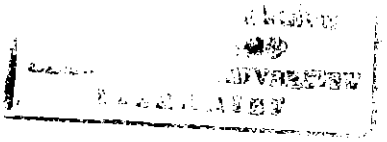
VOLTAMMETRIC BEHAVIOUR OF COBALT(II) AT *N*-p-CHLOROPHENYLCINNAMOHYDROXAMIC ACID MODIFIED CARBON PASTE ELECTRODE



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TO MY MOTHER, SISTERS AND BROTHERS

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Voltammetric Behaviour of Cobalt(II) at *N*-p-Chlorophenylcinnamohydroxamic Acid Modified Carbon Paste Electrode

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Abstract

A new preconcentration and voltammetric method was developed for the determination of Co(II) with *N*-p-chlorophenylcinnamohydroxamic acid (CPCHA) modified carbon paste electrode. The measurements were carried out using cyclic voltammetry and differential pulse anodic stripping voltammetry with closed circuit deposition of cobalt(II) at the electrode surface. The effects of several experimental parameters such as modifier composition in the carbon paste electrode, pH and concentration of supporting electrolyte, deposition potential, deposition time, and other instrumental parameters were studied for analytical application. A linear response was obtained in the concentration range 1×10^{-6} - 4×10^{-5} M Co(II) with a detection limit of 3.3×10^{-7} M for a 5 min deposition time. A relative standard deviation of 3.1% was obtained for eight successive determinations of 1×10^{-5} M Co(II). Many coexisting metal ions had little or no effect on the determination of cobalt(II). The method was applied for the determination of cobalt in vitamin B_{12}. The new electrode offered many attractive properties such as high stability, self cleaning ability, the use of non-dearated solutions and can be used repeatedly without regeneration.

1. Introduction

1.1. Occurrence and Uses of Cobalt

Cobalt constitutes about 0.001 % of the earth's crust [1]. It occurs in meteorites, natural surface waters, sea waters, soils, plants and animals. The principal ores capable of being commercially exploited are the arsenides, sulfides and oxides. These are smaltite ($CoAs_2$), skutterudite ($Co,Ni)As_3$, carrolite ($CuS.Co_2S$), linnaeit (Co_3S_4), cattierite (CoS_2), erythrite ($3CoO.As_2O_5.8H_2O$), and cobaltite (CoAsS). These ores are nearly always associated with ores of other metals, especially with those of nickel. The two leading uses of cobalt are in permanent magnet alloys and in high-strength, high-temperature alloys [2].

Cobalt compounds are used in ceramic industry for decolorizing clay, in glass industry for colouring of glass and in petroleum industry as catalysts for certain processes. Cobalt compounds have biological importance [2]. Cobalt is a vital trace element in animal nutrition [1]. Ruminants grazing upon cobalt-deficient pastures exhibit retarded growth, loss of appetite and anaemia; rapid recovery from these symptoms occurs upon feeding the animals with a cobalt-supplemented diet. Consequently, cobalt sulphate or chloride are mixed with fertilizers or added directly to the feed or to the salt-block licks. To human, small amounts of cobalt salts are invaluable in the treatment of pernicious anaemia. The discovery of the antipernicious anaemia factor in liver in 1926 led to the discovery of vitamin B_{12} in 1948, which was very soon shown to contain cobalt. Concentration of cobalt in whole blood of healthy individuals varies in the range 0.08 - 1.2 $\mu g\ L^{-1}$ [3].

1.2. General Chemistry of Cobalt

Cobalt is in the VIIIB group of the periodic table. Its electronic configuration is $[Ar]4s^2 3d^7$. The principal oxidation states of cobalt are +2 and +3. Cobalt is present as Co(II) in practically all of its simple compounds, where as simple Co(III) compounds are almost non-existent. Cobalt(III) is the principal oxidation state in complex ions, the few known complexes of Co(II) are fairly unstable. Cobalt(II) is able to form some complexes; however, the number is very small in comparison with that of cobalt(III). The complexes of Co(II) are normally tetra-covalent and some hexa-covalency does occur, whereas the cobalt(III) complexes are always

hexa-covalent. Complexes of Co(II) with oxygen donors are less stable than those with nitrogen. Some of the complexes that have been characterized are the carbonato complexes, $K_2Co(CO_3)_2.4H_2O$; oxalato complexes ($K_2Co(C_2O_4)_2.H_2O$) and the non electrolytic β-diketone complexes.

