

# Voltammetric Sensor Based on 1-Benzyl-4-ferrocenyl-1H-[1,2,3]-triazole /Carbon Nanotube Modified Glassy Carbon Electrode; Detection of Hydrochlorothiazide in the Presence of Propranolol

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In this work, 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) and carbon nanotubes has been applied to construct a modified glassy carbon electrode. This modified electrode showed electrocatalytic activity for oxidation of hydrochlorothiazide (HCT) and reduced the overpotential for oxidation of hydrochlorothiazide about 870 mV. Also, the modified electrode can resolve the overlapped voltammetric peaks of hydrochlorothiazide and propranolol into two voltammetric peaks. This property allows to selective determination of hydrochlorothiazide in the presence of propranolol. The transfer coefficient ( $\alpha$ ) and diffusion coefficient of hydrochlorothiazide were also investigated. In phosphate buffer solution (PBS) of pH 8.0, the oxidation currents for hydrochlorothiazide increased linearly from 0.1 to 500.0  $\mu\text{M}$  using square wave voltammetry (SWV). The detection limit ( $3\sigma$ ) was obtained 0.08  $\mu\text{M}$ . The proposed method was successfully applied to the determination of hydrochlorothiazide and propranolol in pharmaceutical and biological samples.

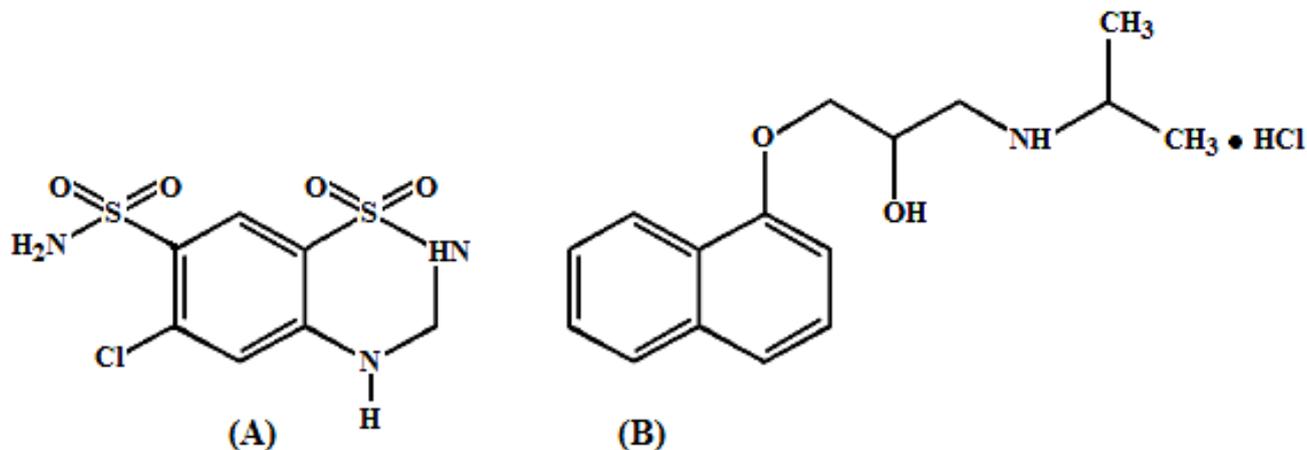
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**Keywords:** Hydrochlorothiazide, Propranolol, Carbon Nanotubes, Chemically modified electrodes

## 1. INTRODUCTION

Hypertension (high blood pressure) adds to the workload of the heart and arteries. If it continues for a long time, the heart and arteries may not function properly. This can damage the blood vessels of the brain, heart, and kidneys, resulting in a stroke, heart attacks or kidney failure. These

problems may be less likely to occur if blood pressure is controlled. Hydrochlorothiazide and propranolol combination is used to treat hypertension (shown in scheme 1).



**Scheme 1.** Chemical structures of a) hydrochlorothiazide and b) propranolol hydrochloride.

Hydrochlorothiazide / propranolol is a non-selective  $\beta$ -adrenergic receptor ( $\beta$ -blocker) and thiazide diuretic combination [1-4]. The hydrochlorothiazide (water pill) is substance that reduces the amount of water in the body by increasing the flow of urine, which helps lower the blood pressure. The propranolol works by affecting the response to some nerve impulses in certain parts of the body, like the heart. As a result, the heart beats slower and decreases the cardiac output, and blood pressure. Hence, the determinations of these drugs in the pharmaceutical and clinical samples have drawn tremendous attention and a reliable and sensitive detection method is highly expected [5-7].

