Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1115 (2006) 260–266
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

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

Yuanhong Xu [a], Ying Gao [a,b,c], Hui Wei [a], Yan Du [a], Erkang Wang [a,*]

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of the Chinese Academy of Science, Changchun, Jilin 130022, China*
[b] *Department of Chemistry, Tianjin University, Tianjin 300072, China*
[c] *Department of Applied Chemistry, Changchun Institute of Technology, Changchun, Jilin 130021, China*

Received 4 November 2005; received in revised form 23 February 2006; accepted 27 February 2006
Available online 17 April 2006

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

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

* Corresponding author. Tel.: +86 431 5262003; fax: +86 431 5689711.
E-mail address: ekwang@ciac.jl.cn (E. Wang).

0021-9673/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.chroma.2006.02.084

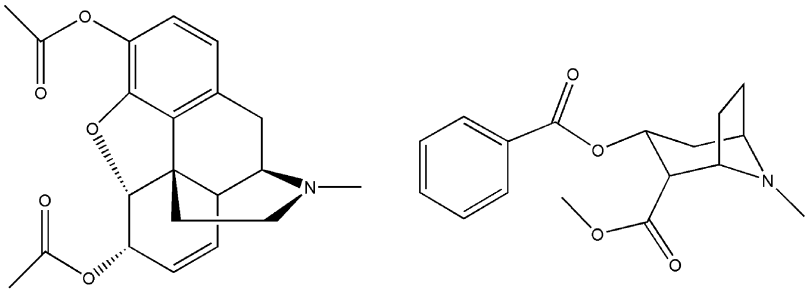

Fig. 1. Molecular structures of heroin and cocaine.

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

recovery studies were prepared by diluting the solution with 0.01 mM acetic acid and filtered through 0.22 μm pore disposable filter membranes just before use.

2.4. Preparation of samples on banknotes

The mimic case-study banknotes were collected directly from general circulation within China. One hundred pieces of banknotes were introduced into this model test and exposed to heroin and cocaine to simulate banknotes that being associated with the trafficking of drugs. About half of these banknotes were directly in contact with standard samples of heroin and cocaine so as to imitate the primary transfer. The rest were used to mimic the secondary transfer: latex surgical gloves that were contaminated with heroin and cocaine worn by the operator, drugs were swabbed on the surface of the banknotes by counting the paper currency one by one. As a result, a bundle of banknotes contaminated with heroin and cocaine was obtained and placed in random environment for 5 days. Finally, banknotes sample treatment was as follows:

A random of approximately one-third of the banknotes was selected for analysis from the top, middle and bottom of the buddle. Analysis can be held for either each banknote or all of the selected ones. In this experiment, all the chosen banknotes were soaked together in appropriate amount of 0.01 mM acetic acid in a beaker to dissolve the drugs on the paper currency. Fifteen minutes later, the banknotes were drawn out from the solution, rinsed with 0.01 mM acetic acid to remove any remanent heroin or cocaine on the paper currency and the rinsing solution was also transferred into the same beaker. Then the mixed solution was adjusted to 300 mL with 0.01 mM acetic acid to obtain the sample solution. The solution was filtered through 0.22 μm pore disposable filter membranes before use. This sampling process was adopted since the banknotes analysed can reasonably be taken as representative of the bundle as a whole. The denomination of each banknote with Arabic numerals and analysis results were recorded. Thirty-three pieces of banknotes drawn from general circulation without illicit drug contamination were also prepared using the same procedure to generate the "blank" solution used for comparison with the contaminated banknotes. All the solutions were stored at 4 °C in a refrigerator.

To determine the validity of the extraction procedure, four groups of banknotes from general circulation without illicit drug contamination were prepared and each group contained 33 pieces of banknotes. The efficiency and reproducibility of the extraction procedure were determined by extracting replicate ($n = 4$) spiked groups of banknotes, which were swabbed with four groups of different masses of heroin and cocaine (heroin was 1.2, 3.0, 6.0 and 9.0 mg, respectively; cocaine was 1.0, 2.5, 5.0 and 7.5 mg, respectively). And the spiked banknotes were dealt with according to the same extraction procedure. Then the extracts were diluted 10-fold, respectively, four different spiked concentrations of heroin and cocaine both at 1.0, 2.5, 5.0 and 7.5 μM were obtained, respectively. The extraction efficiency was estimated by measuring the peak areas of nonextracted standard solutions compared with those of corresponding spiked samples after extracting at each different analyte concentrations.