Cobalt(III) has a very strong tendency to form complex compounds [4]. Normally the most stable complexes are those in which cobalt is bonded to nitrogen. These are followed by the complexes in which cobalt is bonded to carbon (in cyanides), oxygen, sulphur, and the halogens in order of decreasing stability. The relative stability, however, will depend also on the whole molecules of ligands bonded to the cobalt. Some of the complexes of Co(III) that have been characterized are cyano-, isothiocyanato-, nitrito-, nitro-, nitrato-, β-diketone-, carbonato-, oxalato-, dithioxalato-, malonato-, sulfato-, sulfito-, halo-, and bridge complexes.

1.3. Methods of Analysis

Cobalt may be detected and identified by spot tests [2, 5]. When thiocyanate is added to an acid solution of a cobalt(II) salt, a dark blue colour is formed in the presence of acetone. In neutral, ammonical, or acetic acid solution, cobalt reacts with α-nitroso-β-naphthol to form a red-brown precipitate. Cobalt(II) is oxidized, at the expense of the reagent, to cobalt(III) which forms the complex. A blue, chloroform-soluble substance is precipitated when triphenylsulfonium ion is added to a solution containing cobalt(II) and an excess of thiocyanate. The blue colour imparted to the chloroform layer upon extraction is the basis for a sensitive test for cobalt.

Cobalt may be determined gravimetrically [2] by a variety of methods. Cobalt is usually precipitated with α-nitroso-β-naphthol and the precipitate ignited to constant weight as Co_3O_4. Other gravimetric procedures involve precipitation and weighing as $Hg(Co(SCN)_4)$. A rapid method which can be completed in 30 min involves the precipitation of cobalt with pyridine in thiocyanate media and weighing as $(Co(C_5H_5N)_4)(SCN)_2$. Cobalt can also be determined gravimetrically by electrolysis (electrodeposition of the metal on an electrode). Platinum gauze electrodes are usually used in the electrolysis of cobalt(II) solution [1].

Volumetrically cobalt(II) salts may be estimated by potentiometric titration with standard potassium hexacyanoferrate(II) in the presence of high concentrations of ammonium citrate and ammonia solution [2].

Colorimetric [2] methods for estimating cobalt use the blue colour developed by chloride

ions or thiocyanate ions [2]. When only small amounts of cobalt are present, nitroso-R-salts, sodium-1-nitroso-2-hydroxynaphthalene-3,6-disulphonate $C_{10}H_4OH.NO(SO_3Na)_2$, must be used to give a red cobalt complex which is stable in nitric acid.

A highly sensitive method for the determination of cobalt using atomic absorption spectrophotometry uses the cobalt-APDC (ammonium 1-pyrrolidinecarbodithioate) complex which can be extracted by ethylacetate [6] or by MIBK (methylisobutyl ketone) at 240.72 nm [2].

Spectrophotometric methods have been reported for the determination of cobalt. Cobalt(II) was found to react with N^1-hydroxy-N^1,N^2-diphenylbenzamidine to form a yellow-brown complex which can be quantitatively extracted into toluene from the aqueous phase at pH 7.5 - 9.5. The spectrum of the cobalt(II) complex exhibited absorption maximum in the visible region at 405 nm with molar absorptivity of 7000 M^{-1} cm^{-1} [7]. A sensitive spectrophotometric method for determination of cobalt(II) uses cyclohexylthioglycolate in the pH range 8.5 - 10.5 at absorption maxima wave length of 500 nm with molar absorptivity of 20030 M^{-1} cm^{-1} [8].

Cobalt(II) can also be determined polarographically [2]. The half wave potential for the hexaquacobalt(II) ion is about -1.4 V *vs* SCE in supporting electrolyte that form no complexes with the cobalt ion [9]. Polarographic methods usually use the reduction of Co(III) amines. This method allows the determination of cobalt in a one thousand fold excess of nickel. Cobalt may be determined polarographically through reduction of trioxalatocobalt(III) to dioxalatocobalt(II). Lead dioxide is added to a portion of dioxalatocobalt(II) to oxidize the cobalt [2]. Cobalt(II) in ammonical solution may be oxidized to an amine complex of cobalt(III) by potassium permanganate and destroying the excess potassium permanganate upon addition of excess hydroxylammonium sulphate or boiling with sodium perborate, $NaBO_3.H_2O$. The excess permanganate is destroyed upon addition of excess hydroxylammonium sulphate. This method has the advantage over the methods using sodium perborate or lead dioxide in that no refluxing or filtering is necessary to eliminate the excess oxidizing agent. The excess hydroxylamine does not reduce the cobalt(III) complex at a measurable rate at room temperature [2].

