

Effect of metals on silver electrodeposition Application to the detection of cisplatin

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Abstract

In the present work, the influence of several metals (Co, Ru, Pd, Os, Pt, Cu, Pb), deposited on a carbon paste electrode, towards silver electrodeposition was tested. First, adequate conditions for the electrodeposition of metals on the electrode were found. Then, the cyclic voltammograms registered (silver deposition curves and analytical signals) showed that Co, Cu, Pt and Pd were able to accelerate silver electrodeposition. Finally, a valid methodology for the detection of cisplatin was established. It is based on the deposition of silver on a Pt (from cisplatin) modified electrode and the analytical signal corresponds to the anodic stripping of the deposited silver. A limit of detection of $3.2 \times 10^{-9} \text{ mol dm}^{-3}$ (1 ng cm^{-3}) cisplatin was obtained.

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1. Introduction

The modification of an electrode surface employing metals or metallic complexes can give rise to electrodic surfaces able to facilitate and/or accelerate electrochemical processes and also to provoke electrocatalytic reactions. These surfaces can usually be formed by means of chemical deposition of the metal or metallic complex or by means of metal electrodeposition.

Such layers can be formed by just placing a solution of the metallic complex on the surface of the electrode for a time. Cobalt metalophthalocyanines are commonly employed in this way, as they are able to catalyse electrochemical reactions. Electrodes so modified have been employed for the detection of formaldehyde [1], trichloroacetic acid [2] or hydrazine [3]. Also, osmium, rhodium and ruthenium phthalocyanines have been deposited on glassy carbon electrodes for the electrooxidation of cysteine [4].

The bulk electrodeposition of metals on the surface of electrodes can also form electrocatalytic layers. In some cases, the electrocatalytic properties do not rely on the metal itself but on derivatives such as metallic oxides. Wang et al. [5] electrodeposited Pd and Pt on a glassy carbon electrode for the electrocatalytic detection of formaldehyde, acetaldehyde and propionaldehyde in a FIA system. Casella et al. [6] employed Pd modified glassy carbon electrodes as detectors in chromatography for oxalic acid. Pt is also commonly employed for the electrocatalytic detection of different analytes [7,8].

The underpotential deposition (upd) process, discovered by Rogers et al. [9], is known as the phenomenon in which up to a monolayer of metal deposits onto a foreign metal substrate (usually the electrode) at potentials positive from the reversible Nernst potential due to distinct interaction between them. The upd of a metal can form on the electrode

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surface a metallic layer that shows high catalytic activity towards several electroodic processes. Thus, cyclopentanol was electrocatalytically oxidised employing Pt electrodes modified with underpotentially deposited Co, Ge and Pb [10]. Moreover, Pauling and Jüttner [11] showed that the upd co-electrodeposition of Tl and Ag modifies the catalytic properties of a gold electrode.

In our research group, carbon paste electrodes have been modified with colloidal gold by physical adsorption and has been demonstrated that it accelerates silver electrodeposition [12–14]; however, in this case the modification of the electrode was employed to detect colloidal gold and not the reagent that suffers the electrochemical reaction (silver). Colloidal gold facilitates the electrodeposition of silver because silver reduction process occurs at a less negative potential than in the absence of gold on the surface of the electrode. This fact generates a range of potentials in which silver reduction only occurs when the metal is adsorbed on the electrode; therefore, if an anodic scan is performed in 1.0 mol dm^{-3} NH_3 after silver electrodeposition at one of these potentials, an oxidation peak of silver at $+0.100 \text{ V}$ is obtained. The amount of electrodeposited silver is proportional to that of the adsorbed metal, so silver stripping allows the detection of colloidal gold.

Other strategies based on silver amplification for DNA detection (using colloidal gold) [15,16] or for conducting purposes [17] have been described.

In this work, the effect of several metals (electrodeposited on a carbon paste electrode) towards silver electrodeposition is studied. Then, cisplatin (*cis*-[Pt(NH₃)₂Cl₂]) is selected as a model metallic complex that could act as electrochemical label and that contains one of the metals able to accelerate silver electrodeposition. Thus, an adequate methodology, based on the electrodeposition of silver, is developed in order to quantify this complex.