Finally, the banknotes were rinsed with double-distilled water prior to re-circulation to remove any remanent chemicals such as acetic acid on the paper currency and without any damage of the paper currency during the treatment process compared with mass spectrometric methods with which the banknotes needed to be incinerated during the analysis procedure.

3. Result and discussion

3.1. Method optimization

3.1.1. Effect of detection potential

The intensity of the emitted light is dependent on the rate of the light emitting chemical reaction, and this reaction rate is dependent on the potential applied to the working electrode [24]. As the oxidation of $Ru(bpy)_3^{2+}$ needs to be at least 1.0 V, we measured the ECL intensities at a variety of applied potentials from 1.05 to 1.3 V. The highest ECL intensities were obtained at 1.2 V both for heroin and cocaine as shown in Fig. 2, hence, the applied potential was set at 1.2 V.

3.1.2. Effect of separation voltage

A study of the influence of separation voltage on the emission intensities were carried out from 5 to 17.5 kV. As can be seen in Fig. 3, ECL intensities reached highest at 7.5 kV for heroin and 12.5 kV for cocaine, respectively. ECL reaction occurs in the diffusion layer near the electrode when $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$ at the electrode surface and the oxidized $Ru(bpy)_3^{3+}$ contacts the analyte [25]. In CE-ECL system, as separation voltage increased, the electroosmosis flow should increase, thus more analyte in the effluent arrives in the diffusion layer of working electrode within a given time, higher ECL signal and shorter migration time could be obtained [26]. On the other hand, the strong flow of effluent from the capillary may reduce the concentration of $Ru(bpy)_3^{3+}$ at the electrode

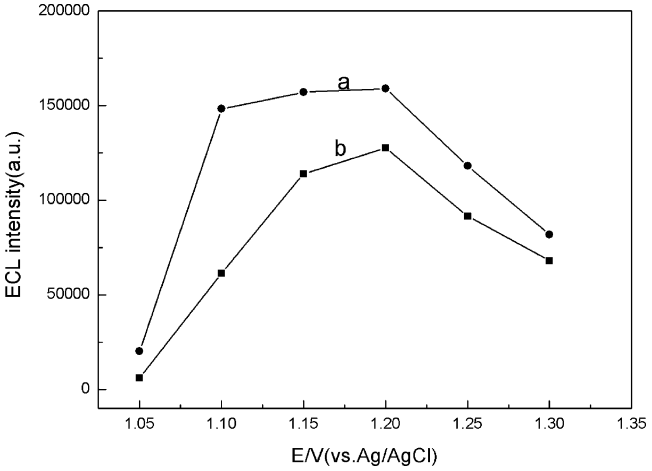

Fig. 2. Effect of detection potential on the ECL intensity: (a) ECL intensity of 10 μM heroin, (b) ECL intensity of 10 μM cocaine. Conditions: running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

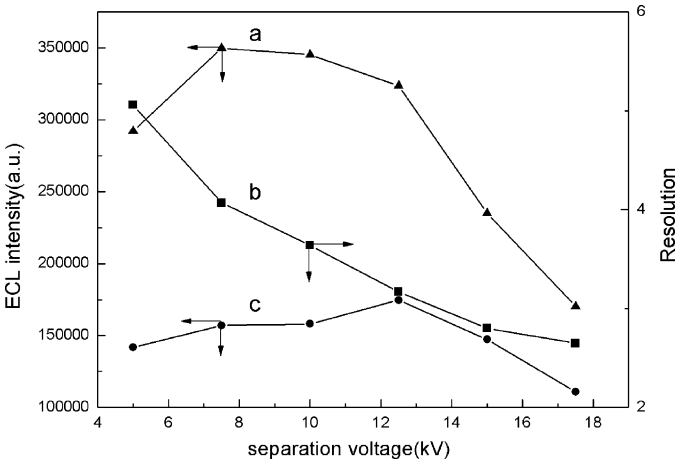

Fig. 3. Effect of separation voltage on ECL intensity and resolution: (a) ECL intensity of 10 μM heroin, (b) resolution between heroin and cocaine, (c) ECL intensity of 10 μM cocaine. Conditions: detection potential, 1.2 V; running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV.

