

Glassy Carbon Electrode Modified with Nickel (II) Tetrasulfophtalocyanine Films and its Behavior as Amperometric Sensor for Nitrite

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Received: 26 August 2013 / *Accepted:* 15 October 2013 / *Published:* 15 November 2013

In this work, a modification of a glassy carbon electrode with a film of Nickel (II) tetrasulfophtalocyanine (f-NiTSPc) was done, which was obtained by a continuous potential cycling in aqueous solution. It was found that a modified electrode with f-Ni(II)TSPc increases its activity versus nitrite oxidation, in comparison to the bare glassy carbon electrode (GC) and the monomer multilayers of this complex (m-Ni(II)TSPc). Its activity was studied versus different pH, and it was found that the better conditions for nitrite oxidation were at pH 7.2. At this pH kinetic calculations were done, finding that it is a diffusional process with a one-electron transference and a Tafel-slope value of 59 mV/dec, postulating a possible reaction mechanism. Finally, the electrode behavior was studied as possible amperometric sensor for nitrite, obtaining and calculating its analytical parameters such as accuracy, exactitude, detection and quantification limits, being a good method for nitrite quantification in aqueous solution.

Keywords: Modified electrode; Nitrite Electro-oxidation; Amperometric Sensor; Nickel tetrasulfophtalocyanine

1. INTRODUCTION

In the last decades, the study of nitrite has gained great importance, because this specie is present in several processes like environmental and biological ones, and also, it is an intermediary in the nitrogen cycle. The nitrites are often used as fertilizers, which produce a high environmental impact through the water pollution, being also added as preservatives in food. It is known that the role that the nitrite has is as a precursor on the N-Nitrosamines formation, which are mostly carcinogenic compounds found in nature [1-3], being a vital importance its study, detection and quantification. A

great variety of techniques have been reported for nitrite determination, for example, chromatography [4,5], spectrophotometry [6-8] and electrochemical techniques [9,10]. The electrochemical techniques often offer advantages versus other ones, because in general they are faster, cheaper and more secure. The electrochemical determination of nitrite can be done through its oxidation or its reduction. The nitrite oxidation has the advantage of being free of interferences such as nitrite and molecular oxygen, which are often present in cathodic determinations [11,12]. The determination of this anion is difficult by using conventional electrodes, because they require high overpotentials [13] and due to that these electrodes are frequently contaminated by the produced species during the electrochemical process [14]. The nitrite oxidation has been widely studied, using modified electrodes of different kind, where we can find, in general, good responses toward nitrite detection and quantification, depending on the type of modification, technique and used material [15-19]. In this work is proposed to determine and quantify nitrite, using a modified electrode with Ni(II)TSPc films, as amperometric sensor. The best electrochemical and experimental conditions were found in order to establish the method, being possible to determine kinetic parameters toward oxidation and establish an oxidation mechanism. The result revealed that the amperometric sensor exhibits, high sensitivity, good reproducibility, long-term stability, and well practical application.

2. EXPERIMENTAL

2.1. Chemical and Solutions

Ni(II)TSPc was purchased from Sigma -Aldrich. Tetrabutylammonium perchlorate (TBAP), monobasic and dibasic potassium phosphate (Sigma Aldrich), sodium nitrite, and NaOH, (Merck) were analytical grade reagents. Deionized water was obtained from a Millipore-Q-system. Argon (99.99% pure) gas was purchased from AGA-Chile. Standard solution sample of Sodium Nitrite in water (1000 mg $\text{NaNO}_2 \text{ L}^{-1}$) was purchased from Merck.

2.2. Equipment

Cyclic voltammetry studies were performed on a CHI instrument 620 C potentiostat galvanostat.

The conventional three-electrode system consisted of a glassy carbon working electrode, Ag/AgCl (3M KCl) reference electrode, and a platinum wire counter electrode.

2.3. Preparation of modified electrode

The glassy carbon electrode was polished to a mirror finish on a felt pad using alumina slurries (3 μm). The monomer-modified electrode (m-Ni(II)TSPc) was obtained by dispensing a drop of 1mM Ni(II)TSPc/NaOH (0.1M) on the glassy carbon electrode surface (dry-drop method).

