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Adsorptive Stripping Voltammetric Determination of Cobalt in the Presence of Nickel and Zinc Using Pyrogallol Red as Chelating Agent

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An adsorptive stripping voltammetric (AdSV) method for the direct determination of Co in the presence of Ni and Zn in natural waters based on metal complexation with pyrogallol red (PR) and subsequent adsorptive deposition onto a hanging mercury drop electrode (HMDE) is presented. Optimal analytical conditions were found to be: pH 7.8 (HEPES buffer 0.05 mol L^{-1}); C_{PR} = 2.0 µmol L^{-1}; E_{ads} = –0.40 V *vs.* Ag/AgCl; and t_{ads} = 60 s. Peak current is proportional to Co concentration over the 0.0–40.0 µg L^{-1} range, with a 3σ detection limit of 0.02 µg L^{-1}. The relative standard deviation for a Co solution (5.0 µg L^{-1}) was 2.1% for six successive assays. The Ni-PR complex is reduced at –0.86 V, free ligand at –0.97 V, and the Co-PR complex at –1.08 V. In the presence of tetrabutylammonium tetrafluoroborate (TBATFB) the Ni-PR complex is reduced at 180 mV more positive potentials and the signal is finer. However, Zn interferes with the determination of Co due to overlapping of the waves. In the presence of 8-hydroxyquinoline (Ox) the Zn-Ox complex is reduced at 130 mV more negative potentials than the Co-PR complex. The method was validated by determining Co in spiked synthetic sea water (ASTM D665), certified reference water (TMDA–61) and was applied to the determination of Co in sea water, tap water, and mineral water samples after UV digestion.

Keywords: Adsorptive stripping voltammetry; Co determination; Pyrogallol red; Water analysis.

1. INTRODUCTION

Cobalt is an essential micronutrient for man, animals and plants and it is a component of cyanocobalamin or vitamin B_{12}. In environmental and biological samples, cobalt is present at a trace level. Surface water and groundwater concentrations of cobalt are low, 1 µg L^{-1} in pristine areas and 1–10 µg L^{-1} in populated areas. Dissolved cobalt occurs in seawater at concentrations ranging from 0.01 to 0.2 nmol L^{-1} and the levels in drinking water are generally 0.1–5.0 µg L^{-1} [1-3].

In trace analysis, mainly of heavy metal ions, anodic stripping voltammetry (ASV) has been the most popular electroanalytical technique because of its speed, good selectivity and sensitivity, and low instrumentation cost compared to other techniques. Traditionally, the hanging mercury drop electrode (HMDE), due to its sensitivity has been used most widely as the working electrode. However, Co, Ni and Cr do not form amalgams with mercury. In these cases adsorptive stripping voltammetry (AdSV) is the adequate technique for their determination in a variety of matrices. In adsorptive voltammetry high sensitivity of the determination can be achieved in the presence of catalytic systems. The catalytic reaction occurs at the surface of the electrode when the reduced analyte is oxidized to its previous by an oxidizing agent. A complete revision of catalytic adsorptive stripping voltammetry for cobalt determination using ligands as dimethylglioxime, nioxime and others was carried out by Bobroski and Zarebski [4,5]. Others ligands used in adsorptive stripping voltammetry of cobalt are: nitroso-S [6], calcon carboxylic acid [7], quercetin [8], 1–nitroso–2–naphthol [9], furyldioxime [10], and 4–(2–pyridylazo)resorcinol [11].

The present paper describes an adsorptive stripping procedure for cobalt determination in natural waters using pyrogallol red (PR) (3,4,5–trihydroxy–9–(2'–sulfophenyl)–6–isoxanthone, pyrogallolsulfonphthalein) as complexing and adsorbing agent. This ligand has been used in AdSV as a chelating agent for molybdenum [12], germanium [13], copper [14], aluminium [15], and antimony [16], but its use in the determination of cobalt in the presence of nickel and zinc has not been reported, and neither has the effect of tetrabutylammonium tetrafluoroborate (TBATFB) or cetylpyridinium bromide (CPB) on the position and resolution of the signals. Because the signals of these metals ions are closed it is important to be able to separate them. The proposed method considerably exceeds the separation obtained with adsorptive methods with DMG and others ligands for Co, Ni and Zn signals.