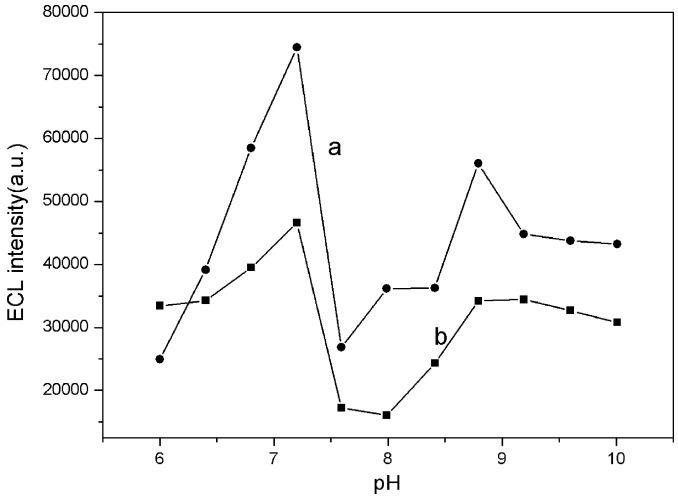

Fig. 4. Effect of buffer pH in the detection reservoir on ECL intensity: (a) ECL intensity of 10 μM heroin, (b) ECL intensity of 10 μM cocaine. Conditions: running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer in the detection reservoir; detection potential, 1.2 V; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

surface and result in the peak broadening as well as resolution (Rs) between heroin and cocaine decreasing. The Rs between heroin and cocaine is calculated with the following equation: $Rs = 2(t_2 - t_1)/(W_{b1} + W_{b2})$, where t_1 and t_2 stand for migration times of heroin and cocaine, respectively. W_{b1} and W_{b2} are the peak widths at half-height of heroin and cocaine. Furthermore, the analytes may not have enough time or space to react with oxidized $Ru(bpy)_3^{3+}$ because of the too strong flow rate of effluent, thereby, the efficiency of light producing reaction was reduced. Considering all these factors, we chose 10 kV as a separation voltage in this experiment to ensure high ECL intensities, moderate resolution, as well as better reproducibility.

3.1.3. Effect of buffer pH

The optimal buffer pH in the detection reservoir has been chosen from a wide range of pH values (from 6.0 to 10.0, 0.4 as a unit). ECL intensities of the sample solutions were increased with increasing pH value of the buffer in the ranges of 6.00–7.20 and 7.40–8.80, respectively. The ECL response decreased when the buffer pH exceeded 8.80. The same phenomenon for both heroin and cocaine was observed. Maximum intensities were achieved at a neutral condition (pH 7.2) (Fig. 4). This pH-dependence might be also related to the phenomenon that maximum ECL activity of tertiary amine occurs at a pH value lower than the pK_a of the amine [27], and the pK_a values of heroin and cocaine are 7.95 and 8.61, respectively. Furthermore, when the buffer pH exceeded 8.00, there was an unknown peak appeared in the electrophoregrams. This unknown peak may be ascribed to the OH^- ion, which assumes considerable concentration levels at high pH values. As can be seen from Fig. 1, heroin is diacetylmorphine, one kind of morphine derivatives. It can be hydrolyzed to morphine and acetate in the presence of alkali solution. Considering all these factors, pH 7.20 was chosen as the optimal buffer pH in the detection reservoir.

As for the running buffer pH, factors considered were similar to optimization of buffer pH in the detection reservoir. As a result, it was also optimized at 7.20. In this condition, moderate resolution, sharper peaks as well as good reproducibility both for heroin and cocaine were obtained.

