Int. J. Electrochem. Sci., 11 **(2016)** 4586 – 4597, doi: 10.20964/2016.06.43

International Journal of
ELECTROCHEMICAL
SCIENCE
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Simple Electrochemical Sensor Based on Carbon-black Paste Electrode Coupled with Derivative Square Wave Voltammetry for the Determination of Sulfites in Rice Wine

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Received: 27 December 2015 / *Accepted:* 26 March 2016 / *Published:* 4 May 2016

A simple electrochemical sensor for the determination of sulfites in rice wine samples based on carbon black paste electrode (CBE) coupled with first-order derivative square wave voltammetry (SWV) was developed. CBE prepared by packing the mixture of carbon black powder and liquid paraffin oil with a ratio of 2:1 (w/w) into a cavity without any additional modification was reported. The cyclic voltammetry and SWV showed that the oxidation current of sulfite at CBE increased significantly compared with bare glassy carbon electrode or graphite paste electrode. Through first-order derivative processing, peaks became narrower and sharper leading to the enhancement of sensitivity. External standard calibration curve was in the range of 0.008~1.0 mmol L^{-1} with a detection limit of 6.0 μmol L^{-1}. This method was applied to the determination of sulfites in the commercial available rice wine samples and the results were compared with a titration method.

Keywords: Electrochemical sensor; Carbon black paste electrode; Derivative square wave voltammetry; Sulfite determination; Rice wine

1. INTRODUCTION

Sulfites are widely used additives in food industry. In wine making process, despite the fact that small amounts of sulfites may form naturally due to some metabolic processes [1, 2], Usually, around 30~90 ppm of additional sulfites are added throughout production both in fermentation and in storage [3] to prevent microbial spoiling [4], as well as to play an important role in reducing quinones formed during oxidation process back to their phenol forms [5], which naturally present in the raw material of wine and reflect the antioxidant capacity of wine [6, 7]. However, ingestion of foods containing large amounts of sulfites is associated with asthmatic reactions and intolerance symptoms

[8-10]. In addition, nutritional quality of treated foods might be reduced due to its interaction with some vitamins such as thiamin, pyridoxal, nicotinamide, and folic acid [11]. Therefore, restricted regulations have been set avoiding over use of sulfites in foodstuffs since the 1980s. For example, United States Food and Drug Administration regulations require food and wine producers to indicate "contains sulfites" on the label of any product that has at least 10 mg L^{-1} sulfite (calculated as SO_2). Accordingly, the development of sensitive, selective, precise and low-cost analytical methods for the determination of sulfite is of vital important.

A couple of useful methods are available to determine sulfites in wine samples, such as titration [12], spectrophotometer [13], ion chromatography [14] and capillary electrophoresis[15]. However, these methods are not fully satisfactory due the tedious sample pretreatment procedure or high cost instrument, and in some cases low sensitivity and selectivity. As a complementary choice, electrochemical sensors, measuring the current generated by direct sulfite oxidation at metallic electrodes, carbon/graphite electrodes or chemically modified electrodes have great potential over other techniques for the determination of sulfite owing to its advantages such as simplicity, sensitivity, reliability and the possibility of on-line applications [16, 17]. As for the electrodes, the electron transfer rate seems quite sluggish at common metal electrodes for the determination of sulfite in aqueous solution [18]. Comparatively, chemically modified electrodes (CMEs) utilizing different modification procedures and sensing materials, possess the advantage of electrocatalysis of slow electron transfer reactions and meanwhile reduce sulfite oxidation potential [19, 20], but their modification procedures are somehow complicated.

During the past few years, a great amount of attention has been paid to the surface property of carbon based material as electrode, such as glassy carbon (GC), graphite, graphene and carbon nano-tube (CNT) particles [21], especially CNT and graphene have been widely used in electroanalysis field. A couple of electrochemical sensors for sulfites have been fabricated based on CNT-based composite electrode [22], modified CNT paste electrode [23], or metal doped graphene modified GC electrode [24] due to their wide operation potential window, rich surface chemistry, chemical inertness and suitability for various sensing and detection [25, 26]. Carbon black, another group of carbon nano material, such as furnace black, channel black, thermal black, lamp black, and acetylene black, made from different sources or technical processes, are extremely favorable due to its good conductivity, significantly lower cost, wide range of sources, mainly used as conductive particle in many types of battery and supercapacitor electrodes [27, 28]. In recent years, some of the carbon black like acetylene black has gradually found its way to be a functional modifier in construction of modified electrode for the determination purpose [29]. Super P® Li is one kind of the carbon black. The main characteristics of Super P® Li are their high purity, high structure and moderate surface area. In our previous work, a Super P® Li based composite electrode (acetylferrocene- Super P® Li-polyvinyl butyral modified glassy carbon electrode) was fabricated for the determination of sulfites in the extraction of muscle foods [30], in which Super P® Li was worked as a conductivity material. Herein, we explore the determination of sulfite in rice wine samples using Super P® Li carbon black paste electrode (CBE) without any additional modification such as addition of electron transfer mediator or specific reagents, coupled with first order derivative square wave voltammetry (first SWV). The behavior of sulfites at CBE electrode and the electrochemical characteristic of CBE were investigated. The proposed method was applied in the commercial rice wine sample analysis and compared with the titration method. To our knowledge, an electrode based on Super P® Li for the sensing of sulfite has not been reported.