2. EXPERIMENTAL PART

2.1. Apparatus

The voltammograms were obtained on a Metrohm model 797 VA Trace Analyzer processor with an Electrode Stand with automated hanging mercury drop electrode. The reference electrode was Ag/AgCl/KCl 3 mol L^{-1} and the auxiliary electrode was a platinum wire. Solutions were stirred during the purging and deposition steps with a rotating PTFE rod. The solutions were deaerated using high–purity nitrogen. pH was measured with an Orion model 430 pH meter. UV–irradiation of water samples was carried out in quartz tubes using a 705 UV–digester (Metrohm).

2.2. Chemical and reagents

Water used for sample preparation, dilution of the reagents, and rinsing purposes was obtained with a Milli–Q system (18.2 Ohm. Millipore, USA). All the chemicals (nitric acid, hydrochloric acid, boric acid, acetic acid, etc.) were analytical grade from Merck. A standard stock solution of 0.5 mg L^{-1} of Co was prepared from standard Co 1000 mg L^{-1} solution (Merck). The stock solutions of pyrogallol red (PR), 8-hydroxyquinoline (Ox), tetrabutylammonium tetrafluoroborate (TBATFB) and cetylpyridinium bromide (CPB) were prepared by dissolving the reagent in methanol (PR, Ox) and water (TBATFB, CPB), respectively. Britton Robinson (BR) buffer solutions were used to investigate pH in the 6–10 range. These buffers (0.4 mol L^{-1}) were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 2.0 mol L^{-1} NaOH solution. N–[2–hydroxyethyl]piperazine–N–[2–ethanesulfonic acid] (HEPES, Aldrich) buffer solutions were used in the pH 7.0–8.1 range (0.5 mol L^{-1}). Synthetic sea water (ASTM D665, Aldrich) and certified reference water (TMDA–61.2, Environment Canada) were used for validation measurements.

2.3. Sample preparation

Sea water samples were obtained from a beach close to several industries and belonging to a highly populated and touristic area (city of Quintero, South Pacific coast, Chile). The samples were placed in plastic bottles previously washed with 1% HNO_3 solution. In the laboratory they were filtered through a 0.45 μm membrane filter and acidified with HNO_3 to pH close to 2. Tap water samples were obtained from the laboratory. Jahuel mineral water was purchase in a supermarket. Before the analysis all the samples were digested by UV irradiation for 90 min at 90 ^{o}C (10.0 mL of sample with 100 μL of 30% H_2O_2).

2.4. Measurement procedure

Water (10.0 mL), 1.0 mL of Britton–Robinson buffer (0.4 mol L^{-1}) or 1.0 mL of HEPES buffer (0.5 mol L^{-1}), 20 μL of pyrogallol red ($1x10^{-3}$ mol L^{-1}), and aliquots of Co(II) solution (0.5 mg L^{-1}) were pipetted into the voltammetric cell. The solution was purged with nitrogen (saturated with water vapor) for 5 minutes. Then, after eliminating some drops, a new mercury drop was extruded to initiate the preconcentration for a given t_{ads} and E_{ads} at a stirring rate of 1600 rpm. After an equilibration time of 10 s, the adsorptive voltammogram was recorded, while the potential was scanned from –0.40 to –1.30 V using square wave modulation with 5 mV step amplitude, 10 mV pulse amplitude, and a frequency of 10 Hz. The calibration curves were obtained and linear regression and detection limits were calculated. The proposed method was applied to the determination of cobalt in tap water, sea water and mineral water; in order to eliminate matrix effects the standard addition method was used.

3. RESULTS AND DISCUSSION

PR contains one sulfonic acid group and three hydroxyl groups. In acidic solutions (pH <1), the–SO_3H group is deprotonated, while the hydroxyl groups at positions 3,4 and 5 have dissociation constants of 2.89, 6.43 and 10.22 respectively [17]. Pyrogallol red forms a complex with Co with a metal:ligand stoichiometry of 1:1, and coordination may occur through the hydroxyl groups at positions 4 and 5 and the xanthene system or through the hydroxyl groups at positions 3 and 4 depending on the pH. During the voltammetric scan free PR exhibits one reduction peak at about –0.97 V and a small signal at –1.02 V. The position of the peaks depends on pH, indicating the involvement of hydroxyl protons in the reduction processes.

