Articles

Voltammetric Determination of Cobalt(II) Using Carbon Paste Electrodes Modified with 1-(2-Pyridylazo)-2-naphthol

Zun-Ung Bae, Yu-Chul Park, Sang-Hak Lee, Woo-Seong Jeon, and Hye-Young Chang

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701, Korea

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A method for the determination of cobalt(II) by differential pulse voltammetry using a carbon paste electrode constructed by incorporating 1-(2-pyridylazo)-2-naphthol(PAN) into a conventional carbon paste mixture composed of graphite powder and Nujol oil has been developed. Several influencing factors for the determination of cobalt(II) were studied in detail and the optimum analytical conditions were found to be as follows: pH, 4.6; composition of electrode, 20%; temperature of deposition, 43 ℃; time of preconcentration, 15 min. Regeneration of the electrode surface for the continuous uses of the electrode was achieved by exposing the carbon paste electrode to an acidic solution. Response of the electrode was reproducible for the uses of five times and the relative standard deviations were 6.7 and 4.6% for 2.0×10^{-5} M and 4.0×10^{-6} M cobalt(II), respectively. The calibration curve for cobalt(II) obtained by differential pulse voltammetry was divided into two linear ranges of 1.7×10^{-6}-1.3×10^{-4} M and 2.0×10^{-7}-8.0×10^{-7} M. The detection limit was estimated to be 1.3×10^{-7} M. The effects of coexisting ions were also investigated to test the applicability of the proposed method to the determination of cobalt(II) in real samples.

Introduction

Chemically modified electrode (CME) was started as a series of endeavor to directly control the chemical characteristics of electrode surface. It has several merits because of its electrocatalytic property,[1,2] enhancement of selectivity[3,4] and prevention of electrode fouling[5,6] in the field of electroanalytical chemistry. The electrochemical properties of CME are influenced by several factors such as material of electrode, the type of modifier and method of immobilization. Among the various types of CMEs, a chemically modified carbon paste electrode is widely used since it is easily fabricated and the regeneration of electrode surface is relatively simple. Selectivity of the analysis using carbon paste electrodes is enhanced by preconcentration and medium exchange procedures. Moreover, there is no need of an applied potential during the preconcentration process. Preconcentration can be extended to analyte that cannot be reductively deposited directly or require excessively negative deposition potentials.

Notwithstanding the good sensitivity offered by carbon paste electrode method, its application to real samples such as biological and environmental samples is limited because of the interferences from the sample matrix. The selection of an appropriate modifier is particularly important and the modifier should be selected according to the mechanism of the reaction involved for the determination. The most commonly used modifiers are complexing agents for the formation of metal complexes. Metals such as cobalt(II),[7] nickel(II),[8,9] copper(I),[10] silver(I)[11~13] and thallium(III)[14] have been analyzed using carbon paste electrodes containing diverse complexing agents. Enzymes[15,16] and an electron mediator[17] were used for catalytic reactions and microorganisms such as alga[18] and moss[19] were utilized for bioaccumulation processes. Organic material20 was also used for solid phases to covalently bind to the other modifier.

In this study for the determination of cobalt(II), we used the carbon paste electrode modified with 1-(2-pyridylazo)-2-naphthol (PAN) which forms very stable complexes with metal ions such as cobalt(II), nickel(II) and copper(II)[21] and is sparingly soluble in water. In the conventional method of determination of metals using extraction technique, PAN is known to be a good chelating agent. In the present analytical method cobalt(II) was deposited on the surface of PAN modified carbon paste electrode, and the deposited cobalt in the form of Co(II)-PAN complex was determined by differential pulse voltammetry. We investigated the optimum experimental conditions, reproducibility of the method in terms of the regeneration of electrode surface, and the interference effects of diverse ions for the determination of cobalt(II) by cyclic and differential pulse voltammetry.

Experimental

Reagents. The graphite powder (Nacalai Tesque), Nujol oil (Sigma Chemical Co.), and PAN (Dodite) used as a modifier were analytical grade. Graphite powder was purified in ethanol and the others were used without further purification. The cobalt(II) standard solution was prepared by dissolving cobalt metal (Wako Co., 99.99%) to be 1,000 μg/mL and was properly diluted before use. Deionized water obtained by a Milli-Q system was used.

