**Dopamine modified electrodes for indirect voltammetric determination of magnesium ions**

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***Abstract***

This article outlines the fabrication process of an electrochemical sensor designed for the innovative determination of magnesium ions based on the electrochemistry of dopamine. The sensor operates under voltammetric conditions, accounting for variations in the electrochemical reversibility of immobilized dopamine in the presence of magnesium ions under conditions of square-wave voltammetry. The immobilization of dopamine on the glassy carbon electrode is achieved through the electrochemical oxidation of its side amino group, leading to covalent grafting onto the electrode surface. All stages of the proposed electrode surface modification procedure were carefully optimized. The dopamine sensor exhibited a linear response in the concentration range of magnesium ions from 0.1 to 10 mmol L-1, with a limit of detection (LOD) value equal to 1.3 × 10−5 mol L−1. To validate the electroanalytical significance of the developed methodology, real food supplement samples were quantitatively analyzed, demonstrating a highly satisfactory rate of recovery. The proposed voltammetric method serves as a simple and cost-effective procedure for the indirect determination of magnesium ions. Additionally, this approach allows for the analysis of real samples without the need for time-consuming preparation steps, as the complex matrices of food supplement samples did not adversely affect the registered currents.

***Keywords***: voltammetry, magnesium, dopamine, grafting, sensing

1. ***Introduction***

Magnesium is one of the most abundant elements in the Earth's crust by mass [1]. Alongside calcium, it is one of the most essential nutrients that ensure a healthy life. Magnesium ions (Mg2+) play significant roles in all living cells, particularly as co-factors in numerous enzymatic reactions. This is especially crucial in reactions related to energy production and the utilization of ATP (adenosine triphosphate). Additionally, magnesium serves as a vital endocrine regulator and a structural component of bones [2]. Maintaining an adequate dietary intake of magnesium is essential for life, and its absorption and elimination are tightly regulated. Disruptions in Mg2+ homeostasis are often implicated in various clinical conditions, including diabetes, cardiovascular disease, hypertension, osteoporosis, anxiety disorders, and migraines [2]. Magnesium is commonly employed as a therapeutic agent in gastroenterology and cardiology, and it may have clinical benefits in neurology and obstetrics as well [2, 3]. Moreover, the role of magnesium in plant growth cannot be overlooked. It is a major constituent of the green pigment in leaves—chlorophyll—and thus plays a significant role in the photosynthetic process [2, 3]. Given its crucial importance for the functioning of all living organisms, it is imperative to monitor magnesium levels in various samples, including water, soil, urine, blood serum, pharmaceuticals, food supplements, and more.

It is worth noting that in certain instances, the presence of magnesium and/or calcium is undesirable, as they are considered contaminants. For instance, during the manufacturing process, these ions may be present in biodiesel samples, leading to corrosion, motor clogging, and the formation of ash in the combustion chamber. This poses a real risk to human health and the environment [4]. Therefore, monitoring these elements in fuel is of utmost importance. In summary, the quantitative determination of Mg2+ is a significant requirement, necessitating sensitive, quick, and reliable methodologies.

Various methodologies have been published for magnesium assay in diverse environmental samples. These include atomic absorption spectroscopic methods [5-8], fluorescent methods [9], enzymatic methods [10], ion chromatography methods [11], ion-selective electrode methods [12], X-ray atomic spectrometric methods [13], colorimetric methods [14], and electrochemical methods [3, 4, 15, 16]. However, many of the mentioned methodologies still exhibit certain drawbacks, such as multi-stage and time-consuming sample preparation procedures, high equipment costs, and the use of numerous toxic solvents. Consequently, in terms of sampling convenience and sensitivity, electroanalytical methods prove to be competitive compared to other techniques for magnesium determination [3, 4]. Regrettably, due to the highly negative potential for the reduction of Mg2+ (approximately −2.2 V vs. SCE), direct determination through electroanalytical methodologies is nearly impractical. The reduction of magnesium ions is significantly hindered by H+ and other ions, such as alkali earth metals [15, 17]. As a result, several electrochemical procedures have been developed for the indirect detection of Mg2+, primarily based on innovative sensor preparation [3, 15, 16, 18]. A crucial component of these sensors is the incorporation of various electroactive ligands capable of forming complexes with magnesium ions.

