



## SHORT COMMUNICATION

# Sensitive determination of buformin using poly-aminobenzoic acid modified glassy carbon electrode

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## KEYWORDS

Chemically modified electrode;  
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**Abstract** Glassy carbon electrode, which is used to electrochemically determine the content of buformin, is modified with an electropolymerized film of *p*-aminobenzoic acid in pH 7.0 acetate buffer solution (ABS). The polymer showed an excellent electrocatalytic activity for the reduction of buformin. In pH 7.0 ABS, the cathodic peak current increased linearly over three concentration intervals of buformin, and the detection limit ( $S/N=3$ ) was  $2.0 \times 10^{-9}$  g/mL. The method was successfully applied to directly determine buformin in tablets with standard addition recoveries of 95.8–102.5%. The proposed method is simple, cheap and highly efficient.

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## 1. Introduction

As a kind of important biguanides drugs, buformin is widely used to treat diabetes. Biguanides can inhibit glycogen xenobiotics, reduce glucose sources, and enhance glucose uptake and utilization. In recent years, buformin has been found to be adulterated in health products. Therefore, it is essential to develop rapid and simple methods for the determination of buformin. Generally, the determination is performed with HPLC [1–2], GC [3], spectrophotometry [4] and potentiometric titration

[5], etc. However, they require a large sample volume, and they are time-consuming and highly costly. Zhou et al. studied metformin electrochemical behavior using dropping-mercury electrode [6]. As is well known, mercury has negative effects in the environment.

Polymer modified electrodes (PMEs) have received great attention in recent years [7]. Glassy carbon electrodes (GCEs) have been widely used because of their biocompatibility with tissue and low residual current [8–9].

In this research, we applied *p*-aminobenzoic acid (*p*-ABA) as a modifier to fabricate PMEs by electropolymerization method. The reason was that *p*-ABA contains electron-rich N atoms and high electron density carboxyl. Hence, the polymeric film is negatively charged. It can distinctly attract buformin cations.

## 2. Experimental

### 2.1. Apparatus and chemicals

Electrochemical measurements were carried out on CHI 1220A electrochemical workstation (CH Instruments, Chenhua Corp,

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Shanghai, China). A conventional three-electrode system was employed with a bare GCE or modified GCE (3.0 mm in diameter) as the working electrode, an Ag–AgCl electrode as the reference electrode, and a platinum electrode as the counter-electrode.

*p*-ABA was obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Buformin hydrochloride was purchased from Toronto Research Chemicals Inc. (Canada). The tablets were purchased from Shenzhen Zhonglian Pharmaceutical Co., Ltd. (Shenzhen, China). All chemicals were of analytical reagent grade and were used without further purification. Acetate buffer solutions (ABS) were prepared by 0.1 M HAc–NaAc; the pH was adjusted with 0.1 M HAc and 0.1 M NaOH. Stock solution buformin ( $1.0 \times 10^{-3}$  M) was prepared by weighing buformin and dilution with water. Solutions with concentrations below  $1.0 \times 10^{-3}$  M were prepared before use.

## 2.2. Methods and procedure

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to study the electrochemical properties of the polymer film.

The bare GCE was polished successively with 0.3 and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  slurry on emery paper. Then it was sonicated in 1:1 nitric acid, acetone and double distilled water for 10 min, respectively. Finally, the electrode was deposited by cyclic sweeping from  $-1.3$  to  $+1.5$  V at 100 mV/s for 10 circles in pH 7.0 ABS containing  $2.0 \times 10^{-3}$  M *p*-ABA.

The DPV was used to determine buformin in pharmaceutical products, commercially available as tablets. 0.5 g of this product was transferred to a 100 mL volumetric flask and diluted to volume with pH 7.0 ABS. Solutions with concentrations below this were prepared before use.

A 5.00 mL volume of ABS containing suitable amounts of buformin was added to the 10.0 mL voltammetry cell. In DPV measurement, potential scanning was performed in the range of  $-1.0$  to  $-0.3$  V. The tablets were analyzed by the standard-addition method. All experiments were conducted at room temperature.

## 3. Results and discussion

### 3.1. Electropolymerization of *p*-ABA

Voltammogram of  $2.0 \times 10^{-3}$  M *p*-ABA at the GCE is shown in Fig. 1. The cathodic peak was observed with the peak potential at  $-0.7$  V. After being scanned 20 segments, the blue polymer film was formed on the GCE surface. The electrochemical behavior of *p*-ABA at the GCE was similar to the references reported [10]. It should be azobenzoic acid reduced to hydrazobenzoic acid [11].

### 3.2. Cyclic voltammograms of buformin at bare and modified electrodes

In Fig. 2, voltammogram of buformin at the modified GCE is presented in comparison with the bare GCE. It only generated a cathodic peak, which indicated that the electrochemical reduction of buformin was irreversible. At the bare GCE (curve B), buformin exhibited a poor electrochemical response. At the modified electrode (curve A), a well formed cathodic peak appeared at about  $-0.65$  V. The reason may be that poly-ABA film is negatively charged as electron-rich N atom and high electron density of carboxyl group. So it can greatly attract buformin cation.

### 3.3. Surface adsorption of buformin

The scan rate ( $v$ ) on the peak current of buformin was investigated. The current was proportional to the scan rate over the range of 40–180 mV/s. The linear regression equation was  $i_p (A) = 8e-9v + 2e-6$  (mV/s) ( $r = 0.998$ ). Therefore, the contribution of adsorption played a more important role in the electrode process.

The adsorbed amount of buformin on the modified electrode should be related to the feature of the polymeric film. With the porous 3D structure, electropolymerized ABA film can provide highly active surface and highly catalytic activities. So the buformin can be sensitively detected. This is consistent with what has been reported [12–13].

