

*Full Paper*

## **Simultaneous Electrochemical Sensing of Methyldopa and Hydrochlorothiazide using a Novel ZnO/Al<sub>2</sub>O<sub>3</sub> Nanocomposite Modified Screen Printed Electrode**

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*Received: 5 April 2017 / Accepted: 29 June 2017 / Published online: 31 December 2017*

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**Abstract-** In this study, ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite modified graphite screen printed electrode (ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE) was fabricated for the simultaneous determination of methyldopa and hydrochlorothiazide. The modified electrode was also employed to study the electrochemical oxidation of methyldopa and hydrochlorothiazide, using cyclic voltammetry (CV), chronoamperometry and differential pulse voltammetry (DPV) as diagnostic techniques. This modified electrode shows excellent electrocatalytic activity towards the oxidation of methyldopa with a potential shift about 240 mV to a less positive potential. Differential pulse voltammetry exhibits linear dynamic ranges from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  M and  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  M for methyldopa and hydrochlorothiazide respectively. Under optimized experimental conditions, the detection limits of methyldopa and hydrochlorothiazide were calculated as 0.5  $\mu$ M and 0.08  $\mu$ M respectively, at this simple construction sensor. Finally, the fabricated sensor was satisfactorily used for the simultaneous determination of methyldopa and hydrochlorothiazide in methyldopa tablets, hydrochlorothiazide tablets and urine samples.

**Keywords-** Methyldopa, Hydrochlorothiazide, ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite, Graphite screen printed electrode

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## 1. INTRODUCTION

Methyldopa (2-amino-3-(3, 4-dihydroxyphenyl)-2-methyl-propanoic acid) (MD) is used to treat high blood pressure. Methyldopa is in a class of medications called antihypertensives. It works by relaxing the blood vessels so that blood can flow more easily through the body. High blood pressure is a common condition and when not treated, can cause damage to the brain, heart, blood vessels, kidneys and other parts of the body. Damage to these organs may cause heart disease, a heart attack, heart failure, stroke, kidney failure, loss of vision, and other problems [1]. Therefore detection and quantification of methyldopa is an important feature in pharmaceutical and clinical method [2].

Hydrochlorothiazide (HCT) (6-chloro-1, 1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide). The hydrochlorothiazide is a benzothiazide diuretic that acts directly on the kidney by increasing the excretion of sodium chloride and water and, to a lesser extent, that of potassium ion. Also, it is an antihypertensive drug which improves the action of other hypotensive substances. Thus, the development of convenient, rapid, selective and sensitive analytical methods for the determination of illicit diuretics, such as hydrochlorothiazide, in human urine samples, especially in the urine samples of athletes has gained great importance. The official method recommended by the United States Pharmacopeia [3].

The combination of methyldopa and hydrochlorothiazide are used to treat high blood pressure. So to establish a simple, accurate, rapid and inexpensive method for simultaneous detection of these drugs is very necessary [4].

Several methods have been reported for determination of methyldopa and hydrochlorothiazide, such as chemometry, spectrophotometry, chromatography, chemiluminescence and  $^1\text{H}$  NMR [5-12]. Some of these methods are not simple and others are time consuming or involve procedures with rigorous control of the experimental conditions or require expensive equipment and consequently are not suitable for routine analysis. Electrochemistry is a simple, inexpensive, sensitive, accurate and without the need for complex prototypes for measuring the species [13-16] such as methyldopa and hydrochlorothiazide individually or simultaneous [17-19].

The development of screen-printed electrodes (SPEs) has become a major revolution in the construction of electrochemical sensors/biosensors. The commonly SPEs are constructed of a commercially purchased ink consisting of graphite and carbon black particles with a polymeric binder which are screen-printed onto a suitable substrate and then cured at a suitable temperature. These simple manufacturing steps of the electrode allow the transfer of electrochemical laboratory experiments to the market for reproducible and disposable on-site detection of various analytes [20-25]. In order to improve their electrochemical performance, SPEs have been modified with nanosized materials.