We can conclude that the same pH for separation buffer and buffer in the detection cell could eliminate the pH changing when the running buffer arrives in the diffusion layer of the working electrode. That pH value at the working electrode surface maintains unchangeable ensures good reproducibility and highest ECL intensities in this experiment.

3.1.4. Choice of background electrolyte

The background electrolyte affects the ECL efficiency, migration time and the separation resolution between compounds directly. The most popular buffer for CE-ECL is phosphate, but as mentioned above, heroin is diacetylmorphine. Heroin hydrolysates are morphine and acetate when presented to basic condition as well as morphine and acetic acid when boiled in acidic solution, respectively. As heroin hydrolysis occurred, accurate quantification could not be achieved. In this experiment, acetic acid was added to the phosphate buffers in order to diminish the hydrolysis as little as possible. And there was also a substantial improvement in peak sharpness and symmetry compared with the pure phosphate buffers.

Acetic acid was added to the phosphate buffers to prepare different concentrations of 5, 10, 20, 30, 40 and 50 mM phosphate–acetate buffers, respectively. The effect of running buffer concentration on ECL intensities and the resolution between heroin and cocaine were investigated, and the results are shown in Fig. 5. When the concentration was below 10 mM, lower ECL intensities and resolution were obtained as a result of the lower ionic strength. Although a higher concentration can decrease the electro-osmotic flow in capillary and improve the resolution [28], but it also gave longer migration time and broader peaks. When the concentration was above 40 mM, the ECL baseline became unstable. This result may be ascribed to

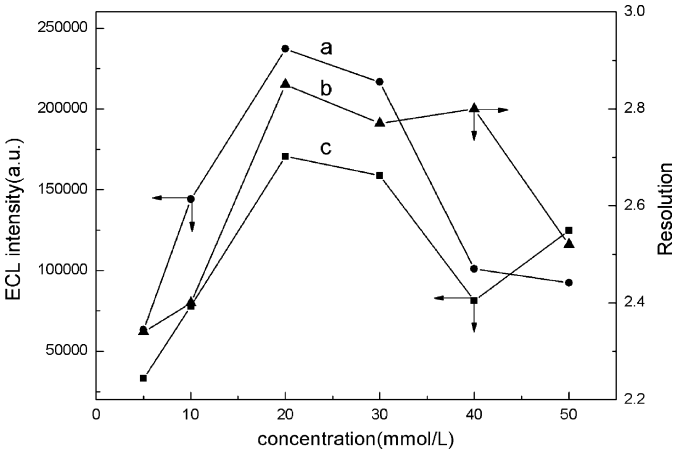

Fig. 5. Effect of running buffer concentration on ECL intensity and resolution: (a) ECL intensity of 10 μM heroin, (b) resolution between heroin and cocaine, (c) ECL intensity of 10 μM cocaine. Conditions: detection potential, 1.2 V; running buffer, phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

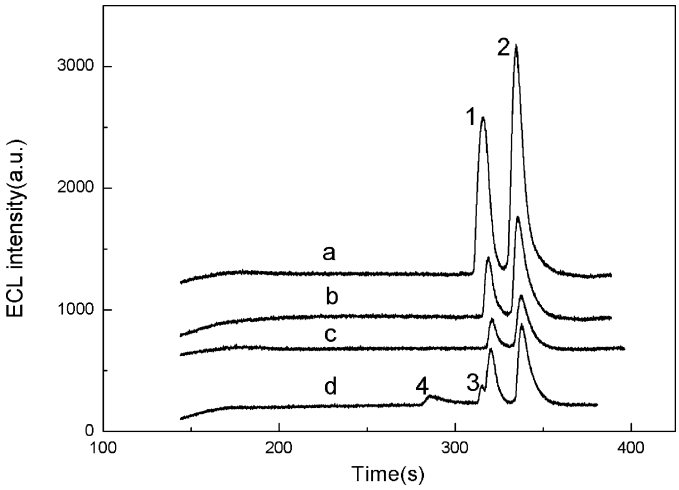

Fig. 6. Electropherograms of (a) 0.01 mM acetic acid as sample solvents, (b) 0.1 mM acetic acid as sample solvents, (c) 1 mM acetic acid as sample solvents, (d) water as sample solvents; (1) ECL intensity of 10 μM cocaine, (2) ECL intensity of 10 μM heroin, (3) ECL intensity of morphine, (4) the peak of an unknown compound. Conditions: detection potential, 1.2 V; running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

