

Analytical Methods

# Electrochemical determination of Sudan I using montmorillonite calcium modified carbon paste electrode

Huogang Lin, Gang Li, Kangbing Wu\*

*Department of Chemistry, Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica,  
Huazhong University of Science and Technology, Wuhan 430074, PR China*

Received 17 May 2007; received in revised form 27 July 2007; accepted 7 August 2007

## Abstract

In the current work, a sensitive, rapid and convenient electrochemical method was developed for the determination of Sudan I utilizing the excellent properties of montmorillonite calcium (MMT-Ca). Compared with the unmodified carbon paste electrode (CPE), MMT-Ca modified CPE not only significantly enhances the oxidation peak current of Sudan I but also lowers the oxidation overpotential, suggesting that the MMT-Ca modified CPE can remarkably improve the determining sensitivity of Sudan I. The experimental conditions such as determining medium, the content of MMT-Ca and accumulation time were optimized for the determination of Sudan I. The oxidation peak current is proportional to the concentration of Sudan I over the range from 0.05 mg L<sup>-1</sup> (2.01 × 10<sup>-7</sup> mol L<sup>-1</sup>) to 1.0 mg L<sup>-1</sup> (4.03 × 10<sup>-6</sup> mol L<sup>-1</sup>), and the limit of detection is 0.02 mg L<sup>-1</sup> (8.06 × 10<sup>-8</sup> mol L<sup>-1</sup>) for 2-min accumulation. Finally this newly-proposed sensing method was successfully employed to detect Sudan I in practical samples and good recovery was achieved. © 2007 Elsevier Ltd. All rights reserved.

*Keywords:* Sudan dye; Voltammetric determination; Modified electrode; Montmorillonite

## 1. Introduction

Food safety analysis is a very important branch of analytical chemistry, and attracts increasing attention since it plays crucial role in human public health. Sudan dyes are phenyl-azoic derivatives extensively used in chemical industries, household commodities, textile, leather and wood industries for coloring materials such as hydrocarbon solvents, oils, fats, plastics, printing inks, shoe and floor polishes (Nohynek, Fautz, Benech-Kieffer, & Toutain, 2004). It is generally known that Sudan dyes mainly include fur types: Sudan I, Sudan II, Sudan III and Sudan IV (see Fig. 1), which have been proved through laboratory experiments to cause cancer to both animals and human beings (Stiborova, Martinek, Rydlova, Hodek, & Frei, 2002). Therefore, Sudan I has been classified as a category 3 carcinogen by the International Agency for Research on Can-

cer (IARC). On this point, developing a sensitive, rapid and convenient method for the determination of Sudan dyes is of great importance and interest.

To date, the most commonly used method for the determination of Sudan dyes is high performance liquid chromatography (HPLC) (Cornet, Yasmine, Goedele, Loco, & Degroot, 2006; Tateo & Bononi, 2004) or HPLC-MS (Calbani et al., 2004; Zhang, Zhang, & Suna, 2006) due to their high sensitivity and excellent selectivity. Otherwise, very limited electrochemical methods have also been proposed for the determination of Sudan dyes. For example, an electrochemically activated glassy carbon electrode (AGCE) was utilized to determine Sudan I based on its reduction (Du, Han, Zhou, & Wu, 2007). The linearity range is from 2.4 × 10<sup>-6</sup> to 1.8 × 10<sup>-5</sup> mol L<sup>-1</sup>, and the detection limit is 7.1 × 10<sup>-7</sup> mol L<sup>-1</sup>. However, to the best of our knowledge, electrochemical determination of Sudan dyes based on its oxidation and using montmorillonite calcium-modified carbon paste electrode has been not reported.

\* Corresponding author. Fax: +86 27 8754 3632.  
E-mail address: [kbwu@mail.hust.edu.cn](mailto:kbwu@mail.hust.edu.cn) (K. Wu).

