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## Electrochemical Behavior And Electrocatalytic Study Of The Manganese (II) Pyrrolidine Dithiocarbamate Modified Carbon Paste Electrode: Use In A Flow Injection System

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### ABSTRACT

The response of a MnPyr<sub>2</sub> modified carbon paste electrode was evaluated by cyclic voltammetry using hydrogen peroxide as a probe. An increase in the reduction peak of Mn<sup>III</sup> Pyr<sub>2</sub> to Mn<sup>II</sup> Pyr<sub>2</sub> was observed in the presence of H<sub>2</sub>O<sub>2</sub>, indicating a mediated reaction for the hydrogen peroxide reduction. After optimization of some experimental parameters it was possible to follow the catalytic reduction of the hydrogen peroxide at -0.49 V (vs. Ag/AgCl) in a flow injection analysis system. The linear relationship between the flow-injection peak currents and the concentrations of H<sub>2</sub>O<sub>2</sub> of 1.0 x 10<sup>-4</sup> to 7.5 x 10<sup>-3</sup> mol L<sup>-1</sup> range with a detection limit of 5.4 x 10<sup>-5</sup> mol L<sup>-1</sup>. © 2007 Trade Science Inc. - INDIA

### KEYWORDS

Carbon paste electrode;  
Mn(II)-  
pyrrolidinedithiocarbamate;  
Hydrogen peroxide;  
FIA

### INTRODUCTION

The existence of natural catalysts with a manganese center raises the question of whether other synthetic complexes can mimic the reactivity of these biological sites. This has prompted the vast interest developed by in manganese complexes as models for catalysts<sup>[1,2]</sup>. Small complexes containing manganese in the +2, +3, +4 and +5 oxidation state have served to define structural possibilities available for man-

gane redox enzymes for oxidation or reduction hydrogen peroxide<sup>[3]</sup>.

Dithiocarbamates (DTC) are the products of the reaction between carbon disulfide and primary or secondary amines in basic medium. These ligands can complex with many metallic ions as mono or bidentate ligands coordinating through the sulfur atoms<sup>[4,5,6]</sup>. The low solubility of the dithiocarbamate complexes suggest them as useful modifiers in the preparation of modified electrodes useful in the de-

termination of several substances. In this case the complex acts as intermediary of electron transfers between the substance and the electrode surface<sup>[7]</sup>.

In this sense Nalini and Narayanan<sup>[8]</sup> described the synthesis of a new ruthenium(III) diphenyldithio carbamate and its use as mediator in modified electrode. The electrochemical behavior of the carbon paste electrode modified with this complex has been investigated by cyclic voltammetry and used for the electrocatalytic oxidation of sulfhydryl compounds<sup>[9]</sup>, as well as in the amperometric determination of ascorbic acid<sup>[10,11]</sup>. We also used the ruthenium(III) piperidinedithiocarbamate in the determination of ascorbic acid<sup>[12]</sup>.

The detection and determination of hydrogen peroxide are of practical importance in chemical, biological, clinical, environment and many other areas. Most of the electroanalytical methods involve the use of peroxidase enzyme immobilized on the electrode material. However serious problems have been observed in such devices mainly in relation to stability, fouling and life-time<sup>[13]</sup>. An increasing number of articles suggested detecting peroxide by modified electrode, in which the ability of some surface-bound redox mediators were exploited to enhance electron-transfer kinetics and thus lowering the operating potential. The modified electrodes prepared by immobilizing complexes of cobalt, iron and manganese phtalocyanine<sup>[14]</sup>, 2,2':6',2''-terpyridyl copper(II) chloride<sup>[15]</sup>, iron-salen and poly(iron-salen)<sup>[16]</sup>, immobilized [Ru(bpy)(3)]<sup>2+</sup> in Nafion and cellulose matrices and macrocyclic cobalt(III)<sup>[17]</sup>, copper-phenanthroline<sup>[18]</sup> and cobaloximes<sup>[19]</sup> on the electrode surface have been prepared for this purpose. The use of metal complex such dithiocarbamates could be an alternative as electrode modifiers in order to improve the sensor performance in addition to sensitivity.

In the present work, the preparation, features and applicability of a carbon paste electrode modified with manganese(II) pyrrolidinedithiocarbamate MnPyr<sub>2</sub>-MCPE in the amperometric determination of H<sub>2</sub>O<sub>2</sub> in flow injection analysis is described. The main proposal of this work is to investigate the performance of the complex as an electrode modifier. The choice of H<sub>2</sub>O<sub>2</sub> as a probe was based on its well-

known redox behavior and its strength as oxidizing agent.

