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The Determination of Riboflavin (Vitamin B_2) Using Manganese Dioxide Modified Glassy Carbon Electrode by Differential Pulse Voltammetry

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A manganese dioxide modified glassy carbon electrode (MnO_2/GCE) was prepared by coating method and used for the determination of riboflavin (VB_2) by differential pulse voltammetry (DPV). The influence of activation, amount of MnO_2, buffer type, buffer pH and concentration on the peak current of VB_2 was investigated, and the experimental results revealed that the DPV peak current of VB_2 shows a linear relationship with its concentration in the range of 2.0×10^{-6} – 1.1×10^{-4} mol L^{-1} with a correlation coefficient of 0.9991. For 1.0×10^{-5} mol L^{-1} vitamin B_2, the RSD is 1.7 % (n=10), and the detection limit is 2.7×10^{-8} mol L^{-1}. The method reveals the excellence of simple, sensitive, good repeatability and anti-interference. It has been applied to the determination of VB_2 in tablet and satisfactory results obtained.

Keywords: Vitamin B_2; differential pulse voltammetry; MnO_2/GCE; determination

1. INTRODUCTION

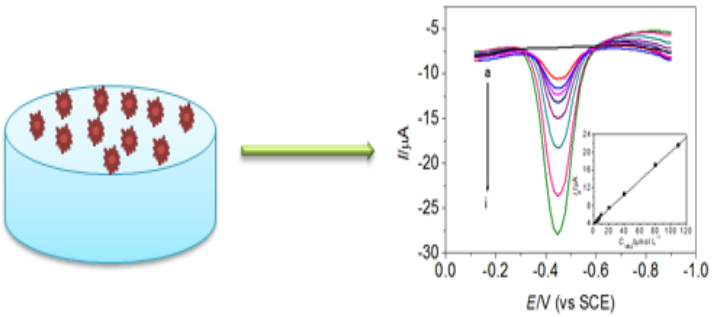
Vitamins B_2 (VB_2) is an organic compound and necessary for the normal organism oxidation and metabolism in the human body [1]. Inadequate intake of VB_2 can have an obvious negative effect on health, and result in serious diseases such as beriberi, microcytic hypochromic anemia, and pellagra or even death [2]. It also has some pharmaceutical values such as antioxidant [3], anti-inflammatory [4], and analgesic [5]. Small quantities of VB_2 required in human diet, but VB_2 cannot be synthesized by the human body and cannot be stored in internal, it must be provided and supplemented by all

kinds of food, such as animal tissues and organs, eggs, milk, green leafy vegetables, beans, and so on [6]. Consequently, it is of great significance to develop a simple, sensitive, reliable and effective quantitative analysis method for VB_2.

Several methods have been reported for the determination of VB_2, including fluorescence [7–10], chemiluminescent [11,12], capillary electrophoresis [13], HPLC [14,15], and LC- MS [16,17]. These methods can be used for the determination of VB_2 in a variety of samples, but they are generally complex, time-consuming, and expensive instruments. Electrochemical methods are becoming increasingly important for quantitative determination of VB_2 owing to their simple, sensitive, cheap instrumentation fast response and online detection ability [18–26].

Manganese dioxide (MnO_2) is another promising electrode material because of its low price, relatively environmentally friendly performance, and distinctive properties. It is a momentous metal oxide and has extensive applications in catalysis, molecular adsorption, biosensor, and energy storage [18,27–30], and has been applied to accelerate direct electron transfer between immobilized or adsorbed some substances and modified electrodes, and attract many interest of researchers [18,28–31]. However, it has intrinsic barrier and hinder the direct electron transfer, result in active centers of many biological molecules are deeply buried [28]. A variety of methods have been established for electron transfer between the biological molecule and the electrode [28,31].

In this work, the MnO_2/GCE was prepared by dropping method and used for the determination of VB_2. On the basis of the voltammetric behavior, a new sensitive, reliable and fast method is proposed by using differential pulse voltammetry (DPV) for the determination of VB_2 in the routine and ultra-trace analysis (Scheme 1).



