DETERMINATION OF ULTRA-TRACE AMOUNTS OF COBALT BY ADSORPTIVE DIFFERENTIAL PULSE VOLTAMMETRY USING ACDA (2-AMINOCYCLOPENTENE-1-DITHIOCARBOXYLIC ACID)

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Abstract

The present work describes a selective, rapid and sensitive method for the determination of cobalt using the adsorptive differential pulse voltammetry technique. The method is based on the accumulation of Co(II) complex with 2-aminocyclopentene-1-dithiocarboxylic acid on a hanging mercury drop electrode, followed by measurement of the current of the adsorbed complex. The effects of experimental parameters on the peak current were investigated. The current was linear from 0.010 to 0.150 μg/ml of Co(II), with detection limit of 1.5 ng/ml. The relative standard deviation for ten replicate analyses of 0.02 and 0.06 μg/ml Co(II) was 2.3% and 1.2%, respectively. The method was used for the determination of Cobalt in steel sample.

Introduction

Cobalt is an essential element in biology. This metal ion is among the significant toxic metals for environmental surveillance, food control, occupational medicine, toxicology and hygiene. For studying environmental problems and environmental control, simple and sufficiently sensitive methods for the determination of the metal ion are necessary. For the determination of trace element in aquatic systems, voltammetric techniques are very suitable owing to their low cost, sensitivity and relative simplicity [1].

Keywords: Cobalt; Differential pulse; Stripping

The applications of adsorptive-voltammetry for the determination of trace and ultra-trace metals have been reviewed elsewhere [2]. The advantages and disadvantages of advanced electroanalytical techniques versus AAS (Atomic Absorption Spectrometry), ICP (Inductively Coupled Plasma)-AES (Atomic Emission Spectroscopy) and ICP-MS (Mass Spectrometry) in analysis have also been reviewed elsewhere [3]. Electroanalytical methods have been particularly successful for determination traces of Cobalt. In particular, the differential pulse method following adsorptive accumulation of Co(II)-dioxime complex [4], Co(II)-dimethylglyoxime [5], Co(II)-triethanolamine [6], Co(II)-diphenylglyoxime [7] and Co(II)-1,10-phenanthroline [8] was used for the determination of Cobalt at ng/ml level. But these methods have interferences from Ni(II), Zn(II), Fe(II) and Fe(III).

2-Aminocyclopentene-1-dithiocarboxylic acid

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(ACDA) is a dithiol compound that can be solved with Co(II) as $Co(ACDA)_2^{2+}$ [9]. The polarographic behaviour of the reagent has previously been studied by Safavi and Gholivand [10]. In this paper, a sensitive and selective method for the adsorptive differential pulse voltammetric determination of Co(II) is presented. The method was applied for the determination of Co(II) in steel samples.

Experimental Section

Reagents

Double distilled water was used throughout the experimental work. Chemical reagents were of analytical reagent grade.

2-Aminocyclopentene-1-dithiocarboxylic acid (ACDA) was prepared and purified according to Takeshima and Yokoyama [11] and Bordas *et al.* [12]. 1.0×10^{-3} M aliquot solution of ACDA was made by dissolving 0.016 g of ligand in 100 ml of methanol in a volumetric flask. This solution was prepared daily.

Analar grade nitrate, chloride and sulfate salts were used for preparing a standard solution of the metal ions (Merck). The buffer was prepared from Na_2HPO_4 and $NaHPO_4$.

A stock solution of Co(II) (1000 μg/ml) was prepared from Cobalt(II) nitrate (Merck) and standardized complexometrically with EDTA. Working standards were made by successive dilution of the stock solution as required.

Apparatus

The measurements were performed by a PAR Model 384B polarographic analyzer equipped with a Model 303 electrode system (EG&G) and a Model DMP40-44 plotter. A conventional three electrode system, comprising a medium sized HMDE electrode with a surface area 1.8 mm^2, a platinum wire counter electrode and a Ag/AgCl (in saturated KCl) reference electrode, was used in all experiments. All potentials reported are referred to as Ag/AgCl reference electrode. Solutions were deoxygenated with high-purity nitrogen for 4 min prior to each experiment and all experiments were performed under a nitrogen atmosphere.