## EXPERIMENTAL

### Apparatus

Cyclic voltammetric and amperometric measurements were carried out with an AUTOLAB PGSTAT-30 (Ecochimie) controlled by the GPES 4.8 software. The measurements were performed in a three-electrode cell using a manganese(II) pyrrolidinedithiocarbamate modified carbon paste electrode as working electrode and Ag/AgCl reference and platinum plate auxiliary electrode. For cyclic voltammetry a potential window from 0.5 to -0.7 V vs. Ag/AgCl at 20 mV s<sup>-1</sup> scan rate was used. An electrochemical flow cell (Figure 1A) was fabricated from polyurethane resin<sup>[20]</sup>, with an effective cell volume of 77 mL for amperometric measurements in flow injection system.

### Reagents and solutions

All the solutions were prepared using water treated in a Milli-Q system. All chemicals were of analytical grade and used without any further purification. The supporting electrolyte used for all experiment was 0.10 mol L<sup>-1</sup> KCl solution (pH 5.0). A 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> hydrogen peroxide solution was prepared and standardized daily<sup>[21]</sup> and used to prepare the hydrogen peroxide reference solution in 0.10 mol L<sup>-1</sup> KCl, at pH 5.0.

### Synthesis of the anhydrous MnPyr<sub>2</sub>

The ammonium pyrrolidinedithiocarbamate, NH<sub>4</sub>Pyr, was prepared according to a procedure earlier described<sup>[22]</sup>, recrystallized from ethanol-water 1:1 (v/v) and then dried in a vacuum oven at 40°C, for 12 hour. The MnCl<sub>2</sub>.4H<sub>2</sub>O was dehydrated according to the procedure described by Pray<sup>[23]</sup>, using thionyl chloride. The metallic complex was obtained by direct reaction of the previously dehydrated MnCl<sub>2</sub> and NH<sub>4</sub>Pyr dissolved in isopropanol, previously dried and purified according to Perrin<sup>[24]</sup>.

The synthesis was performed in a glove bag, under nitrogen atmosphere in order to prevent oxidation of the complex, which occurs easily at humid air<sup>[25]</sup>. The complex was characterized by elemental

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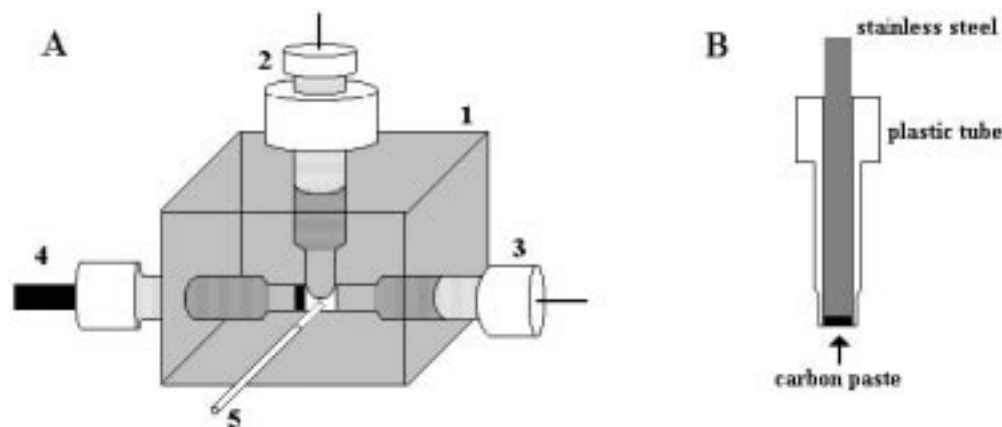


Figure 1: Schematic diagram of the electrochemical flow cell used in the amperometric measurements in flow injection system. (a): 1 -polyurethane resin block; 2-reference electrode (Ag/AgCl); 3-platinum electrode; 4-carbon paste electrode; 5-polyethylene tubing (flow). (b): carbon paste packed into an electrode body.