Scheme 1. The determination diagram of VB_2 at MnO_2/GCE by DPV.

2. EXPERIMENTAL

2.1. Chemicals and instrumentation

The electrochemical experiment was carried out on an electrochemical workstation of LK2005 Electrochemical Workstation (Tianjin Lan Le Croy Chemical Electronic High-Tech Co., Ltd.) instrument. A conventional three-electrode system was applied to the determination of VB_2, including a MnO_2 modified or a bare GCE (ϕ=3 mm) working electrode, a saturated calomel reference electrode (SCE, 217), and a platinum wire counter electrode (ϕ=0.5 mm), respectively. All the pH values were performed using a pH meter (pHS-3C, Shanghai, P.R. China).

All reagents used were analytical grade and no further purification (Shanghai Chemicals Co., Ltd., P.R. China). Phosphate buffer solution (PBS) was prepared with NaH_2PO_4-Na_2PO_4. All aqueous solutions were prepared using double deionized water. VB_2 (1000 mg L^{-1}) stock standard solution was prepared daily and kept at 4 °C.

2.2. Preparation of MnO_2

Potassium permanganate and manganese sulfate are dissolved and mixed with a molar ratio of 1:1.5, stirred and let stand for 30 min. Manganese dioxide precipitation and water were obtained after reaction, and then a sufficient amount of sodium sulfite solution was added until purple disappear and shows gray and black. The reaction is indicated by equation (1). The reaction mixture was filtered, and the production rinsed several times using a low concentration of sodium sulfate and then using water [32]. The production was dried at 110 ° C, and crushed using a mortar for further use.

$$3MnSO_4 + 2\ KMnO_4 + 2\ H_2O = 5\ MnO_2\downarrow + 2\ K_2SO_4 + 2\ H_2SO_4 \qquad (1)$$

2.3. Preparation of MnO_2/GCE

Before modification, the bare GCE was polished with 0.05 μm alumina slurry, rinsed with double deionized water, then sonicated with nitric acid (1:1), ethanol, and double deionized water for 5 min, respectively. The bare GCE was activated using 0.5 mol L^{-1} sulfuric acid solution at the scan rate of 0.1 V s^{-1} by cyclic scanning for 20 cycles in the potential range from –1.0 V to 1.0 V.

3 mg of MnO_2 was added into 2 mL of N, N-dimethyl formamide (DMF), and sonicated for 30 min. Certain amount of MnO_2 and DMF dispersion was dropped onto the surface of the GCE using syringe, and carefully placed in an oven and baked for 20 min at 70 °C, then aired to room temperature. The MnO_2/GCE was scanned for 20 circles by CV between –0.9 and –0.1 V in 0.1 mol L^{-1} pH 6.5 PBS until a stable cyclic voltammetric background was chalked up for further use.

2.4. Procedure

10 mL of PBS and certain volume of VB_2 stock standard solution were added into the electrolytic cell, and the concentration of VB_2 was determined using the MnO_2/GCE by DPV.

3. RESULTS AND DISCUSSION

3.1 The electrochemical behavior of VB_2

The electrochemical behavior of VB_2 was studied on a bare GCE and a MnO_2/GCE by DPV. It can be seen that there is an oxidation peak at around −0.45 V at bare GCE and MnO_2/GCE, the peak current of VB_2 is obviously increased at MnO_2/GCE (Fig 1 b) compared with that at a bare GCE (Fig. 1 a). This is mainly attributed to the higher surface area of the MnO_2/GCE, resulting in an increase of VB_2 amount adsorbed at MnO_2/GCE surface [18].

