Analytical Methods

A novel conducting poly(p-aminobenzene sulphonic acid)-based electrochemical sensor for sensitive determination of Sudan I and its application for detection in food stuffs

Bang Lin Li, Jun Hua Luo, Hong Qun Luo *, Nian Bing Li *

Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

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ABSTRACT

In the present work, a new method for the determination of Sudan I has been developed based on a conducting poly(p-aminobenzene sulphonic acid) (poly(p-ABSA)) film modified electrode. The new electrochemical sensor showed strong accumulation ability and excellent electrocatalytic activity for Sudan I. Electrochemical oxidation signal of Sudan I at the poly(p-ABSA) modified glassy carbon electrode (poly(p-ABSA)/GCE) was significantly increased when compared to that at the bare GCE. The experimental conditions such as amount of alcohol, pH of buffer solution, accumulation time, and instrumental parameters for square wave anodic stripping voltammetry were optimised for the determination of Sudan I. Under optimum conditions, the linear regression equation of Sudan I was $i_p = 1.868 + 0.1213c$ (i_p: μA, c: $\mu g\,L^{-1}$, $R = 0.9981$) from 1 to 500 $\mu g\,L^{-1}$ with a detection limit of 0.3 $\mu g\,L^{-1}$. Finally, this sensor was successfully employed to detect Sudan I in some hot chili and ketchup samples.

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1. Introduction

Sudan azo dyes are synthetic chemical colorants that are used for different industrial and scientific applications (Rebane, Leito, Yurchenko, & Herodes, 2010). Because of their bright and vivid red colour (Capith, Capith-Vallvey, Fernkdez, Orbe, & Avidad, 1996), low cost, and wide availability, Sudan dyes are also attractive as food colorants. However, Sudan dyes are categorised as class 3 carcinogens by the International Agency for Research on Cancer (IARC) and due to their carcinogenicity, they are banned in food in most countries including those in the European Union (EU) (European Commission Decision 2004/92/EC) (Chailapakul et al., 2008; Rebane et al., 2010). Thus, it is important to have

sensitive, rapid, simple and reliable methods for determining Sudan dyes in foodstuffs.

To date, there have been many methods for the determination of Sudan I, including liquid chromatography (Chailapakul et al., 2008; Qi, Zeng, Wen, Liang, & Zhang, 2011; Qiao, Geng, He, Wu, & Pan, 2011; Xin et al., 2011; Yan et al., 2012; Zhang et al., 2012), capillary electrophoresis (Mejia, Ding, Mora, & Garcia, 2007), immunoassay (Chang et al., 2011; Oplatowska, Stevenson, Schulz, Hartig, & Elliott, 2011; Wang, Yang, Ga, & Deng, 2011), high-resolution ^{1}H nuclear magnetic resonance spectrometry (Anibal, Ruisánchez, & Callao, 2011), partial filling micellar electrokinetic chromatography (Fukuji, Castro-Puyana, Tavares, & Cifuentes, 2011), and plasmon resonance light scattering (Wu, Li, Huang, & Zhang, 2006). The determination of Sudan I using these techniques shows high sensitivity, but they require expensive instruments, pre-treatment steps, skilled operators, and large quantity of organic solvents. Electroanalysis has been established

* Corresponding authors. Tel./fax: +86 23 68253237.
E-mail addresses: hongqunluo@163.com (H.Q. Luo), linb@swu.edu.cn (N.B. Li).

as rapid, simple, reliable, and inexpensive technique widely used in analytical determination. Some voltammetric techniques (Ensaif, Rezaei, Amini, & Heydari-Bafrooei, 2012; Lin, Li, & Wu, 2008; Yang, Zhu, & Jiang, 2010; Yin et al., 2011; Wu, 2010) have been applied to the detection of Sudan I.

