engineering proceedings

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Proceeding Paper

Oxidative Grafting of Adrenaline onto Carbon Electrode Surface: Preliminary Studies †

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† Presented at the 2nd International Electronic Conference on Chemical Sensors and Analytical Chemistry, 16–30 September 2023; Available online: https://csac2023.sciforum.net/.

Abstract: In the present work, we performed the optimization of electrografting of adrenaline onto a glassy carbon electrode surface. The cyclic voltammetry technique was used to immobilize the compound on the electrode surface by immersing it in an acidic adrenaline solution. This grafting was achieved by conducting 20 successive CV scans over a wide potential range. The stability of the obtained layer was analyzed using the SWV technique. The conducted research shows that it is possible to create a stable adrenaline layer on the GCE surface using voltammetric techniques. Additionally, once a stable layer was immobilized, its sensitivity to certain metal cations—which cannot be directly detected electrochemically—was verified. After exposing the sensor to designated cationic solutions, there was a significant decrease in the adrenaline signal. This suggests potential future applications in cation determination.

Keywords: voltammetry; adrenaline; epinephrine; grafting; glassy carbon electrode

Citation: Machura, G.; Seroka, J.; Smarzewska, S.; Koszelska, K. Oxidative Grafting of Adrenaline onto Carbon Electrode Surface: Preliminary Studies. *Eng. Proc.* **2023**, *48*, 65. https://doi.org/10.3390/CSAC2023-16285

Academic Editor: Nicole Jaffrezic-Renault

Published: 16 November 2023

1. Introduction

Electrochemical modification of an electrode entails a process where the electrode undergoes electrochemical treatments to deposit specific chemical species on its surface. Such modifications are conducted to increase sensitivity, reduce detection limits, enhance selectivity, increase specificity, or enable the analysis of electrochemically inactive compounds [1]. In the case of amines, such modifications are denoted as grafting. This process involves the formation of a covalent bond between the amino group and the electrode surface [2].

Adrenaline, also known as epinephrine (*Adn*, Figure 1), is an organic chemical molecule that belongs to the catecholamine group of neurotransmitters [3].

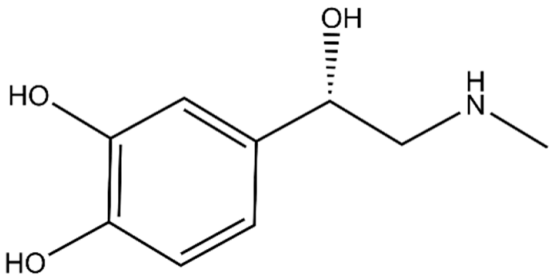

Figure 1. Chemical structure of adrenaline.

Compounds possessing a quinone–hydroquinone system, such as dopamine or adrenaline, are electrochemically active. When subjected to the appropriate potential, the quinone form can be reversibly reduced to its hydroquinone form [4,5]. A strategy for

altering the surface of the electrodes using a dopamine solution is described in the existing literature [5–7]. The amino group within the dopamine structure, due to its available free electron pair, can form a covalent bond with the glassy carbon electrode (GCE) surface. This results in a thin dopamine layer on the electrode [5]. In the mentioned study, an irreversible signal from the oxidation of the amino group was obtained, which gradually decreased during the deposition process. This trend indicates successful dopamine deposition and affirms the effective covalent attachment of dopamine to the electrode surface. Due to the significant structural similarity between adrenaline and dopamine, we considered it reasonable to attempt immobilizing *Adn* on the surface of the working electrode. Once a stable *Adn* layer formed on the electrode surface, we sought to investigate whether the developed sensor could detect the presence of selected metal cations (Ca^{2+}, Mg^{2+}, and Fe^{3+}). Notably, Ca^{2+} and Mg^{2+} ions are not electrochemically active and hence cannot be directly determined using electrochemical techniques. Demonstrating the sensitivity of the developed sensor to Ca^{2+} and Mg^{2+} cations can establish an analytical method for their indirect determination.

The aim of this study was to assess the suitability of adrenaline as a modifier for working electrode surfaces in voltammetry. The investigations involved the electrochemical deposition of adrenaline onto a GCE surface. This process was initially optimized. Subsequently, an attempt was made to verify whether the developed sensor allows for the detection of selected metal cations.