Cisplatin has been employed as an anticancer drug since 1969, when Rosenberg et al. [18] discovered its chemotherapeutic properties. When cisplatin enters into the cells it coordinates to different molecules such as enzymes (affinity for sulphur groups), RNA or DNA, being the interaction with DNA the responsible of the therapeutic action. Cisplatin can coordinate to N7 of two neighbouring guanine and/or adenine bases, as this nitrogen does not form H bonds with other bases, in the same or in opposite DNA strands. As a consequence of the employment of cisplatin in cancer treatment, it became necessary to detect the molecule in biological samples [19–26]. The most employed technique has been HPLC coupled to different kinds of detection (electrochemical, spectrophotometric) but the electrochemical detection of cisplatin, by differential pulse polarography, without previous separation has also been described [26]. Moreover, Sadik and co-workers [27–29] have described some silver based methodologies for the electrochemical sensitive detection of cisplatin on avidin covered, silver coated (electrochemically deposited) gold electrodes modified with biotinylated double-stranded DNA.

The employment of platinum complexes as electrochemical labels in biological assays is based on the ability of square planar Pt(II) complexes with a free coordination site to bind to DNA (as previously described) or to proteins. This is commonly employed to attach markers, i.e. enzymes or fluorochromes previously coordinated to the Pt complex, to the target molecule via the proprietary Universal Linkage System (ULS™) labelling technology from Kretech Biotechnology [30].

2. Experimental

2.1. Reagents

Carbon paste was prepared by thorough mixing of 0.24 cm^3 of Uvasol paraffin oil (Merck) with 1 g of Ultra “F” purity graphite powder (Ultra Carbon). It was prepared weekly.

Water was obtained from an ultrapure Millipore Milli-Q water system.

Analytical grade (Merck) H_2SO_4 , HNO_3 , HCl , NH_3 , NaCl and AgNO_3 were used.

The following reagents were employed: $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (all of them from Fluka), OsCl_3 , $(\text{NH}_4)_2[\text{PtCl}_4]$ (both from Riedel-de Haën), $\text{Pb}(\text{NO}_3)_2$ (from Merck) and *cis*-[Pt(NH₃)₂Cl₂] “cisplatin” (from Sigma). Solutions were prepared in 0.1 mol dm^{-3} HNO_3 , excepting the $(\text{NH}_4)_2[\text{PtCl}_4]$ solutions, which were prepared in 0.1 mol dm^{-3} HCl ; solutions of cisplatin were prepared daily in NaCl 0.9% and stored at 4°C protected from light with aluminium foil.

The 0.04 mol dm^{-3} silver nitrate solutions were made daily and 0.134 cm^3 were added to a 25 cm^3 cell containing 1.0 mol dm^{-3} NH_3 to obtain a final concentration of $2 \times 10^{-4} \text{ mol dm}^{-3}$ Ag^+ for each experiment.

2.2. Apparatus

Voltammetric measurements were performed with an ECO CHEMIE μ Autolab Type II potentiostat/galvanostat coupled to a PC and controlled by Autolab GPES software version 4.6 for Windows.

The electrochemical arrangement used was a conventional three-electrode cell. A homemade carbon paste electrode with a surface diameter of 3 mm was used as the working electrode. It is made of a hollow Teflon tube in which the carbon paste is packed under pressure into a 2 mm deep well; a stainless steel rod acts as the electrical contact between the carbon paste and the potentiostat; the paste is further compacted by polishing manually on a sheet of paper. The reference electrode was an Ag/AgCl electrode; the counter electrode was a $1.5 \text{ mm} \times 1 \text{ mm}$ platinum wire. Cells were protected from light with aluminium foil when silver solutions or cisplatin solutions were employed.