2. MATERIAL AND METHODS

2.1. Chemicals and reagents

Chemical standard of sodium sulfite (Acros, Belgium) was used as purchased without further purification. Reagents including sodium nitrate, sodium chloride, lead acetate, sodium hydroxide, hydrochloric acid, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, iodine solution are of analytical grade purchased from Aladdin, China. Carbon black (Super P® Li) was obtained from Timcal, Belgium. Graphite powder was purchased from Shanshan, China. 0.2 mol L^{-1} phosphate buffer （pH 7.40）obtained by well mixing appropriate volume of 0.2 mol L^{-1} NaH_2PO_4 and 0.2 mol L^{-1} Na_2HPO_4 was used as support electrolyte. To stabilize sulfite inhibiting oxidation to their sulfate constituents, propyl alcohol (2%, v/v) solution was added when preparing sulfite solution [31] The working standard solutions of sodium sulfite were prepared daily in supporting electrolyte. Rice wine samples were randomly purchased from the local market.

2.2. Apparatus

All cyclic voltammetric experiments were performed on a computer-controlled LK2005A Electrochemistry Workstation (Lanlike, China) with a conventional three-electrode configuration. A platinum electrode was served as the counter electrode, the saturated calomel electrode（SCE）was used as a reference in all electrochemical experiments. The working electrode (4.5 mm diameter) was Super P® Li carbon black paste electrode (CBE) or graphite paste electrode (GE). The working electrode for cyclic voltammograms scanning and square wave voltammetry (SWV) was operated within a potential range of 0 to 0.8 V (vs. SCE) at scan rate of 50 mV s^{-1}, peak potential (E_P) and peak current (i_P) were recorded. The chronocoulometry was conducted with the initial potential of 0 V, the step potential of 0.65 V, sample time of 0.5 s and sample point of 200. All tests were conducted at room temperature. The pH was measured using a Sartorius pH-meter, model PB-10, employing a glass composite electrode with a SCE as external reference electrode. Scanning electron microscope (SEM) images were obtained on a Hitachi S-3400N field scanning electron microscope (Japan).

2.3. Preparation of Super P® Li carbon paste electrode

CBE was prepared by hand-mixing Super P® Li powder and liquid paraffin oil with a ratio of 2:1 (w/w). The paste was packed into the cavity of a Teflon tube (4.5-mm diameter). An electrical contact was established via a copper rod handle. A new surface was obtained by smoothing the electrode onto a weighing paper. GE was made for comparison study following the same procedure except for using graphite powder instead of Super P® Li powder. Before use, The freshly polished

GCE was pretreated by cycling the potential several times between -0.2~1.2V vs. SCE at a scan rate of 50 mV s^{-1} in 0.2 mol L^{-1} phosphate buffer solution until a steady signal was obtained.

2.4. Sample analysis

Rice wine samples produced by local wineries were randomly purchased from the local markets and kept in a refrigerator for further use. Prior to analysis, 1.0 mL wine sample was accurately mixed with 2.0 mL phosphate buffer (1 mol $L^{-1)}$ and diluted to 10 mL with 3% (v/v) propyl alcohol for further electrochemical detection. The content of sulfite in these samples was quantified by the external standard calibration method. For comparison study, titration method was used for the determination of splitting samples according to GB/T5009.34-2003, which was regarded as the standard reference method based on the release of sulfite at acid distillation in the form of bisulfite and then titrated by NaOH.

3. RESULTS AND DISCUSSION

3.1. Surface morphology of Super P® Li carbon paste electrode

The surface morphology of GE and CBE was characterized by SEM images (Figure 1).

