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Electrochemical Determination of Dopamine with Ruthenium (III)-Modified Glassy Carbon and Screen-Printed Electrodes

Safeta Redžića, Emira Kahrovićb, Adnan Zahirovićb, and Emir Turkušić b

ABSTRACT
Here is reported for the first time the application of sodium bis[N-2-oxyphenyl-5-bromosalicylideneiminato-ONO]ruthenate(III) as a mediator with multiwalled carbon nanotubes and Nafion at glassy carbon and screen-printed electrodes for the determination of dopamine in the presence of ascorbic acid. Electrochemical studies were performed using cyclic voltammetry, differential pulse voltammetry, and flow injection amperometry. In flow injection mode, the flow rate was 0.4 mL min⁻¹, the injection volume 250 µL, and the operation potential 0.05 V vs. Ag/AgCl. In 0.1M pH 7.5 phosphate buffer, the sensor provided a linear dynamic range up to 50 mg L⁻¹ dopamine with a detection limit of 0.11 ± 0.04 mg L⁻¹. The sensor was used for the determination of dopamine in ampoules of dopamine hydrochloride by cyclic voltammetry, differential pulse voltammetry, and flow injection amperometry.

Introduction
Dopamine is an important neurotransmitter that controls motor activity, autonomic and endocrine functions, and mental and emotional health of humans (Zhang et al. 2009; Jackowska and Krysinski 2013). The concentrations of dopamine in biological fluids range from $10^{-8}$ to $10^{-6}$ M (Li et al. 2011). Decreased dopamine in biological systems leads to Parkinson’s disease, while increased concentrations are associated with psychosis and schizophrenia (Li et al. 2011; Jackowska and Krysinski 2013). Therefore, the development and improvement of methods for dopamine determination, especially electrochemical methods, are of analytical interest.

Many electrochemical sensors have been developed for the determination of dopamine, based on carbon electrodes modified with various electron-transfer mediators, such as iron nanoparticles (Lai, Zhang, and Han 2008a), poly(2-picolinic acid), poly(sulfosalicylic acid) (Zhao, Zhang, and Yuan 2001), poly(3-acetylthiophene) (Aslanoglu et al. 2007), L-cysteine (Martinez-Huitlóa, Cerro-Lopezb, and Quirozb 2009), iron oxide/reduced graphene oxide (Peik-See et al. 2014), and copper nanocubes (Luo et al. 2014). In addition, some ruthenium complexes were used as modifiers including ruthenium(III) biphosphine complex (Wohnrath et al. 2005; Santos et al. 2007) and ruthenium complex with picoline...
and pyridine ligands (Ferreira et al. 2004), \( \text{Et}_4\text{NH}[\text{RuCl}_2L_2] \) where \( L \) represents the bromo and chloro derivatives of the salicylideneimine Schiff base (Kahrović et al. 2012; Turkušić and Kahrović 2012). To improve the oxidation of dopamine, carbon nanoparticles are being used, which may be single-walled carbon nanotubes (Chuekachang et al. 2010) or multiwalled carbon nanotubes (Britto, Santhanam, and Ajayan 1996).

Multiwalled carbon nanotubes are widely used in the development of sensors due to their favorable electrochemical properties, resulting from the presence of reactive groups on the surface, broad exploitable potential window and compatibility with dopamine in improving electron transfer on electrodes, selectivity, and reproducibility (Noroozifar et al. 2011; Esnafi et al. 2014). In complex biological systems, interferences may occur. One interference is ascorbic acid, which is found in biological fluids at much higher concentrations than dopamine (Alwarappan, Liu, and Li 2010; Zhou et al. 2010). Selective determination of dopamine in the presence of ascorbic acid is possible due to their differences in structure and ionic charge at physiological \( \text{pH} \) where dopamine is a cation \( (pK_b = 8.87) \), while ascorbic acid is an anion \( (pK_a = 4.10) \) (Zhou et al. 2010).