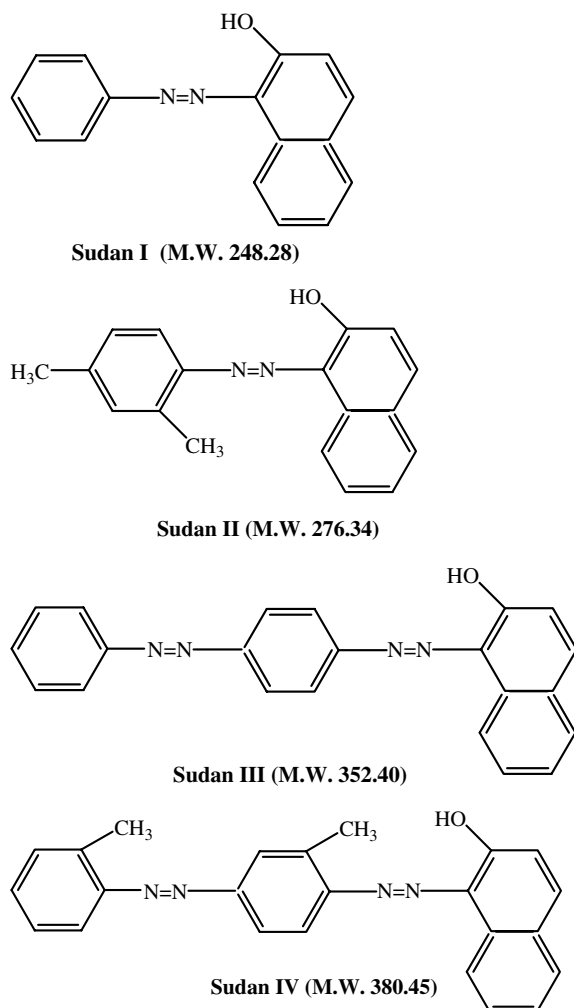


Fig. 1. Chemical structures of Sudan I, Sudan II, Sudan III and Sudan IV.

The main objective of the current work is to develop a sensitive and convenient electrochemical method for the determination of Sudan dyes utilizing the excellent properties of montmorillonite calcium (MMT-Ca). Montmorillonite belongs to the smectite group of clays with a layer lattice and includes two types: montmorillonite sodium (MMT-Na) and montmorillonite calcium (MMT-Ca). Because montmorillonite has high chemical and mechanical stability, a well-layered structure, strong adsorptive properties attributed to the expandability of the internal layers, it has been widely used in electroanalytical chemistry for different purposes (Shumyantseva et al., 2004; Xiang, Sato, Umemura, & Yamagishi, 2005; Zen & Kumar, 2004).

To complete the goal, MMT-Ca was homogeneously mixed with graphite powder and paraffin oil, and then a MMT-Ca modified carbon paste electrode (CPE) was achieved. In pH 7.0 phosphate buffer, the oxidation peak current of Sudan I significantly increases and the oxidation peak potential shifts negatively at the MMT-Ca modified CPE, suggesting that MMT-Ca facilitates the electron

transfer of Sudan I and then remarkably improves the determining sensitivity. After all the experimental parameters were optimized, a novel electrochemical method was proposed for the determination of Sudan I, demonstrating with chilli and ketchup samples. This new sensing and determining system possesses following advantages: high sensitivity, extreme simplicity, good accuracy and low cost.

## 2. Experimental section

### 2.1. Reagents

Montmorillonite calcium (MMT-Ca) was obtained from source clay Minerals Repository, University of Missouri (Columbia Mo). Graphite powder (spectral reagent) and paraffin oil were purchased from Sinopharm Group Chemical Reagent Co., Ltd., China (<http://www.sinoreagent.com>).

Sudan I (1-[(2,4-dimethylphenyl)azo]-2-naphthalenol), Sudan II (1-(phenylazo)-2-naphthalenol), Sudan III (1-(4-phenylazophenylazo)-2-naphthalenol), Sudan IV (*o*-tolylazo-*o*-tolylazo-beta-naphthalenol), were purchased from Beijing Chemical Reagent Company, China. 0.10 mg mL<sup>-1</sup> Stock solutions of Sudan I, Sudan II, Sudan III and Sudan IV were prepared in ethanol, and stored at 4 °C in the dark.

Other chemicals used were of analytical reagents, and all the chemicals were used without further purification.