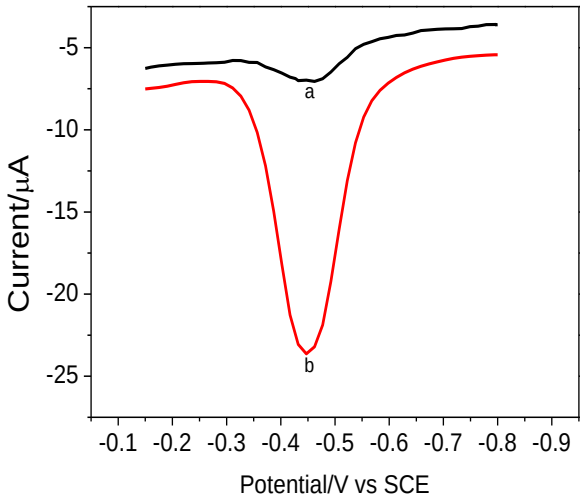


Figure 1. DP voltammograms of VB_2 at a bare GCE (a) and a MnO_2/GCE (b) surface. Buffer solution: 0.1 mol L^{-1} pH 6.5 PBS, C_{VB2}: 5.0×10^{-5} mol L^{-1}, DPV: increase 0.015 V, amplitude 0.085 V, pulse width 0.05 s, pulse period 0.125 s, and quiet time 10 s.

3.2 Influence of GCE pre-activation on the peak current of VB_2

The influence of activation before modification on the performance of MnO_2/GCE on the peak current of VB_2 was studied. The results indicated that the electrode was activated in 0.5 mol L^{-1} sulfuric acid for 20 cycles by cyclic voltammetry between –1.0 V to 1.0 V before modification can increase the response of the MnO_2/GCE to VB_2 (Fig. 2). Thus, the activation was adopted to pretreat GCE before preparation. Nagaoka and Yoshino reported that this type of oxidation will result in the formation of porous nature on electrode surface [34]. The oxidation method of GCE has been used for the preparation of some sensors [35,36].

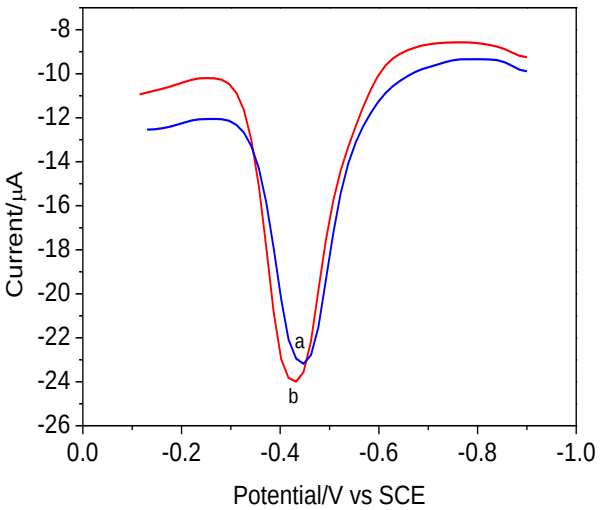


Figure 2. DP voltammograms of VB_2 on activated electrode (a) and unactivated electrode (b); Buffer: pH 6.5 PBS; C_{VB2}: 5.0×10^{-5} mol L^{-1}, DPV conditions: potential range of –0.9– –0.1 V, Other conditions are the same as Fig. 1.

3.3 Influence of amount of MnO_2

The influence of amount of MnO_2 dispersion on the response to 5.0×10^{-5} mol L^{-1} VB_2 was studied, and the results indicated that the peak current of VB_2 is first increased with the increase amount of MnO_2 and then decreased. The peak current is highest as the amount of MnO_2 is 4 μL (Fig. 3). The reason probably is the conductivity of MnO_2/GCE reduced with the increase of the amount of MnO_2. The peak current of VB_2 is highest as the amount of MnO_2 is 4.0 μL, but the peak shape is asymmetric. The peak current of VB_2 is about the same high as the amount is 6.0 μL compared with that is 4.0μL, but the peak shape of VB_2 is relatively symmetrical symmetry as the amount MnO_2 is 6.0 μL symmetric, thus, 6.0 μL of MnO_2 dispersion was selected for the preparation of MnO_2/GCE. This is attributed to the increase of amount of manganese dioxide, which increases the area of the modified GCE. Excessive manganese dioxide leads to poor conductivity of the modified electrode [28, 37].

