**RESEARCH PAPER**

# A Certain Electrochemical Nanosensor Based on Functionalized Multi-Walled Carbon Nanotube for Determination of Cysteine in the Presence of Paracetamol

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## ARTICLE INFO

## ABSTRACT

The modified glassy carbon electrode (GCE) was prepared with 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (pyrazole derivative (AMPC)) and functionalized multi-walled carbon nanotubes. In this research, electrocatalytic activity of nanocomposite (AMPC/MWCNTs) has been studied by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA) methods. The electrocatalytic properties of the AMPC/MWCNTs nanocomposite for cysteine oxidation was considerably enhanced as compared to only AMPC. The kinetic parameters including the electron transfer coefficient ($\alpha$) and the heterogeneous constant rate (k') for oxidation of cysteine was studied by CV method. The diffusion coefficient of cysteine was calculated with aid of chronoamperometry (D=$9.51 \times 10^{-6}$ cm$^2$/s). The AMPC/MWCNTs modified electrode shows a linear response to cysteine in the range of 0.7 nM to 200.0 μM with detection limit of 0.16 nM. Also, differential pulse voltammetry was applied for the simultaneous determination of cysteine (CYS) and paracetamol (or acetaminophen, AC). Finally, the modified electrode was used for the detection of CYS and AC in human serums (real samples). The sensor produced good sensitivity, selectivity, reproducibility and stability features.

## INTRODUCTION

Cysteine, a thiol-containing amino acid, is one of the 20 amino acids which are found in proteins which play very important roles in many physiological processes such as protein synthesis, detoxification and metabolism [1]. Cysteine is an unnecessary category of alpha amino acids, because it is synthesized in the body under physiological conditions [2]. The thiol group in cysteine increases its reactivity by ionization and acts as a nucleophile. Due to the ability of this group to react with oxidation-reduction, cysteine has antioxidant properties. Cysteine plays an important role in biological systems and is widely applied in medicinal chemistry and nutritional chemistry [3] and has various pharmaceutical applications, including those that can be used in some antibiotics for the treatment of skin lesions [4] and protective against radio waves. Cysteine has the ability to combine with free radicals and low-level elements, which acts as a poisoning agent [5]. Cystinuria is a hereditary disease in which cysteine and some of the basic amino acids are damaged in brain cells. Therefore, measurement of cysteine in biological fluids and pharmacology is of great importance [6]. Different methods for measuring

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cysteine have been reported, including mass spectrometry [7], liquid chromatography [8] UV-Vis spectroscopy [9] HPLC [10] and electrochemical sensors [11]. Although the methods mentioned above are capable of measuring cysteine, but most of these techniques usually are expensive and complicated. On the other hand, cysteine measurement requires methods that have high sensitivity and high selectivity and can be measured in biological environments. Among these methods, electrochemical methods have great attention because electrochemical equipment is usually sensitive, simple in detection, rapidity and economical in comparison to the traditional equipment [12-14]. One of the methods that has been considered is the use of modified chemical electrodes that can facilitate selective oxidation of cysteine and by reducing its oxidation overvoltage can be measured in different samples.

Electrochemical investigations have been widely used for sensitive detections, particularly in trace compound contents. To do this, electrochemical methods have the advantage of chemically modified electrodes (CMEs).

