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Electrooxidation and determination of dopamine using a Nafion®-cobalt hexacyanoferrate film modified electrode

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Sensors **2008**, *8*, 1950-1959

sensors

ISSN 1424-8220
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Full Research Paper

Electrooxidation and Determination of Dopamine Using a Nafion®-Cobalt Hexacyanoferrate Film Modified Electrode

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Received: 29 May 2007 / Accepted: 17 March 2008 / Published: 19 March 2008

Abstract: The electrocatalysis of dopamine has been studied using a cobalt hexacyanoferrate film (CoHCFe)-modified glassy carbon electrode. Using a rotating disk CoHCFe-modified electrode, the reaction rate constant for dopamine was found to be 3.5×10^5 cm^3 mol^{-1} s^{-1} at a concentration of 5.0×10^{-5} mol L^{-1}. When a Nafion® film is applied to the CoHCFe-modified electrode surface a high selectivity for the determination of dopamine over ascorbic acid was obtained. The analytical curve for dopamine presented linear dependence over the concentration range from 1.2×10^{-5} to 5.0×10^{-4} mol L^{-1} with a slope of 23.5 mA mol^{-1} L and a linear correlation coefficient of 0.999. The detection limit of this method was 8.9×10^{-6} mol L^{-1} and the relative standard deviation for five measurements of 2.5×10^{-4} mol L^{-1} dopamine was 0.58%.

Keywords: Cobalt hexacyanoferrate; chemically modified electrode; dopamine; voltammetry; rotating disk electrode.

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1. Introduction

There is an increasing demand for simple and sensible analytical methods for the determination of biological compounds. In this context, dopamine is an important neurotransmitter in the mammalian

central nervous system and plays a pivotal role in the regulation and control of movement, motivation and cognition. Abnormalities in brain dopamine levels are associated with many neurological and psychiatric disorders including Parkinson's disease, schizophrenia and the use of substances of abuse. The dopamine system is therefore an important topic in neuroscience research and an important target for the development of pharmaceutical products.

The electrochemical oxidation of dopamine has been studied on carbon base electrodes, for *in vivo* and *in vitro* determinations [1-5]. Although dopamine exhibits a characteristic cyclic voltammetric oxidation wave, it is sensitive to the nature of the carbon surface exposed [6] and its electrochemical oxidation at glassy carbon electrode proceeds with a large overpotential, making its quantitative evaluation very difficult. One promising approach for minimising these effects is the use of chemically modified electrodes, which use the ability of certain surface bound redox mediators to enhance the electron-transfer kinetics and thus decrease the operating potential.

The chemical modification of electrodes using inorganic films is an attractive approach in the development of electrochemical sensors [7]. One electrode modification scheme that has attracted significant interest is the generation of films of transition metal hexacyanoferrates such as Prussian Blue and its analogues [8]. Such modified electrodes are useful for a variety of charge-transfer studies including efforts to enhance rates of electron transfer of solution substrates. The ability of solution substrates to enter (or exit) the film can be controlled by choice of suitable derivatising layer. This can be evidenced by several electrocatalytic studies that have been reported in the literature [9-26], which include the study of the determination of dopamine using nickel hexacyanoferrate (NiHCFe)-modified microdisk platinum electrodes [12]. Such results were shown to be promising, with the catalytic current increasing linearly with the concentration of dopamine in the range from 1×10^{-4} to 1.5×10^{-2} mol L^{-1}.

In this context, cobalt hexacyanoferrate (CoHCFe)-modified glassy carbon electrodes have been applied as biological sensors to the determination of hydrogen peroxide [13], ascorbic acid [14] and glucose [15]. Additionally, CoHCFe has also presented electrocatalytic activity for oxidation of dopamine [16,17], whose electrochemical behaviour has been well reported. However, no electroanalytical measurements for selective determination of dopamine at μmol L^{-1} level in the presence of ascorbic acid were reported in the literature, using glassy carbon modified with CoHCFe/Nafion® film. Furthermore, in an attempt to develop an amperometric sensor to quantify dopamine, we present the utilisation of a Nafion®-cobalt (II) hexacyanoferrate (CoHCFe) film modified glassy carbon electrode for the oxidation and determination studies of this compound. Considering that ascorbic acid, also present in the extracellular fluid found in the central nervous system, is the main interferent in the dopamine determination, a study of selectivity between these compounds was also realised.