The f-Ni(II)TSPc was obtained through electroadsorption which was made with a continuous potential cycling of Ni(II)TSPc/NaOH (0.1M) between -0.6V and +1.2V vs vs Ag/AgCl. The modified electrodes were carefully rinsed with water to remove excess electrolyte and finally with Milli-Q water. The modified electrode was stabilized in phosphate buffer by cycling the potential within the potential window at which nitrite oxidation is performed. All experiments were carried out in triplicate.

3. RESULTS AND DISCUSSIONS

3.1. Obtention of NiTSPc film (f-NiTSPc)

Figure 1 shows the voltammetric profile of the electroadsorption of the modified electrode with f-NiTSPc, obtained in NaOH 0.1 M, 15 cycles, at a scan rate of 25 mV/s. As it is seen in Figure 1, when the number of cycles grows, the pair Ni(II)/Ni(III) increases in terms of current between 0.4 and 0.6 V, as well as the irreversible signal at 1V, which is displaced in more negative potentials. This behavior indicates the increase of the film on the electrode surface. The mechanism of NiTSPc film production has been reported previously [20-21]. It is known that the fixation of the nickel complex to the electrode surface is related to the oxidation of OH⁻ anions at potentials higher than 0.8 V. Also, the pH has an important role in the film formation, because at pH 13 the oxidation of OH⁻ creates a great variety of functional groups on the electrode surface, which are necessary to form –O-Ni(II) bonds. For this reason, the rate-determining step is the coupling of the complex to the electrode surface through –O-Ni(II) bonds. Subsequently, the deposition of Ni(II) complex is formed due to the oxidation of Ni(III) [21,22].

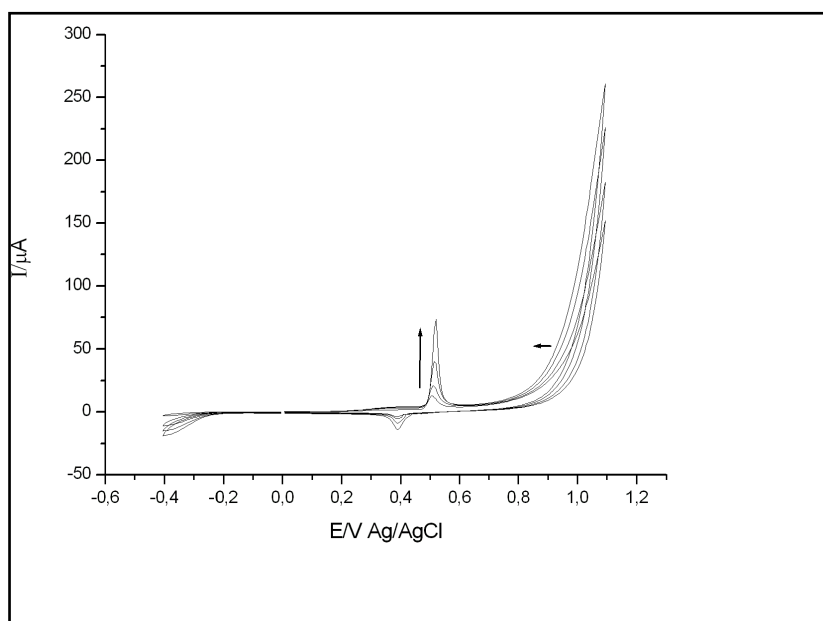


Figure 1. Voltammetric profile of the Ni(II)TSPc electroadsorption, 15 cycles, at a scan rate of 25 mV/s, in a NaOH 0.1M solution in Ar atmosphere, between -0.4V and +1.2V vs Ag/AgCl

Figure 2 shows the voltammetric profile of the modified electrode with f-NiTSPc, in NaOH 0.1M, at 200mV/s. As it is seen in the figure, it is clearly seen that the response of the metallic couple is obtained, which is very stable at 5 successive cycles of potential.

