

# Electrocatalytic behaviour of several cobalt complexes: Determination of hydrazine at neutral pH

G. CEPRIÁ\*, J. R. CASTILLO

*Group of Analytical Spectroscopy and Sensors, Department Analytical Chemistry, Faculty of Sciences, University of Zaragoza, Campus Plaza San Francisco E-50009 Zaragoza, Spain*

Received 11 November 1996; revised 9 April 1997

Four cobalt complexes (cobalt(II) acetylacetonate and 8-hydroxyquinolate and cobalt(III) 8-hydroxyquinolate and diethyldithiocarbamate) were tested as mediators to modify carbon paste electrodes with a view to obtaining a catalytic effect for the hydrazine. Cobalt(II) acetylacetonate was found to exert no catalytic effect as the likely result of ligand having to stabilize higher oxidation states of Co potentially involved in the catalytic process. The effects of the electrolyte and pH were examined and found to be important. The proposed chronoamperometric determination for hydrazine features limits of detection at the 99% confidence level of 1.6 mM with cobalt(III) diethyldithiocarbamate, 1.5 mM with cobalt(III) 8-hydroxyquinolate and 2.0 mM with Co(II) 8-hydroxyquinolate. The RSD for 2 mM hydrazine was always less than 8%.

Keywords: carbon paste electrode, mediator, electrocatalysis, hydrazine, cobalt complexes

## 1. Introduction

A variety of compounds have been tested as additives for carbon paste electrodes to improve the responses to analytes that are nonelectroactive over their typical working range at the carbon electrodes [1]. Doped carbon paste has been favoured because it is easy to handle and has low cost. Redox couples have been included in the composition of the carbon paste in recent years [2]. Among them, the complexes of transition metals such as Ni, Fe, Co and Ru are the most popular because they combine high chemical stability with favourable electrochemical properties.

The addition of cobalt complexes and other transition metals to carbon paste electrodes has been the subject of much recent study (particularly macrocyclic species such as phthalocyanines and porphyrins, which are chemically stable and have good electrochemical properties). A wide variety of applications have developed many different applications for these cobalt macrocycles, especially as electrochemical catalysts for several compounds of environmental and biological interest [3].

Hydrazine is one of the most commonly analysed compounds in industrial and environmental samples owing to its toxic effect on humans. It has found many applications in the pharmacological and chemical industry, as well as some in the aeronautical field, for example, as a rocket propellant. Unfortunately, hydrazine compounds have a large overpotential at ordinary carbon electrodes. One promising approach to minimize overvoltage effects is the use of

electrocatalytic modified electrodes based on a variety of catalysts including metals [4], polymer films [5] and metal complexes particularly cobalt complexes, largely cobalt phthalocyanines and porphyrins [6, 7].

The cobalt in all these macrocyclic compounds is bound to four nitrogen atoms in a square-planar configuration with the two axial positions free [9]. This is the case with Co(III) diethyldithiocarbamate, which has a distorted octahedral geometry in which all coordination positions are occupied by sulfur atoms. The redox electrochemistry of this complex has been the subject of much controversy, because it depends strongly on the solvent, electrolyte and electrode used. Nevertheless, an explanation for the behaviour of the Co(III) dithiocarbamates in different solvents and at different electrodes was provided by Bond *et al.* [10].

The aim of this work was to find cobalt complexes that provide good catalytic properties to an electrochemical probe to detect and quantify hydrazine in the environment. Such complexes have to be chemically stable and exhibit a suitable response range in the conditions that normally occur in a natural medium: high ionic strength and neutral pH. The economic aspects of the electrochemical sensor must also be taken into account, so this complex has to be easily prepared in the laboratory through a simple method. We looked for ligands that provide a similar structure to the metal complex as the macrocyclic ligands. Considering this, we used ligands that coordinate through N and O atoms as in 8-hydroxyquinone; oxygen donors such as acetylacetonates and sulfur-containing ligands such as diethyldithiocarbamate.

\* Author to whom correspondence should be addressed.

## 2. Experimental details

### 2.1. Reagents

8-Hydroxyquinoline, sodium diethyldithiocarbamate and acetylacetone and silicone oil were purchased from Aldrich; hydrazine, methylisobutyl ketone and methanol from, Panreac; acetonitrile for HPLC from Lab Scan; and  $\text{Co}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$  and graphite from Merck. Tetrabutylammonium perchlorate was purchased from Eastman.