3.1. Effect of operational parameters

3.1.1. Influence of pH

In order to select the optimum pH value at which peak current of the Co–PR complex is achieved and there is minimum overlap between free ligand and complex, the influence of the pH of the medium was studied in the 6.0–10.0 range using Britton–Robinson buffers (fig.1). The peak potentials of both cobalt and the free PR peak shifted towards more negative values with increasing pH, and maximum peak current was obtained at pH 7.8. At pH below 6.0 sensitivity is slightly lower because the second hydroxyl group is protonated ($pKa_{(2)}$=6.43). The pH range was further reduced to 7.0–8.2 and HEPES buffer solutions (0.5 mol L^{-1}) were used, reaching maximum peak current at pH 7.8.

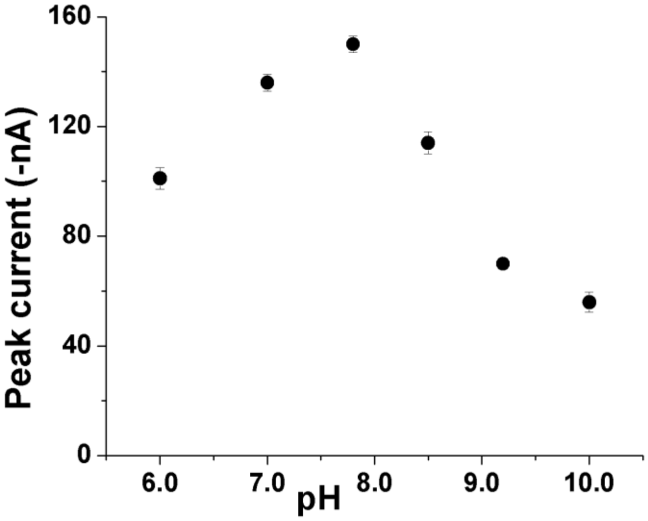

Figure 1. Influence of pH on the peak current of the Co–PR complex. Conditions: Co(II) 9.7 μg L^{-1}; C_{PR}: 2.1 μmol L^{-1}; t_{ads}: 60 s; E_{ads}: −0.20 V; step amplitude: 10 mV; pulse amplitude: 50 mV; and frequency: 10 Hz.

3.1.2. Influence of ligand concentration

PR concentration had a considerable effect on the method's linear range and sensitivity. The signal of Co in the absence of ligand is not observed, making this study somewhat difficult. The effect of C_{PR} (range 0.0 to 3.0 μmol L^{-1}) was studied for Co at concentration levels of 5.0 and 20.0 μg L^{-1} (pH 7.8, HEPES buffer, E_{ads} –0.20 V; t_{ads} 60 s) and it is illustrated in fig. 2. The results show that peak current increases with increasing ligand concentration up to 1.5 to 2.0 μmol L^{-1}, while at higher PR concentration the peak current remains almost constant, indicating that the ligand does not compete with the complex for the surface of the mercury electrode. Therefore, an optimum C_{PR} of 2.0 μmol L^{-1} was chosen for further optimization studies with synthetic solutions. However, when the spiked or real water samples contained several metal ions, a higher ligand concentration (5.0 μmol L^{-1}) was used to ensure complete complex formation.

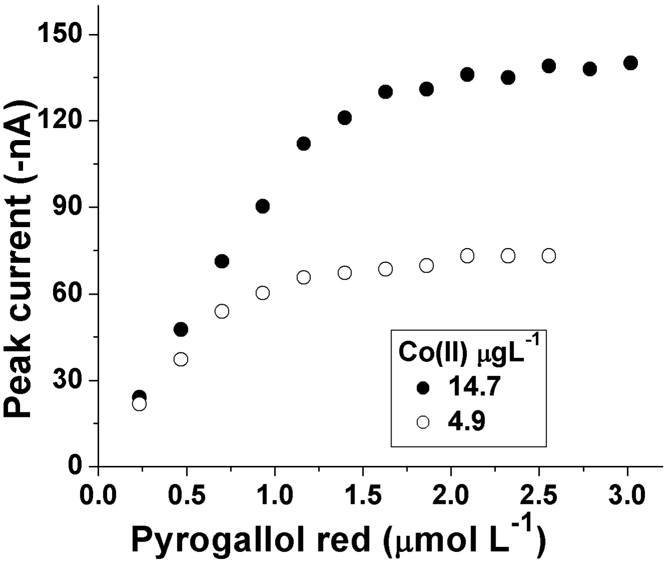

Figure 2. Influence of C_{PR} on the peak current of the Co–PR complex. Conditions: Co 4.9 (o) and 14.7 (•) μg L^{-1}; pH 7.8 (HEPES 0.05 mol L^{-1}); t_{ads}: 60 s; E_{ads}: −0.20 V; step amplitude 5 mV; pulse amplitude 10 mV; and frequency 25 Hz.