Nanostructures offer numerous unique features and show great promise for faster responses and higher sensitivity than planar sensor configurations. Major advantages

obtained from NPs in modified electrodes are facilitation in electron kinetics by provision of high surface area, increased mass transport rates, better control of NPs surface and controllable functionalization of desired groups. Recently, nanoparticles have attracted great attention in area of electrocatalysis because of their unusual physical and chemical conduct. MNPs modified electrodes show reasonably fast redox activity towards the compounds which show sluggish electron kinetics at bare electrodes. In many cases, use of MNPs modified electrodes helped in resolving overlapped peaks of analytes with close oxidation potentials. Moreover, such modified electrodes provide good peak to peak separations [26-42]. Metal oxide nanoparticles have been extensively developed in the past decades. They have been widely used in many applications such as catalysts, sensors, semiconductors, medical science, capacitors, and batteries [43-48]. Among the metal oxide nanoparticles, zinc oxide (ZnO-NPs) has attracted much attention owing to its fascinating properties such as lack of toxicity, wide direct band gap (3.37 eV at room temperature), large exciton binding energy (60 meV) [49], a high isoelectric point (IEP) (~9.5) [50], large surface area, and versatile surface chemistry. So, zinc oxide nanoparticles deserve further investigation as an extraordinary and promising candidate for support material in the construction of the biosensors.

It is widely accepted that ZnO-NPs acts both as an electronic and structural promoter exhibiting a major influence on the catalytic activity, while alumina or other refractory oxides mainly increase the long-term stability as structural promoter of the catalyst system. Al<sub>2</sub>O<sub>3</sub> generally refers to corundum. It is a white oxide. Alumina has several phases such as gamma, delta, theta, and alpha. However, the alpha alumina phase is the most thermodynamically stable phase. In general, alumina has many interesting properties, for example high hardness, high stability, high insulation, and transparency. Alumina is also widely used in the fire retard, catalyst, insulator, surface protective coating, and composite materials [51].

In the present work, the ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite-modified SPEs were used for the first time as a simple, inexpensive, rapid and sensitive electrochemical biosensor for determination of methyl dopa and hydrochlorothiazide in pharmaceutical formulations and human fluids. The SPEs showed high sensitivity for determination of methyl dopa and hydrochlorothiazide in real samples.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. The screen-printed electrode (DropSens, DRP-110, Spain) consists of three main parts which

are a graphite counter electrode, a silver pseudo-reference electrode and a graphite working electrode.

All solutions were freshly prepared with double distilled water. Methyldopa, hydrochlorothiazide, and all other reagents were of analytical grade and were obtained from Merck chemical company (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0.

## **2.2. Synthesis of ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite**

The aluminum hydroxide was prepared by dissolving of 3 g of Al (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O in 100 ml of distilled water. The pH of solution was set to 8 by ammonia solution and it was kept at 60 °C for 18 h. The precipitate was washed by ethanol and acetone three times, respectively. The Al(OH)<sub>3</sub> was prepared by aging of precipitate at 75 °C for 24 h.

A solution of zinc nitrate (0.3 M) was prepared in 80 ml of distilled water. The pH of solution was set to 9.5 by ammonium solution (25%) and the 0.13 g of aluminum hydroxide was added to the solution and the solution was mixed for 2 h at room temperature. The solution was aged at 90 °C for 4 h at 250 rpm stirring rate. The precipitate of ZnO-Al<sub>2</sub>O<sub>3</sub> was washed by ethanol and distilled water, respectively.

## **2.3. Preparation of modified electrode**

The bare screen-printed electrode was coated with ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite as follows. A stock solution of ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite in 1 mL aqueous solution was prepared by dispersing 1 mg ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite with ultrasonication for 1 h, and a 2 µl aliquot of the ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite/H<sub>2</sub>O suspension solution was casted on the carbon working electrodes, and waiting until the solvent evaporation in room temperature.

## **2.4. Preparation of real samples**

Five methyldopa tablets (labeled 250 mg per tablet, DarouPakhsh Holding, Iran) were grinding. Then, the tablet solution was prepared by dissolving 250 mg of the powder in 25 mL water by ultrasonication. Then, different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0).