Procedure

2 ml phosphate buffer solution (0.06 M), pH=6.0, 1.0 ml of 5.0×10^{-5} M ACDA solution 7 ml of distilled water were pipetted into the cell and purged with nitrogen for 4.0 min. After 30 sec of accumulation at –0.6 V, the differential pulse voltammogram was recorded from –0.8 to –1.5 with a potential scan rate of 10 mV/sec and pulse height of 0.02 V. After the background voltammogram had been obtained, aliquots of the Co(II) standard solution were added into the cell and the voltammogram was also recorded. Nitrogen atmosphere was maintained over the solution. All data were obtained at room temperature. The calibration graph was obtained by plotting I_p vs. Co(II) concentration.

Results and Discussion

Figure 1 shows differential pulse voltammograms for different concentrations of Co(II)-ACDA and of a blank solution. For the blank system, no current peak was observed between –0.6 and –1.5 V. But, in the presence of Co(II), the peak current increases with increasing Cobalt concentration with limit of detection 1.5 ng/ml. It was demonstrated that a complex of $CO(ACDA)_2^{2+}$ is formed under the experimental condition [9]. Evidence of the absorptive nature of the complex was obtained as follows: the peak current increased with increasing accumulation time before the potential scan. Small amounts of surfactants such as Triton X-100, and sodium dodecyl sulfate strongly suppressed the peak current. In addition, the influence of scan rate shows that the peak currents increase with potential scan rate from 40 to 10 mV/sec. These three phenomena indicate that the complex was strongly adsorbed on mercury electrode surface.

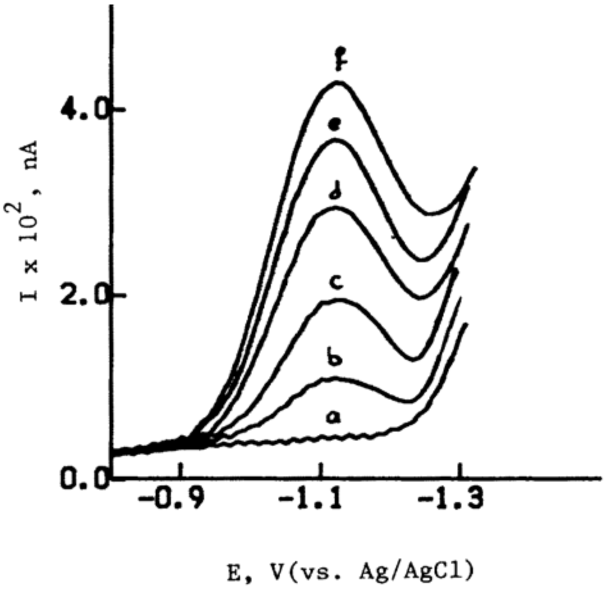

Figure 1. Differential pulse voltammograms for Co(II)-ACDA and a blank solution; Conditions: pH, 6.0, ACDA, 5.0×10^{-6} M; initial potential, -0.80 V, final potential, -1.50 V; accumulation potential, -0.60 V; accumulation time, 30 sec; pulse height, 0.02 V; scan rate, 10 mV/sec. a): 0.00, b): 50, c): 80, d) 100, e): 130, and f): 150 ng/ml Co(II) concentration.

Influence of Experimental Parameters

Various experimental parameters affecting sensitivity were explored.

The effect of pH on the peak current was studied with

5.0×10^{-6} M ACDA and 100 ng/ml of Co(II) (Fig. 2). Variation of pH produced a maximum peak current between 5.5-6.0 of pH values. A substantial decrease in peak current was observed at higher pH values. This effect is due to the interaction of Cobalt(II) with hydroxyl ion. On the other hand, in acidic media (pH<5.5), Co(II) is not completely complex formed with ACDA. Thus, a pH of 6.0 was selected for the study.