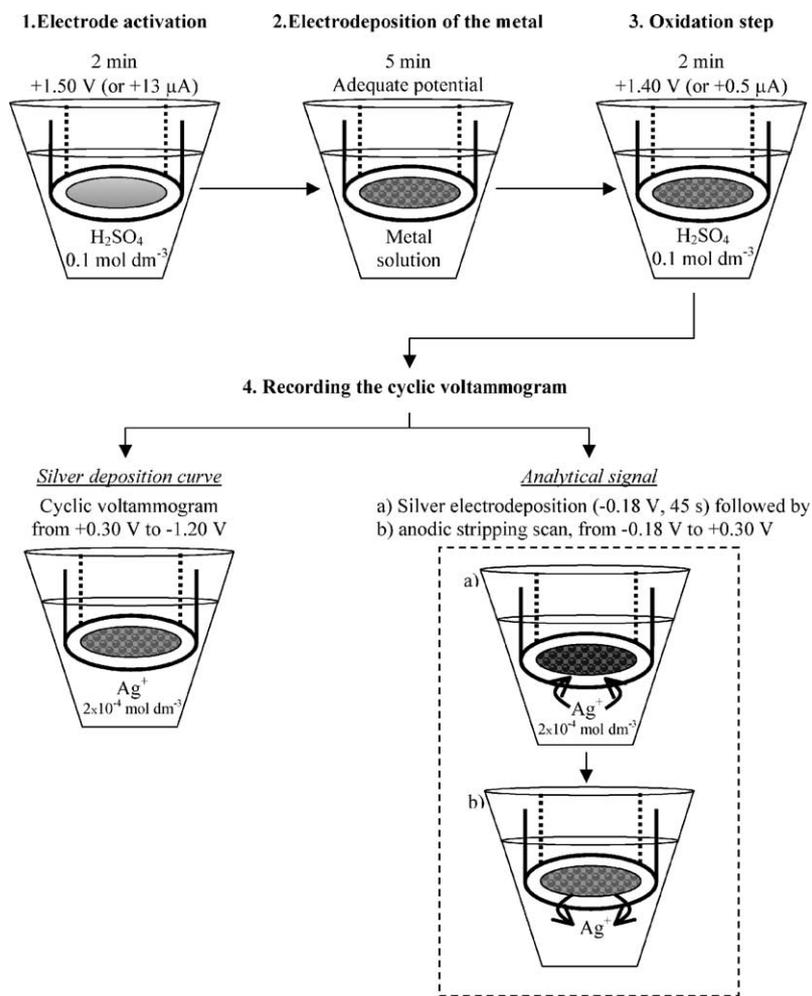


Fig. 1. Analytical procedures developed to evaluate the effect of deposited metals on silver electrodeposition.

2.3. Analytical procedures

2.3.1. Electrodeposition of metals

The following procedures were developed in order to test if metals were electrodeposited on the surface of a carbon paste electrode.

Procedure 1: First, the surface of the electrode was activated using a $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ stirred solution for 2 min at +1.50 V. Then, the electrode was immersed in a metal solution and a cyclic voltammogram from +1.50 V to -0.90 V, at a scan rate of 50 mV s^{-1} , was recorded. Rinsing with water was carried out between each step. Doing this, an adequate electrodeposition potential for each metal could be selected.

Procedure 2: First, the surface of a new electrode was activated as in *Procedure 1*. Then, the electrode was immersed in a metal solution and the adequate electrodeposition potential (different for each metal) selected in *Procedure 1* was held for 2 min with stirring. Finally, the electrode was introduced in the electrolyte solution (without metal) and a cyclic voltammogram from the electrodeposition potential to +1.50 V was recorded. Rinsing with water was carried out between each step.

2.3.2. Evaluation of the effect of metals on silver electrodeposition

The following procedure is depicted in Fig. 1:

- 1. Electrode activation.** The surface of the electrode was activated using a $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ stirred solution for 2 min at +1.50 V (for cisplatin, a constant current of +13 μA was employed).
- 2. Electrodeposition of the metal.** The electrode was immersed in a metal solution and the adequate electrodeposition potential (different for each metal) was held for 5 min with stirring.
- 3. Oxidation step.** It was performed employing a $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ stirred solution for 1 min at +1.40 V (for cisplatin, a constant current of +0.5 μA was employed).
- 4. Recording the cyclic voltammogram.** As different kinds of studies were developed, a *silver deposition curve* or an *analytical signal* was recorded for an electrode.
 - *Silver deposition curves* were obtained in the following way: the electrode was immersed in a silver solution ($2 \times 10^{-4} \text{ mol dm}^{-3}$ silver nitrate contained in

Table 1
Half-wave potentials of oxidation and reduction processes of metals on carbon paste electrodes

Metal	Concentration (mmol dm ⁻³)	Potential of reduction process ($E_{1/2}$) (V)	Potential of oxidation process ($E_{1/2}$) (V)	Electrodeposition potential selected (V)
Ru	1	+0.93	+1.20	+0.70
Os	1	+0.24	+0.72	0.00
Cu	1	-0.01	+0.10	-0.20
Co	1		+0.35	-0.30
Pt	0.1	-0.01	+0.91	-0.40
Pd	0.01	-0.21	+0.25	-0.40
Pb	1	-0.57	-0.40	-0.60

1.0 mol dm⁻³ NH₃) and a cyclic voltammogram from +0.30 V to -1.20 V at a scan rate of 50 mV s⁻¹ was recorded.

