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ARTICLE

Hydrazine electrooxidation mediated by transition metal octaethylporphyrins-modified electrodes

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This work presents the generation of new systems composed of glassy carbon electrodes (GC) modified with commercially available transition metal octaethylporphyrins, M-OEP (M = Co[II], Cu[II], Zn[II], Ru[II], Fe[III], Ni[II]) for the electrooxidation of hydrazine at neutral pH. It was found that the most active system corresponds to GC electrodes modified with Co[II]-OEP adsorbed on the surface, evidencing the importance of the central metal. This system, whose preparation is quick and easy, has great reported electrocatalytic activity on systems and unmodified GC electrode, which has been corroborated by using electrochemical impedance spectroscopy techniques. In addition, this system provides a very good linear response to the analyte concentration, as well as high accuracy and exactitude. Thus, limits of detection and quantification of 0.0518 and 0.173 mmol L^{-1}, respectively, were determined. These good characteristics envisage the possibility of developing a sensitive amperometric sensor. Furthermore, SEM, AFM and Raman studies revealed the actual modification produced on the electrode surface.

Keywords: hydrazine oxidation, glassy carbon electrodes, porphyrins, electrocatalysis.

Introduction

Hydrazine (N_2H_4) is a highly reactive basic compound used in many industrial applications, *e.g.* fuel cells, propellants, corrosion inhibitors, explosives, as well as in medical antidepressants development.[1,2] However, despite the many applications of this compound, hydrazine is a highly toxic and irritating compound, which is recognized as a carcinogenic, mutagenic and hepatotoxic substance.[3-5] Consequently, EPA has classified this compound as a group B2, indicating it would likely cause cancer in humans, affecting liver and brain glutathione.

This compound displays no characteristic color but has an ammonia-like odor and its use in fuel cells takes great importance in the field of electrocatalysis, especially in the development of catalysts capable of decreasing the oxidation overpotential of this compound.[6] In this regard, many materials have been tested in order to reduce overpotential, among which are quinizarin, chlorogenic acid, cobalt hexacyanoferrate, cobalt tetraphenylporphyrin,[7] making it possible to obtain electrodes modified with compounds that possess high electrocatalytic activity towards hydrazine electrooxidation. Hence, the overpotential required for this

reaction to occur, basically depends on the used electrode material. Although Pt, Au and Ag electrodes are very active in hydrazine anodic oxidation, these materials are also quite expensive, so that the use of cheaper materials becomes a challenge. Unfortunately, carbon electrodes are inactive to this reaction, and its direct use for detection and quantification of this analyte is not possible. However, metallic octaethylporphyrin complexes electrooxidize hydrazine in aqueous medium, which provides a great opportunity to detect and quantify this compound using glassy carbon electrodes modified with commercial porphyrin complexes. In this regard, the carbon surfaces may be modified due to the presence of inherent functional groups, which is a great advantage in the field of electrocatalysis. Thus, when glassy carbon is used as substrate, the chemistry of its surface controls catalyst dispersion, electrocatalytic activity, selectivity and stability. Particularly, glassy carbon electrodes can be functionalized by non-covalent molecular interactions. These interactions, despite being weaker, leave intact the characteristics of the supporting structure and thus their conducting properties.[8] This way, metalloporphyrins involve π-π type interactions occurring with sp² type carbons of the electrode, and then lead to π-interactions between the same porphyrins (π-stacking). Although such direct electrode modifications may eventually affect the electronic characteristics of metalloporphyrins, great advantages exist, within which is included the obtainment of a highly active system towards reactions of interest, such as hydrazine oxidation, in a simple, fast and effective manner. In the current work, the great applicability of these arrays developed both to

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detect and quantify hydrazine in aqueous medium at neutral pH is demonstrated. To achieve this goal, a porphyrin modified glassy carbon electrode, which is highly electroactive and possesses good electrical properties, was utilized.

Results and discussion

Voltammetric studies

In order to establish the best system for hydrazine electrooxidation, the effect of the central metal ion contained into different octaethylporphyrins was studied. Figure 1A shows the voltammetric profiles of hydrazine oxidation using GC electrodes modified with the different available M-OEPs (M = Co^{II}, Cu^{II}, Zn^{II}, Ru^{II}, Fe^{III} and Ni^{II}).

As can be seen, a great electrocatalytic effect of the Co^{II}-OEP GC modified electrode is obtaining through dipping, while the other porphyrin compounds provokes an electrode passivation effect regarding this reaction (fig. 1A inset), since its electrocatalytic effect is even lower than that observed for unmodified GC. Then, figure 1B shows the response of the modified system in presence and absence of hydrazine, where it is possible to corroborate that the anodic peak observed is due to hydrazine oxidation and not due to the metal center (Co^{II}) of the porphyrin complex.

