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Electrochemical reduction of C.I. Acid Red 18 on multi-walled carbon nanotubes and its analytical application

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ABSTRACT

The electrochemical reduction of C.I. Acid Red 18 on the surface of multi-walled carbon nanotube-modified glassy carbon electrode was investigated using cyclic voltammetry. A novel, simple, sensitive and inexpensive method for determination of C.I. Acid Red 18 in soft drinks was proposed and the accuracy and reproducibility of this determination method were evaluated. The method was satisfactorily applied for the determination of C.I. Acid Red 18 in soft drinks in the concentration range 3.30×10^{-7}–1.24×10^{-4} M, with a detection limit of 1.65×10^{-7} M.

1. Introduction

C.I. Acid Red 18 (E-124, C.I. 16255) is a synthetic azo food dye that is routinely found in many common food products such as beverages, sweets, dairy produce and bakery products. As the genetic toxicity of some azo dyes has been confirmed [1,2], accurate and reliable methods for the determination of azo dyes in foods are required. Although spectrophotometry [3–6], adsorptive voltammetry [7,8], reversed-phase liquid chromatography (RPLC) [9–11], ion-pair RPLC [12] and capillary electrophoresis [13–18] have been used for the determination of various water-soluble synthetic dyes, many of these methods are time-consuming.

Since carbon nanotubes (CNTs) were discovered in 1991, CNTs have attracted much research attention. The modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) has been shown to result in enhanced sensitivity, electron-transfer promotion, increased resistance to surface fouling and reduction of over-potential. It has been reported that CNT modified electrodes can be successfully applied in the determination of many organic molecules [19–25].

To the best of our knowledge, the voltammetric determination of C.I. Acid Red 18 using an MWCNT modified glassy carbon electrode (GCE) has not hitherto been reported. This paper concerns the electrochemical reduction of C.I. Acid Red 18 at the surface of a multi-walled carbon nanotube-modified glassy carbon electrode and the development of a simple, rapid and effective cyclic voltammetric (CV) method for the determination of C.I. Acid Red 18 in soft drinks.

2. Experimental

2.1. Chemicals

C.I. Acid Red 18 (E-124, C.I. 16255), C.I. Acid Yellow 23 (E-102, C.I. 19140), C.I. Acid Red 27 (E-123, C.I. 16185), C.I. Food Yellow 3 (E-110, C.I. 15985), C.I. Acid Blue 74 (E-132, C. I. 73015), C.I. Acid Red 51 (E-127, C.I. 45430), and C.I. Acid Blue 9 (E-133, C.I. 42090) were purchased from National Research Center for CRMS (Beijing, China). The purity of C.I. Acid Red 18 was determined by means of melting point, UV–visible, infrared spectra and HPLC: no impurities were found. A 0.0100 M aq solution of C.I. Acid Red 18 was prepared using double-distilled water. The impurities of other dyes were not examined. MWCNTs were purchased from Shenzhen Nanotechnology Port Co. Ltd. (China). 0.2–2.0 g L^{-1} solutions of MWCNTs was prepared in *N*, *N*-dimethylformamide. All other reagents were of analytical grade. 0.1 M phosphate buffer solution was prepared by dissolving 0.1 mol NaCl and 0.1 mol Na_2HPO_4 in 1 L of double-distilled water and adjusting the pH using 6 M aq HCl or 1 M NaOH solution.

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2.2. Instrumentation

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of three electrodes, a 3 mm diameter glassy carbon disc electrode and MWCNT composite modified GCE were used as working electrode, a platinum wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode.

2.3. Preparation of MWCNTs and modified GCE

The MWCNTs were purified in boiling concentrated nitric acid for 4 h, followed by rinsing with deionized water and drying under ambient atmosphere. Open-end MWCNTs with hydrophilic surface were thus obtained. Before modification, the GCE was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water, and then sonicated in ethanol and doubly distilled water for 10 min, sequentially. The modifier suspension was prepared by dispersing the MWCNTs in 5.0 mL of *N*,*N*-dimethylformamide under sonication for 30 min. The MWCNT modified GCE was prepared by casting 5 μL of the mentioned above black suspension on the GCE surface using a micropipette and left to dry at room temperature. Before the voltammetric measurements, the modified electrode was cycled between −1 and 1 V (scan rate 100 mV s^{-1}) in 0.1 M phosphate buffer solution for several times until acquiring the reproducible responses.