Several techniques for the analytical determination have been reported in the literature for these drugs determination which includes chromatography, capillary electrophoresis, spectrophotometry and conductometry [8]. However, these techniques have the insufficiency of being expensive, laborious and require pre-treatment or multi-solvent extraction of samples. Among various analytical methods, modern electrochemical techniques have attracted considerable interest due to the good simplicity, sensitivity, selectivity, stability and often do not require any pre-treatments or pre-separation [9-15]. These methods also have potential to provide valuable information into the redox reactions of biologically active drugs [16-23].

Glassy carbon electrodes (GCEs) are very versatile as electrode material for trace level determination of organic molecules because they provide negligible porosity, high sensitivity, and good mechanical rigidity. Yet, very few methods have been reported in literature on direct voltammetric behavior of drugs since the over-potential of them are very high at bare GCE [24, 25]. To overcome this problem, various inorganic and organic materials have been applied to modify electrodes [26-28]. Modifier such as nanoparticles, polymers, carbon ionic liquid, carbon-ceramic and carbon nanotubes could enhance the transfer rate of the electron and reduce the over-potential for the oxidation of substrates [29-36].

Multi-wall carbon nanotube (MWCNT) is one kind of the most extensively used materials to modify electrodes due to a huge, cylindrical surface area and graphene sheet MWCNT have

extraordinary properties, such as high thermal and electrical conductivity, chemical stability, high tensile strength, high elasticity, and in some instances, metallic conductivity and catalyst support [108-119]. In addition, similar to the electrically conducting polymers, the MWCNTs present functional groups anchored onto them, viz. carboxyl, hydroxyl, and carbonyl, making these materials a great support that can be modified with several species [37-40]. Therefore, in comparison to the traditional carbon electrodes, MWCNT-based sensors generally have higher sensitivities, faster electron transfer kinetics, lower limits of detection, low background current, wide potential window, reduction of overpotentials and resistance to surface fouling [41-45].

Thus, we described the preparation of a 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) modified glassy carbon nanotube electrode (BFTGCNE) as a new sensor in the determination of hydrochlorothiazide. Then simultaneous determination of hydrochlorothiazide and propranolol was evaluated.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). An Ag/AgCl/KCl (3.0 M) electrode was used as reference electrode, a platinum wire was used as auxiliary electrode, and the BFTGCNE used as the working electrode.

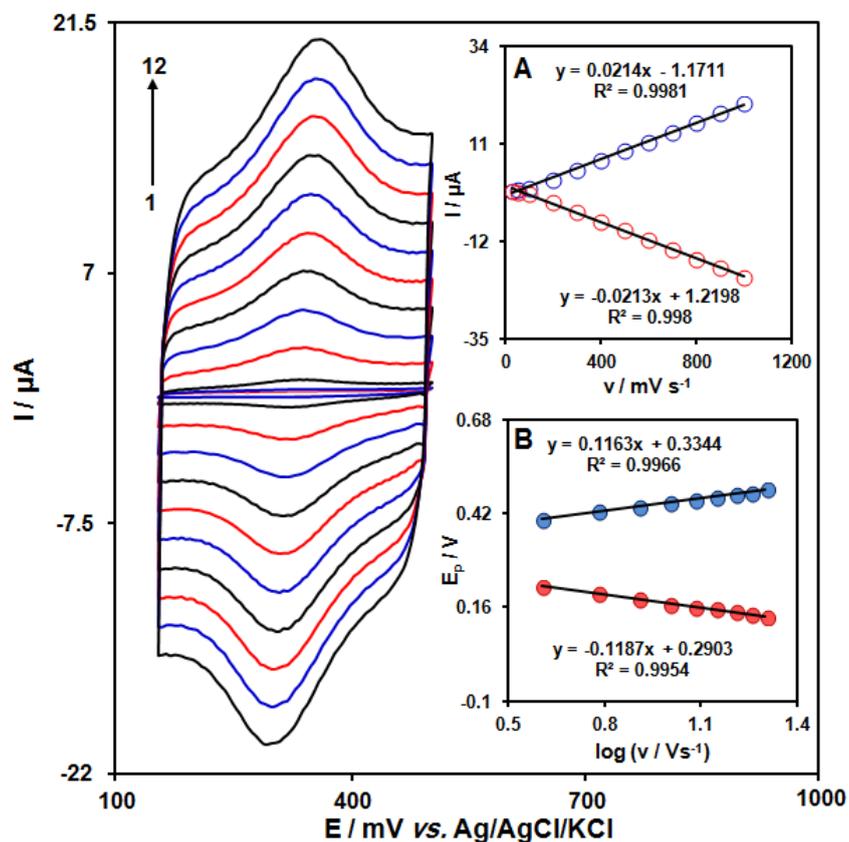
All the reagents were of analytical grade from Merck. Multiwalled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 0.5 to 200  $\mu\text{m}$  were prepared from Nanostructured & Amorphous Materials, Inc. 1-Benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) was synthesized in our manuscript as reported previously [43].