Therefore, electrochemical methods are best for the determination of electroactive compounds CYS and paracetamol (AC). Paracetamol is widely used for the headaches, and also applied for relief of fever, and other types of minor pains. Paracetamol (AC) is often used in combination with other medications, like cold medications [15]. Paracetamol is a medication which is used for severe pain, like cancer pain and pain after surgery [16]. Due to the high over potential and low electron transfer rate of cysteine, the working electrode should be modified by modifier to promote a better electron transfer between the cysteine and electrode. A variety of materials such as polymer [17], metal oxide nanoparticles [18], and carbon based nanomaterials [19,20], have been applied for modification of electrode to improve the electrochemical performance of sensor. Among of carbon based nanomaterials, carbon nanotubes having extensive potential applications as electrocatalysts in electrochemical sensors due to the catalytic properties. In this research, 6-amino-4-(3,4-dihydroxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile was applied as a mediator in the electrode oxidation of CYS. Recent papers showed that some composite based on carbon nanotubes such as RuOx carbon nanotube [21], HCF multi-walled carbon nanotubes (MWCNTs) [22] and metal nanoparticles on multi-walled carbon nanotubes [23] could also act as platform in electrochemical sensors. We developed a pyrazole derivative functionalized carbon nanotubes composite as an excellent electrocatalyst for the detection of cysteine in human serums (real samples). The nanocomposite of pyrazole derivative and carbon nanotubes improved the sensivity and detection limit of the proposed sensing platform.

## MATERIALS AND METHODS
### Instrumentals and chemicals

$H_2SO_4$, $HNO_3$, cysteine, paracetamol, KCl, ethyl acetoacetate, and ethanol were purchased from Merck (Darmstadt, Germany). The MWCNTs (Outer diameter: 5–20 nm; Innerdiameter: 2–6 nm; length: 1–10 m and 95% pure) were bought from Plasma Chem (Germany). The AMPC were synthesized by a mixture of ethyl acetoacetate and hydrazine derivatives following the method reported in the literature [24]. Deionized water (DW) was applied for the preparation of all solutions. Morphologies of the CNTs were characterized applying a (SEM scanning electron microscopy, Hitachi S-4160). The electrochemical investigations were done via a potentiostat/galvanostat (SAMA 500, Iran). A platinum wire was applied as an auxiliary electrode, saturated calomel electrode (SCE) was applied as a reference electrode and AMPC/MWCNTs/GCE was applied a working electrode. A Metrohem model 691 pH/mV meter was applied for measuring the pH of solutions.

### Preparation of the nanocomposite (AMPC/MWCNTs)

The functionalized carbon nanotubes composite were prepared by mixture of one gram MWCNTs was suspended in 1 mL of concentrated $H_2SO_4$ and $HNO_3$ in 3:1 ratio (v/v) and ultrasonicated for 2 h to finally get a dispersed black colored solution of MWCNTs. It was allowed to cool down to room temperature for overnight. The suspension was centrifuged and washed several times with double distilled water and ethanol to remove the acid. Then, drying at 60 ºC for 24 h and characterized by SEM (Fig. 1). When oxidation is performed in the nanotubes top peaks are still identifiable. The SEM image demonstrate that this work do not damage the structure of carbon nanotube. The presences of functional
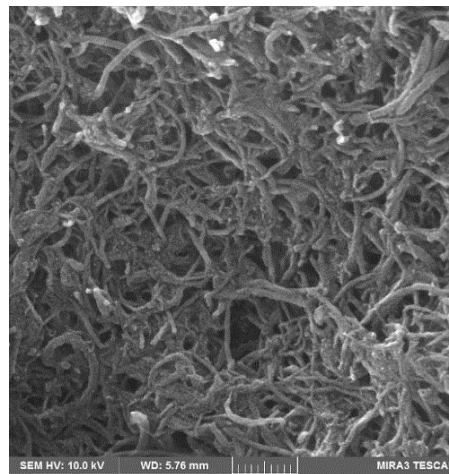
Fig. 1. The SEM image of the functionalized MWCNTs.

group on the surface of the nanotubes was confirmed by infrared spectroscopy. The AMPC/ MWCNTs nanocomposite was made by mixing 1.0 mg functionalized MWCNTs and 4.0 mg AMPC in 4.0 mL of double distilled water under stirring for 24 h at room temperature. The suspensions were centrifuged, and the samples were thoroughly rinsed with water to removal of the free AMPC from MWCNTs and then dried.

*Preparation of the electrode*

The bare GCE was polished successively on special cloth with alumina ($Al_2O_3$) powder and then washed well by distilled water. After that, a suspension was prepared by dispersing a 1 mg of nanocomposite in 1 mL double distilled water for 15 minutes in ultrasonic. Then, 2.5 µL of solution drop casting on GCE and at room temperature was placed to dry.