Poly(p-aminobenzene sulphonic acid) (poly(p-ABSA)) modified electrodes have been employed in recent years (Chen et al., 2010; Wu, Li, & Luo, 2008; Xie, Luo, & Li, 2010; Xiong, Luo, & Li, 2011) because the polymer film has some excellent characteristics including stability, more active sites, reproducibility and homogeneity in electrochemical deposition, and it can adhere strongly to the electrode surface (Jin et al., 2008). There are large numbers of π–π bonds, electron-rich N atoms, and high electron density among sulphonic group in poly(p-ABSA) film. Hence, the poly (p-ABSA) film adsorbs Sudan I strongly through π–π stacking interactions and electrostatic forces. Therefore, Sudan I may be accumulated, largely on the surface of poly(p-ABSA) film, leading to an increased electrochemical signal during the anodic stripping process using poly(p-ABSA)/GCE.

To our best knowledge, the electrochemical determination of Sudan dyes, based on oxidation and the use of poly(p-ABSA)/GCE, has not been reported. A novel method for the determination of Sudan I with simple, stable, and sensitive characteristic was developed. The modified electrode exhibited a good electro-catalytic activity for the oxidation of Sudan I. The proposed method was used to the determination of Sudan I in some hot chili and ketchup samples with satisfactory results.

2. Experimental method

2.1. Chemicals and reagents

Sudan I, Sudan II, Sudan III, and Sudan IV were obtained from Kemiou Chemical Plant, Tianjin, China. Aminobenzene sulphonic acid was purchased from Tianjin Chemical Plant (Tianjin, China). Ethanol (99.7%) was purchased from Chuan Dong Chemical Plant (Chongqing, China). All chemicals employed in this work were of analytical reagent grade and were used without further purification. All of the experiments were carried out at room temperature (approximately 25 °C) without removing oxygen. All solutions were prepared with doubly distilled water. P-ABSA (20 mmol L^{-1}) was used for preparation of the poly(p-ABSA) film electrode. Phosphate buffer solutions (PBS) were prepared by step-wise adjustment with 0.1 mol L^{-1} Na_2HPO_4 and 0.1 mol L^{-1} NaH_2PO_4. PBS (0.1 mol L^{-1}, pH 7.6) was used as the supporting electrolyte for preparation of poly(p-ABSA)/GCE whilst PBS (0.1 mol L^{-1}, pH 8.5) for Sudan I detection.

2.2. Apparatus

Preparation of the poly(p-ABSA) film electrode and determination of Sudan I were performed using a CHI660B electrochemical station (CHEN HUA Instruments Co., Shanghai, China) with a bare or poly(p-ABSA) modified glassy carbon working electrode (3 mm diameter and 80 mm length), an Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. All the electrodes were purchased from CHEN HUA Instruments Co. (Shanghai, China). All potentials were given with respect to the Ag/AgCl electrode. A pHs-3B pH meter (Dazhong, Shanghai, China) was used for measuring pH. A magnetic stirrer was used during accumulation period. The KQ-250B ultrasonic bath (250 W, Kun Shan Ultrasonic Instruments Co., Ltd, China) was adopted for sample preparation and the centrifugation was carried out in a TGL-16M high-speed refrigerated centrifuge (Xiangyi, China).

2.3. Sample preparation

The samples of chilli powder and ketchup were bought from a local supermarket. According to previous reports (Yang, Zhu, Jiang, & Guo, 2009; Yin et al., 2011), the chilli powder and ketchup samples were treated as follows: briefly, 1 g of sample was added to 10 mL ethanol and subjected to ultrasonication for 30 min. After centrifugation (6000 rpm, 10 min) to remove the sediments, the supernatant was collected in a 100 mL volumetric flask. After repeating the above operation three times, the supernatant was diluted to 100 mL with ethanol. Spiked samples were prepared by adding a specified amount of 0.1 g L^{-1} Sudan I standard solution (333, 667 or 1000 µL) to a sample (1 g) before performing the extraction. For electrochemical determination, 10 mL of the mixed solution containing 0.1 mol L^{-1} phosphate buffer (3 mL, pH 8.5) and 1 mL sample in ethanol was measured for 20 times using square wave anodic stripping voltammetry (SWASV), under the optimised conditions.

