January 2008 Volume 7 Issue 2

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 7(2) 2008 [89-94]

# Determination of cobalt(II) at a 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine modified carbon paste electrode by differential pulse cathodic voltammetry

**Mohammad Reza Nateghi*, Ali Hadji-Shabani, Majid Fakheri**
[1]Department of Chemistry, Azad University-Yazd Branch, Yazd, (IRAN)
Tel. : 0098 351 8211391-9; Fax : 0098 351 5210681
E-mail : m_nateghi60@hotmail.com

*Received: 11th August, 2007 ; Accepted: 16th August, 2007*

## ABSTRACT

The feasibility of a carbon paste electrode(CPE) for practical use in analysis of cobalt(II) was investigated. The procedure involves an accumulation of cobalt on a 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine modified CPE, followed by medium exchange to a 'clean' solution where the accumulated Co(II) was oxidized and then a stripping voltammetric reduction current of cobalt(III) was measured at the 150mV *versus* Ag/ACl. The optimum conditions for determination of cobalt were found to be 0.09mol/l, $NH_3$(pH=10.60) as accumulation medium, 180s accumulation time in open circuit condition and stirred sample solution, 0.1mol/l KOH as measurement medium, and 3% ligand in the composition of electrode. The relative standard deviations for 5 successive determinations were 5.55% and 7.05% for $1.00\times10^{-5}$mol/l and $1.00\times10^{-6}$mol/l cobalt(II) respectively. The detection limit was estimated to be $8.90\times10^{-8}$mol/l(5.25 ppb). Excess amounts of Cu(II) interfering with cobalt peak were precipitated by potassium hexacyanoferrate(II) in acidic solution. The developed method was tested by analyzing a reference sample(Canadian certified reference materials NICKEL-COPPER-COBALT ORE SU-1a) and then applied to determine Co(II) in natural water and welding electrode samples tion was found to be 20 and 4ng/ml for CT and AM respectively.

KEYWORDS

Cobalt;
Cathodic voltammetry;
Carbon paste electrode;
Differential pulse;
Salicyl aldimine.

## INTRODUCTION

Although cobalt at trace levels is an essential element for the functioning of many vital processes in plants, animals and humans, however, it can be toxic at higher concentrations[1]. Also it is an important element for fabrication of hard alloys. For this reason, it often requires methods capable of quantitatively monitoring its presence at trace levels in the natural environment, and various other real samples. A variety of analytical techniques including spectrochemical and electrochemical methods have been utilized to determine cobalt in real samples[2-8]. Amongst the various analytical methods, adsorptive stripping voltammetry technique using modified electrodes is becoming a widely accepted analytical tool, as a high sensitive and economic method in determination of some ions in real samples[4,6,9-11].

Although these determinations by adsorptive stripping have very good detection limits, the adsorptive stripping peaks usually occur at high negative potentials(in the region of -1.0V or even more negative). In real samples, operations at such highly negative potentials involve a high probability of occurrence of interferences from the coexisting substances. Chemically modified electrodes with surfaces specifically designed for the ability to react with and bind the target solute have attracted considerable attention for their application in analytical chemistry[12-13]. Coupled with a medium exchange step, additional discrimination against background interferents can be achieved.

Amongst CMEs, carbon paste electrodes have low background current, wide range of usable potential, rapid renewability and easy fabrication[14,15]. Several studies on the use of modified carbon paste electrodes for selective and sensitive determination of metal ions have been reported, however there are a few reports in the literature on the use of MCPEs for Co(II) determination[14-17].

In the present article we report the application of a new MCPE for Co(II) determination by cathodic adsorptive stripping voltammetry. 5-[(4-choloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine Schiff base was chosen as modifier to determine Co(II) because it is new, and never been studied for Co(II), has a good ability for complexing Co(II) selectively and has low solubility in water. We investigated the optimum experimental conditions, reproducibility of the method and the interference effects of diverse ions for the determination of Co(II). Finally, the method was applied to the determination of cobalt in natural water and welding electrode samples.