**RESULTS AND DISCUSSION**
*Electrochemical study of AMPC/MWCNTs nanocomposite*

Electrochemical methods are the simplest and best method used to study oxidation and reduction mechanisms of different species. In the section, cyclic voltammetry technique was used as valuable method for evaluation the AMPC behavior electrochemical. A pair of reversible peak are observed at $E_{pa}$=135 mV and $E_{pc}$=65 mV versus SCE, and $\Delta E_p = (E_{pa}-E_{pc})$ was 70 mV. Given that the peak separation potential is greater than the 59/n mV, then the reaction are quasi-reversible. CVs of the AMPC/MWCNTs/ GCE were

recorded at different potential scan rate (20-2600 mV/s), Fig. 2. Plots of both $I_{pa}$ and $I_{pc}$ were linearly dependent on scan rate, indicating that the redox properties of AMPC is not controlled by diffusion. Also, $\Delta E_p$ has increased with the scan rate. The surface coverage of the AMPC on the electrode estimated by sharp [25]. Using the slope $I_{pa}$ versus scan rate (inset A in Fig. 2) the estimated surface coverage of the AMPC on the nanocomposite is mol/cm$^2$ for n=2. The peak potential ($E_p$) shifted to less negative amounts on increasing the scan rate. A linear relationship between peak potential and logarithm of scan rate (inset C in Fig. 2) was observed. The slope of inset B Fig. 2 can be used calculate the electron-transfer rate constant ($k_s$) and transfer coefficient (α) for oxidation of CYS by laviron method [26]. The estimated value for the $α_a$=0.48 and $α_c$=0.52. The value of $k_s$=4.04 s$^{-1}$ was calculated by laviron equation (1).

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log\left(\frac{RT}{nF\upsilon}\right) - \alpha(1-\alpha)nF(\frac{\Delta Ep}{2.3RT}) \quad (1)$$

The electrochemical response of AMPC/ MWCNTs is generally pH dependent. Therefore, the electrochemical behavior of the modified electrode was investigated at different pHs (3.0-11.0) using CV. $E_p$ of AMPC/MWCNTs were shifted to less positive value with increasing in pH.

*Electrocatalytic oxidation of CYS at AMPC/ MWCNTs/GCE*

Fig. 3 show A comparison of the CV of AMPC/ MWCNTs/GCE in buffer solution (pH=7.0) at the scan rate of 25 mV/s in the presence 0.5 mM
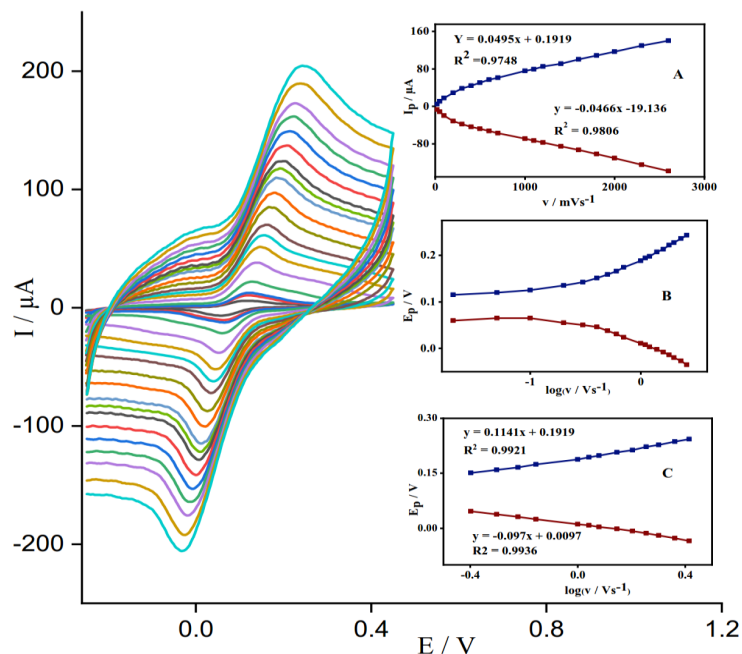
Fig. 2. CVs of AMPC/MWCNTs/GCE in 0.1 M Phosphate buffer (pH=7.0) at different scan rates, down to up at 20 to 2600 mV/s, a) variation of Ip versus scan rate, b) Ep versus logarithm of scan rates, c) magnification of ( inset b) for high scan rates.