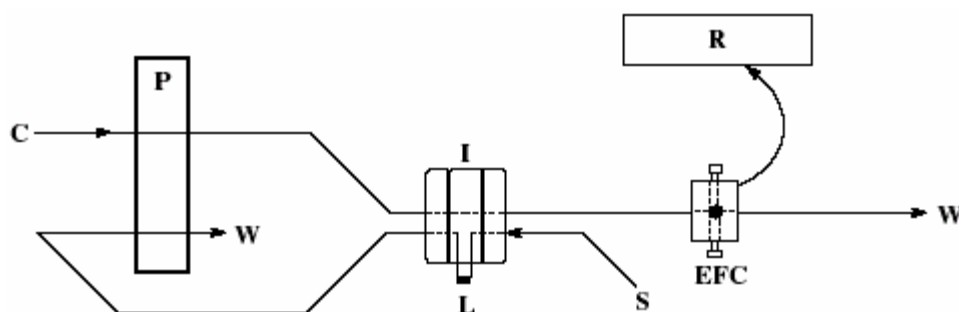


Figure 2: Schematic diagram of the flow system used for evaluation of the carbon paste electrode for dipyrone determination. P-peristaltic pump; I-manual injector; S sample or reference solutions; L-sample volume; C-carrier solution; EFC electro chemical flow cell; R-amperometer (recorder); W-waste

analysis, IR and mass spectroscopy<sup>[22]</sup>.

### Preparation of the modified carbon paste electrode

The carbon paste electrode was prepared by mixing 50% (w/w) of graphite powder (1-2  $\mu\text{m}$  particle size - Aldrich), 25% (w/w) of mineral oil (Aldrich) and 25% (w/w) of manganese(II) pyrrolidinedithio carbamate complex. The carbon paste was packed into an electrode body (Figure 1B), consisting of a plastic cylindrical tube (o.d. 7 mm, i.d. 4 mm) equipped with a stainless steel staff serving as an external electric contact. Appropriate packing was achieved by pressing the electrode surface (area of 12.6 mm<sup>2</sup>) against a piece of filter paper.

### Amperometric measurements in flow injection analysis

The electrochemical cell was inserted into a one-channel flow injection analysis system. The system (Figure 2) consisted of a peristaltic pump (Ismatec, model 7618-40, Switzerland) and a homemade manual injector made of Perspex® with two fixed sidebars and a sliding central bar<sup>[26]</sup>. The connections were made with polyethylene tubing (0.76 mm i.d.).

A 0.10 mol L<sup>-1</sup> KCl solution was used as the carrier (C) at a flow rate of 2.5 mL min<sup>-1</sup>. Standard hydrogen peroxide in 0.10 mol L<sup>-1</sup> KCl solution contained in the sample volume (L, 408.6  $\mu\text{L}$ ) was injected and transported by the carrier stream after the baseline had reached a constant value. The analytical path was 30 cm and the entire flow injection analy-

sis system was maintained at 25°C.

### Preparation and analysis of bleaching sample

The sample was a commercial bleaching formulation containing hydrogen peroxide, and did not require any preparation previously to the amperometric flow determination. For the analysis of  $\text{H}_2\text{O}_2$  in the bleaching formulation, an accurate amount of 19.5  $\mu\text{L}$  was transferred to a 100 mL volumetric flask and this volume completed with KCl (pH 5.0) solution. The percentage content of hydrogen peroxide in this sample was determined by the standard addition method and compared with the permanganate titration<sup>[21]</sup>.

## RESULTS AND DISCUSSION

### Electrochemistry of the MnPyr<sub>2</sub>-MCPE

Figure 3 shows the cyclic voltammograms obtained for MnPyr<sub>2</sub>-MCPE and non-modified CPE at a scan rate of 20  $\text{mV s}^{-1}$ , in 0.10  $\text{mol L}^{-1}$  KCl solution (pH 5.0). It can be seen that in potential range 0.5 to

-0.7 V vs. Ag/AgCl, no redox peak at the non-modified CPE, figure 3.a, is observed. A typical cyclic voltammogram of the MnPyr<sub>2</sub>-MCPE is illustrated in figure 3.b. In this curve two couples of not well-defined peaks around 0.22 V and -0.18 V (vs. Ag/AgCl) at 20  $\text{mV s}^{-1}$  scan rate are observed. This electrochemical behavior is related to the surface Mn<sup>III</sup>Pyr<sub>2</sub>/Mn<sup>IV</sup>Pyr<sub>2</sub> and Mn<sup>II</sup>Pyr<sub>2</sub>/Mn<sup>III</sup>Pyr<sub>2</sub> redox couples respectively<sup>[27]</sup>. Bond and Martin<sup>[27]</sup> discussed in details the ability of the dithiocarbamates (DTC) in stabilizing different oxidation states of metal complexes and the redox behavior of several DTC complexes. In potentials higher than 0.5 V the oxidation of the ligand takes place, involving the formation of a sulphur-sulphur bond generating the pyrrolidine-thiuramdisulphide<sup>[28,29]</sup>.