2.4. Experimental procedure

Prior to each electrochemical experiment, the surface of GCE was thoroughly polished with water slurry containing 0.3 and 0.05 µm alumina powder on a polishing cloth to a mirror-like appearance, rinsed and ultrasonicated in 1:1 (v/v) HNO_3 aqueous solution, absolute ethanol (99.7%), and water for 3 min, respectively. The well-polished GCE was then placed in a 5 mL electrochemical cell containing 0.1 mol L^{-1} PBS (pH 7.6) and 2 mmol L^{-1} p-ABSA, and was treated with 10 cycles of potential sweep between −1.0 and 2.0 V (vs. Ag/AgCl) at a scan rate of 0.2 V s^{-1} for the preparation of poly(p-ABSA)/GCE. Subsequently, the modified GCE was voltammetrically cycled in a 10 mL electrochemical cell containing 0.1 mol L^{-1} PBS (pH 8.5) and 1 mL of ethanol until a stable cyclic voltammogram was obtained. The electrode was then rinsed with doubly distilled water and used for the following experiments.

Square wave anodic stripping voltammetric measurements were performed in a 10 mL electrolyte solution containing appropriate amounts of Sudan I, 3 mL of 0.1 mol L^{-1} PBS (pH 8.5), and 1 mL of ethanol (or sample ethanol solution). After accumulation at open circuit for 80 s whilst being stirred and 10 s equilibration, the voltammogram was recorded by applying a positive-going square wave stripping voltammetric potential scan from 0.3 to 0.9 V (vs. Ag/AgCl) with a frequency of 35 Hz, pulse height of 50 mV, and step increment of 2 mV. The oxidation peak current of Sudan I was obtained at about 0.51 V (vs. Ag/AgCl).

2.5. Interference analysis

To explore the interference of foreign species to the determination of Sudan I, the oxidation peak current for 100 µg L^{-1} Sudan I, in the absence and presence of foreign species at various concentrations, was measured using the poly(p-ABSA)/GCE and when a change exceeded 10% it is considered to be causing interference. In order to investigate the interference of the natural pigments in chilli powder and ketchup samples, 10 mL of mixed solutions containing 200 µg L^{-1} Sudan I and 3 mL of PBS (0.1 mol L^{-1}, pH 8.5) were measured in the presence of 1 mL of ethanol or sample ethanol solution and the experimental results were recorded.

3. Results and discussion

3.1. Electropolymerisation of p-aminobenzene sulphonic acid at the glassy carbon electrode surface

Cyclic voltammetry was used to form the poly(p-ABSA) film. Electropolymerisation of p-ABSA was carried out in the potential

range of −1.0 to 2.0 V with a scan rate of 200 mV s^{-1} for 10 cycles in 0.1 mol L^{-1} PBS (pH 7.6) containing 2 mmol L^{-1} p-ABSA. The cyclic voltammogram was analogous to that of Jin, Zhang, and Cheng (2005), and the electrochemical polymerisation mechanism of p-ABSA on the GCE was explored.

3.2. Electrochemical behaviour of Sudan I at the poly(p-aminobenzene sulphonic acid) modified glassy carbon electrode

Fig. 1 shows the square wave anodic stripping voltammograms of Sudan I and blank solution on the poly(p-ABSA)/GCE (curves a and d) and the unmodified GCE (curves b and c), respectively. No redox peak was observed at the bare GCE (curve c) and poly(p-ABSA)/GCE (curve d) for the blank solution, indicating that poly(p-ABSA) was non-electrochemically active in the potential range of 0.3–0.9 V, and the background current was very low. When 500 µg L^{-1} Sudan I was added to the PBS (0.1 mol L^{-1}, pH 8.0), a well-defined oxidation peak was observed. The peak current achieved on the poly(p-ABSA)/GCE was twice that at the GCE alone. The superior analytical performance of poly(p-ABSA)/GCE over the GCE alone may be ascribed to unique properties of the poly(p-ABSA) film (e.g. much π–π interactions, strong electrostatic forces, and high specific surface areas), and its capability to adsorb more Sudan I and so enhance the voltammetric response of Sudan I.