Moreover, electroactive ligands sensitive to magnesium ions should preferably be immobilized on the electrode surface to enhance the sensitivity of electrochemical measurements. An outstanding example of such a ligand is dopamine (*Dop*) [19], a well-known neurotransmitter that plays a significant role in the functioning of the cardiovascular, nervous, and renal systems [20]. The electrochemical activity of *Dop* is based on the redox turnover of the quinone/hydroquinone redox couple, which is one of the most important redox reactions in the chemistry of living systems [21]. Specifically, compounds with a catechol moiety, such as *Dop*, can easily transform from a stable *o*-quinone form to a catechol one. Both redox forms exhibit significant differences in their chemical reactivity. The catechol redox form is a well-known ligand for transition metal complexation. Moreover, upon initial deprotonation, it is prone to strong electrostatic interactions with various metal cations, such as Ca2+ and Mg2+ [22-24].

What is more important in the context of this study is that *Dop* and other catechols have been utilized in the surface coatings of electrodes [19, 25], whereas polydopamine coatings have proven to be a versatile platform for secondary reactions, allowing for the customization of electrode surface coatings for various functional uses [26, 27]. The immobilization of *Dop* on the electrode surface can be achieved through the electrochemical oxidation of the amino group in its side ethylamine tail. It is noteworthy that the electrooxidation of amines, coupled with the electrochemical reduction of aryldiazonium salts, represents one of the most powerful routes for electrochemical grafting [28, 29], resulting in the formation of a thin organic film covalently attached to the electrode surface [19, 29, 30].

In this study, electrochemical techniques were utilized for the preparation of a dopamine sensor and its novel application in the indirect determination of magnesium ions. The grafting of *Dop* was carried out through the electrochemical oxidation of the amino group on a glassy carbon (GC) electrode [19]. All stages of the proposed electrode surface modification procedure were optimized. The electroanalytical relevance of the developed methodology was demonstrated through the quantitative analysis of the pharmaceutical formulation/dietary supplement Magnum Forte.

1. ***Experimental***

*2.1 Apparatus and instrumentation*

Cyclic voltammetric (CV) and square wave voltammetric (SWV) experiments were conducted using an EmStat 3 potentiostat operated with PsTrace 4.7 software (PalmSens, The Netherlands), coupled with an M164 electrode stand (mtm‐anko, Poland). A conventional three-electrode system was employed for the experiments, featuring a glassy carbon electrode as the working electrode (Mineral, Poland), Ag/AgCl (3 mol L-1 KCl) as the reference electrode, and a Pt wire as the counter electrode. All electrochemical measurements were performed in a voltammetric cell with a volume of 10 mL. pH measurements were carried out using a digital pH/mV/ion meter (Elmetron, Poland) equipped with a glass electrode. The experiments were conducted at the ambient laboratory temperature (21-23 ⁰C).

*2.2 Chemicals and solutions*

All chemicals utilized in this study were of analytical grade. Dopamine was procured from Merck (Germany). A stock standard *Dop* solution of 1.0 × 10-2 mol L-1 was prepared by dissolving an appropriate mass of the *Dop* powder in distilled water and stored at 4 °C in the refrigerator. A solution of Mg(NO3)2 at a concentration of 1.0 × 10-1 mol L-1 was prepared by dissolving the required mass of the salt in distilled water. Supporting electrolytes, namely Britton–Robinson (BR) buffers (pH 2.0−9.0) and sulfuric acid solution, were also prepared. All components used for buffer preparation were purchased from Avantor company (Poland). Deionized and triple-distilled water were used for all measurements.

The pharmaceutical formulation Magnum Forte (ZDROVIT) was obtained from a local pharmacy. Tablets were powdered in a mortar, and an appropriate mass of the powder was dissolved in distilled water, resulting in a Mg2+ concentration of 8.0 × 10−4 mol L−1.

