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Field-amplified sample stacking capillary electrophoresis with electrochemiluminescence applied to the determination of illicit drugs on banknotes

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Abstract

Capillary electrophoresis (CE) with $Ru(bpy)_3^{2+}$ electrochemiluminescence (ECL) detection system was established to the determination of contamination of banknotes with controlled drugs and a high efficiency on-column field-amplified sample stacking (FASS) technique was also optimized to increase the ECL intensity. The method was illustrated using heroin and cocaine, which are two typical and popular illicit drugs. Highest sample stacking was obtained when 0.01 mM acetic acid was chosen for sample dissolution with electrokinetical injection for 6 s at 17 kV. Under the optimized conditions: ECL detection at 1.2 V, separation voltage 10.0 kV, 20 mM phosphate–acetate (pH 7.2) as running buffer, 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate (pH 7.2) in the detection cell, the standard curves were linear in the range of 7.50×10^{-8} to 1.00×10^{-5} M for heroin and 2.50×10^{-7} to 1.00×10^{-4} M for cocaine and detection limits of 50 nM for heroin and 60 nM for cocaine were achieved (S/N = 3), respectively. Relative standard derivations of the ECL intensity and the migration time were 3.50 and 0.51% for heroin and 4.44 and 0.12% for cocaine, respectively. The developed method was successfully applied to the determination of heroin and cocaine on illicit drug contaminated banknotes without any damage of the paper currency. A baseline resolution for heroin and cocaine was achieved within 6 min.

Keywords: Capillary electrophoresis; Electrochemiluminescence; Field-amplified sample stacking; Heroin; Cocaine; Banknotes

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1. Introduction

Drug-trafficking frequently involves the exchange of large sums of cash, which may be contaminated with the drugs. Contamination can occur through events that bring banknotes into direct contact with bulk drugs (primary transfer) or surfaces bearing traces of drugs (secondary transfer) [1]. The presence of trace levels of illicit drugs on banknotes is often used as a part of the evidence to establish a link between an individual and these drugs [2]. Heroin and cocaine are representatives of stimulants that belong to tertiary amino groups and the molecular structures are shown in Fig. 1. Several methods for the analysis of heroin or cocaine on paper currency have been developed. Mass spectrometric methods are most commonly used to detect the presence of illicit drugs on banknotes [1–3]. Raman microspectroscopy was also applied to detect and identify individual drug crystals on paper currency [4]. Unfortunately, methods such as mass spectrometry are destructive because the banknotes need to be incinerated during the analysis procedure and Raman spectroscopy may suffer fluorescence disturbance from the banknotes.

$Ru(bpy)_3^{2+}$ ECL has been applied to a wide variety of compounds and ions as a simple but sensitive detection technique. Its applications have been extensively reviewed [5–7]. Flow injection $Ru(bpy)_3^{2+}$ ECL has been used to detect heroin [8,9] and cocaine in urine [10]. CE possesses the advantages of short analysis time, small consuming sample, high separation efficiency, simple experiment operation and so on. All these characteristics make it a new powerful tool of investigation in the hands of forensic toxicologists. Nonaqueous capillary electrophoresis

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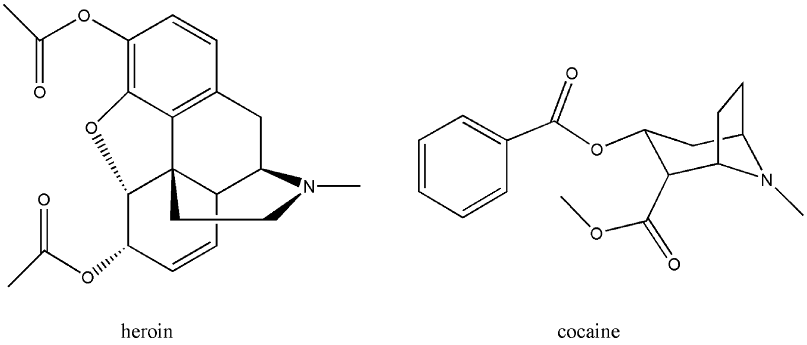