Several reports exist wherein the electrocatalytic effect of cobalt complexes modified electrodes[9,10] is set; consequently, this metal is a good candidate for hydrazine electrooxidation. These systems report similar peak potentials but at very alkaline pH, where hydrazine is mostly on its unprotonated form (N_2H_4). At this point, GC-Co^{II}OEP can catalyze the same reaction at neutral pH, where hydrazine is protonated and less analyte is available to oxidize.
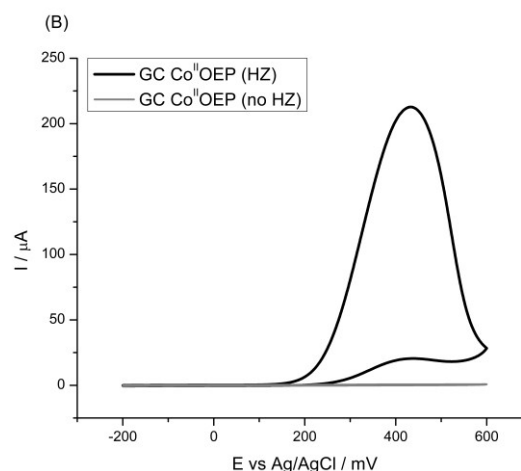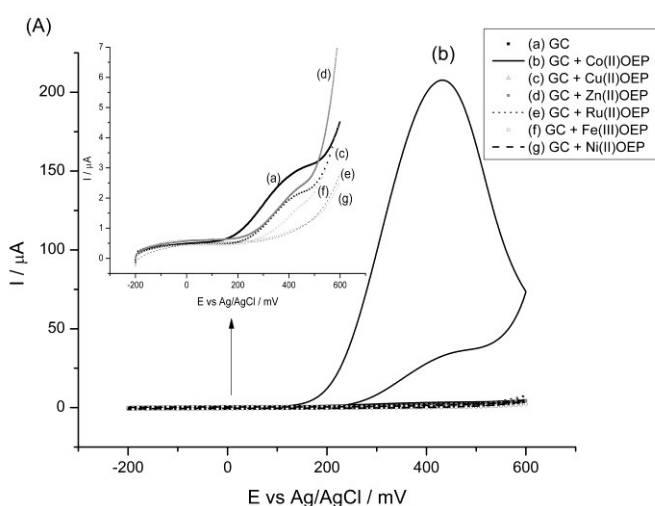

(A)

Figure 1. Voltammetric profile of **(A)** different GC modified systems with metalloporphyrins towards hydrazine oxidation and **(B)** GC-Co^{II}OEP system in presence and absence of hydrazine (HZ) in phosphate buffer solution (pH 7.0) 0.066 M. Concentration of hydrazine: 5.00 mmol L^{-1}. Potential scanned between −200 and 600 mV at 100 mV s^{-1}

The Co^{II} with its d^7 electronic configuration and a respective low-spin (strong field) field would have e_g orbital with an unpaired electron and an empty orbital; hence, no significant repulsive effects exist for the reception of electron density and to facilitate hydrazine oxidative processes to finally generate N_2 as reaction product.

Kinetic studies

To obtain information on the kinetics of the hydrazine oxidation, the effect of potential scan rate using the GC-Co^{II}-OEP electrode was studied. Figure 2 shows the voltammetric profile corresponding to the analyte electrooxidation at different scan rates. It can be appreciated thereof that this is a diffusion-controlled process, since a high linear correlation between I_p and $v^{1/2}$ exists ($R^2 = 0.996$).

Given this information, the number of electrons involved in the hydrazine oxidation reaction is calculated using the Randles-Sevcik equation for an irreversible, diffusion-controlled process,[11,12] which relates the current peak (I_p) versus the scan rate (v):