2. Materials and Methods

2.1. Instrumentation and Working Electrode Preparation

Cyclic (CV) and square wave (SWV) voltammetric experiments were conducted using an EmStat3 potentiostat, managed by PSTrace 4.7 software. An electrode stand from mtm-anko, equipped with a three-electrode system, was utilized. This system included a GCE as the working electrode, a silver/silver chloride electrode (Ag/AgCl) as the reference electrode, and a platinum wire (Pt) as the auxiliary electrode. All chemicals used were of analytical grade. Adrenaline was purchased from Merck (Darmstadt, Germany). A stock standard solution of *Adn* was prepared by dissolving the appropriate amount of the analyte in H_2SO_4 at a concentration of $C = 1.6 \times 10^{-2}$ mol·L^{-1}. Given that *Adn* is more soluble in aqueous solutions containing mineral acids, the solution was stored at 4 °C. Sulfuric acid with a concentration of $C = 1.0 \times 10^{-2}$ mol·L^{-1} was used as a supporting electrolyte.

Before the deposition procedures, the working electrode surface was thoroughly cleaned by polishing with alumina slurry. Additionally, the electrode underwent electrochemical cleaning using the cyclic voltammetry technique. This cleaning involved sweeping the potential between 0.1 and 2.0 V in the supporting electrolyte (H_2SO_4 with $C = 1.0 \times 10^{-2}$ mol·L^{-1}), a process that was repeated six times.

2.2. Research Methodology

All measurements were performed using both CV and SW voltammetry. Unless stated otherwise, the voltammetric experiments during the adrenaline immobilization consisted of the following steps (Table 1). Stage I: Deposition of *Adn* onto a GCE using cyclic voltammetry. Stage II: Evaluation of the stability of the obtained adrenaline layer. This was achieved by immersing the modified electrode into a pure supporting electrolyte solution (H_2SO_4 with $C = 1.0 \times 10^{-2}$ mol·L^{-1}) and subsequently recording the signal from this layer using square wave voltammetry. Before proceeding to the next stage, the electrode was immersed in metal cation solutions (Ca^{2+}, Mg^{2+}, and Fe^{3+}). Stage III: After a specific incubation time in the metal cation solution, the electrode was thoroughly rinsed. Subsequent measurements were then conducted, mirroring those in Stage II, to assess whether the metal cations had any impact on the signals detected.

Table 1. Detailed description of research methodology.

Stage	Performed Actions	Measurement Conditions
	Cleaning of the working electrode surface	
I	Deposition of the adrenaline on the GCE surface	CV technique, 20 scans, measurement cell: $C_{Adn} = 1.0 \times 10^{-3}$ mol·L^{-1}, $C_{H_2SO_4} = 1.0 \times 10^{-2}$ mol·L^{-1}
	Thorough rinsing of the electrode using distilled water	
II	Verification of the stability of the deposited layer	Technique SWV, 1 scan, measurement cell: $C_{H_2SO_4} = 1.0 \times 10^{-2}$ mol·L^{-1}
	Immersion of the electrode in a metal cation solution (5 min), thorough rinsing of the electrode using distilled water	
III	Evaluation of the sensitivity of the formed layer towards chosen metal cations	Technique SWV, 1 scan, measurement cell: $C_{H_2SO_4} = 1.0 \times 10^{-2}$ mol·L^{-1}

3. Results and Discussion

3.1. Deposition of Adrenaline on the Surface of GCE

Adn deposition onto the GCE surface was carried out within a potential range of 0.1–2.0 V, through 20 successive scans. To investigate the reproducibility of this process, several measurement series were conducted, ensuring uniform electrode modification each time. During the experiments, reversible signals were detected from the quinone–hydroquinone redox pair present in the epinephrine. Voltammograms obtained from Stage I, as part of a selected measurement series, are depicted in Figure 2.