- *Analytical signals* were obtained in the following way: the electrode was immersed in a silver solution (2 × 10⁻⁴ mol dm⁻³ silver nitrate contained in 1.0 mol dm⁻³ NH₃) and silver electrodeposition, developed at a potential of -0.18 V for 45 s, followed by an anodic stripping scan, from -0.18 V to +0.30 V with a scan rate of 50 mV s⁻¹, were performed, giving rise to the cyclic voltammogram corresponding to the analytical signal.

Rinsing with water was carried out between each step. *Background silver deposition curves* and *background analytical signals* were recorded before each experiment following the same procedure but employing only the electrolyte (without metal) in Step 2.

A new electrode was employed for each measurement.

2.3.3. Oxidation of metals in NH₃

The following procedure was developed in order to test which electrodeposited metals could interfere in the *analytical signal* obtained as described above.

Firstly, the steps “Electrode activation” and “Electrodeposition of metals” were performed as Steps 1 and 2 described above, respectively, employing 1 × 10⁻⁴ mol dm⁻³ metal solutions in “Electrodeposition of metals” step. Then, the electrode was immersed in 1.0 mol dm⁻³ NH₃ and a cyclic voltammogram was recorded from -0.70 V to +1.20 V at a scan rate of 50 mV s⁻¹.

3. Results and discussion

3.1. Electrodeposition of metals on a carbon paste electrode

In order to evaluate which metals were able to catalyse the electrodeposition of silver, they must be previously deposited on the surface of the carbon paste electrode. Therefore, the first assays were focused on the selection of an adequate electrodeposition potential, as well as on demonstrating that the metals remained deposited on the electrode.

Thus, following the *Procedure 1* described in Section 2.3.1, the cyclic voltammograms obtained showed the reduction process for each metal (as well as the oxidation process in the anodic scan). Taking it into account, an adequate reduction potential was chosen for each case. Table 1 lists the half-wave potentials ($E_{1/2}$) of the oxidation and reduction processes, as well as the electrodeposition potential selected for each metal. When cobalt solutions were used, no reduction process appeared. However, if the cathodic scan in *Procedure 1* was recorded from +1.50 V to less negative potentials than -0.30 V the oxidation peak in the anodic scan was not obtained. Thus, -0.30 V was selected and demonstrated to be an adequate electrodeposition potential for cobalt. In order to prove that the metals remained deposited on the surface of the electrode after their reduction, *Procedure 2* of Section 2.3.1 was carried out. In the cyclic voltammograms obtained, an oxidation process for each metal appeared, as well as a change in its intensity proportional to the concentration of the solution employed. This confirmed that all the metals were electrodeposited on the surface of the carbon paste electrode.

3.2. Effect of deposited metals on silver electrodeposition

As previously mentioned, the ability of a metal for accelerating silver electrodeposition would be indicated in the shift, towards less negative potentials, of the silver reduction process. The higher the shift, the higher the effect.

In order to test it, *silver deposition curves*, recorded following the analytical procedure described in Section 2.3.2, similar to the one showed in Fig. 2 were obtained for each metal. Concretely, this figure shows the voltammogram obtained when a 1 × 10⁻⁵ mol dm⁻³ Cu²⁺ solution was employed (voltammogram “b”, thick line) and the one obtained in absence of metal (voltammogram “a”, thin line). Thus, this metal accelerates silver electrodeposition because silver reduction process is shifted towards less negative potentials. ΔE (0.086 V) indicates the difference between the half-wave potential of the silver reduction process on the electrode surface without metal ($E_{1/2[n]}$, in this case -0.540 V) and the half-wave potential of the silver reduction process when the metal is electrodeposited on the electrode surface ($E_{1/2[s]}$, in this case -0.454 V). Thus, the higher ΔE , the higher the effect. Table 2 lists the ΔE values for all the metals tested. Only

