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*Original scientific paper*

# Voltammetric determination of epinine using carbon paste electrode modified by $ZnO/Al_2O_3$ nanocomposite

Safana Ahmed Farhan[1,✉], Mohammed Nawfal Alkhafaji[2], Noor Faraj Kadhem[3], Athraa H. Oraibi[3] and Hussein Ali Al-Bahrani[4]

[1]*Chemistry Department, College of Science, Mustansiriyah University, Baghdad, Iraq*
[2]*Department of Chemistry, College of Education for Pure Science, University of Kerbala, Iraq*
[3]*Polymer Research Unit, College of Science, Mustansiriyah University, Baghdad, Iraq*
[4]*College of Nursing, University of Al-Ameed, Department of Chemistry, College of Education for Pure Science, University of Kerbala, Iraq*

*Corresponding Author:* ✉*safanah@uomustansiriyah.edu.iq*

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***Abstract***

*We created a $ZnO/Al_2O_3$ nanocomposite and used it to modify a carbon paste electrode (ZAO/CPE) for epinine (EPNN) electro-oxidation, as EPNN is a sensitive electroactive material. The results showed a significant improvement in the electron-transfer reaction rate and catalytic performance of the as-produced $ZnO/Al_2O_3$ nanocomposite, which increased EPNN's current responses. The electrochemical activity of the EPNN on the ZAO/CPE was examined using chronoamperometry, cyclic voltammetry and differential pulse voltammetry. In the wide concentration range (0.05 to 290.0 µM), a linear calibration plot with high sensitivity was achieved. For the EPNN, the estimated limit of detection (S/N = 3) was 0.01 µM. The ZAO/CPE's repeatability, reproducibility, and stability were examined; the results showed better repeatability, reproducibility, and stability. The as-built sensor satisfactorily detected the research analytes in actual specimens.*

**Keywords**

Catecholamines; voltammetric sensor; deoxyepinephrine; sympathomimetic drugs

## Introduction

Catecholamines are a major group of drugs, with broad uses in biological systems [1]. Catecholamines make up the most important part of sympathomimetic drugs, which are often proposed for management of blood pressure issues and for cardiac arrest [1]. Epinine (EPNN) is a natural catecholamine compound, detected in certain plants and insects. It behaves similarly to epinephrine in terms of pharmacological effects. EPNN is suggested for the treatment of congestive

heart failure, mostly because it can work as a cleavage product of the prodrug ibopamine [2]. Still, Barger and Dale reported that EPNN may increase blood pressure, so it is not always "quiet" [3].

Besides, EPNN is also described as a replacement for epinephrine. If someone takes too much EPNN, it can be damaging for the human body, so the administration of this drug must be properly controlled in patients. To the best of our understanding, HPLC has been used to determine EPNN in biological samples [4]. Although HPLC has strong capacity for analysing many different drugs at low levels [4], it still has drawbacks: it usually requires expensive instruments and add-ons like an isolation system and temperature control, and the whole process can be costly and time-consuming [4,5].

The accurate detection of EPNN is thus critical not just for pharmaceutical quality control, but also for biological and clinical studies. Because EPNN includes an electroactive catechol moiety, it may be oxidised at electrode surfaces, making electrochemical methods particularly appealing for its detection. However, direct electrochemical oxidation of catecholamine compounds using ordinary electrodes may be hampered by sluggish electron-transfer kinetics, surface fouling, and poor analytical sensitivity.

Electrochemical technologies provide great sensitivity and selectivity. These approaches are often regarded as eco-friendly analytical methods because they use minimal reagents and are low-cost [6,7]. Carbon paste electrodes (CPEs) are commonly utilized as working electrodes (WE). They are often manufactured by combining graphite powder with a non-conductive binder, such as paraffin oil, which has several benefits. Furthermore, CPEs can be easily modified with electroactive chemical materials and nanomaterials to increase sensitivity and enhance electron transfer by increasing the electrode surface area [8]. NPs and metal oxides have been employed successfully to improve voltammetric signals and overall analytical performance [9].

Nanostructures offer many unique traits and seem promising for faster responses and higher sensitivity than planar sensor setups. The biggest benefits of using nanoparticles (NPs) to modify electrodes include improved electron-transfer kinetics, increased electroactive surface area, faster mass transport, better control over the NP surface, and controllable functionalization for specific functional groups [10]. In many situations, using NP-modified electrodes also made it easier to resolve overlapping peaks of analytes with close oxidation potentials [11].

