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Screening determination of pharmaceutical pollutants in different water matrices using dual-channel capillary electrophoresis coupled with contactless conductivity detection

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ABSTRACT

In this study, the employment of purpose-made dual-channel compact capillary electrophoresis (CE) instrument with capacitively coupled contactless conductivity detection (C^4D) as a simple and inexpensive solution for screening determination of various pharmaceutical pollutants frequently occurring in surface water and hospital wastewater in Hanoi, Vietnam is reported. Five negatively charged pharmaceutically active compounds, namely ibuprofen, diclofenac, bezafibrate, ketoprofen and mefenamic acid were determined using the first channel whereas three positively charged ones, namely diphenhydramine, metoprolol and atenolol were determined with the second channel of the CE-C^4D instrument. Two different background electrolytes (BGEs) were used in these two CE channels independently. The best detection limits achieved were in the range of 0.2–0.8 mg/L without sample preconcentration. Enrichment factors up to 200 were obtainable with the inclusion of a solid phase extraction step. Good agreement between results obtained from CE-C^4D and those with the standard confirmation method (HPLC-DAD) was achieved, with correlation coefficients higher than 0.98.

1. Introduction

Many pharmaceutically active compounds are classified as environmental contaminants due to their low biodegradability and their potential to cause undesirable ecological and human health effects [1–5]. While having positive effects on the treatment of various pathologies and diseases, the use of pharmaceutical products results in the contamination of the aquatic environment, mainly through municipal and hospital effluents [6–8]. The occurrence of a large number of pharmaceutical contaminants in the environment has been reported for different developed countries (see some recent examples in [7,9–12]). In emerging countries, although the situation is often worse, only limited information is available as the regulations for environmental protection are not well established. In Vietnam, the first study on pharmaceutically active compounds contamination was recently reported by Tran et al., focusing on hospital wastewater and surface water in Hanoi [13]. Water contamination in Hanoi caused by direct discharge of domestic and industrial wastewater to rivers and lakes poses a big threat to public health. This leads to an urgent need for regular control of these contaminants in different water sources.

So far, various analytical methods for determination of pharmaceutical contaminants in different environmental matrices have been proposed [14,15]. Among all techniques, high performance liquid chromatography (HPLC) is the most common due to its high degree of confidence, reliability and reproducibility. The utilization of HPLC nevertheless requires long analysis time, a large amount of costly HPLC-grade solvents as mobile phases as well as high setup and maintenance costs (especially for the high pressure pumps and accessories). In Vietnam, only a few central environmental monitoring agencies or companies with abundant funding and sufficient expertise can afford the installation, long-term operation and maintenance of such instruments. On the other hand, capillary electrophoresis (CE), relying on a high voltage rather than high pressure for driving the analytes in a micro separation channel, offers a more economic and higher-throughput alternative. The determination of pharmaceutical residues in water with CE using UV or mass-spectrometric detection has been reported repeatedly (see refs. [16–22] for example).

Three additional positive features of CE that make it even more suitable for screening analysis purposes are portability for mobile

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deployment (see [23–26] and references listed therein), customer-oriented CE configuration for adaptation to different financial and expertise situations [27,28] and the possibility of using dual-channel setup for the concurrent determination of positively and negatively charged analytes [29–31]. The portability and the use of more than one channel were enabled when CE was used together with capacitively coupled contactless conductivity detectors (C^4D). In these detectors, the difference between the conductivities of the analytes and that of the background electrolyte (BGE) can be measured by employing a pair of tubular electrodes fitted around the capillary wall. Some notable advantageous features of C^4D include high versatility, ease in construction and operation, low power consumption and the potential of miniaturization (for more details see [32,33] and the references listed therein). CE-C^4D has been repeatedly used by Richter et al. for determinations of active ingredients together with their counter ions or degradation products in pharmaceutical formulations [34–39]. Simultaneous determination of cations and anions in these pharmaceutical applications were implemented through the use of BGEs with pH above 7 to produce high magnitudes of electro-osmotic flow (EOF) in fused silica capillaries for sweeping the anions with low and opposite electrophoretic mobilities towards the detector. In environmental applications, the employment of CE-C^4D has been communicated for separation of negatively and positively charged pharmaceutical contaminants in standard solutions [40] and for tracing of some negatively charged ones in a hospital wastewater sample [41]. Only one single CE channel was used and no cross check with another well established analytical method was realized in both cases.