$$Ip = 2.99 \times 10^5 n[(1-\propto)n_\propto]^{1/2} A C_b D^{1/2} v^{1/2}$$

where A is the electrode area (0.07 cm^2), D hydrazine diffusion coefficient (9.2 x 10^{-6} cm^2 s^{-1},[1,13-15] C_b analyte concentration (5.00 mmol L^{-1}), α the electronic transfer coefficient, n and n_α the number of transferred electrons on the overall reaction and the rate determining step, respectively. These data enables the number of electrons involved in the reaction to be worked out.
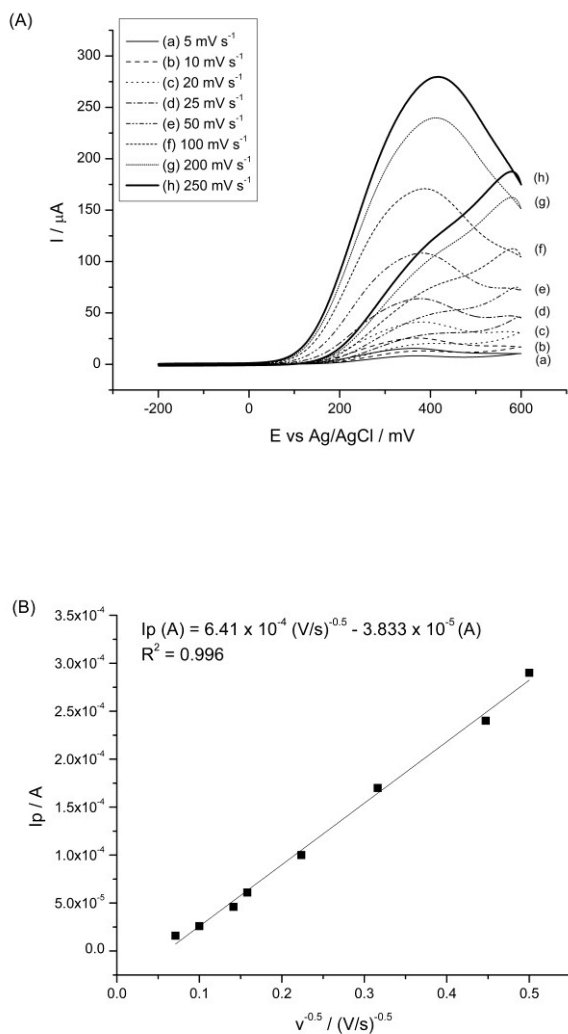
Figure 2. (A) Effect of scan rate on the current response of a 5.00 mM hydrazine electrooxidation at pH 7.0, phosphate buffer solution 0.066 M and **(B)** Ip $vs.$ $v^{1/2}$ plot.

Considering the relationship between the potential peak (E_p) and the half-potential peak ($E_{p/2}$):

$$[(1-\propto)n_\propto = \frac{47.7 \text{ mV}}{E_p - E_{\frac{p}{2}}}$$
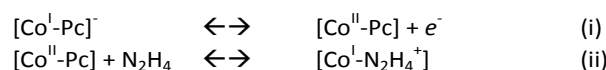
then,

$$[(1-\alpha)n_a]^{1/2} = 0.45$$

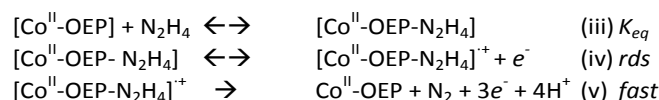Finally,

$$n = \frac{2.01}{0.45} = 4.4 \text{ electrons}$$

Which corroborates hydrazine oxidation involves 4 electrons. Concomitantly, the Tafel equation (equation 1) was used to establish a global reaction mechanism (fig. 3). From that equation, a 99 mV per decade Tafel slope was measured (β), implying that there is a first determining step (rds) involving the transfer of one electron,[9] giving then rise to a second step that produces dinitrogen gas as final product.[16]

$$E \text{ (V)} = \beta \log I \qquad \text{Equation 1}$$

These results differ from those previously observed at cobalt(II) phthalocyanine (Co-Pc) modified electrodes, whose slopes had a value $ca.$ 60 mV per decade[9,17]. In the latter case, the overall reaction involves the Co^{II} metal center reduction to Co^I as follows:

$$[Co^I\text{-Pc}]^- \quad \longleftrightarrow \quad [Co^{II}\text{-Pc}] + e^- \qquad \text{(i)}$$
$$[Co^{II}\text{-Pc}] + N_2H_4 \quad \longleftrightarrow \quad [Co^I\text{-}N_2H_4^+] \qquad \text{(ii)}$$

Consequently, reactions (i) and (ii) would not be part of the overall process. Given this background, the following reaction mechanism at pH close to 7.0 is proposed:[18]

$$[Co^{II}\text{-OEP}] + N_2H_4 \longleftrightarrow [Co^{II}\text{-OEP-}N_2H_4] \qquad \text{(iii) } K_{eq}$$
$$[Co^{II}\text{-OEP-}N_2H_4] \longleftrightarrow [Co^{II}\text{-OEP-}N_2H_4]^{\cdot+} + e^- \qquad \text{(iv) } rds$$
$$[Co^{II}\text{-OEP-}N_2H_4]^{\cdot+} \rightarrow Co^{II}\text{-OEP} + N_2 + 3e^- + 4H^+ \quad \text{(v) } fast$$

Due to the large porphyrins π-clouds, they are able to stabilize the radical produced in the rds,[19] which remains stable thanks to Co^{II}-OEP and thus the oxidation is allowed to proceed. The intermediate radical cation $[Co^{II}\text{-OEP-}N_2H_4)]^+$ is rapidly oxidized to regenerate the catalyst (Co^{II}-OEP) and forming N_2 as final product of the reaction. Hence, when N_2H_4 catalytic electrooxidation occurs via 4-electrons, the Co^{II}-OEP system enters a new catalytic cycle.
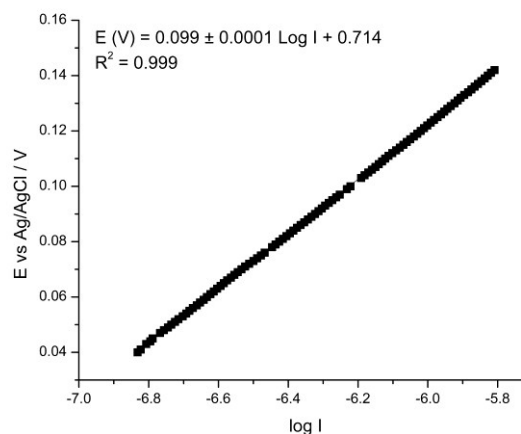

Figure 3. Tafel plot slope for the GC system plus Co^{II} porphyrin-monomer multilayers for hydrazine oxidation in phosphate buffer (pH 7.0) 0.066 M and 5 mV s^{-1} scan rate.