2. Experimental

2.1 - Apparatus and chemicals

Cyclic voltammetric measurements were carried out using a model 273A EG&G potentiostat, under the control of M270 EG&G electrochemical software. A three-electrode EG&G cell was employed with a CoHCFe-modified glassy carbon electrode (0.013 cm^2), a Ag/AgCl (saturated aqueous KCl)

reference electrode and a platinum plate auxiliary electrode. To perform the measurement of the reaction rate constant, an EG&G - PAR, model 616 disk electrode system was utilised.

All chemical reagents were of analytical grade and all solutions were prepared using deionised water. Nafion®, as a 5 wt.% ethanol solution and the dopamine hydrochloride were obtained from Aldrich and Sigma, respectively. Dopamine solutions were prepared immediately before use by dissolution in 1.0 mol L^{-1} aqueous NaCl solution and the electrochemical experiments were carried out with a previous flow of nitrogen gas through all solutions during 10 minutes.

2.2 - Electrode preparation

Glassy carbon electrodes (GCE) were polished until a mirror-like appearance with alumina powder (0.05 μm), then rinsed with water, cleaned in an ultrasonic aqueous bath and again rinsed with water before use. Cobalt hexacyanoferrate (CoHCFe) films were prepared by successive potential cycling, from 0.00 to 1.00 V vs. Ag/AgCl, in an oxygen free solution containing 0.50 mmol L^{-1} of $K_3Fe(CN)_6$ and 1.0 mmol L^{-1} of $CoCl_2$ in 0.50 mol L^{-1} NaCl, at a scan rate of 100 mV s^{-1}, in similar conditions as described in the literature [28]. After film formation, electrodes was rinsed with deionised water and cycled in 1.0 mol L^{-1} NaCl between 0 and 0.75 V vs. Ag/AgCl, at a scan rate of 50 mV s^{-1} until a steady current-voltage profile was obtained, then subjected to further experiments. The amount of cobalt hexacyanoferrate adsorbed on the electrode was calculated as 1.9×10^{-8} mol cm^{-2} from the charge measured on integration of the voltammetric oxidation currents of the adsorbent. To prepare a Nafion®-coated surface, the cobalt hexacyanoferrate film modified electrode was dipped into the 5 wt.% alcoholic solution containing the polymer in a small vial. The electrode surface was subsequently dried for 30 minutes at room temperature without gas flow.

3. Results and Discussion

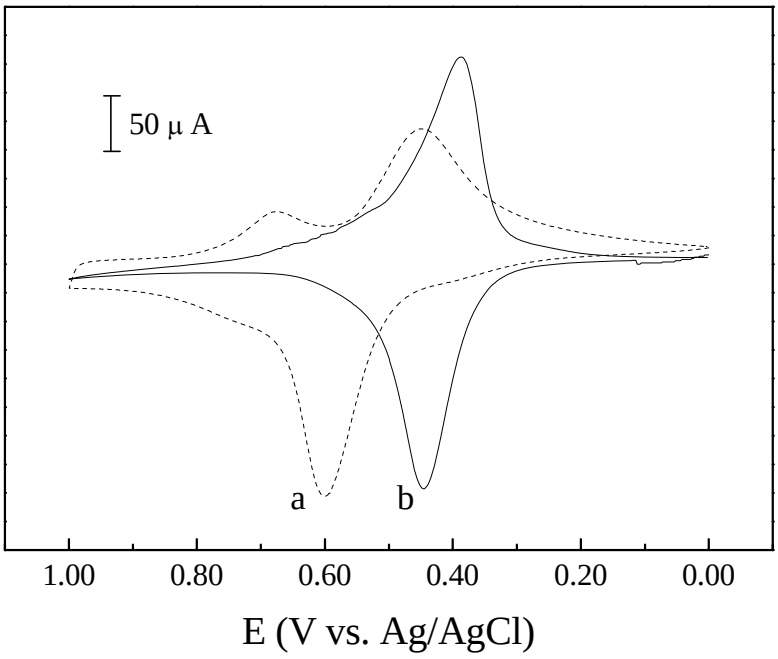
3.1 - Electrochemical behaviour of the modified electrode

When the films were investigated in pure supporting electrolytes, similar characteristics as reported in literature [27] were observed. Figure 1 shows cyclic voltammetric responses of cobalt hexacyanoferrate (CoHCFe) films in 1.0 mol L^{-1} KCl (curve a) and in 1.0 mol L^{-1} NaCl (curve b).