Apparatus. EG&G PAR Model 174A polarographic analyzer, 175 universal programmer and RE0091 X-Y recorder were used in this experiment. Three electrode type was applied to all the measurements. Working and reference electrodes were carbon paste electrode and SCE and auxiliary electrode was platinum wire. Electrolysis cell was cylindrical type and temperature of the cell was controlled using a water bath circulator (Neslab RTE 210-D).

Preparation of Electrodes. A purified graphite powder was used to prepare PAN-modified and unmodified electrodes. The unmodified carbon paste electrode was constructed by mixing graphite powder and Nujol oil to a ratio of 6 : 2.5 (w/v). The chemically modified carbon paste electrode was made by the following procedure. The modifier was dissolved in acetonitrile to be dispersed uniformly and the solution was mixed with graphite powder to be a constant ratio (w/w%). Acetonitrile was then removed ultrasonically and dried at 70 ℃ for one day in vacuum.

The surface of carbon paste electrode prepared with a polyethylene syringe (1 mL, 5-mm ID) was cut with a fine nichrome wire and was polished to have smooth surface with a transparent paper. After being immersed in 0.1 M HCl for a few seconds, and subsequently in a buffer (pH 2.7, 43 ℃) solution, the electrode was rinsed with deionized water. This procedure was repeated for five or six times.

Analytical Procedure. The activated PAN modified electrode was immersed in 50 mL of a buffer solution (phthalate buffer medium, pH 4.6) containing cobalt(II) without the applied potential while stirring the solution. Temperature was controlled at 43 ℃. After preconcentration was carried out the electrode was rinsed with deionized water and subsequently by a buffer solution. The cobalt(II)-deposited electrode was transferred to a new medium (0.1 M KNO_3), and was prereduced at -0.45 V at 25 ℃ for 1 min. Dissolved oxygen in the electrolyte solution was removed by purging with nitrogen. Voltammograms were obtained in the range of -0.45 to $+0.10$ V. The peak current of cyclic voltammogram was measured to obtain the optimum experimental conditions, and differential pulse voltammograms were used for the calibration curve.

Results and Discussion

The cyclic voltammograms(A) and the differential pulse voltammograms(B) are presented in Figure 1. The dashed line and the solid line in Figure 1 are the cyclic voltammograms obtained using 20% PAN modified carbon paste electrode for the blank and the solution which contains 2.0×10^{-5} M cobalt(II), respectively. The relatively reversible redox waves in the cyclic voltammograms (A in Figure 1) were obtained at potential between -0.27 and -0.13 V. The oxidation wave in differential pulse voltammograms (B in Figure 1) was obtained at -0.12 V. On the basis of the increase of the peak current at a fixed potential with the increase of deposition time and concentration of cobalt(II), we confirmed that the peaks observed were the redox peaks of cobalt (II)-PAN complex.

In other to further investigate the peaks we recorded cyclic voltammograms with a carbon paste electrode which was not modified with PAN under the same experimental conditions as those used in Figure 1 (scan rate, 50 mV/s; supporting electrolyte, 0.1 M KNO_3; temperature, 43.0± 0.1 ℃). The result representsd in Figure 2 shows the disappearance of redox peaks of PAN obtained at $+0.3$, $+0.08$ and -0.37

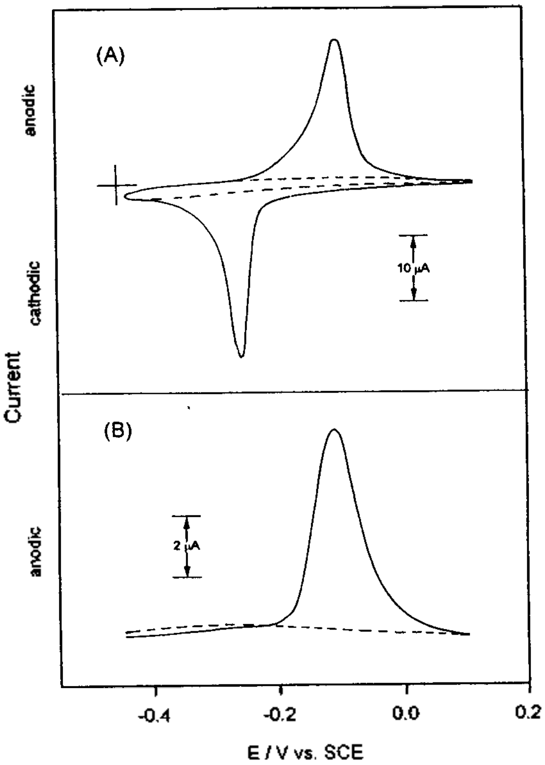

Figure 1. Cyclic voltammograms (A) and diffrential pulse voltammograms (B) for 2.0×10-5 M cobalt(II) solution obtained using 20% PAN modified carbon paste electrode: electrolyte solution, 0.1 M KNO_3; preconcentration time, 8 min in phthalate buffer (pH 4.6) at 43 ℃; reduction time, 1 min; scan rate, 50 and 10 mV/s for cyclic and differential pulse voltammograms, respectively; pulse amplitude, 50 mV. The voltammograms for the blank solution is presented as dashed line.

