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Highly sensitive trivalent copper chelate-luminol chemiluminescence system for capillary electrophoresis detection of epinephrine in the urine of smoker

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ABSTRACT

Epinephrine (EP) is one of the most important neurotransmitters and hormones. Some previous literatures show that there is a close relation between its release and smoking. To compare the levels of EP in urines of smokers and nonsmokers, a sensitive chemiluminescence (CL) system, luminol-diperiodatocuprate (III) ($K_5[Cu(HIO_6)_2]$, DPC), has been developed and validated for the determination of EP after CE separation. The DPC-luminol-EP CL reaction showed very intensive emission and fast kinetic characteristics, thus led to a high sensitivity in the flow-through detection mode for capillary electrophoresis. With the peak height as a quantitative parameter, the relative CL intensity was linear with the EP concentration in the range of 2.0–400 ng/mL, with a limit of detection of 0.82 ng/mL (S/N = 3). The reproducibility was assessed by intra- and inter-day relative standard deviations (RSDs) for 11 replicate determinations of EP standard samples at low, medium and high concentrations. The intra- and inter-day RSDs for CL signals were 5.5%–6.6% and 6.1%–7.5%, respectively, and those for migration times were 3.4%–5.8% and 4.3%–6.3%, respectively. The presented method was successfully applied to the determination of EP in EP injection and urine samples of smokers and nonsmokers. The recovery test results for urine samples ranged from 86.5 to 112.0%, which demonstrated the reliability of this method. The results for urine sample detection indicate that the average level of EP in the urines of the smoker group is obviously higher than that in the urines of the nonsmoker group, which may demonstrate that smoking can stimulate the release of EP in human body.

1. Introduction

Epinephrine (EP) or adrenaline, chemically named 1-(3,4-dihydroxyphenyl)-2-methyloamino-ethanol, has been well known as one of the important catecholamines, and plays a crucial role as a neurotransmitters or a hormones in the function of brain and during the signal transduction of the nervous system [1]. It exists in the form of organic cation in the nervous tissue and body fluid. Some studies have demonstrated that many diseases are related to the change of EP concentration in body fluid [2]. Some previous reports have proved that there is a close relationship between the release of EP and smoking, due to the acute effect of nicotine on hypothalamic-pituitary-adrenal axis [3–5]. In addition, almost 50% of the secreted hormone in human body will appear in urine as free and conjugated forms [6]. Therefore, there is a demand for the development of a rapid, simple, and sensitive analytical method to detect EP in urine sample of smoker.

Numerous analytical methods have been developed for determination of EP, including fluorimetric method [7,8], flow injection analysis coupled with chemiluminescent (CL) [9,10], amperometric [11] and biamperometric detections [12], microchip electrophoresis coupled with CL detection [13], capillary electrophoresis (CE) coupled with ultraviolet-visible (UV) [14] and amperometric detections [15], liquid chromatography coupled with mass spectrometry [16,17], electrochemical [18,19] and ultraviolet-visible detections [20]. Since the methods based on fluorimetry and flow injection are lack of separation process prior to detection, their reliability is limited when they are applied for biological sample detection. Therefore, efficient separation method combined with high sensitive detection will be preferred for detection of EP in complex biological samples such as urine and serum. Although liquid chromatography has been one of the most frequently utilized methods, long analytical time and toxic organic solvent are still unfavorable. CE has been proven to be one of the most powerful alternative techniques for biological samples analysis, owing to its high separation efficiency, short analysis time, and low sample consumption [21].

CL detection is one of the most sensitive detection techniques for analysis of trace amount of analyte [22]. CE coupled with CL detection has been successfully applied for quantifying some compounds including peptides [23,24], amino acids [25,26], drugs [27,28] and metal ions [29,30]. For the determination of EP using CE-CL strategy, EP is usually derivatized by CL reagent

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such as *N*-(4-aminobutyl)-*N*-ethylisoluminol [13,28]. However this pre-column derivatization process is always time-consuming and labor-intensive. For direct detection strategy without using of derivatization reagent, some oxidants such as potassium periodate [9] and hexacyanoferrate (III) [31] have been reported to trigger the CL emission of luminol and produce the detectable signal for EP. Unfortunately, the sensitivity of these traditional oxidants-based CE-CL methods is not high enough for detecting trace amount of EP in biological sample. Furthermore, CE-CL strategy for the investigation of the relation between EP release and cigarette smoking has not been reported so far.