3. Results and discussion

3.1. Electrochemical behavior of C.I. Acid Red 18 at MWCNT/GCE and selected buffer solution

The electrochemical response of C.I. Acid Red 18 at bare GCE and MWCNT/GC electrode in purged N_2 0.1 M phosphate buffer solution of pH 8.3 is shown in Fig. 1. It could be seen that the reduction peak for the C.I. Acid Red 18 at bare GCE and MWCNT/GCE were observed at −0.812 V and −0.670 V, respectively, the reduction potential of C.I. Acid Red 18 at MWCNT/GC electrode shifted to positive potentials, and the peak current increased.

These results indicated that the MWCNT modified electrode promoted the electrochemical reduction of C.I. Acid Red 18 by considerably accelerating the rate of electron transfer. Purified MWCNTs are functionalized with −OH and −COOH, which could interact with hydroxyl and sulfonyl in C.I. Acid Red 18 to form hydrogen bond. The π−π conjugated bonds between MWCNTs and the C.I. Acid Red 18 probable increase reduction current. The MWCNT interface has a large surface area, a great deal of active sites, better conductivity and favorable electrocatalytic power, all of them led to the dissimilar conjugation effect of C.I. Acid Red 18 with the bare electrode interface.

The similar electrochemical behavior for C.I. Acid Red 18 in acetate buffer or Britton–Robinson buffer (pH 8.3) was observed. However, the background current of MWCNT/GC electrode in acetate buffer or Britton–Robinson buffer was great. Therefore, 0.1 M phosphate buffer solution of pH 8.3 was selected.

3.2. Amount of the modifier

The reduction current for C.I. Acid Red 18 at modified electrode can be affected by the amount of MWCNTs on the electrode surface. This can be controlled by using the same volume (5 μL) of the suspensions with the different concentrations of MWCNTs, casted on the surface of GCE. The experiments showed that the reduction peak current for 9.00×10^{-5} M C.I. Acid Red 18 increased quickly by increasing the concentration of MWCNT suspension deposited on the surface of GCE up to 0.8 g L^{-1} (from 0.00 to 0.80 g L^{-1}). Further increase, caused a gradual decrease in the cathodic peak current of C.I. Acid Red 18 with increase in background current. As a result, 5 μL of 0.8 g L^{-1} MWCNT suspension was selected as optimum volume for preparation of the modified electrode.

3.3. Influence of pH

The influence of pH on the electrochemical behavior of C.I. Acid Red 18 was investigated at different pH values in the range of 2.0–10.0. Fig. 2 shows the CVs of 9.00×10^{-5} M C.I. Acid Red 18 on the surface of the modified electrode over the discussed pH range at the scan rates of 100 mV s^{-1}. It was found that the peak potential shifted negatively with pH increasing and a good linear relationship was observed between the *E* and pH values in the range of 2.0–10.0

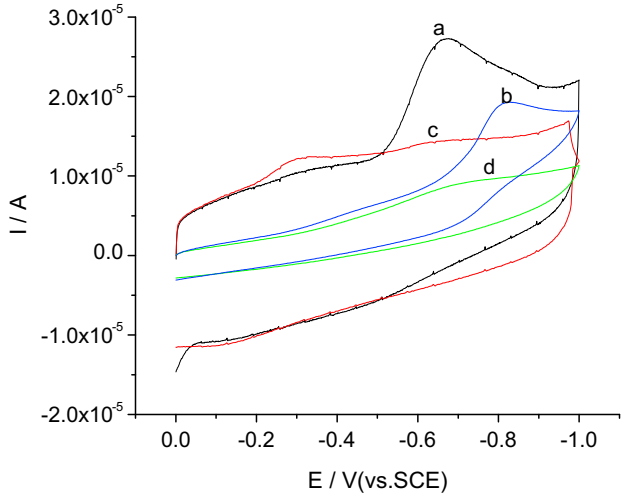

Fig. 1. CVs of 9.00×10^{-5} M C.I. Acid Red 18 at MWCNT/GCE (a) and bare GCE (b); CVs of MWCNT/GCE (c) and bare GCE (d). Scan rate: 100 mV s^{-1}; supporting electrolyte: 0.1 M phosphate buffer with pH 8.3; accumulation volume of 0.8 g L^{-1} MWCNT suspension: 5 μL.