Fig. 1. Molecular structures of heroin and cocaine.

and electrochemical detection was applied to the determination of illicit drugs [11]. Complementary use of capillary zone electrophoresis and micellar electrokinetic capillary chromatography for mutual confirmation of results in forensic drug analysis has been reported [12]. Excellent reviews of applications of CE to forensic drug analysis have been presented [13–15]. CE has the potential to be a powerful analytical tool that combines the inherent properties with the sensitivity and selectivity of $Ru(bpy)_3^{2+}$ ECL detection. The development of ECL detection for CE has been critically reviewed [16].

Field-amplified sample stacking (FASS), one of the on-column concentration techniques, is based on a mismatch between the electric conductivity of the sample and that of the separation buffer [17–19]. Applications of FASS-CE to illicit drug analysis have been reported recently. For example, FASS has been applied to the analysis of abused drugs in hair [20,21]; FASS capillary zone electrophoresis with β-cyclodextrin and UV detection was applied to the determination of heroin metabolites in human urine [22]. The sensitivity of simple electrokinetic injection was insufficient for analysis of heroin and cocaine on banknotes due to their low concentration in the complex matrix and the inherent property of heroin was also considered, as a result, optimized FASS injection before the separation was applied for this experiment.

In this paper, an original experimental strategy was established for the simultaneous detection of heroin and cocaine on paper currency. By adopting field-amplified sample stacking CE-ECL, improved sensitivity and lower detection limits of heroin and cocaine were obtained. And it is possible to determine whether the banknotes are contaminated with illicit drugs. Experimental details of the technique are given and an imitational case study is presented. These results exploited a new scope both for CE-ECL applications and for court judgments of illicit drug seizures.

2. Experimental

2.1. Chemicals and materials

Tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). Heroin and cocaine was purchased from the State Narcotic Laboratory (Beijing, China). The buffers used both in the detection cell and as migration electrolyte were phosphate–acetate. All chemicals and reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water processed with Milli-Q ultra-high purity water system (Millipore, Bedford, MA, USA). They were stored in the refrigerator at 4 °C and filtered through 0.22 μm pore disposable filter membranes before use.

2.2. Apparatus and equipments

All ECL experiments were carried out with a computer controlled CE-ECL system (Xi'an Remex Electronics Co. Ltd. Xi'an, China), including a high voltage power supply for electrophoretic separation and electrokinetic injection, an electrochemical potentiostat, a multifunctional chemiluminescence detector and a multichannel data processor. A three-electrode configuration was used in the detection cell consisting of a 500-μm Pt disk as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode. The axes of working electrode and separation capillary was aligned setting the distance 125 μm between each other with the aid of a optical microscope (40× magnification). ECL detection reservoir used herein is the same as the one reported previously [23].

All separations were performed in a 45-cm-long fused-silica capillary with 25 μm i.d. and 360 μm o.d. (Yongnian Optical Conductive Fiber Plant, Hebei, China). The capillary was rinsed with 0.1 M NaOH overnight, washed for 5 min with 0.1 M NaOH, followed by double-distilled water and equilibrated with the running buffer for 5 min before use so as to maintain an active and reproducible inner surface. The voltage of photomultiplier tube for collecting the ECL signal was set at 800 V in the process of detection. Electrokinetic injections were performed at 17 kV for 6 s. The inlet end of the capillary was held at a positive potential and the outlet end was maintained at ground. $Ru(bpy)_3^{2+}$ (5 mM) with 50 mM phosphate–acetate was added in the detection cell.

2.3. Preparation of standard solutions

The stock solutions of 5 mM heroin and cocaine were prepared by dissolving the standard samples in 0.01 mM acetic acid solution and stored at 4 °C in a refrigerator, respectively. A series of standard solutions for calibration curve, reproducibility and