### 2.2. Apparatus

All measurements were made on an Eco Chimie PGstat 10 using a Pt wire as auxiliary electrode and Ag/AgCl as reference electrode. Laboratory-made carbon paste electrodes were used in aqueous media and a Metrohm glassy carbon and platinum disc electrodes were employed for cyclic voltammetry in acetonitrile.

A piece of Teflon tubing of 1.6 mm i.d. was used as the body for the carbon paste electrode, a copper wire served as electrical contact and as a piston to pack the paste into the tube. Carbon paste was prepared by careful mixing of 60% graphite with 40% silicone oil, 190 mg of the paste was then thoroughly mixed with 10 mg of the corresponding crushed complex.

A glassy carbon electrode was polished with 0.25  $\mu\text{m}$  alumina slurry on a piece of cloth. Platinum was polished twice, first with 6  $\mu\text{m}$  diamond powder and then with 1  $\mu\text{m}$  diamond powder. Both electrodes were carefully rinsed with deionized water.

Cobalt(II) acetylacetonate ( $\text{CoACA}_2$ ) was precipitated from  $\text{Co}(\text{NO}_3)_2$  in acetic/sodium acetate by adding a solution of acetylacetone in methanol, as reported previously [11]. The complex was dissolved in hot benzene and supplied with 10 to 15 mL of petroleum ether added. The solution was allowed to cool at 0 °C in an ice bath and then filtered and dried at 100 °C.

Cobalt(III) diethyldithiocarbamate ( $\text{CoDTC}_3$ ) [12] was prepared by mixing two hot solutions containing aqueous  $\text{Co}(\text{NO}_3)_2$  and the ligand, respectively. The mixture was stirred with heating for 30 min. The resulting product was dissolved in 1 : 1 (v/v) ethanol : water and allowed to recrystallize. The green crystals formed were filtered, rinsed with water and dried at 80 °C.

Cobalt (II) 8-hydroxyquinolinatate ( $\text{CoOX}_2$ ) [13] was prepared by mixing a  $\text{Co}(\text{NO}_3)_2$  solution with a 8-hydroxyquinoline solution in acetic acid. The complex thus formed was filtered, rinsed and dried at 120 °C. Cobalt(III) 8-hydroxyquinolinatate was similarly prepared; Co(II) was previously oxidized to Co(III) with  $\text{H}_2\text{O}_2$ . Black crystals appeared within 24 h; these were filtered, rinsed with dilute HCl and dried at 120 °C. None of the complexes used was water soluble.

The purity of the complexes was assured by two means. (i) The cobalt content of the complexes syn-

thesized in the laboratory was determined by flame atomic absorption spectroscopy and the purity of the complexes was within the range 95 to 100%. To carry out this determination, the complexes were dissolved in hot concentrated sulfuric acid in a closed glass container. (ii) The purity of the complexes was also established via melting points: these differed slightly (4 °C) from the expected values.

### 2.3. Procedure

Cyclic voltammetry was performed either with a glassy carbon or with a platinum disc electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate. All scans were carried out from -1.25 to 1.25 V except for  $\text{CoDTC}_3$  which was scanned from -1.5 to 1.5 V. The scan rate was always 100  $\text{mV s}^{-1}$ . Only carbon paste electrodes were used in aqueous media. The potential range was -0.1 to 0.8 V and the scan rate 100  $\text{mV s}^{-1}$ .

To perform chronoamperometry the electrode was held at 0 V for 3 s and then the potential was increased to +0.45 and this value was maintained for 45 s, the time required for the current to reach steady state. The measurement was performed just at the end of this time.

## 3. Results and discussion

### 3.1. Assignment of peaks

The electrochemistry of the cobalt complexes was studied by using cyclic voltammetry (CV) with two different working electrodes in acetonitrile containing 0.1 M tetrabutylammonium perchlorate. An amount of 5 mg of each complex was dissolved in acetonitrile. Oxygen was removed by bubbling pure nitrogen through the solution for 5 min. Figure 1 shows typical cyclic voltammograms for the four complexes on Pt.