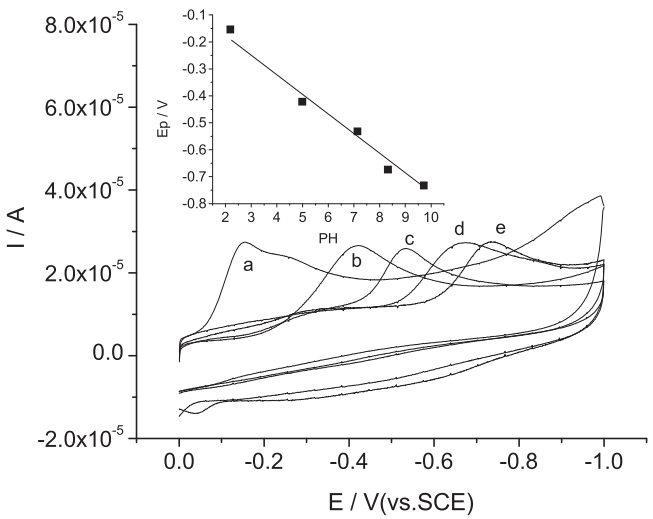

Fig. 2. Influence of pH on the shape of cathodic peak of 9.00×10^{-5} M C.I. Acid Red 18. pH: 2.0 (a), 5.0 (b), 7.0 (c), 8.3(d) and 10.0 (e). Inset: plot of the peak potential against pH. Scan rate: 100 mV s^{-1}; accumulation volume of 0.8 g L^{-1} MWCNT suspension: 5 μL.

with the following equation: $E\,(\mathrm{mV}) = -67.14\,\mathrm{pH} - 3.78 \times 10^{-3}$ (R: correlation coefficient; $R = 0.9926$). A value of about −67.14 mV per pH unit clearly indicates that equal numbers of electrons and protons are involved in the electro-reduction of C.I. Acid Red 18 on the surface of the modified electrode. On the other hand, the peak current showed to be increased by the pH from 10.0 to 2.0. In order to avoid the oxygen influence on the reduction of C.I. Acid Red 18, the phosphate buffer solution of pH 8.3 was used as supporting electrolyte in all voltammetric determinations.

3.4. Effect of potential scan rate

The information involving electrochemical mechanism usually can be obtained from the investigation of CVs in the different potential sweep rates. Therefore, the CV investigations for 9.00×10^{-5} M C.I. Acid Red 18 were performed on the surface of the MWCNT/GCE in buffered solution of pH 8.3 at different potential sweep rates. Fig. 3 illustrates the influence of scan rate on the CVs of C.I. Acid Red 18 in the range of 10–250 mV s^{-1}.

The linear relation between the peak current (I) and square root of scan rates ($\nu^{1/2}$) in the range of 10–100 mV s^{-1}(Fig. 3 inset Fig.) indicating a diffusion controlled process on the surface of the modified electrode. The regression equation for this relationship was given as $I = 1.3236\nu^{1/2} + 0.5287$ ($R = 0.9999$, I: μA, ν: mV s^{-1}).

The relationship between the reduction peak potential and scan rate showed that the reduction peak potential shifts negatively with increasing scan rate. There was a linear relationship between E and the logarithm of the scan rate (Fig. 4).