Here, diperiodatocuprate (III) ($K_5[Cu(HIO_6)_2]$, DPC), a transition metal chelate at unstable high oxidation state, was found to react with luminol to generate a CL emission in a basic medium. Moreover, EP could greatly enhance this CL reaction to produce very strong CL signal. This CL system was utilized to develop a rapid and sensitive CE-CL method for the determination of EP. The result for biological sample detection showed an acceptable agreement with that of high performance liquid chromatography (HPLC). This method was successfully applied in the comparison of EP levels in urines of smoker group and nonsmoker group, and provided an evidence to demonstrate that smoking can stimulate EP release.

2. Experiment

2.1. Chemicals and material

Potassium persulphate ($K_2S_2O_8$), potassium hydroxide (KOH), cupric sulphate ($CuSO_4{\cdot}5H_2O$) and potassium periodate (KIO_4) were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Luminol and standard preparation of EP were obtained from Sigma–Aldrich (St. Louis, MO, USA). The EP injection was purchased from Wuhan Grand Pharmaceutical Group Co. Ltd. (Wuhan, China). Its content was claimed by the manufacturer to be 1 mg/ampoule. All other chemicals used were of analytical grade and used without further purification. Ultra-pure water (18.2 MΩ) was purified by ELGA PURELAB classic system (Veolia Water Solutions & Technologies Co. Ltd.), and used throughout this investigation. The luminol stock solution at 10.0 mmol/L was prepared by dissolving 0.18 g of luminol in 100 mL of NaOH solutions at 0.10 mol/L, and stored in the refrigerator at 4 °C. The urine samples were collected from seven smokers and seven nonsmokers in Southwest University. All the volunteers are healthy males, and ages 22–26 years.

2.2. Synthesis of DPC solution

The DPC stock solution at 10.0 mmol/L was prepared by oxidizing Cu(II) in a strong alkaline medium according to the previously reported method [32]. In briefly, KIO_4 (0.23 g), $CuSO_4{\cdot}5H_2O$ (0.12 g), $K_2S_2O_8$ (0.14 g) and KOH (0.80 g) were mixed and dissolved in 30 mL of water. The solution was heated to boiling and kept temperature for about 20 min with constant stirring. The dark red product solution was then cooled to room temperature and diluted to 50 mL with water. The obtained DPC solution was stored in the refrigerator at 4 °C, and could keep stable for no less than 5 months. The DPC solution was characterized by the ultraviolet–visible spectrum (PERSEE TU-1901, China), which exhibited two absorption peaks near 262 and 421 nm.

2.3. Apparatus and procedures

The home-assembled CE-CL apparatus was shown in Supplementary data (Fig. S1), which was constructed in a post-column flow-through detection mode. All flow components of this system were connected using Teflon tubes with i.d. of 0.80 mm. A fused-silica capillary with a length of 50 cm and an i.d. of 75 μm (Yongnian Optical Fiber Factory, Hebei, China) was used for CE separation. In this study, the new capillaries were rinsed sequentially with 1.0 mol/L NaOH solution for 30 min and water for another 30 min prior to the first use. Between two consecutive injections, the capillary was flushed sequentially with 0.10 mol/L NaOH solution, water and running buffer (RB) for 2 min for each. A 1.0-cm polyimide coating section of one end of the capillary was burned and removed. The burned tip of the capillary was directly inserted into an optical glass tube (3.0 cm × 1.0 mm i.d.) acting as the CL detection window. The CL detection window was located above a photomultiplier (PMT) operated at −800 V for performing CL signal collection. Both the detection window and the PMT were sealed in a dark box to avoid interference from the external light.

The RB used for CE separation was 2.5 mmol/L phosphate buffer (pH 6.0) containing 0.10 mmol/L luminol, and the separation voltage was 12 kV. The solution of 0.10 mmol/L DPC in 40.0 mmol/L NaOH was siphoned into the detection window with an altitude difference of 20 cm, to trigger the CL reaction. After a stable baseline was obtained, the sample was loaded by gravity injection for 15 s at an altitude difference of 10 cm. The peak height of the electropherogram was applied as the quantitative parameter to evaluate the level of EP. Data acquisition and treatment were performed using an IFFM software package (Remex, Xi'an, China). CL spectra were measured using a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan).