To develop selective sensors for dopamine in the presence of ascorbic acid, various modified electrodes have been developed that include electropolymerized macrocyclic \( \text{Ni(II)} \) complex (Yi et al. 2007), oxidized polypyrrole/graphene-modified glassy carbon electrode (Zhuang et al. 2011), and graphene-modified glassy carbon electrode (Ma, Chao, and Wang 2012). Nafion surface modification of electrodes by negatively charged ion-exchange membranes for selective determination of dopamine was successful at removing and blocking anionic interferences such as ascorbic acid (Zhang and Gorski 2005; Alothman et al. 2010; Quan et al. 2011; Zhao et al. 2013). The goal of this work is the development of a new selective sensor for dopamine in the presence of ascorbic acid. Here we report, for the first time, the application of a sodium bis[\( N\)-2-oxyphenyl-5-bromosalicylideneiminato-ON\( O \)]ruthenate(III) complex (hereinafter referred to as \( \text{Na[RuL}_2 \text{]} \) complex) as a redox mediator for dopamine oxidation in the presence of multiwalled carbon nanotubes and Nafion at glassy carbon and screen-printed electrodes.

**Experimental**

**Reagents and solutions**

The synthesis of \( \text{Na[RuL}_2 \text{]} \) complex was performed according to a previously published procedure (Kahrović, Zahiropvić, and Turkušić 2014). Multiwalled carbon nanotubes (type: L.MWCNTs-1030) were purchased from Advanced Chemicals. Dopamine hydrochloride and sodium ascorbate were purchased from Sigma-Aldrich; sodium dihydrogen phosphate and disodium hydrogen phosphate from Merck. Analytically pure 0.1M, \( \text{pH} \) 7.5 phosphate buffer was prepared from \( \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} \) and \( \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} \) in double-distilled and deoxygenated water with helium (99.995%, Messer Griesheim, Gumpoldskirchen, Austria). Solutions of dopamine and ascorbic acid were prepared in 0.1M, \( \text{pH} \) 7.5 phosphate buffer immediately before use. An ampoule of dopamine hydrochloride 40 mg mL\(^{-1}\) was obtained from Rotex Medica Trittau, Germany. A total of 20 mg L\(^{-1}\) Dopamine hydrochloride was prepared by diluting the dopamine hydrochloride (USP, 40 mg mL\(^{-1}\)) with deoxygenated 0.1M \( \text{pH} \) 7.5 phosphate buffer.
Electrode preparation

The glassy carbon electrodes were polished with 0.05 µm Al₂O₃ until a mirror was obtained, washed out with distilled water, and dried. The screen-printed electrodes were printed on inert porcelain plates (Coors Ceramic GmbH, Chattanooga, TN, USA). Four modified electrodes with Na[RuL₂] complex, Nafion, and multiwalled carbon nanotubes were prepared. The mixture for electrode modification was prepared by mixing the ruthenium complex (4 mg) dissolved in 50 µL of ethanol (depending on the modification), 2 mg of multiwalled carbon nanotubes, and 5 µL of 0.05% Nafion. The mixtures were homogenized for 15 min with ultrasound (Ultraschallgenerator PHYWE) before electrode modification. The glassy carbon and screen-printed electrodes were modified by adding 5 µL of homogenous suspension and dried for 30 min at room temperature.

Apparatus

All measurements were performed with Autolab PGSTAT-12 potentiostat/galvanostat with GPES software (Autolab software version 4.9). Modified and unmodified glassy carbon and screen-printed electrodes were used as working electrodes. The flow injection system consisted of a high-performance liquid chromatographic pump (Model 510, Waters, Milford, MA, USA), a sample injection valve (U6K, Waters), and a thin-layer electrochemical cell (CC5, BAS Bioanalytical systems Inc., West Lafayette, IN, USA). Teflon spacers (MF-1047, MF-1048, BAS) were used to adjust the thickness of the flow-through cell. A conventional three-electrode flow cell BAS 100 (BASi Dual 3-mm glassy carbon electrode MF-1000 for thin-layer flow cells, BAS CC-5) was used for measurements. An Ag/AgCl electrode (3M KCl, model RE-1, BAS) and the back plate of flow cell were used as the reference and counter electrode, respectively. For cyclic voltammetry and differential pulse voltammetry, a three-electrode cell was used with a platinum wire as the counter electrode, Ag/AgCl (Model 6.1227.000; Metrohm) as the reference electrode, and a modified glassy carbon or screen-printed working electrode. The pH values were measured using a meter (Thermo Orion, model 210+; Orion, Model SA 720) with the appropriate pH electrodes (SenTix 22 plus; A043019007).