3.3. Optimisation of experimental conditions

3.3.1. Effect of pH

Protons are always involved in the electrochemical reaction of organic compound and exert significant influence on the reaction speed (Yang, Zhu, Jiang, & Guo, 2009). Therefore, pH value of phosphate buffer solution (0.1 mol L^{-1}) should have a measurable influence on the peak potential and peak current of Sudan I. Fig. 2 shows the effect of solution pH on the response of Sudan I, which was investigated over the pH range of 6.0–11.0. When the pH changed from 6.0 to 11.0, the anodic peak potential of Sudan I shifted in the negative direction, indicating that a proton took part in the oxidation of Sudan I. The relationship between the oxidation peak potential and pH was constructed and obeyed the linear regression equation Epa(V) = 0.789–0.032 pH (R = 0.9921), meaning that the electron transfer in electrochemical process is accompanied by proton transfer. As to the deviation of the slope to 32 mV/pH from the

theoretical value (58.6 mV/pH) derived from Nernst equation, it can be ascribed to the influence of the slower electrode reaction (Mo et al., 2010). The oxidisation process of Sudan I includes transfer of electrons and protons, which is attributed to the oxidation of the –OH group (Yang et al., 2010). The anodic peak current increased rapidly with increasing solution pH until it reached 8.5 and then it decreased slightly at pH > 8.5. When pH is higher than 3.23 (pKa of p-ABSA is about 3.23), the terminal sulphonic acids will be gradually deprotonated and act as electrostatic adsorption sites (Wu et al., 2008). The experimental investigation showed the poly(p-ABSA) film allows proton transmission and has sufficient negatively charged sites for electrostatic adsorption of Sudan I (pKa of Sudan I is 9.0 (Gao, Zhang, & Xu, 2010)) at pH 8.5. As a result, pH 8.5 phosphate buffer solution (0.10 mol L^{-1}) was chosen as the background electrolyte for further determination.

3.3.2. Effect of amount of co-solvents

The effect of co-solvents on the oxidation current of Sudan I was investigated because of the comparatively weak solubility of Sudan I in water. It had been discussed that Sudan I can be dissolved in alcohol (Du, Han, Zhou, & Wu, 2007). In this experiment, the influence of different ratios of alcohol in the working solution on the voltammetric response of Sudan I was studied. Fig. 3 illustrates the influence of volume ratio of alcohol in the working solution on the voltammetric response of Sudan I. The highest sensitivity and well-defined peak shape were obtained in the solution containing 10% alcohol. When the amount of alcohol was more or less than 10%, the peak current of Sudan I was reduced. Considering the solubility and voltammetric response of Sudan I in 10% (v/v) aqueous solution, this mixture was chosen for subsequent experiments.

3.3.3. Effect of accumulation time

Sudan I (500 µg L^{-1}) was accumulated onto the poly(p-ABSA)/GCE surface, whilst being stirred, prior to recording the voltammogram. The accumulation time had a distinct influence on the analytical sensitivity. Fig. 4 shows that the peak current increased sharply with increasing time when accumulation was less than 80 s, and then reached a constant limiting value. This demonstrates that the adsorption of Sudan I was fast and easily reached saturation. Therefore, 80 s was chosen for subsequent analytical procedures.

3.3.4. Effect of voltammetric parameters

For achieving the best square wave anodic stripping voltammetric responses for Sudan I, some voltammetric parameters were investigated in detail such as step increment, pulse height, and frequency. The effect of the step increment on the peak current of Sudan I was measured in the range of 1–4 mV. The peak current of Sudan I increased with increasing step increment from 1 to 2 mV and then decreased when the step increment was higher than 2 mV. Hence, 2 mV was selected as the optimum step increment.