### 2.2. Apparatus

All the electrochemical measurements were carried out using a VersaStat™ II Potentiostat/Galvanostat (Princeton Applied Research, USA), which was controlled by a PC using the Powersuit Software.

A conventional three-electrode system, consisting of a carbon paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed. The body of working electrode was a polytetrafluoroethylene (PTFE) cylinder that was tightly packed with carbon paste, while a copper wire inserts into the carbon paste to provide electrical contact.

### 2.3. Fabrication of MMT-Ca modified CPE

At first, 30.0 mg of MMT-Ca and 150.0 mg graphite powder were mixed uniformly by milling in a small carnelian mortar, then 30.0 μL paraffin oil was added into and milled again to give a homogenous MMT-Ca modified carbon paste. After that, the MMT-Ca modified carbon paste was pressed into the end cavity (3-mm in diameter, 1-mm in depth) of the electrode body, and the surface was smoothed against weighing paper. It is necessary to note that the amount of paraffin oil must be carefully controlled because excessive paraffin oil will lower the conductivity, while insufficient paraffin oil is not beneficial to obtain uniform MMT-Ca modified carbon paste.

## 2.4. Analytical procedure

Unless otherwise stated, 0.1 mol L<sup>-1</sup> phosphate buffer (pH = 7.0) was used as determining medium for Sudan I analysis. The analytical procedure mainly contains two steps: accumulation step and determining step. Firstly, Sudan I was preconcentrated at the MMT-Ca modified CPE surface under open-circuit for 2-min stirring. After that, Sudan I was oxidized during the following square wave voltammetric sweep from 0.30 to 0.90 V, resulting in a sensitive oxidation peak at 0.62 V, which measured as the analytical signal for Sudan I.

After each measurement, the used paste was carefully removed from the end cavity and another new MMT-Ca modified CPE was fabricated again.

## 2.5. Sample preparation

Various samples possibly contained Sudan I were obtained from a local market, and then treated as following method to give sample solution. Otherwise, the spiked sample solution was prepared as the same method after adding known-amount of Sudan I standard.

### 2.5.1. Hot chilli powder sample

Various hot chilli powders were treated as described with minor modifications [7]. Chilli powder (1.00 g) was exactly weighed, and then 20 mL ethanol was added into. After 30-min ultrasonication, the mixture was filtrated and the liquid phase was collected in a 100.0-mL volumetric flask. The treatment was repeated three times, and finally the filtrate extract was diluted to volume with ethanol.

### 2.5.2. Ketchup sample

The ketchup sample was treated as follows: 10.00 g ketchup was exactly weighed, and then 20 mL ethanol was added into. After 20-min ultrasonication, the mixture was filtrated and the liquid phase was collected in a 100.0-mL volumetric flask. The treatment was repeated three times, and the filtrate extract was diluted to volume with ethanol.

### 2.5.3. Chilli juice sample

The chilli juice was just filtrated, and the filtrate was collected for further measurement.

## 3. Results and discussion

### 3.1. Cyclic voltammetric behaviors of Sudan I

The electrochemical behaviors of Sudan I at the unmodified CPE and MMT-Ca modified CPE were investigated using cyclic voltammetry (CV). In 0.1 mol L<sup>-1</sup>, pH 7.0 phosphate buffer, unmodified CPE and MMT-Ca modified CPE have different responses to 0.50 mg L<sup>-1</sup> (2.01 × 10<sup>-6</sup> mol L<sup>-1</sup>) Sudan I. At the unmodified CPE (Fig. 2a), an oxidation peak is observed at 0.67 V during the first anodic