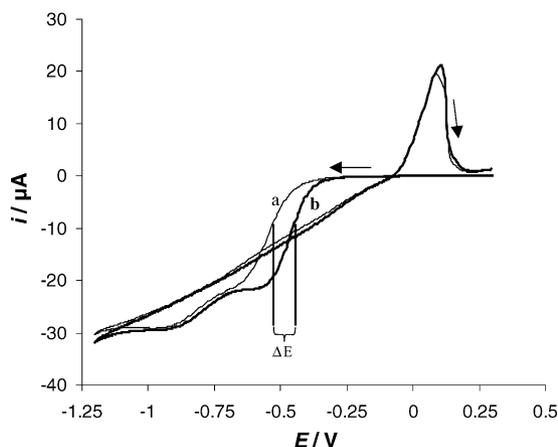


Fig. 2. Cyclic voltammograms (silver deposition curves) recorded in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$ containing $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$, from $+0.30 \text{ V}$ to -1.20 V at a scan rate of 50 mV s^{-1} , when (a) (thin line) Cu is not deposited on the electrode and (b) (thick line) Cu is deposited on the electrode employing a $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Cu}^{2+}$ solution. Cu^{2+} electrodeposition conditions: -0.20 V , 5 min.

Table 2

Difference between the half-wave potential of the silver reduction process on the carbon paste electrode in absence and in presence of electrodeposited metals

Metal	ΔE (V)
Os	0.029
Pb	0.049
Ru	0.051
Cu	0.086
Co	0.096
Pt	0.171
Pd	0.252

Pd, Pt, Co and Cu facilitate silver electrodeposition; for Os, Pb and Ru there are hardly differences in the silver reduction processes. Moreover, as deduced from ΔE values, the effect is higher for Pd and Pt.

Fig. 2 also shows that there is a range of potentials in which silver reduction only occurs when the metal is deposited on the electrode. So, if silver is electrodeposited at an

adequate potential in this range, an anodic scan gives rise to a silver oxidation process only if the metal was previously deposited on the surface of the electrode. This is shown in Fig. 3 for Cu and Os, where cyclic voltammograms correspond to the analytical signals recorded following the procedure described in Section 2.3.2. When there is no metal on the electrode (Fig. 3A(b) and B(b)) silver is not electrodeposited at -0.18 V , so there is no oxidation process. Moreover, only the electrodeposited Cu is able to provoke silver electrodeposition and an oxidation peak of silver is obtained (Fig. 3B(a)); the electrodeposited Os does not show this effect, so -0.18 V is not enough to electrodeposit silver and register its oxidation peak (Fig. 3A(a)).

3.3. Electrochemical behaviour in NH_3 of electrodeposited metals

The aim of this work is to show the possibility of detecting a metallic complex (cisplatin, as described below) using the accelerated electrodeposition of silver provoked by the metal. Then, a future research will deal with the employment of the metallic complex as electrochemical label of biomolecules (proteins or DNA) that would be used in immuno- or genosensing devices, where the labelled molecules would be captured to give the analytical signal based on the accelerated electrodeposition of silver. Therefore, as the detection of the metallic label would be achieved via the commonly used sequential heterogeneous assays on immuno- or genosensors, there would be no possibility of finding other metals on the sensor device that could interfere in the detection of the metallic label.

However, the accelerated deposition of silver could also be used to detect a metallic complex (i.e. cisplatin) in biological samples (which is out of the scope of this work). In this case, metallic interferences present in the sample would need to be considered. For this reason, the next study shows, for the metals used in this work, the way in which they could be evaluated.

Of course, those metals that accelerate silver electrodeposition are potential interferences for the detection of other