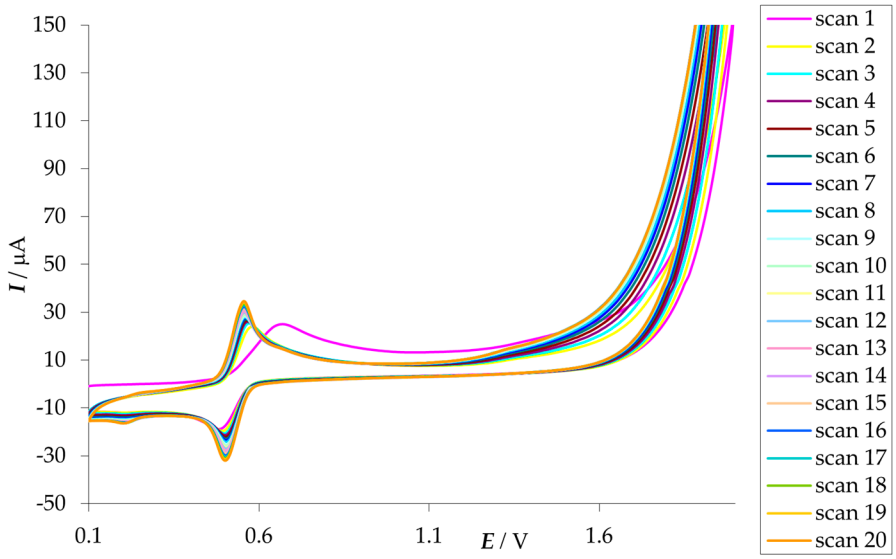

Figure 2. CV voltammograms obtained for the selected measurement series during Stage I—deposition of adrenaline on the surface of GCE recorded in sulfuric acid at pH 1.7.

Several measurement series were conducted, with the electrode modification process consistently carried out in the same way each time. This resulted in the formation of a stable adrenaline layer on the surface of GCE. In the subsequent stage of the study, the optimization of this process was conducted to increase its efficiency.

3.2. Optimization of the Initial Potential—Stage I

In this study, the potential window, specifically the initial deposition potential, was optimized as it significantly influenced the signal from the deposited layer. The aim was to determine the most suitable potential window that ensured an efficient and repeatable deposition of adrenaline molecules onto the electrode surface. For this purpose, the initial potential (E_i) was performed, employing a potential range from −0.2 to 0.25 V. The other parameters related to this process are detailed in Table 2.

Table 2. Parameters applied during the optimization of the initial potential E_i.

	Measurement Cell	E_i	E_f	ν	ΔE_i	E_{sw}	f	Number of Scans	Technique
Stage I	C_{Adn} =1.0 × 10^{-3} mol·L^{-1} and C_{H2SO4} = 1.0 × 10^{-2} mol·L^{-1}	−0.2–0.25 V	2.0 V	0.060 V·s^{-1}	0.005 V	-	-	20	CV
Stage II	C_{H2SO4} = 1.0 × 10^{-2} mol·L^{-1}	0.0 V	1.0 V	-	0.005 V	0.025 V	25 Hz	1	SWV

Stage II focused on testing the stability of the adrenaline layer on the GCE surface. This involved comparing the peak heights obtained from various E_i values used in Stage I. During these tests, the measurement cell contained only the supporting electrolyte. Therefore, the signals recorded were exclusively from the oxidation of the *Adn* layer. For a detailed comparison of peak heights, all signals from Stage II are displayed in a single voltammogram (Figure 3).