Measurement protocols

All electrochemical determinations of dopamine were performed in 0.1M pH 7.5 phosphate buffer at ambient temperature. Flow injection analyses were performed at applied potentials of 0.00 and 0.05 V vs. the reference Ag/AgCl electrode. The typical flow rate was 0.40 mL min⁻¹ and the injection volume was 250 µL. Cyclic voltammograms were recorded from an initial potential of −0.30 to a second vertex potential of +0.40 V. The scan rates were 50 and 400 mV s⁻¹. The number of scans was 2; the equilibrium time was 5 s, and the step potential was 0.01998 V. Differential pulse voltammograms were recorded from an initial potential of −0.75 to the end potential of +0.75 V. The other differential pulse voltammetric parameters were an equilibrium time of 2 s, a modulation time of 0.006, an interval time of 0.6 s, a step potential of 0.1195 V, and a modulation amplitude of 0.40005 V.
Results and discussion

The ruthenium(III) complex, Na[RuL₂], is found to be suitable for electrode modification because it meets some basic requirements: water insolubility; availability in +2, +3, and +4 oxidation states; suitable stability; and reversible catalytic properties.

Electrochemistry of dopamine at modified and unmodified glassy carbon electrodes

The electrochemical behavior of the modified electrodes was characterized by cyclic voltammetry. Figure 1 shows typical cyclic voltammograms of dopamine in pH 7.5 phosphate buffer solution at an unmodified glassy carbon and a Na[RuL₂]-modified glassy carbon electrode at scan rate of 50 mV s⁻¹ for 50 mg L⁻¹ dopamine. The anodic current response on the modified Na[RuL₂]/glassy carbon electrode shows a significant increase for the oxidation of dopamine (Iₚₐ = 98.50 µA), that is, six times higher compared to the unmodified glassy carbon electrode (Iₚₐ = 15.26 µA) (Figure 1), confirming the mediating role of the Ru^{III}/Ru^{II} pair. A well-defined redox couple with highly improved peak current was observed on the Na[RuL₂]/modified glassy carbon electrode with a peak separation of 121 mV. The ratio of the anodic and cathodic peak current was 1 to 1, indicating that the process was quasi-reversible.

The reaction mechanism for the oxidation of dopamine at the Na[RuL₂] surface-modified glassy carbon electrode is shown in Scheme 1. Dopamine reacts with Na[Ru^{II}L₂] producing Na[Ru^{II}L₂] complex species at lower oxidation states and o-dopamine quinone. Na[Ru^{II}L₂] was reoxidized to Na[Ru^{III}L₂], generating an oxidation current proportional to the dopamine concentration.

Additional electrode modifications with carbon nanotubes and Nafion significantly improved the electrochemical response of dopamine (Figure 2). Nafion, a negatively charged ion-exchange membrane, attracted positive molecules of dopamine (pKₐ = 8.87).

Figure 1. Cyclic voltammograms at the unmodified glassy carbon electrode (curves a, b) and Na[RuL₂]-modified glassy carbon electrode (curves c, d) in the absence and presence of 50 mg L⁻¹ dopamine. The scan rate was 50 mV s⁻¹.
through electrostatic interaction and enhanced the anodic signal ($I_{pa} = 82 \mu A$). The voltammetric response of dopamine was increased at the Na[RuL2]/multiwalled carbon nanotubes/glassy carbon electrode with a current of ($I_{pa} = 185 \mu A$) at peak potential of 0.180 V compared to the Na[RuL2]/glassy carbon electrode and Na[RuL2]/Nafion/glassy carbon electrode. The multiwalled carbon nanotubes and Nafion significantly enhanced the current response to 225 $\mu A$ at the peak potential of 0.197 V.