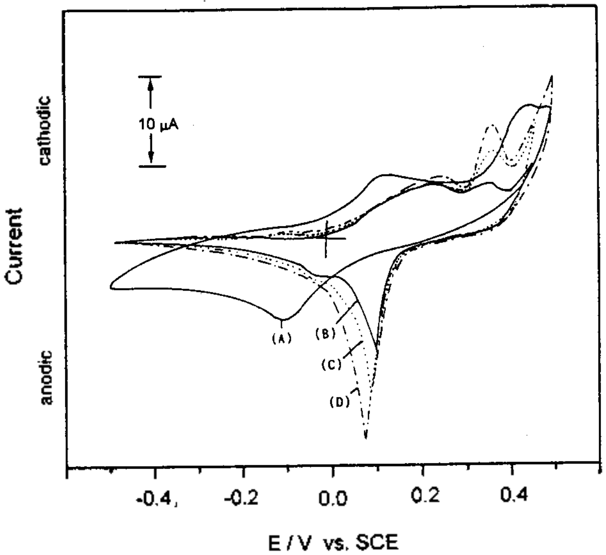

Figure 2. Effect of cobalt (II) ion concentration on the cyclic voltammograms obtained using PAN unmodified carbon paste electrode: (A) 5.88×10^{-3} M PAN. (B), (C) and (D); 8.15×10^{-4}, 1.50×10^{-3} and 2.07×10^{-3} M cobalt(II) are added to 5.88×10^{-3} M PAN, respectively. The other experimental conditions are the same as those for Figure 1A.

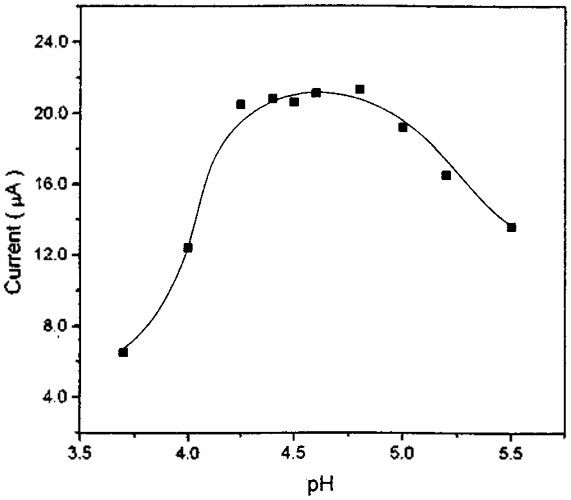

Figure 3. Effect of pH on the peak current of cyclic voltammograms for 2.0×10^{-5} M cobalt(II) solution obtained using 20% PAN modified carbon paste electrode: preconcentration time, 8 min at 43 ℃; reduction time, 1 min; scan rate, 50 mV/s.

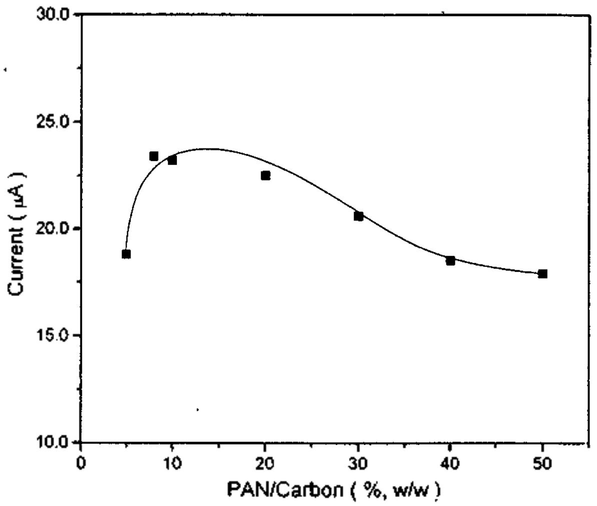

Figure 4. Effect of PAN composition (w/w%) for PAN-modified carbon paste electrode on the peak current for the stripping voltammetric determination of 2.0×10^{-5} M cobalt(II) solution: pH, 4.6; preconcentration time, 8 min at 43 ℃; reduction time, 1 min; scan rate, 50 mV/s.