## EXPERIMENTAL

### Reagents

All of the chemicals used were of AR grade. A stock solution of Co(II)($1.00\times10^{-2}$mol/l) was prepared by dissolving cobalt(II) nitrate(Merck) in doubly distilled water. This was stored in a darkened glass bottle. More dilute cobalt(II) standards were prepared daily by dilution of the solution. Britton-Robinson buffer was obtained by first preparing a mixture of phosphoric, acetic and boric acids, each 0.04mol/l. This B-R acid mixture was then titrated to the required pH with sodium hydroxide. The graphite powder(Fluka), paraffin(boiling range 300-400$^0$C Merck) and 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine(was prepared according to method cited in reference 18) were used as received for fabrication of CPE and MCPE.

### Apparatus

Cathodic stripping voltammograms and also cyclic linear sweep voltammograms for characterization of MCPEs were obtained with a 746 electrochemical analyzer, Metrohm Switzerland. A one-compartment electrochemical cell with a three-electrode configuration containing 10ml of 0.1mol/l KOH supporting electrolyte served as the measurement cell. A platinum wire was used as the counter electrode and the reference was an Ag/AgCl electrode. pH measurements were made with a Horiba instruments model M-12.

### Electrode preparation

5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)] salicyl aldimine coated graphite powder(for 1% to 5% w/w) were prepared by dissolving weighed amount of 5-[(4-choloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine in $CH_2Cl_2$, adding the required amount of graphite powder, and stirring the slurry thus formed until essentially all the solvent had evaporated. A completely dry powder was obtained by keeping the mixture at 30$^0$C for 24hr. The chemically modified carbon paste electrode was made by first thoroughly mixing of 0.5g coated graphite powder and 0.1ml of paraffin oil in a mortar .The unmodified carbon paste electrode was constructed by graphite powder and paraffin oil to a ratio of 5/1(w/V).

Electrode bodies were made from Teflon(4mm i.d.), the tips of which had been cut off with a razor blade. Smooth surfaces were obtained by applying manual pressure to the copper piston(which connect the electrical contact to the paste) while holding the electrode surface against a smooth, solid support. Fresh electrode surfaces were obtained by squeezing out small amount of paste, scraping off excess and smoothing on a piece of stiff, white paper until the surface had a shiny appearance.

### Analytical procedure

In each determination cobalt(II) was accumulated at open circuit, by immersing the modified electrode in 25.00ml of a stirred 0.09mol/l $NH_3$ solution containing Co(II) for 3min accumulation time. The electrode was then removed, rinsed with water and placed in the electrochemical cell containing deaerated 0.1mol/l KOH solution. Differential pulse voltammetric experiments were performed after the oxidation step at a potential +0.40V for a time interval 30s, without stirring.

### Preparation of samples for cobalt determination

A standard sample used for method testing contained the following constituents: Ni(12330±80), Cu (9670±50), Co(410±10), Ag(4.3±0.3), Pt(0.41±0.06), Pd(0.37 ±0.03), where the number in brackets are the concentrations, in μg/g. This sample was prepared by weighting 0.2g into a calibrated flask and making to mark with 0.09mol/l $NH_3$.

### Natural water sample

24.0ml of natural water sample was taken in a beaker. Concentrated ammonia was added to adjust the pH on 10.6. After 2hr the sample was filtered and again the pH adjusted by adding required amount of 0.09 mol/l $NH_3$.

### Welding electrode sample

1.5g of electrode was covered with 20ml of 1:1 $HNO_3$ and allowed to stand 20min until all of sample is dissolved. Concentrated ammonia was added to adjust the pH on the 10.6. After 2hr the sample was filtered. 5.0ml of the filtered solution was transferred to a beaker and potassium hexacyanoferrate(II) was added to precipitate the $Cu^{2+}$ interfering ions. The sample was filtered and transferred to a 50ml volumetric flask and made to mark with 0.09 mol/l $NH_3$. The cobalt concentration was then determined by the optimized method.