Figure 3 shows the influence of ACDA concentration on peak current at pH 6.0 and 100 ng/ml Co(II). The results show that by increasing the ligand concentration up to 5.0×10^{-6} M, the peak current increases, whereas greater amounts of the ligand decreased the peak current. This effect may be due to competitive adsorption of ACDA in HMDE. Thus, 5.0×10^{-6} M ACDA concentration was selected.

The accumulation potential on the peak current was examined over the range 0.10-–0.60 V. As illustrated in Figure 4, the peak current increased gradually when the adsorption potential became increasingly negative up to –0.60 V.

The accumulation time was also studied for the 100 ng/ml of Co(II) with the other variables at the optimum conditions (Fig. 5). The results show that the peak current increased when increasing accumulation time up to 120 s and then started to level off between 120-180 sec.

Calibration Graph, Precision and Limit of Detection

Under the optimum conditions described above, with increasing Co(II) concentration, the peak current increases linearly from 10 to 150 ng/ml with r=0.9995 for n=10.

The precision of the determination of Cobalt was evaluated from repeated determination at 20 and 60 ng/ml of Co(II). The relative standard deviation for ten replicate measurements of 20 and 60 ng/ml of Co(II) was 2.3% and 1.2%, respectively.

The detection limit was calculated as three times the standard deviation of the blank ($3S_b$), and was found to be 1.5 ng/ml Co(II).

Interferences Study

The effect of existing ions is tested on 100 ng/ml Cobalt. The results are shown in Table 1. From the results, it is concluded that many ions do not affect the determination of Co(II) when present in a 1000-fold to 50-fold excess.

Surface-active substance, such as Triton X-100 interferes as a result of competitive adsorption at the electrode peak surface. For example, addition of 50 μg/ml of Triton X-100 depressed stripping peak current. Higher concentration of complexing agents,

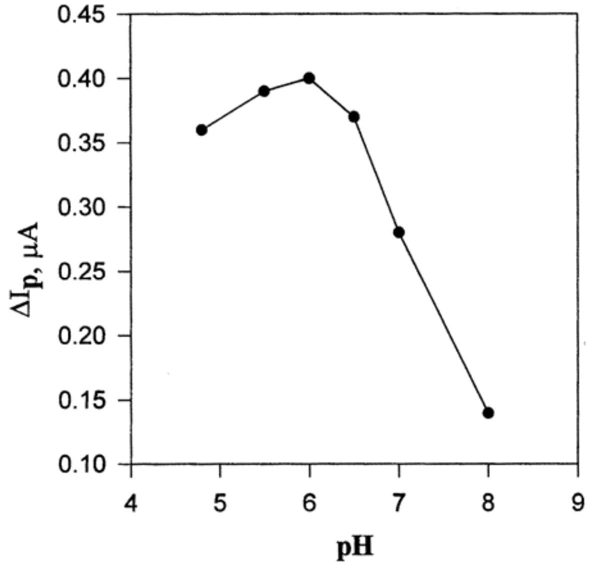

Figure 2. Effect of pH on the determination of Co(II); Conditions: ACDA, 5.0×10^{-6} M; initial potential, -0.80 V; final potential, -1.50 V; accumulation potential, -0.10 V; accumulation time, 30 sec; pulse height, 0.02 V; scan rate, 10 mV/sec.