(curve f) and absence (curve d) of CYS, no traceable signal is obtained on GCE (curve a), however in the presence of cysteine a weak CV signal is observed (curve b). The comparison of Fig. 3 c and f indicates that the anodic peak current ($I_{pa}$) of modifier was highly increased in the present of CYS over that usually observed only for the AMPC/AMPC' redox couple in GCE, while the cathodic peak ($I_{pc}$) was disappeared of the reverse scan of the potential. Based on these results $E_p$ for CYS oxidation at the AMPC/MWCNTs/GCE shifted toward less potential compared with GCE. However, the modified electrode (curve f) demonstrated higher current toward CYS compared to AMPC/GCE (curve e), indicating that the presence of AMPC on the functionalized MWCNTs could enhance the peak currents, which may because of the good catalytic features of MWCNTs including privileged electrical conductivity, high surface and high chemical stability. The comparison of these voltammograms shows that the increase of CYS to the electrolyte solution, the cathodic peak eliminated and the anodic peak current increasing. The fact represents an EC' catalytic mechanism (Fig. 4). The effect of potential scan rate (υ) on the electrocatalytic oxidation CYS of modified electrode by AMPC/MWCNTs composite investigated in the ranges of

5-40 mV/s in buffer solution (pH=7.0) (Fig. 5). As shown in Fig. 5, peak current little moved to high potential with increase in υ. Also, inset a Fig. 5 show that $I_p$ is related to the oxidation of the CYS linearly with square root of the scan rate potential increased. Therefore, it can be concluded that the electrocatalytic oxidation process of the CYS is under the control diffusion. A plot of scan rate normalized current ($I_p/\upsilon^{1/2}$) versus υ (inset b Fig. 5) demonstrate the characteristic shape of an EC' process. The Tafel plot obtained inset c at Fig. 5, which shows that one electron transfer process is a rate-limiting step (RDS) assuming a transfer coefficient (α=0.35).