## RESULTS AND DISCUSSION

Figure 1 shows the CVs at the CPE and modified CPE in 0.1mol/l KOH after preconcentration in the blank and 2.0×10$^{-5}$mol/l Co(II) accumulation solutions with 3min accumulation. The presence of a cathodic peak at $E_{pc}$=+0.158mV is clear when the MCPE was employed for the open circuit accumulation(Figure 1c) which is a very reasonable evidence that the presence of 5-[(4-chloro phenyl)azo-n-(4'-methyl phenyl)]salicyl aldimine in the MCPE enabled the preconcentration of Co(II) at the electrode surface.

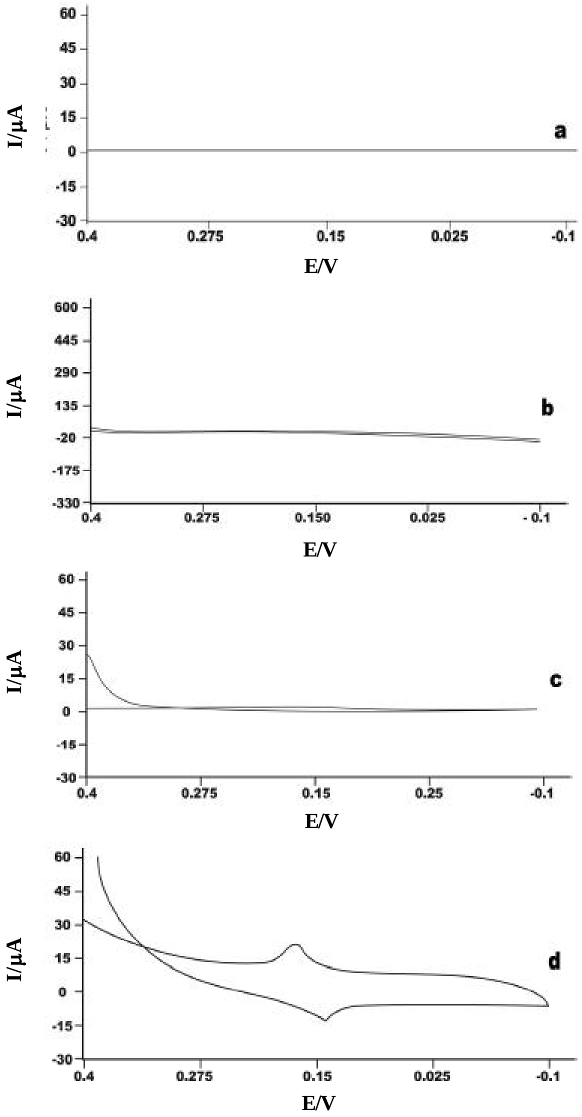

**Figure 1 : Cyclic voltammograms in 0.10mol/l KOH. Open circuit accumulation in 0.09 mol/l $NH_3$; $t_a$=180s; (a) CPE, no Co(II) in accumulation medium; (b) CPE, 2.00×10$^{-5}$mol/l Co(II) in accumulation medium; (b) MCPE, no Co(II) in accumulation medium; (c) MCPE, 2.00×10$^{-5}$mol/l Co(II) in accumulation medium; scan rate=50mV/s. Cathodic currents are negatively polarized.**

Although the anodic peak was potentially more sensitive than cathodic peak, in order to the better selectivity, an oxidation step was employed followed by cathodic voltammetry for subsequent works.

### Effect of carbon paste composition

The effect of composition ratios of 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine to carbon powder(w/w %) from 1.0% to 5.0% on the peak current was studied. Maximum current was observed when the 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine content in the paste was 3%. Higher concentrations(>3%) of ligand decreased the voltammetric signal which can be possibly attributed to the increase of electrode resistance. Hence a 3% 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)] salicylaldimine loading was employed in all subsequent experiments.