**Influence of pH**

The electrochemical behavior of dopamine in 0.1M phosphate buffer at pH values from 3.0 to 9.0 was characterized by flow injection amperometry at an applied potential of 0.0 V at the Na[RuL2]/glassy carbon electrode. The comparison of the background current and

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**Figure 2.** Cyclic voltammograms of 50 mg L$^{-1}$ dopamine at the (a) bare glassy carbon electrode, (b) the Na[RuL2]/glassy carbon electrode, (c) Na[RuL2]/Nafion/glassy carbon electrode, (d) the Na[RuL2]/multiwalled carbon nanotube/glassy carbon electrode, and the (e) Na[RuL2]/multiwalled carbon nanotube/Nafion/glassy carbon electrode in 0.1M pH 7.5 phosphate buffer. The scan rate was 400 mV s$^{-1}$. 

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dopamine current shows that the background current is relatively stable over a wide range of pH values. At pH values from 6.00 to 9.00, the dopamine current increased. Hence, analytical measurements were performed at physiological pH 7.50.

**Influence of scan rate**

The influence of scan rate for dopamine in 0.1M pH 7.50 phosphate buffer was studied at the Na[RuL₂]/multiwalled carbon nanotube/Nafion/glassy carbon electrode by cyclic voltammetry (Figure 3). Linear relationships between the peak current and the scan rate from 20 to 700 mV s⁻¹ and the peak current and the square root of the scan rate (ν¹/₂) are shown.
in Figures 4 and 5, respectively. Anodic and cathodic peak currents increased with scan rate from 20 to 700 mV s$^{-1}$. However, the redox peak potential slightly shifted in the positive and negative directions for the anodic and cathodic reactions, respectively.

The redox peak current was plotted as a function of square root of scan rate and clearly showed that the linear dependence of peak current on the scan rate ended at 400 mV s$^{-1}$ (Figure 5). It has been reported that the relationship between the redox peak current and the scan rate may be expressed by the following relationships (Bard and Faulker 1980; Kim et al. 2004; Gal et al. 2008):

\begin{equation}
I_{pa} = kv^x
\end{equation}

\begin{equation}
\log I_{pa} = \log k + x \log v,
\end{equation}

Figure 5. Plots of peak current for the oxidation of dopamine at the Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode as a function of the square root of the scan rate: (a) anodic and (b) cathodic.

Figure 6. Plot of the logarithm of peak current for the oxidation of dopamine at the Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode as a function of the logarithm of the scan rate.
where $I_{pa}$ is the peak oxidation current density (mA cm$^{-2}$), $v$ is scan rate (mV s$^{-1}$), $k$ is a proportionality constant, and $x$ is the exponent of the scan rate. Since the electrode kinetics meet (1), the electrochemical redox reaction is under the electron transfer process control, where $x = 1$, or the reactant diffusion process, where $x = 0.5$. The oxidation current density ($\log I_{pa}$) was plotted as a function of scan rate ($\log v$), showing an approximately linear relationship ($r^2 = 0.9968$) from 20 to 400 mV s$^{-1}$ as shown in Figure 6.

The exponent of the scan rate is found to be 0.817. A slope larger than 0.5 may indicate that the electron transfer is also a limiting factor. This phenomenon may occur if additional processes take place, such as dopamine adsorption and restricting movement through the inner and outer Helmholtz planes.

**Analytical figures of merit**

The linear relationship between the current response and the concentration of dopamine was investigated by flow injection amperometry, cyclic voltammetry, and differential pulse voltammetry at the Na[RuL$_{2}$]/multiwalled carbon nanotube/Nafion/glassy carbon and screen-printed electrodes. A linear dependence between the amperometric response and concentration was found for flow injection amperometry (Figure 7) from 0.25 to 50 mg L$^{-1}$. The calibration relationship was dopamine $I$ (µA) = 0.0114 $\gamma$ (mg L$^{-1}$) + 0.0158, $r^2 = 0.9922$.

The current peak heights corresponding to dopamine concentrations (Figure 7) clearly demonstrate rapid response and reproducibility for dopamine. Dopamine was oxidized to dopamine quinone according to the mechanism shown in Scheme 1. The linear dynamic range by cyclic voltammetry (Figures 8 and 9) and differential pulse voltammetry (Figure 10) was consistent with the results obtained by flow injection amperometry.