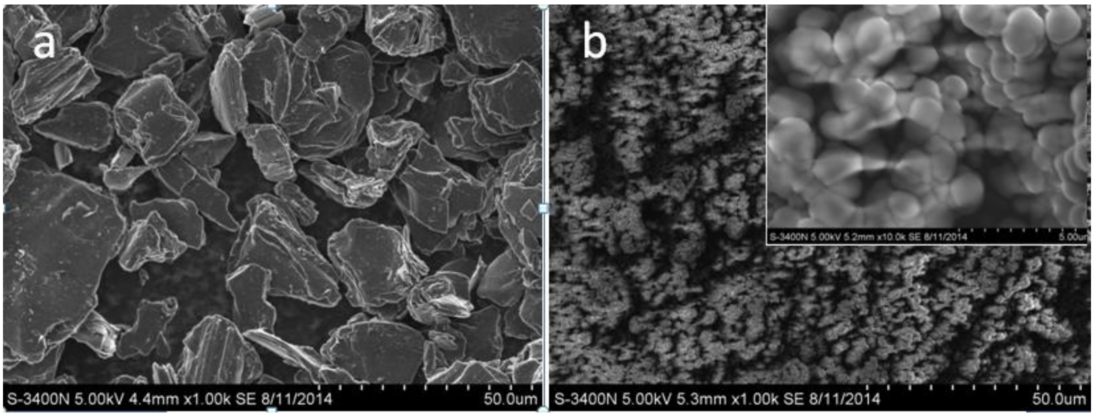

Figure 1. SEM images of GE (a) and CBE (b). (Inset of b, 10 x magnification image of CBE).

As seen, a uniform surface of both GE and CBE was observed. Compared with the rather big particle size, irregular shape and well dispersed-layered-structure of the surface of GE (Figure 1a), a compact film comprising nano-loose-porus-structured surface was observed at CBE, which made up of spherical nano-particles of carbon black as indicated in the inset of Figure 1b. It might be inferred that the nano-loose-porus-structured surface can not only improve the effective surface area of the electrode at CBE but can greatly increases the electron transfer rate.

3.2. The electrochemical response of sulfite at the CBE

The typical cyclic voltammograms of 0.2 mol L^{-1} phosphate buffer (pH 7.4) containing 1.0 mmol L^{-1} sulfite at bare glassy carbon electrode (GCE) (b), GE (a), and CBE (c) were shown in Figure 2A. As seen, only one anodic peak was shown at all the electrodes, indicating the irreversible electrochemical process of the oxidation of sulfite at these electrodes.

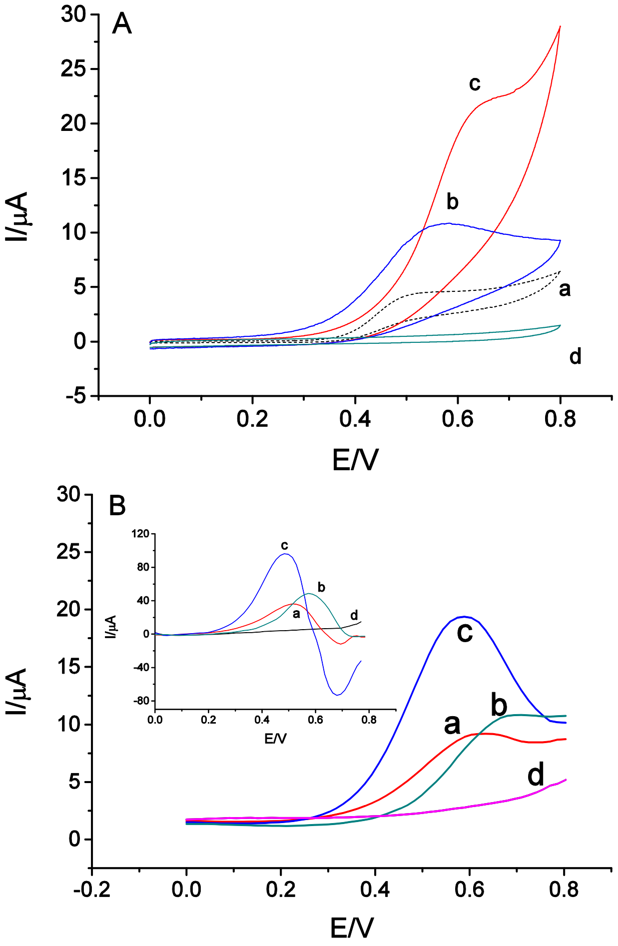

Figure 2. Voltammograms of 1.0 mmol L^{-1} sulfite at GE (a), GCE (b) and CBE (c) in 0.2 mol L^{-1} phosphate buffer (pH 7.40) with a scan rate of 50 mV s^{-1}, Curve d corresponds to the voltammogram at CBE of 0.2 mol L^{-1} phosphate buffer (pH 7.40) only. (A) Cyclic Voltammograms of the electrodes. (B) SWV behavior of the electrodes. Inset of (B) is first SWV behavior of the electrodes.

In Figure 2A-b, with the use of bare GCE, a cyclic voltammogram with one anodic peak at 0.590 V was yielded, showing a small current value around 10.0 μA. When CBE was used, a much enhanced anodic peak occurring at a little bit higher potential of 0.645 V with much higher current of 20.0 μA was observed (Figure 2A-c), which shifted positively by about 0.055 V vs GCE. Comparatively, sulfite possesses relatively lower potential of 0.527 V on the GE but with a smaller oxidation peak of 4.5 μA (Figure 2A-a), probably due to the relatively sluggish electron transfer rate at GE. Whereas the remarkably higher signal of sulfite at CBE might be due to the nanostructure of carbon black, which facilitated the electron transfer rate and thus effectively promoted the electrochemical oxidation of sulfite.