*2.3 Measurement procedure*

Electrochemical measurements were conducted using CV and SW voltammetry. Unless otherwise specified, all steps during dopamine immobilization comprised the following procedures: (I) direct electrochemical oxidation of *Dop* on a working electrode in acidic media, (II) meticulous washing of the working electrode surface with water, and (III) verification of the stability of the obtained *Dop* layer.

In the (I) stage, 20 successive CV scans were performed in the potential range from +0.1 to +2.0 V, with the final scan stopping at +0.1 V. For the (II) step, the GC electrode surface was thoroughly rinsed with distilled water to eliminate any impurities and unbound *Dop* molecules. Finally, in the last (III) step, CV was utilized during the optimization procedure or SW voltammetry in the analytical part, in potential range of 0.0 to +1.0 V in a sulfuric acid solution. All stages of the described methodology were optimized to obtain stable signals with the highest possible peak current values.

Before each immobilization procedure, the working GC electrode underwent careful cleaning by polishing on Al2O3 0.3 µm slurry, followed by sonication for 15 minutes in ethanol, and thorough rinsing with distilled water.

For analytical purposes, specifically the indirect determination of magnesium ions, the immobilization of *Dop* was carried out as described above (I – III stages). Following the immobilization procedure, the modified electrode was incubated in a solution of magnesium cations with varying concentrations for a duration of 5 minutes. Subsequently, the electrode was thoroughly rinsed with distilled water, immersed in a sulfuric acid solution free of magnesium ions, and SW voltammograms were recorded. The differences in the peak current values of the dopamine layer obtained before and after immersion in the cation solution formed the basis of the analytical approach in this study. In the SWV experiments the parameters were as follows: an amplitude of 25 mV, a step potential of 5 mV, and a frequency of 25 Hz. All measurements were conducted in triplicate.

1. ***Results and discussion***
   1. *Immobilization of dopamine on the glassy carbon electrode surface*

The first part of the present work is devoted to the immobilization of *Dop* onto a GC electrode surface. Every stage of the proposed procedure was carefully optimized, including the applied potential range, number of scans, and the scan rate during immobilization step (I), as well as pH and composition of the supporting electrolyte.

The grafting of dopamine was initially carried out in a strongly acidic medium (0.01 mol L-1 sulfuric acid solution) through 20 successive CV scans in the potential range of 0.0 to +1.9 V (Fig. 1A). Typically, as suggested by literature data, amines are challenging to oxidize, and the corresponding anodic peak, if present at all, is generally very weak and tends to disappear during repetitive potential cycling [30-32]. In this system, the oxidation of the amine group is evident as a strong anodic current tail emerging at potentials more positive than 1.0 V (Figure 1A, main plot). Throughout the subsequent potential cycles, the typical response of the *Dop* redox couple (quinone/hydroquinone) around the formal potential of about 0.350 V gradually intensifies, while the anodic current tail attributed to amine oxidation gradually diminishes.

Obraz zawierający diagram, szkic, rysowanie, Grafika liniowa

Opis wygenerowany automatycznie

Fig. 1. **(A)** Cyclic voltammograms of *Dop* (c(*Dop*) = 1.0 × 10−3 mol L−1), recorded during immobilization stage (I) in 1.0 × 10−2 mol L−1 H2SO4 at scan rate of 0.06 V s-1. Black-solid line represents the 1st scan; gray-solid line is the 10th scan, and the gray-dotted line is the 20th scan. The inset shows enlarged part of the voltammograms within the potential region of the *Dop* (quinone/hydroquinone) redox couple. **(B)** Cyclic voltammogram of *Dop*-modified GC electrode (III stage) recorded in 1.0 × 10−2 mol L−1 H2SO4; at scan rate of 0.06 V s-1.

In reference to the amine oxidation process attempted for the grafting of *Dop*, it has been suggested to occur through the formation of a neutral aminyl radical [30]. Specifically, this radical generation involves a multistep process, beginning with the initial one-electron-one-proton oxidation of the protonated amino group of *Dop*, leading to the formation of a radical cation (RCH2NH2+•). Subsequent to the electrochemical step, deprotonation of the α-methylene group results in a carbon radical (RCH•NH2), which ultimately rearranges into an aminyl radical (RCH2NH•) that binds to the electrode surface (Figure 2A) [28, 30]. The scheme of the immobilization of *Dop* onto surface of the working electrode is presented in the Figure 2B.