High Tafel slopes values in completely reversible systems (as here), have been associated with the great interaction between the catalyst and analyte,[20] wherein the substrate (analyte) strongly binds to the catalyst during the interaction as reaction intermediate.

On the other hand, the change of pH is important in the hydrazine oxidation reaction, which can lead to a different reaction mechanism.[21] In this regard, the porphyrinic catalysts may be affected at alkaline pHs, owing to the irreversible porphyrin ring electrooxidation,[18,19] despite the fact that, concomitantly, more analyte is available. This effect is unfavorable for the catalytic process involving electron transfer since the electrocatalytic activity is reduced. For this reason, all studies were performed at pH near to 7.0.

Morphological studies

In order to substantiate the GC electrodes modification, SEM, AFM and Raman studies were conducted and compared with unmodified electrodes. The latter study was carried out at gold electrodes in order to obtain clearer signals coming from molecular vibrations. Also, glassy carbon itself is not a suitable substrate for Raman studies due to its inappropriate optical and electronic properties, and any enhancement on carbon would be very small. Then, by using gold substrates, it is possible to get better responses from different vibrations.

Figure 4 shows SEM images corresponding to GC modified (GC-Co^{II}OEP) and bare GC electrodes. As seen, metalloporphyrins deposition over the electrode surface is corroborated, so that this result adds up evidence to the morphological tests previously accomplished for these systems employing AFM.[22] Figure 5 shows the results obtained in this study by using this technique.
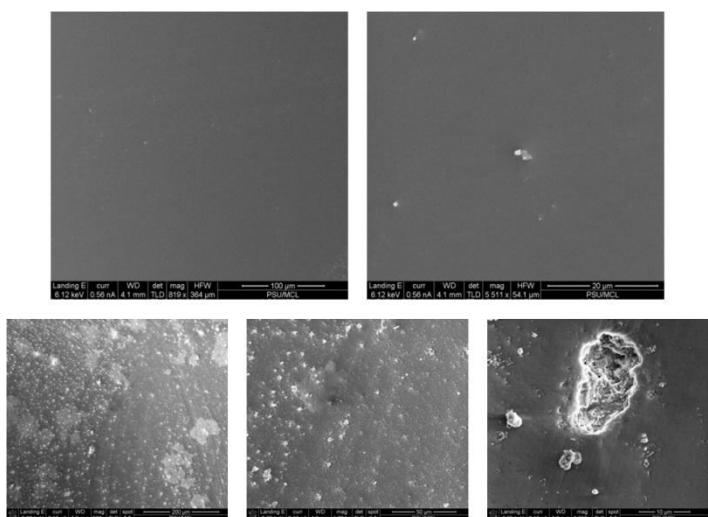

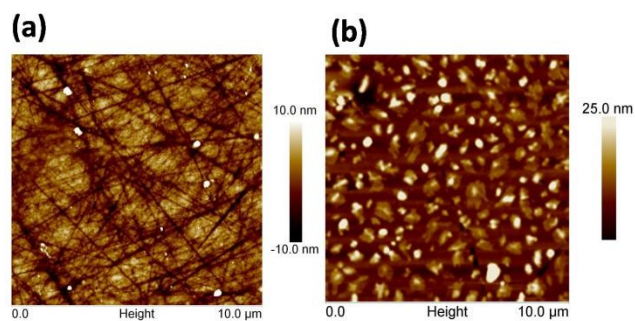**Figure 4.** SEM images of bare GC electrode (up) and GC-Co^{II}OEP (down)

Figure 5. AFM images corresponding to **(a)** GC and **(b)** GC-Co^{II}OEP system.

At this point, roughness values (Rq) change from 10.0 nm to 25.0 nm, which corroborates the results observed on SEM images concerning to morphological changes on the GC surface after modification with Co^{II}OEP.

From figure 1, the amount of Co^{II}-OEP adsorbed in the system was determined, whose value was 4.4 x 10^{-8} mol cm^{-2}, considering the respective I vs. t (Q) integral curve.

Thus, the morphological change of the electrode surface is evidenced. Similarly, RAMAN tests on gold electrodes were performed and signals vibration changes observed. Figure 6 shows the results of this study.