Among metal oxide nanoparticles, zinc oxide (ZnO-NPs) acts as both an electronic and structural helper; it has a major impact on catalytic activity, while alumina or other refractory oxides offer long-term stability mostly as structural promoters [12]. Alumina can exhibit several phases, such as gamma, delta, theta, and alpha. Still, the alpha alumina form is the most thermodynamically stable phase. Broadly, alumina has many interesting properties, including high hardness, high stability, strong insulation, and even transparency. It is also used extensively in fire-retardant applications, catalysts, insulators, surface-protective coatings, and composite materials [13].

The analytical performance of an electrochemical sensor is strongly influenced by the physicochemical properties of the electrode surface. In this context, surface modification with nanostructured materials has emerged as an effective strategy to improve electrocatalytic activity and overcome limitations associated with conventional electrode materials. Nanocomposites are particularly attractive because combining two or more components can provide complementary properties that are difficult to achieve with a single material [14].

The $ZnO/Al_2O_3$ nanocomposite carbon paste-modified electrode (ZAO/CPE) was employed in this work as a straightforward, affordable, rapid, and sensitive electrochemical biosensor for EPNN determination. When determining EPNN in actual samples, the ZAO/CPEs demonstrated great sensitivity.

## Experimental

### *Apparatus and chemicals*

An Autolab potentiostat/galvanostat (PGSTAT 12N, Eco Chemie) was used for electrochemical measurements. A traditional three-electrode cell was employed at 25 ± 1°C. The working, auxiliary, and reference electrodes were ZAO/CPE, platinum wire, and a saturated calomel electrode. Analytical-grade EPNN and all other reagents were obtained from Merck Company. Orthophosphoric acid and its salts were used in the pH range of 4.0 to 9.0 to prepare the buffer solutions (PBS).

### *Synthesis of $ZnO/Al_2O_3$ nanocomposite*

Three grams of Al $(NO_3)_3.9H_2O$ were dissolved in 100 mL of pure water to create aluminium hydroxide. Ammonia solution was used to bring the pH to 8, and the solution was maintained at 60 °C for 18 hours. Acetone and ethanol were used to wash the precipitate three times each. The precipitate was aged at 75 °C for 24 hours to produce $Al(OH)_3$. Zinc nitrate (0.3 M) was dissolved in 75 millilitres of distilled water. After adding 0.14 g of aluminium hydroxide and adjusting the pH of the solution to 9.5 using a 20 % ammonium solution, the mixture was stirred for two hours at room temperature. The mixture was aged at 100 °C for four hours while being stirred at 300 rpm. Ethanol and distilled water were used to wash the $ZnO\text{-}Al_2O_3$ precipitate, respectively.

### *Preparation of $ZnO/Al_2O_3$ nanocomposite modified carbon paste electrode*

Using a mortar and pestle, 0.7 mL of paraffin oil, 0.95 g of graphite powder, and 0.05 g of $ZnO/Al_2O_3$ nanocomposite were combined to create a homogeneous paste for the ZAO/CPE. The paste was then put inside a glass tube. The surface of the carbon paste was polished with fine paper at the start of each experiment. The unmodified CPE was prepared without the $ZnO/Al_2O_3$ nanocomposite for comparison.

### *Preparing the real samples*

30 mL urine samples were centrifuged for 15 minutes at 3500 rpm. Following that, 30 mL of the solution was transferred into a 50 mL volumetric flask and diluted with phosphate-buffered (PBS) to a final volume of 50 mL and adjusted to pH 7.0. In the next stage, the diluted urine samples were spiked with various EPNN contents, and EPNN content was determined by differential pulse voltammetry (DPV) using the conventional addition procedure to prevent additional matrix effects.

## Results and discussion

### *Influence of pH*

The EPNN was then tested using DPV in different buffered solutions at pH values between 4.0 and 9.0. The highest anodic peak current ($I_{pa}$) was observed at pH 7.0; therefore, pH 7.0 was the appropriate pH (Figure 1). Additionally, for the voltammetric analysis, we chose 0.1 M PBS at pH 7.0 as the appropriate electrolyte (Figure 2A), since $I_{pa}$ is highest at pH 7.