*Obraz zawierający tekst, diagram, Czcionka, zrzut ekranu

Opis wygenerowany automatycznie*

Fig. 2 (A) Schematic illustrating of the electrooxidative grafting mechanism of amines [28]; (B) Schematic Illustrating the immobilization of *Dop* onto surface of the working electrode [19].

The electrochemical response of *Dop*/GC electrode in sulfuric acid solution obtained during the (III) stage of experiment is presented in Figure 1B. The morphology of the voltammetric response taking into account the shape of voltammetric peak and the linear dependency of the peak current on the scan rate are typical for a quasireversible electrode reaction of an immobilized redox couple, inferring that *Dop* was successfully immobilized on the electrode surface. The overall electrode reaction is two-electron-two-proton redox turnover of dopamine (catechol form) to *o*-quinone form [24].

In the subsequent experimental phase, we optimized several parameters crucial for both the first (I) and third (III) stages of the procedure. Initially, we focused on optimizing the pH and composition of the supporting electrolyte. This was examined in Britton-Robinson buffers within a pH range of 1.5 to 9.0, as well as in a sulfuric acid solution with a pH interval from 1.5 to 2.5. Figure 3 illustrates typical voltammograms of *Dop* using different Britton-Robinson buffers for the immobilization (stage I) and the subsequent recording of voltammograms in the corresponding buffer (stage III). The primary criterion for optimization was the intensity of the voltammetric response and the stability of the response during repetitive cyclization in the (III) stage. It is noteworthy that the *Dop* voltammetric response was observed across the entire applied pH range (Fig. 3B). The dependency of the anodic peak current on the pH of Britton-Robinson’s buffer is complex one, chiefly increasing by decreasing the pH. However, the most significant signals and the longest stability were achieved when the immobilization procedure occurred in sulfuric acid at pH 1.7, which was selected as a medium for further optimisation.

Obraz zawierający diagram, Wykres, tekst

Opis wygenerowany automatycznie

Fig. 3. **(A)** Cyclic voltammograms of *Dop*/GCE obtained in (III) stage of the procedure when the immobilization stage was performed in BR buffers of different pH values: black-dotted line represents pH 1.5; black-solid line pH 1.7; gray-solid line pH 3.0; gray-dotted line pH 5.0. **(B)** The dependence of the anodic peak-current of *Dop*/GCE electrode on the pH of BR buffer. The buffer for immobilization (stage I) and recording the voltammogram (stage III) is identical.

The next optimized parameter during the immobilization procedure was the applied potential range, recognizing that the overall potential range significantly influences the morphology and chemical composition of the GCE surface [33], the physisorption of *Dop* [34], and the stability and morphology of the dopamine film chemically bonded to the electrode surface through the amino group oxidation. Both the values of the initial potential (*E*i) and the end potential (*E*e) were investigated.

Initially, the initial potential was varied within the range of ‒0.10 to +0.25 V, and the results are presented in Figure 4A. Analysis of the voltammograms revealed that the highest peak currents in the (III) stage of experiments were observed when the initial potential during *Dop* immobilization was set at +0.10 V. This observation can be attributed to the dependency of the physisorption of *Dop* on the electrode potential [34]. Considering the subsequent analytical application, where the highest signal correlates with the procedure's highest sensitivity, the initial potential of +0.10 V in the (I) experimental stage was selected.

Subsequently, the end potential (*E*e) employed during the immobilization stage was adjusted within the range of +1.5 to +2.0 V, and corresponding voltammograms recorded in the course of the (III) stage are depicted in Figure 4B. Notably, the peak current of the deposited *Dop* layer increased as the end potential of the applied potential window in the (I) stage became more positive. This trend aligns with the requirement for a higher overpotential to drive the sluggish oxidation of the amino-group and facilitate grafting to the electrode. The most substantial signals of the *Dop* layer were achieved with an end potential of +2.0 V. Consequently, the potential window selected for further analysis during the (I) stage was in the range of +0.1 to +2.0 V.