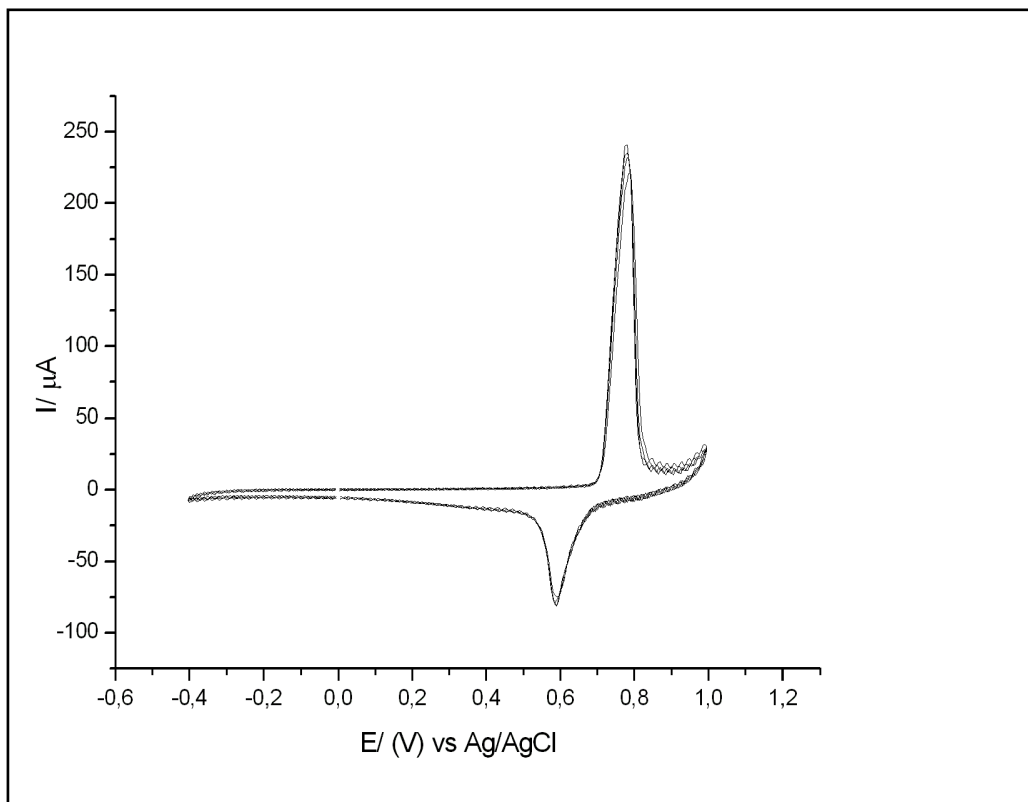


Figure 2. Voltammetric profile of f-Ni(II)TSPc, 5 cycles, in NaOH 0.1M solution, at a scan rate of 200 mV/s, Ar atmosphere, between 0.4V and +1.2V vs Ag/AgCl

3.2. Electrocatalytic activity versus nitrite oxidation on f-NiTSPc

Figure 3 shows the activity of the modified electrode, f-NiTSPc, in comparison to the electrode without modification (GC) and to the modified electrode with monomer multilayers m-NiTSPc (dry drop method), versus nitrite oxidation. As it is seen in the figure, the f-NiTSPc electrode presents a slight potential displacement and a current increase, in comparison to the bare GC electrode and m-NiTSPc. It is interesting to notice that the m-NiTSPc electrode decreases the own activity of the GC, which indicates that this system blocks the active sites, showing an oxidation at more positive potentials. It is also demonstrated that the obtained film by continuous cycling of potential, is a different system, more active and coherent with what is described on literature [20-22].