The square wave voltammetry (SWV) responses of the same 1.0 mmol L^{-1} sulfite (0.2 mol L^{-1} phosphate buffer as supporting solution, pH 7.4) at bare GCE(b),GE(a) and CBE(c) are shown in Figure 2B. As seen, an obviously narrow oxidation peak appears at CBE with a little bit lower potential of 0.60 V (Figure 2B-c), whereas, a relatively small and broad peak is observed at both GCE (Figure 2B-b) and GE (Figure 2B-a).Compared with the cyclic voltammograms, the peaks in SWV seem much narrower but the oxidation current is nearly the same. To improve the sensitivity and increase the signal to noise ratio, the method of first SWV was employed. As shown in the inset of Figure 2B, the oxidation peaks became narrower and sharper at the three electrodes through first-order derivative processing. The sensitivity was improved to a large extent nearly 4-folded at CBE for sulfite determination based on the signal of peak current. The curve d without any peak in Figure 2 presents the voltammograms at CBE of blank sample of 0.2 mol L^{-1} phosphate buffer only, further proving the oxidation peak in Figure 2 was attributed the oxidation of sulfite.

3.3. Effective electrode area determined by Chronocoulometry

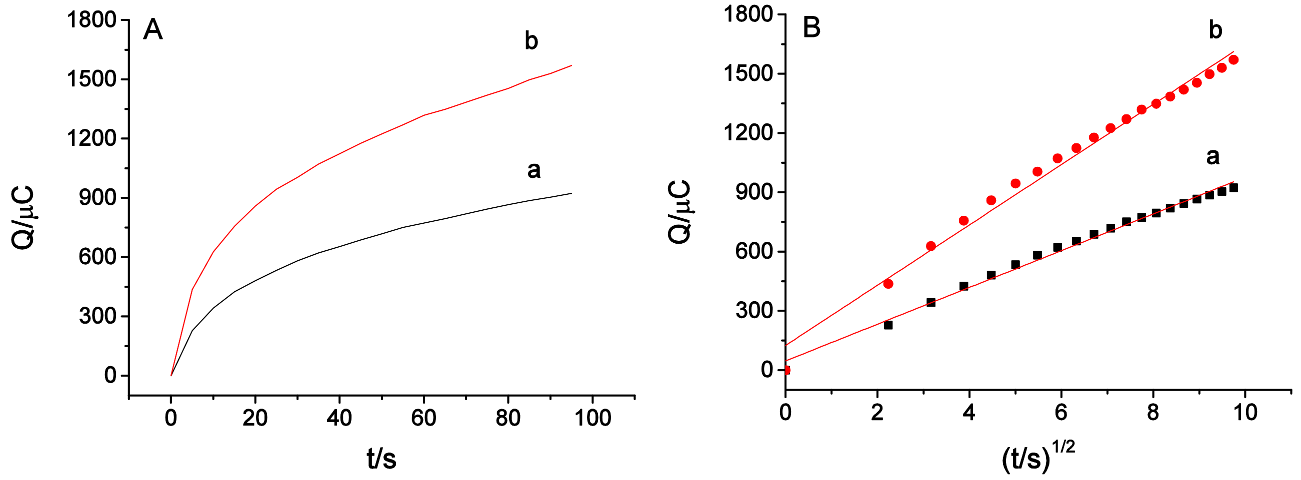

Figure 3. The chronocoulometry curves (A) at GE (a) and CBE (b) and (B) the relationship of $Q\text{-}t^{1/2}$.

Figure 3A shows the Chronocoulometry of GE (a) and CBE (b) in 0.1 mol L^{-1} KCl containing 1.0 mmol L^{-1} $[Fe(CN)_6]^{3-}$, and Figure 3B shows the relationship between the charge (Q) and the square root of time($t^{1/2}$). As seen, the plot of Q of $[Fe(CN)_6]^{3-}$ changes linearly with $t^{1/2}$ at both GE (a) and CBE (b), which can be expressed as $Q = 93.0t^{1/2}+47.18$ and $Q=152.6t^{1/2}+125.61$, respectively. According to the Anson's equation,

$$Q = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ad} \qquad (1)$$

Where c is the bulk concentration of $[Fe(CN)_6]^{3-}$, Q_{dl} is the double-layer charge, Q_{ad} is the Faradaic charge due to the oxidation of $[Fe(CN)_6]^{3-}$, D is the diffusion coefficient of $[Fe(CN)_6]^{3-}$, which is a constant of 7.6×10^{-6} cm^2 s^{-1} in the given 1.0 mmol L^{-1} $[Fe(CN)_6]^{3-}$ in 0.1 mol L^{-1} KCl solution. *A* is the surface area of working electrode, and other symbols have their usual meanings. Here n=1. Comparing of the slopes of the two electrodes with equation (1), the effective area of GE and CBE was calculated to be 0.3098 and 0.5084 cm^2 respectively, revealing that the effective area of CBE is much larger than that of GE, and showing that the formation of carbon black nanostructures on CBE can obviously increase the surface area leading to the enhancement in the current response and thus improve the sensitivity of the sensor.