3.1.3. Influence of potential, time and stirring speed on the accumulation step

The influence of adsorption potential and time were also evaluated (figs. 3A and 3B). The effect of the adsorption potential on the stripping peak current was studied over the 0.00 to –0.80 V range. The peak current is maximum between –0.20 and −0.50 V.

However, it decreased slightly when the potential was changed to −0.60 V. An accumulation potential of −0.40 V gives the best sensitivity and was selected for further measurements. On the other hand, the effect of accumulation time was examined in the 0–350 s range. Peak current increases with increasing accumulation time prior to the potential scan, indicating that the PR and Co–PR complex are readily adsorbed on the HMDE (fig. 3B).

At first, the peak current of Co–PR increased almost linearly with accumulation time until 250 s and then it tended to a steady value, while the peak current of the ligand increased linearly with accumulation time until 60 s and then it tended to level off. However, at longer adsorptive times (above 180 s) the signal of the Co–PR complex is very broad, losing selectivity. On that basis and considering the speed of the measurement, t_{ads} of 60 s was used for further studies, but in the analysis of real samples higher times can be used to achieve good sensitivity.

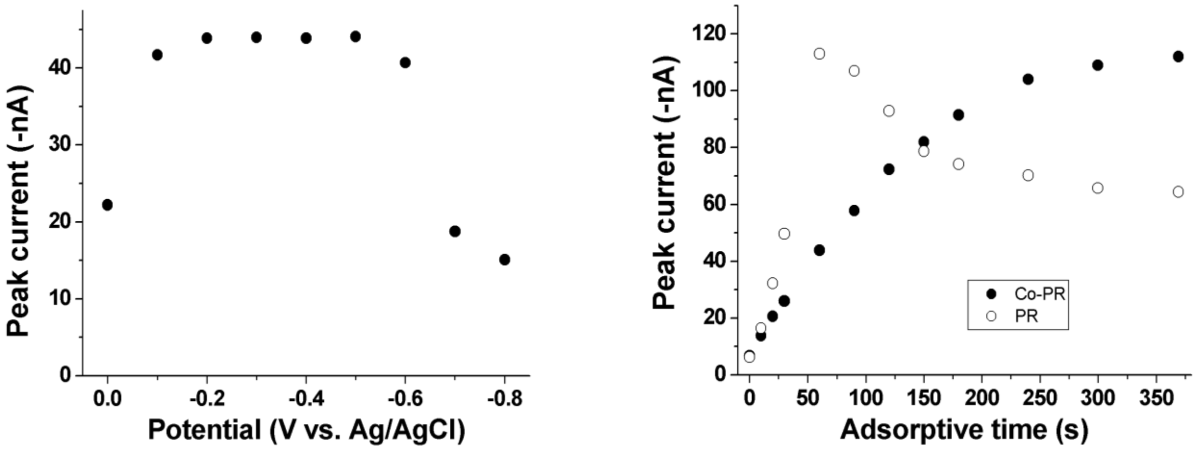

Figure 3. (A) Influence of E_{ads} on the peak current of the Co–PR complex. Conditions: Co(II) 4.9 µg L^{-1}; C_{PR}: 2.0 µmol L^{-1}; t_{ads}: 60 s. (B) Influence of t_{ads} on the peak current of the PR ligand (o) and Co–PR complex (•). Conditions: Co(II) 4.9 µg L^{-1}; C_{PR}: 2.0 µmol L^{-1}; pH 7.8.

Another not less important parameter is stirring speed in the accumulation step; normally, if the complex is weakly adsorbed, a low stirring speed is recommended. Fig. 4 shows plots of the cathodic peak current *vs.* stirring speed for free ligand and the Co–PR complex. Peak current of Co–PR complex increased linearly with stirring speed until 1000 rpm and then it tended to a steady value, while the peak current of the ligand increased linearly with stirring speed until 1000 rpm and then it tended to level off. A stirring speed of 1600 rpm was used for further studies.