![Figure 7](image-url). Amperometric flow injection response of dopamine at the screen-printed/Na[RuL$_{2}$]/multiwalled carbon nanotube/Nafion/carbon electrode. The concentrations of dopamine were (a) 0.25, (b) 0.5, (c) 1, (d) 2, (e) 5, (f) 10, (g) 20, (h) 40, (i) 50, (j) 60, and (k) 80 mg L$^{-1}$. The potential was 0.05 V vs. Ag/AgCl in 0.1M pH 7.5 phosphate buffer at a flow rate of 0.4 mL min$^{-1}$ and an injection volume of 250 µL.
The limit of detection (3σ) by flow injection amperometry, calculated from six injections of 250 µL volume of dopamine, corresponding to 0.25 mg L$^{-1}$, was 0.11 ± 0.04 mg L$^{-1}$. The comparison of these results for linear dynamic range and limit of detection with methods for dopamine is presented in Table 1. The reported device provided comparable (Liu, Sun, and Hu 2012) or lower detection limits (Bezzera et al. 2003; Ferreira et al. 2004; Lai et al. 2008a; Alothman et al. 2010; Noroozifar et al. 2011) for dopamine. In addition, the linear dynamic range was suitable for dopamine determination.

![Cyclic voltammograms](image1.png)

**Figure 8.** Cyclic voltammograms of (a) 2, (b) 4, (c) 5, (d) 10, (e) 20, (f) 30, (g) 40, and (h) 50 mg L$^{-1}$ dopamine in 0.1M pH 7.5 phosphate buffer at the modified Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode. The scan rate was 400 mV s$^{-1}$.

![Linear dependence](image2.png)

**Figure 9.** Linear dependence of the (a) anodic and (b) cathodic current response as a function of dopamine concentration in 0.1M pH 7.5 phosphate buffer at the modified Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode. The scan rate was 400 mV s$^{-1}$.
Electrochemical determination of dopamine in the presence of ascorbic acid at the Na[RuL₂]/multiwalled carbon nanotube/Nafion/glassy carbon electrode

The primary limitation for electrochemical determination of dopamine in biological fluids is the presence of ascorbic acid that may be oxidized at the same potential at an unmodified electrode. In addition, the concentration of ascorbic acid is typically higher than dopamine in biological samples. This problem may be solved using differential pulse voltammetry and appropriate electrode modification. In this work, differential pulse voltammetry was used to examine the influence of ascorbic acid upon the response of dopamine on the

Figure 10. Differential pulse voltammograms of the concentration of dopamine at the Na[RuL₂]/multiwalled carbon nanotube/Nafion/glassy carbon electrode in 0.1M pH 7.5 phosphate buffer. The concentrations of dopamine were (a) 2.5, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, (g) 50, and (h) 100 mg L⁻¹.

Table 1. Analytical figures of merit of the reported electrodes with values from literature references.

<table>
<thead>
<tr>
<th>Method</th>
<th>Linear dynamic range [µm]</th>
<th>Limit of detection [µm]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential pulse voltammetry</td>
<td>2–60</td>
<td>0.83</td>
<td>Lai et al. (2008a)</td>
</tr>
<tr>
<td></td>
<td>0.05–100</td>
<td>0.02</td>
<td>Esnafi et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>3–200</td>
<td>0.8</td>
<td>Alothman et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>1–210</td>
<td>0.19</td>
<td>Babaei, Babazadeh, and Momeni (2011)</td>
</tr>
<tr>
<td></td>
<td>10–110</td>
<td>3.3</td>
<td>Lai et al. (2008b)</td>
</tr>
<tr>
<td></td>
<td>5.0–500</td>
<td>1.5</td>
<td>Yang and Li (2014)</td>
</tr>
<tr>
<td></td>
<td>10–100</td>
<td>5</td>
<td>Plovman et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>5–25</td>
<td>3</td>
<td>Tsai et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>4–52</td>
<td>0.6</td>
<td>Liu, Sun, and Hu (2012)</td>
</tr>
<tr>
<td>Cyclovoltammetry</td>
<td>40–1200</td>
<td>40</td>
<td>Ferreira et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>5–200</td>
<td>2</td>
<td>Fan et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>1–30</td>
<td>0.35</td>
<td>Mani et al. (2015)</td>
</tr>
<tr>
<td>Linear sweep voltammetry</td>
<td>7.35–833</td>
<td>1.05</td>
<td>Noroozifar et al. (2011)</td>
</tr>
<tr>
<td>Constant potential amperometry</td>
<td>5–41</td>
<td>3</td>
<td>Fooladsaz et al. (2012)</td>
</tr>
<tr>
<td>Flow injection amperometry</td>
<td>200–20,000</td>
<td>150</td>
<td>Bezzera et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>1.31–263</td>
<td>0.61</td>
<td>This work</td>
</tr>
</tbody>
</table>
Na[RuL₂]/multiwalled carbon nanotube/glassy carbon electrode (Figure 11) and Na[RuL₂]/multiwalled carbon nanotube/Nafion/glassy carbon electrode (Figure 12).