The urine samples were also assayed using HPLC method to evaluate the reliability of the proposed CE-CL method. The HPLC experiments were performed on a HITACHI LC system (Column Oven L-2300, Pump L-2130, Autosamper L-2200, Diode Array Detector L-2455) equipped with a Lichrospher RP-C_{18} analysis column (250 mm × 4.6 mm, 5.0 μm, Hanbon Science & Technology Co. Ltd, Jiangsu, China). The column temperature was maintained at 40 °C, and the detection wavelength was set at 210 nm. A degassed mobile phase was prepared with acetonitrile-water (25:75, v/v), and the flow rate was set at 1.0 mL/min.

2.4. Sample preparation

2.4.1. Pharmaceutical preparation

The EP injection was suitably diluted with RB before the determination so that the analysis concentration fell in the linear range of proposed method. The diluted samples were filtered through a 0.22-μm membrane filter before loading.

2.4.2. Urine samples of smokers and nonsmokers

The urine samples of seven healthy smokers were collected in 20 min after 2 cigarettes-smoking, and the urine samples of seven nonsmokers were also collected as the control. All the volunteers were in a resting stage during the time of sample collection. A 200-μL urine sample in a 1.5-mL centrifuge tube was mixed with 400 μL of acetonitrile and shaken vigorously for 2 min to precipitate proteins. After filtration with a 0.22-μm membrane filter, the obtained solution was diluted with RB if necessary before loading.

3. Results and discussion

3.1. Kinetic characteristic of EP-luminol-DPC CL reaction

The preliminary experiment demonstrated that luminol could be oxidized by DPC to produce CL emission in alkaline solution, and this CL emission could be greatly enhanced in the present of EP. The kinetic characteristics of luminol-DPC CL reactions in the absence and presence of EP were studied by using a static mode, and the typical response curves (CL intensity versus times) were

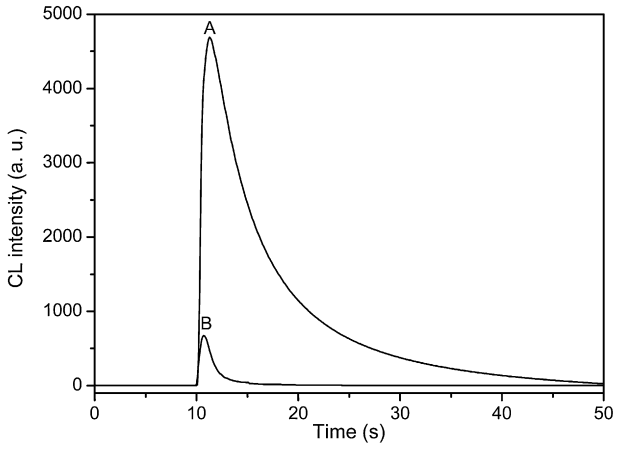

Fig. 1. Kinetic curves for (A) luminol-DPC-EP and (B) luminol-DPC CL systems. (A) One hundred microlitre of 5.0 μmol/L DPC solution was injected into a mixture of 1.0 mL of 1.0 μmol/L luminol (in 40 mmol/L NaOH) and 1.0 mL of 0.10 μg/mL EP solution; (B) one hundred microlitre of 5.0 μmol/L DPC solution was injected into a mixture of 1.0 mL of 1.0 μmol/L luminol (in 40 mmol/L NaOH) and 1.0 mL of water.