The redox peak current of the voltammograms is linearly proportional to the square root of the scan rate between 5 and 100  $\text{mV s}^{-1}$ , which was expected for a surface-controlled process. Scanning the potential of the electrode continuously in the interval of -0.7 to 0.5 V showed the stability of the modified

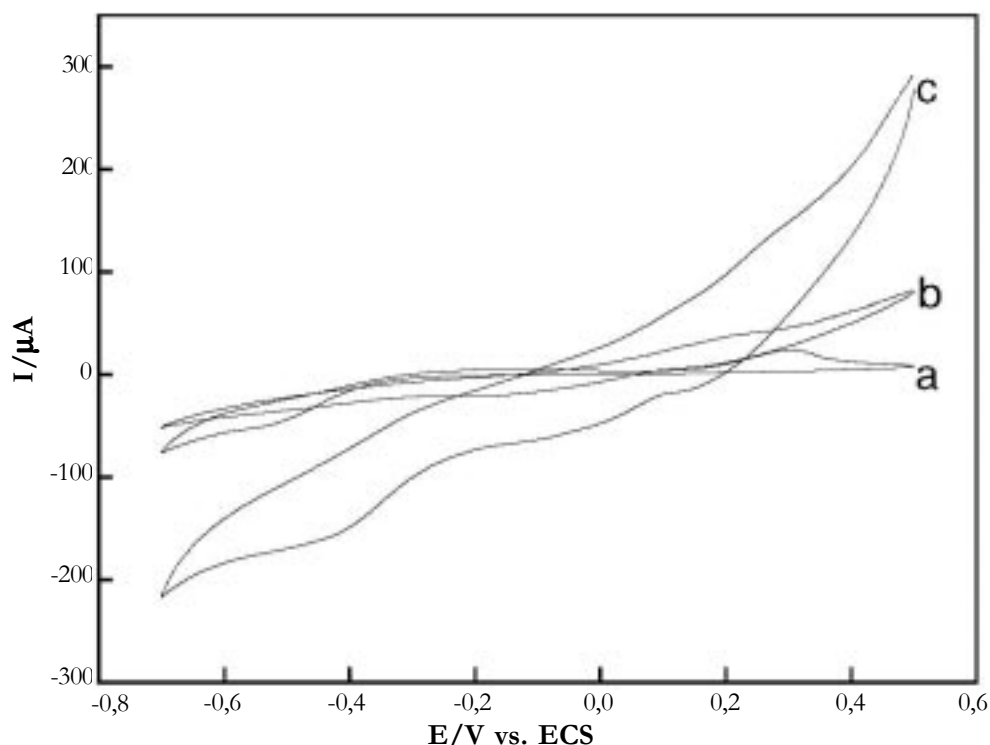


Figure 3: Cyclic voltammogram for (a) unmodified carbon paste electrode in the  $\text{H}_2\text{O}_2$  presence; (b) modified carbon paste electrode in the absence of  $\text{H}_2\text{O}_2$  and (c) modified carbon paste electrode in the  $\text{H}_2\text{O}_2$  presence;  $\nu = 20 \text{ mV s}^{-1}$

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electrode. No decrease of current was detected even for 30 cycles indicating that the complex in the paste is not washed out from the electrode surface.

Anions should to diffuse on and out of the electrode surface to maintain electroneutrality. The influence of the electrolyte anion is therefore related to the various coordinating abilities of the anions and to differences in the coordination of the Mn(III) and Mn(IV) complexes. The voltammetric behavior of the modified electrode was investigated in four different supporting electrolytes (phosphate buffer, acetate buffer, KCl and tetrabutylammonium bromide -TBABr). In phosphate buffer and TBABr, the electrochemical behavior of the modified electrode was unstable and the redox peaks are not clear. This is due to the fact that the manganese(II) cation in the complex interact with phosphate anion forming a insoluble salt at electrode surface and consequently degrading the complex MnPyr<sub>2</sub>. For TBABr, probably the anion has low interaction with the metallic center, due to its size. In acetate buffer, although well-defined peaks were observed for the Mn<sup>II</sup>/Mn<sup>III</sup> and Mn<sup>III</sup>/Mn<sup>IV</sup> couples, this event occurs in poten-

tials higher than those observed in KCl solution. These results are consistent with those reported by Taraszewska et al.<sup>[30]</sup>, who studied effect of the electrolyte in the stability of nickel tetraazamacrocyclic complexes for highest oxidation states of the metal. In KCl solution, the voltammetric profiles are very similar and stable.