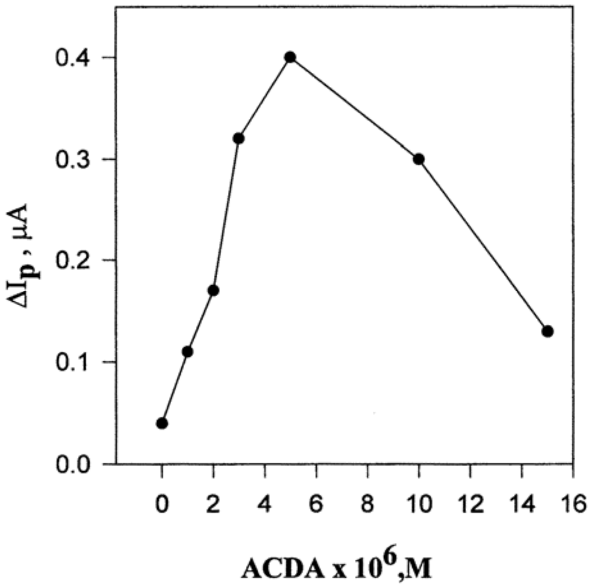

Figure 3. Effect of ACDA concentration on the sensitivity; Conditions: pH, 6.0; initial potential, -0.80 V; final potential, -1.50 V; accumulation potential, -0.10 V; accumulation time, 30 sec; pulse height, 0.02 V; scan rate, 10 mV/sec.

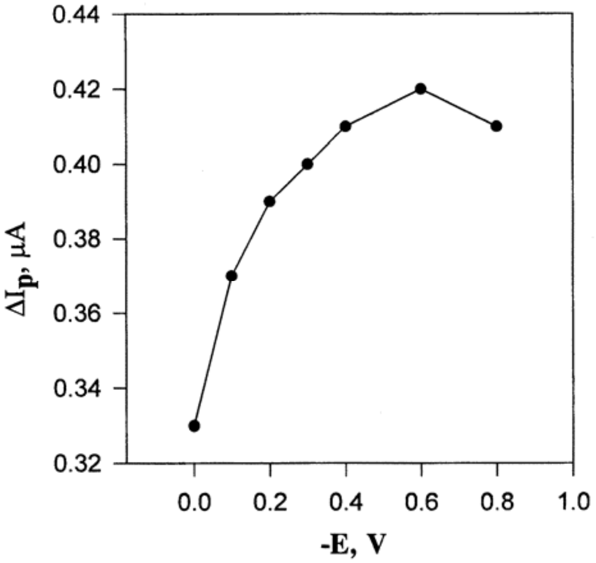

Figure 4. Effect of accumulation potential on the sensitivity; Conditions: pH, 6.0; ACDA, 5.0×10^{-6} M; initial potential, -0.80 V; final potential, -1.50 V; accumulation time, 30 sec; pulse height, 0.02 V; scan rate, 10 mV/sec.

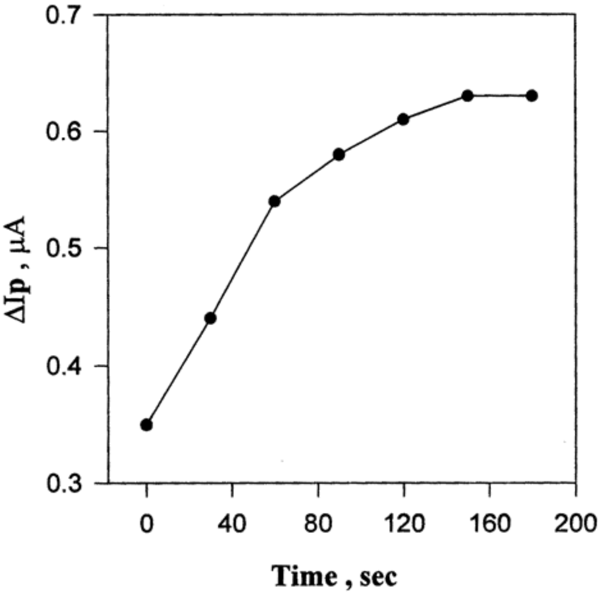

Figure 5. Effect of accumulation time on the sensitivity; Conditions: pH, 6.0; ACDA, 5.0×10^{-6} M; initial potential, -0.80 V; final potential, -1.50 V; accumulation potential, -0.60 V; pulse height, 0.02 V; scan rate, 10 mV/sec.

such as EDTA is also found to suppress the response of the system. For example, signal is almost completely eliminated by addition of 0.05% EDTA. Depending on the complexity of the sample for direct determinations of Cobalt, complexing agents and natural surface-active substances must be removed before the determination.