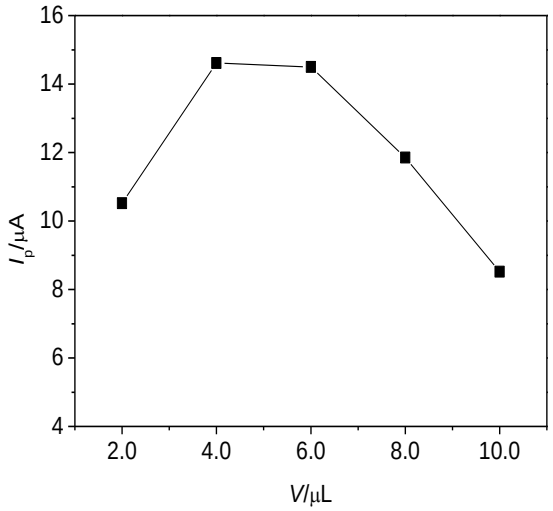


Figure 3. The influence of amount of MnO_2 and DMF dispersion on the peak current of VB_2. Other conditions are the same as Fig. 1.

3.4 Influence of different buffers

The influence of different kinds of buffers including 0.1 mol L^{-1} pH 6.0–8.0 phosphate, borate, sodium carbonate - sodium hydroxide, and ammonia - ammonium chloride on the peak current of VB_2 at MnO_2/GCE was investigated. The experimental results showed that the CV peak current of VB_2 is relatively large and the peak shape is more symmetrical in phosphate buffer as shown in Fig. 4. Consequently, the subsequent electrochemical determination of VB_2 was carried out in 0.1 mol L^{-1} PBS.

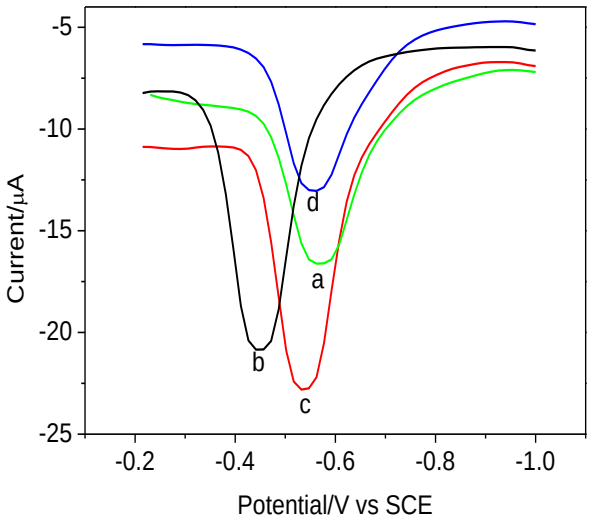


Figure 4. DP voltammograms of VB_2 in different buffers. a: $NaCO_3$-NaOH; b: PBS; c: NH_3-NH_4Cl; d: $Na_2B_4O_7 \cdot 10H_2O$. Other conditions are the same as Fig. 1.

3.5 Influence of solution pH

The influence of buffer on the peak current of VB_2 was investigated. The experimental results showed that the peak current of VB_2 reached the highest value when the pH of PBS is 6.5 (Fig. 5.), and then the peak current of VB_2 decreases with further increase of the pH. There is a negative shift of the peak potential of VB_2 with the increase of buffer pH in the range from 6.5 to 8.0. The linear regression equation is E_p/mV=982–70.2 pH (r= 0.9930) for VB_2. The slope of E_p vs. pH for VB_2 is very close to the theoretical value of 59 mV/pH. The result could be suggesting the number of protons and electrons involved in the reversible electrochemical process of VB_2 [28]. Thus, the subsequent DPV determination experiment was performed in 0.1 mol L^{-1} pH 6.5 PBS.