Two redox couples and a single cathodic peak were found for  $\text{CoDTC}_3$  at platinum and glassy carbon electrodes (Table 1); the peak potential was very similar at both working electrodes, but the single reduction peak was shifted to highly negative potentials at the glassy carbon electrode.

The first redox couple at highly positive potentials is related to the Co(III)/Co(IV) oxidation (IIIa, IIIc). At high potentials,  $\text{CoDTC}_3$  is oxidized to  $(\text{CoDTC}_3)^+$  which is difficult to isolate since the dimer  $(\text{Co}_2\text{DTC}_5)^+$ , more stable, is formed. This oxidation reaction was previously reported to occur in several solvents such as dimethylformamide [14], acetone [15] and acetonitrile [16]. Also, it is reportedly reversible at a Pt electrode in  $\text{CH}_2\text{Cl}_2$  [11].

The first one electron reduction of  $\text{CoDTC}_3$  is reversible at Pt and Hg electrodes in polar solvents such as acetone [11]. However, we found the process to be irreversible in acetonitrile. Bond *et al.* [10] suggested that the constant of charge transfer may be smaller in acetonitrile because the  $(\text{Co}^{\text{II}}\text{DTC}_3)$  formed may be more stable in this solvent and they concluded that

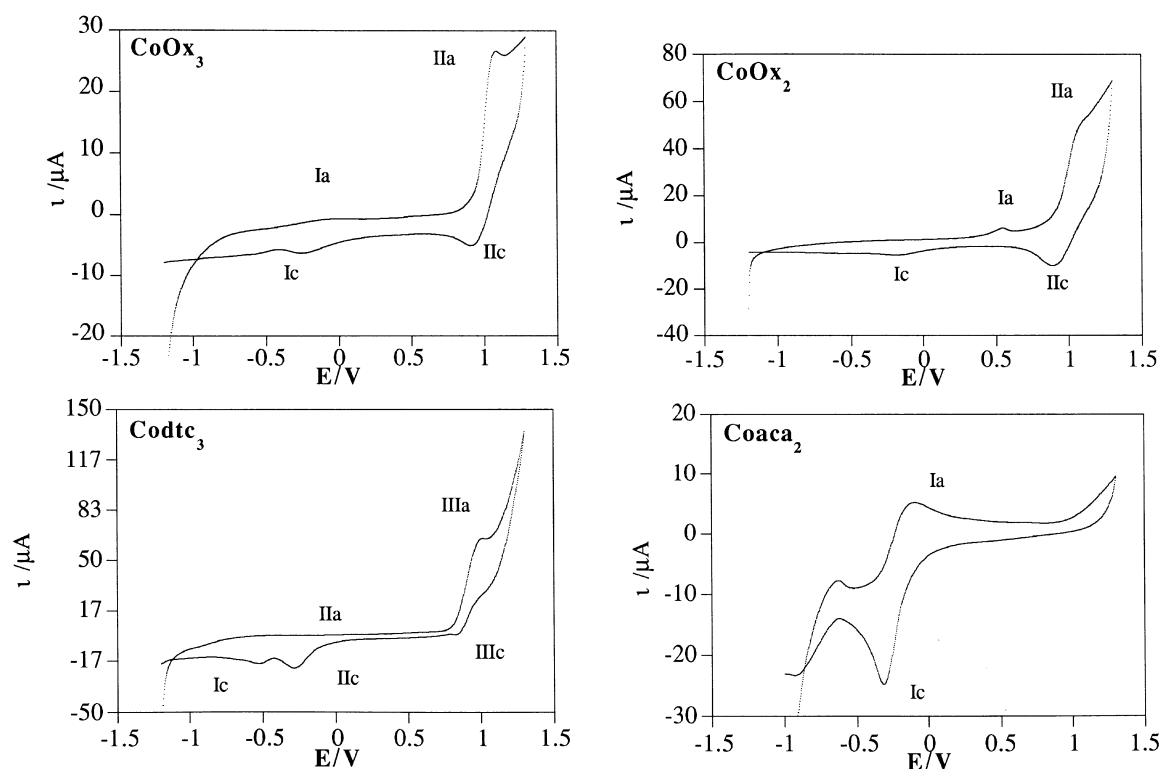


Fig. 1. Cyclic voltammograms for cobalt(III) diethyldithiocarbamate and 8-hydroxyquinolinate, cobalt(II) acetylacetonate and 8-hydroxyquinolinate ( $0.5 \text{ mg mL}^{-1}$ ) at a Pt electrode in acetonitrile containing  $0.1 \text{ M}$  tetrabutylammonium perchlorate. Reference electrode Ag/AgCl, auxiliary electrode: Pt. Scan rate:  $100 \text{ mV s}^{-1}$ .