The regression equation for this relationship was obtained as $E = -0.0948 \log \nu - 0.7657$ ($R = 0.9940$, E: V; ν: V s^{-1}). Such a behavior revealed the irreversible nature of the electrochemical process for the C.I. Acid Red 18. As for an irreversible electrode process, E_p is given by the following equation [26,27]:

$$E_p = E^{o'} + \frac{2.303RT}{\alpha nF}\log\frac{RTk_s^o}{\alpha nF} - \frac{2.303RT}{\alpha nF}\log\upsilon$$

where α is the transfer coefficient, k^o is the standard heterogeneous rate constant of the reaction, n is the number of electrons, υ is the scan rate and $E^{o\prime}$ is the formal redox potential. Thus the value of αn

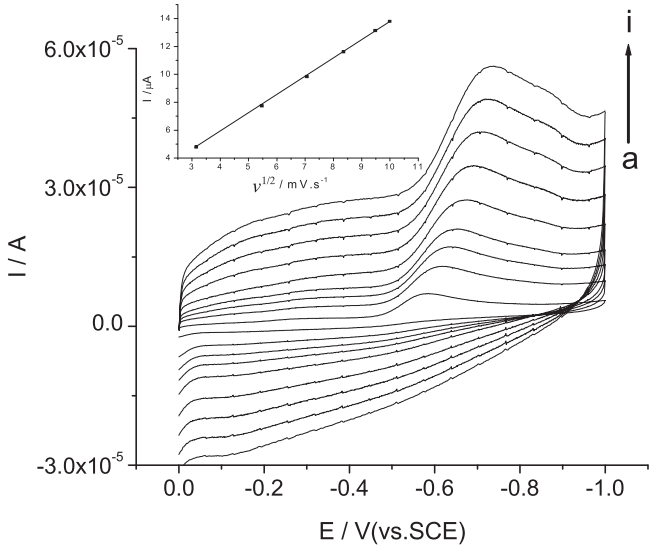

Fig. 3. CVs of 9.00×10^{-5} M C.I. Acid Red 18 at MWCNT/GCE with different scan rates. (a)–(i) was 10, 30, 50, 70, 90, 110, 150, 200 and 250 mV s^{-1}, respectively. Inset Fig.: plot of the peak current against square root of scan rates. Other conditions are as in Fig. 1.

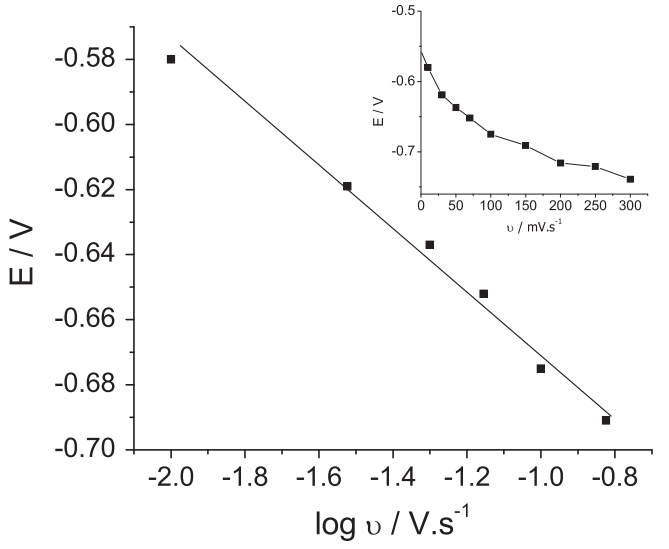

Fig. 4. Dependence of the reduction peak potential of 9.00×10^{-5} M C.I. Acid Red 18 on the logarithm of scan rates. Inset: plot of the peak potential against scan rates.

can be easily calculated. The αn was calculated to be 0.6238. According to Bard and Faulkner [28], α can be obtained as

$$\alpha = \frac{47.7}{|E_p - E_{p/2}|}\,\mathrm{mV}$$

where $E_{p/2}$ is the potential where the current is at half the peak value. The α is calculated to be 0.5889. Furthermore, the number of electron (n) transferred in the electro-reduction of C.I. Acid Red 18 was calculated to be 1.10 ± 0.10. The value of $E^{o'}$ could be obtained from the intercept of E_p vs. υ curve by extrapolating to the vertical axis at $\upsilon = 0$. The intercept for E_p vs. log υ plot was −0.7657 and $E^{o'}$ was obtained to be −0.5588 V, thus k^o was calculated to be 0.16 s^{-1}.