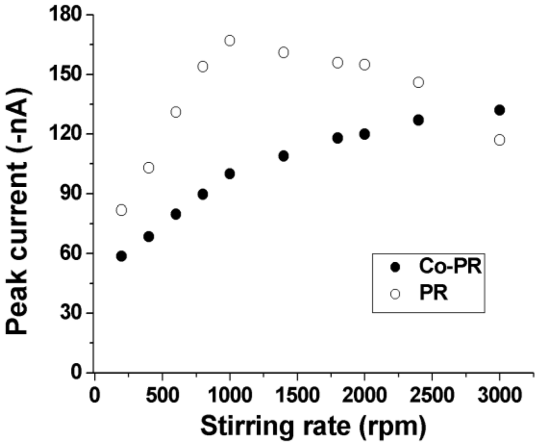

Figure 4. Influence of stirring speed on the peak current of the PR ligand (o) and Co–PR complex (•) in the accumulation step. Conditions: Co(II) 4.9 µg L^{-1}; C_{PR}: 2.0 µmol L^{-1}; pH 7.8 (HEPES 0.05 mol L^{-1}); t_{ads}: 60 s.

3.1.4. Effect of instrumental variables (frequency, step potential and amplitude)

The SW parameters studied were frequency, step amplitude, and pulse amplitude. Peak current increased as all the parameters increased. However, when the frequency was higher than 25 Hz the peak of the Co–PR complex was very broad and the separation of the free PR peak of the electrochemical reaction was smaller, losing resolution. A step amplitude of 5 mV, and a pulse amplitude of 10 mV at a frequency of 25 Hz (scan rate = 0.126 V s^{-1}) were selected for further experiments.

3.2. Linear range, detection limit, and reproducibility of the method

Optimal analytical conditions were found to be a PR concentration of 2.0 μmol L^{-1}, pH 7.8 (HEPES buffer 0.05 mol L^{-1}), and an adsorption potential of –0.40 V with an adsorption time of 60 s (stirring speed 1600 rpm; step amplitude 5 mV; pulse amplitude 10 mV; and frequency 25 Hz). Under these conditions the peak current was proportional to the concentration of cobalt over the 0.0–40.0 μg L^{-1} range, with a 3σ detection limit of 0.02 μg L^{-1} with an accumulation time of 60 s. Reproducibility for a 5.0 μg L^{-1} cobalt solution was 2.1% (n = 6). The results were lower compared to other results reported for cobalt(II) considering the conditions applied to this work. For instance, Mohadesi et al. [6] obtained a detection limit of 1.8 μg L^{-1} using AdSV in the presence of nitroso-S with a carbon paste electrode. Lower limits of detection were achieved in the presence of nitrite due to its catalytic effect. Ensafi and Abbasi [18] reported a detection limit of 0.08 μg L^{-1} for Co(II) in the presence of ammonium 2-aminocyclohexene-1-dithiocarboxylate using a deposition potential of –1.2 V during 60 s. Bobrowski and Nowak [19] got a detection limit of 0.07 μg L^{-1} with a bismuth film electrode for the catalytic determination of Co(II) in the presence of dimethylglyoxime, and the peak current was linear up to 10 μg L^{-1}, while Jugade and Joshi [20] used 2,2′-bipyridine as ligand and achieved a detection limit of 0.05 μg L^{-1} for Co(II). On the other hand, Bobrowski [10] reported detection limits of 0.02 μg L^{-1} for Co(II) and 0.2 μg L^{-1} for Ni(II) by catalytic AdSV in the presence of α-furildioxime using only an accumulation time of 20 s with linear ranges of 0.03 to 2.4 μg L^{-1} for Co(II) and 0.3 to 9 μg L^{-1} for Ni(II). The limit of detection achivied by Korolczuk et al. [21] was much lower (0.0007 μg L^{-1}) when they used dimethylglioxime in the presence of cetyltrimethylammonium bromide, achieving linearity from 0.0029 to 0.23 μg L^{-}1.

3.3. Interference studies

Metal ions can interfere with the measurement by complexing with PR, and this consumes the ligand or both by complexing and producing reduction peaks that overlap with, or even completely suppress, the Co–PR complex peak. The first problem is solved by adding excess ligand and using the standard addition method for the determination. In the voltammetric determination of Co the main interference may be caused by the presence of Ni and Zn because of their reduction potential close to that of Co, and normally in real samples they occur together with higher concentrations of Ni and Zn.