Additionally, as the solution pH increased, the anodic peak potentials ($E_{pa}$) shifted linearly toward less positive values with a slope of -56.6 mV *per* pH unit, as shown in Figure 2B. This slope suggests that 2 electrons and 2 protons are transferred during the oxidation process of EPNN. Scheme 1 shows the suggested mechanism for the oxidation process of EPNN [5,6].

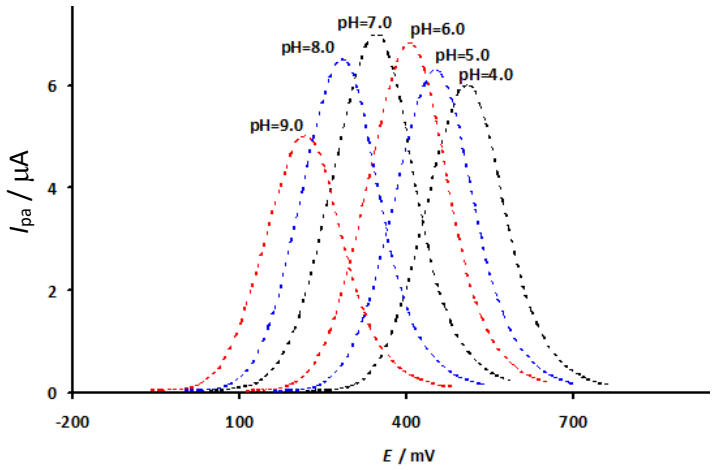



***Figure 1.*** *DPV responses of ZAO/CPE in 0.1 M PBS containing 50.0 µM EPNN at different pH*

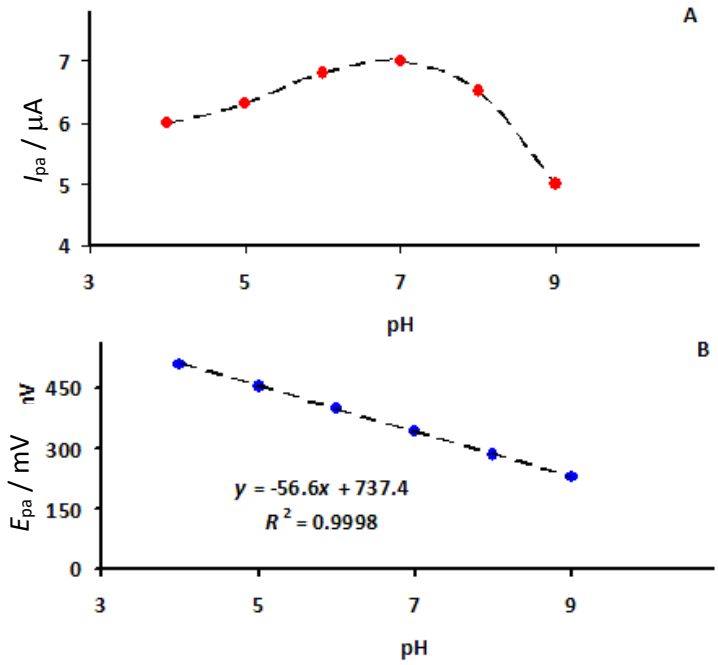
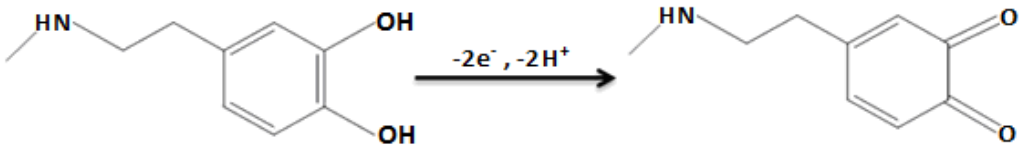



***Figure 2.*** *Dependence of (A)* $I_{pa}$ *and (B)* $E_{pa}$ *on pH of 0.1 M PBS with EPNN at ZAO/CPE*




***Scheme 1.*** *Schematic representation of the proposed mechanism for EPNN electro-oxidation at the ZAO/CPE*

*Electrochemical behaviour of epinine at $ZnO/Al_2O_3$ nanocomposite modified carbon paste electrode*

Cyclic voltammetry (CV) was used to examine the behaviour of EPNN (Figure 3) at the ZAO/CPE (curve B) and the unmodified CPE (curve A).