The effect of the square wave pulse height from 25 to 75 mV was investigated. The peak potential shifted toward slightly low values (shifted about 0.02 V) and the peak current increased with increasing pulse height. The peak current increment was relatively large and the peak potential changed slightly at pulse height of 50 mV; therefore, a pulse height of 50 mV was chosen for the following experiments. The stripping peak current of Sudan I increased with increasing frequency of SWASV from 15 to 35 Hz, and then decreased gradually with increasing frequency from 35 to 75 Hz. Therefore, 35 Hz was chosen.

3.4. Analytical properties

3.4.1. Reproducibility

Considering the active sites of poly(p-ABSA) film bind strongly with analytes, it was necessary to polish the electrode and
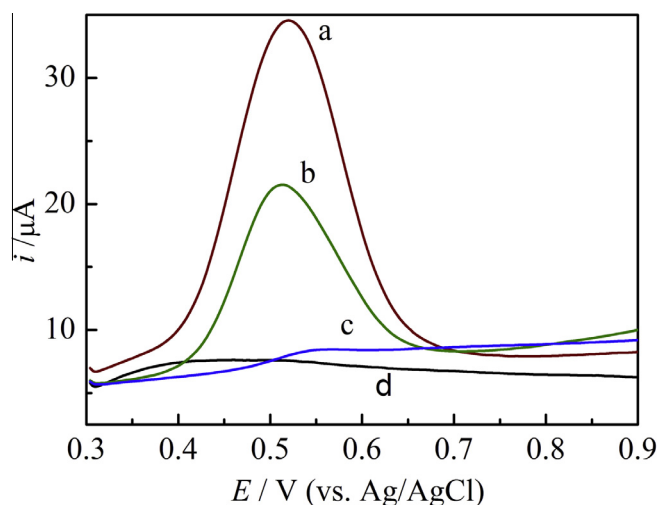

Fig. 1. Square wave anodic stripping voltammetric responses of 500 µg L^{-1} Sudan I and blank solution at the poly(p-ABSA)/GCE (a and d) and bare GCE (b and c) in 3.0 mL of 0.1 mol L^{-1} PBS (pH 8.0) and 1.0 mL of ethanol. Accumulation time: 80 s; quiet time: 10 s; frequency: 50 Hz; pulse height: 35 mV; step increment: 4 mV.
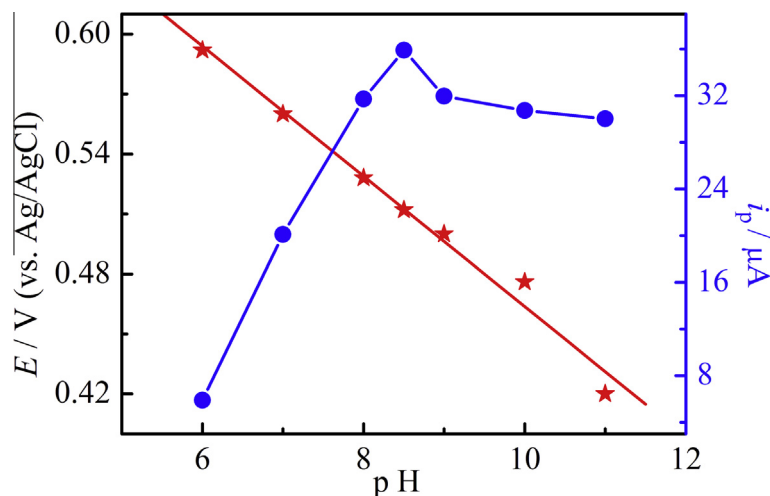
Fig. 2. Effects of the pH of solution on the peak potential (★) and peak current (●) of 500 µg L^{-1} Sudan I at the poly(p-ABSA)/GCE. Other conditions are the same as in Fig. 1.