## Effect of accumulation and stripping media

Various media including acetate buffer(pH 3.39, 4.93 and 5.00) citrate buffer(pH 3.09, 4.98) and B-R buffer(pH 5.50), 0.1mol/l $NH_4Cl$, 0.1mol/l $NH_4CH_3COO$, 0.1mol/l KOH, 0.1mol/l sodium borate(pH 9.13), 0.1mol/l $NH_3$(pH 10.35), 0.1mol/l sodium carbonate(pH 11.01), borate buffer(pH 10.09), B-R buffer(pH 9.37, 10.36), $NaHCO_3$-NaOH(pH 10.06), phosphate-borax buffer(pH 9.00), ammonia-ammonium chloride buffer(pH 9.77, 10.51) and ammonia-ammonium carbonate buffer(pH 8.64, 9.72) were tested for Co(II) accumulation and no voltammetric peaks were observed in acidic or neutral media. The best sensitivity was obtained with $NH_3$ and this was chosen for further studies. The ammonia concentration of the accumulation medium was optimized and found to be 0.09mol/l (Figure 2).

Solutions of $HNO_3$, HCl, $H_2SO_4$, $HClO_4$, KCl, KOH, $NH_3$, $Na_2CO_3$, $NaNO_3$ and $NaClO_4$ investigated for the differential pulse voltammetry. The alkaline media were more suitable compared to the acidic and neutral media in terms of sensitivity. Amongst the basic media, 0.1mol/l KOH was found to be the most suitable supporting electrolyte. The concentration of KOH was varied from 0.03M to 1.0M with other parameters kept constant. The peak current was found to increase with the concentration of KOH up to 0.5M. The redox potential of the $Co^{II}/Co^{III}$ couple shifted to more positive values with decreasing $OH^-$ concentration. It was observed that as KOH decreased from 1.0M to 0.03M, the peak potential increased from 0.235 V to 0.045V. This could explain the decrease in peak height at low concentration end of figure 3. Since, the applied oxidation potential of +0.40V may not be sufficient for complete oxidation of the accumulated $Co^{II}$. The higher solubility of ligand at high concentration of KOH causes deterioration of the electrode surface and decreases the peak height. In all further studies, 0.1M KOH, was selected as the optimum concentration.

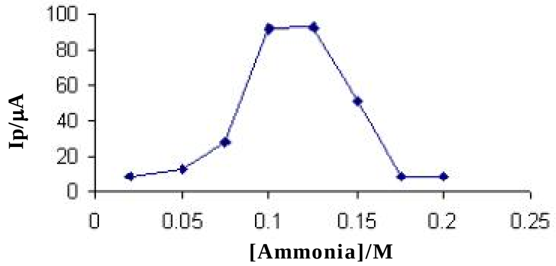

**Figure 2 : Plot of differential pulse voltammetric peak current *versus* concentration of $NH_3$ in accumulation medium: 3% ligand; accumulation, ammonia solution containing $1.00\times10^{-4}$mol/l Co(II); differential pulse voltammetry, 0.10mol/l KOH; $t_a$=180s, $t_o$=30 s, $E_0$=$E_i$= 0.30V; Scan rate=10mV/s.**

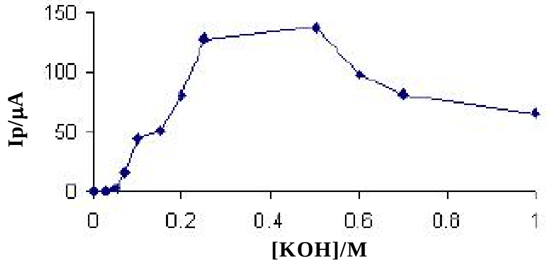

**Figure 3 : Plot of differential pulse voltammetric peak current versus concentration of KOH in voltammetric medium: 3%mol/mol ligand accumulation, 0.09M $NH_3$ containing $2.00\times10^{-5}$M$Co^{II}$; differential pulse Voltammetry**

## Effect of oxidation potential, oxidation time and accumulation time

The differential cathodic peak current increased with increasing oxidation potential and reached a maximum at about +0.40V. Potentials less than +0.40V not be sufficient for complete oxidation of $Co^{II}$ and potentials more than +0.4V can causes the irreversible oxidation of ligand. Hence +0.4V was the potential of choice. A 30s oxidation time at this potential was found to be suitable for complete oxidation of accumulated $Co^{II}$.