3.4. Effect of scan rate

The effect of scan rate (*v*) on the oxidation of 1.0 mmol L^{-1} sulfite (0.2 mol L^{-1} phosphate buffer, pH 7.4) was investigated by linear cyclic voltammetry (LSV) with scan rate in the range of 0.05~0.90 V/s (Figure 4A). It was found that the oxidation peak current of sulfite increased linearly with the increase of square root of scan rates, following the equation of $i_p = 130.4v^{1/2}+16.82$ with a correlation coefficient (r^2) of 0.9913 (Figure 4B).

Simultaneously, peak potential shifted positively with the increase of scan rates. Such results suggested that the process of electrode reaction was controlled by diffusion. Furthermore, for the totally irreversible electrochemical process, the diffusion coefficient could be calculated base on the Randles-Sevcǐk equation

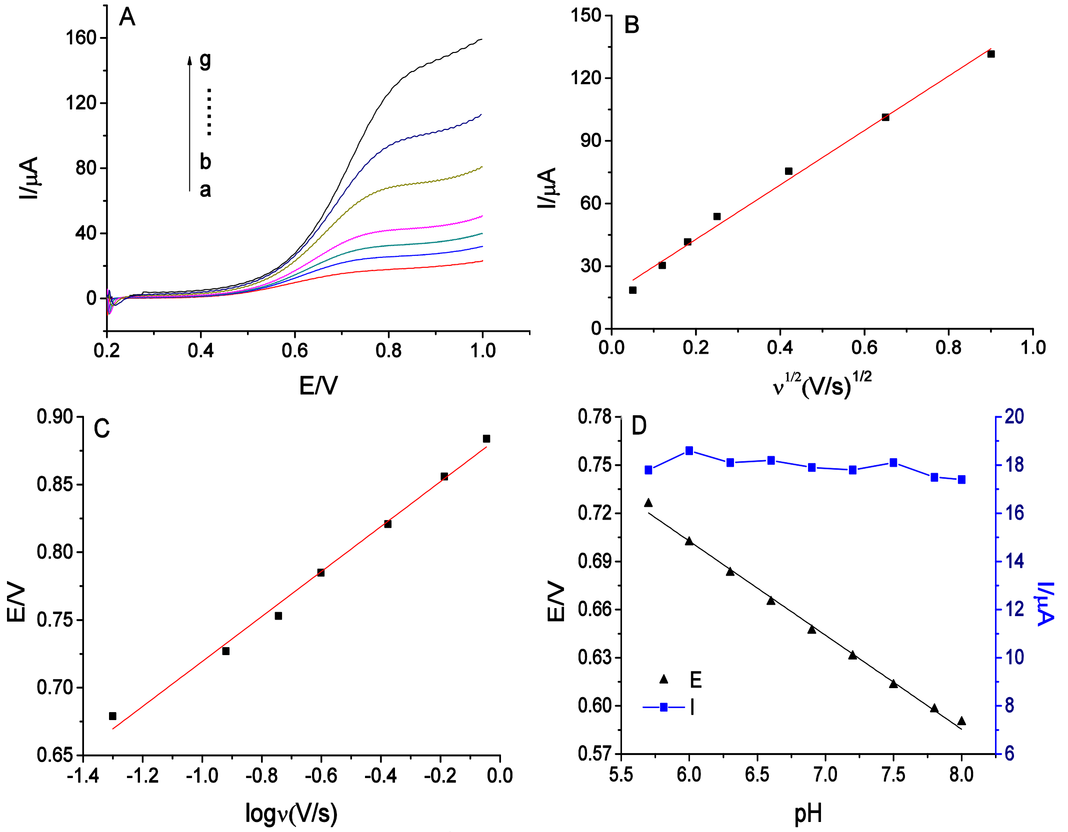

Figure 4. (A) LSV behaviors of 1.0 mmol L^{-1} sulfite at CBE at various scan rates: 0.05(a)，0.12(b), 0.18(c), 0.25(d), 0.42(e), 0.65(f), and 0.90(g) V s^{-1}, and (B) the linear dependence of the i_p vs. $v^{1/2}$ and (C)Ep vs. lgv. (D) Influence of pH on the peak potential and peak current based on cyclic Voltammograms.

$$i_p = (2.687 \times 10^5) n^{3/2} A D^{1/2} c v^{1/2} \qquad (2)$$

Where, *n* is the number of electron transferred, *D* is the diffusion coefficient of sulfite, *c* is the bulk concentration of sulfite, from the above equation (i_p=130.4$v^{1/2}$+16.82), *D* was calculated to be 1.14×10^{-7} cm^2/s.