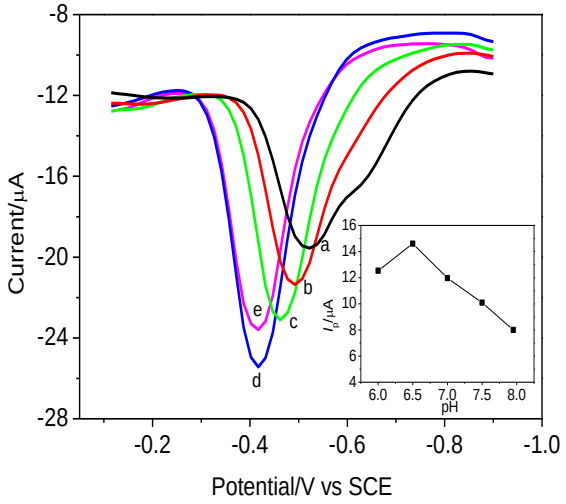


Figure 5. DP voltammograms of VB_2 in different buffer pH. Buffer: 0.1 mol L^{-1} PBS. pH a-e: 8.0, 7.5, 7.0, 6.5, 6.0. Inset: The relationship between the peak current of VB_2 and buffer pH. Other conditions are the same as Fig. 1.

3.6 Calibration curve and detection limit

Differential pulse voltammetry was used to investigate the relationship between the peak current and the concentration of VB_2 due to its higher sensitivity. As can be seen from Fig. 6, under the optimal conditions, the oxidation peak current is proportional to the concentration of VB_2 in the range of 2.0×10^{-6} and 1.1×10^{-4} mol L^{-1} with a linear regression equation of $I_{pa}(\mu A) = 0.160\ C_{B2}(\mu M) + 4.07$ ($r = 0.9993$) (Fig. 5). The detection limit is 2.7×10^{-8} mol L^{-1} calculated as 3σ blank, which is lower than that at most of modified electrodes (Table 1), closed to that at p-AMTa/GCE (4.5×10^{-8} mol L^{-1}) [21], PEDOT/$Fe(CN)_6^{4-}$/GCE (2.0×10^{-8} mol L^{-1}) [23], and PEDOT/Fc^-/GCE (5.0×10^{-8} mol L^{-1}) [23], and lower than that at PEDOT/ClO_4^-/GCE (8.0×10^{-8} mol L^{-1}) [23] and Nano-Ti-ZSM-5/GCE (6.0×10^{-7} mol L^{-1}) [27]. However, the linear range obtained in this work is wider than that at MnO_2/CPE (2.0×10^{-8}–9.0×10^{-6} mol L^{-1}) [19]. Compared with other methods, the proposed electrochemical method in our work showed several advantages, such as no need complex pretreatment, high sensitivity, easy to preparation, good stability and cheap.

3.7 Reproducibility

Under optimum conditions, the RSD ($n = 10$) for 5.0×10^{-5} mol L^{-1} VB_2 is 1.7%, which indicates that the MnO_2/GCE shows good reproducibility. The detection limit (DL) of this method for VB_2 determination is 2.7×10^{-8} mol L^{-1} calculated as 3σ blank.

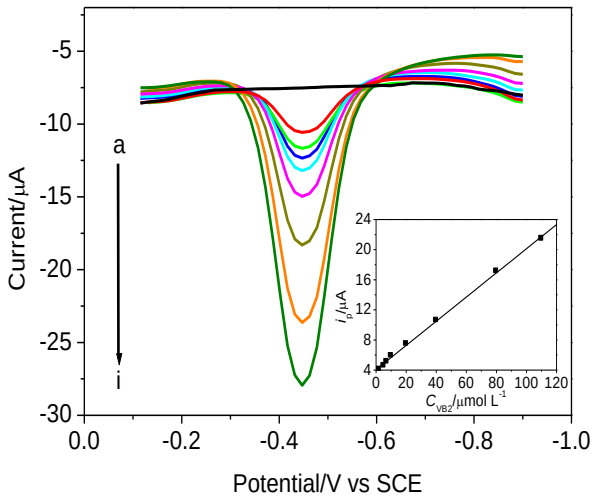


Figure 6. DPV responses changed with concentration of VB_2. Buffer: 0.1 mol L^{-1} pH 6.5 PBS. Inset: The relationship between peak current and concentration of VB_2. C_{VB2} a→i: 0, 2.0×10^{-6}, 5.0×10^{-6}, 7.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5}, 4.0×10^{-5}, 8.0×10^{-5} and 1.1×10^{-4} mol L^{-1}. Other conditions are the same as Fig. 1.