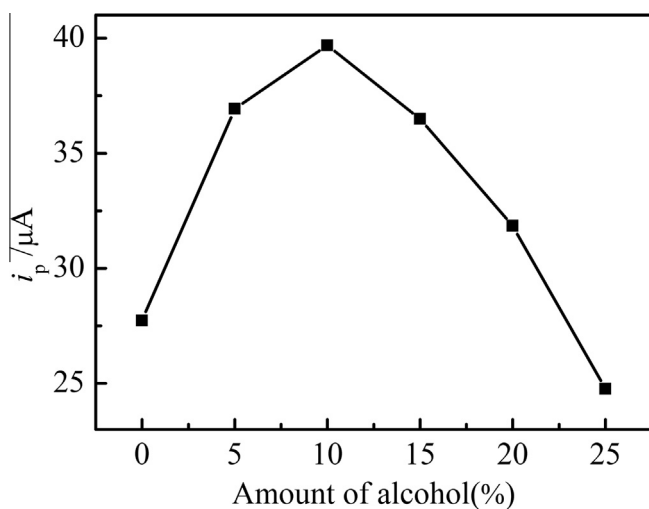**Fig. 3.** Effect of the amount of alcohol (%) on the peak current of 500 µg L^{-1} Sudan I at the poly(p-ABSA)/GCE in 0.1 mol L^{-1} PBS (pH 8.5). Other conditions are the same as in Fig. 1.
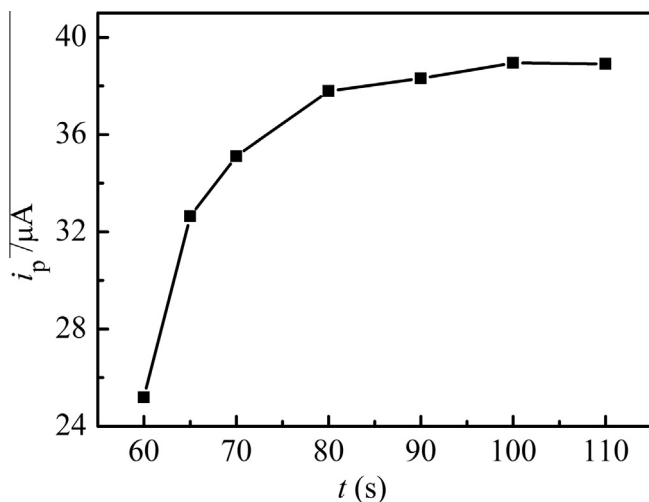
construct a new film after each analysis in order to obtain a polymer film with good stability, more active sites, and good reproducibility (Xie et al., 2010; Xiong et al., 2011). The reproducibility of the poly(p-ABSA)/GCE was estimated by comparing the oxidation peak current of a constant Sudan I concentration. To determine reproducibility, three concentrations of Sudan I (5, 50, and 500 µg L^{-1}) were measured, and the relative standard deviations (RSDs) for the peak currents of each in SWASV (based on 11 repeated tests) were 6.3%, 4.7%, and 5.1%, respectively, indicating good reproducibility in the response of the modified electrode.

3.4.2. Linear range and detection limit

Under the optimum conditions, the relationship between the oxidation peak current and the concentration of Sudan I was studied using SWASV. Fig. 5 shows a linear relationship between the oxidation peak current and the concentration of Sudan I in the range of 1–500 µg L^{-1}. The linear regression equation of Sudan I was $i_p = 1.868 + 0.1213c$ (i_p: µA, c: µg L^{-1}) with a correlation