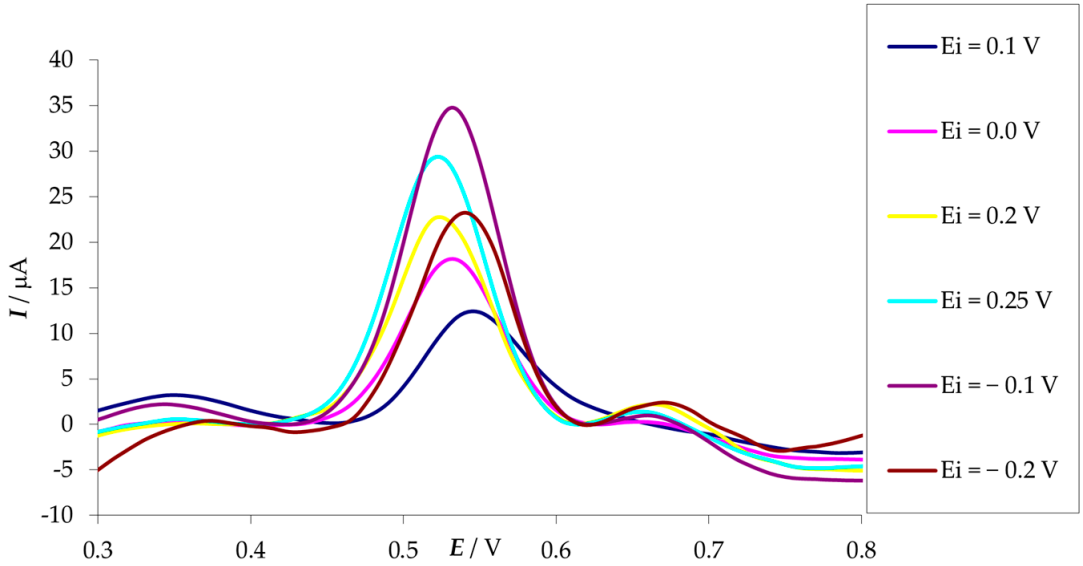

Figure 3. Comparison of voltammograms obtained during Stage II of the procedure for different values of E_i used in Stage I.

From the obtained results, it is concluded that the signals originating from the oxidation of *Adn* in Stage II were highest when adrenaline deposition in Stage I began at the potential E_i = −0.1 V. Based on the observed dependency, −0.1 V was chosen as the initial potential for adrenaline deposition in subsequent investigations.

3.3. Sensitivity Study of the Formed Layer to Selected Metal Cations

Upon achieving a stable epinephrine layer, using the procedure previously outlined, the research proceeded to Stage III. The electrode, now modified, was incubated for 5 min in solutions containing metal cations (Ca^{2+}, Mg^{2+}, and Fe^{3+}), each at a concentration of C = 1.0 × 10^{-6} mol·L^{-1}. The influence of each cation was analyzed separately. Following this incubation, the electrode was thoroughly rinsed, and voltammograms were recorded in the same way as in Stage II, using the SWV technique in a pure supporting electrolyte solution. The optimized parameter E_i = −0.1 V was consistently applied across all measurements.

Three measurement series were conducted for each of the analyzed cations. To facilitate a comparison between the signals from Stages II and III, they were summarized into a single graph for each cation (Figure 4A–C). These graphs show the signals from one chosen measurement series.