the effect of increased electrophoretic current on the ECL detector. When the concentration was above 50 mM, the resolution decreased sharply. This phenomenon is due to the Joule heating which resulted in band broadening. Considering all influence factors, the concentration of running buffer was set at 20 mM for further experiment.

3.1.5. On-column field-amplified sample stacking

Because the low concentrations of illicit drugs present in the complex matrix of banknotes, on-column field-amplified sample stacking was applied in this experiment. If the sample conductivity is lower than that of the background electrolyte (BGE), the higher electric filed and consequently the higher migration velocities of the analytes result in an injected sample plug in comparison with the running buffer, and this produces a sharpening and stacking of the analyte zone at the boundary with BGE [20]. Theoretically speaking, the highest samples stacking was obtained when water was used as sample solvents, but as can be seen in Fig. 6d, heroin would be hydrolyzed to morphine during storage and unknown peak was also observed in the electrophoretogram. In order to increase the sample loading without excessive band broadening and maintain the optimal stability of heroin, low-concentration acetic acid solution was used as sample solvents. In method development, different concentrations of acetic acid were tested. The comparison among 1, 0.1 and 0.01 mM acetic acid as sample solvents showed obvious differences in terms of ECL intensities. Fig. 6 summarizes the results obtained by injecting heroin and cocaine simultaneously both at 10 μM electrokinetically. When acetic acid used, the unknown peak and morphine, which was observed in Fig. 6d were eliminated. A remarkable ECL intensity improvement was obtained by using 0.01 mM acetic acid as sample solvents without loss of resolution and efficiency, which was about five-fold for heroin and 10-fold for cocaine, respectively, more than solution using 1 mM acetic acid as solvents. As a result, 0.01 mM acetic acid was chosen for sample dissolution. Injection time and voltage were also optimized and the best compromise between sample loading and efficiency was 6 s at 17 kV.

3.1.6. Repeatability, linearity, detection limit of heroin and cocaine

Under the optimized conditions: ECL detection at 1.2 V, separation voltage at 10 kV, 20 mM phosphate–acetate running buffer at pH 7.20, 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate buffer at pH 7.20 in the detection reservoir, FASS electrokinetical injection for 6 s at 17 kV, a standard mixture solution containing heroin and cocaine both at 10 μM was injected consecutively six times to determine the repeatability of ECL intensity based on peak area and migration time. 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 high reproducibility indicates that this approach is accurate for detection of heroin and cocaine. To evaluate the linearity of the established method, standard curves were prepared by analyzing different concentrations of mixture of two drugs between 1 nM and 1 mM. 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, respectively. The calibration equations and regression coefficients were: $y = 2.08 \times 10^{10}x - 1967.78$ and $R = 0.9993$ ($n = 7$) for heroin, $y = 5.23 \times 10^{9}x - 4274.40$ and $R = 0.9990$ ($n = 9$) for cocaine in terms of peak area response as a function of analytes concentration. Detection limits of 50 nM for heroin and 60 nM for cocaine were achieved (S/N = 3), respectively.

Compared with detections limits of 1.1 μM for heroin by flow injection electrogenerated chemiluminescence (ECL) [9], 6.50×10^{-7} M for cocaine by Tris(2,2′-bipyridyl)ruthenium(II) electrogenerated chemiluminescence with solid phase extraction

sample preparation [10] and 2.6 μg/mL (~8.5 μM) for cocaine by nonaqueous capillary electrophoresis with electrochemical detection [11], improved sensitivity and lower detection limits of heroin and cocaine were obtained by adopting field-amplified sample stacking CE-ECL method.