the irreversibility is not related to the displacement of the ligand but to the different stability of the complexes involved in the electrode process:



The second reduction step (Co(III)/Co(II)) is also very difficult to observe because the Co(II) species involved react immediately with oxygen to produce Co(III), and then the peaks due to Co(II) cannot be seen, this is why we deoxygenated the solutions. We observed the reduction peak at highly negative potentials and at the Pt electrode (IIa, IIc).

The last reduction peak (Ic) is related to a process that takes place at highly negative potentials:

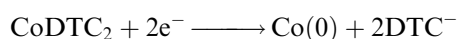


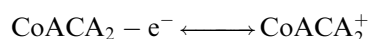
Table 1. Peak potentials (in V) for cobalt couples at glassy carbon (GC) and platinum (Pt) electrodes in acetonitrile containing  $0.1 \text{ M}$  tetrabutylammonium perchlorate

| Complex                 | Co(IV)/Co(III)<br>$E_{pa}; E_{pc}/\text{V}$ | Co(III)/Co(II)<br>$E_{pa}; E_{pc}/\text{V}$ | Co(II)/Co(0)<br>$E_{pa}; E_{pc}/\text{V}$ |
|-------------------------|---|---|---|
| CoACA <sub>2</sub> (GC) | —   | —   | —   |
| CoACA <sub>2</sub> (Pt) | —   | -0.10; -0.40                                | —   |
| CoOX <sub>2</sub> (GC)  | 1.07; 0.89                                  | —   | —   |
| CoOX <sub>2</sub> (Pt)  | 1.06; 0.91                                  | 0.02; -0.13                                 | —   |
| CoOX <sub>3</sub> (GC)  | 1.10; 0.93                                  | —   | —   |
| CoOX <sub>3</sub> (Pt)  | 1.10; 0.93                                  | —; -0.24                                    | —   |
| CoDTC <sub>3</sub> (GC) | 0.99; 0.83                                  | 0.08; -0.43                                 | —; -1.23                                  |
| CoDTC <sub>3</sub> (Pt) | 1.00; 0.82                                  | 0.09; -0.20                                 | —; -0.49                                  |

$E_{pc}$ : cathodic peak potential;  $E_{pa}$ : anodic peak potential.

No adsorption was detected in 10 scans of the same solution.

For CoACA<sub>2</sub> we found only one pair of peaks (Ia, Ic) corresponding to the process



Peak potentials of CoACA<sub>2</sub> are close to the corresponding ones for CoDTC<sub>3</sub>. The difference in peak potential was also quite large (212 mV) and the cathodic peak was larger than the anodic one. The process was considered irreversible, even at the platinum electrode. No adsorption was detected in 10 scans of the same solution.

8-Hydroxyquinolinate exhibited a couple at highly positive potentials which is attributable to the Co(III)/Co(IV) (IIa, IIc) process and lay close to those for CoDTC<sub>3</sub>. This couple was observed at both platinum and graphite electrodes. We found one other irreversible couple, at  $-0.243 \text{ V}$  (Ia, Ic), with the Pt electrode only, the anodic peak for which was scarcely perceptible. This peak can be attributed to the Co(III)/Co(II) process.

8-Hydroxyquinolinate were found to polymerize on both glassy carbon and platinum electrodes [9]. Two couples were observed for both complexes at both electrodes. Through several scans the anodic peak corresponding to the Co(IV)/Co(III) couple decreased and shifted to less positive potentials, and the corresponding cathodic peak increased and shifted to less positive potentials, in successive scans another anodic peak appeared at  $0.76 \text{ V}$  in addition to a cathodic peak at  $-0.30 \text{ V}$  at the Pt electrode. The

electrode was coated with a yellow or greenish–yellow film that was insoluble in methanol and could not be removed by rubbing on paper tissue.