In potassium ion-containing electrolyte, the CoHCFe film undergoes a double oxi-reduction peak, due probably to the existence of two distinct forms. The form that contains less potassium ion and thus is less strongly paired by K^+ ions shows electroactivity at more negative potentials. Nevertheless, in sodium ion-containing electrolyte, the CoHCFe film is characterised by a single set of well-defined peaks that appear at more negative potentials when compared to their respective peaks in the potassium ion-containing electrolyte.

Considering the fact that the electrochemical catalysis of dopamine oxidation is of fundamental importance for its determination, all the subsequent studies were realised in NaCl-containing supporting electrolyte. It was also important to establish the optimum concentration of supporting electrolyte for the dopamine study.

Figure 1. Cyclic voltammetric responses of CoHCFe films in 1.0 mol L^{-1} KCl (curve a) and in 1.0 mol L^{-1} NaCl (curve b). v = 50 mV s^{-1}.



In agreement with the Nernst equation, the formal potential of the CoHCFe film redox couple is also related to the concentration of the cation in solution [29]

$$E = E^{o\prime}_{Na+} + (RT/nF) \ln (a_{CoHCFe\ ox} \times a_{Na+} / a_{CoHCFe\ red}) \quad (1)$$

Therefore, cyclic voltammetric studies in different concentrations of NaCl (0.01, 0.1 and 1.0 mol L^{-1}) were realised. Due to the increase in the activity of Na^+, the cathodic peak shifted to more positive potential and a larger reversibility was observed, in agreement with that described in literature [29]. So, cyclic voltammetric studies with variation of scan rates, using 1.0 mol L^{-1} NaCl supporting electrolyte, were realised. The results showed that the electron transfer between the substrate and the CoHCFe film is the faster transport process. The peak currents increase linearly with scan rate and the relation i_{pc}/i_{pa} is equal to the unity, being consistent with reversible redox system behaviour. The formal potential of +0.45 V vs. Ag/AgCl was obtained by averaging the cathodic and anodic peak potentials. Because the cobalt(II) cannot be reduced in this potential range, the redox peaks correspond to the surface-confined hexacyanoferrate(II/III) redox couple. The redox process can be represented by general equation:

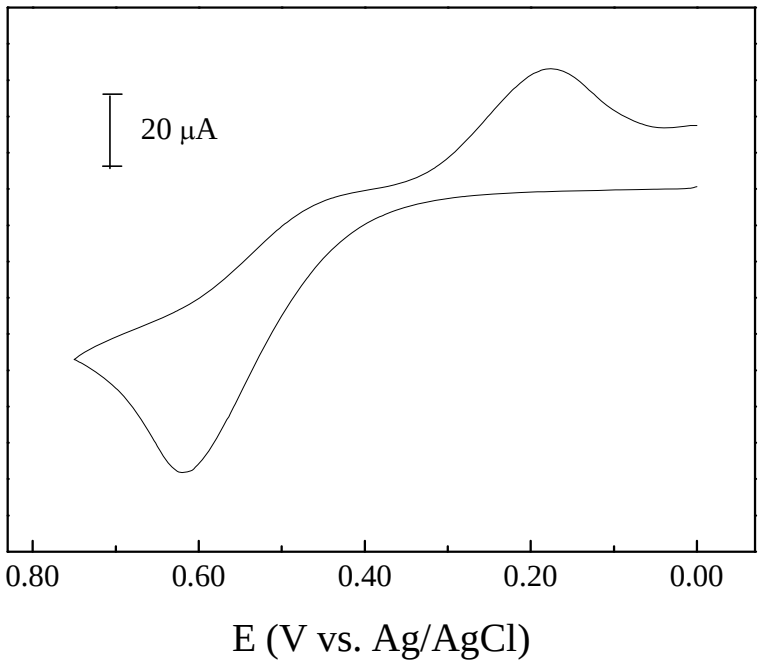
$$NaCo^{II}[Fe^{III}(CN)_6] + Na^+ + e^- \rightleftharpoons Na_2Co^{II}[Fe^{II}(CN)_6] \quad (2)$$

Successive potential scanning in 1.0 mol L^{-1} NaCl solution showed that, after 100 cycles, there was a decrease of only 7% in the peak current, indicating good stability of the CoHCFe-modified electrode.