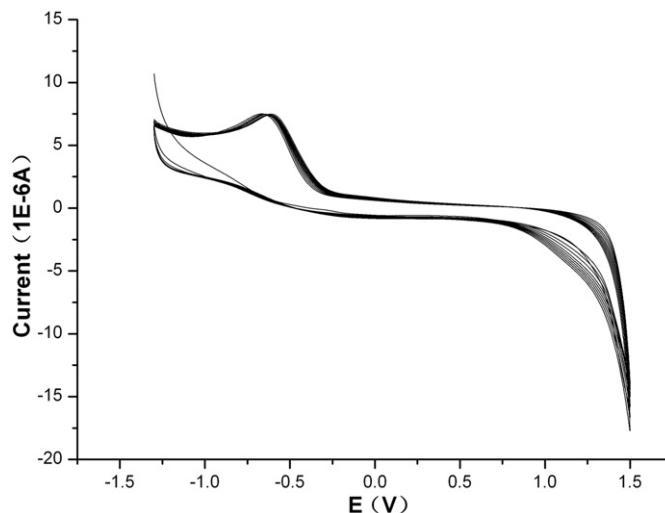
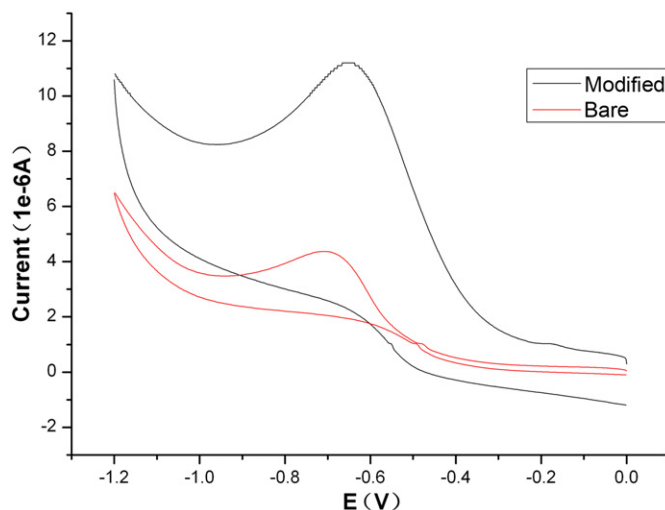
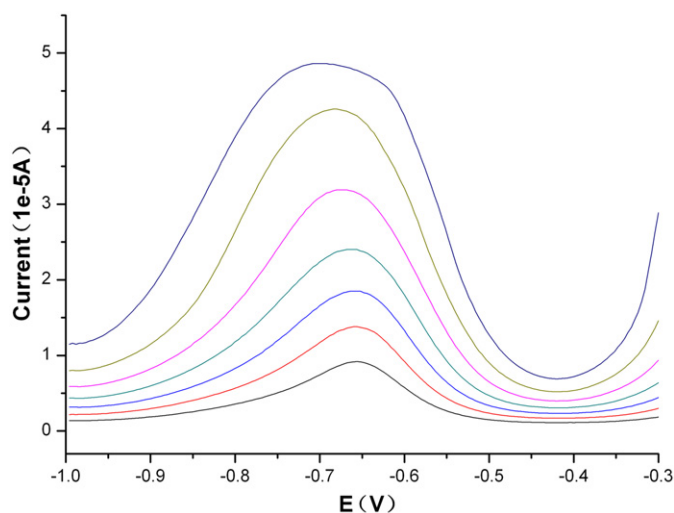


Figure 1 Repetitive cyclic voltammograms of  $2.0 \times 10^{-3}$  M *p*-ABA.



**Figure 2** Cyclic voltammograms of  $1.0 \times 10^{-6}$  M buformin at the modified GCE (A) and the bare GCE (B).



**Figure 3** DPV recordings of buformin at the modified electrode.

**Table 1** Determination results of buformin in tablets ( $n=6$ ).

Sample	Labeled ( $\mu\text{g}$ )	Added ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery (%)	Average (%)	RSD (%)
1	2.0002	2.0017	3.9439	97.1	98.5	2.5
2	2.0010	2.0017	3.9186	95.8		
3	1.9998	2.0017	4.0515	102.5		

### 3.4. Determination of buformin

Buformin concentration at the modified electrode was determined with DPV. Fig. 3 shows that peak current  $i_p$  is proportional to the concentration over three concentration intervals, namely,  $2.0 \times 10^{-8}$ – $2.0 \times 10^{-7}$  g/mL,  $2.0 \times 10^{-7}$ – $2.0 \times 10^{-6}$  g/mL and  $2.0 \times 10^{-6}$ – $2.0 \times 10^{-5}$  g/mL. The linear regression equation was  $i_p$  ( $\mu\text{A}$ ) =  $3.8411 + 0.1820C$  ( $\mu\text{g/mL}$ ),  $i_p$  ( $\mu\text{A}$ ) =  $3.6844 + 0.0281C$  ( $\mu\text{g/mL}$ ) and  $i_p$  ( $\mu\text{A}$ ) =  $3.4448 + 0.0373C$  ( $\mu\text{g/mL}$ ), with  $r=0.9984$ ,  $0.9973$  and  $0.9921$ , respectively. The detection limit ( $S/N=3$ ) was  $2.0 \times 10^{-9}$  g/mL. The relative standard deviation of 10 successive scans was

2.8% for  $2.0 \times 10^{-6}$  g/mL buformin, indicating excellent reproducibility of modified electrode. The linear range was wider and detection limit was lower than those reported in the literature [14]. The results showed that this method is more sensitive.

### 3.5. Analytical application

Under the optimum conditions, the modified electrode was applied to determine buformin in tablets. The results are listed in Table 1.

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