At a potential of 330 mV, which is over 100 mV less than the potentials at the unmodified CPE, EPNN was oxidized at the surface of the ZAO/CPE. Additionally, compared with the unmodified CPE, the $I_{pa}$ for EPNN at ZAO/CPE was 2.57 times larger. It should be mentioned that the addition of the $ZnO/Al_2O_3$ nanocomposite increased the electrochemical activity of bare CPE. This could be attributed to the nanomaterial's exceptional electron-transfer capacity and larger surface area.

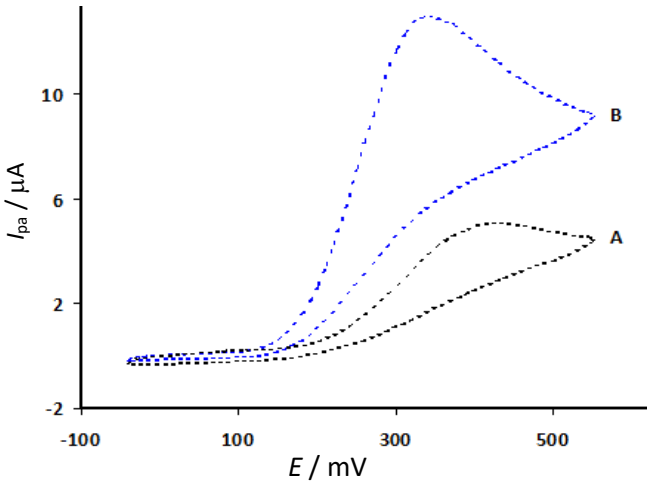



***Figure 3.*** *CVs at the unmodified (A) CPE and (B) ZAO/CPE in 0.1 M PBS containing 100.0 µM EPNN at* v = *50 mV* $s^{-1}$

*The effect of scan rate*

The effect of scan rate (*v*) on the oxidation process of 50.0 µM EPNN in pH 7.0 PBS at ZAO/CPE was examined. As shown in Figure 4, $I_{pa}$ increased with increasing scan rate. The results showed that peak currents for EPNN increased linearly with increasing $v^{1/2}$ (Figure 5), supporting both a diffusion-controlled mechanism for the oxidation reaction of EPNN on ZAO/CPE and the investigated *v* range.