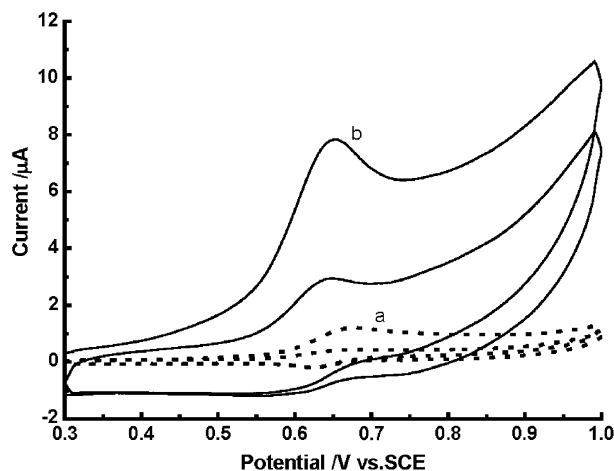


Fig. 2. Cyclic voltammograms of 0.50 mg L<sup>-1</sup> (2.01 × 10<sup>-6</sup> mol L<sup>-1</sup>) Sudan I in pH 7.0 phosphate buffer at (a) unmodified CPE; and (b) MMT-Ca modified CPE. Scan rate = 100 mV s<sup>-1</sup>.

sweep from 0.30 to 1.00 V; on the reverse scan, a non-sensitive reduction peak appears at 0.63 V. During the second cyclic sweep, the oxidation peak current remarkably decreases while the reduction peak current almost keeps unchangeable.

Fig. 2b shows the successive cyclic voltammograms of 0.50 mg L<sup>-1</sup> Sudan I at the MMT-Ca modified CPE. During the first anodic sweep from 0.30 to 1.00 V, a sensitive and well-shaped oxidation peak appears at 0.65 V. On the reverse scan, a poorly-defined reduction peak is observed. Additionally, the oxidation peak current shows obvious decline during the second cyclic sweep, while the reduction peak current slightly decreases. Therefore, the oxidation peak current in the first anodic sweep is recorded for Sudan I to achieve higher sensitivity and better reproducibility in the following studies.

Compared with the unmodified CPE, it is very clear that the MMT-Ca modified CPE not only significantly enhances the oxidation peak current, but also lowers its oxidation peak potential from 0.67 V to 0.65 V. The obvious peak current enhancement and negative shift of oxidation peak potential indicate that MMT-Ca exhibits catalytic ability to the oxidation of Sudan I.

Moreover, the effects of scan rate on the oxidation peak current and peak potential of 0.50 mg L<sup>-1</sup> Sudan I were also studied using linear sweep voltammetry (LSV) in pH 7.0 phosphate buffer. It is found that the oxidation peak potential shifts positively as increasing scan rate, revealing that the oxidation of Sudan I at MMT-Ca modified CPE is irreversible. Otherwise, the oxidation peak current increases linearly with scan rate over the range from 25 to 150 mV s<sup>-1</sup>, suggesting that the oxidation of Sudan I is adsorption-controlled.

### 3.2. Square wave voltammetric responses of Sudan I

Square wave voltammetry (SWV) is widely used in electrochemical determination because of high sensitivity and

excellent resolution. Therefore, the electrochemical responses of low concentration of Sudan I at unmodified CPE and MMT-Ca modified CPE were compared using SWV, which depicted in Fig. 3. After 2-min open-circuit accumulation in pH 7.0 phosphate buffer,  $0.1 \text{ mg L}^{-1}$  ( $4.03 \times 10^{-7} \text{ mol L}^{-1}$ ) Sudan I yields an oxidation peak at 0.64 V at the unmodified CPE (Fig. 3a). However, the oxidation peak current of Sudan I significantly increases at the MMT-Ca modified CPE under the identical conditions, accompanied by negative shift of oxidation peak potential from 0.64 V to 0.62 V (Fig. 3b). From the comparisons of curves (a) and (b), it is well-known that MMT-Ca can greatly improve the determining sensitivity of Sudan I. MMT-ca is an excellent smectite clay with a well-layered structure and has strong adsorptive ability attributed to the expandability of the internal layers. Therefore, the MMT-Ca modified CPE exhibits much higher accumulation efficiency to Sudan I and then greatly improves the surface concentration. Without a doubt, the oxidation peak current of Sudan I significantly increases at the MMT-Ca modified CPE, compared with the unmodified CPE.