Real Sample Analysis

In order to validate the proposed method, it was examined by the determination of Cobalt in steel and water samples. The results are shown in Tables 2 and 3 and are satisfactory. For water analysis that contains low concentration of Cobalt, it must be digested by UV irradiation for 2 h before analysis. The results are given in Table 3.

Table 1. Influence of foreign ions on the determination of 100 ng/ml of Co(II) at the optimum conditions

Species	Tolerance limit ($W_{ion}/W_{Co(II)}$)
Ba(II), Cs^+, Cu(II), Sr^{2+}, Mg(II), Cr(III), La(III), Ca(II), Hg(I), Mn(II), Pb(II), U(VI), $S_2O_8^-$, HCO_3^-, SO_3^{2-}, Cl^-, $B_4O_7^{2-}$, OAC^-, WO_4^{2-}, SO_4^{2-}, BrO_3^-, CrO_4^{2-}, $S_2O_3^{2-}$, NO_3^-, ClO_3^-, I^-, Br^-, V(V), K^+, Na^+	1000
Cd(II), Th(IV), Ce(IV), NO_2^-, CO_3^{2-}, Te(IV), SCN^-	500
Ni(II), Fe(III), IO_3^-	200
Zn(II)	50

Table 2. Determination of Co(II) in steel samples

Steel type	Co(II)% present	Co(II)% found	RSD% n=5
CuNiCo(I)	30.0	28.9	2.7
CuNiCo(II)	24.0	23.7	2.2
Lemaiguand	8.0	7.6	3.2

Table 3. Determination of Co(II) in water sample

Sample	Co(II) added (ng/ml)	Co(II) found (ng/ml)	RSD% (n=5)	Recovery%
Water(I)	0.0	0.0	—	—
Water(I)	15.0	15.5	2.8	103.3
Water(I)	40.0	41.0	2.7	102.5
Water(I)	100.0	102.0	2.6	102.0
Water(I)	140.0	144.0	2.4	103.2
Water(II)	20.0	21.0	2.8	104.0
Water(II)	50.0	51.5	2.5	103.0
Water(II)	100.0	102.0	2.3	102.0

References

1. Stulik, K. and Kalvoda, R. *Electrochemistry for environmental protection,* (Ed.) Chales University and Academy of Science of the Czech Republic, Prague, pp. 128-152, (1995).
2. Paneli, M. G. and Voulgaropoulos, A. N. *Electroanalysis*, **5**, 335, (1993).
3. Bersier, P. M., Howell, J. and Bruntett, C. *Analyst,* **119**, 219, (1994).
4. Flora, C. J. and Nieboer, E. *Anal. Chem.,* **52**, 1013, (1980).
5. Gilbert, M. J. M., Powell, H. K. and Fardy, J. J. *Anal. Chim. Acta,* **207**, 103, (1988).
6. Meyer, A. and Neeb, R. *Fresenius J. Anal. Chem.,* **315**, 118, (1983).
7. Bobrowski, A. and Bond, A. M. *Electroanalysis,* **3**, 157, (1991).
8. Bebeki, V. J. and Voulgaropoulos, A. N. *Fresenius J. Anal. Chem.,* **342**, 352, (1992).
9. Nag, K. and Joardar, D. S. *Inorg. Chim. Acta,* **17**, 111, (1976).
10. Safavi, A. and Gholivand, M. B. *Anal. Lett.,* **25**, 1309, (1992).
11. Takeshima, T. and Yokoyama, M. *J. Org. Chem.,* **34**, 730, (1969).
12. Bordas, B., Sohar, D., Matolesy, G. and Berenesi, P. *J. Org. Chem.,* **37**, 727, (1972).