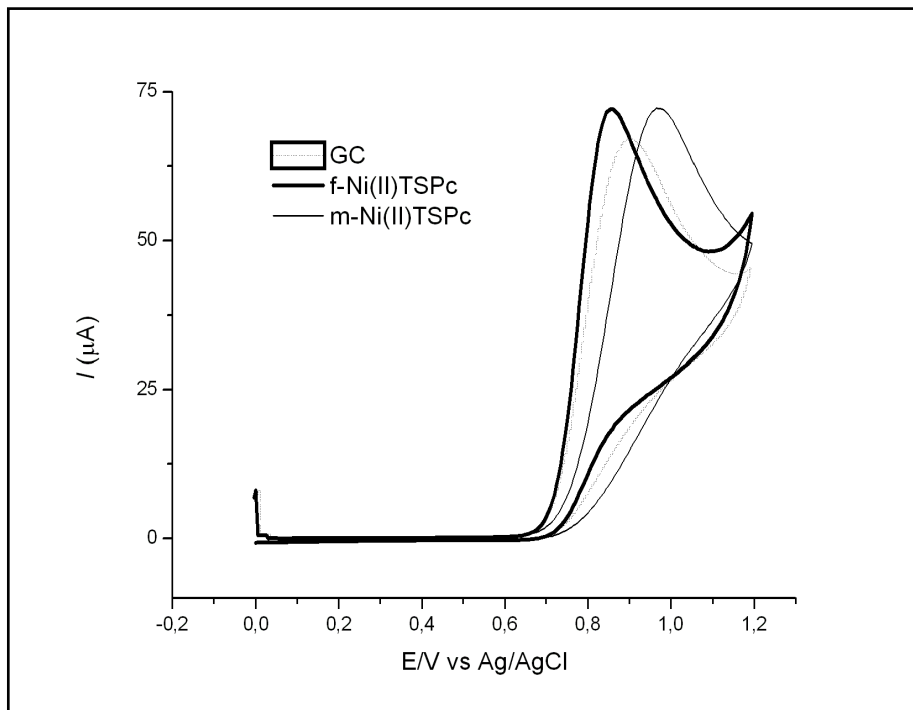


Figure 3. Voltammetric profile of f-Ni(II)TSPc (wide line), GC (dotted line) and m-Ni(II)TSPc (narrow line) towards nitrite oxidation 2mM, at pH 7.2 and Ar atmosphere, at a scan rate of 0.1 V/s, between 0.0V and +1.2V Ag/AgCl

3.3. Influence of pH versus nitrite oxidation

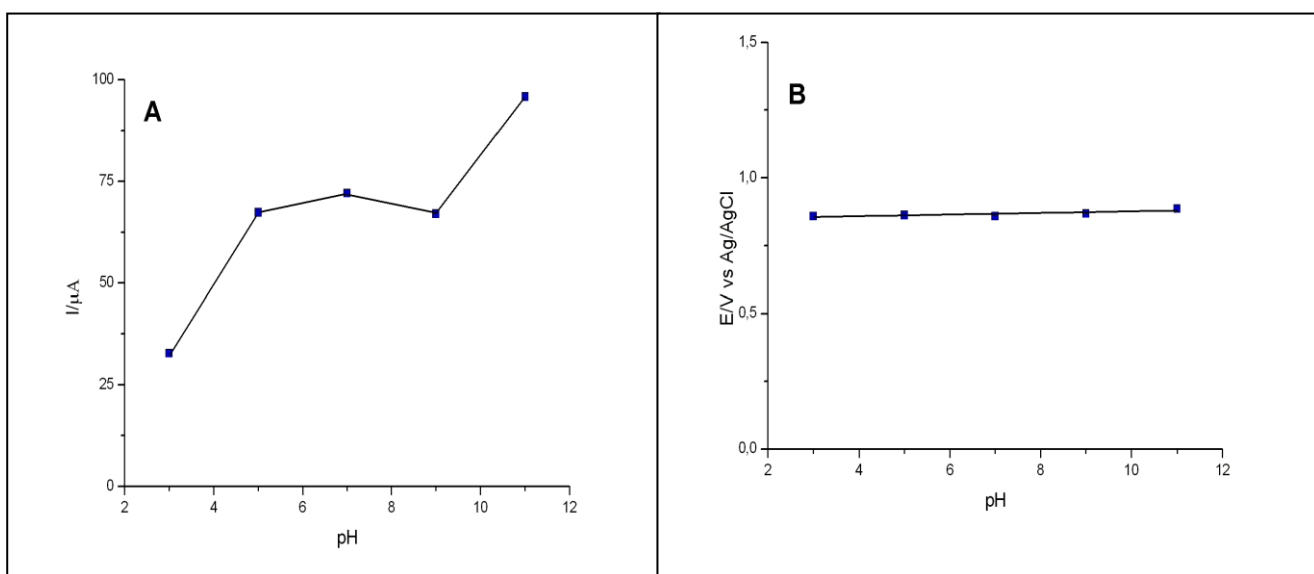
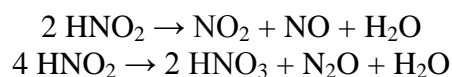