It is generally admitted that azo molecules are reduced at the mercury drop in two steps [29]:

Step 1: R–N = N–R′ + $2e^-$ + $2H^+$ = R–NH–NH–R′,
Step 2: R–NH–NH–R′ + $2e^-$ + $2H^+$ = $R–NH_2$ + R′–NH_2.

When the pH value is below 3, steps 1 and 2 occur simultaneously, while for media close to neutrality, the second step does not occur. Consequently, reduction potentials and intensities are strongly influenced by the media pH.

Taking into account that the C.I. Acid Red 18 contains N=N group, which presents a basic center of electron and proton acceptor. So, we may assume that the reduction step of C.I. Acid Red 18 is located on the N=N group. The C.I. Acid Red 18 accepts a proton and an electron to form a free radical, and the free radical rapidly accept another proton and an electron. The mechanism is shown in Fig. 5.

3.5. Linearity range and the detection limit

The relationship between the reduction peak current and the concentration of C.I. Acid Red 18 was examined by CV on the surface of MWCNT/GCE (Fig. 6). Under the previous mentioned optimum conditions, the reduction peak currents were proportional to the C.I. Acid Red 18 concentrations over two intervals in the range of 3.30×10^{-7} to 1.24×10^{-4} M in 0.1 M phosphate buffer solution of pH 8.3. The linear regression equation was obtained as $c\,(\times 10^{-6}\,\mathrm{M}) = 6.800\,\mathrm{I}\,(\mu\mathrm{A})\text{-}14.872$ ($R = 0.9985$). The detection limit

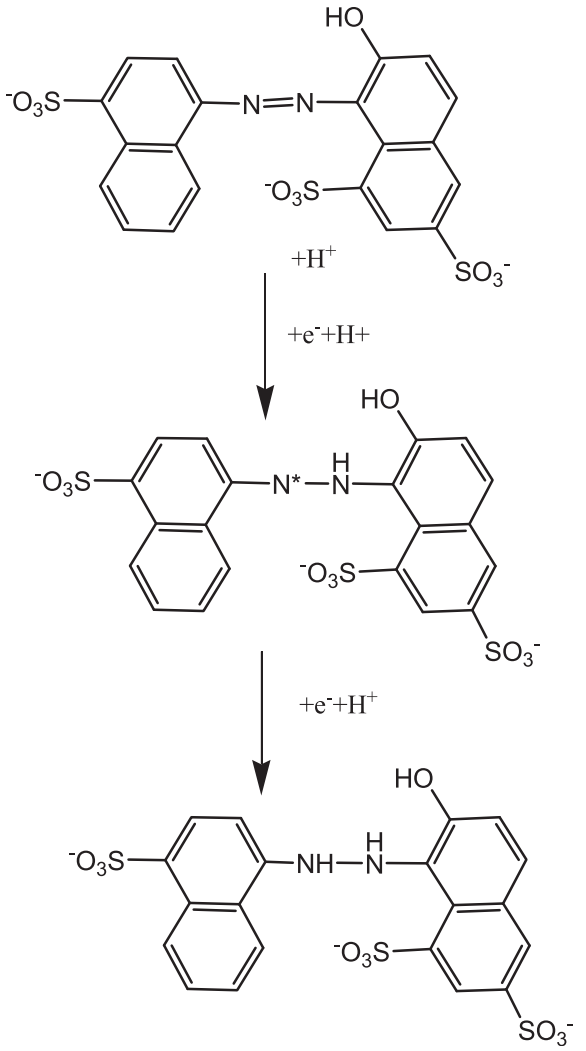

Fig. 5. Mechanism for the electrochemical reduction of C.I. Acid Red 18.

(3σ/slope, where σ is the standard deviation of the intercept and s is the slope of the calibration curve) observed for the C.I. Acid Red 18 was 1.65×10^{-7} M.