3.2. Applications

The detailed extraction procedure was described in Section 2.4. This method was validated through investigating samples spiked with four different concentrations of heroin and cocaine. Table 1 shows the recovery rates of heroin and cocaine after the extraction procedure and corresponding relative standard deviations. The recoveries at the four different concentrations for heroin were 97.3, 96.4, 97.6 and 95.2%, respectively, and the relative standard deviations were 4.73, 5.89, 5.26 and 4.27% ($n=6$), respectively; for cocaine were 95.7, 96.8, 95.4 and 96.1%, respectively, and the relative standard deviations were 3.68, 4.68, 3.47 and 4.42% ($n=6$), respectively.

The optimized field-amplified sample stacking CE-ECL methods was adopted to the determination of heroin and cocaine extracted from the contaminated banknotes sample. The sample showed well-separated and symmetrical peaks of heroin and cocaine, which were obviously distinguishable from the background. Heroin and cocaine were quantified by the calibration curve, and were 5.52×10^{-7} M for heroin and 2.91×10^{-6} M for cocaine, respectively. Confirmation of the analytes in the banknotes sample was operated by comparing the electropherograms of the sample with that of sample spiked with heroin and cocaine both at 1.50×10^{-6} M, where the increase of peak area at equivalent migration time was directly proportional to the amount spiked with heroin or cocaine. The "blank" banknotes sample showed no significant peaks, for example, fluorescence disturbance from the paper currency that could interfere with investigated drugs in the time window from 150 to 550 s. The electrophoregrams are shown in Fig. 7.

Table 1
The efficiency and reproducibility of the extraction for banknotes spiked with heroin and cocaine

Amount added (μM)	Amount found (μM)	RSD (%) ($n=6$)	Recovery (%)
Heroin			
1.00	0.973	4.73	97.3
2.50	2.41	5.89	96.4
5.00	4.88	5.26	97.6
7.50	7.14	4.27	95.2
Cocaine			
1.00	0.957	3.68	95.7
2.50	2.42	4.68	96.8
5.00	4.77	3.47	95.4
7.50	7.21	4.42	96.1

Conditions: detection potential, 1.2 V; running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

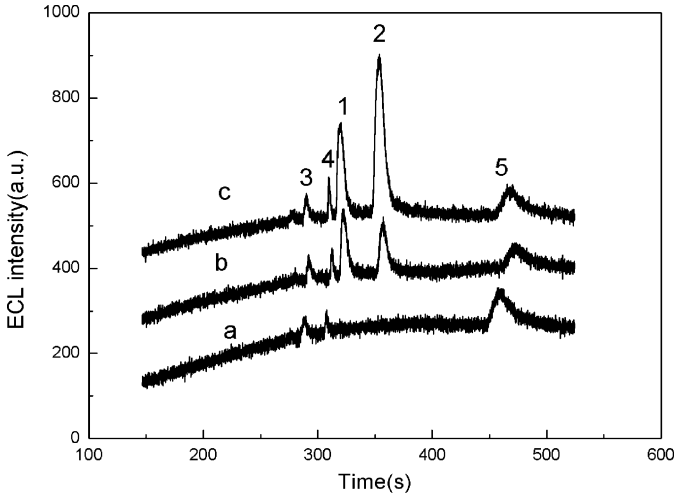

Fig. 7. Electropherograms of (a) the "blank" banknotes extract and, (b) the banknotes sample extract, (c) the banknotes sample extract spiked with 1.5×10^{-6} M heroin and 1.5×10^{-6} M cocaine; (1) ECL intensity of cocaine; (2) ECL intensity of heroin; (3), (4) and (5) the peaks of unknown compounds in extract. Conditions: detection potential, 1.2 V; running buffer, 20 mM phosphate–acetate (pH 7.2); 5 mM $Ru(bpy)_3^{2+}$ with 50 mM phosphate–acetate buffer (pH 7.2) in the detection reservoir; electrokinetic injection, 6 s at 17 kV; separation voltage, 10 kV.