3.8 Interference experiment

In order to evaluate the selectivity of the method for the determination of VB_2, the effect of possible interfering substances was investigated under selected conditions. Some possible interfering compounds were determined, such as Ca^{2+}, Mg^{2+}, K^+, Cl^-, Na^+, vitamin B_1, B_6, B_{12}, ascorbic acid,

starch and glucose. For 5.0×10^{-5} mol L^{-1} VB_2, 1000 times of Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, 200 times of ascorbic acid, starch and glucose do not interfere with the determination of VB_2.

Table 1. Comparison of the linear range and limit of detection obtained using MnO_2/GCE for VB_2 determination with other methods

Methods or electrodes	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Reference
MWCNTs/[BMPi]PF_6/GCE	2.6×10^{-8}–1.3×10^{-6}	4.7×10^{-9}	[6]
Fluorescence	1.6×10^{-6}–2.5×10^{-4}	1.4×10^{-8}	[8]
Fluorescence	0–1.3×10^{-6}	4.0×10^{-8}	[9]
MnO_2/CPE	2.0×10^{-8}– 9.0×10^{-6}	1.5×10^{-9}	[19]
BDDE	2.0×10^{-8}– 3.5×10^{-5}	3.7×10^{-9}	[20]
p-AMTa/GCE	1.0×10^{-5}–9.0×10^{-5}	4.5×10^{-8}	[21]
sparked-BiSPEs	1.0×10^{-9}–1.0×10^{-7}	7.0×10^{-10}	[22]
PEDOT/ClO_4^-/GCE	1.5×10^{-7}–3.0×10^{-4}	8.0×10^{-8}	[23]
PEDOT/Fc^-/GCE	1.0×10^{-7}–3.0×10^{-4}	5.0×10^{-8}	[23]
PEDOT/$Fe(CN)_6^{4-}$/GCE	4.0×10^{-7}–2.0×10^{-4}	2.0×10^{-8}	[23]
Nano-Zr-ZSM-5/GCE	3.0×10^{-8}–5.0×10^{-4}	3.0×10^{-9}	[27]
Nano-Ti-ZSM-5/GCE	1.0×10^{-6}–3.0×10^{-4}	6.0×10^{-7}	[27]
Nano-Al-ZSM-5/GCE	5.0×10^{-6}–2.0×10^{-4}	1.0×10^{-6}	[27]
Zr-ZSM-5	1.0×10^{-5}–1.0×10^{-4}	5.0×10^{-6}	[27]
Ti-ZSM-5	1.0×10^{-5}–1.0×10^{-4}	5.0×10^{-6}	[27]
Al-ZSM-5	1.0×10^{-5}–1.0×10^{-4}	5.0×10^{-6}	[27]
P3MT/GCE	1.0×10^{-7}–2.0×10^{-4}		[33]
Au-ECTG	1.0×10^{-6}–1.0×10^{-2}	5.0×10^{-8}	[38]
Mn(III)-TPP-CPE	1.0×10^{-8}–1.0×10^{-5}	9.0×10^{-9}	[40]
MB-SO_3H-MSM-GCE	1.0×10^{-8}–1.5×10^{-5}	5.0×10^{-9}	[41]
Fluorescence	3.3×10^{-7}–5.3×10^{-5}	8.0×10^{-8}	[39
HPLC	5.3×10^{-7}–1.9×10^{-5}	2.0×10^{-7}	
Fluorescence	1.9×10^{-8}–1.4×10^{-7}	5.0×10^{-9}	[43]
Co^{2+}-Y zeolite-CPE	1.7×10^{-6}–3.4×10^{-5}	7.1×10^{-7}	[44]
OLA-NiO/MWCNTs/GCE	1.7×10^{-6}–3.4×10^{-5}	7.1×10^{-7}	[45]
Cr-SnO_2-GCE	2.0×10^{-7}–1.0×10^{-4}	1.1×10^{-7}	[46]
MnO_2/GCE	2.0×10^{-6}–1.1×10^{-4}	2.7×10^{-8}	This work