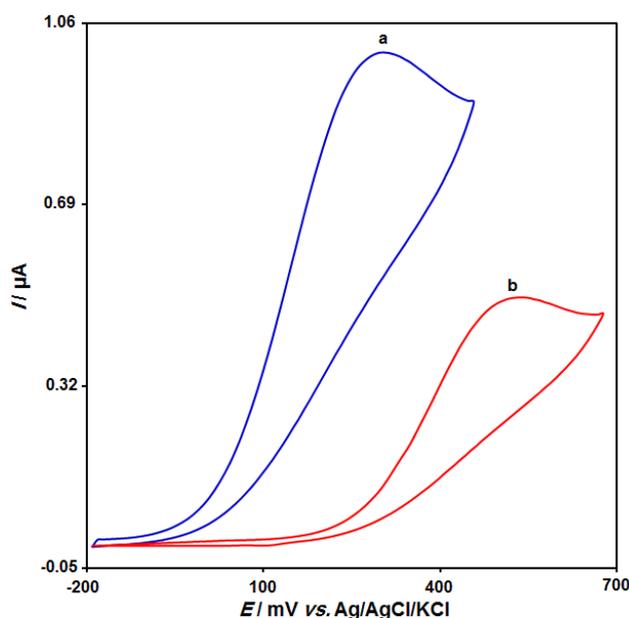
Ten hydrochlorothiazide tablets (labeled 50 mg per tablet, Irandarou Company, Iran) were grinding. Then, the tablet solution was prepared by dissolving 50 mg of the powder in 25 mL water by ultrasonication. Then, different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The hydrochlorothiazide content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 15 min at 2000 rpm. The supernatant was filtered out using a 0.45  $\mu\text{m}$  filter. Then, different volume of the solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine sample was spiked with different amounts of methyldopa and hydrochlorothiazide.

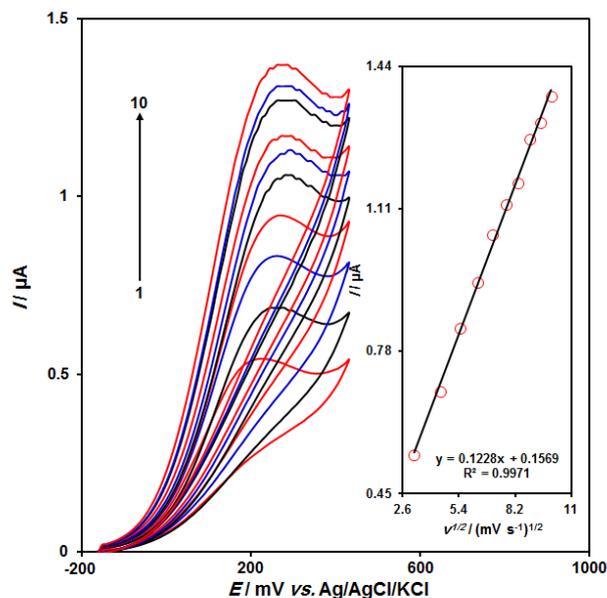
### 3. RESULT AND DISCUSSION

#### 3.1. Electrocatalytic oxidation of methyldopa at a ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE

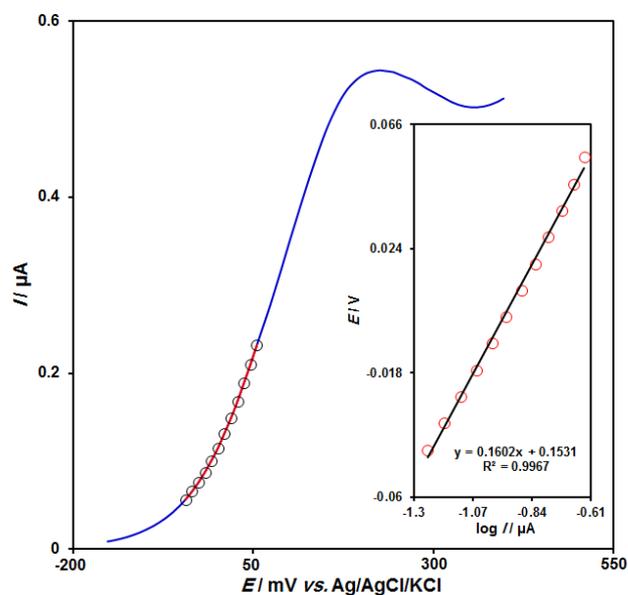
The electrochemical behavior of methyldopa was studied in 0.1 M PBS in pH=7 at the surface of ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE by CV. Fig. 1 depict the cyclic voltammetric responses for the electrochemical oxidation of 100.0  $\mu\text{M}$  methyldopa at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE (curve a) and bare SPE (curve b). The anodic peak potential for the oxidation of methyldopa at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE (curve a) is about 300 mV compared with 540 mV for that on the bare SPE (curve b). Similarly, when the oxidation of methyldopa at the ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE (curve a) and bare SPE (curve b) are compared, an extensive enhancement of the anodic peak current at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE relative to the value obtained at the bare SPE (curve b) is observed. In other words, the results clearly indicate that the combination of ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposites improve the methyldopa oxidation signal.