Additionally, the oxidation peak current of Sudan I at MMT-Ca modified CPE was examined as a function of its concentration. When the concentration of Sudan I increases to  $0.2 \text{ mg L}^{-1}$  ( $8.06 \times 10^{-7} \text{ mol L}^{-1}$ ), the oxidation peak current also increases by 100% (Fig. 3c); if the concentration decreases to zero (without Sudan I), the oxidation peak will vanish (Fig. 3d). These phenomena reveal that the oxidation peak at 0.62 V corresponds to Sudan I and what's more, the peak current has good linearity with its concentration.

### 3.3. Electrochemical behaviors of Sudan I, Sudan II, Sudan III and Sudan IV

Because Sudan dyes include four types: Sudan I, Sudan II, Sudan III and Sudan IV, it is very necessary to investi-

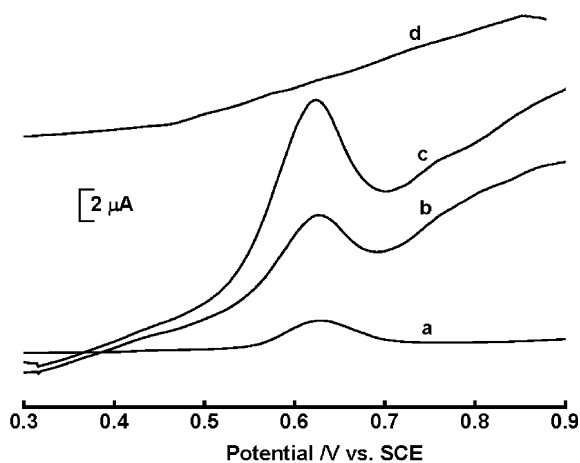


Fig. 3. Square wave voltammetric responses of Sudan I after 2-min accumulation. (a)  $0.1 \text{ mg L}^{-1}$  Sudan I at unmodified CPE; and (b–d)  $0.1$ ,  $0.2$  and  $0 \text{ mg L}^{-1}$  Sudan I at MMT-Ca modified CPE. Pulse height =  $25 \text{ mV}$ , pulse wide =  $10 \text{ ms}$ , scan rate =  $100 \text{ mV s}^{-1}$ .

gate their electrochemical behaviors at the MMT-Ca modified CPE. Fig. 4 shows the square wave voltammetric responses of four kinds of Sudan dyes at MMT-Ca modified CPE after 2-min accumulation.

In pH 7.0 phosphate buffer,  $0.3 \text{ mg L}^{-1}$  ( $1.21 \times 10^{-6} \text{ mol L}^{-1}$ ) Sudan I yields a well-defined and most sensitive oxidation peak at 0.62 V (Fig. 4a). Regarding to Sudan II, a well-shaped and relative lower oxidation peak is also observed at 0.62 V (Fig. 4b). The peak potentials of Sudan I and Sudan II are very close since their chemical structures are very similar and contain the same electrochemical active group.

Curves (c) and (d) depict the square wave voltammetric response of  $0.3 \text{ mg L}^{-1}$  Sudan III and Sudan IV at MMT-Ca modified CPE, respectively. There are two oxidation peaks are observed at 0.66 V and 0.67 V, respectively. Compared with Sudan I and Sudan II, their oxidation peak currents are relatively lower and the peak potentials are more positive.

Besides, the square wave voltammetric response of MMT-Ca modified CPE in pH 7.0 phosphate buffer after 2-min accumulation was also given for better comparison (Fig. 4e). It is found that the curve is very smooth and has no reduction peaks.

From Fig. 4, it is very clear that the electrochemical responses of 4 types of Sudan dyes are very similar at the MMT-Ca modified CPE. Therefore, this method can detect the total amount if they exist together. Considering that Sudan I is commonly used and much sensitive at MMT-Ca modified CPE, it was only examined in the following studies.