As seen, the signals of the pure reagent (Co^{II}-OEP) are different from those found for the modified electrode (Au + Co^{II}-OEP), where the pure reagent shows more intense signals in comparison to the modified electrode. Also, when the substrate is modified, mostly of the molecular vibrations that are between 1500 and 4000 cm^{-1} disappear. Assignations of molecular vibrations are shown in table 1.
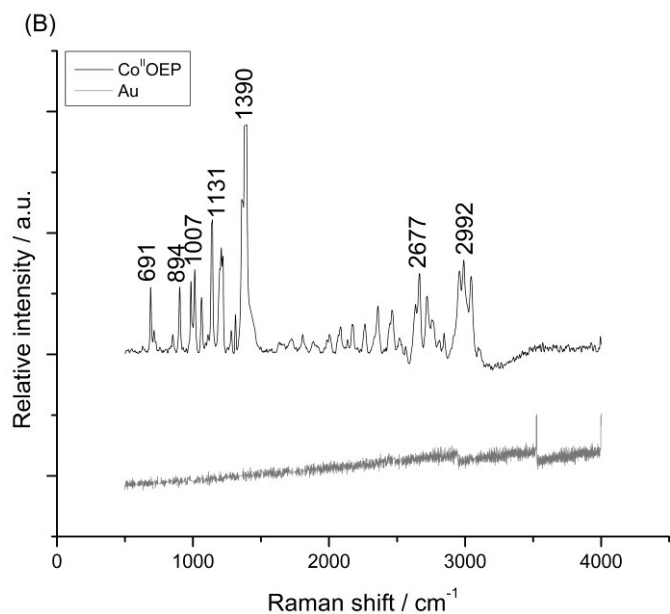
(B)
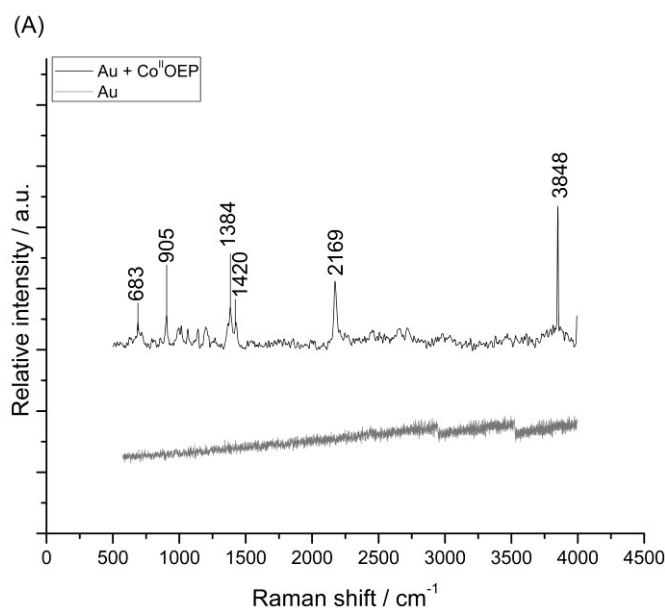
Figure 6. Raman spectra of **(A)** Au, Au–Co^{II}OEP electrodes and **(B)** Au electrode and Co^{II}OEP pure reagent. λ_{exc} = 532 nm

Table 1. RAMAN assigned signals for Au-Co^{II}OEP and Co^{II}OEP (v = stretch, δ = deformation vibration about the C_2 axis of pyrrole ring)

Au – Co^{II}OEP Raman frequency (cm⁻¹)	Assignment
3848	v (C-H)
2169	v (C-H)
1420	v (C-C), v (C-Et)
1384	v (C-C), v (C-Et)
905	v (C-C), v (C-N), v (C-Et)
683	δ (C-C-N), v (C-C)

Co^{II}OEP Raman frequency (cm⁻¹)	Assignment
2992	v (C-H)
2677	v (C-H)
1390	v (C-C), v (C-Et)
1131	v (C-Et), v (C-N)
1007	v (C-C), v (C-N), v (C-Et)
894	v (C-Et), δ (C-C)
691	δ (C-C-N), v (C-C)

Then, evidence concerning electrodes modification with cobalt porphyrins was confirmed.

According to the general interpretation of porphyrins vibrational spectra, such as that used in this study,[23] only A_{1g} and B_{1G} symmetry vibrations are active for D_{4h}, and symmetry types such as A_{1g} B_{1G} and B_{2g} for D_{4h} symmetry (metal porphyrins). Any explanation concerning the nature of the porphyrin ring vibrations involves an experimental and theoretical problem. This way, it is known that signals around 1600 cm⁻¹ correspond to the vibrations set involving C = C bonds at the methine bridges.

Consequently, it can be concluded that as the MN (pyrrole) bond become stronger, the shorter the distance between C–N and therefore, the greater the frequency corresponding to the ring stretching. This metal-dependent effect results in a balance of attractive conjugated interactions between the 4p orbital of the metal and porphyrin a_2u orbital and a corresponding repulsion between the metal dx^2-y^2 orbital and $2px$, and nitrogen orbital. This interaction phenomenon is crucial when the dx^2-y^2 orbital is occupied.[24] It is noteworthy that, usually, the vibrations assigned in the current study present greater frequencies values in the modified system than in the pure salt, demonstrating the actual modification of the electrode.

