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Short communication

Electrophoretic concentration and sweeping-micellar electrokinetic chromatography analysis of cationic drugs in water samples

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ABSTRACT

Sample preparation by electrophoretic concentration, followed by analysis using sweeping-micellar electrokinetic chromatography, was studied as a green and simple analytical strategy for the trace analysis of cationic drugs in water samples. Electrophoretic concentration was conducted using 50 mmol/L ammonium acetate at pH 5 as acceptor electrolyte. Electrophoretic concentration was performed at 1.0 kV for 50 min and 0.5 kV and 15 min for purified and 10-fold diluted waste water samples, respectively. Sweeping-micellar electrokinetic chromatography was with 100 mmol/L sodium phosphate at pH 2, 100 mmol/L sodium dodecyl sulfate and 27.5%-v/v acetonitrile as separation electrolyte. The separation voltage was −20 kV, UV-detection was at 200 nm, and the acidified concentrate was injected for 36 s at 1 bar (or 72% of the total capillary length, 60 cm). Both purified water and 10-fold diluted waste water exhibited a linear range of two orders of concentration magnitude. The coefficient of determination, and intra- and interday repeatability were 0.991–0.997, 2.5–6.2, and 4.4–9.7%RSD ($n = 6$), respectively, for purified water. The values were 0.991–0.997, 3.4–7.1, and 8.7–9.8%RSD ($n = 6$), correspondingly, for 10-fold diluted waste water. The method detection limit was in the range from 0.04–0.09 to 1.20–6.97 ng/mL for purified and undiluted waste water, respectively.

1. Introduction

Electric field-assisted sample preparation has attracted much recent interest because of the enhanced analyte extraction selectivity resulting from the introduction of an electric field. The goals are to achieve efficient sample clean-up within a short period of time, at low cost, and in an environmentally-responsible way. A useful strategy to accomplish these goals is to superimpose an electric field onto traditional extraction techniques, such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), and dialysis. The electric field enhances the transfer of charged analytes across a physical boundary, which can be the interface of two immiscible liquids (i.e., electroextraction) [1], a solid–liquid phase (i.e., electric field-assisted solid-phase extraction, EA-SPE) [2–5] or two or more miscible phases separated by a membrane or filter (i.e., electromembrane extraction or EME [6,7] and electrodialysis [8]). In EA-SPE, the electric field can also be used to support the elution of the analyte from the sorbent. High enrichment factors and low limits of detection have been achieved by the implementation of electroextraction, EME, and EA-SPE [9,10].

Concentration of microliter scale sample volumes using an electric field and careful manipulation of sample and supporting electrolyte was proposed more than two decades ago [11–13]. We have previously reported a selective electrophoretic concentration (EC) scheme for ionised and ionisable analytes from aqueous or water samples. This scheme was initially demonstrated for ionised anionic analytes. Eight anionic analytes were injected electrokinetically from 20 mL of a low conductivity sample into 20 μL of acceptor electrolyte held inside a micropipette [14]. The principle of concentration is based on field-enhanced sample injection [15] where the analytes from a low conductivity sample were injected into a high conductivity electrolyte (i.e., acceptor electrolyte) inside the micropipette. EC did not use organic solvents or a physical barrier to separate the sample and acceptor phases. Using only an electric field as driving force, the concentrations of anionic analytes in the sample were increased by up to more than two orders of concentration. The experimental set-up for EC can be found in Fig. 1(a) of [14]. Briefly, a micropipette filled with acceptor electrolyte was inserted into to a plug of hydrogel housed in a syringe and the other end of the micropipette was submerged into the sample solution. The hydrogel at the top end of the micropipette prevented the flow of

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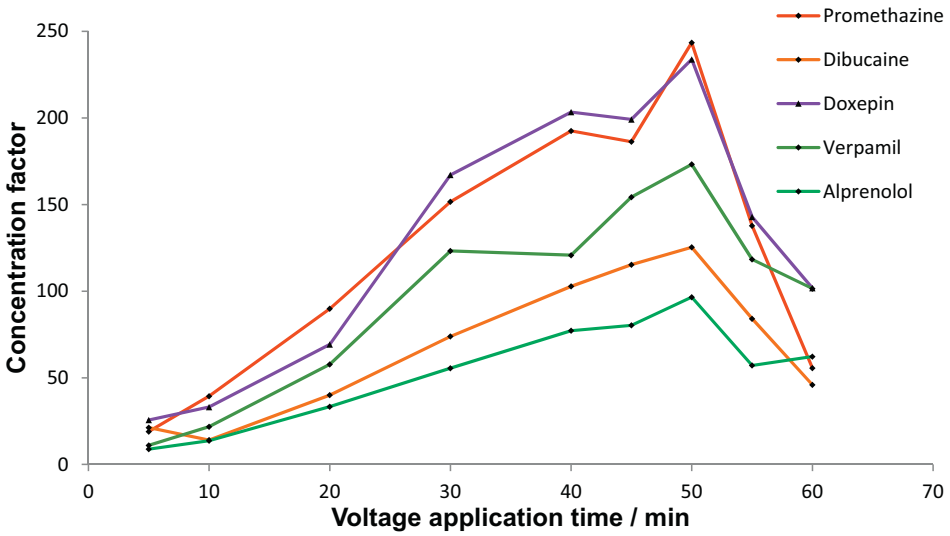