Adsorptive stripping voltammetric methods have been used for trace analysis of cobalt(II). Adsorptive stripping voltammetry at hanging mercury drop electrode using 2-quinolinethiol [10], 1,10-phenanthroline [11], and dimethylglyoxime [12], and at dropping mercury electrode with 5-bromo-4-(2-pyridylazo)-1,3-dihydroxynaphthalene (5-Br-PADNM) [13], α-benzyldioxime [14] and diphenylglyoxime [15] have been reported.

1.4. Chemically Modified Carbon Paste Electrodes

Carbon paste electrodes have been widely applied in electroanalysis mainly as substitute for noble metals because, depending on the nature of the supporting electrolyte, they can be used at both positive and negative potentials ranging from -1.4 to +1.3 V versus the saturated calomel electrode (SCE). Carbon paste possesses many advantages such as that it is inexpensive, easy to handle, and easy to prepare [16].

The modification of carbon paste electrodes began in 1964 with the fundamental studies of Kuwana and co-workers [17, 18], who dissolved elecroactive organic compounds like ferrocene, anthraquionone, or 5-aminobenzophenone in the liquid component of the paste. Work in France followed this route by modifying carbon pastes with solid additives (ferrocene, vanadic oxide, iron oxide) and using electrolytic binders instead of paraffin for voltammetric and chronoamperometric studies [19 - 21]. In 1981, Ravichandran and Baldwin suggested direct mixing of the modifier with the plain carbon paste [22]. The idea was to mix an insoluble particulate component into the carbon powder, with the pasting liquid.

Chemically modified carbon paste electrodes (CMCPEs) have attracted a great deal of attention for accumulation of target analytes prior to their electrochemical quantitations. One of the main reasons for modification is to improve the sensitivity and selectivity of the electrochemical measurement by preconcentrating the analyte on the electrode surface [16]. Several types of modifiers such as ion exchangers, adsorbents, and ligands are used.

Some ligands are electrochemically active. In such cases, it is necessary that the redox potential of the ligand and metal complex differ substantially. These ligands can be exploited for the indirect determination of elements which can not be easily reduced or oxidized electrochemically. Adsorptive stripping voltammetry mainly relay on a knoweledge of the chealating agent. The resulting complex should be surface active and/or electroactive. Thus selective complexation can be used to enhance the overall selectivity.

Preconcentration of analytes can be performed with or without the use of applied potential. Closed circuit accumulation may involve an electrochemical reaction (oxidation, reduction) whereas open circuit accumulation is based on physicochemical processes such as ion exchange, complexation, or the formation of insoluble salts. With the open-circuit approach it is possible to separate the species under consideration and eliminate interference from other components by proceeding to a medium exchange step after the accumulation phases. Thus, the

preconcentrated substances are extracted from the test solution and parameters such as acidity and ionic strength can be optimized separately for the analyte and the solution in which the electrode is polarized during the measurement. Of course, the modifier's affinity and specificity for the species to be extracted and the value of the formation constant determine the quality of the analysis. The kinetics of the reaction should be moderately fast both to shorten the time of the analysis and to avoid diffusion of the adduct from the surface into the bulk of the paste where it is not accessible for the measurements [16].

Chemically modified carbon paste electrodes are exceedingly easy to fabricate and can be generated rapidly and reproducibly in quantity. Some of the techniques used for the preparation of chemically modified carbon paste electrodes include direct mixing [23 - 25], solvent volatilization [26], dissolving the modifier in the pasting liquid [27], electrode coating [28] or *in situ* [29] modification.

As a general rule, the modifiers used with direct addition should meet the following criteria. The first requirement is that, they should be insoluble in the analyte solution, or they should be at least strongly adsorb to the paste components in order to avoid dissolution of the molecules from the electrode surface during the measurement. The phenomenon of "bleeding" causes modifier concentration gradients in the surroundings of the electrode surface as well as variable amounts in the interface. This results in barely reproducible currents. The other important requirement is that the modifier itself should not undergo electrochemical transformations within the potential range of the voltammetric response of the analyzed species except for catalytic applications, otherwise, the high background current would reduce or even impair the desired analytical properties of the electrode because the concentration of the modifier in the paste is rather high [19].