3.2 - Electrochemical catalysis of dopamine oxidation at a CoHCFe modified electrode

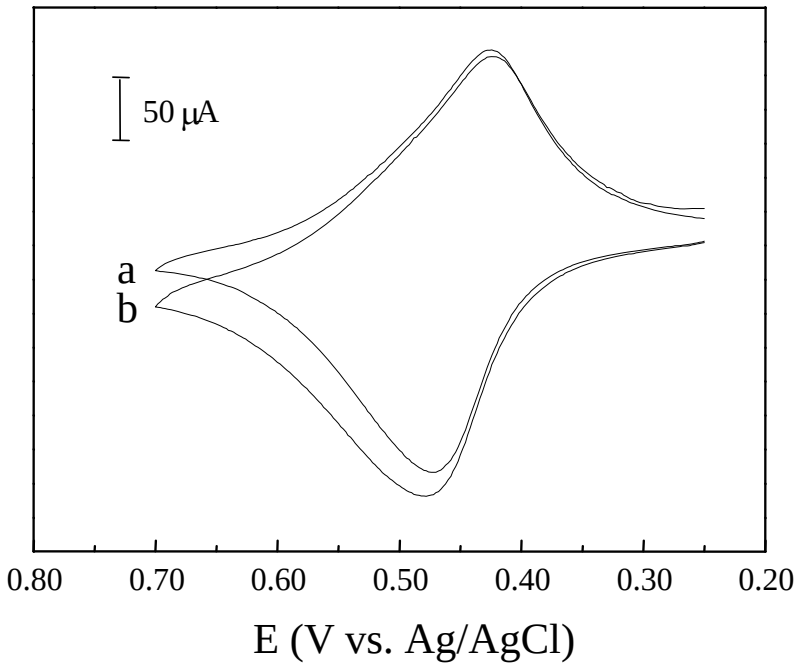
Figure 2 shows the cyclic voltammogram obtained for 2.8×10^{-4} mol L^{-1} dopamine, in 1.0 mol L^{-1} NaCl solution, at bare glassy carbon electrode (GCE). The electrochemical oxidation process reveals one anodic peak at 0.62 V vs. Ag/AgCl and one cathodic peak in 0.18 V vs. Ag/AgCl.

Figure 2. Cyclic voltammogram of 2.8×10^{-4} mol L^{-1} dopamine in 1.0 mol L^{-1} NaCl at glassy carbon electrode. $\nu = 50$ mV s^{-1}.



On the other hand, when the electrochemical oxidation of dopamine is investigated at CoHCFe-modified electrode (Figure 3), in the same experimental condition, a reversible electron transfer process is observed.

Figure 3. Cyclic voltammograms of the CoHCFe film-modified electrode in (a) 1.0 mol L^{-1} NaCl solution and (b) 2.8×10^{-4} mol L^{-1} dopamine in 1.0 mol L^{-1} NaCl. $\nu = 50$ mV s^{-1}.



The peak potential of dopamine oxidation at the CoHCFe film-modified electrode is shifted 170 mV to more negative potential range in relation to the unmodified GCE. In addition, there is an increase in the anodic peak current, proportional to the concentration of dopamine, corresponding to the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ of the CoHCFe film. The catalytic activity of the redox couple at 0.45 V clearly mediates the oxidation of dopamine and reduces the overpotential effect, otherwise observed at the solid electrode. The electrochemical process can be represented by the general equation:

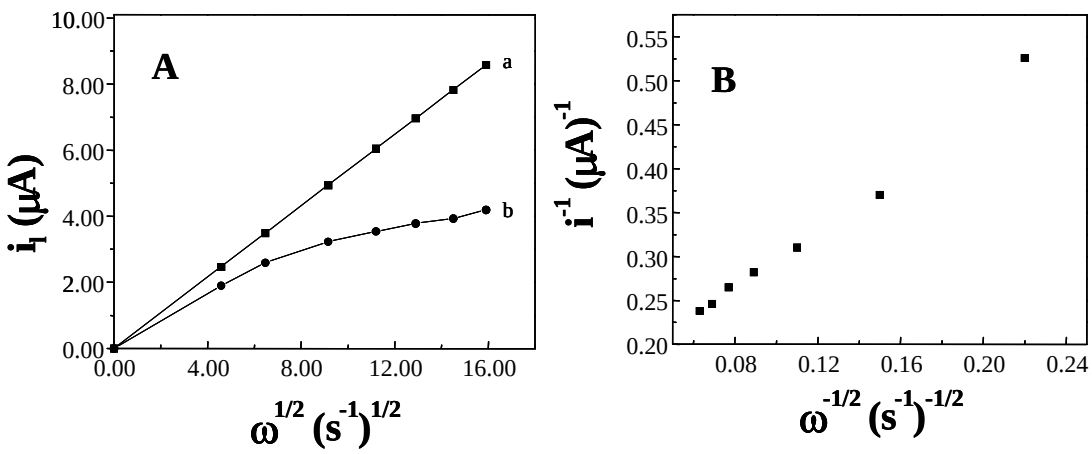
$$2NaCo\,[Fe(CN)_6] + 2Na^+ + Dop_{red} \rightleftharpoons 2Na_2Co\,[Fe(CN)_6] + Dop_{ox} \quad (3)$$

It was noteworthy that the limiting current of dopamine oxidation at the CoHCFe film was lower than at the unmodified GCE. This indicates that the overall reaction rate of the system is mainly controlled by the catalytic reaction, rather than diffusion of the dopamine.