Fig. 4. Effect of accumulation time on the peak current of 500 µg L^{-1} Sudan I in 0.1 mol L^{-1} PBS (pH 8.5). Other conditions are the same as in Fig. 1.
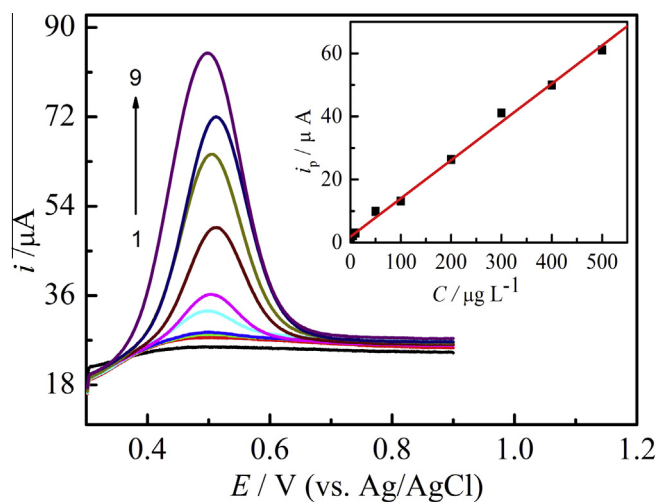

Fig. 5. Square wave anodic stripping voltammetric responses of different concentrations of Sudan I in 0.1 mol L^{-1} PBS (pH 8.5) at the poly(p-ABSA)/GCE. Concentration of Sudan I (from 1 to 9, µg L^{-1}): 1, 5, 10, 50, 100, 200, 300, 400, and 500, respectively; accumulation time: 80 s; quiet time: 10 s; frequency: 35 Hz; pulse height: 50 mV; step increment: 2 mV. The inset shows the relationship between i_p and different concentrations of Sudan I.

Table 1
A particle list of literature on electrochemical sensors of Sudan I.

Sensor	Linear range ($\mu g\ L^{-1}$)	Detection limit ($\mu g\ L^{-1}$)	References
MMT-Ca[a]/CPE[b]	50–1000	20	Lin et al. (2008)
MWNT[c]/GCE	10–1000	5	Gan, Li, and Wu (2008)
OMC[d]/GCE	100–16386	0.6	Yang, Zhu, Jiang, and Guo (2009)
Ionic liquid-MWNT/GCE	12.2–496.6	7.4	Mo et al. (2010)
Fe_3O_4-NPs[e]/GCE	2.5–4965.6	0.25	Yin et al. (2011)
Activated GCE	597–4469	176	Du et al. (2007)
Graphene/GCE	18.6–1862.1	9.9	Ma, Chao, and Wang (2013)
Poly(p-ABSA)/GCE	1–500	0.3	This work

[a] MMT-Ca: montmorillonite calcium.
[b] CPE: carbon paste electrode.
[c] MWNT: multi-walled carbon nanotube.
[d] OMC: ordered mesoporous carbon.
[e] Fe_3O_4-NPs: Fe_3O_4 nanoparticles.

coefficient of 0.9981. The detection limit of $0.3\ \mu g\ L^{-1}$ was estimated from the signal-to-noise characteristics of these data (S/N = 3) and the determination performance of the developed sensor based on poly(p-ABSA) film was compared with other modified electrodes. From Table 1, it can be seen clearly that poly(p-ABSA)/GCE exhibits a lower detection limit than those shown in most of previous methods, which can be ascribed to the good adsorptivity and electrocatalytic ability of poly(p-ABSA) to Sudan I.

3.4.3. Selectivity

For exploring the selectivity of poly(p-ABSA) modified GCE on the determination of Sudan I, the electrochemical responses of Sudan II, Sudan III, and Sudan IV at the modified GCE were investigated and the results are shown in Fig. 6. Obviously, when compared to Sudan II, Sudan III, and Sudan IV, Sudan I exhibited a higher electrochemical response and lower oxidation potential at the poly(p-ABSA)/GCE and it is shown that the four Sudan possess a similar electrochemical behaviour and well-defined catalytic oxidation peak, making the determination of Sudan I be disturbed by other Sudan compounds. Therefore, it is impossible to determine single Sudan compound only if they are separated from their mixture. The interference of some common metal ions and organic compounds coexisting in samples undergoing Sudan I analysis was considered. The experimental results suggest that 500-fold concentration of K^+, Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, NO_3^-, and SO_4^{2-} and 100-fold concentration of capsorubin, cryptoxanthin, and capsaicin had no influence on the determination of Sudan I.