Similarly, a linear relationship between E_{pa} and logarithm of *v* (*lgv*) was also obtained ranging from 0.05 to 0.90 V/s (Figure 4C). The equation can be expressed as: E_{pa}=0.166 lg*v*+0.8855, with r^2=0.9908. Theoretically, as for the diffusion-controlled and totally irreversible surface electrochemical reaction, the relationship between the peak potential (E_{pa}) and the scan rate *(v)* can be expressed as the equation

$$E_{pa} = E^{0'} + m(0.78 + 2.303\lg(D^{1/2} K_s^{-1}) - 1.15\lg m) + 1.15 m \lg v \quad (3)$$

With

$$m = RT/(1-\alpha)nF$$

where α is transfer coefficient, K_s is the standard rate constant of the surface reaction , *n* is electron transfer number, *v* is scan rate, $E^{0'}$ is formal redox potential, *R* is the gas constant, *T* is the absolute temperature, and *F* is the Faraday constant. According to the linear correlation of E_{pa} vs. *lgv* as mentioned above, the slope of the line (0.166) is equal to (2.3RT/n(1-α)F)/2, therefore, when n=2, α was calculated to be 0.911, which means that the reaction process is highly irreversible.

3.5. Effect of pH

The pH of phosphate buffer on the response of sulfite peak potential and peak current was investigated and the result is shown in Figure 4D. As seen, the peak potential gradually shifted negatively and a good linear relationship between E_p and pH was observed following the equation of E_p (*V*) =1.0543-0.0586pH with a relation coefficient (r^2) of 0.9949. A shift of typically 58.6 mV per pH unit is approximately close the theoretical value of 57.6 mV per pH unit. According to Nernst's equation

$$\partial E_p / \partial pH = -2.303 RTm/nF \quad (4)$$

Where *m* is transfer proton number; *n* is transfer electron number, *T* (293K) and *F*（96485 C mol^{-1}） are constant，therefore m/n=1.01≈1，indicating that the electron transfer is accompanied by an equal number of protons in the electro-oxidation of sulfite at CBE. As discussed in the above section, the electron transfer number involved in the oxidation process of sulfite is 2, thus the electro-oxidation of sulfite at CBE involved a two-electron and two-proton transfer process. The optimal pH was around 7.4 as shown in Figure 4D. At this pH, sulfite presents mainly as its free form,[14] which is more responsible for the hypersensitive reaction.

3.6. Detection limit and reproducibility

Under the optimal working conditions, the first SWV experimental parameters were employed to acquire the analytical curve for sulfite. First SWV obtained after increasing additions of the sulfite standard solution at CBE are shown in Figure 5A with the concentration ranged from 0.008 to 1.0 mmol L^{-1} in 0.2 mol L^{-1} phosphate buffers (pH 7.4).

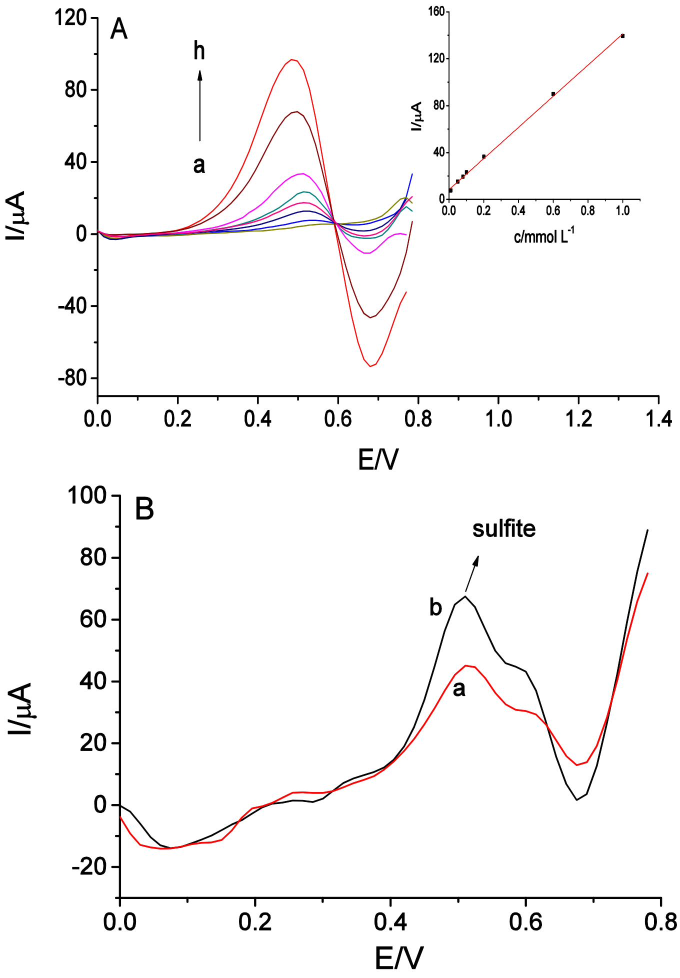

Figure 5. (A) First SWV behaviors of sulfite concentration ranging from 0.008 to 1.0 mmol L^{-1} at CBE in 0.2 mol L^{-1} phosphate solutions (pH 7.40) as electrolyte; the inset of is the calibration curve constructed by plotting current response vs. sulfite concentration. (B) Typical First SWV of commercial wine samples (a) and the corresponding spiked sample at level of 1.56 mM L^{-1} of sulfite (b) at CBE.