Obraz zawierający szkic, diagram, rysowanie, Wykres

Opis wygenerowany automatycznie

Fig. 4. **(A)** Cyclic voltammograms of *Dop*/GCE obtained after applying various initial potential (*E*i) in the immobilization stage (I): (1) ‒0.1 V, (2) 0.0 V, (3) 0.1 V and (4) 0.25 V. **(B)** Cyclic voltammograms of *Dop*/GCE obtained after applying various end potential (*E*e) in the immobilization stage (I): (1) 1.5 V; (2) 1.6 V; (3) 1.7 V; (4) 1.8 V; (5) 1.9 V and (6) 2.0 V, recorded in 1.0 × 10−2 mol L−1 H2SO4 Scan rate = 0.06 V s-1. All experiments have been conducted in 1.0 × 10−2 mol L−1 H2SO4 and the scan rate was *v* = 0.06 V s-1.

The final parameters subjected to optimization were the number of potential cycles (stage I) and the potential scan rate applied, which is important for both stages (I) and (III). Initially, the number of scans was varied within the range of 3 to 30 (data not shown). It was observed that the highest peak current was achieved when employing 20 consecutive potential cycles, which might be rationalized with frequently observed phenomena related to the formation of a multilayer film with unfavourable morphology for extended deposition processes [35].

Additionally, the scan rate value played a crucial role. In the (I) stage, the scan rate impacts the total time of the deposition process, encompassing the kinetics of the overall complex electrode mechanism involving amino-group oxidation, chemical reorganization of the initially formed radical, and ultimately the grafting process. Furthermore, in the (III) stage, which pertains to the redox turnover of immobilized *Dop*, the scan rate is critically important for the electrochemical reversibility of the quasi-reversible electrode reaction of *Dop*, thereby influencing the intensity of the voltammetric response. In light of these considerations, the scan rate during the immobilization stage was varied broadly within the range of 0.01 to 1.0 V s-1. Taking into account the intensity of the peaks, the peak potential separation of the *Dop* response recorded in the (III) stage as criteria for optimization, along with the overall duration of the immobilization procedure, a scan rate value of 0.06 V s-1 was chosen as optimal. In summary, the (I) stage involved performing 20 successive potential cycles in CV scans within the potential range from +0.1 to +2.0 V, in a 0.01   
mol L-1 aqueous H2SO4 solution at pH 1.7, with a potential scan rate of 0.06 V s-1.

* 1. *Analytical application*

For analytical purposes, specifically the indirect determination of magnesium ions, we conducted the immobilization of *Dop* using the optimized procedure outlined in the previous section. In stage (III), SWV was employed, as this technique is more frequently utilized in analytical procedures, mainly due to the elimination of capacitive current [36]. Following the immobilization procedure, the modified electrode underwent incubation in Mg(NO3)2 solutions with varying concentrations for a duration of 5 minutes, as detailed in the Experimental Section.

To establish a calibration curve, we plotted the differences in peak current values of the *Dop* layer before and after immersion in the magnesium containing solution (referred to as signal decrease and expressed as a percentage decrease %) against the corresponding magnesium cation concentrations. Figure 5A showcases typical net SW voltammograms for different Mg2+ concentrations, comprising a well-defined, sharp net SW peak that enables the precise measurement of its intensity and position. The inset of Fig. 5A represents the forward (anodic; dashed lines), backward (cathodic; dotted lines), and the net component (full lines) of the SW voltammetric response of *Dop* in the absence and in the presence of Mg2+ ions. The morphology of the SW voltammetric response clearly reveals the strong influence of Mg2+ ions on the overall electrochemical reversibility of the electrode reaction of *Dop*. The degree of electrochemical reversibility (i.e., the rate of interfacial electron exchange) diminishes in proportion to the concentration of magnesium ions, presumably as a consequence of strong electrostatic interactions between magnesium ions and the catechol moiety of the reduced form of covalently grafted *Dop*. However, electrostatic interactions between magnesium ions and one of the redox intermediates (i.e., semiquinone forms) of *Dop* obtained in the course of the complex two-electron-two-proton redox transformation of dopamine cannot be ruled out. Considering the fact that the net response in SWV is highly sensitive to the kinetics of the surface immobilized electrode reaction [37-39], the disparities in the obtained net peak-currents exhibited a linear decrease with magnesium ions concentration, spanning from 1.0 × 10−2 to 1.0 × 10−3 and from 1.0 × 10−3 to 1.0 × 10−4 mol L−1 (Fig. 5A).