V and the appearance of new redox peaks at −0.10 and −0.27 V with the addition of cobalt(II). The increase of peak currents with the increase of concentration of cobalt(II) in the range from 8.15×10^{-4} to 2.07×10^{-3} M indicates that the new peaks are redox peaks of cobalt(II)-PAN complex. Furthermore the redox peak potentials of these new peaks are consistant with those of the redox peaks shown in Figure 1. The values of oxidation current for the continuous measurements were found to be more reproducible than those of reduction currents. Therefore, the optimum experimental conditions were investigated at the oxidation peak of cobalt(II)-PAN complex.

Effect of pH. The effect of pH on preconcentration of cobalt(II) from sample solution to the PAN-modified electrode was studied. The result is shown in Figure 3. In the pH range of 4.3 to 4.8, Co(II)-PAN complex was found to be formed quantitatively at the PAN-modified electrode surface. The decrease of peak currents at the lower pH region and at a pH region greater than about 4.8 can be explained that efficiency of complexation is reduced by the protonated PAN and by the hydrolysis of cobalt(II), respectively. The resulted narrow pH region for maximum currents is similar to the case of copper(II) obtained using PAN modified carbon paste electrode.[22] Therefore, pH 4.6 was used for the optimum pH condition for the determination.

Composition of Electrode. To obtain the optimum composition of the PAN-modified electrode, the voltammograms were obtained using electrodes prepared by changing the composition ratios of PAN to carbon powder (w/w%). The effect of electrode composition on the peak current is presented in Figure 4. When the amounts of PAN was between 8 to 20%, the peak current was found to be nearly constant. When the percentage of PAN is above 20%, the current was decreased with the increase of the amounts of PAN. This phenomenon is probably due to the increase of the electode resistance with the increase of the amounts of PAN. This result is similar to that of Baldwin *et al.*[9] In this experiment 20% PAN modified electrode was used for the determination of cobalt(II) since this composition was found to be better in reproducibility than the 8% and 10% PAN-modified electrodes.

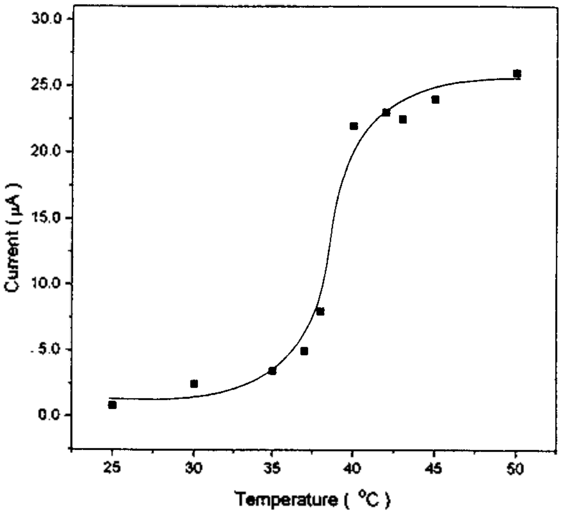

Figure 5. Effect of temperature on the peak current for 2.0×10^{-5} M cobalt(II) solution obtained using 20% PAN modified carbon paste electrode: pH, 4.6; preconcentration time, 8 min at 43 ℃; reduction time, 1 min; scan rate, 50 mV/s.

Effect of Temperature. We investigated the effect of temperature on the peak currents for the preconcentration since temperature is an important factor for the stability of metal complexes with PAN. Figure 5 shows the effect of temperature on the peak currents for the solution which contains 2.0×10^{-5} M cobalt(II) at pH 4.6. In the temperature ranges of 20 to 30 ℃ and over about 40 ℃, the peak current slowly increases. Between 30 and 40 ℃, however, the peak current was found to rapidly increase. The general increase of current can be explained by the increase of the activities of ion and the amounts of preconcentrated cobalt(II) due