3.6. Repeatability of the modified electrode

The repeatability of the modified electrode was investigated by repetitive recording at a fixed C.I. Acid Red 18 concentration of 9.00×10^{-5} M. The relative standard deviation (RSD) for the peak currents in CVs based on 6 replicates was 1.3%, indicating excellent repeatability of the response of the modified electrode. Also, on using the MWCNT/GCE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 97.3% of its initial peak current response for a C.I. Acid Red 18 concentration of 9.00×10^{-5} M. The results indicate that the modified electrode has an excellent repeatability.

3.7. Interference

The influence of some organic compounds was tested. If the presence of an interferent altered the average current signal of 9.00×10^{-5} M C.I. Acid Red 18 concentration by less than ±5% we considered that caused no interference. The reduction of dyes is related to both electrode and supporting electrolyte. The peak of sodium saccharin in 0.1 M KCl–0.1 M NaOH solution is found at −1.864 V (vs. SCE) by the second derivative linear scanning voltammetry [30], and the reduction peaks of C.I. Acid Red 51 and C.I. Acid Blue 9 at the hanging mercury electrode in acetate buffer of pH 9.0 are observed at about −0.96 and −1.17 V, respectively (vs. Ag/AgCl/3 M KCl) [31], while the reduction peaks of saccharin sodium, C.I. Acid Red 51 and C.I. Acid Blue 9 at MWCNT/GC electrode in the phosphate buffer solution of pH 8.3 were not found. The reduction peak of dye C.I. Acid Red 27 at Pt electrode in Britton–Robinson buffers of pH 7.9 is about −0.989 V (vs. Ag/AgCl/3 M KCl) [32], while the reduction peak of C.I. Acid Red 27 at MWCNT/GC electrode in the phosphate buffer solution of pH 8.3 was observed at −0.82 V in this work. The reduction peaks of C.I. Acid Yellow 23 and C.I. Food Yellow 3 closed to that of C.I. Acid Red 18. The results showed that 100-fold of glucose, cane sugar, saccharin sodium, 50-fold of ascorbic acid, and dye C.I. Acid Blue 74, C.I. Acid Red 27, C.I. Acid Blue

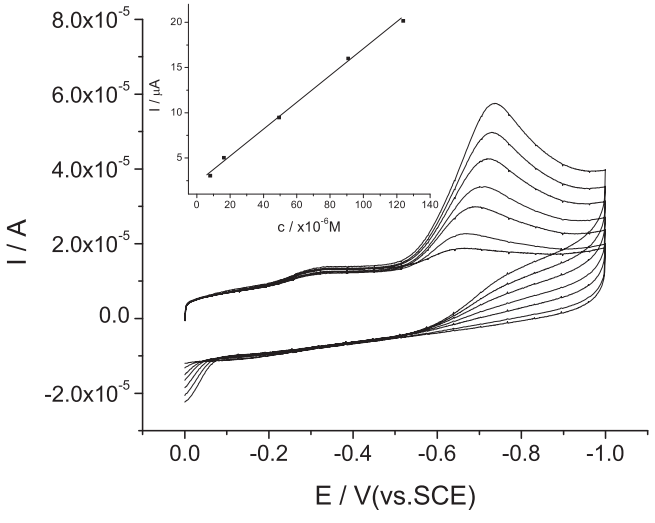

Fig. 6. CVs of different concentrations of C.I. Acid Red 18 at MWCNT/GCE. Inset: plot of the peak current against the concentration. Other conditions are as in Fig. 1.