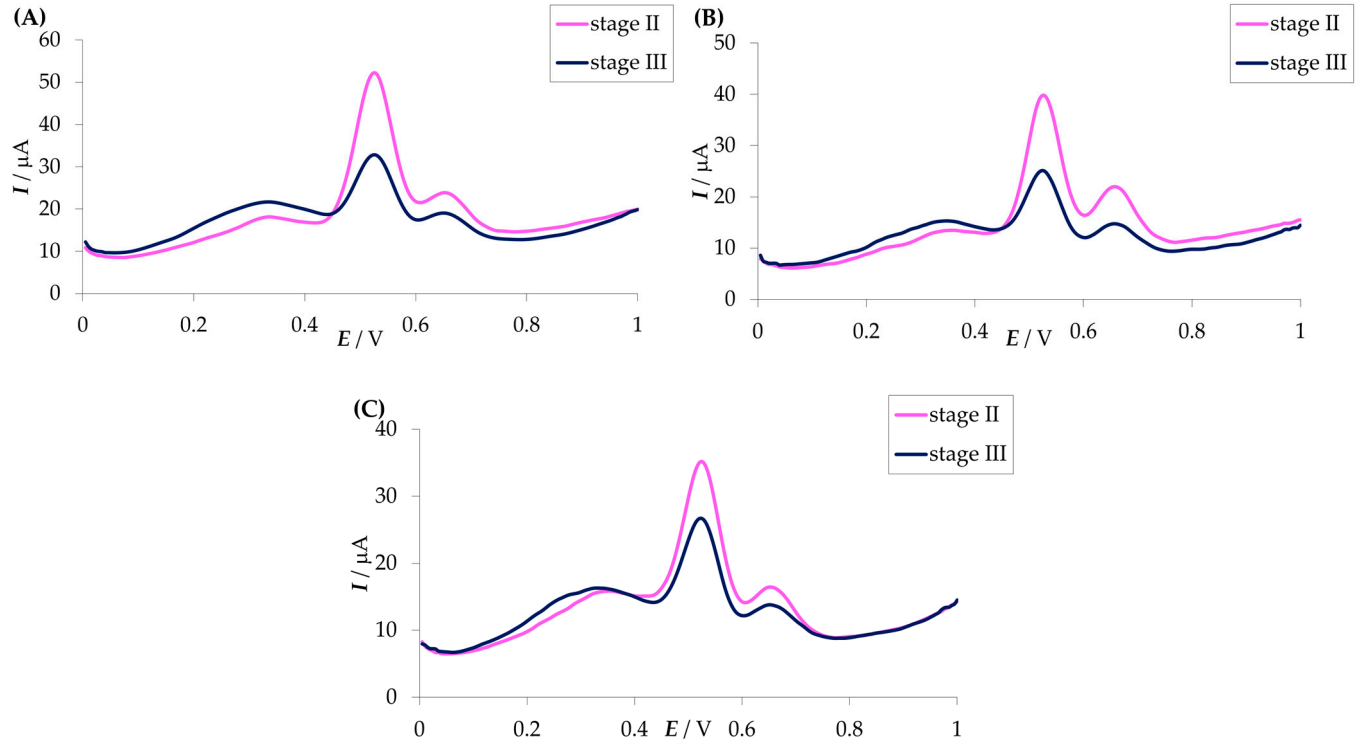

Figure 4. SWV voltammograms obtained during Stages II and III, after immersing the electrode in solutions of metal cations: (**A**) Ca^{2+}, (**B**) Mg^{2+}, and (**C**) Fe^{3+} at a concentration of $C = 1.0 \times 10^{-6}$ mol·L^{-1}.

During Stage III, there was a noticeable reduction in the signal originating from the oxidation of *Adn* upon exposure to all three cations under analysis. The percentage decrease in signal from Stage III compared to Stage II is presented in Table 3. This diminished current signal could be associated with the formation of a complex between the adrenaline layer and the metal cations. The most significant reduction in the measured current was observed after immersing the working electrode in the calcium cation solution. This suggests that Ca^{2+} forms the most stable complex with adrenaline.

Table 3. The percentage decrease in the current of the signals between Stages II and III.

Metal Cation	Signal Decrease (%)			Average Value of Signal Decrease for the Three Measurement Series (%)
	Series 1	Series 2	Series 3	
Ca^{2+}	55.18	54.65	56.01	55.28
Mg^{2+}	51.62	51.88	50.46	51.32
Fe^{3+}	33.97	30.46	31.96	32.13

4. Conclusions

During these investigations, we successfully developed a stable sensor based on adrenaline, indicating its utility for modifying working electrode surfaces in voltammetry. In the first stage of the research, a preliminary optimization of the adrenaline deposition procedure on the surface of glassy carbon electrodes was conducted. The deposition process was carried out using cyclic voltammetry, and the verification of signals originating from adrenaline was subsequently performed using square wave voltammetry. The optimized potential window used during the deposition stage ranged from −0.1 to 2.0 V. Additionally, the developed sensor showed sensitivity to the selected metal cations, suggesting its potential for developing an analytical method for their indirect determination. This is particularly important for ions like calcium and magnesium, given their inability to be directly determined using electrochemical techniques.

Author Contributions: Conceptualization, K.K.; methodology, K.K.; investigation, G.M., S.S., and J.S.; writing—original draft preparation, G.M., K.K and J.S.; writing—review and editing, G.M., J.S., S.S. and K.K.; supervision, K.K.; project administration, K.K.; funding acquisition, K.K.. All authors have read and agreed to the published version of the manuscript.

Funding: The research was financed by the PRELUDIUM grant of the National Science Centre in Cracow, Poland (B2211100001202100).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is available from authors upon request.

Conflicts of Interest: The authors declare no conflict of interest.

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