3.3 - Electrochemical catalysis of dopamine oxidation at a CoHCFe film-modified rotating glassy carbon disk electrode

The catalytic reaction of dopamine at a CoHCFe-modified rotating disk electrode was also studied, to enable the acquisition of more detailed information about the kinetics of the catalytic process. Figure 4A shows the shape of the curves of limiting current (i_l) vs. square root of the rotation rate. The Levich plot shows that the oxidation current of dopamine increases with the rotation rate of electrode but does not vary linearly with the square root of the rotation rate.

Figure 4. A) Levich plot for dopamine oxidation at CoHCFe film modified electrode in 1.0 mol L^{-1} NaCl solution. The curve (a) is the expected mass transport limited current and the curve (b) was obtained experimentally for concentration of 5.0×10^{-5} mol L^{-1} dopamine. B) Koutecky-Levich plot for equal experimental condition as in Figure 4A.



Furthermore, i_l is always found to be lower than the value calculated by using the Levich equation, which describes a purely mass transport limited process:

$$i_{lev} = 0.620\, n\, F\, A\, D^{2/3}\, \nu^{-1/6}\, C\, \varpi^{1/2} \quad (4)$$

In this equation, D and C are diffusion coefficient and bulk concentration of the solution species, respectively, ϖ is the rotation rate and ν is the kinematic viscosity of the aqueous electrolyte. This fact indicates that at low rotation rate values the current was controlled by the transport of dopamine through the rather thick Levich layer so that the behaviour of i_l vs. $\varpi^{1/2}$ appeared to be linear. At higher values of ϖ, the thickness of the Levich layer decreased and the current becomes controlled by rate of chemical reaction between the dopamine and the film such as indicated by cyclic voltammetry.

The catalytic currents (i_l) corresponding to the mediated reaction depend on the current (i_k) of the electron transfer between the dopamine and the whole of the CoHCFe film and the Levich current (i_{lev}) representing the mass transfer of dopamine in the solution, described by Koutecky-Levich equation:

$$1/i_l = 1/i_{lev} + 1/i_k \quad (5)$$

The i_k presents no dependence in relation to rotation rate, as expressed by equation:

$$i_k = n\,F\,A\,k\,\Gamma\,C \quad (6)$$

where k is the reaction rate constant between the solution species and the redox centre of the film and Γ is the surface coverage. So, by means of plots of i_l^{-1} vs. $\varpi^{-1/2}$ the linear relation of Koutecky and Levich was obtained, as shown in Figure 4B. From intercept of the Koutecky-Levich plot the heterogeneous charge transfer rate constant, k, for the concentration of 5.0×10^{-5} mol L^{-1} was calculated at 3.5×10^5 cm^3 mol^{-1} s^{-1}. This value is in the same order of magnitude as that reported for the electrocatalytic oxidation of dopamine at a NiHCFe-modified electrode (8.5×10^5 cm^3 mol^{-1} s^{-1}) [12].