### Electrocatalytic behaviour of the MnPyr<sub>2</sub>-MCPE

Using a non-modified CPE a not well defined reduction peak around -0.53 V is observed while an oxidation process appears at +0.30 V (vs. Ag/AgCl) in the cyclic voltammograms in a  $1.0 \times 10^{-2}$  H<sub>2</sub>O<sub>2</sub> in 0.10 mol L<sup>-1</sup> KCl solution at 20 mV s<sup>-1</sup> scan rate (Figure 3a), referent to the redox process of the hydrogen peroxide. The direct reduction of hydrogen peroxide at the non-modified CPE is therefore is low sensitive for analytical purposes. To test the electrocatalytic activity of the MnPyr<sub>2</sub>-MCPE toward peroxide hydrogen reduction, cyclic voltammograms were taken in pH 5.0 KCl solution in the absence and presence of hydrogen peroxide (Figure 3). At the MnPyr<sub>2</sub>-MCPE, the electrocatalytic reduction of

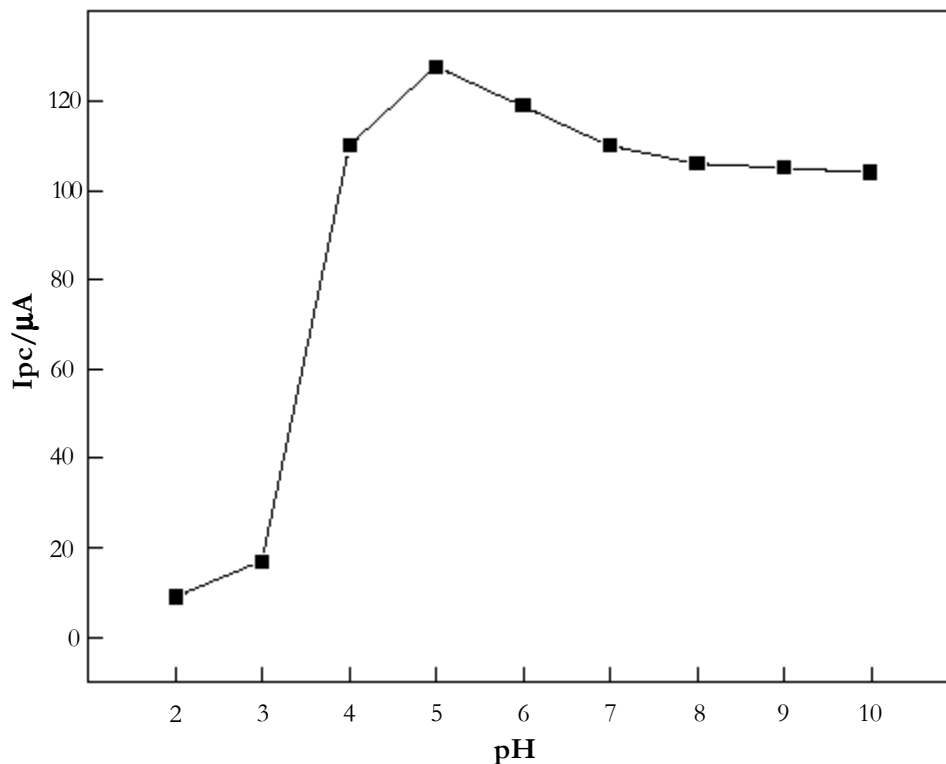
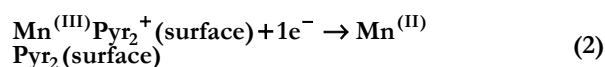
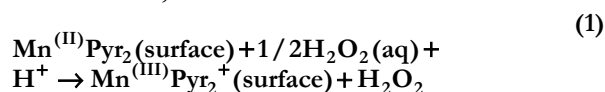


Figure 4: Voltammetric behavior of  $1.00 \times 10^{-2}$  mol L<sup>-1</sup> hydrogen peroxide in KCl solution on a carbon paste electrode in different pHs. Scan rate 20 mV s<sup>-1</sup>

hydrogen peroxide occurred at around -0.44 V. The reduction potential of hydrogen peroxide changes by c.a. 90 mV when compared with that observed at the non-modified CPE. The cathodic response current of hydrogen peroxide is about 3 times larger at MnPyr<sub>2</sub>-MCPE than that at unmodified CPE. The catalytic reduction current increases linearly with the square root of the scan rate between 5 and 100 mV s<sup>-1</sup>, indicating that the process is controlled by diffusion. Moreover, with increasing scan rate, the reduction peak potentials moved towards more negative direction. In the scan rate range from 5 to 100 mV s<sup>-1</sup>, the peak reduction potential is linear with logarithm of scan rate.