*Chronoamperometric study*

Chronoamperometric measurement of CYS at AMPC/MWCNTs/GCE were done at potential of 200 mV for different concentration of CYS (Fig. 6), with a diffusion coefficient (D), the current has been seen for the electrochemical reaction at the mass transport limited condition is described for an electroactive material (cysteine) with cottrell equation [27]. A plot of I versus $t^{-1/2}$ will be linear for different concentration of CYS, according to slope and equation cottrell the value of D was estimated to be cm²/s (inset B Fig. 6). CHA can also
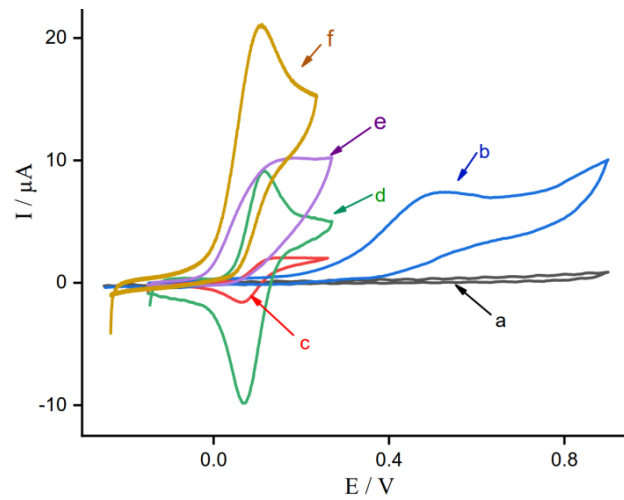
Fig. 3. CVs of a) GCE in 0.1 M PBS (pH 7.0) at υ = 20 mV/s and b) as (a) with 0.5 mM cysteine; c) as (a) at the surface of AMPC/GCE; d) as (a) at the surface of AMPC/MWCNTs/GCE; e) as (c) + 0.5 mM CYS; f) as (b) at the surface of AMPC/MWCNTs/GCE.
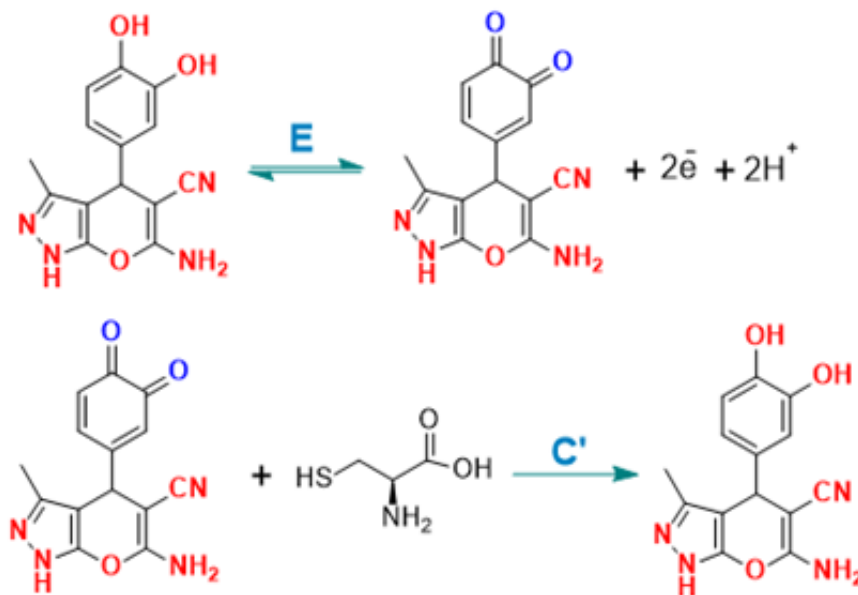


Fig. 4. Schematic of EC' catalytic mechanism.

be employed to study the catalytic rate constant (k'), for the reaction among AMPC/MWCNTs composite and CYS by Galus method [28] equation 2. According to this method the mean value of k'=991/64($M^{-1}s^{-1}$) was found.

$$\frac{I_c}{I_L} = \pi^{1/2}\Upsilon^{1/2} = \pi^{\frac{1}{2}}(kC_b t) \qquad for\ \Upsilon > 2 \qquad (2)$$