Figure 4. A:Dependence between peak current (I_p) in function of pH for f-Ni(II)TSPc towards nitrite electro-oxidation 2mM, at pH 7.2. **B:**Dependence between potential (E/V) in function of pH towards nitrite electro-oxidation 2mM, at pH 7.2

The response of the f-NiTSPc electrode versus the nitrite electro-oxidation was studied, at pH 3.0, 5.0, 7.2, 9.2 and 11, between -0.4 and +1.2V, at a scan rate of 100 mV/s and a nitrite concentration of 2mM. Figure 4A shows the pH influence, where the peak current, I_p , reaches a maximum at pH 7.2, followed by pH 11. However, at pH 11 the peak current of the voltametric profile (non-shown), is quite defined, so it is discarded for future studies. At lower pH the current decreases, so the reaction is less favorable. This is coherent with what is known by literature, considering that at lower pH, the nitrite tends to decompose in various species, due to dismutation processes (Scheme 1). For this reason, the effective concentration of nitrite as anion (NO_2^-) is low, because a percentage of the initial concentration is part of resulting species of such dismutation processes (Scheme 1). This behavior provokes a diminution of the current of the oxidation process of nitrite, considering that this response is proportional to its concentration. For this same consideration, while the pH value is closer to its pKa (3.4), the equilibrium will favour the more protonated specie (HNO_2), so a lower effective concentration of the anion is obtained [23]



Scheme 1: Examples of dismutation of HNO_2

However, E stays practically independent of pH (Figure 4B). Similar behaviors have been observed in other studies [11,19,24] and it is recommended that on the nitrite oxidation kinetics, the rate-determining step is proton-independent in the range of pH studied [24].

3.4. Kinetic studies in nitrite oxidation

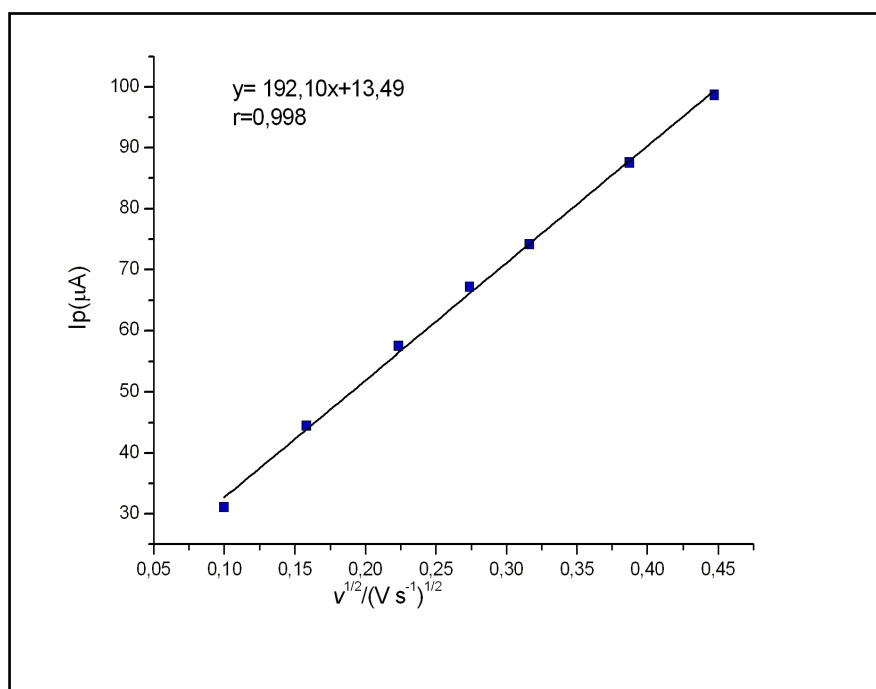


Figure 5. Peak current (I_p) versus square root of the scan rate for f-Ni(II)TSPc, pH 7.2 in nitrite 2mM.