A mixture of dopamine and ascorbic acid at Na[RuL₂]/multiwalled carbon nanotube/glassy carbon electrode distinguished two separate peaks belonging to ascorbic acid at −0.363 V and dopamine at +0.0625 V (Figure 11). Additional electrode modification with Nafion significantly diminished the ascorbic acid peak, as shown in Figure 12. The oxidation peak of ascorbic acid on −0.352 V is almost imperceptible, which can be attributed to strong electrostatic blocking of ascorbate ions due to the presence of Nafion. The oxidation peak of dopamine occurs at +0.110 V. The separation of dopamine and

**Figure 11.** Differential pulse voltammograms of 20 mg L⁻¹ dopamine and 200 mg L⁻¹ of ascorbic acid in 0.1M pH 7.5 phosphate buffer at the Na[RuL₂]/multiwalled carbon nanotube/glassy carbon electrode.

**Figure 12.** Differential pulse voltammograms of 20 mg L⁻¹ dopamine and 200 mg L⁻¹ ascorbic acid in 0.1M pH 7.5 phosphate buffer at the Na[RuL₂]/multiwalled carbon nanotube/Nafion/glassy carbon electrode.
Ascorbic acid peaks of 0.242 V contributes to the selective determination of dopamine in the presence of ascorbic acid.

Selectivity for dopamine in the presence of ascorbic acid on Na[RuL₂]/multiwalled carbon nanotubes/Nafion/glassy carbon electrode

Differential pulse voltammetric responses of various concentrations of dopamine, in the presence of 10 times higher concentration of ascorbic acid, on Na[RuL₂]/multiwalled carbon nanotubes/Nafion/glassy carbon electrode.

**Figure 13.** Differential pulse voltammograms of dopamine (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mg L⁻¹ in 10-fold excess ascorbic acid in 0.1 M pH 7.5 phosphate buffer at the Na[RuL₂]/multiwalled carbon nanotubes/Nafion/glassy carbon electrode.

Amperometric flow injection response for various concentrations of dopamine at the screen-printed/Na[RuL₂]/multiwalled carbon nanotube/Nafion/carbon electrode. The concentrations of dopamine were (a) 5, (b) 10, (c) 40, and (d) 20 mg L⁻¹ of dopamine hydrochloride injection. The potential was 0.05 V vs. Ag/AgCl in 0.1 M pH 7.5 phosphate buffer. The flow rate was 0.4 mL min⁻¹ and the injection volume was 250 µL.

**Figure 14.** Amperometric flow injection response for various concentrations of dopamine at the screen-printed/Na[RuL₂]/multiwalled carbon nanotube/Nafion/carbon electrode. The concentrations of dopamine were (a) 5, (b) 10, (c) 40, and (d) 20 mg L⁻¹ of dopamine hydrochloride injection. The potential was 0.05 V vs. Ag/AgCl in 0.1 M pH 7.5 phosphate buffer. The flow rate was 0.4 mL min⁻¹ and the injection volume was 250 µL.
carbon nanotube/Nafion/glassy carbon electrode are shown in Figure 13. Differential pulse voltammogram responses of dopamine provided a linear relationship ($r^2 = 0.9921$) for 5–50 mg L$^{-1}$ dopamine in the presence of 10-fold excess ascorbic acid. At a potential of +0.110 V, the oxidation of dopamine occurred, confirming a linear increase in the response with increasing dopamine concentration. The calibration curve was

![Figure 15](image1.png)

**Figure 15.** Differential pulse voltammograms for various concentration of dopamine at the Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode in 0.1M pH 7.5 phosphate buffer. The fortified concentrations of dopamine were (a) 0, (b) 5, (c) 10, (d) 35, and (e) 20 mg L$^{-1}$ of dopamine hydrochloride injection and 200 mg L$^{-1}$ of ascorbic acid.