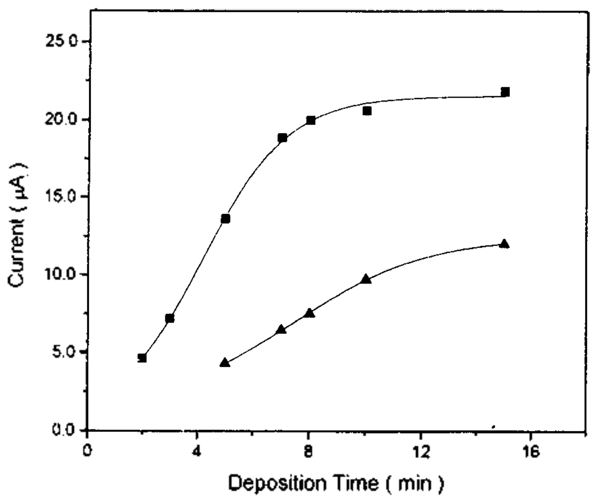

Figure 6. Effect of preconcentration time on the peak current obtained using 20% PAN modified carbon paste electrode: ■, 2.0×10^{-5} M cobalt(II); ▲, 4.0×10^{-6} M cobalt(II); preconcentration time, 8 min at 43 ℃; reduction time, 1 min; scan rate, 50 mV/s.

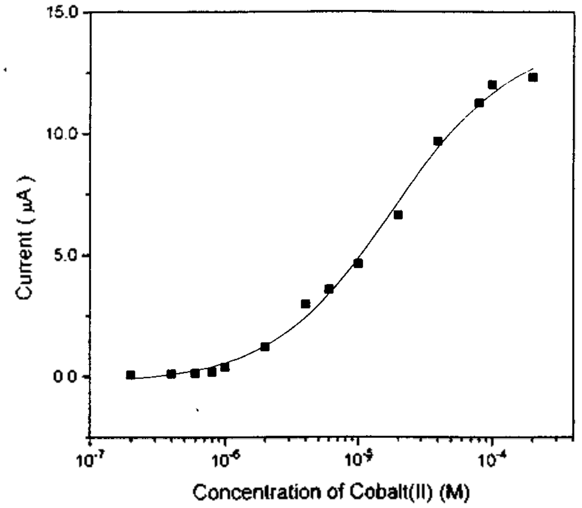

Figure 7. Calibration curve for the determination of cobalt(II) obtained by the differential pulse voltammetric method using 20% PAN modified carbon paste electrode: preconcentration time, 15 min at 43 ℃; pH, 4.6; reduction time, 1 min; scan rate, 10 mV/s; pulse amplitude, 50 mV.

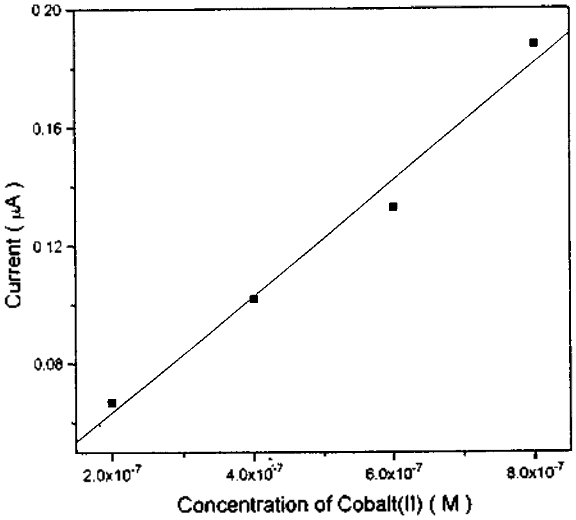

Figure 8. Calibration curve expanded in the low concentration range of Figure 6 for the determination of cobalt(II) obtained by differential pulse voltammetric method using 20% PAN modified carbon paste electrode: preconcentration time, 15 min at 43 ℃; pH, 4.6; reduction time, 1 min; scan rate, 10 mV/s; pulse amplitude, 50 mV.

to the increase of the complex formation constant with the increase of temperature. The rapid increase in the range of 30 to 40 ℃ is probably due to the fact that PAN is oriented to easily make bond with cobalt(II) at the electrode surface since viscosity of Nujol oil rapidly decreases in this temperature range. It is also considered that the rate of the formation of complex in the high temperature contributes more largely than the stability of the complex. Since we found that the renewal of electrode surface was relatively difficult and the possible number of continuous uses for the determination was reduced at temperature over 45 ℃, the temperature of 43 ℃ was suggested for the optimum temperature during the preconcentration of cobalt(II).