### 3.4. Choice of supporting electrolyte

The electrochemical oxidation signals of Sudan I at the MMT-Ca modified CPE in pH 5.0, 5.5, 6.0, 6.5, 7.0, 8.0 phosphate buffer ( $0.1 \text{ mol L}^{-1}$ ) were examined. It is found that the oxidation peak current is highest in  $0.1 \text{ mol L}^{-1}$ ,

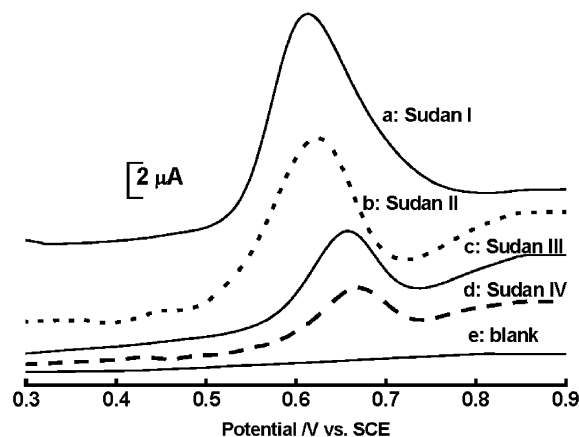


Fig. 4. Square wave voltammetric responses of  $0.3 \text{ mg L}^{-1}$  Sudan dyes at the MMT-Ca modified CPE after 2-min accumulation time. (a) Sudan I; (b) Sudan II; (c) Sudan III; (d) Sudan IV; and (e) blank voltammograms.

pH 7.0 phosphate buffer. Otherwise, the background current is very low and the oxidation peak is well-shaped. Therefore, 0.1 mol L<sup>-1</sup> phosphate buffer (pH 7.0) was used as supporting electrolyte for the determination of Sudan I.

### 3.5. Influence of the content of MMT-Ca

It is well clear that MMT-Ca can remarkably improve the oxidation peak current of Sudan I from Figs. 2 and 3. However, the mass ratio between MMT-Ca and graphite powder also influences the oxidation peak current of Sudan I. As gradually improving the content of MMT-Ca, the oxidation peak current of Sudan I firstly increases, then changes slightly, and finally decreases. When improving the amount of MMT-Ca, the sites for adsorption of Sudan I also increase, resulting in much higher accumulation efficiency. Thus, the oxidation peak current shows obvious enhancement. However, the conductivity of MMT-Ca modified CPE will lower as further improving the amount of MMT-Ca, blocking the electron transfer and increasing the background current. So, the oxidation peak current of Sudan I contrarily decreases when the content of MMT-Ca is too high. In this work, the optimized mass ratio between graphite powder and MMT-Ca is chosen as 5:1.

### 3.6. Effect of accumulation time

Open-circuit accumulation is a simple and effective way to enhance the determining sensitivity in electrochemical determination. The influence of accumulation time on the oxidation peak current of 0.1 mg L<sup>-1</sup> (4.03 × 10<sup>-7</sup> mol L<sup>-1</sup>) Sudan I was examined. It is found that the oxidation peak current gradually increases as extending the accumulation time. The longer accumulation time will cause more and more Sudan I to be preconcentrated at MMT-Ca modified CPE surface, subsequently lead the oxidation peak current to enhance. This phenomenon tells that the sensitivity of determination of Sudan I will increase as extending accumulation time.

However, the oxidation peak current begins to increase slightly when the accumulation time is too long (4.0 min in this work), presumably indicating that the limiting value of Sudan I at the MMT-Ca modified CPE surface has been achieved. Considering both sensitivity and working efficiency, an accumulation time of 2.0 min was used.

## 3.7. Analytical properties

### 3.7.1. Reproducibility

After each measurement, the MMT-Ca modified carbon paste was carefully removed from the end cavity and another new MMT-Ca modified CPE was remade as above-mentioned procedure. The reproducibility between multiple MMT-Ca modified electrodes was estimated by comparing the oxidation peak current of 0.1 mg L<sup>-1</sup> (4.03 × 10<sup>-7</sup> mol L<sup>-1</sup>) Sudan I. The relative standard deviation (RSD) is 5.6% for 10 MMT-Ca modified CPEs, revealing that this method possesses good reproducibility.

ation (RSD) is 5.6% for 10 MMT-Ca modified CPEs, revealing that this method possesses good reproducibility.