In order to obtain information that concerns to the rate-determining step involved in the electro-oxidation of nitrite, the Tafel slope for this reaction was calculated as shown in Figure 6. The value was 59 mV per decade, indicating that the rate-determining step corresponds to a chemical reaction, after the transfer of the first electron. Figure 5 shows the graph I_p versus the square root of the scan rate. A good linear relationship was obtained, which indicates that is a process controlled by diffusion, where this result that is consistent with a high rate-constant catalytic system [25, 26]. The number of transferred electrons, n , can be calculated from this graph (Figure 5) using equation 1 that is valid for a totally irreversible process, controlled by diffusion [25,26]

$$I_p = (2,99 \cdot 10^5) n [(1-\alpha) na]^{1/2} C_0 A D_0^{1/2} v^{1/2} \tag{Equation 1}$$

Where α is the electronic transference coefficient, n represents the number of electrons implied in the slow step of the reaction, D_0 is the diffusional coefficient of the electroactive species (cm^2s^{-1}), A is the area of the electrode (cm^2), C_0 is the concentration of the electroactive specie. For this study, a concentration of 2mM is used and a diffusional coefficient of $3,7 \cdot 10^{-5} \text{ cm}^2\text{s}^{-1}$ is considered [11,19,27]. Also considering that $(1-\alpha) na$ must be known, an approximation based upon its dependence on the difference between the peak potential E_p and the mean peak potential $E_p/2$, given by equation 2, was employed [11, 19, 25, 26].

$$(1-\alpha) na = 47.7 \text{ mV} / (E_p - E_p/2) \tag{Equation 2}$$

Where $(1-\alpha) na$ has a value of 0.51. Inserting this value in equation 1, and considering that the value of the slope of the graph I_p vs $v^{1/2}$ (Figure 5) is $192,10 \text{ mA}/(\text{Vs}^{-1})^{1/2}$, yields $n=1.055$, which indicates that the number of transferred electrons is 1, number that differs from other related reports [11,19,24].

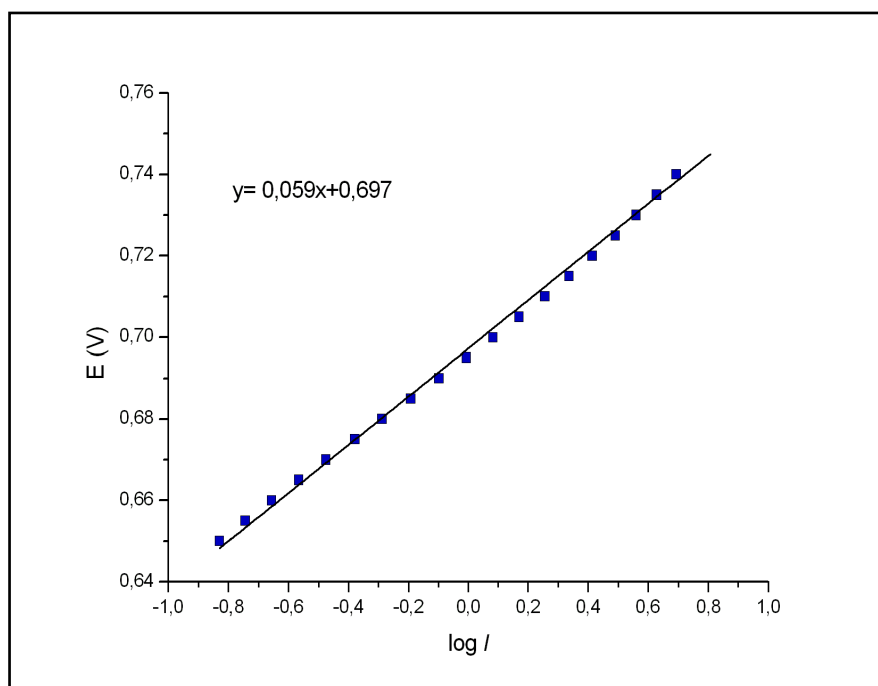
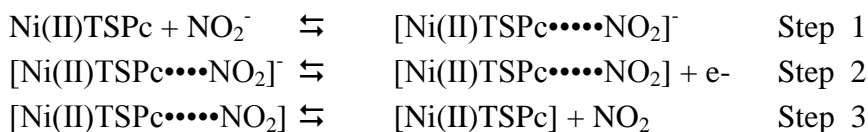