It should be pointed out that the number of peaks in the voltammogram was related to the ligand and electrode used. We only observed the Co(III)/Co(II) couple for all the complexes when using Pt electrodes. The peaks were strongly affected by the material of the working electrode and they appeared at more negative potentials when the graphite electrode was used. We observed no peaks for the Co(II)/Co(0) couple, except for a single reduction peak. The Co(IV)/Co(III) couple was more markedly affected by the ligand in the complex than by the electrode material. It seems that the ligand has to stabilize the Co(IV) for a long enough period for the peak to be detected. Acetylacetonate cannot stabilize Co(III). The resulting complex is very difficult to synthesize as it is rapidly reduced by water; therefore one cannot expect acetylacetonate to stabilize higher oxidation states such as Co(IV) [11].

### 3.2. Mechanism of the catalytic oxidation of hydrazine

CoOX<sub>2</sub>, CoOX<sub>3</sub> and CoDTC<sub>3</sub> were found to lower the oxidation potential of hydrazine. As can be seen in Fig. 2, the voltammograms for 10 mM hydrazine exhibit an increase in the anodic current and a decrease in the cathodic one, as expected for an electrocatalytic oxidation process. It should be noted that the catalytic effect was found to be exerted only by those complexes whose ligands can stabilize higher oxidation states of Co, but not by the acetylacetonate.

The oxidation of hydrazine is believed to take place in two steps. One electron oxidizing mediators such as ours yield N<sub>2</sub>H<sub>3</sub> in the first step through a one electron process. The following step, however has been interpreted in various ways that lead to N<sub>2</sub> and H<sub>2</sub>O or N<sub>2</sub> and NH<sub>3</sub> [17].

Chronoamperometry at different potentials of a 2 mM hydrazine solution, at pH 7, was performed in order to identify the minimum working potential at which the catalytic effect was exerted. The results are shown in Fig. 3. As can be seen 0.45 V allowed hydrazine to be detected, so this potential was chosen for all chronoamperometric experiments.

### 3.3. Effect of pH

The performance of cobalt-based electrodes is strongly influenced by pH because the stability of the species that may take part in the electrode processes involved are affected by this variable. In most cases, cobalt electrodes [18] and cobalt complex modified electrodes [19] only work at a high pH where various cobalt oxides are formed that favour the formation of Co(IV), a potential mediator for many processes, including the oxidation of sugars. As a result, pH has been a serious drawback when using cobalt based electrodes, since basic pH was always necessary.

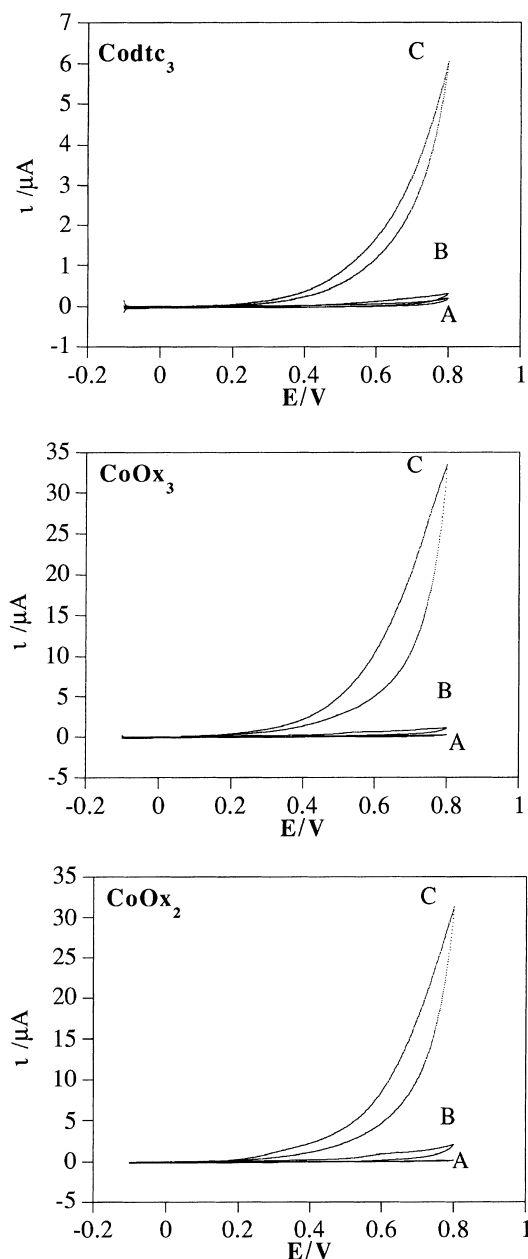


Fig. 2. Cyclic voltammogram obtained with the chemically modified electrodes (C) for hydrazine (10 mM) in phosphate buffer at pH 7, and at plain carbon paste electrode (A). (B) denotes blank solution (phosphate buffer at pH 7) at the chemically modified electrodes.