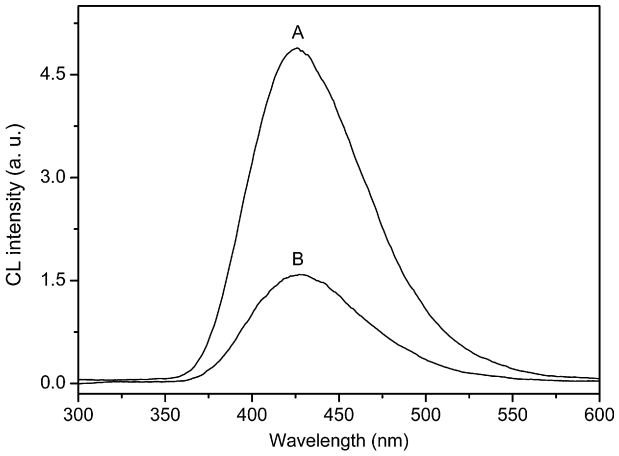

Fig. 2. The CL spectra of (A) luminol-DPC-EP and (B) luminol-DPC systems. Experimental conditions: luminol, 0.10 mmol/L; DPC, 0.15 mmol/L; EP, 0.20 μg/mL; NaOH, 40 mmol/L.

shown in Fig. 1. It was found that the both CL reactions were very quick, and the CL emissions only took 1.3 s (10.0–11.3 s) to reach the peak values after triggering the reactions for the two systems. Such a rapid kinetic characteristic for DPC-luminol-EP CL reaction was very helpful to obtain a high sensitivity since the contacting time of DPC and the effluent from the capillary was very short in the flow-through detection interface.

3.2. Condition optimization

To obtain a good analytical performance, we investigated the dependence of the column efficiency and the relative CL intensity on the RB conditions. The results showed that a basic RB led to a very poor asymmetric peak, whereas an acidic RB depressed the CL emission. Phosphate buffer at pH 6.0 (2.5 mmol/L) was finally chosen as the optimal RB because it provided a symmetric peak and an acceptable relative CL signal intensity. The influence of the luminol concentration in RB was investigated in the range of 0.020–0.50 mmol/L, and the optimum concentration for the CL reaction was found to be 0.10 mmol/L.

DPC was used as an efficient oxidant in this CL reaction, and showed a great influence on the generation of CL signal. The sensitivity of the proposed method was closely related to the concentration of DPC; hence, relative CL intensities were recorded at different DPC concentrations (0.025–0.40 mmol/L) using this CE-CL strategy. As seen in Fig. S2A of Supplementary data, the relative CL intensity increased with the concentration of DPC, and achieved the maximum when the latter was 0.10 mmol/L. The decreased CL intensity at higher DPC concentration could be attributed to the self-absorption of the DPC solution, since DPC showed a peak absorbance at 421 nm, which was very near the maximum emission wavelength of luminol (425 nm). The effect of the NaOH concentration on the relative CL intensity was investigated in the range of 10–80 mmol/L, and the results are shown in Fig. S2B of Supplementary data. The results indicated that the maximal relative CL intensity was reached when the NaOH concentration was 40 mmol/L, and higher concentration of NaOH also decreased the CL signal. Thus, 40 mmol/L was chosen as the optimized NaOH concentration.

Some physical conditions, including the separation voltage and the sample-loading time, were examined to obtain a high sensitivity and a high column efficiency. To avoid the effect of the electrical discrimination for the biological samples, the samples were loaded into the capillary by gravity injection at a height difference of 10 cm, instead of electromigration injection. Although a long loading time led to a high CL signal, the loading time longer than 15 s resulted in a decreased column efficiency. Thus, 15 s was chosen as the optimal loading time. In the further investigation, a separation voltage of 12 KV was adopted since it provided an acceptable column efficiency and run time.

3.3. Analytical performance

Under the optimum conditions, a seven-point calibration curve of relative CL intensity versus EP concentration was achieved in the range of 2.0–400 ng/mL. The limit of detection was 0.82 ng/mL (S/N = 3). The regression equation was ΔI (a.u.) = 12.16 C (ng/mL) + 189.95 (R^2 = 0.9978), where the ΔI and C were the relative CL intensity and the concentration of EP, respectively. The reproducibility was assessed by intra- and inter-day RSDs for 11 replicate determinations of EP standard samples at the lowest (2 ng/mL), medium (50 ng/mL) and highest (400 ng/mL) concentrations. As shown in the Table 2, the intra- and inter-day RSDs for CL signals were 5.5%–6.6% and 6.1%–7.5%, respectively, and those for migration times were 3.4%–5.8% and 4.3%–6.3%, respectively. The intermediate precision was evaluated to be 8.2% for a standard sample at 50 ng/mL, by three operators with a same procedure.