Fig. 5 shows adsorptive voltammograms of PR solution in the presence of Ni and Co, and the calibration curve (1.2-15.0 μg L^{-1}, pH 7.8; C_{PR} 2.0 μmol L^{-1}). Peak reduction of the Ni–PR complex occurs at –0.86 V, free PR at –0.97 V and Co-PR complex at –1.08 V. This difference indicates that the determination of cobalt in the presence of higher nickel concentration is possible, but this method (with optimum parameters for Co determination) is not sensitive for determining Ni because the peak current is smaller than the Co peak current for the same concentration.

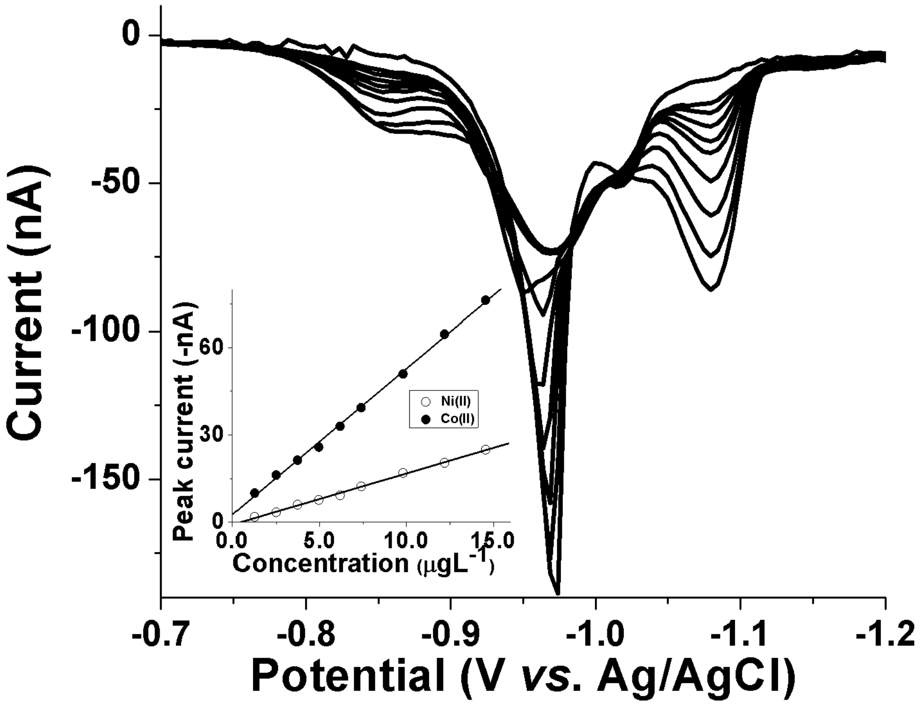

Figure 5. AdV and calibration curve of PR solution in the presence of Ni(II) and Co(II); concentration range: 1.2-15.0 μg L^{-1}.

With the purpose of determining Ni and Co simultaneously by changing the charge of the complexes or producing electrostatic interaction with the mercury electrode, tetrabutylammonium tetrafluoroborate (TBATFB) or cationic surfactant (cetylpyridinium bromide, CPB) were added to the electrochemical cell.

Fig. 6A shows adsorptive voltammograms and the calibration curve of Ni-PR solutions in the presence of TBATFB (2.4-27.8 μg L^{-1}, pH 7.8; C_{PR} 2.0 μmol L^{-1}; C_{TBATFB} 12.0 μmol L^{-1}). The reduction potential of the Ni-PR complex was displaced from –0.86 to –0.68 V and the peak is finer compared to the voltammograms in the absence of TBATFB. However, when Co solution was added, the signal of the Ni–PR complex decreased substantially because the Co complex is more stable than the Ni complex and the equilibrium is displaced towards the formation of the latter, whose reduction was observed at –1.08 V.