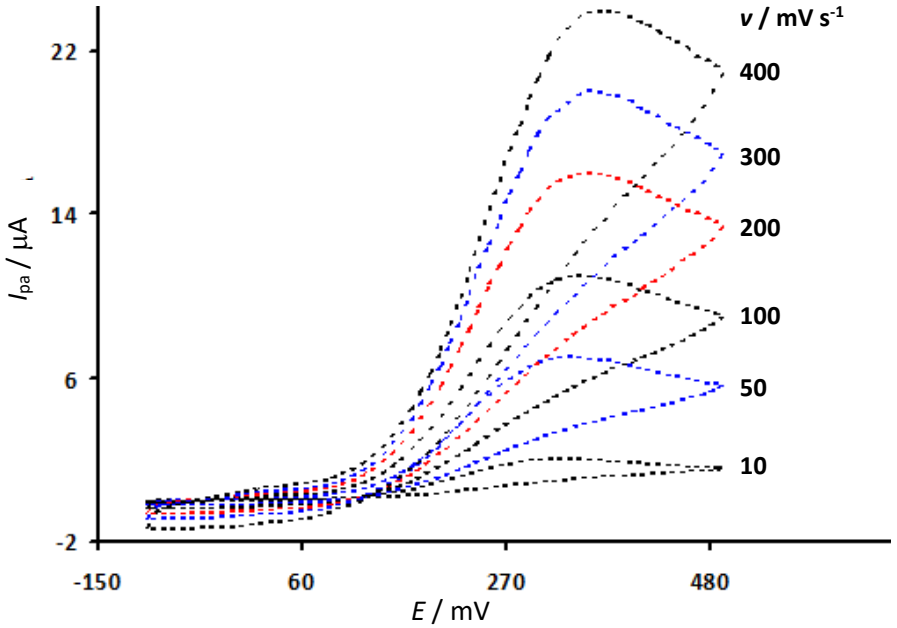



***Figure 4.*** *CVs of the ZAO/CPE in the presence of 50.0 µM EPNN at different scan rates*

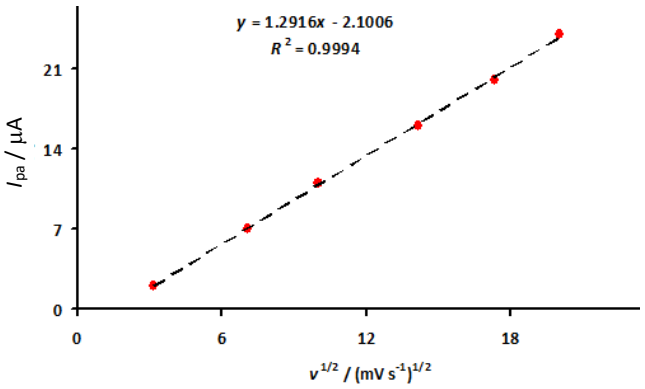



***Figure 5.*** *Relation of* I vs. $v^{1/2}$, *obtained from CVs in Figure 4*

*Chronoamperometric measurements*

Current *vs.* time curves were recorded for various EPNN concentrations at a ZAO/CPE surface (Figure 6).

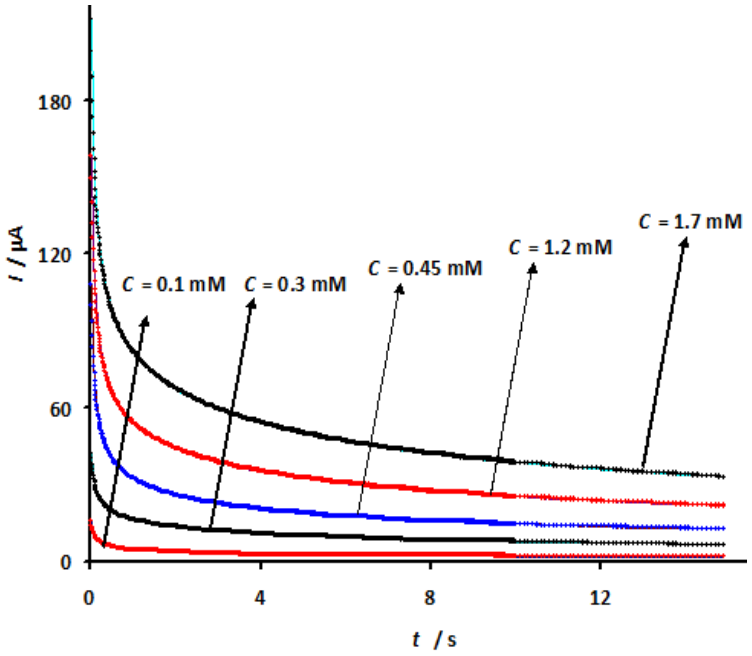



***Figure 6.*** *Single step chronoamperograms of ZAO/CPE in the presence of various concentrations of EPNN*

The Cottrell Equation (1) characterizes the electrochemical reaction's current (at a mass transport-limited rate):

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-½} \quad (1)$$

In the Cottrell equation, $D$ / cm$^2$ s$^{-1}$ represents the diffusion coefficient, and $C_b$ / mol cm$^{-3}$ represents the bulk concentration. Figure 7A displays the $I$ *vs.* $t^{-1/2}$ relationships at various EPNN concentrations. The linearity of the electrocatalytic current with respect to $t^{-1/2}$ indicates that EPNN oxidation takes place under diffusion control (Figure 7B). $D$ was found from the slopes to be $6.6\times10^{-6}$ cm$^2$ s$^{-1}$.