Electrochemical impedance (EIS) study

To establish the electrical characteristics of the systems, GC and GC-Co^{II}OEP were studied with regard to hydrazine (5.00 mmol L⁻¹) electrochemical oxidation at pH 7.0, utilizing electrochemical impedance spectroscopy technique.

Figure 7 shows Nyquist plots obtained for the studied systems. As appreciated, the GC-Co^{II}-OEP modified system tends to close the semicircle at lower Z'' values, indicating a lower charge transfer resistance towards hydrazine electrooxidation. Next, the simulation of the electrical parameters using different equivalent circuits (fig. 7 inset) was accomplished. The obtained values are summarized in Table 2.

Noticeable differences with respect to the R_{ct} values of both systems exist. In this respect, the modified system possesses lower charge transfer resistance, facilitating the hydrazine oxidation, corroborating thus the results found in the voltammetric study. Differences in the Constant Phase Element (CPE) values show that the modified electrode increases the uniformity of the porphyrin immobilized film.[25] The apparent electron-transfer rate constant (k_{app}) is calculated using equation 2 where R is the gas constant (8314 J mol⁻¹ K⁻¹), T the absolute temperature of the system (298 K), F the Faraday constant (96485 C mol-1) and C the analyte concentration in the system (5.0 x 10⁻⁶ mol cm⁻³).

$$k_{app} = \frac{RT}{F^2 R_{ct} C} \quad \text{Equation 2}$$
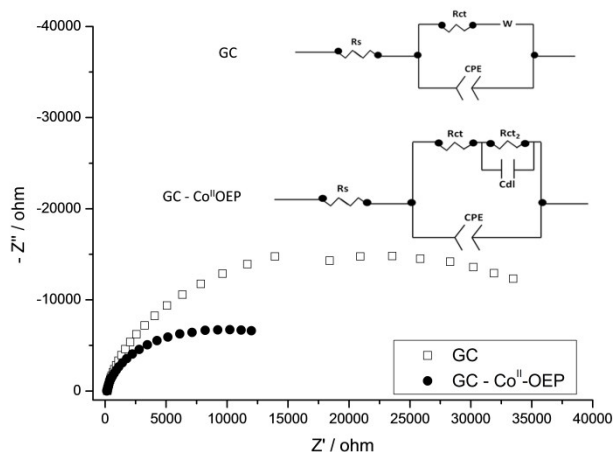
Figure 7. GC and GC-Co^{II}OEP systems Nyquist-diagrams in 5.00 mmol L^{-1} N$_2$H$_4$, pH 7.0 phosphate buffer, solution. Frequency range 100,000 – 0.1 Hz, constant potential 0.35 V and equivalent circuits utilized in this study. Equivalent circuits (inset)

Table 2. GC and GC–Co^{II}OEP electrical parameters obtained by EIS

Parameters	GC	GC-Co^{II}OEP
R_s (Ω)	160	128
R_{ct} (Ω)	37.8	11.9
CPE (F cm^{-2})	0.89	0.67
W (Ω cm^{-2} s$^{1/2}$)	0.57	-
C_{dl} (F cm^{-2})	-	6.9E-6
R_{ct2} (Ω)	-	4.6

Thus, k_{app} would have a value 1.4×10^{-12} cm s^{-1} and 4.5×10^{-12} cm s^{-1} for GC and GC-Co^{II}-OEP systems, respectively. A greater k_{app} value in the modified system is an indication that the electron transfer is faster compared to the unmodified electrode. This effect also suggests the existence of a short "electron-tunnel" distance between the porphyrin layers and the GC electrode surface.[26]

On the other hand, it is evident that the modified system, unlike the bare electrode, possesses no significant diffusional effects altering the electron transfer (W), therefore its electrical component is zero. Besides, this system has a new interface corresponding to GC and octaethylporphyrin. Hence, a new electric element (R$_{CT2}$) exists corresponding to a second charge transfer resistance between these materials, and, along with it, its corresponding electrical double layer (C$_{dl}$). In this case, the value of R$_{ct}$ would correspond to the charge transfer resistance of the entire system, whose value is lower than that reported for GC.

Analytical studies

Once the optimal electrochemical parameters for hydrazine identification was established, the validation of the proposed technique is conducted, by studying analytical parameters, which would allow to propose the system as a prospective amperometric sensor for hydrazine.

Linearity, limit of detection and limit of quantification study. Increasing the analyte concentration in the system, the current peaks become better defined at a potential close to 0.35 V. Figure 8 shows the voltammetric responses of the GC-Co^{II}-OEP electrode for hydrazine electrooxidation and the respective calibration curve. Given the observed linearity (R^2 = 0.999), the use of cyclic voltammetry for hydrazine quantification in aqueous media at neutral pH seems possible.