The effect of pH on the catalytic current of 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> is presented in figure 4. In the whole pH range investigated, the response current was practically constant for pH higher than 5.0. In acidic media (pH < 5.0) the current response had decreased, probably due to the fact that in lower pH values decomposition of the ligand takes place<sup>[26,31,32]</sup>. However, any change in the potential was observed as a function of the pH.

This behavior is compatible with an electrocatalytic mechanism, which can be written as:



### Application (Flow injection analysis)

On the basis of the voltammetric results described, it appears likely that amperometric detection of hydrogen peroxide by MnPyr<sub>2</sub>-MCPE in a flow injection system is possible. The hydrodynamic voltammograms for the hydrogen peroxide reduction at the non-modified CPE and MnPyr<sub>2</sub>-MCPE were obtained under flow-injection. The applied potential was also evaluated from -0.55 to +0.30 V (vs. Ag/AgCl). If a non-modified electrode was used, the hydrogen peroxide did not contribute significantly to the current when the applied potentials were less than -0.50 V. Only a relative small reduction current of hydrogen peroxide was found after the applied potentials were higher than -0.50 V. However, greatly enhanced response currents are observed at MnPyr<sub>2</sub>-

MCPE. The amperometric response currents increased with the applied potential from -1.0 to -0.5 V (vs. Ag/AgCl), then the currents remained almost constant when the applied potential was increased further. Although the hydrodynamic voltammogram shows the maximum response at the applied potentials of more than -0.50 V, an amperometric operating potential of -0.49 V was selected, both to minimize the potential interference at the higher negative potentials and to maintain a relative low background signal.

The influence of the experimental conditions was exploited to optimize the flow system in terms of analytical performance. The effect of the sample volume from 81.7 to 817.1 μL has been evaluated by injecting 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> of hydrogen peroxide in 0.10 mol L<sup>-1</sup> KCl solution (pH 5.0). In this case was possible to observe a fast current increase up to 408.6 μL. For sample volumes higher than 408.6 μL the current tends to an almost constant value and the increase is not so high and implies in lower analytical frequency with high reagent consumption. Thus, a sample volume of 408.6 μL was selected for showing better engagement between sensibility and analytical frequency. The effect of the flow rate on the magnitude of the amperometric response was investigated by applying a working potential of -0.49 V and sample volume of 408.6 μL. The results showed that the flow injection response current is dependent on the flow rate as presented in figure 5. The current increased as a function of the flow rate reaching a maximum value at 2.5 mL min<sup>-1</sup>. The peak current increases with the flow rate and is in agreement with theoretical expectations based on laminar flow assumptions, which indicate the increase of the flow rate would increase the response current due to the increased hydrodynamics (increase in convective component of mass transport) and the reduced diffusion layer thickness<sup>[33]</sup>. Higher flow rates led to a decrease in the current due to the fast passage of the sample zone which difficult the redox reaction between the MnPyr<sub>2</sub> and the H<sub>2</sub>O<sub>2</sub>, in addition to the dispersion of the sample. A flow rate of 2.5 mL min<sup>-1</sup> was used in the following experiments, which presented good sensitivity and a stable amperometric response.

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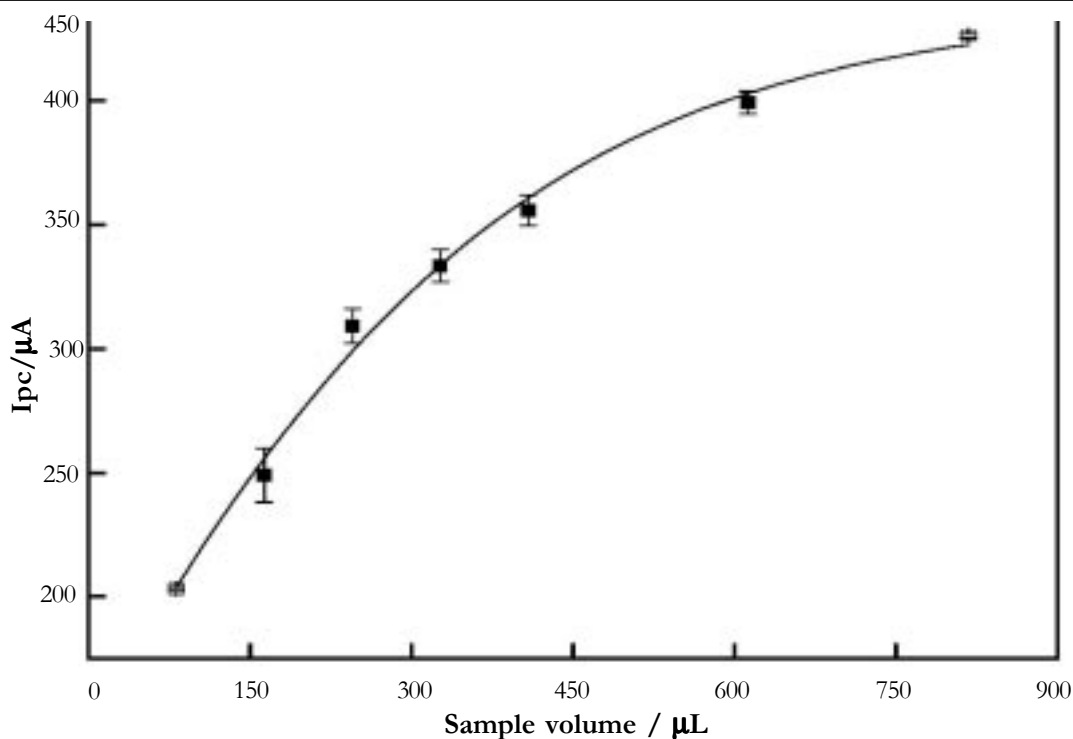