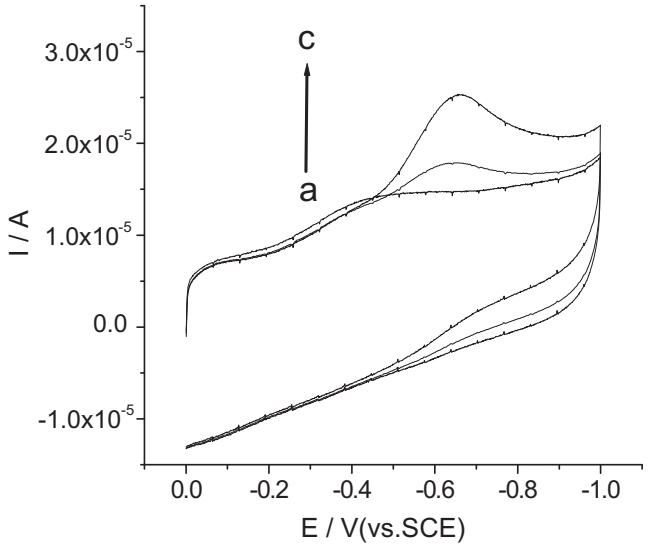

Fig. 7. CVs of soft drink and added standard samples. Sample (a), sample + 3.00×10^{-5} M C.I. Acid Red 18 (b) and sample + 9.00×10^{-5} M C.I. Acid Red 18 (c) at MWCNT/GCE. Other conditions are as in Fig. 1.

Table 1
Comparative study for C.I. Acid Red 18 in soft drink by the proposed and literature method.

No.	Sample[a] ($\times 10^{-6}$ M) This method	RSD%[a]	Added ($\times 10^{-6}$ M)	Found[a] ($\times 10^{-6}$ M)	Recovery (%)	Sample[a] ($\times 10^{-6}$M) HPLC method [33]
1	0.00	0.0	30.00	29.02	96.7	0.00
2	9.25	4.0	40.00	49.56	100.8	8.60
3	27.56	3.1	50.00	75.81	96.5	28.62
4	29.94	2.7	60.00	91.97	103.4	28.28

[a] Average of six replicate measurements.

9 and C.I. Acid Red 51 did not interfere on the determination, while the dye C.I. Acid Yellow 23 and C.I. Food Yellow 3 interfered severely. This suggests the modified electrode had certain resistance to some interferences.

3.8. Application

The MWCNT/GCE was used to determination of the content of C.I. Acid Red 18 in soft drinks by applying CV method. The comparison between the present biosensor and reliable high performance liquid chromatography (HPLC) [33] was also carried out. 2.00 mL of soft drink was diluted to 5.0 mL with 0.1 M phosphate buffer solution of pH 8.3. The CVs of sample and added standard samples are shown in Fig. 7.

The determination results using the standard addition method are shown in Table 1. It could be seen that the results measured by the present biosensor showed a good agreement with those measured by HPLC method. The recoveries were in the range from 96.5 to 103.4%. Using this standard addition method, the content for the C.I. Acid Red 18 in soft drinks was obtained to be 0.00–3.00 $\times$ 10^{-5} M with RSD of 0.0–4.0% ($n = 6$).

The determination results obtained by the developed electrochemical method and HPLC method were statistically evaluated by *F*-test and paired *t*-test. The *F* value is calculated as

$$F = \frac{s_2^2}{s_1^2}$$

s is the standard deviation, the values of s_2 for this method and s_1 for HPLC method were 0.76 and 0.52 $\times$ 10^{-6} M, respectively. (Determine number of 5.00 $\times$ 10^{-5} M C.I. Acid Red 18 is 10.) *F* value was calculated to be 2.14, which is less than 3.18($t_{0.95,\,9}$, from *F* value Table).

The *t* value of paired *t*-test is calculated as

$$t = \frac{\overline{X}}{SD} \times \sqrt{N}$$

where *SD* is standard deviation of the differences for the content of paired samples, $\overline{X}$ is the mean value of the differences, and *N* is the determine number of sample pairs. The *t* value calculated from datum in Table 1 was 0.55, which is less than 3.18($t_{0.95,3}$, from *t* value Table).

The *F*-test and paired *t*-test indicated there was no significance between this method and HPLC method.

4. Conclusions

In present work, it was demonstrated that modification of GCE with MWCNTs is a simple and effective method for the determination of C.I. Acid Red 18 in soft drinks. The procedure enables preparation of highly stable and reproducible uniform modifier film, which leads to a considerable enhancement in repeatability and reproducibility in the voltammetric measurements. High sensitivity and improved detection limit of the MWCNT/GCE are promising for the determination of trace amounts of C.I. Acid Red 18 in soft drinks.

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