Hence, a total of 6 calibration curves were constructed from voltammograms obtained using 0.05 to 5.00 mmol L^{-1} hydrazine solutions under the same working conditions. This concentration range was chosen having in mind to cover the widest possible concentration range, so that the technique can be applied to a variety of aqueous samples.

The slope and standard deviation values were different for each curve, however, these values kept their order of magnitude (table 3). As shown, all calibration curves displayed high linearity since all R^2 are very close to unity.

From these data the LOD and LOQ for each curve was determined. These values were calculated from the slope of the line obtained using the equations below.

$$LOD = \frac{3 \times \sigma}{slope} \qquad LOQ = \frac{10 \times \sigma}{slope}$$

Mean LOD and LOQ was 0.0518 and 0.173 mmol L^{-1}, respectively. These values are comparable to previously reported studies with other systems[27-29] (table S1), considering the quick and simple way to obtain this modified system, and, on the other hand, the pH of the solution, lower than hydrazine pKa of 7.9,[30,31] which means that most of the hydrazine available at the solution is its protonated form (more difficult to oxidize).

Finally, from the obtained curves, an average calibration curve is worked out, whose linear regression fits the relationship Ip (A) = 3.25 x 10^{-5} ± 1.13 x 10^{-6} [N$_2$H$_4$] (mmol L^{-1}) + 4.32×10^{-6} (A), with a correlation coefficient (R^2) 0.998. This curve will support or back up the upcoming analytic-statistical determinations that are carried out in this study.
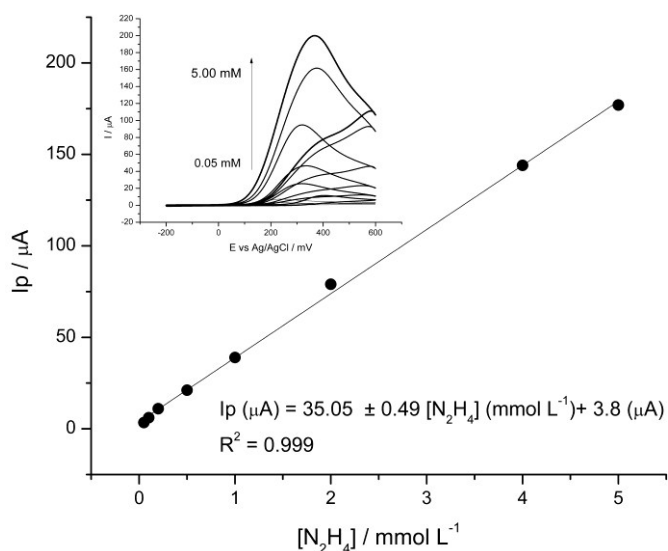
Figure 8. Voltammograms from hydrazine electrooxidation at the GC-Co^{II}OEP system using different concentrations, at phosphate buffer solution, pH 7.0, 0.066 M and 100 V s^{-1} scan rate (inset) and calibration curve corresponding to the voltammetric response of the modified electrode.

Table 3. Calibration curves data obtained from Ip (µA) vs. hydrazine concentration (mmol L^{-1}). Standard deviation (σ) and correlation coeficient (R^2) are also included.

Curve	Intercept (µA)	Slope (mM)	Σ	R^2	LOD (mM)	LOQ (mM)
1	3.63	38.5	1.90	0.997	0.0633	0.211
2	5.77	34.5	1.76	0.997	0.0635	0.212
3	5.11	39.6	2.10	0.997	0.0668	0.223
4	3.08	26.0	0.62	0.999	0.0302	0.101
5	4.13	22.0	0.78	0.998	0.0455	0.152
6	4.86	35.1	1.17	0.999	0.0416	0.139

Accuracy study. In an analytical study, it is always important to know how high the level of agreement between a set of measurements is. In this accuracy study, the parameter was analyzed at two levels and the scatter of the data was observed with respect to its mean.

a) Replicability.

For this assay, the cyclic voltammograms of 8 aliquots were recorded under the same previously used working conditions at pH 7.0. From the obtained results mean ($\overline{X}$), variance (σ^2), standard deviation (σ) and coefficient of variance (C$_V$) statistic

parameters were calculated. Measurements were carried out within the same day, using the same modified electrode.

b) Repeatability.

Similarly, the repeatability test was accomplished. In this case, the measurements were performed within the same day but using different modified electrodes (2 electrodes, 4 aliquots measured for each system).

Table 4 shows the values of the analytic statistical parameters for each conducted test. As observed in Table 4, the repeatability test is slightly more heterogeneous than that of replicability, due to the variation of the systems used. However, it is possible to establish that at both levels, the method is quite homogeneous, since the values found for the statistical parameters showed that the variation is small and consequently, the method is precise, independent of the utilized measuring system. Also, this study indicates that the system shows a good stability, since all current responses are similar, as well as linearity study showed. Chronoamperometry at fixed potential was also carried out in order to corroborate this information (figure S1).