From the calibration curve (Fig. 5B), the limit of detection (LOD) and the limit of quantification (LOQ) for the procedure as kSD/b were calculated, where k = 3 for LOD and k = 10 for LOQ, and b represents the obtained slope of the calibration curve, while SD is the standard deviation of the intercept [32]. The computed values for LOD and LOQ were found to be 1.3 × 10−5 and 3.9 × 10−5 mol L−1, respectively.

Obraz zawierający tekst, diagram, mapa, Plan

Opis wygenerowany automatycznie

Fig. 5. **(A)** Typical net SW voltammograms of *Dop*/GCE obtained before (black-solid line) and after the immersion in magnesium solutions for chosen concentrations of Mg2+: black-dashed line represents *c*Mg2+= 1.0 × 10−4 mol L−1; gray-dashed line *c*Mg2+= 1.0 × 10−3 mol L−1, and light-gray-dashed line *c*Mg2+= 1.0 × 10−2 mol L−1, all recorded in 1.0 × 10−2 mol L−1 H2SO4; Insets represent net (solid line), forward (anodic, dashed line) and backward (cathodic, dotted line) component of the SW voltammetric response of *Dop* in the absence (upper inset) and in the presence of Mg2+ ions (lower inset). **(B)** Corresponding calibration lines.

The suitability of the proposed methodology for indirectly determining magnesium cations was assessed by quantifying them in a commercially available food supplement, namely Magnum Forte. In this study, the working electrode Dop/GCE was immersed in a solution containing the dissolved food supplement. The calculation of magnesium ions in the dietary supplement was performed based on the results obtained, specifically the differences in peak currents and the calibration curve mentioned above. The quantified amount of magnesium ions is presented in Table 1. The results obtained clearly indicate that the developed methodology can be effectively utilized for the indirect determination of magnesium in food supplement samples without encountering any interference.

Table 1. Results obtained from the indirect determination of Mg2+ in food supplement samples using the *Dop*/GC electrode and SWV technique.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Magnum Forte samples | | | | |
| Sample | Declared content  (mg/tablets) | Calculated content  (mg/tablets) | Precision  (%) | Recovery  (%) |
| 1 | 375 | 374 |  | 99.7 |
| 2 | 375 | 383 | 7.1 | 102.1 |
| 3 | 375 | 380 |  | 101.3 |

1. ***Conclusions***

This study explored the preparation of a *Dop* sensor and its innovative application for the indirect determination of magnesium ions. It has been demonstrated that *Dop* can be effectively immobilized via electrochemical oxidation of the amino group, resulting in covalent grafting to the surface of the GC electrode. The optimal immobilization procedure involves 20 successive potential cycles under CV conditions in sulfuric acid of pH 1.7, within the potential range from 0.1 to 2.0 V, with an optimal scan rate of 0.06 V s-1.

The electrochemical reversibility of the immobilized *Dop* is highly sensitive to magnesium ion concentration, forming the basis for the proposed analytical procedure conducted with SWV. The analytical efficacy of the proposed methodology is validated through the analysis of real food supplement samples. This approach enables indirect analysis of real samples without the need for time-consuming preparation steps. The complex matrices of food supplement samples do not interfere with the determination of Mg2+ on the *Dop-*modified GC electrode. Consequently, the developed methodology can be considered an environmentally friendly and cost-effective procedure for the determination of Mg2+ in real samples.

In conclusion, it is reasonable to assume that Ca2+ ions could potentially interfere, given the similarities between both types of cations in a physiological context, as well as their comparable electrostatic interactions with various quinone systems. Therefore, our upcoming study will focus on elucidating the impact of Ca2+ in the current experimental system.

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Declarations of interest: none

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