Figure 6. Plot of E_p vs. $\log I$ (Tafel plot), for f-Ni(II)TSPc, pH 7.2, in nitrite 2 mM. Scan rate: 0.005 Vs^{-1}

Consequently, it is possible to put forward a mechanism for the oxidation of nitrite, consistent with the above findings, where the limiting stage corresponds to step 3 of the following mechanism:



4. ANALYTICAL PARAMETERS

The nitrite electro-oxidation system was evaluated in analytical terms such as linearity, accuracy and exactitude, using a GC modified electrode with f-Ni(II)TSPc and cyclic voltammetry as technique.

4.1. Linearity

Four calibrate curves were done considering a fixed potential of 0.9484 mV. Based on these curves, an average curve is calculated as it is seen in Figure 7. The correlation coefficient is very close to 1, so the linearity parameter is favorable. Also, it is possible to calculate the lower and upper limits of linearity, whose values are 3.41×10^{-5} and 3.77×10^{-5} , respectively.

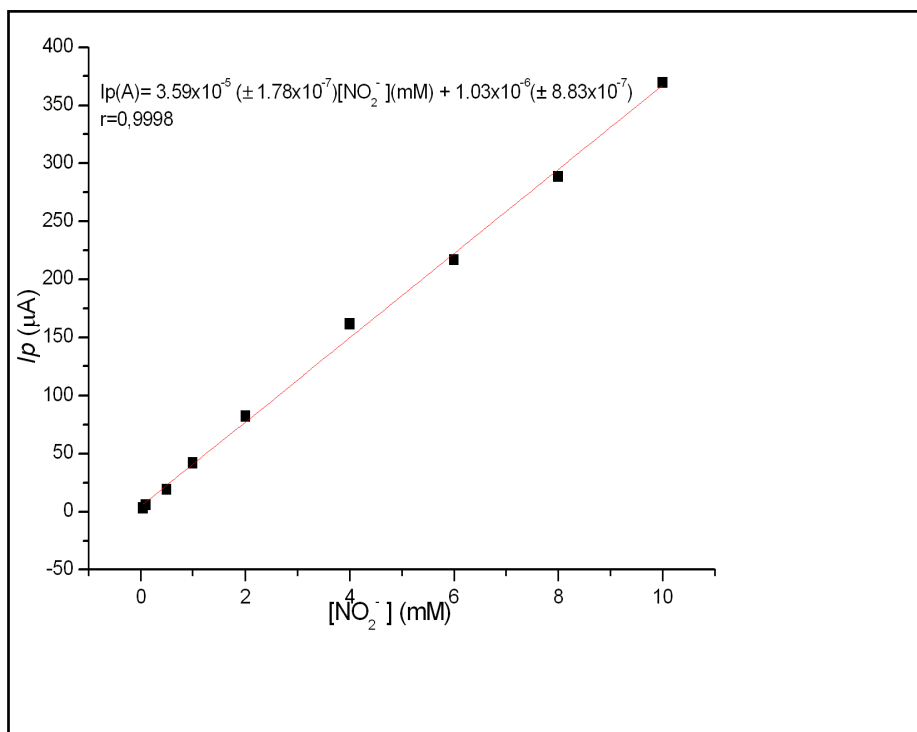


Figure 7. Peak current (Ip) versus nitrite concentration at fixed potential of 0.9484 V on nitrite oxidation, using a GC modified electrode with f-Ni(II)TSPc, at a scan rate of 100mV/s, in buffer solution of pH 7.2.

Parallel to this, it is possible to obtain the limits of detection (LOD) and quantification (LOQ) for this system with values of 0.149 mM and 0.0496 mM respectively.

4.2. Accuracy and exactitude

The accuracy was studied at a level of replicability and repetibility. In the last one, the days of the nitrite determinations were varied. In Table 2 the average responses of 10 aliquots are shown with the concentrations of them obtained from linear regressions set forth previously. It is also shown their standard deviations (SD) and their coefficients of variance (CV).