MWCNTs/[BMPi]PF_6/GCE: Multi-walled carbon nanotubes and ionic liquid [BMPi]PF_6 modified electrode; MnO_2/CPE: Manganese dioxide-modified carbon paste electrode; BDDE: boron-doped diamond electrode; p-AMTa/GCE: 3-amino-5-mercapto-1,2,4-triazole modified glassy carbon electrode; Sparked-BiSPEs: Sparked-bismuth oxide screen-printed electrodes; PEDOT/ClO_4^-/GCE: ClO_4^- doped poly(3,4-ethylenedioxythiophene) modified glassy carbon electrode PEDOT/Fc^-/GCE: ferrocenecarboxylic acid doped poly(3,4-ethylenedioxythiophene) modified glassy carbon electrode; PEDOT/$Fe(CN)_6^{4-}$/GCE: $Fe(CN)_6^{4-}$ doped poly(3,4-ethylenedioxythiophene) modified glassy carbon electrode; Nano-Ti-ZSM-5/GCE: Nanocrystalline Zr-ZSM-5 modified glassy; Poly (3-methylthiophene) modified glassy carbon electrode; mesoporous carbon modified glassy carbon electrode. Au–ECTG: Ethyl[(methythio)carbonothioyl] glycinate monolayer modified gold electrode. Mn(III)-TPP-CPE: Manganese (III) tetraphenylporphyrin modified carbon paste electrode. MB-SO3H-MSM-GCE: methylene blue incorporated sulfonic acid functionalized mesoporous silica microspheres. OLA-NiO/MWCNTs/GCE: Oleylamine capped nickel oxide nanoparticles onto the acid functionalized multiwalled carbon nanotubes glassy carbon electrode. CE-LIF: capillary electrophoresis with laser-induced fluorescence. Cr-SnO_2-GCE: Cr doped SnO_2 nanoparticles modified electrode. PEG: polyethylene glycol.

3.9 Determination of VB_2 in vitamin B_2 tablets

10 tablets of commercially vitamin B_2 tablets (the content is 5 mg per tablet) were grinded. Accurately weighed powder samples were dissolved into a 100 mL of brown volume metric flask and with distilled water and accurate sizing, and standing for 12 h. 100 μL of the supernatant was added to 9.9 mL PBS buffer (pH 6.5). Under optimum conditions, the content of VB_2 was determined by DPV. The content of VB_2 was calculated according to the standard curve linear regression equation. The determination results were presented in table 2.

Table 2. Determination results of VB_2 in VB_2 tablets (n=3).

Sample	Detected (μmol L^{-1})	Added(μmol L^{-1})	Found(μmol L^{-1})	Recovery (%)
1	2.0	2.0	3.93 ± 0.02	96.5
2	2.0	4.0	5.89 ± 0.04	97.3
3	2.0	6.0	8.18 ± 0.03	103

4. CONCLUSIONS

In the present work, the MnO_2/GCE was developed and used to the determination of VB_2. Under the optimized experimental conditions, the DPV peak current of VB_2 is a linear relationship with its concentration in the range of 2.0×10^{-6} and 1.1×10^{-4} mol L^{-1}. The DL is 2.7×10^{-8} mol L^{-1}, which is more sensitive than that at some previous reported methods. The MnO_2/GCE has been successfully applied to the detection of VB_2 in VB_2 tablet with satisfactory recoveries from 96.5 % to 103 %. The proposed electrochemical method for VB_2 determination in our work showed several advantages, such as no need complex pretreatment, cheap, easy to preparation, good stability and repeatability.

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