Herein we report a straightforward and cost-effective method based on purpose-made dual-channel compact CE-C^4D for concurrent screening determination of different positively charged pharmaceutical residues (diphenhydramine, metoprolol and atenolol) and negatively charged ones (ibuprofen, diclofenac, bezafibrate, ketoprofen and mefenamic acid) in various water matrices in Hanoi, Vietnam. Compared to the recently reported dual-channel CE instruments that share a common BGE for both channels [31,42–44], the system reported herein allows the employment of two different BGEs, allowing the separations of analytes belonging to different categories.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). Stock solutions (1 mM) of diphenhydramine, metoprolol, atenolol, ibuprofen, diclofenac, ketoprofen, bezafibrate and mefenamic were used for the daily preparation of the standard solutions. Chemicals used for the preparation of BGEs included: Acetic acid (Ace), histidine (His), 2-(N-morpholino)ethanesulfonic acid (MES), lactic acid (Lac), tris(hydroxymethyl)aminomethane (Tris), 3-(N-morpholino)propanesulfonic acid (MOPS) and hydroxypropyl-beta-cyclodextrin (HP-β-CD). Fused silica capillaries of 50 μm ID and 365 μm OD were obtained from Polymicro Technologies (Phoenix, AZ, USA). Prior to their use, the capillaries were pre-conditioned with 1 M NaOH for 10 min and de-ionized water for 10 min, followed by flushing with the BGE. The capillaries were then used continuously for successive separations. De-ionized water, purified using a water purification system from Millipore - model Simplicity UV (Bedford, MA, USA), was used for the preparation of all standard solutions and for sample dilution if required. Commercial solid phase extraction (SPE) cartridges, including (i) LiChrolut RP-18 with the cartridge volume of 3 mL containing 500 mg sorbents (Merck) and (ii) hydrophilic modified, styrene-based polymer (hydrophilic lipophilic balance, HLB) SPE cartridges (200 mg sorbents per cartridge, 30 μm particle size, Waters Corporation), as well as the SPE vacuum manifold (Visiprep 5-7030, Sulpelco) were used for sample treatment and pre-concentration. Cross-checking was carried out using an HPLC instrument (LC-20AB) equipped with a UV–VIS-based diode array detector (DAD) from Shimadzu Corp. (Japan).

2.2. Instrumentation

All experiments were performed on a purpose-made dual-channel CE instrument. The high voltage (HV) modules (DX250 series) capable of providing up to 25 kV were obtained from EMCO (Sutter Creek, CA). The HV end of the capillary was isolated with a safety cage made from Perspex, which was equipped with a microswitch to interrupt the HV on opening. The miniature membrane pumps (NF-5-DCB) for sample aspiration were purchased from KNF (Balterswil, Switzerland). Micro-graduated needle valves were obtained from IDEX (P-470, Oak Harbor, WA) and solenoid valves from NResearch (product nos. 116T021 and 116T031, West Caldwell, NJ). All fluidic connections were made with 0.02″ I.D. and 1/16″ O.D. Teflon tubing and with polyether ether ketone (PEEK) flangeless nuts and ferrules 10-32 or ¼-28 UNF (IDEX). The injection interface that accommodates the grounded end of the capillary and the ground electrode was machined from a Perspex block (2 cm × 2 cm × 3 cm). Detection was carried out with in-house built miniature HV - C^4D according to a design reported previously [43,45]. The resulting signals were recorded with an ADC-20 data acquisition system (Pico Technology, St. Neots, UK) connected to the USB-port of a personal computer. A lithium battery pack of 14.8 V (CGR 18650CG 4S3P, Contrel, Hünenberg, Switzerland) and a separate pair of smaller Li-ion batteries (CGR 18659CG 4S1P, Contrel) fitted with 12 V regulators of appropriate polarities were used for powering the CE-C^4D system. Mains power can be utilized whenever available.

2.3. Field sampling

The sampling sites are located in Hanoi - the capital of Vietnam (see details in Fig. S1). Surface water samples were collected from the Nhuệ river (SN1, SN2 and SN3), Tô Lịch river (TL1–TL5), Lừ river (SL1), Sét river (SS1), Kim Ngưu river (KN1), the lake near Hanoi Medical University (YHN) and West Lake (HT2). The distances between the sampling sites from the same river or lake were at least 500 m. The samples from these rivers and lakes were collected near the municipal discharges at the distance of 1 m from the borders and at the depth of 20–30 cm below the surface. Untreated and treated wastewater samples were collected from the influents and effluents of wastewater treatment plants of the central pharmaceutical manufactory (TW1 and TW2, respectively) and the VCP pharmaceutical manufactory (VCP1 and VCP2, respectively). Water samples from discharges to the receiving points in residential zones were also collected. These samples came from a wastewater discharge (NCT2), Vietnam sports hospital (TT1) and Vietnam national hospital of pediatrics (NH). Totally 20 samples representative for different surface water bodies in Hanoi that may be contaminated by pharmaceutical pollutants were collected for analyses. Water samples were firstly filtered with 0.45 μm membrane filters (Sartorius, Göttingen, Germany), then collected in amber glass bottles and stored at 4 °C (up to one week). The collected water samples, especially wastewater samples may contain microorganisms whose activity can lead to modification of the concentrations of pharmaceutical pollutants via microbial degradation of pharmaceutical compounds [46]. The samples therefore were stored at 4 °C rather than at room temperature in order

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