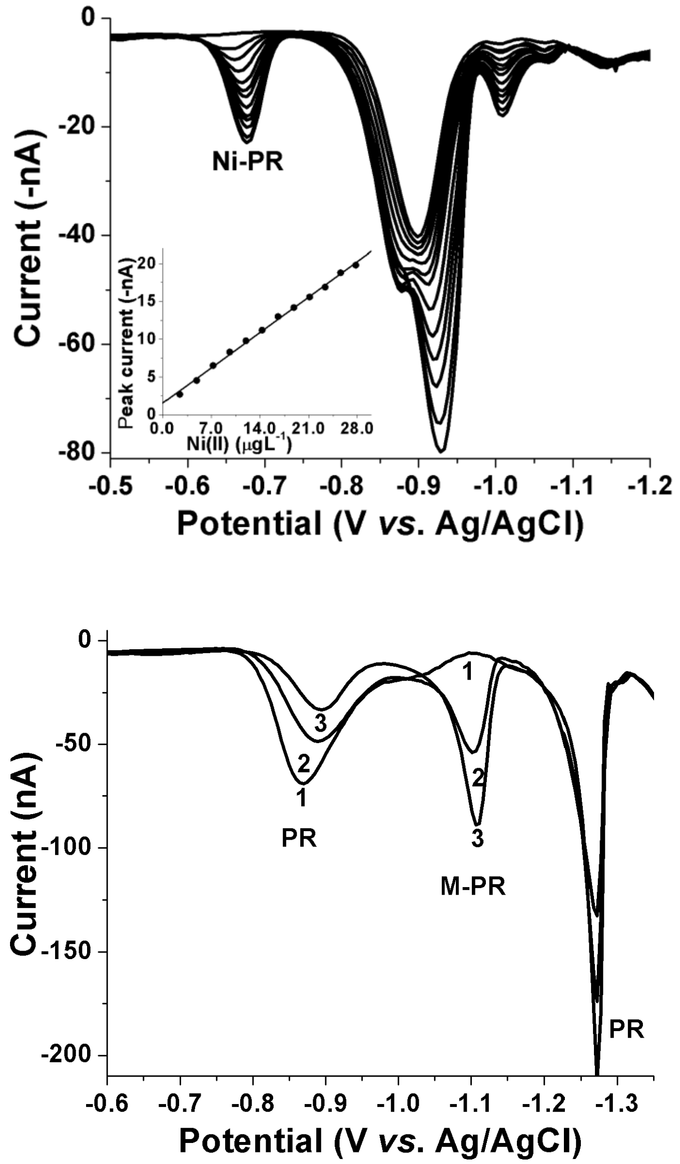

Figure.6 (A) AdV and calibration curve of Ni-PR solutions in the presence of TBATFB; Ni(II) 2.4-27.8 μg L^{-1}; pH 7.8; C_{TBATFB} 9.0 μmol L^{-1}. (B) AdV in the presence of CPB; PR ligand (curve 1), Ni(II) 30.0 μg L^{-1} (curve 2), and Co(II) 4.6 μg L^{-1} (curve 3). Conditions: C_{PR}: 2.0 μmol L^{-1}; C_{CPB}: 2.0 μmol L^{-1}; pH 7.8 (HEPES 0.05 mol L^{-1}); E_{ads} = –0.40 V; t_{ads}: 60 s.

When aliquots of CPB solution were added to a PR ligand, the voltammograms presented a great change, the reduction peak of the free ligand was slowly displaced to a less negative potential (from –0.97 to –0.87 V), peak current decreased from –0.24 to –0.064 μA, and a new peak at –1.27 V was seen (fig. 6B. curve 1). The signal due to the nickel complex appeared at –1.10 V (Ni(II) 30.0 μg L^{-1}, curve 2), which is more sensitive and finer than in the absence of CPB. However, in the presence of cobalt the same signal was increased (Co 5.0 μg L^{-1}, curve 3). This means that with CPB in solution it is not possible to determine Co in the presence of Ni.

Under the optimal conditions selected, Co-PR and Zn-PR complexes were reduced at the same potential. $NaNO_2$ was added with the purpose of increasing the Co signal by a catalytic effect and minimizing interference by Zn. The Co signal increased substantially and the wave was narrower than in the absence of nitrite, however the linear range reached was until 5.0 μg L^{-1} and the Zn signal did not change. Several ligands were added to the solution with the purpose of displace the reduction potential of the Zn complex to more negative values. When Ox was added the reduction potential of Co-PR did not change (–1.08 V), the Zn-Ox wave was seen at –1.21 V, and the linear range reached 35.0 μg L^{-1}.

On the other hand, Cu(II), Pb(II) and Cd(II) form complexes with PR which present electrochemical reactions at –0.34; –0.63 and –0.67 V, respectively, so they did not interfere with the determination of Co, and it was only necessary to increase the ligand concentration until the free ligand peak was observed.