### 2.2. Preparation of the modified electrodes

The preparation of modified GCE was performed by mechanically polishing a glassy carbon electrode with 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  in water slurry then, it was electrochemically activated in a 0.1 M sodium bicarbonate solution, and pouring 5  $\mu\text{L}$  of CNT suspension (0.01 g/mL) onto the activated GCE surface. Finally for the preparation of BFT-CNT-GCE, CNT modified GCE was placed in a solution of 5% V/V ethanol and 0.1M PBS (pH 6.0) containing 1.0 mM BFT. It was modified by 8 cycles of potential scan rate between 0.1 V and 0.55 V at 30  $\text{mVs}^{-1}$ . In order to fabricate BFT modified GCE (BFT-GCE), the activated GCE was immersed in a solution of 5% V/V ethanol and 0.1M PBS (pH 6.0) containing 1.0 mM BFT. The modification was performed with the same procedure that has been described for BFT-CNT-GCE.

### 3. RESULTS AND DISCUSSION

#### 3.1. Electrochemical properties of BFTGCNE



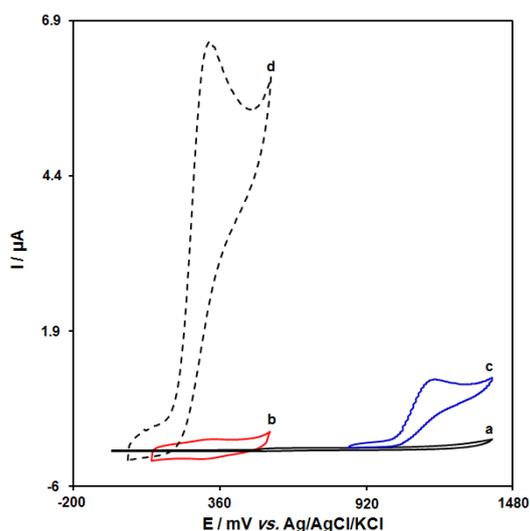
**Figure 1.** CVs of BFTGCNE in 0.1M PBS (pH 8.0), at different scan rates, (30, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000  $\text{mV s}^{-1}$ ). Insets: variation of (A)  $I_p$  vs. potential scan rate; (B) Variation of  $E_p$  versus the logarithm of the high potential scan rates.

The cyclic voltammetric results for BFTGCNE in a 0.1 M PBS (pH 8.0) showed anodic and cathodic peaks with  $E_{pa} = 330.0$  mV,  $E_{pc} = 300.0$  mV and  $E^{\circ} = 315.0$  mV vs. Ag/AgCl/KCl (3.0 M) respectively.

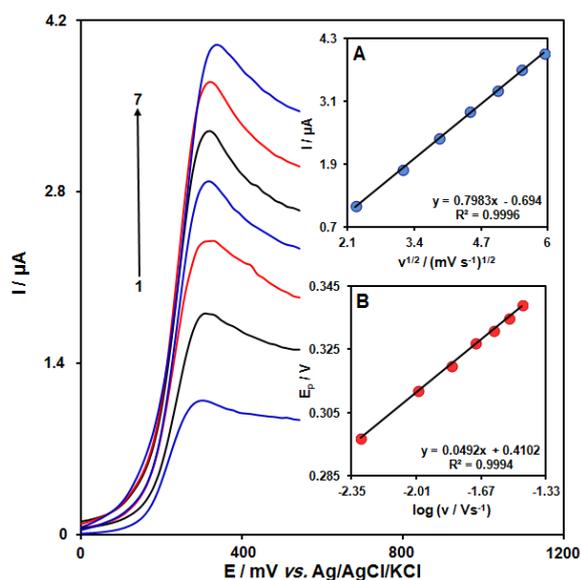
The potential scan rate ( $v$ ) effect of the on electrochemical behavior of the BFTGCNE was studied. Plots of the both anodic and cathodic peak currents ( $I_p$ ) were linearly dependent on potential scan rate within the range of 30 to 1000  $\text{mV s}^{-1}$  (Fig. 1A). These results indicate that the redox process of BFT at the surface of glassy carbon electrode is diffusionless in nature [47].