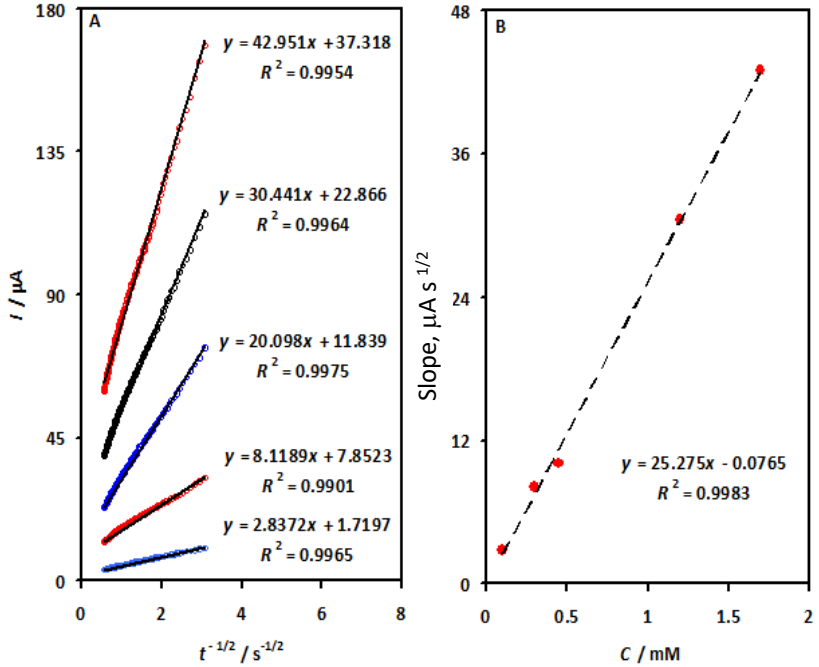



***Figure 7.*** *(A) Plot of I versus $t^{-1/2}$ for each of the chronoamperograms and (B) the plot of slope* vs. *different concentrations of EPNN*

*Quantitative determination of epinine using differential pulse voltammetry*

Quantitative measurements of EPNN were performed using the DPV method. Figure 8 shows the DPV responses of ZAO/CPE used to identify different EPNN concentrations. The $I_{pa}$ values of the recorded voltammograms progressively increased as the EPNN concentration increased. Additionally, the oxidation peak current of EPNN increased linearly from 0.05 to 400.0 µM, as shown in Figure 9 (calibration plot for EPNN determination at the ZAO/CPE). The limit of detection (LOD) was determined as 0.01 µM.