### 3.7.2. Interference

The interferences of many foreign species (especially contained in chilli sample) on the determination of Sudan I were studied by SWV under the above-optimized conditions. The oxidation peak currents of 0.1 mg L<sup>-1</sup> (4.03 × 10<sup>-7</sup> mol L<sup>-1</sup>) Sudan I in the absence and presence of foreign species with various concentrations were measured, respectively. Based on this, the peak current change can be achieved. Herein, when the peak current change exceeds 10%, it is considered that this substance causes obvious interference, and the corresponding concentration was defined as tolerance level. The results are listed in Table 1, suggesting that 200-fold concentration of capsanthin, capsorubin, zeaxanthin, β-carotene, cryptocapsin, cryptoxanthin, and capsanthin diacetate almost have no influence. Otherwise, some metal ions such as 500-fold concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, 200-fold concentration of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> almost do not influence the determination of Sudan I.

### 3.7.3. Linear range

The relationship between the oxidation peak current and the concentration of Sudan I was studied by SWV under the optimized conditions. The oxidation peak current (*i<sub>p</sub>*) is proportional to the concentration of Sudan I over the range from 0.05 mg L<sup>-1</sup> (2.01 × 10<sup>-7</sup> mol L<sup>-1</sup>) to 1.0 mg L<sup>-1</sup> (4.03 × 10<sup>-6</sup> mol L<sup>-1</sup>), obeying the following equation: *i<sub>p</sub>* = 0.135 + 37.65 *c* (*r* = 0.9889, *i<sub>p</sub>* in μA, *c* in mg L<sup>-1</sup>).

### 3.7.4. Limit of detection

The limit of detection was estimated utilizing the method of gradually decreasing the concentration of Sudan I. When the concentration decreases to 0.02 mg L<sup>-1</sup>, an observable oxidation peak appears after 2-min accumulation. As further decreasing the concentration, the oxidation peak almost disappears. So, the limit of detection is evaluated to be 0.02 mg L<sup>-1</sup> (8.06 × 10<sup>-8</sup> mol L<sup>-1</sup>) for 2-min accumulation. Additionally, the limit of detection will lower as increasing accumulation time. If the accumulation time extends to 4 min, the limit of detection are 0.01 mg L<sup>-1</sup>.

Table 1  
Interference on the determination of Sudan I

Foreign species	Tolerance level (mg L <sup>-1</sup> )
Capsanthin, capsorubin, zeaxanthin, β-carotene, cryptocapsin, cryptoxanthin, capsanthin diacetate	20.0
Ca <sup>2+</sup> , Mg <sup>2+</sup> , Fe <sup>3+</sup> , Al <sup>3+</sup> , Zn <sup>2+</sup>	50.0
Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup>	20.0

Table 2  
Determination of Sudan I in chilli and ketchup samples

Sample	Spiked	Expected	Found	RSD (%)	Recovery (%)
Powder A	0.00		0.00		
	30.00 $\mu\text{g g}^{-1}$	30.00 $\mu\text{g g}^{-1}$	27.72 $\mu\text{g g}^{-1}$	4.2	92.4
Powder B	0.00		36.46 $\mu\text{g g}^{-1}$		
	30.00 $\mu\text{g g}^{-1}$	66.46 $\mu\text{g g}^{-1}$	60.21 $\mu\text{g g}^{-1}$	3.8	90.6
Powder C	0.00		0.00		
	40.00 $\mu\text{g g}^{-1}$	40.00 $\mu\text{g g}^{-1}$	35.44 $\mu\text{g g}^{-1}$	4.3	88.6
Ketchup A	0.00		0.00		
	20.00 $\mu\text{g g}^{-1}$	20.00 $\mu\text{g g}^{-1}$	18.58 $\mu\text{g L}^{-1}$	4.6	92.9
Ketchup B	0.00		9.26 $\mu\text{g g}^{-1}$		
	10.00 $\mu\text{g g}^{-1}$	19.26 $\mu\text{g g}^{-1}$	17.95 $\mu\text{g g}^{-1}$	5.5	93.2
Juice A	0.00		0.36 $\text{mg L}^{-1}$		
	0.50 $\text{mg L}^{-1}$	0.86 $\text{mg L}^{-1}$	0.77 $\text{mg L}^{-1}$	5.6	89.5
Juice B	0.00		0.62 $\text{mg L}^{-1}$		
	0.50 $\text{mg L}^{-1}$	1.12 $\text{mg L}^{-1}$	1.02 $\text{mg L}^{-1}$	5.4	91.1

### 3.8. Sample analysis

In order to ascertain the potential applications in practical sample analysis, this newly-proposed method was used to detect Sudan I in different kinds of samples such as chilli powder, chilli juice and ketchup. Under the optimized conditions, a known-amount of sample solution was added into pH 7.0 phosphate buffer, and then analyzed according to the above-described procedure.