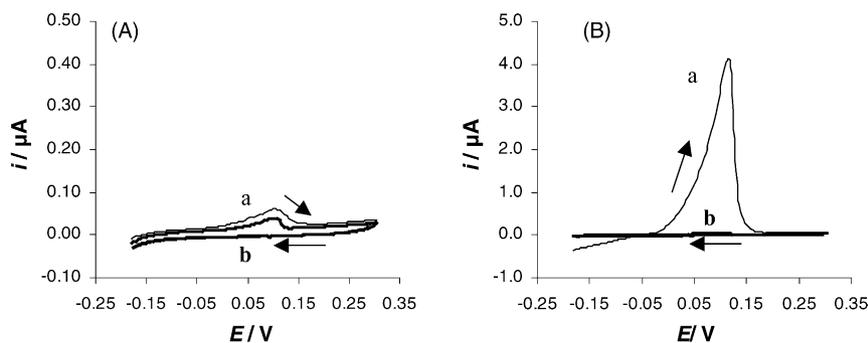


Fig. 3. Cyclic voltammograms (analytical signals) recorded in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$ containing $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$, from -0.18 V to $+0.30 \text{ V}$ at a scan rate of 50 mV s^{-1} , when (A) Os and (B) Cu are employed (a) (thin line) metal is deposited on the electrode [from a $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ OsCl}_3$ solution in (A) and from a $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution in (B)]; (b) (thick line) metal is not deposited on the electrode (background analytical signals). Os^{3+} electrodeposition conditions: 0.00 V , 5 min. Cu^{2+} electrodeposition conditions: -0.20 V , 5 min. Ag^+ electrodeposition conditions: -0.18 V , 45 s.

metal whose electrodeposition potential is more negative. For example, Co would interfere in the detection of Pd or Pt.

Another interference could be the oxidation process of metals at high concentrations in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$. As previously showed, the *analytical signal* obtained is due to the reoxidation of silver, which occurs in NH_3 at $+0.100 \text{ V}$. Thus, it is important that in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$ there is no other anodic peak at that potential, which could interfere with the *analytical signal*. Therefore, it was necessary to study the electrochemical behaviour of metals electrodeposited at high concentrations on a carbon paste electrode when an anodic scan is performed in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$. Following the analytical procedure described in Section 2.3.3, Pd, Pt, Cu and Os did not show any anodic process. Co, Pb and Ru showed anodic processes at $+0.955 \text{ V}$, $+0.897 \text{ V}$ and $+0.528 \text{ V}$, respectively, but none of these processes interfere with the one of silver at $+0.100 \text{ V}$.

Other metals usually present in biological samples such as Fe or Zn were also tested. However, results obtained following the procedures described in Section 2.3.1 (data not shown) showed that none of them remained deposited to the electrode surface after applying an adequate electroreduction potential on the metal solution, so they could not affect silver electrodeposition nor show an anodic process in NH_3 and, therefore, would not interfere.

Anyway, possible specific metallic interferences should be evaluated (in a similar way than the one showed here) and further research should be carried out in order to avoid them for the detection of a metallic complex in a biological sample using the accelerated silver electrodeposition.

3.4. Detection of cisplatin

From the four metals able to catalyse silver electrodeposition, Pt was selected as the most adequate one to develop an analytical methodology for the detection of a metal that can act as electrochemical label of biological molecules. The reason is the existence of *cis*-diamminedichloro platinum(II) (cisplatin). Cisplatin and other similar Pt complexes are molecules able to bind to DNA and other biomolecules. Thus, detection of cisplatin would allow the detection of biomolecules labelled with cisplatin (or other similar Pt complex). So far, the employment of cisplatin (apart of being an anti-cancer drug) is just to act as linker between a biomolecule and a label (mainly enzymes or fluorochromes) [30] but it has never been detected as a label itself. Thus, if cisplatin (or a similar Pt complex) could be detected, the other labels (enzymes, fluorochromes) used for the detection of the biomolecule would not be necessary and electrochemical detection of the Pt-labelled biomolecules could be performed, which would allow employing cisplatin (or other similar Pt complex) as a label itself and not only as linker.

The *analytical signal* for cisplatin is similar to the one showed for Cu^{2+} in Fig. 3. However, a solution of $1 \times 10^{-7} \text{ mol dm}^{-3}$ cisplatin (100-fold lower concentration than Cu) gives rise to an oxidation peak of silver of about