3.4.4. Sudan I assay in food samples

The poly(p-ABSA)/GCE showed high sensitivity and good selectivity towards the detection of Sudan I under the optimum conditions. In order to illustrate its application in practical analysis, the poly(p-ABSA)/GCE was used to detect Sudan I in chilli powder and ketchup samples. However, no Sudan I signal was observed in electrochemical measurement and it was considered that the effects of the natural pigments in hot chili powder and ketchup samples should be explored according to interference analysis. Experimental results showed the natural pigments did not interfere with the Sudan I detection using poly(p-ABSA)/GCE, which was in accordance with previous reports on determination of Sudan I dyes on the MWNT/GCE (Yang et al., 2010), activated GCE (Du et al., 2007), and Fe_3O_4-NPs/GCE (Yin et al., 2011). As no Sudan I was detected in the food samples, different amounts of Sudan I were added to the sample matrices to determine recovery. The results are shown in Table 2, including the RSD of three parallel determination and recovery, which was calculated based on the concentration determined and the concentration of Sudan I added. The analytical results showed that the developed electrochemical
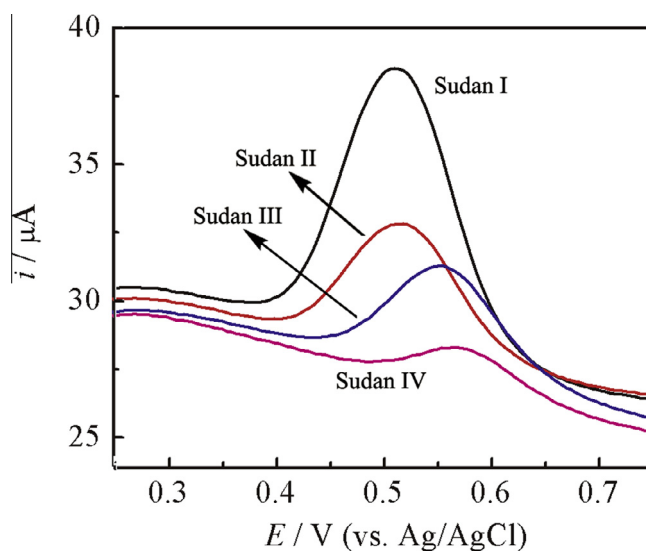

Fig. 6. Square wave anodic stripping voltammetric responses of $100\ \mu g\ L^{-1}$ Sudan I, Sudan II, Sudan III, and Sudan IV at the poly(p-ABSA)/GCE in $0.1\ mol\ L^{-1}$ PBS (pH 8.5). Other conditions are the same as those described in Fig. 5.

Table 2
Recovery of the determination of Sudan I in food samples.

Sample	Added ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	RSD (%)	Recovery (%)
Chilli powder	100	98.0	3.23	98.0
	200	202.2	2.39	101.1
	300	296.9	3.21	98.9
Ketchup	100	97.4	1.98	97.4
	200	204.1	3.07	102.0
	300	297.2	1.78	99.0

[a] Mean of three determinations.

sensor could be applied to the determination of Sudan I in practical samples with satisfactory results.

4. Conclusions

In summary, this study established a novel method to detect Sudan I using a poly(p-ABSA)/GCE. Due to the strong adsorption and excellent electrocatalytic activity of poly(p-ABSA) for Sudan I, the fabricated electrode offered a low detection limit for Sudan I detection, which was less than those of most previous reports. The method developed was successfully applied to the determination of Sudan I in food samples.

Acknowledgments

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