electromembrane extraction (μ-EME) approach. The FLM acts as a selective phase interface between the aqueous donor and the acceptor solution that facilitates the electrically induced transfer of charged species in transparent tubing. This offline three-phase extraction showed the feasibility to efficiently retreat the samples with complex matrices e.g. high concentrations of salts and proteins and allowing the resulting acceptor solutions to be analysed directly by means of CE techniques. Various applications including the quantification of basic drugs in undiluted biological samples [26], as well as perchlorate in drinking water samples [28] were successfully implemented.

In this present work, the unique features of FLM were adopted and directly integrated into the existing EKS method in order to further enhance the detection sensitivity in capillary electrophoresis. The proposed new approach was evaluated for the analysis of paraquat and diquat present in the environmental water sample. Paraquat and diquat are bipyridylium herbicides widely employed for agricultural productivity. Among the reported analytical approaches, CE was proven to be a promising approach for the simultaneous separation of paraquat and diquat in various complex sample matrices after treating with either the offline [29–32] or online [33–35] sample pretreatment step. The operational parameters in the proposed FLM-EKS approach were comprehensively elucidated. A comparison was also made between the proposed approach and the typical hydrodynamic injection, FASI, as well as the EKS in the absence of the FLM.

2. Experimental

2.1. Chemicals and reagents

Sodium chloride (NaCl), ammonium acetate (Am-Ac), glacial acetic acid, sodium hydroxide (NaOH), potassium chloride (KCl), methanol (MeOH), and 1-octanol were purchased from Merck (Darmstadt, Germany). Paraquat, diquat, tris(2-ethylhexyl) phosphate (TEHP), 2-nitrophenyl octyl ether (NPOE), and cetyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Ultrapure deionised (DI) water was produced using a Direct-Q3 ultrapure water system (Merck Millipore, Darmstadt, Germany). The stock solutions of each herbicide at a concentration of 100 μg/mL were prepared in DI water and stored at 4 °C. Working standard solutions at lower concentrations were prepared by dilution in DI water prior to the analysis. All other reagents were of the analytical grade and used without any further purification.

2.2. Apparatus and procedures

The CE experiments were performed on a PrinCE 500 series instrument (Prince Technologies, Emmen, Netherlands) equipped with an external ECD 2600 UV–vis detector (ECOM, Prague, Czech Republic). A bare fused-silica capillary of 50 μm I.D. and 365 μm O.D. with total and effective lengths of 130 and 90 cm, respectively, was employed (Polymicro Technologies, Phoenix, AZ, USA). Data acquisition was carried out using the PowerChrome 280 data recording system equipped with a Chart software package (eDAQ, NSW, Australia). New capillaries were conditioned by flushing with 1 M NaOH for 15 min, water for 5 min, and buffer solution for 10 min. After each separation, the capillary was rinsed with the running buffer solution for 5 min in order to maintain the repeatability of the analysis. The background electrolyte (BGE) was adopted from reported work [36] with slight modifications and consisted of 12 mM of ammonium acetate and 30 mM NaCl with 20% MeOH at pH 4 (adjusted with acetic acid) in all case studies. A typical hydrodynamic injection (HI) procedure was performed at the optimum condition of 50 mbar for 50 s (2% of the total capillary volume). Note that the injection volume was calculated based on the Poiseuille equation [37]. The separation was performed at +25 kV. The UV detection was performed at 205 nm.

2.3. Field-amplified sample injection (FASI)

The FASI was performed by applying an injection voltage of +10 kV and an injection time of 300 s after filling the capillary with the BGE. The sample solutions were prepared in pure DI water and as a result the latter had a lower conductivity compared to the BGE. All running solutions were filtered through 25 mm diameter syringe filters with a 0.2 μm pore-size PTFE membrane (Macherey-Nagel, Düren, Germany). The CE separation was performed at +25 kV. The UV detection was performed at 205 nm.

2.4. Electrokinetic supercharging (EKS)

In the case of EKS, the capillary was initially filled with the BGE, followed by a short plug of 20 mM KCl which served as the LE. The LE was hydrodynamically injected at 50 mbar for 75 s (3% of the total capillary volume). Subsequently, the sample solution containing the targeted analytes was injected at +10 kV for 360 s. Lastly, a small volume of 20 mM CTAB which serves as the TE was injected hydrodynamically at 50 mbar for 50 s (2% of the capillary volume). A separation voltage of +25 kV was applied to re-stack the diffuse band of injected analytes between the LE and TE, followed by the CZE separation. The UV detection was performed at 205 nm.

2.5. Free liquid membrane – electrokinetic supercharging (FLM-EKS)

In order to integrate a FLM into the existing EKS protocol, the separation capillary was initially filled with the BGE, followed by a hydrodynamic injection of 20 mM KCl as LE at 50 mbar for 75 s (3% of the total capillary volume). Then, a short plug of TEHP, which served as the FLM, was hydrodynamically injected at 50 mbar for 7.8 s (0.1% of the total capillary volume based on the TEHP plug)