In our case, we can expect the electrode response to be affected in two different ways: through the mechanism of oxidation of hydrazine and through electrode processes involving the cobalt complexes.

The effect of pH was examined using chronoamperometry ( $E = +0.45$  V) in 0.05 M phosphate medium. As expected, the electrode response was strongly influenced by pH, see Fig. 4a. At low pH the signal decreased abruptly consistent with the fact that the oxidation of hydrazine takes place at alkaline pH. From pH 6 to pH 10 the signal increased; above pH 10, the CoOX<sub>2</sub> and CoDTC<sub>3</sub> signals increased sharply and a plateau appeared at pH 11. On the other hand, the signal for CoOX<sub>3</sub> decreased above pH 10, possibly through destruction of the complex

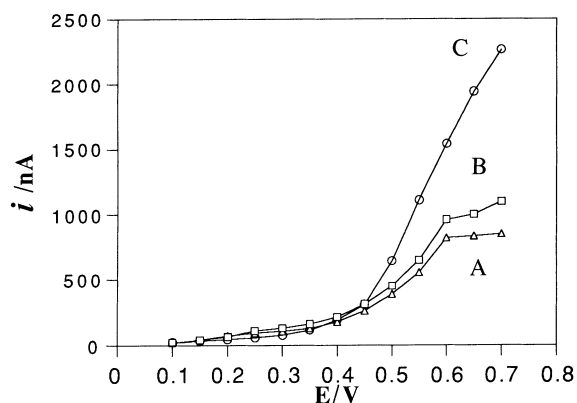


Fig. 3. Dependence on the applied potential of the chronoamperometric signal for a 2 mM hydrazine solution in phosphate buffer. (A) denotes  $\text{CoOX}_2$ , (B)  $\text{CoDTC}_3$  and (C)  $\text{CoOX}_3$ .