Accumulation of the complex was carried out for different periods from 30 s to 420 s. Initially, there was an increase in the peak current however equilibrium was

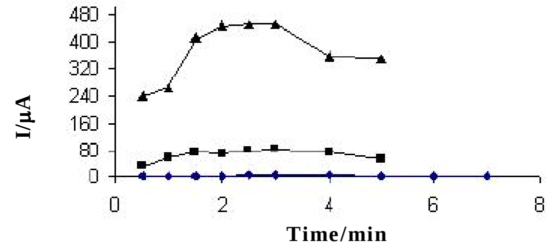

**Figure 4 : Plot of differential pulse voltammetric peak current *versus* accumulation time, $t_a$: accumulation, 0.09mol/l $NH_3$ containing(♦) $5.0\times10^{-6}$mol/l Co(II)(■) $5.0\times10^{-5}$mol/l Co(II)(▲) $5.0\times10^{-4}$mol/l Co(II); DPV 0.1mol/l KOH. All other parameters same as for figure 2**

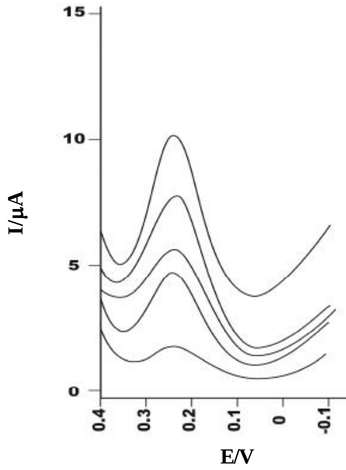

**Figure 5 : Differential pulse cathodic voltammograms at the MCPE; accumulation medium standard sample containing, 0.09mol/l $NH_3$ by standard addition method; DPV 0.1mol/l KOH**

**TABLE 1: Determination of Co(II) in standard(ORE SU-1a) natural water, electrode welding**

| Sample | Co (Proposed method) | Co (GF. AAS) | Spark-emission spectroscopy | Certified |
|---|---|---|---|---|
| Standard (ORE SU-1a) | 396μg/g | - | - | 410μg/g |
| Natural water | 19 ppb(ng/ml) | 18.04 ppb(ng/ml) | - | - |
| Electrode welding | 111μg/g | - | 108μg/g | - |

reached in about 180s(Figure 4). Therefore, the time for accumulation was kept 3.0min for the present method. Obviously, the rate of accumulation of $Co^{II}$ decreases with decreasing the concentration of cobalt(II) and more time is needed for complete accumulation of the analyte. Under the optimum conditions, two portions of good linearity were observed in the concentration ranges from $9.0\times10^{-7}$ to $9.0\times10^{-6}$mol/l and $1.0\times10^{-5}$ to $3.0\times10^{-4}$mol/l. The equations of regression lines are:

**Ip(μ A)=1.1989C(μ M) -1. 3554 r =0.9936(10 points)**
**Ip(μ A)=12.304C(μ M)+3.0946 r =0.9958(7 points)**

The detection limit calculated as 3-times the standard deviation of the blank, was found to be 5.25 ppb.

The reproducibility of the CME preconcentration approach was evaluated in two ways. First, the analytical responses obtained after 180 s accumulation from 5.0μM $Co^{II}$ in $NH_3$ solution were measured and compared for a series of different CME surfaces. Fresh electrode surfaces were generated simply by scraping off the old surface and smoothing the newly exposed layer of paste on a glassy paper. Alternatively, the same-initially conditioned-electrode surface, subjected after each accumulation/oxidation-reduction cycle to the EDTA or nitric acid cleaning solutions. The resulting reproducibility computed as the relative standard deviation of 10 consecutive measurements for each manner, was 5.55% and 7.05% respectively, and indicates the superiority of the scraping regeneration procedure. This may be attributed to the deleterious effect of acid or EDTA on the electrode surface and or dissolve of ligand-$Co^{II}$ complex into the aquase solution.