The apparent charge transfer rate constant,  $k_s$ , and the charge transfer coefficient,  $\alpha$ , of a surface-confined redox couple can be evaluated from CV experiments according to the method of Laviron [47]. As can be seen in Fig. 1B  $E_p$  values are proportional to the logarithm of scan rate for scan rate values higher than  $4.0 \text{ V s}^{-1}$ . The slopes these plots can be used to extract the transfer coefficients. The  $\alpha = 0.5$  was obtained. Using Laviron theory  $k_s = 12.7 \text{ s}^{-1}$  was obtained.

## 3.2. Catalytic electro-oxidation of hydrochlorothiazide at the surface of BFTGCNE



**Figure 2.** CVs of BFTGCNE in PBS (b), CV of BFTGCNE in PBS and 0.3 mM hydrochlorothiazide (d), CV of bare GCE in PBS and 0.3 mM hydrochlorothiazide and (c) CV of bare GCE in PBS (a). In all cases the scan rate was  $10 \text{ mV s}^{-1}$ .



**Figure 3.** LSVs of BFTGCNE in PBS containing 0.15 mM hydrochlorothiazide at various scan rates; numbers 1-7 correspond to 5, 10, 15, 20, 25, 30 and 35  $\text{mV s}^{-1}$ , respectively. Insets: Variation of (A) anodic peak current vs.  $v^{1/2}$ ; (B) anodic peak potential vs.  $\log v$ .

Fig. 2 shows the CV responses for the electrochemical oxidation of 0.3 mM hydrochlorothiazide at BFTGCNE (curve d), and bare GCE (curve c). As can be seen, the anodic peak potential for the oxidation of hydrochlorothiazide at BFTGCNE (curve d) is about 330 mV, while at the bare GCE (curve c) peak potential is about 1200 mV.

The obtained data show that the combination of CNTs and BFT improved the characteristics of hydrochlorothiazide oxidation. The BFTGCNE in 0.1M PBS (pH 8.0), in the absence of hydrochlorothiazide in solution, exhibits a well-behaved redox reaction (curve b) upon the addition of 0.3 mM hydrochlorothiazide, there is a dramatic enhancement of the anodic peak current (curve d), which indicates a strong electrocatalytic effect [46].

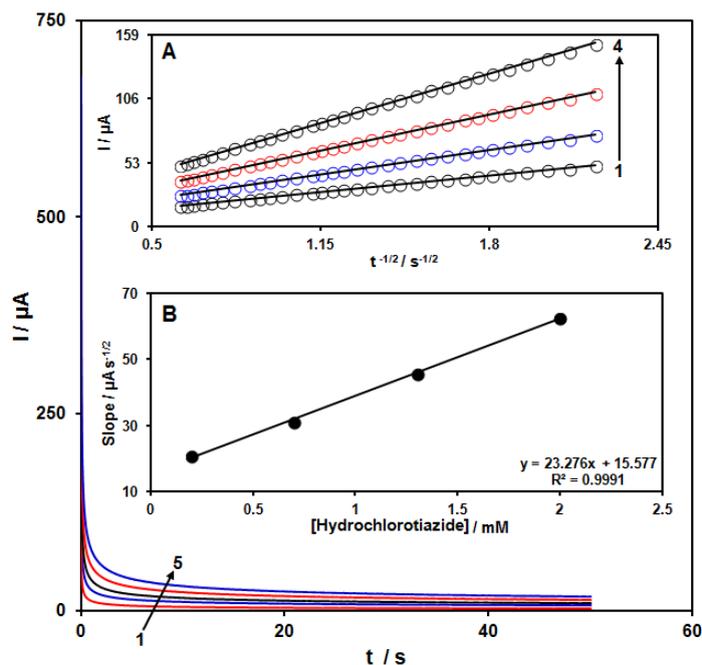
The effect of scan rate on the electrocatalytic oxidation of hydrochlorothiazide at the BFTGCNE was investigated by linear sweep voltammetry (LSV) (Fig. 3). As can be observed in Fig. 3, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height ( $I_p$ ) vs. the square root of scan rate ( $v^{1/2}$ ) was found to be linear in the range of 5-35  $\text{mV s}^{-1}$ , suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 3A) [46].