Table 1. Replicability level accuracy up to 10 aliquots of 2.00 mM nitrite solution

	Ip (μA)	[NO₂⁻] (mM)		Ip (μA)	[NO₂⁻] (mM)
Aliquot 1			Aliquot 7		
\bar{X}	7,108E-05	1,995	\bar{X}	6,348E-05	1,780
SD(±)	4,099E-07	0,002	SD(±)	1,879E-07	0,008
CV%	0,576	0,098	CV%	0,296	0,462
n=3			n=3		
Aliquot 2			Aliquot 8		
\bar{X}	7,047E-05	1,978	\bar{X}	7,040E-05	1,976
SD(±)	9,168E-08	0,011	SD(±)	7,175E-08	0,012
CV%	0,130	0,554	CV%	0,102	0,583
n=3			n=3		
Aliquot 3			Aliquot 9		
\bar{X}	7,053E-05	1,980	\bar{X}	7,019E-05	1,970
SD(±)	5,920E-08	0,012	SD(±)	7,509E-08	0,011
CV%	0,084	0,600	CV%	0,107	0,580
n=3			n=3		
Aliquot 4			Aliquot 10		
\bar{X}	7,047E-05	1,978	\bar{X}	7,041E-05	1,976
SD(±)	1,838E-08	0,013	SD(±)	1,351E-07	0,010
CV%	0,026	0,659	CV%	0,192	0,492
n=3			n=3		
Aliquot 5					
\bar{X}	7,117E-05	1,998			
SD(±)	9,402E-07	0,013			
CV%	1,320	0,652			
n=3					
Aliquot 6			Inter-average		
\bar{X}	7,069E-05	1,984	\bar{X}	6,989E-05	1,962
SD(±)	1,108E-07	0,010	SD(±)	2,789E-07	0,003
CV%	0,157	0,525	CV%	0,399	0,166
n=3			n=30		

Therefore the procedure was repeated during two different days in order to evaluate the accuracy at a level of repetibility. The results are shown in Table 2. As it is seen, at replicability level the method has a greater grade of accuracy, since its standard deviations and its coefficient of variance

have a tendency to be lower in comparison to a repetibility level. This behavior was expected due to the instability of nitrite, so when the days of measurements are different, the responses would be quite different too.

Finally, the system was evaluated in terms of exactitude. Table 3 shows the obtained values for 6 samples of nitrite with a concentration of 4.415 mM. These were compared with a standard solution sample (1000 mg NaNO₂ L⁻¹) from which the relative error is obtained. This value is low (under 5%), so it is possible to consider that this system may be a possible amperometric sensor.

Table 2. Repeatability accuracy level of 60 aliquots of 2.00 mM nitrite solution

	I(μA)	[NO ₂ ⁻] (mM)
Day 1		
\bar{X}	6,99E-05	1,962
SD	2,21E-06	0,049
CV%	3,163	2,497
Day 2		
\bar{X}	6,31E-05	1,769
SD(±)	1,33E-06	0,024
CV%	2,113	1,357
n=30		
Average		
\bar{X}	6,65E-05	1,865
SD(±)	6,2225E-07	0,018
CV%	0,936	0,948
n=60		

Table 3. Evaluation of exactitude parameter for nitrite samples in comparison to a standard sample. SD, CV and relative error (RE) are shown.

	[NO ₂ ⁻] (mM)
\bar{X}	4,415 mM
SD (±)	0,008
CV (%)	0,186
RE (%)	1,57
n=6	

5. CONCLUSIONS

A modified electrode with a Ni(II)TSPc film (f-Ni(II)TSPc) was generated, which was the more active one towards nitrite oxidation, in comparison to the non-modified electrode (GC) and the modified electrode with monomer multilayers (m-Ni(II)TSPc). The modified electrode with f-Ni(II)TSPc had its best response, in terms of potential and current, at pH 7.2. At this pH the kinetic

parameters were calculated, being possible to determine that the process occurs with transference of one electron, with a Tafel slope of 59 mV/dec, which allows establishing a possible reaction mechanism. At pH 7.2, the analytic studies were done and it was found that the systems behaves as a good amperometrical sensor in a large range of concentrations, showing good properties in terms of accuracy, exactitude, and detection and quantification limits.

ACKNOWLEDGEMENTS

The authors wishes to acknowledge, project FONDECYT N° 1120049 and project FONDECYT N° 1130094, for their support in this work.

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