*Sensitivity of the electrochemical sensor and limit of detection*

The differential pulse voltammetry is a high sensitive method, (compare to the other methods such as cyclic voltammetry), it was applied to calculate the detection limit of cysteine. The dynamic linear range, current sensitivity and detection limit for CYS were evaluated by DPV.
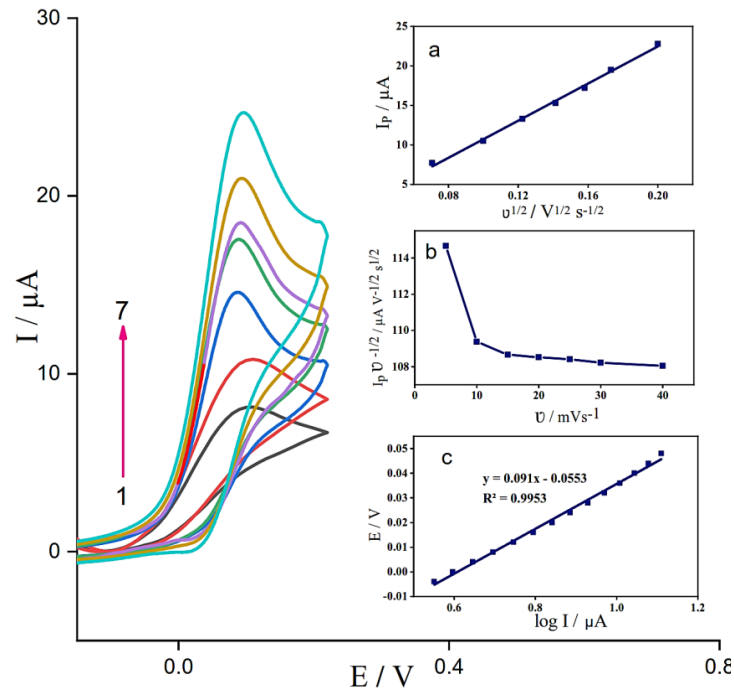
Fig. 5. CVs of AMPC/MWCNTs/GCE in 0.1 M PBS (pH 7.0) in percent of 0.5 mM cysteine at scan rates of 5-40 mV/s. Inset: a) Variations of Ip versus $\upsilon^{1/2}$, b) Variations in $\upsilon$ normalized current (Ip / $\upsilon^{1/2}$) versus $\upsilon$ and c) Tafel plot derived from the rising part of voltammogram recorded at $\upsilon$ = 20 mV/s.
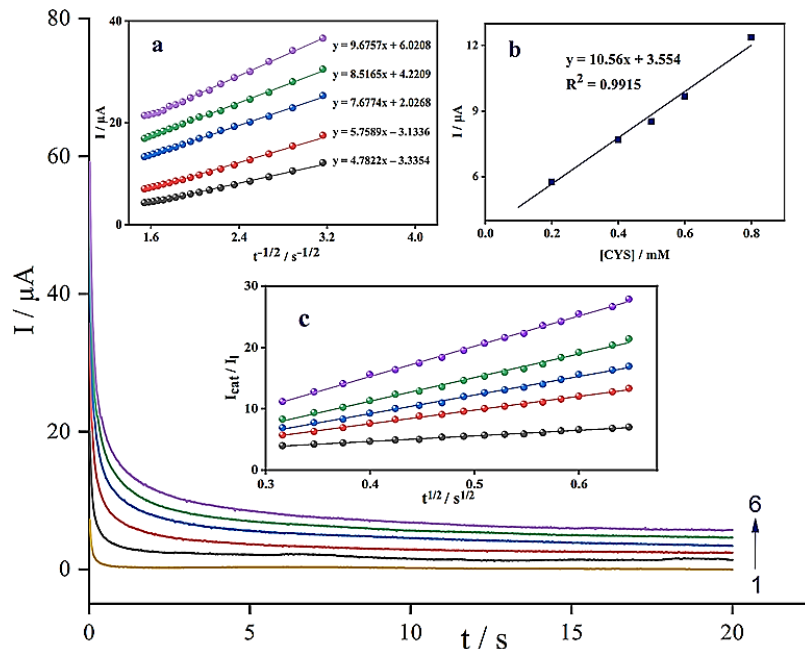


Fig. 6. Chronoamperograms obtained at AMPC/MWCNTs/GCE in 0.1 M PBS (pH=7.0) for the following concentration of CYS: 0.0-0.2-0.4-0.6-0.8 and 1.0 mM by setting potential step at 200 mV. Insets: a) plots of current versus $t^{-1/2}$, b) plot of the slope of the straight lines versus the CYS concentration.

Fig. 7 shows the differential pulse voltammograms obtained for variety concentration of CYS in PBS (phosphate buffer solution) (pH=7.0) for oxidation of CYS at the modified electrode. The $I_{pa}$ enhanced with the increase of cysteine. This inset (a) at Fig. 7 shows that the plot of $I_p$ versus different concentrations of CYS including of two linear part with various slopes. Based these results, the linear dynamic range 0.7 nM to 200.0 μM and a limit of detection of 0.16 nM were obtained.