Exactitude study. To determine the exactitude of the developed analytical procedure using the modified system, a real sample consisting of a standard 5.00 mmol L^{-1} hydrazine solution was analyzed. To this purpose, three aliquots of a 35wt. % hydrazine solution were quantified. The mean peak current was 1.75×10^{-4} A. From this value and the calibration curve found in the linearity study, statistical results were obtained and they are summarized in Table 5.

Consequently, considering that the relative error is lower than 5%, the modified system is considered exact,[32] and therefore a prospective amperometric sensor for hydrazine.

Table 4. Analytic statistical parameters for testing accuracy at repeatability and replicability level

Parameters	Replicability	Repeatability
Mean ($\overline{x}$)	2.082×10^{-4} A	2.027×10^{-4} A
Standard deviation (σ)	5.779×10^{-6}	9.236×10^{-6}
Variance (σ^2)	3.340×10^{-11}	8.530×10^{-11}
Variance coefficient (%)	2.78	4.56

Table 5. Exactitude of N$_2$H$_4$ 5.00 mmol L^{-1} determination using the GC-Co^{II}OEP system

Exactitude parameter	N$_2$H$_4$ 5.00 mM
Mean (mM)	5.17
Absolute error (mM)	0.17
Relative error (%)	3.28
Samples number (n)	3

Experimental

Chemicals and Solutions

KCl, NaOH and Cl_2CH_2 p.a. reagents were purchased from Merck. Deionized water was obtained from a Millipore-Q system (18.2 MΩ·cm). Argon (99.99 % pure) and dioxygen gas were purchased from AGA, Chile. Metalloporphyrins (2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine cobalt(II), 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine copper(II), 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine zinc(II), 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine ruthenium(II) carbonyl, 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine iron(III) chloride and 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine nickel(II)), sodium dibasic phosphate, potassium monobasic phosphate, hydrazine salt and hydrazine standard solution (35 wt. % in water) were all Sigma-Aldrich, Chile.

Instrumentation

Cyclic voltammetry studies were performed on a CH Instruments 750D potentiostat galvanostat. The conventional three-electrode system consisted of a glassy carbon (GC) working electrode (0.071 cm^2), Ag/AgCl (3M KCl) reference electrode, and a platinum wire counter electrode.

Scanning Electron Microscopy (SEM) studies were conducted on a Nova NanoSEM™ 630 and Raman spectra were obtained on a Renishawmicro Raman instrument. For the latter experiment, gold electrodes were used in order to obtain improved responses. AFM studies were carried out on an Innova1 Atomic Force Microscope (AFM). Tapping mode was employed in all samples.

Preparation of modified electrodes and analysis

The GC electrode was polished to a mirror finish on a felt pad using alumina slurries (3 μm), sonicated for 120 s in deionized water and finally stabilized by scanning the potential between -0.7 V and 0.7 V in a 0.1 M NaOH solution under Ar atmosphere with the aim of removing all substances adsorbed to the surface (by oxidizing/reducing them) and get reproducible responses.

Cleaned and stabilized electrodes were immersed into a 0.2 mM metalloporphyrin solution, M-OEP (M = Co^{II}, Cu^{II}, Zn^{II}, Ru^{II}, Fe^{III} and Ni^{II}) dissolved in CH_2Cl_2 for 20 minutes at room temperature (GC-M-OEP). The electrodes were then dried at room temperature for 1 min.

Hydrazine electrooxidation was carried out by scanning the potential between -0.2 and 0.6 V, in 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0 and 5.00 mM hydrazine solutions prepared in pH 7.0 phosphate buffer solutions (Na_2HPO_4/KH_2PO_4) 0.066 M, using GC and modified electrodes (GC-M-OEP).

Morphological studies were accomplished using SEM and AFM. These studies were all conducted on glassy carbon substrates.

Raman spectra were obtained by modifying gold electrodes, following the same procedure utilized for GC electrodes. Gold-coated glass slides (EMF Corp. CA134, 100 nm Au deposited onto a 5 nm Cr adhesion layer on float glass) were used as gold electrodes. These electrodes were cleaned by sonication in acetone for 40 minutes before each modification, followed by stabilization in a 0.1 M NaOH solution by sweeping the potential between -1.0 and 1.0 V. 532 nm laser excitation wavelength was used.

Conclusions

A highly active system was found (GC-Co^{II}-OEP) for hydrazine electrooxidation at neutral pH. SEM, AFM and Raman studies corroborated the actual modification over the electrode surface by Co^{II}-OEP adsorption, while EIS studies established that the GC-Co^{II}-OEP modified array exhibited lower resistance to electron transfer than the unmodified GC electrode.

The system presents a linear I_p current *vs.* analyte concentration relationship, exhibiting low detection and quantification limits, *e.i.* the system proved to be accurate and exact.

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