The Tafel slope (b) can be obtained from the slope of  $E_p$  vs.  $\log v$  using Eq. (1) [46]:

$$E_p = b/2 \log v + \text{constant} \quad (1)$$

The Tafel slope was found to be 0.0984 V (Fig. 3, inset B), which indicates that one-electron transfer process is the rate limiting step assuming a transfer coefficient ( $\alpha$ ) is about 0.4.

### 3.3. Chronoamperometric measurements



**Figure 4.** Chronoamperograms obtained at the surface of BFTGCNE in PBS for different concentrations of hydrochlorothiazide. The numbers 1–5 correspond to 0.0, 0.2, 0.7, 1.3, and 2.0 mM of hydrochlorothiazide. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 2–5. (B) Plot of the slope of the straight lines against hydrochlorothiazide concentrations.

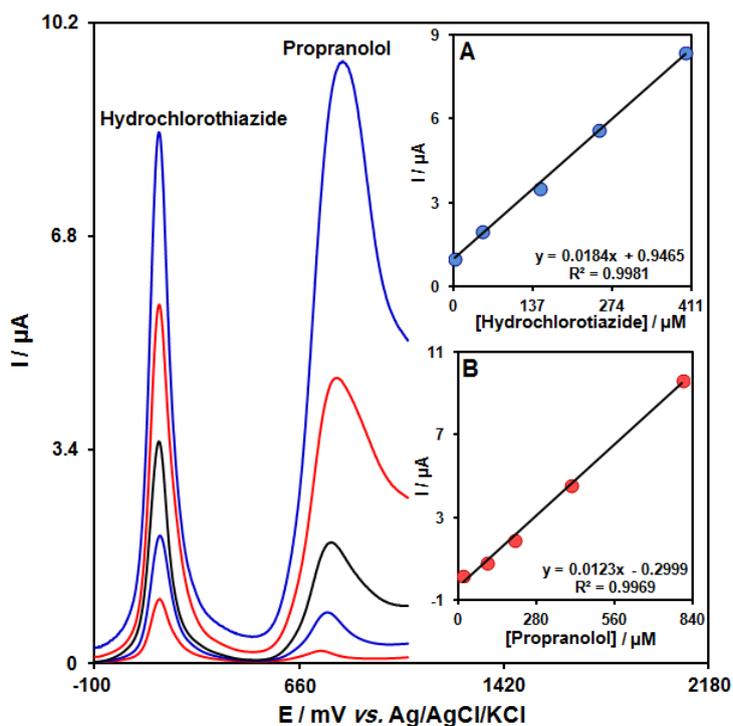
Chronoamperometric measurements of hydrochlorothiazide at BFTGCNE were carried out by setting the working electrode potential at 0.4 V vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of hydrochlorothiazide in PBS (pH 8.0) (Fig. 4). Using Cottrell equation the mean value of the D was found to be  $5.6 \times 10^{-6} \text{ cm}^2/\text{s}$ .

### 3.4. Calibration plot and limit of detection

SWV method was used to determine the concentration of hydrochlorothiazide. The plot of peak current vs. hydrochlorothiazide concentration consisted of a linear segment in the concentration range of 0.1 to 500.0  $\mu\text{M}$ . The detection limit ( $3\sigma$ ) of hydrochlorothiazide was found to be 0.08  $\mu\text{M}$ . These values are comparable with values reported by other research groups for electro-oxidation of hydrochlorothiazide at the surface of chemically modified electrodes by other modifiers (see Table 1).

### 3.5. Simultaneous determination of hydrochlorothiazide and propranolol

One of the main object of this study was to detect hydrochlorothiazide and propranolol simultaneously using BFTGCNE. This was performed by simultaneously changing the concentrations of hydrochlorothiazide and propranolol, and recording the SWVs. The voltammetric results showed well-defined anodic peaks, indicating that simultaneous determination of these compounds is feasible at the BFTGCNE as shown in Fig. 5.



**Figure 5.** SWVs of BFTGCNE in 0.1 M PBS (pH 8.0) containing different concentrations of hydrochlorothiazide+propranolol in  $\mu\text{M}$ , from inner to outer: 3.0+15.0, 50.0+100.0, 150.0+200.0, 250.0+400.0 and 400.0+800.0 respectively. Insets (A) plots of  $I_p$  vs. hydrochlorothiazide concentrations and (B) plot of  $I_p$  vs. propranolol concentrations.