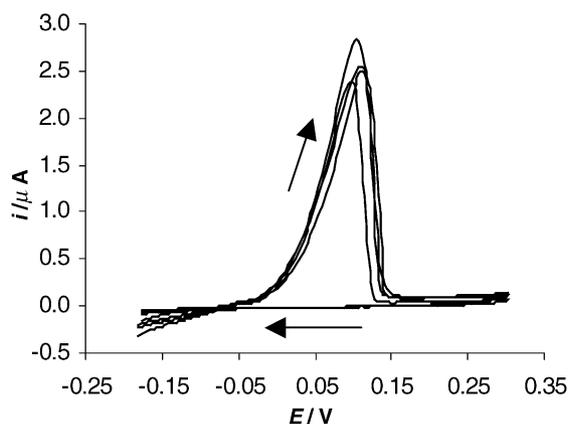


Fig. 4. Reproducibility of the *analytical signal* of cisplatin ($n=4$). Cyclic voltammograms (*analytical signals*) recorded in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$ containing $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$, from -0.18 V to $+0.30 \text{ V}$ at a scan rate of 50 mV s^{-1} , when Pt (from a $3 \times 10^{-8} \text{ mol dm}^{-3}$ cisplatin solution) is deposited on the electrode. Cisplatin electrodeposition conditions: -0.40 V , 5 min. Ag^+ electrodeposition conditions: -0.18 V , 45 s.

$50 \mu\text{C}$ (10-fold higher peak area than for Cu), due to the higher activity of Pt towards silver electrodeposition.

In this analytical procedure, the “Oxidation step” and the “Electrode activation” step are carried out at constant current. Doing this, the reproducibility in the analytical signal is better than the one obtained if constant potentials were applied. Thus, a relative standard deviation of 11.1% was observed for five measurements with a mean peak area of $3.55 \mu\text{C}$ when a $3 \times 10^{-8} \text{ mol dm}^{-3}$ cisplatin solution was employed (see Fig. 4).

3.4.1. Influence of the “Oxidation step”

If the “Oxidation step” in H_2SO_4 , performed after the “Electrodeposition” step, is not carried out, silver is electrodeposited on the carbon paste electrode in absence of metals. This effect was studied employing cisplatin. Fig. 5 shows the *silver deposition curves* recorded when the oxidation step is not carried out (Fig. 5A; $E_{1/2[\text{n}]} = -0.451 \text{ V}$, $E_{1/2[\text{s}]} = -0.381 \text{ V}$) and when it is carried out (Fig. 5B; $E_{1/2[\text{n}]} = -0.545 \text{ V}$, $E_{1/2[\text{s}]} = -0.359 \text{ V}$). A comparison of these curves and values of the half-wave potentials shows that if the oxidation step is not included in the analytical procedure, the silver reduction process is shifted towards less negative potentials in absence of Pt. Therefore, at -0.18 V silver is electrodeposited and high peak areas are obtained for *background analytical signals*.

Hydrogen evolution during the electrodeposition step, performed at negative potentials (-0.40 V for cisplatin), is probably the responsible of this behaviour. If the oxidation step is not carried out, H_2 is not removed from the surface of the electrode and, even in absence of Pt, silver electrodeposits at low cathodic potentials. If the oxidation step is carried out, hydrogen is removed from the electrode and silver electrodeposition only occurs in the presence of Pt. When the influence of the oxidation current applied in the oxidation

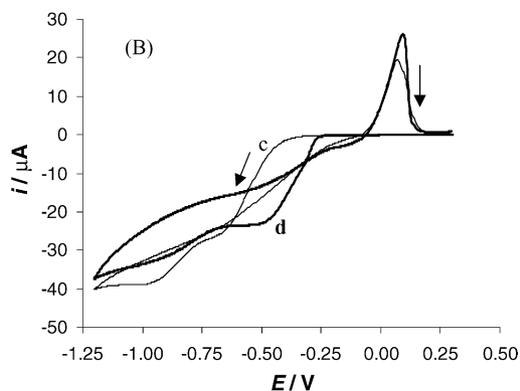
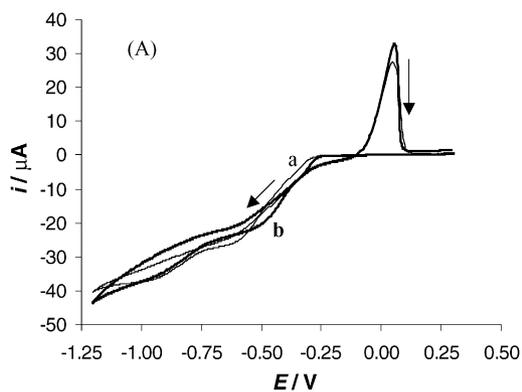