3.4. Validation of the method

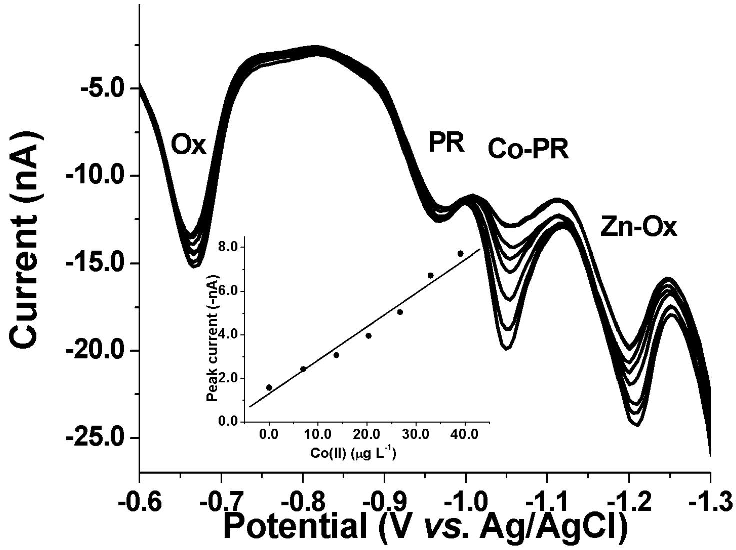

Figure 7. AdV of certified reference water (TMDA–61.2) and calibration curve of Co. Conditions: C_{PR}: 3.7 μmol L^{-1}; C_{Ox}: 15.0 μmol L^{-1}; pH 7.8 (HEPES 0.10 mol L^{-1}); E_{ads} = –0.40 V; t_{ads}: 60 s; step amplitude 5 mV; pulse amplitude 10 mV; and frequency 10 Hz.

An aliquot of synthetic sea water (ASTM D665) was contaminated with Co and Ni solutions (5.0 μg L^{-1}) and the determination was carried out using the standard addition method, getting 5.1 ± 0.1 μg L^{-1} (RE 2.0 %) for Co. The composition of synthetic sea water is NaCl 24.54; $MgCl_2x6H_2O$ 11.10; Na_2SO_4 4.09; $CaCl_2$ 1.16; KCl 0.69; $NaHCO_3$ 0.20; KBr 0.10; H_3BO_3 0.03; $SrCl_2x6H_2O$; and NaF 0.003 g L^{-1}. The usefulness of the present method was also evaluated by determining Co in certified reference water (TMDA–61.2) containing Al 57.9; As 34.4; Cd 58; Co 63; Cu 63.5; Fe 79.7; Mn 75.7; Ni 57.5; Pb 61.4; V 71.1; Zn 71.3 μg L^{-1} and others. The value obtained for Co was 62.0 ±

0.3 μg L^{-1} (certified value Co 63 μg L^{-1}. RE 1.6%). Fig. 7 shows the results obtained when 1.0 mL of reference water was added to 6.0 mL of water and 2.0 mL of HEPES 0.5 mol L^{-1}.

3.5. Real samples analysis

The proposed method was applied to the determination of cobalt in seawater, domestic tap water, and mineral water previously digested under UV radiation in the presence of HNO_3–H_2O_2 solution. Co in seawater samples was 3.2 ± 0.7 μg L^{-1} (three samples) and Co in Jahuel mineral water was 5.1 ± 0.4 μg L^{-1} (three samples). In tap water samples Co was not detected. To check the reliability of the method the samples were analyzed by ICP-AES, however the results obtained with this technique were below 5.0 μg L^{-1}, which is the detection limit of the procedure. The sea water samples were collected close to several industries and belongs to a highly populated and tourist area, however the levels are below the limit proposed by the EPA.

4. CONCLUSIONS

The determination of Co in the presence of Ni and Zn was made by forming Co–PR, Ni-PR and Zn-Ox complexes which are adsorbed on the HMDE. In the presence of TBATFB the reduction potentials of Co-PR and Ni-PR complexes are separated by about 300 mV, however, in the presence of cationic surfactant (CPB) both complexes shows reduction peaks at the same potential. In the presence of oxine Zn complex is reduced 130 mV more negative than Co-PR complex. The proposed method using PR as main ligand considerably exceeds the separation obtained with the adsorptive method with other ligands for the determination of Co in the presence of Ni and Zn.

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