![Figure 16](image2.png)

**Figure 16.** Cyclic voltammograms in 0.1M pH 7.5 phosphate buffer at Na[RuL$_2$]/multiwalled carbon nanotube/Nafion/glassy carbon electrode following the addition of dopamine. The concentrations of dopamine were (a) 10, (b) 30, (c) 50, and (d) 20 mg L$^{-1}$ dopamine hydrochloride injection and 200 mg L$^{-1}$ ascorbic acid. The scan rate was 400 mV s$^{-1}$. 
Table 2. Determination of dopamine in dopamine hydrochloride injection by differential pulse voltammetry, cyclovoltammetry, and flow injection amperometry ($n = 3$).

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration of dopamine (mg L$^{-1}$) (labelled)</th>
<th>Concentration of ascorbic acid (mg L$^{-1}$) (added)</th>
<th>Regression equation</th>
<th>Concentration of dopamine (mg L$^{-1}$) (found)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow injection amperometry</td>
<td>20</td>
<td>–</td>
<td>$I_{pa}$ (µA) = 0.0267 γ (mg L$^{-1}$) + 0.1780, $r^2 = 0.9991$</td>
<td>20.01 ± 0.04</td>
<td>100.05</td>
</tr>
<tr>
<td>Differential pulse voltammetry</td>
<td>20</td>
<td>200</td>
<td>$I_{pa}$ (µA) = 1.2903 γ (mg L$^{-1}$) + 905.16, $r^2 = 0.9925$</td>
<td>20.07</td>
<td>100.35</td>
</tr>
<tr>
<td>Cyclovoltammetry</td>
<td>20</td>
<td>200</td>
<td>$I_{pa}$ (µA) = 1.3575 γ (mg L$^{-1}$) + 43.241, $r^2 = 0.9968$</td>
<td>20.08</td>
<td>100.40</td>
</tr>
</tbody>
</table>
$I_{pa} (\mu A) = 1.0684 \gamma (mg L^{-1}) + 907.39, r^2 = 0.9921$. The measurements were performed at the physiological pH of 7.50 according to the published results (Zhou et al. 2010).

**Determination of dopamine in pharmaceuticals in the absence and presence of ascorbic acid**

The Na[RuL2]/multiwalled carbon nanotube/Nafion/glassy carbon electrode was used to determine and analyze a dopamine hydrochloride injection with a labeled concentration of 40 mg mL$^{-1}$ used for heart treatment. Dopamine was determined by flow injection amperometry (Figure 14), differential pulse voltammetry (Figure 15), and cyclic voltammetry (Figure 16) with $r^2$ greater than 0.99 for all methods. The results are shown in Table 2. The recoveries were acceptable for all methods, showing these protocols were suitable for the determination of dopamine in injections.

**Conclusion**

A simple, rapid, and direct modification of glassy carbon and screen-printed electrodes with stable Na[RuL2] complex, multiwalled carbon nanotubes, and Nafion provided selective determination of dopamine in the presence of large concentrations of ascorbic acid. The electrocatalytic properties of the Na[RuL2] complex were enhanced in the presence of multiwalled carbon nanotubes and Nafion. The modified Na[RuL2]/multiwalled carbon nanotubes/Nafion/glassy carbon electrode exhibited a wider linear range (1.31–263 µmol L$^{-1}$) and lower limit of detection (0.61 µmol L$^{-1}$) using flow injection analyses for dopamine compared with previously reported sensors for dopamine. The modified electrode demonstrated a rapid current response, good reproducibility, and was suitable for the selective determination of dopamine in pharmaceutical formulations by flow injection amperometry, differential pulse voltammetry, and cyclic voltammetry in the absence and presence of ascorbic acid with the recovery values 100.05, 100.35, and 100.4%, respectively.

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**References**


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