4. Conclusion

In this paper, an original experimental method was proposed for analysis of banknotes that are under suspicion of being associated with controlled drugs such as heroin and cocaine. By adopting field-amplified sample stacking CE-ECL it is possible to determine whether the banknotes are contaminated with illicit drugs. The proposed strategy in this paper avoided the fluorescence disturbance from the banknotes as well as any damage of the paper currency during the treatment process. It was found to be a suitable approach to analyze illicit drugs on banknotes such as heroin and cocaine simultaneously. Furthermore, due to fast separation, lower detection limits, good selectivity, high sensitivity and effective resolution of this method, it has the potential to be a powerful tool for the analysis of illicit drugs in other complex matrices in forensic investigations.

Acknowledgements

This work is supported by the National Natural Science Foundation of China with the grant Nos. 20335040 and 20427003.

References

[1] K.A. Ebejer, R.G. Brereton, J.F. Carter, S.L. Ollerton, R. Sleeman, Rapid Commun. Mass Spectrom. 19 (2005) 2137.
[2] R. Sleeman, I.F.A. Burton, J.F. Carter, D.J. Roberts, Analyst 124 (1999) 103.
[3] J.F. Carter, R. Sleeman, J. Parry, Forensic Sci. Int. 132 (2003) 106.
[4] K.A. Frederick, R. Pertaub, N.W.S. Kam, Spectrosc. Lett. 37 (2004) 301.
[5] M.M. Richter, Chem. Rev. 104 (2004) 3003.
[6] K.A. Fahnrich, M. Pravda, G.G. Guilbault, Talanta 54 (2001) 531.
[7] A.W. Knight, TrAC 18 (1999) 47.
[8] G.M. Greenway, A.W. Knight, P.J. Knight, Analyst 120 (1995) 2549.

[9] Y.F. Zhuang, D.M. Zhang, H.X. Ju, Analyst 130 (2005) 534.
[10] Q.J. Song, G.M. Greenway, T. McCreedy, Analyst 126 (2001) 37.
[11] U. Backofen, F.M. Matysik, W. Hoffmann, C.E. Lunte, Fresen. J. Anal. Chem. 367 (2000) 359.
[12] F. Tagliaro, F.P. Smith, S. Turrina, V. Equisetto, M. Marigo, J. Chromatogr. A 735 (1996) 227.
[13] N. Anastos, N.W. Barnett, S.W. Lewis, Talanta 67 (2005) 269.
[14] F. Tagliaro, S. Turrina, P. Pisi, F.P. Smith, M. Marigo, J. Chromatogr. B 713 (1998) 27.
[15] G. Manetto, F. Crivellente, F. Tagliaro, Ther. Drug Monit. 22 (2000) 84.
[16] X.-B. Yin, E. Wang, Anal. Chim. Acta 533 (2005) 113.
[17] W. Thormann, C.-X. Zhang, Anal. Chem. 68 (1996) 2523.
[18] W. Thormann, C.-X. Zhang, Anal. Chem. 70 (1998) 540.
[19] G. McGrath, W.F. Smyth, J. Chromatogr. B 681 (1996) 125.
[20] G. Manetto, F. Tagliaro, F. Crivellente, V. Pascali, M. Marigo, Electrophoresis 21 (2000) 2891.
[21] F. Tagliaro, G. Manetto, F. Crivellente, D. Scarcella, M. Marigo, Forensic Sci. Int. 92 (1998) 201.
[22] A. Alnajjar, B. McCord, J. Pharm. Biomed. Anal. 33 (2003) 463.
[23] J. Liu, J. Yan, X. Yang, E. Wang, Anal. Chem. 75 (2003) 3637.
[24] K.E. Haapakka, J.J. Kankare, Anal. Chim. Acta 138 (1982) 263–275.
[25] W.-Y. Lee, T.A. Nieman, Anal. Chem. 67 (1995) 1789.
[26] J. Liu, W. Cao, X. Yang, E. Wang, Talanta 59 (2003) 453.
[27] S.N. Brune, D.R. Bobbitt, Talanta 38 (1991) 419.
[28] Y. Deng, J. He, High Performance Capillary Electrophoresis (Chinese), Science Press, Beijing, 1998, 66.