*Simultaneous determination of cysteine and paracetamol at AMPC/MWCNTs/GCE*

The oxidation potential of paracetamol (AC) is very close to the peak potential of CYS when an unmodified electrode (GCE) is used as the working electrode, hence it could be concluded that the GCE (unmodified electrode) is not a good choise for investigation of the CYS in presence of the AC. Fig. 8 shown that CYS and AC oxidation can be separated using the modified electrode (AMPC/MWCNTs/ GCE) and the capability of the mentioned modified electrode for the determination of cysteine in the presence of different concentrations of AC is confirmed which denies its interference in the total electrochemical response. The DPV results, with two preferable anodic peak at potentials of 135 and 350 mV, corresponding to the oxidation

of CYS and AC at the AMPC/MWCNT/GCE was possible (Fig. 8).

*Interference study*

The effect of different interfering species on the determination of 100 μM cysteine studied. The tolerance limit (which was assumed as the maximum concentration of the interfering material), was about a nearly ±5% relative error in the detection. The tolerated concentration of interfering material was 0.1 M for asparagine, glucose, glycine, glutathione, tryptophan and folic acid.

*Real samples analysis*

To examine the capability of the mentioned modified sensor (AMPC/MWCNTs/GCE) for characterizing of cysteine, a blood serum sample was analyzed and the test results were repeated for five times. The results (RSD< 5%) showed that the AMPC/MWCNTs modified sensors has a good applicability for monitoring cysteine in real life samples. The result of real sample investigation are listed in table 1.

*The stability and repeatability of AMPC/MWCNTs/ GCE*
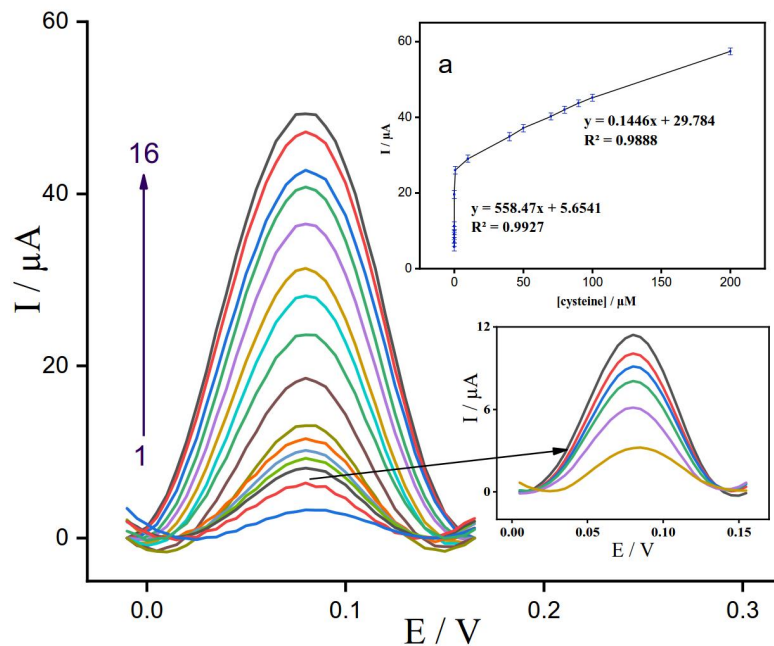
The reproducibility of the electrode surface