3.4. Discussion of possible CL mechanism

In order to explore the possible mechanism of enhancement on luminol-DPC CL reaction by EP, the following investigations were performed. The CL spectra were obtained using a fluorescence spectrophotometer with an emission slit of 10 nm and a scanning rate of 1200 nm/min, while the exciting slit was closed. As seen in Fig. 2, the results showed that the maximum emission wavelengths of luminol-DPC and EP-enhanced luminol-DPC CL reactions were both appeared at 425 nm, and a much stronger CL signal was obtained in the latter reaction. It is well known that 3-aminophthalate ion is a luminophor, and its maximum emission wavelength is 425 nm. This phenomenon demonstrated that the luminophor of EP-enhanced luminol-DPC CL reaction was still 3-aminophthalate ion, which was the oxidation product of luminol.

Literature survey demonstrated that reactive oxygen species (ROS) could be generated by the reaction between EP and dissolved oxygen in a basic medium [9]. It was also reported that the CL reaction of luminol-DPC could be greatly enhanced in the presence of

Table 1
Results of determination of EP in urine samples of smokers and nonsmokers by using CE-CL and HPLC methods ($n = 5$).

Sample	Found by proposed method (ng/mL)	Found by HPLC method (ng/mL)	Added (ng/mL)	Total found (ng/mL)	Recovery (%)
Nonsmoker					
1	16.2 ± 0.62	16.7 ± 0.45	20.0	35.2 ± 1.97	95.0 ± 6.73
2	13.4 ± 0.48	13.0 ± 0.53	20.0	31.7 ± 1.33	91.5 ± 4.62
3	15.4 ± 0.75	15.2 ± 0.46	20.0	36.6 ± 1.39	106.0 ± 7.15
4	12.8 ± 0.44	13.0 ± 0.65	20.0	33.9 ± 2.20	105.5 ± 9.20
5	16.7 ± 0.42	17.8 ± 0.38	20.0	35.6 ± 1.57	94.5 ± 6.60
6	25.7 ± 1.38	26.2 ± 1.27	20.0	47.6 ± 1.85	109.5 ± 8.68
7	22.8 ± 1.17	21.0 ± 0.74	20.0	42.0 ± 2.39	96.0 ± 9.55
Smoker					
1	31.4 ± 1.20	30.7 ± 1.19	20.0	53.8 ± 2.21	112.0 ± 7.86
2	24.2 ± 1.16	23.8 ± 0.86	20.0	41.5 ± 1.45	86.5 ± 5.90
3	20.4 ± 0.61	21.1 ± 0.72	20.0	39.0 ± 1.99	93.0 ± 6.12
4	28.8 ± 1.23	29.3 ± 1.45	20.0	50.3 ± 2.16	107.5 ± 9.88
5	30.2 ± 1.75	31.0 ± 1.33	20.0	49.6 ± 1.78	97.0 ± 6.74
6	23.7 ± 1.58	22.8 ± 0.84	20.0	42.5 ± 1.36	94.0 ± 7.32
7	35.5 ± 1.37	34.9 ± 1.45	20.0	54.6 ± 1.42	95.5 ± 8.95

ROS [33–35]. Based on the above discussion, a possible mechanism could be shown as following:

$$\text{EP} + \text{dissolvedoxygen} + \text{NaOH} \rightarrow \text{ROS} + \text{otherproducts}$$

$$\text{luminol} + \text{DPC} + \text{ROS} \rightarrow \text{3-aminophthalateion}*$$

$$\text{3-aminophthalateion}* \rightarrow \text{3-aminophthalateion} + h\nu(\lambda = 425\,\text{nm})$$

3.5. Application

3.5.1. Pharmaceutical preparation analysis

The application of the proposed method in pharmaceutical analysis was performed by the analysis of EP injection. Under the optimum conditions, the CL intensity of the diluted injection was detected. The content of the EP injection was measured to be 1.04 mg with a RSD of 2.6% for 5 replicate determinations. In addition, to check the accuracy of the proposed method, the recovery studies of injection for EP at two spiked levels of 1.0 mg/mL and 5.0 mg/mL were performed, and the recoveries were found to be 103.0% and 95.6% respectively. The results showed that the proposed method is accurate and sensitive enough for the content determination of EP injection.