The sensitivity of the modified electrode towards the oxidation of hydrochlorothiazide was found to be  $0.0184 \mu\text{A } \mu\text{M}^{-1}$ . This is very close to the value obtained in the absence of propranolol ( $0.0182 \mu\text{A } \mu\text{M}^{-1}$ , see Section 3.4), indicating that the oxidation processes of these compounds at the BFTGCNE are independent and therefore, simultaneous determination of their mixtures is possible without significant interferences.

**Table 1.** Comparison of the efficiency of some modified electrodes used in the determination of hydrochlorothiazide.

Electrode	method	LOD (M)	LDR(M)	Ref.
Carbon paste	Voltammetry	$9.0 \times 10^{-8}$	$6.0 \times 10^{-7} - 3.0 \times 10^{-4}$	4
Carbon paste	Voltammetry	$2.0 \times 10^{-8}$	$5.0 \times 10^{-8} - 2.0 \times 10^{-4}$	29
Glassy carbon	Voltammetry	$4.3 \times 10^{-9}$	$4.0 \times 10^{-6} - 4.0 \times 10^{-5}$	27
Boron-doped diamond	Voltammetry	$6.39 \times 10^{-7}$	$1.97 \times 10^{-6} - 8.81 \times 10^{-5}$	34
Carbon paste	Voltammetry	$8.0 \times 10^{-8}$	$1.0 \times 10^{-7} - 5.0 \times 10^{-4}$	This work

### 3.6. Real sample analysis

In order to evaluate the analytical capability of the proposed method, also it was applied to the determination of hydrochlorothiazide and propranolol in hydrochlorothiazide and propranolol tablets and urine samples. The results are listed in table 2 and show satisfactory recoveries for hydrochlorothiazide and propranolol.

**Table 2.** The application of BFTGCNE for simultaneous determination of hydrochlorothiazide and propranolol in real samples (n=3).

Sample	Spiked ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )		Recovery (%)		R.S.D. (%)		
		Propranolol	Hydrochlorothiazide	Propranolol	Hydrochlorothiazide	Propranolol	Hydrochlorothiazide	
Hydrochlorothiazide tablet	0	0	13.0	ND <sup>a</sup>	-	-	3.4	-
	2.5	20.0	15.4	20.5	99.3	102.5	2.8	2.6
	5.0	30.0	18.5	29.8	102.8	99.3	2.9	3.5
	7.5	40.0	20.9	38.9	101.9	97.2	1.9	2.2
	10.0	50.0	22.4	50.9	97.4	101.8	3.3	1.7
Propranolol tablet	0	0	ND	10.0	-	-	-	2.8
	10.0	10.0	10.3	19.8	103.0	99.0	3.5	2.1
	15.0	20.0	14.8	30.5	98.7	101.7	3.2	2.2
	20.0	30.0	20.3	38.9	101.5	97.2	1.7	2.9
	25.0	40.0	24.8	51.5	99.2	103.0	2.2	3.1
Urine	0	0	ND	ND	-	-	-	-
	12.5	25.0	12.4	25.5	99.2	102.0	2.7	2.9
	17.5	35.0	17.9	34.8	102.3	99.4	2.8	1.9
	22.5	45.0	22.9	44.1	101.8	98.0	2.2	1.7
	27.5	55.0	26.9	55.9	97.8	101.6	3.1	2.1

<sup>a</sup> ND: Not detected

#### 4. CONCLUSION

The BFTGCNE was prepared and used for the investigation of the electrochemical behavior of hydrochlorothiazide. The BFTGCNE showed excellent electrocatalytic activity for the hydrochlorothiazide. The SWV currents of hydrochlorothiazide at the surface of BFTGCNE increased linearly with the hydrochlorothiazide concentration in the range from 0.1-500.0  $\mu\text{M}$  with a detection limit of 0.08  $\mu\text{M}$ . The modified electrode exhibited excellent electrocatalytic activity towards the detection of hydrochlorothiazide and propranolol where co-oxidized at the electrode with a wide potential difference. Thus, simultaneous as well as independent electrochemical determinations of hydrochlorothiazide and propranolol are possible without electrochemical interference from each other. Finally, this method was used for the determination of hydrochlorothiazide and propranolol in some real samples.

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