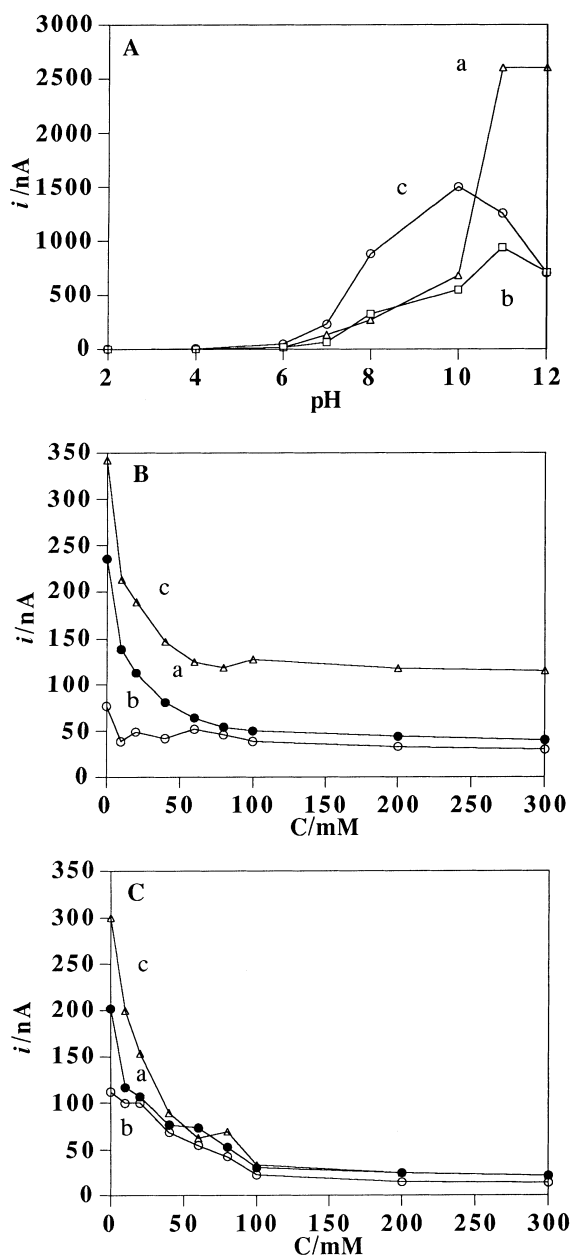


Fig. 4. Influence of pH (A) and the sulfate (B) and chloride (C) concentrations on the chronoamperometric response of the chemically modified carbon paste electrodes with  $\text{CoOX}_2$  (A),  $\text{CoDTC}_3$  (B) and  $\text{CoOX}_3$  (C) to a 2 mM hydrazine solution in phosphate buffer (pH 7 in (B) and (C)).

to form more stable species such as cobalt(III) and (IV) oxides at alkaline pH values.

### 3.4. Effect of the electrolyte

Anions were found to diffuse into and out of the carbon paste to maintain electroneutrality. If they could coordinate with the cations in some of the oxidation states potentially formed, then a shift in the peak potential would be expected. 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  $\text{Co(II)}$ ,  $\text{Co(III)}$  and  $\text{Co(IV)}$  complexes [20]. Because cations did not influence the electrode response they were not studied here.

The effects of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were examined as they are frequently used as electrolytes in electrochemical experiments and they are regular occurring ions in environmental samples as well as biological ones. All experiments were performed in 0.05 M phosphate buffer solution to which increasing amounts of sodium sulfate or chloride were added. Data were obtained for 2 mM hydrazine at +0.45 V, and are shown in Fig. 4(b) and (c). All the modified electrodes studied were affected by an increase in electrolyte concentration. It turned out that  $\text{CoOX}_2$  is less affected by the anions, followed by  $\text{CoDTC}_3$ . The influence of these anions on the response suggested the importance of performing an *in situ* calibration of the electrode to overcome this problem. This is a necessary step every time a real sample is concerned, especially with polluted samples or biological samples, due to their complexity.

These results are consistent with those reported by Taraszewska *et al.* [20], who claim that anions help stabilize the complexes of the highest oxidation states of the metal acting as the catalyst.

### 3.5. Electrocatalytic oxidation of hydrazine

Chronoamperometry was used at a working potential of 0.45 V, in phosphate buffer at pH 7 to study the relationship between the hydrazine concentration and the signals provided by the three chemically modified working electrodes. The logarithm of the concentration was found to be linearly related to the current once the steady state was reached. We obtained a good regression factor ( $r^2 = 0.996$ ) for the three complexes. The slopes of the linear calibration plots were similar for  $\text{CoOX}_3$  and  $\text{CoDTC}_3$  (258 and 251 nA, respectively), and slightly different for  $\text{CoOX}_2$ , (237 nA).

Detection limits were calculated following the advices given by Clayton *et al.* [21]. These authors take into account the influence of the number of standards and observations as well as the quality of the calibration. The upper limit (UL) was calculated as the point where an inflection in the calibration curve is observed.

LODs were calculated from three determinations of each standard. The concentrations tested were 0.5,

1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0 mM. The LOD thus obtained at a 99% confidence level was 1.6, 1.5 and 2.0 mM for CoDTC<sub>3</sub>, CoOX<sub>3</sub>, and CoOX<sub>2</sub>, respectively. The UL turned out to be 9 mM for CoDTC<sub>3</sub>, 10 mM for CoOX<sub>3</sub> and 8 mM for CoOX<sub>2</sub>. The dynamic linear range was narrow, but the minimum amount of hydrazine detected with 99% confidence was satisfactory for the low working potential and, especially, the low pH at which the determination was performed.

The repeatability was found to be 7.2% for CoDTC<sub>3</sub>, 4.8% for CoOX<sub>3</sub> and 2.6% for CoOX<sub>2</sub> as calculated from ten determinations of a 2 mM hydrazine solution in phosphate buffer at pH 7.

#### 4. Conclusions

High oxidation states of complexed cobalt play a prominent role in the catalytic behaviour of these complexes. These oxidation states are only apparent when stabilized through the formation of complexes lasting long enough for their redox electrode process to be observed. 8-Hydroxyquinoline and diethyl-dithiocarbamate complexes turned out to have a catalytic effect on the oxidation of hydrazine and they are proposed as mediators in the design of the corresponding electrochemical sensor.