Figure 5: Hydrodynamic responses for FIA hydrogen peroxide on the MCPE-MnPyr<sub>2</sub> with to a sample volume

After optimizing the best operating conditions for the FIA procedure, amperometric measurements were carried out in 0.10 mol L<sup>-1</sup> KCl solution (pH = 5.0) containing different hydrogen peroxide concentrations in order to obtain the analytical curve. Figure 6 illustrates the FIA current-time response for different concentrations of H<sub>2</sub>O<sub>2</sub>. The current values (base peak 1) obtained showed a linear relationship with the hydrogen peroxide concentrations from 1.0 x 10<sup>-4</sup> to 7.5 x 10<sup>-3</sup> mol L<sup>-1</sup> represented by the equation:

$$I_{\text{cathodic}}/\mu\text{A} = 103.2 + 25.60 \text{mmolL}^{-1} [\text{H}_2\text{O}_2] \quad (3)$$

with a correlation coefficient of 0.9999 (see detail in Figure 6). To concentrations higher than 5.0 x 10<sup>-3</sup> mol L<sup>-1</sup> a deviation from the linearity was observed. The detection limit was of 5.4 x 10<sup>-5</sup> mol L<sup>-1</sup> and quantification limit of 17.8 x 10<sup>-5</sup> mol L<sup>-1</sup> hydrogen peroxide, those values were calculated from 3 and 10 times the standard deviation in the current of the blank divided by the slope of the analytical curve<sup>[34]</sup>, respectively. Analyzing 17 replicates of 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> hydrogen peroxide tested the precision of the method. The variation coefficient was 0.9% and the

analytical frequency was 50 determinations per hour.

The optimized method was applied in the determination of H<sub>2</sub>O<sub>2</sub> in a bleaching formulation and the result was compared with those from a classical titration with potassium permanganate<sup>[21]</sup>. The comparison is presented in TABLE 1 and the result suggested the proposed electrode as an alternative to the determination of peroxide in quality control of commercial samples in short time and low reactive consumption in the flow injection analysis procedure. The limit of detection also suggests the MnPyr<sub>2</sub>-

TABLE 1: Results for the determination of hydrogen peroxide in the bleaching formulation using the MnPyr<sub>2</sub>-MCPE, compared with the classical titration with potassium permanganate

Label	% H <sub>2</sub> O <sub>2</sub> <sup>a</sup> (m/m)		Relative error <sup>b</sup> / %
	Proposed flow method	Permanganate titration	
2.50-5.80	4.35	4.66	3.20