**Fig. 1.** Cyclic voltammograms of (a) ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 100.0  $\mu\text{M}$  methyldopa at the scan rate  $50 \text{ mVs}^{-1}$



**Fig. 2.** Cyclic voltammograms of ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE in 0.1 M PBS (pH 7.0) containing 100.0 μM methyldopa at various scan rates; numbers 1-10 correspond to 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV s<sup>-1</sup>, respectively. Inset: variation of cathodic peak current vs. v<sup>1/2</sup>

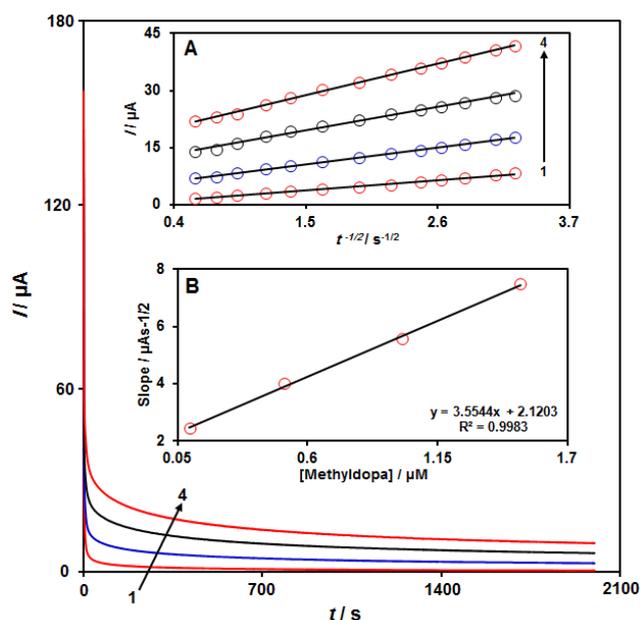


**Fig. 3.** LSV (at 10 mV s<sup>-1</sup>) of electrode in 0.1 M PBS (pH 7.0) containing 100.0 μM methyldopa. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

The effect of potential scan rates on the oxidation current of methyldopa has been studied (Fig. 2). The results showed that increasing in the potential scan rate induced an increase in the peak current. In addition, the oxidation process is diffusion controlled as deduced from

the linear dependence of the anodic peak current ( $I_p$ ) on the square root of the potential scan rate ( $v^{1/2}$ ) over a wide range from 10 to 100  $\text{mV s}^{-1}$ .

Fig. 3 shows a Tafel plot that was drawn from points of the Tafel region of the LSV. The Tafel slope of 0.1602 V obtained in this case agrees well with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of  $\alpha=0.63$  [52].



**Fig. 4.** Chronoamperograms obtained at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE in 0.1 M PBS (pH 7.0) for different concentration of methyl dopa. The numbers 1–4 correspond to 0.1, 0.5, 1.0 and 1.5 mM of methyl dopa. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1–4; (B) Plot of the slope of the straight lines against methyl dopa concentration

### 3.2. Chronoamperometric measurements

Chronoamperometric measurements of methyl dopa at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE were carried out by setting the working electrode potential at 0.4 V for the various concentration of methyl dopa in PBS (pH 7.0) (Fig. 4). For an electroactive material (methyl dopa in this case) with a diffusion coefficient of  $D$ , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [52].

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (1)$$

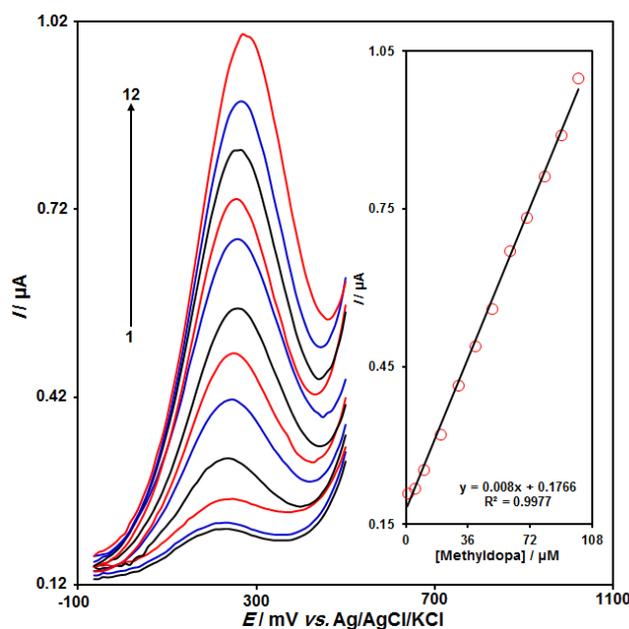
Where  $D$  and  $C_b$  are the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) and the bulk concentration ( $\text{mol cm}^{-3}$ ), respectively. Experimental plots of  $I$  vs.  $t^{-1/2}$  were employed, with the best fits for different concentrations of methyl dopa (Fig. 4A). The slopes of the resulting straight lines

were then plotted vs. methyldopa concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the  $D$  was found to be  $1.1 \times 10^{-6} \text{ cm}^2/\text{s}$ .