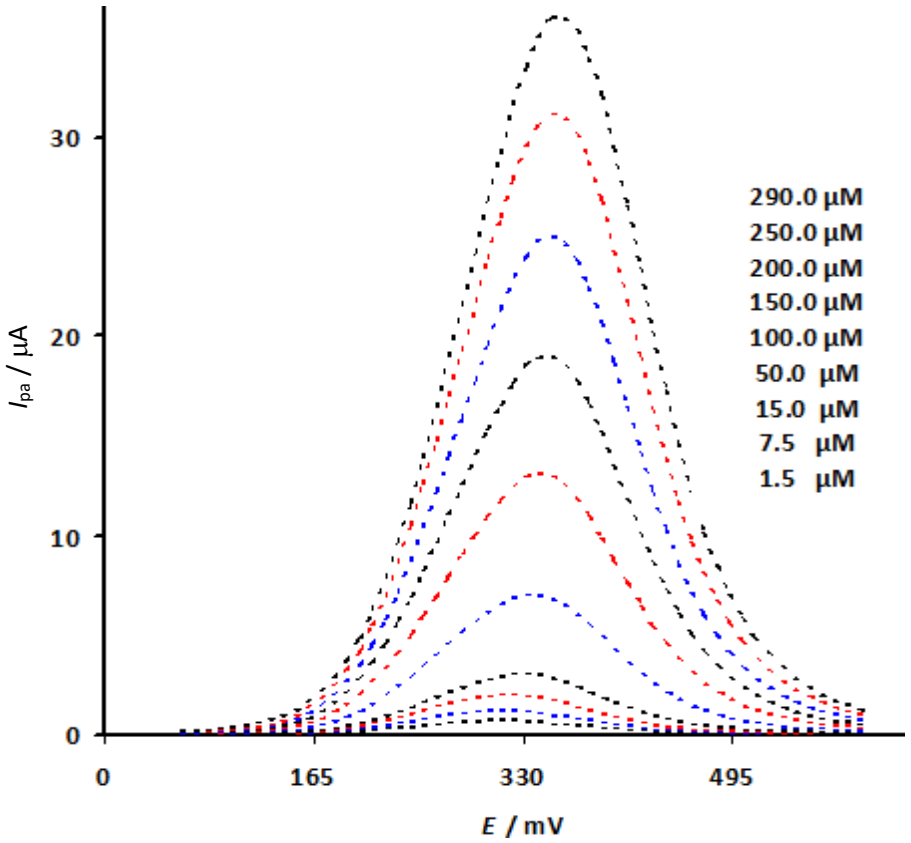



***Figure 8.*** *DPV responses of ZAO/CPE for various concentrations of EPNN under optimized voltammetric parameters*

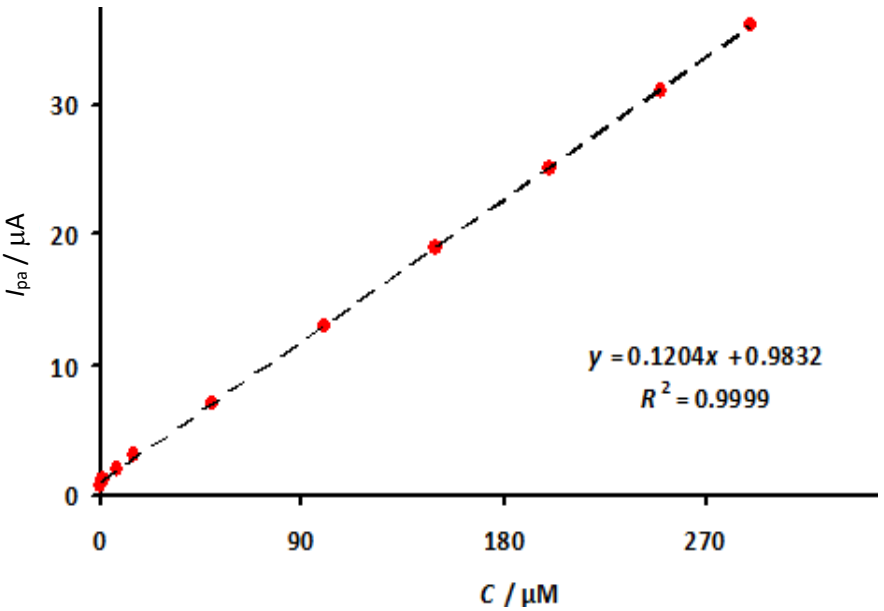



***Figure 9.*** *linear plot of the* $I_{pa}$ *vs. EPNN concentrations*

*The repeatability, reproducibility, and stability of the $ZnO/Al_2O_3$ nanocomposite modified carbon paste electrode*

Six consecutive measurements of 25.0 µM EPNN were used to assess the repeatability of the ZAO/CPE, with a relative standard deviation (RSD) of 5.0 %. This low RSD demonstrates excellent repeatability. Six ZAO/CPEs were separately made using the same process to evaluate fabrication repeatability. The 25.0 µM EPNN readings produced an RSD of 3.8 %, indicating the method's outstanding dependability. Additionally, the electrode was stored under ambient laboratory conditions to assess the ZAO/CPE's long-term stability. After three weeks of storage, the electrode retained 97.5 % of its initial electrochemical response. These findings showed that the stability of the ZAO/CPE is adequate.

*Analytical application*

The ZAO/CPE sensor was used to detect EPNN in the urine samples. The conventional addition method was used to calculate the EPNN concentration values. Table 1 summarizes the results; recovery ranged from 98.0 to 102.8 %, and all RSDs were less than or equal to 3.4 %. The testing results indicate that the ZAO/CPE sensor has strong potential for analytical applications.

***Table 1.*** *Experimental results from the analysis of EPNN in the urine sample using ZAO/CPE*

| Added | Found | Recovery, % | RSD, % |
|---|---|---|---|
| 0 | - | - | - |
| 5.0 | 4.9 | 98.0 | 3.0 |
| 7.0 | 7.2 | 102.8 | 2.1 |
| 9.0 | 8.9 | 98.9 | 1.8 |
| 11.0 | 11.1 | 100.9 | 3.4 |

## Conclusion

This work describes preparation of $ZnO/Al_2O_3$ nanocomposite (ZAO) using a straightforward method and assessed its electrochemical performance for epinine (EPNN) detection. The ZAO/CPE sensor was straightforward to prepare and required no intricate steps before detection. The results showed that the $ZnO/Al_2O_3$ nanocomposite has remarkable activity for EPNN detection, with a wide linear dynamic range between 0.05 and 440.0 µM and a low LOD of 0.01 µM. Additionally, this sensor successfully identified EPNN in spiked specimens.

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***Conflict of interest****: The authors have no conflict of interest.*

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