Fig. 5. Cyclic voltammograms (*silver deposition curves*) recorded in $1.0 \text{ mol dm}^{-3} \text{ NH}_3$ containing $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$, from $+0.30 \text{ V}$ to -1.20 V at a scan rate of 50 mV s^{-1} , when cisplatin is not deposited on the electrode surface (voltammograms a and c, thin lines) and after cisplatin electrodeposition (voltammograms b and d, thick lines). (A) Oxidation step is not carried out; (B) Oxidation step is carried out. Cisplatin concentration: $1 \times 10^{-7} \text{ mol dm}^{-3}$. Cisplatin electrodeposition conditions: -0.40 V , 5 min.

step on the *analytical signal* was studied, it was observed that a minimum oxidation ($+0.05 \mu\text{A}$) was enough to avoid the electrodeposition of silver in absence of Pt.

3.4.2. Effect of silver electrodeposition conditions and cisplatin electrodeposition time on the analytical signal

Silver electrodeposition potential, silver deposition time and cisplatin electrodeposition time effects were studied employing a $1 \times 10^{-7} \text{ mol dm}^{-3}$ solution of cisplatin; optimised values are those applied in the analytical procedure described in Section 2.3.2.

First, it was observed that, at potentials less negative than -0.18 V , the more negative the silver electrodeposition potential, the higher the *analytical signal* and also constant *background analytical signals* were obtained. But when the deposition potential was more negative than -0.18 V , *background analytical signals* increased, and faster than the *analytical signals*, so the most adequate potential was -0.18 V .

Then, the effect of silver electrodeposition time was studied; the voltammetric signals increased with the deposition time, obtaining a good signal to background ratio at 45 s.

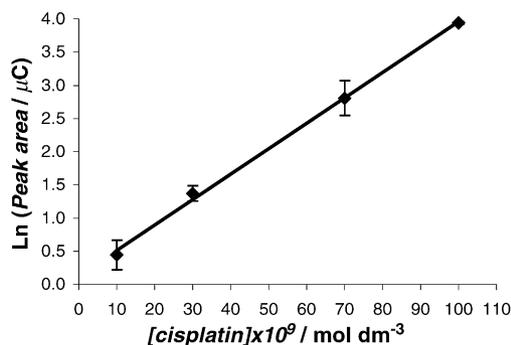


Fig. 6. Calibration plot of cisplatin concentration.

These results agreed with the behaviour showed by silver when its electrodeposition was accelerated by colloidal gold [13].

Finally, the study of the effect of cisplatin electrodeposition time showed that the signals increased with the electrodeposition time, reaching a maximum at 5 min.

3.4.3. Effect of cisplatin concentration on the analytical signal

Fig. 6 shows the evolution of the *analytical signal* with the cisplatin concentration. The calibration curve was linearly fitted on a $\ln(y) - x$ form from $1 \times 10^{-8} \text{ mol dm}^{-3}$ to $1 \times 10^{-7} \text{ mol dm}^{-3}$ cisplatin, according to the following equation ($r = 0.9990$):

$$\ln(\text{peak area}/\mu\text{C}) = 0.13 + 3.83 \times 10^7 [\text{cisplatin}]/\text{mol dm}^{-3}$$

A limit of detection of $3.2 \times 10^{-9} \text{ mol dm}^{-3}$ (1 ng cm^{-3}) cisplatin was calculated considering the three times of the standard deviation divided by the slope of the calibration curve.

4. Conclusions

For the first time, in this work the electrodeposition of silver on carbon paste electrodes modified with several electrodeposited metals (Co, Ru, Pd, Os, Pt, Cu, Pb) has been studied. It was demonstrated that Os, Ru and Pb do not affect silver electrodeposition but Pd, Pt, Co and Cu do, being Pd and Pt those who show a higher accelerating effect. When these metals are electrodeposited on the surface of the electrode, silver reduction process occurs at a less negative potential than on the bare electrode and the anodic stripping of electrodeposited silver gives rise to an oxidation peak at $+0.100 \text{ V}$ in NH_3 . Also, an adequate methodology based on the electrodeposition of silver for the determination of cisplatin, a Pt containing complex, has been described. The proposed procedure is sensitive but susceptible to interference of some metals and the precision is not so high.

Work is in progress to show the feasibility of the employment of square planar Pt(II) complexes as electrochemical

labels in biological assays, for example in the detection of Pt-labelled target oligonucleotides in genosensors.

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