Fig. 1. Effect of voltage application time on concentration factor of cationic drugs in purified water. Applied voltage was 1.0 kV. The analyte concentration in the sample was 100 ng/mL. The concentration factor was calculated by dividing the CE peak area obtained from the concentrate by the peak area from a standard sample and then multiplied by the dilution factor (=500). CE analysis of standard and sample see Section 2.

electrolyte out of the pipette due to gravity. During voltage application, the hydrogel also supported the electric current and provided a zero net flow of liquid inside the pipette [16]. The anions were concentrated in the acceptor electrolyte as a result of electrophoretic migration towards the anode situated at the hydrogel end of the pipette.

Popular approaches to improve the detection sensitivity of CE techniques (including micellar electrokinetic chromatography (MEKC) [17]) coupled to UV detection are based on on-line sample concentration or stacking [18–20]. Sweeping, a mode of on-line sample concentration in MEKC, uses a pseudostationary phase (in this case, micelles) to accumulate the analytes into sharp zones [21,22]. Concentration factors (CF) of one to more than three orders of magnitude can be achieved [23,24]. However, sample preparation is often required in order to convert the sample into a form which is amenable to sweeping-MEKC, in particular by the use of a diluent devoid of the micelles. Examples of such preliminary sample treatment procedures include solvent–solvent extraction [25], dispersive liquid–liquid microextraction [26,27], magnetic solid particle extraction [28], solid-phase microextraction [29], and single drop microextraction [30]. In these techniques, the sample was ultimately extracted into an organic solvent, requiring that the extracts were first evaporated and the target analytes then reconstituted in a micelle-free diluent prior to sweeping-MEKC.

In the present study, EC was examined for the off-line sample preparation of cationic drugs in simple and complex water samples. Promethazine, dibucaine, doxepin, verapamil, and alprenolol were used as model ionisable analytes, while purified and waste water were used as sample matrices. EC provided a micelle-free concentrate, thus a sweeping-MEKC method was also optimised to separate the target analytes and to obtain good analyte detection sensitivities. In EC, the type and concentration of the acceptor electrolyte and the voltage application time were investigated. In sweeping-MEKC, the injection time and the effect of acidic buffer addition to the concentrate were studied. The performance of the combined analytical procedure of EC and sweeping-MEKC (i.e., linearity, method detection limit (MDL), method quantitation limit (MQL), repeatability, and concentration factor (CF)) was also investigated. MDL and MQL are the minimum analyte concentrations in the sample for detection and quantification of the whole method (i.e., EC combined with sweeping-MEKC).

2. Experimental

2.1. Reagents and stock solutions

Purified water was obtained from a Milli-Q system (Millipore, MA, USA). All reagents (acetonitrile, acrylamide, ammonium acetate, phosphoric acid, sodium hydrogen carbonate, sodium carbonate, 2-amino-2-hydroxymethyl-propane-1,3-diosodium hydroxide, Tris, and sodium dodecyl sulfate, SDS) were obtained from Sigma–Aldrich (New South Wales, Australia) and used as delivered. Stock electrolyte solutions of 1 mol/L sodium phosphate at pH 2 and 0.5 mol/L ammonium acetate at pH 5 were prepared in purified water. The pH of the stock solutions was adjusted when needed using 1 mol/L sodium hydroxide or acetic acid. The pH and conductivity of solutions were measured using a Bench-Top Meter (Sper Scientific, Australia). All stock solutions were sonicated and filtered using 0.45 μm filter prior to use. Wastewater effluent was donated from a local sewerage company (TasWater, Moonah, Australia) and filtered through a paper filter (Grade 1, Whatman, GB) prior to use. The analytes were also obtained from Sigma–Aldrich. Analyte stock solutions of 1 mg/mL each in methanol were prepared and stored at 5–8 °C when not in use. The analyte mixture consisted of hydrochloride salts of promethazine, dibucaine, doxepin, verapamil, alprenolol, and clomipramine (internal standard).

2.2. Hydrogel preparation

Hydrogels were prepared directly in 3 mL capacity polypropylene syringes without plunger where the narrower end was sealed with parafilm. The polymer mixture was made by mixing 700 μL of 50%-wt aqueous acrylamide (monomer), 120 μL of 0.5 mol/L ammonium acetate at pH 5, 320 μL purified water, and 60 μL of 5%-wt potassium persulfate (initiator). The mixture was heated at 60 °C for 10 min.

2.3. Electrophoretic sample concentration

The set-up for EC consisted of a high voltage power supply (Matsusada, Japan) capable of providing voltages up to 30 kV (0.1 kV increments), two platinum electrodes connected to the voltage power supply, 20 μL micropipettes with a length of 6.4 cm