The influence of the medium on the response of an amperometric sensor based on the catalytic effect on the oxidation of hydrazine was evaluated. The anions present in the medium affect the catalytic response of the electrode through potential competition for coordination positions. This causes a shift in the peak potential that decreases the intensity obtained at a given concentration of hydrazine. The effect of sulfate was found to be slightly more marked than chloride effects because these complexes are stronger than chloride ones.

pH strongly affects the electrode response. At low pH the signal decreased because hydrazine cannot be oxidized in acidic medium. At alkaline pH the signal increased for the three modified carbon paste electrodes owing to the catalytic effect of OH<sup>-</sup> anions, up to pH 10. Above such a pH the CoOX<sub>2</sub> and CoDTC<sub>3</sub> modified electrodes exhibited a sharp increase in their signals, followed by a stable response; on the other hand, the signal for CoOX<sub>3</sub> decreased through de-

composition of the mediator to oxides of Co in a high oxidation state.

The main advantage of the three complexes studied is their compatibility with neutral pH, and the low working potential required (0.45 V) to obtain low enough LOD at a high confidence level. In addition, none of the complexes is water-soluble, so no leakage from the electrode into the solution is possible, which further stabilizes the electrode. CoDTC<sub>3</sub> and CoOX<sub>2</sub> are slightly affected by anions present in the medium that allows us to use them as chemical constituents of electrochemical sensors to detect hydrazine in water samples. This constitutes the future scope of our work.

#### References

- [1] S. A. Wring and J.P. Hart, *Analyst* **117** (1992) 1215.
- [2] J. Cox, R. K. Jarowski and P. J. Kulesza, *Electroanalysis* **3** (1991) 869.
- [3] J. Wang, J. Golden, K. Varughese and I.El-Rayis, *Anal. Chem.* **61** (1989) 508.
- [4] W. Zhou, L. Xu, M. Wu, I. Xu and E. Wang, *Anal. Chim. Acta* **299** (1994) 189.
- [5] J. E. Bennett and T. Malinski, *Chem. Mater.* **1** (1991) 490.
- [6] J. J. Zhang, W. J. Pietro and A. B. P. Lever, *J. Electroanal. Chem.* **403** (1996) 93.
- [7] D. W. Pang, H. B. Deng and Z. L. Wang, *Electrochim. Acta* **39** (1994) 847.
- [8] M. C. Pham, J. E. Dubois and P. C. Lacaze, *J. Electrochem. Soc.* **130** (1983) 346.
- [9] T. Brennan and I. Bernal, *J. Phys. Chem.* **73** (1969) 443.
- [10] A. M. Bond, R. L. M. Hendrickson, J.E. Moir and D. R. Page, *Inorg. Chem.* **22** (1983) 3440.
- [11] R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal  $\beta$ -diketonates and Allied Derivatives', Academic Press, London (1978).
- [12] R. G. W. Hollingshead, 'Oxine and its Derivatives', Vol. 1, Butterworths Scientific, Sevenoaks, UK (1954–1956), p. 227.
- [13] M. L. Riekkola, O. Makitie and M. Sundberg, *TIAFT-Bull.* **1** (1979) 23.
- [14] G. S. Patterson and R. H. Holm, *Inorg. Chem.* **11** (1972) 2285.
- [15] R. Chant, A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Aust. J. Chem.* **26** (1973) 2533.
- [16] L. R. Gahan and M. J. O'Connor, *J. Chem. Commun.* **68** (1974) 310.
- [17] C. Lin and A. B. Bocarsly, *J. Electroanal. Chem.* **300** (1991) 325.
- [18] T. R. J. Cataldi, A. Guerrieri, I. G. Castella and E. Desimoni, *Electroanalysis* **7** (1995) 305.
- [19] J. Zhou and E. Wang, *ibid.* **4** (1992) 473.
- [20] J. Taraszewska and G. Roslonek, *J. Electroanal. Chem.* **371** (1994) 223.
- [21] C. A. Clayton, J. W. Hines and P. D. Elkins, *Anal. Chem.* **59** (1987) 2506.