### 3.3. Calibration plot and limit of detection

The peak current of methyldopa oxidation at the surface of the modified electrode can be used for determination of methyldopa in solution. Therefore, differential pulse voltammetry (DPV) experiments were done for different concentrations of methyldopa (Fig. 5). The oxidation peak currents of methyldopa at the surface of a modified electrode were proportional to the concentration of the methyldopa within the ranges 1.0 to 100.0  $\mu\text{M}$ . The detection limit ( $3\sigma$ ) of methyldopa was found to be  $5.0 \times 10^{-7} \text{ M}$ .

In the case of hydrochlorothiazide peak currents of hydrochlorothiazide oxidation at the surface of  $\text{ZnO}/\text{Al}_2\text{O}_3/\text{SPE}$  were linearly dependent on the hydrochlorothiazide concentrations, over the range of  $1.0 \times 10^{-7}$ – $1.0 \times 10^{-4} \text{ M}$  (with a correlation coefficient of 0.9983) and the detection limit ( $3\delta$ ) was obtained  $8.0 \times 10^{-8} \text{ M}$ .

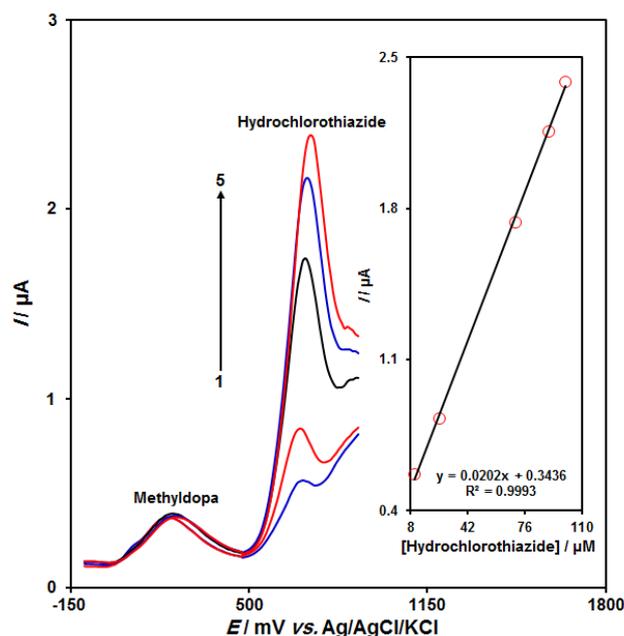


**Fig. 5.** DPVs of  $\text{ZnO}/\text{Al}_2\text{O}_3/\text{SPE}$  in 0.1 M (pH 7.0) containing different concentrations of methyldopa. Numbers 1–12 correspond to 1.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0  $\mu\text{M}$  of methyldopa. Inset: a plot of the electrocatalytic peak current as a function of methyldopa concentration in the range of 1.0–100.0  $\mu\text{M}$

### 3.4. Simultaneous determination of methyldopa and hydrochlorothiazide

It is pertinent to note that the use of modified electrode for simultaneous determination of methyldopa and hydrochlorothiazide has not reported so far and we believe that this work is

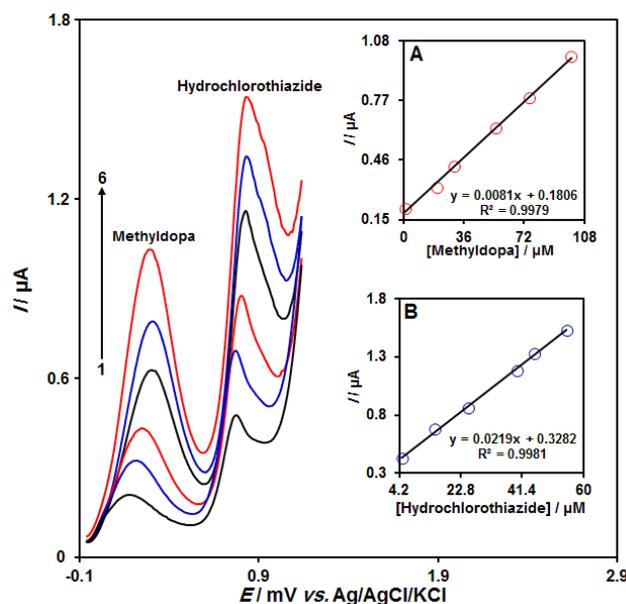
the first report on the simultaneous determination of methyldopa and hydrochlorothiazide using ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE.