The inset in this figure depicted the analytical curve obtained for sulfite with the corresponding regression equation i_p (µA) = 8.309+ 132.84×10^{-3} Cso_3^{2-} (mol L^{-1}) and correlation coefficient (r^2) 0.9987. The limit of detection (LOD), based on a signal to noise ratio of three ($S/N=3$) was found to be 6.0 µM (calculated as SO_2), which was in the approximate order of magnitude compared with other electrochemical sensor based on carbon ionic liquid electrode [32], and was an order of magnitude lower than glassy carbon electrodes modified with films of Prussian Blue for the determination of sulfite in wine.[19] The LOD was also comparable with other technique such as ion chromatography [14].

The intraday repeatability of the peak current was determined by successive measurements (n=11) of a 1.0 mmol L^{-1} sulfite solution and the relative standard deviation (RSD) of 3.0% was obtained. Additionally, eleven separate CBE electrodes made parallel in the same day exhibited acceptable stable responses with RSD being less than 4.8% (n=11) in the same 1.0 mmol L^{-1} sulfite solution, showing thus the good repeatability of the electrode.

3.7. Interference Study

In order to apply the developed sensor for commercial sample analysis, the influence of various possible interferences presented in rice wine samples were tested. Interference studies were conducted by exposing CBE to 1.0 mmol L^{-1} sulfite solution in 0.2 mol L^{-1} phosphate buffer (pH 7.4) containing interferences at certain concentrations in their proper forms. The tolerance limit was defined as the amount of the foreign substance causing an error of less than ±5% of the peak current intensity reading. The comparison of first SWV obtained with the presence or absence of each interfering substance showed that at least 1000-fold of K^+, Fe^{3+}, Cu^{2+},Ca^{2+}, Na^+, Cl^- , SO_4^{2-}, and 50-fold of L-lactic acid and citric acid did not interfere with the determination of 1.0 mmol L^{-1} sulfite. In wine samples, it is particularly important to investigate the interference of polyphenolic acids, such as caffeic acid, catechuic acid, ferulic acid and chlorogenic acid, which naturally present in the raw material of wine at much low levels of concentration, but they are usually a group of serious interference for sulfite determination in wine samples in many analytical methods. In the interference test of this work, caffeic acid, as one of major constituent in many wines, was chosen as the representative polyphenolic acid, it was observed that oxidation of caffeic acid occurred at relatively lower potential at CBE surface, moreover, no interference was observed when less than 0.55 mmol L^{-1} (100 mg L^{-1}) caffeic acids coexisted and selectivity was thus improved.

3.8. Sample Analysis and Comparison with Titration Method

Five rice wine samples were randomly collected from the local markets and analyzed using the proposed method soon after purchase, at the same time, compared with a titration method using the splitting samples. To evaluate the recovery of the proposed method, wine samples spiked with sulfite at the levels of 1.56 mmol L^{-1} (100 mg L^{-1}) was detected (calculated as SO_2) simultaneously. The results showed that the content of sulfite of the samples were around 1.56 mmol L^{-1} , the recovery were between 83.5-99.4%, the relative error were in the range of -4.8~5.2%, showing no remarkably difference between the proposed method and titration method ($p>0.05$) as illustrated in Table 1. The first SWV of one selected commercial sample and its corresponding spiked sample at level of 1.56 mmol L^{-1} are shown in Figure 5B.

Table 1. Comparison of the proposed method with the reference method (titration method) in the determination of sulfite in rice wine samples and their fortification samples

Sample	Fortification level (mM L^{-1})	Proposed method (mM L^{-1})	Titration method (mM L^{-1})	Relative error (%)	Recovery (%)	RSD of the proposed method (%) (n=3)
1	/	1.84	1.75	5.2	/	3.6
	1.56	3.22	3.21	0.5	88.4	1.1
2	/	1.98	2.00	-1.6	/	1.6
	1.56	3.53	3.62	2.4	99.4	1.2
3	/	1.47	1.55	-5	/	4.9
	1.56	2.78	2.91	-4.8	83.5	3.3
4	/	1.34	1.40	-4.5	/	0.9
	1.56	2.74	2.85	-3.7	90.0	1.6
5	/	1.58	1.65	-4.1	/	2.5
	1.56	3.04	3.15	-2.5	92.9	1.4

4. CONCLUSIONS

A simple and highly sensitive electrochemical sensor for sulfite determination was fabricated based on carbon black paste electrode. The oxidation peak current of sulfite was significantly increased compared with bare GCE and GE due to the good conductivity and high surface area to volume ratio of carbon black powder. First SWV was proved to be a sensitive analytical method for the quantification of sulfite. The proposed method was accurate, reproducible and sensitive enough for sulfite determination in commercial rice wine samples, and has no remarkable difference ($p>0.05$) compared with the titration method.