3.5.2. Urine sample analysis for smoker and nonsmoker

It has been reported that the smoking can stimulate a much more release of EP in human body [3–5]. In this work, the proposed method was applied to detect EP in urine samples of nonsmokers (Fig. 3A) and smokers (Fig. 3B). Using the CE-CL method, the EP levels for the above two groups were found to be 12.8–25.7 ng/mL and 20.4–35.5 ng/mL, respectively. To verify the reliability of the proposed method, all urine samples were also analyzed using HPLC as reference method, and the values obtained by the two methods showed acceptable agreement (Table 1). Furthermore, the obtained levels of EP in urine samples were also in good agreement with the previously reported data [36,37]. The urine samples were also spiked with EP standard solutions, and assayed using the proposed method to perform the recovery experiment (Fig. 3C). Acceptable recoveries ranging from 86.5 to 112.0% were obtained. To assess the repeatability, five consecutive determinations of EP in urine samples of both smokers and nonsmokers were performed. The RSDs for the peak heights and the migration time were less than 6.8% and 4.7%, respectively. No obvious difference of the migration times was found between the electropherograms of the standard sample and the urine sample, which also demonstrated the selectivity of this CE-CL method.

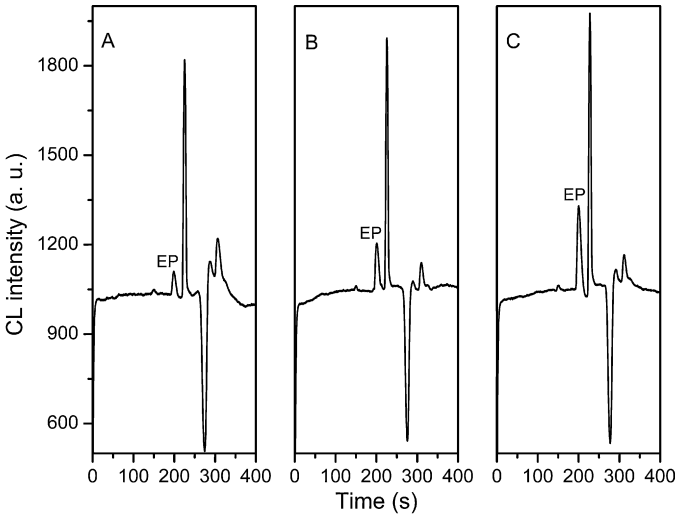

Fig. 3. Electropherograms for analysis of (A) nonsmoker urine sample (16.7 ng/mL), (B) smoker urine sample (28.8 ng/mL) and (C) smoker urine sample spiked with EP at 20.0 ng/mL. All the conditions were the selected optimal conditions.

Table 2
Reproducibility (RSD) for the EP determination ($n = 11$).

Reproducibility	Intra-day		Inter-day	
EP	CL intensity (%)	Migration time (%)	CL intensity (%)	Migration time (%)
2.0 ng/mL	6.6	5.8	7.5	6.3
50.0 ng/mL	5.6	3.4	6.1	4.3
400.0 ng/mL	5.5	3.7	6.3	4.5

The results indicated that the average level of EP was 17.6 ng/mL in the nonsmoker group and 27.7 ng/mL in the smoker group, with a significant difference between them ($P < 0.01$). These obtained EP levels for the two groups provided a proof demonstrating that smoking behavior can stimulate EP release of human body. Hence, it is concluded that the newly proposed method for the EP determination shows a promise in diagnosis of some diseases relating to the changes of EP level in body fluid [2].

4. Conclusion

In this work, a novel, rapid and sensitive CE-CL system was developed for the determination of EP. DPC, a transition metal chelate at unstable high oxidation state, was synthesized in a strong

basic solution, and acted as oxidant in this novel CL reaction. This proposed method was successfully applied in the comparison of EP levels in urines of smoker group and nonsmoker group, and provided an evidence to demonstrate that smoking can elevate the level of EP in human urine. A comparison of the results with HPLC and the recovery experimental indicated that the measurement accuracy and precision were favorable.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jchromb.2012.10.017.

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