**Fig. 6.** DPVs of ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE in 0.1 M PBS (pH 7.0) containing 25.0 μM methyldopa and different concentrations of hydrochlorothiazide. Numbers 1-5 correspond to 10.0, 25.0, 70.0, 90.0, and 100.0 μM of hydrochlorothiazide. Inset: plot of the electrocatalytic peak current as a function of hydrochlorothiazide concentration

The determination of methyldopa and hydrochlorothiazide in mixtures were performed at the ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE using DPV. The concentration of hydrochlorothiazide was varied, while keeping the methyldopa concentration constant. The results are shown in Fig. 6. When the concentration of methyldopa is kept constant at 25.0 μM, the peak current of hydrochlorothiazide is proportional to its concentration. No changes in the peak current and potential of methyldopa can be found.

Also, determination of two compounds was performed by simultaneously changing the concentrations of methyldopa and hydrochlorothiazide, and recording the DPVs (Fig. 7). The voltammetric results showed well-defined anodic peaks at potentials of 230 and 770 mV, corresponding to the oxidation of methyldopa and hydrochlorothiazide, respectively, indicating that simultaneous determination of these compounds is feasible at the ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE as shown in Fig. 7.



**Fig. 7.** DPVs of ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of methyldopa + hydrochlorothiazide in  $\mu\text{M}$ , from inner to outer: 1.0+5.0, 20.0+15.0, 30.0+25.0, 55.0+40.0, 75.0+45.0 and 100.0+55.0 respectively. Insets: (A) plot of  $I_p$  vs. methyldopa concentrations and (B) plot of  $I_p$  vs. hydrochlorothiazide concentrations

**Table 1.** The application of ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE for simultaneous determination of methyldopa and hydrochlorothiazide in methyldopa tablet, hydrochlorothiazide tablet and urine samples (n=5). All concentrations are in  $\mu\text{M}$

Sample	Spiked		Found		Recovery (%)		(%R.S.D.)	
	MD	HCT	MD	HCT	MD	HCT	MD	HCT
Methyldopa tablet	0	0	14.0	-	-	-	3.1	-
	2.5	5.0	16.9	4.9	102.4	98.0	2.9	3.2
	7.5	10.0	21.3	10.1	99.1	101.0	2.4	1.6
	12.5	15.0	26.1	15.5	98.5	103.3	2.7	2.9
	17.5	20.0	31.7	19.8	100.6	99.0	1.9	2.7
Hydrochlorothiazide tablet	0	0	-	10.0	-	-	-	2.9
	5.0	2.5	5.1	12.4	102.0	99.2	3.1	1.9
	10.0	7.5	9.7	17.8	97.0	101.7	2.8	3.2
	15.0	12.5	15.2	22.0	101.3	97.8	2.4	2.5
	20.0	17.5	19.8	28.5	99.0	103.6	2.5	2.1
Urine	0	0	-	-	-	-	-	-
	5.0	7.5	5.1	7.4	102.0	98.7	1.7	2.4
	15.0	17.5	14.9	17.9	99.3	102.3	3.2	2.1
	25.0	27.5	25.3	27.3	101.2	99.3	2.2	3.3
	35.0	37.5	34.1	37.9	97.4	101.1	1.9	2.9

### 3.5. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of methyldopa in methyldopa tablet, hydrochlorothiazide tablet and urine samples. The results for determination of the two species in real samples are given in Table 1. Satisfactory recovery of the experimental results was found for methyldopa and hydrochlorothiazide. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

### 4. CONCLUSION

ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE electrode was fabricated. Compared to bare SPE, the oxidation peaks of methyldopa and hydrochlorothiazide at ZnO/Al<sub>2</sub>O<sub>3</sub>/SPE were significantly amplified. The current increase is not only due to an increase in surface area but also due to facilitate in electron transfer by introducing ZnO/Al<sub>2</sub>O<sub>3</sub> nanocomposite. The modified electrode shows excellent analytical performance so that it can be utilized for simultaneous determination of methyldopa and hydrochlorothiazide in real samples.

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