ACKNOWLEDGEMENTS

Financial supports from Public Project of Zhejiang Province (2014C37083), Food science and engineering- the most important discipline of Zhejiang province (JYTsp20141061) are gratefully acknowledged.

References

1. R. Eschenbruch, *American journal of Enology and Viticulture*, 25 (1974) 157-161.
2. W. Dott, H.G. Trüper, *Archives of Microbiology*, 108 (1976) 99-104.
3. A.W. Burgstahler, M.A. Robinson, *Fluoride*, 30 (1997) 142-146.
4. H. Li, A. Guo, H. Wang, *Food chemistry*, 108 (2008) 1-13.
5. O. Makhotkina, P.A. Kilmartin, *Journal of agricultural and food chemistry*, 61 (2013) 5573-5581.
6. C. Rice-Evans, N. Miller, G. Paganga, *Trends in plant science*, 2 (1997) 152-159.
7. M. Lopez-Velez, F. Martinez-Martinez, C.D. Valle-Ribes, *Crit. Rev. Food Sci. Nutr.*, 43 (2003) 233.
8. H. Vally, A. Carr, J. El-Saleh, P. Thompson, *Journal of allergy and clinical immunology*, 103 (1999)

41-46.
9. H. Vally, P. Thompson, *Thorax*, 56 (2001) 763-769.
10. A. Armentia, *Current opinion in allergy and clinical immunology*, 8 (2008) 266-269.
11. M.V. Navarrro, M.R. Payán, M.A.B. López, R. Fernández-Torres, M.C. Mochón, *Talanta*, 82 (2010) 2003-2006.
12. D. Lowinsohn, M. Bertotti, *Food Additives & Contaminants*, 18 (2001) 773-777.
13. P. Stratil, V. Kuban, J. Fojtova, *Czech Journal of Food Sciences*, 26 (2008) 242-253.
14. M. Koch, R. Köppen, D. Siegel, A. Witt, I. Nehls, *Journal of agricultural and food chemistry*, 58 (2010) 9463-9467.
15. M. Masár, M. Danková, E. Ölvecká, A. Stachurová, D. Kaniansky, B. Stanislawski, *Journal of Chromatography A*, 1026 (2004) 31-39.
16. A. Isaac, J. Davis, C. Livingstone, A.J. Wain, R.G. Compton, *TrAC Trends in Analytical Chemistry*, 25 (2006) 589-598.
17. C.S. Pundir, R. Rawal, *Analytical and bioanalytical chemistry*, 405 (2013) 3049-3062.
18. K. Scott, W. Taama, *Electrochimica acta,* 44 (1999) 3421-3427.
19. T. García, E. Casero, E. Lorenzo, F. Pariente, *Sensors and Actuators B: Chemical,* 106 (2005) 803-809.
20. T.R. Dadamos, M.F. Teixeira, *Electrochimica Acta*, 54 (2009) 4552-4558.
21. K. Kalcher, J.M. Kauffmann, J. Wang, I. Švancara, K. Vytřas, C. Neuhold, Z. Yang, *Electroanalysis*, 7 (1995) 5-22.
22. H. Zhou, W. Yang, C. Sun, *Talanta*, 77 (2008) 366-371.
23. L.S.T. Alamo, T. Tangkuaram, S. Satienperakul, *Talanta*, 81 (2010) 1793-1799.
24. X.-R. Li, J. Liu, F.-Y. Kong, X.-C. Liu, J.-J. Xu, H.-Y. Chen, *Electrochemistry Communications*, 20 (2012) 109-112.
25. J. Wang, *Electroanalysis*, 17 (2005) 7-14.
26. Y. Shao, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y. Lin, *Electroanalysis*, 22 (2010) 1027-1036.
27. R. Alcántara, J.M. Jiménez-Mateos, P. Lavela, J.L. Tirado, *Electrochemistry Communications*, 3 (2001) 639-642.
28. A. Pandolfo, A. Hollenkamp, *Journal of power sources*, 157 (2006) 11-27.
29. W. Yazhen, Q. Hongxin, H. Siqian, X. Junhui, *Sensors and Actuators B: Chemical*, 147 (2010) 587-592.
30. L. Wang, L. Xu, *Journal of agricultural and food chemistry*, 62 (2014) 10248-10253.
31. L.M. de Carvalho, G. Schwedt, *Fresenius' journal of analytical chemistry*, 368 (2000) 208-213.
32. A. Safavi, N. Maleki, S. Momeni, F. Tajabadi, *Analytica chimica acta*, 625 (2008) 8-12.

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