Table 2 shows the content of Sudan I in different samples, which measured by the standard addition method. Each sample undergoes three parallel measurements, and the RSD is below 6%, suggesting that this method possesses good reproducibility. Otherwise, the recovery of Sudan I standard that added into the samples was also measured, and the results were in the range from 88.6% to 93.2%, indicating that this method has good accuracy.

### 4. Conclusion

On account of the strong adsorptive ability of MMT-Ca, the oxidation peak current of Sudan dyes greatly increases at the MMT-Ca modified CPE. Based on this, a sensitive and convenient electrochemical method was developed for the determination of Sudan dyes. Compared with other electrochemical method, this new method possesses higher sensitivity, extreme simplicity and rapid response.

### Acknowledgements

The authors are grateful to the financial support from the National Natural Science Foundation of China (No. 20507006).

### References

- Calbiani, F., Careri, M., Elviri, L., Mangia, A., Pistara, L., & Zagnoni, I. (2004). Development and in-house validation of a liquid chromatography – electrospray-tandem mass spectrometry method for the simultaneous determination of Sudan I, Sudan II, Sudan III and Sudan IV in hot chilli products. *Journal of Chromatography A*, 1042, 123.
- Cornet, V., Yasmine, G., Goedele, M., Loco, J. V., & Degroodt, J. M. (2006). Development of a fast analytical method for the determination of sudan dyes in chilli- and curry-containing foodstuffs by high-performance liquid chromatography-photodiode array detection. *Journal of Agricultural and Food Chemistry*, 54, 639.
- Du, M. J., Han, X. G., Zhou, Z. H., & Wu, S. G. (2007). Determination of Sudan I in hot chilli powder by using an activated glassy carbon electrode. *Food Chemistry*, 105, 883.
- Nohynek, G. J., Fautz, R., Benech-Kieffer, F., & Toutain, H. (2004). Toxicity and human health risk of hair dyes. *Food and Chemical Toxicology*, 42, 517.
- Shumyantseva, V. V., Ivanov, Y. D., Bistolos, N., Scheller, F. W., Archakov, A. I., & Wollenberger, U. (2004). direct electron transfer of cytochrome P450 2B4 at electrodes modified with nonionic detergent and colloidal clay nanoparticles. *Analytical Chemistry*, 76, 6046.
- Stiborova, M., Martinek, V., Rydlova, H., Hodek, P., & Frei, E. (2002). Sudan I is a potential carcinogen for humans: evidence for its metabolic activation and detoxication by human recombinant cytochrome P450 1A1 and liver microsomes. *Cancer Research*, 62, 5678.
- Tateo, F., & Bononi, M. (2004). Fast determination of sudan I by HPLC/APCI-MS in hot chilli, spices, and oven-baked foods. *Journal of Agricultural and Food Chemistry*, 52, 655.
- Xiang, H. J., Sato, H., Umemura, Y., & Yamagishi, A. (2005). Sensing of molecular chirality on an electrode modified with a clay-metal complex hybrid film. *Journal of Physical and Chemical B*, 109, 4679.
- Zen, J. M., & Kumar, A. S. (2004). The prospects of clay mineral electrodes. *Analytical Chemistry*, 76, 205A.
- Zhang, Y. T., Zhang, Z. J., & Suna, Y. H. (2006). Development and optimization of an analytical method for the determination of Sudan dyes in hot chilli pepper by high-performance liquid chromatography with on-line electrogenerated  $\text{BrO}^-$ -luminol chemiluminescence detection. *Journal of Chromatography A*, 1129, 34.