Time for Deposition. To obtain the optimum time for the deposition of cobalt(II) on the electrode surface, peak currents for the different immersing times of the electrode in the two solutions of containing different amounts of cobalt were measured. Figure 6 shows the changes of peak currents with increasing deposition time for 2.0×10^{-5} and 4.0×10^{-6} M solutions. The oxidation current was found to be increasing with increasing time up to about 8 min for the solution of 2.0×10^{-5} M cobalt(II). The current was almost constant after this time. For the dilute solution it took about 13 min for completing the deposition process. Therefore, the time for deposition was kept 15 min for the present method.

Reproducibility for Continuous Uses of the PAN-Modified Electrode. The repeated uses of the PAN-modified electrode affect the reproducibility of the electrode. The renewal of electrode used in this experiment is accomplished by immersing the electrode in a 3.0×10^{-3} M HCl solution at 43 ℃ for five seconds followed by rinsing with deionized water. The relative standard deviations of peak currents for five consecutive uses of the electrode were found to be 6.7 and 4.6% for 2.0×10^{-5} and 4.0×10^{-6} M cobalt(II) solutions, respectively. Results of the investigation on reproducibility suggested that the electrode could be reusable for about 7 consecutive measurements. Further uses induced the peak currents to slowly decrease possibly due to the loss of PAN at the electrode surface and the increase of background current for the repeated uses.

Determination of cobalt(II) by Differential Pulse Voltammetry. Figure 7 shows the calibration curve for the determination of cobalt(II) in water obtained by differential pulse voltammetry. We divided the curve into two linear ranges. Figure 8 shows the calibration curve in the low concentration range with the expanded scale of peak currents. The correlation coefficients were 0.990 and 0.991 for the linear ranges of 1.7×10^{-6} to 1.3×10^{-4} M and 2.0×10^{-7} to

Table 1. Effects of foreign ions on the oxidation peak current of cobalt(II) ion obtained by differential pulse voltammetry usig PAN modified carbon paste electrode[a]

Foreign	2.0×10^{-5} M		2.0×10^{-4} M	
ion	i (μA)	Interference ratio (%)	i (μA)	Interference ratio (%)
Cu^{2+}	1.99	−69.9	0.63	−90.0
Ni^{2+}	3.91	−40.8	2.20	−64.9
Mn^{2+}	7.53	+13.9	7.87	+19.1
Zn^{2+}	6.61	0	6.61	0
Pb^{2+}	6.61	0	6.61	0
Mg^{2+}	6.61	0	6.61	0
EDTA	0.21	−96.7	0.10	−98.4
CN^-	5.74	−8.6	4.80	−23.6
$Oxalate^{2-}$	6.19	−6.3	5.77	−23.6

[a] Concentration of Co(II) solution is 2.0×10^{-5} M. The peak current obtained using 20% PAN modified carbon paste electrode for the Co(II) solution containing no interferent ions is 6.61 μA: electrolyte solution, 0.1 M KNO_3 at 25℃; preconcentration time, 15 min in phthalate buffer(pH 4.6) at 43 ℃; reduction time, 1 min; scan rate, 10 mV/s; pulse amplitude, 50 mV.

8.0×10^{-7} M, respectively. Detection limit was found to be 1.3×10^{-7} M. Response was reproducible for the uses of five times and the relative standard deviations for five measurements were 6.7 and 4.6% for 2.0×10^{-5} M and 4.0×10^{-6} M cobalt(II), respectively.

Influence of Coexisting Ions. To test the applicability of the proposed method to the determination of cobalt(II) in a real sample the effects of diverse ions were investigated. To the aqueous solutions of 2.0×10^{-5} M cobalt(II), nine diverse ions of 2.0×10^{-5} and 2.0×10^{-4} M were added separately and the peak current for each spiked solution was measured. The results are presented in Table 1. The peak currents did not change in the cases of zinc(II), lead(II) and magnesium(II). For manganese(II) the peak current was slightly increased and for cyanide and oxalate it was slightly decreased. On the other hand, the peak currents were significantly decreased for copper(II), nickel(II) and EDTA. The decrease of peak currents for the metals is as expected based on the similar formation constants (logK>12 for Co(II), logK=16 for Cu(II) and 12.7 for Ni(II)[23]). The observation for anions may be explained by the reduced activity of cobalt(II) due to the electrostatic interaction with anions and the complex formation of cobalt(II) with these anions which occurs competitively with PAN.

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