## Interferences

The effect of various ions on the peak current was determined at $2.0\times10^{-4}$M concentration. It was observed that Ca(II), Ag(I), Cd(II), Mn(II), Sn(II), Mg(II), Al(III), Bi(III), Ba(II), Fe(III), Sb(III), As(III), Cr(III), V(II), Si(IV), Zn(II), Be(II), Ni(II), W(IV), $Na^+$ and Pb(II), did not interfere, even when present in 20-times excess of Co(II). However, the presence of $2.0\times10^{-4}$ M Cu(II) and Ce(III) caused depression of the Co(II) peak. Interference from Cu(II) ions could be eliminated by adding ferrocyanide and precipitation of Cu(II) ion in acidic pH, filtration and then adjusting the sample pH at desired level by $NH_3$.

## Practical applications

The above-developed method was applied to the determination of Co(II) in a standard sample, natural water and welding electrode. The concentration of Co(II) in the samples was determined by the standard addition method(Figure 5). Three determinations ware made on each addition, the results are summarized in TABLE 1. The experimental values correspond with the values obtained from the method of GFAAS and spark emission spectroscopy.

## CONCLUSION

Our investigations show that the ppb levels of cobalt can be determined in real samples by a new chemically modified CPE using 5-[(4-chloro phenyl) azo-N-(4'-methyl phenyl)]salicyl aldimine as modifier by differential pulse cathodic voltammetry. Compared to other modified electrode for determination of Co(II), our electrode has a comparable detection limit and is not interfered so strongly by other metal ions.

## REFERENCES

[1] A.Carlocena, M.Gallego, M.Valcarcel; J.Anal.At. Spectrom., **12**, 479 **(1997)**.
[2] S.Codore, R.D.Goi, N.Baccan; J.Braz.Chem.Soc., **16**, 957 **(2005)**.
[3] A.S.Ribeiro, M.A.Vieira, A.F.Silva, D.L.G.Borges, B.Welz, U.Heitmann, A.J.Curtius; Spectrochim. Acta, **60**, 693 **(2005)**.
[4] M.Grabarczyk, K.Tyszyna, M.Korolezuk, Electroanalysis, **18**, 70 **(2006)**.
[5] J.Du, J.Lu, X.Zhang; Microchim.Acta, **153**, 21 **(2006)**.
[6] J.Opydo; Microchim.Acta, **137**, 157 **(2001)**.
[7] Y.A.Zolotov, G.I.Malofeeva, O.M.Petrokhin, A.R. Timerbaev; Pure & Appl.Chem., **59**, 497 **(1978)**.
[8] L.Husakova, A.Bobrovski, J.Sramkova, A.Krolicka, K.Vytras; Talanta, **66**, 999 (**2005**).
[9] R.D.DeMars; Anal.Chem., **33**, 342 **(1961)**.
[10] M.Nimmo, G.Fones; Analytica Chim.Acta, **291**, 321 **(1994)**.
[11] P.Ostapczuk, P.Valenta, H.W.Nurnberg; J. Electroanal.Chem., **214**, 51 **(1986)**.
[12] M.R.Nateghi, M.H.Mosslemin, H.Hadjimohammadi; Reac.& Func.Polymers, **64**, 103 **(2005)**.
[13] J.A.Lori, A.Morrin, A.J.Killard, M.R.Smyth; Electroanalysis, **18**, 77 **(2006)**.
[14] N.S.Lawrence, R.P.Deo, J.Wang; Anal.Chem., **76**, 3735 **(2004)**.
[15] Z.Bae, Y.Park, S.Lee, S.Jeon, H.Chang; Bull. Korean.Chem.Soc., **17**, 995 **(1996)**.
[16] M.R.Khan, S.B.Khoo; Analyst, **123**, 1351 **(1998)**.
[17] X.Lu, Z.Wang, Z.Geng, J.Kang, J.Gao; Talanta, **52**, 411 **(2000)**.
[18] M.Jalali Heravi, A.A.Khandar, I.Sheikshoaie; Spectrochim Acta, Part A, **55**, 2537 **(1999)**.