a-mean of three determinations

b-[(Permanganate titration -Proposed flow method)/ Permanganate titration] x 100

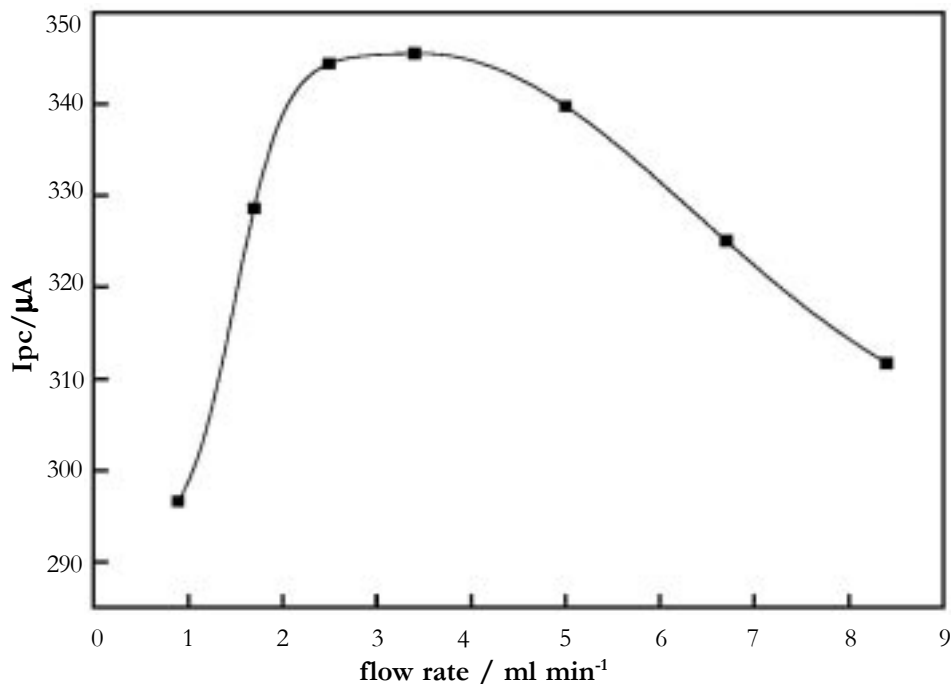


Figure 6: Hydrodynamic responses for FIA hydrogen peroxide on the MCPE-MnPyr<sub>2</sub> with to a flow rate

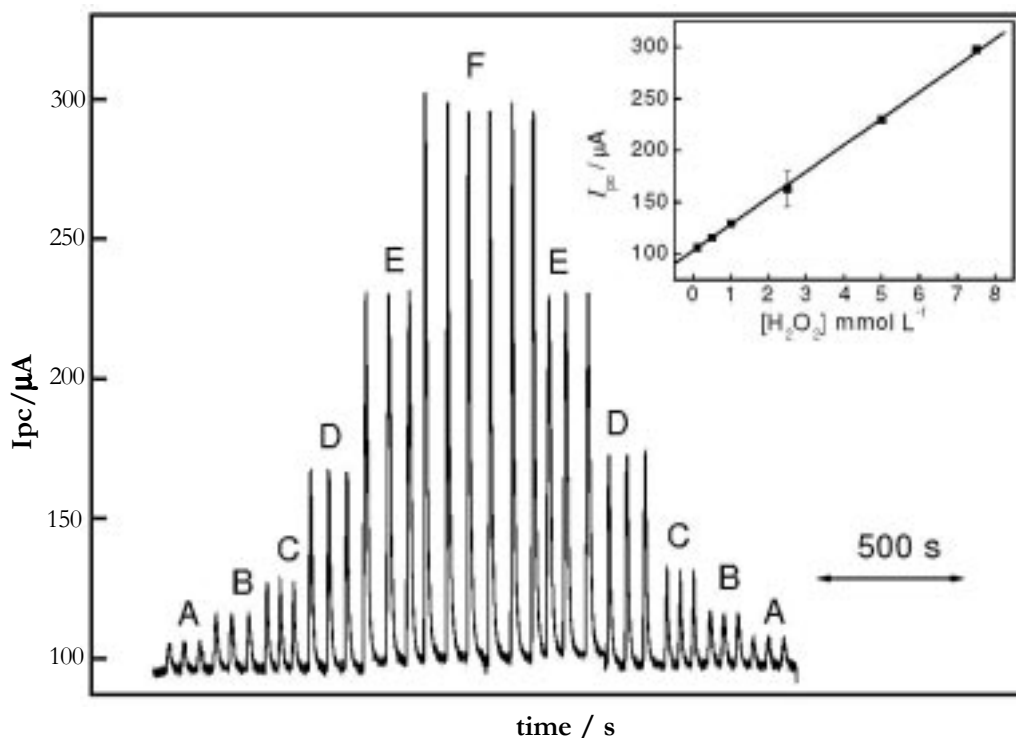


Figure 7: Transient current signals obtained in triplicate for hydrogen peroxide solutions: (a) 0.1; (b) 0.5; (c) 1.0; (d) 5.0 mmol L<sup>-1</sup> hydrogen peroxide. The inset shows the analytical curve for hydrogen peroxide. Applied working potential = -0.494 V vs. Ag/AgCl; sample volume = 408.6 μL of hydrogen peroxide; flow rate = 2.5 mL min<sup>-1</sup>



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MCPE as a promising alternative in the determination of peroxides in environmental samples.

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