Fig. 7. DPVs of AMPC/MWCNTs/GCE in CYS solution at various concentration: 0.0007-0.002-0.004-0.006-0.008-0.01-0.09-0.4-0.8-10.0-40.0-50.0-70.0-90.0-100.0 and 200.0 μM. Inset, plot of peak current versus the concentration of CYS.
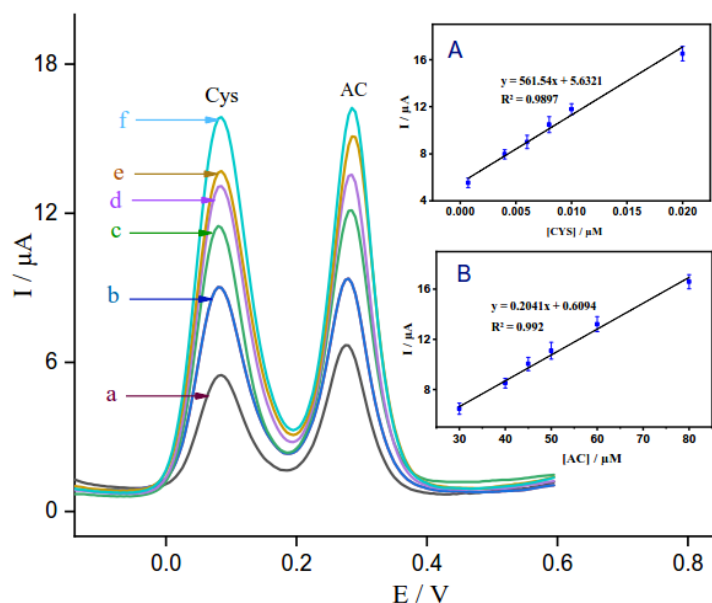
Fig. 8. DPVs of AMPC/MWCNTs/GCE in 0.1 M PBS (pH 7.0) containing various concentrations of AC+CYS mixed solutions: (a) 30.0+0.002, (b) 40.0+0.004, (c) 45+0.006, (d) 50.0+0.008, (e) 60.0+0.009, (f) 80+0.02. Insets A and B are plots of peak currents as a function of CYS and AC concentration.

Table 1. Determination of cysteine in real sample (blood serum) using DPV method (n=5)

| Cysteine Added (µM) | Found (µM) | (%) Recovery | (%) RSD |
|---|---|---|---|
| 0 | - | - | - |
| 1.0 | 1.05 | 105.0 | 2.7 |
| 5.0 | 5.19 | 103.8 | 2.3 |
| 10.0 | 9.61 | 96.1 | 3.1 |

was examined with DPV method for four different AMPC/MWCNTs/GCEs, which were prepared in the same optimum conditions. According to the results (RSD < 5%) the sensor has a good reproducibility (Fig. 9)

To investigate the long-term stability of the AMPC/MWCNTs/GCE, the mentioned modified sensor was kept under optimum condition for a whole week. According to the results (DPV investigations).

## CONCLUSIONS

In this research, a certain electrochemical sensor based on pyrazole derivatives and functionalized MWCNTs were engaged for simultaneous detection of cysteine and paracetamol.

According to the data, the diffusion coefficient of cysteine was about $cm^2/s$. The AMPC/MWCNTs modified electrode shows a good linear response to cysteine in the range of 0.7 nM to 200.0 µM with detection limit 0.16 nM.

According to the results, the sensor shows good repeatability and have applicability for monitoring paracetamol in real life samples.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.
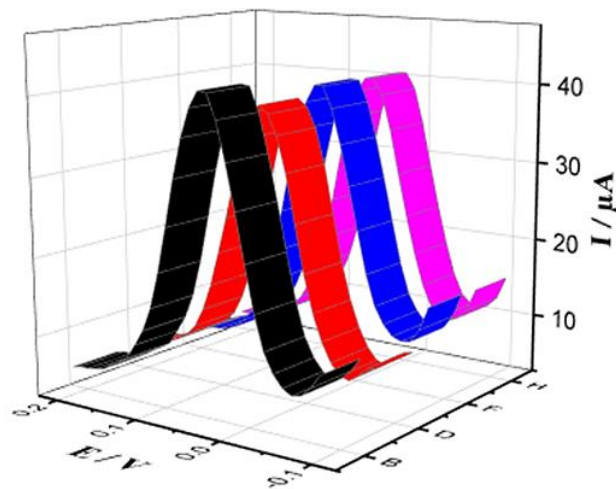
Fig. 9. Reproducibility of AMPC/MWCNTs/GCE in solution of 100.0 μM of CYS.

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