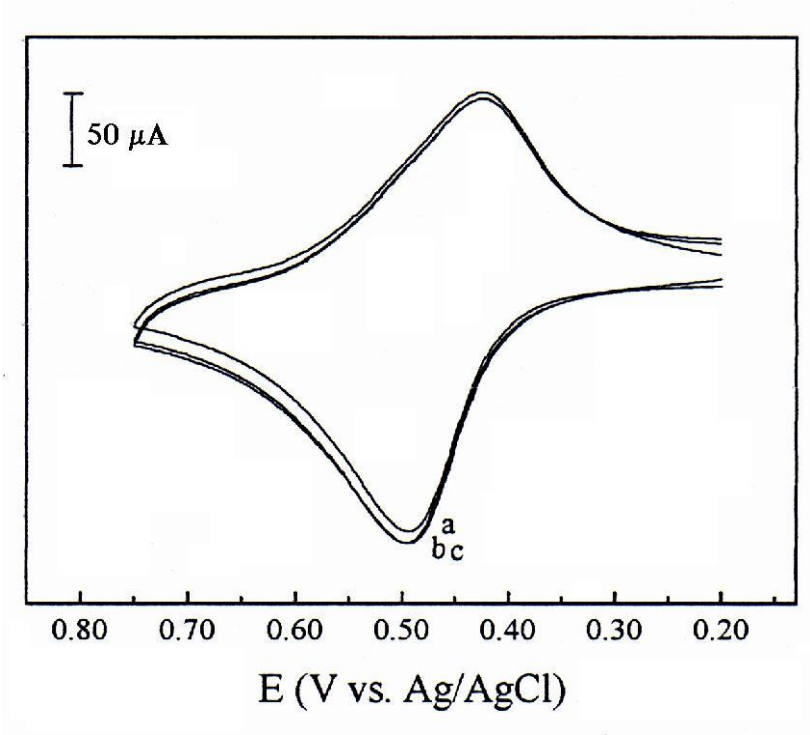
3.4 - Interference of ascorbic acid

Considering the fact that ascorbic acid is the main interferent in the dopamine determination and that the electrochemical oxidation of ascorbic acid occurs at a potential value near of the CoHCFe film oxidation potential, which catalyses the oxidation of dopamine, a study about the selectivity between these compounds was realised. Classically, this problem has been resolved with the use of Nafion®-coated electrode, a perfluorosulfonated derivative of Teflon® [29]. This polymer is very inert, has a high chemical resistance and presents cation exchange property. The negatively charged sulfonate groups permit the permeability of positively charged species by electrostatic interaction but it forms a selective polymeric net to anionic species.

The addition of 1.4×10^{-4} mol L^{-1} dopamine at the Nafion®-coated CoHCFe film modified electrode caused an increase in the anodic peak current when compared to the respective peak in pure supporting electrolyte, as shown at Figure 5.

The positively charged dopamine provides an ion exchange reaction with the Nafion® film, that is, the cation initially present as counter-ion of the $-SO_3^-$ in the Nafion® film is substituted by positively charged dopamine, that diffuses through the Nafion® membrane to the CoHCFe film-modified electrode surface. On the other hand, the ascorbic acid is a negatively charged species, and its behaviour was opposite to that observed for dopamine in relation to the Nafion® film, being observed no amperometric response in the cyclic voltammogram. This behaviour was observed for the dopamine determination in the presence of a concentration of ascorbic acid thirteen times higher than dopamine.

Figure 5. Effect of selectivity of Nafion® film for dopamine using cyclic voltammetry (ν = 50 mV s^{-1}.): a) CoHCFe-Nafion® film; b) addition of dopamine at final concentration of 1.4 x 10^{-4} mol L^{-1}; c) addition of ascorbic acid at final concentration of 1.8 × 10^{-3} mol L^{-1}.



3.5 - Determination of dopamine at Nafion®-CoHCFe modified electrode

The last factor that was determined in the analytical characterisation of this detector was the linear dynamic range. The analytical curve for dopamine was linear over the concentration range from 1.2 × 10^{-5} to 5.0 × 10^{-4} mol L^{-1}. A linear least squares fit of the data yielded a slope of 23.5 mA mol^{-1} L and a linear correlation coefficient of 0.999. The detection limit of this method was 8.9 × 10^{-6} mol L^{-1} using the criterion of a signal of three times the noise. The relative standard deviation between five measurements for the concentration of 2.5 × 10^{-4} mol L^{-1} of dopamine was of 0.58%.

4. Conclusion

A cobalt (II) hexacyanoferrate modified glassy carbon electrode has been shown to be effective for dopamine determination, with a linear range from 1.2 × 10^{-5} until 5.0 × 10^{-4} mol L^{-1}, and a detection limit of 8.9 × 10^{-6} mol L^{-1}. The studies have shown that the permselectivity ion exchange characteristics and transport properties of Nafion® films allow Nafion®-coated CoHCFe- modified electrode for the selective determination of the studied neurotransmitter in presence of ascorbic acid. The catalytic reaction of dopamine at a CoHCFe-modified rotating disk electrode was also studied and the heterogeneous charge transfer rate constant, *k*, for the concentration of 5.0 × 10^{-5} mol L^{-1} was calculated as 3.5 × 10^{5} cm^{3} mol^{-1} s^{-1}.

Acknowledgements

The authors are grateful for the financial support of FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo.

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