The number of chemically modified carbon paste electrodes (CMCPEs) reported for the voltammetric determinations of cobalt(II) are very few. Kasem, *et al.* [30] reported carbon paste electrode (CPE) modified with 1,10-phenanthroline for the electroanalysis of cobalt(II) in 1988. A 5% 1,10-phenanthroline modified CPE was used. A linear calibration was obtained with a range from 1×10^{-6} M to 3×10^{-4} ($r = 0.98$). It is a known fact that 1,10- phenanthroline is soluble in aqueous solution. Therefore, it is easy to conclude that the 1,10-phenanthroline modified CPE would not be stable due to leaching of the modifier in aqueous solution. This problem has been sought by Gao and co-workers [31, 32] who employed 1,10-phenanthroline and 2,2-bipyridyl to modify CPEs for determination of cobalt(II). This group of workers reported Nafion-1,10-

phenanthroline [31] and Nafion-2,2-bipyridyl [32] modified CPEs for the determination of cobalt(II) in 1991. Nafion was reported to act as a cation exchanger. The cobalt complex on the electrode surface is a cation that can be accumulated by Nafion to form an insoluble complex with a $(-SO_3)$- site on the Nafion modified electrode surface.

Nafion-1,10-phenanthroline [31] modified CPE was used for the determination of cobalt(II) with in the linear range of 1×10^{-7} to 4×10^{-6} M cobalt(II) for 3 min open circuit preconcentration time.The detection limit was 8×10^{-8} M. The CMCPE was regenerated in stirred 1 M NaOH solution for several minutes.

The Nafion-2,2-bipyridyl [32] modified CPE was used for the determination of cobalt(II) with linear range of Co(II) concentration from 7×10^{-7} to 1×10^{-5} M for 5 min open circuit precon- centration time. The detection limit was 3×10^{-7} M (S/N = 3). Ten fold molar excess of Cd^{2+}, Pb^{2+}, Zn^{2+}, Pd^{2+}, Mn^{2+}, In^{3+}, Sn^{2+} and Ag^{+} were found not to interfere in the determination of Co(II). But equal molar concentrations of Cu^{2+}, Fe^{2+}, Ru^{3+} and Ni^{2+} were found to interfere in the determination of cobalt(II). The method was applied for the determination of cobalt(II) in certified standard reference materials (steel and peach leaf). Regeneration of the electrode was done in stirred 1 M HCl acid solution for several minutes.

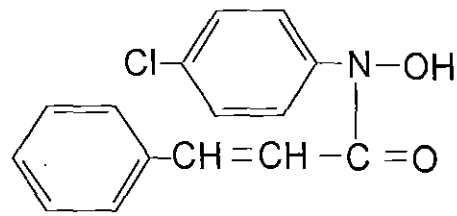
Even though the incorporation of Nafion with 2,2-bipyridyl and 1,10-phenanthroline, made the CMCPEs stable for the determination of cobalt(II), the method has some drawbacks. These are the difficulty in regenerating the electrode, the preparation of the electrodes itself, and the transfer of the electrode from one cell to another cell. The electrode had to be immersed in stirred cleaning solution for 5 to 10 min for regeneration. Because the modified electrode preparation required the use of two modifiers the electrode preparation was not as such simple.

Cobalt(II) has also been determined at trace level in sea water using CPE by *in situ* modification with α-nitroso-β-naphthol *via* adsorption under open circuit conditions [33]. Cobalt(II) oxidised by the reagent itself forms Co(III)-α-nitroso-β-naphthol complex on the electrode surface. The cobalt(II) concentration was determined by cathodic stripping voltammetry after reducing the cobalt(III) complex to cobalt(II) state. The used CPE was replaced by new CPE surface and the modifier was frequently added to solution containing the analyte. The linear range reported was from 5×10^{-6} to 4×10^{-8} M. The base line was deformed owing to the reduction of oxygen. The reduction of oxygen dissolved in the paste and the Co(III) to Co(II) reduction takes place in the same potential range. For the determination of cobalt(II) a frequent injection of the ligand was required. Therefore, it is necessary to look for another CMCPE for the

determination of cobalt(II) that could overcome the problems mentioned above.

1.5. Objectives of the Project

N-Arylhydroxamic acids have a number of desirable properties as potential analytical reagents for the determination of metal ions: (i) they contain an acid group with a replaceable hydrogen atom and a basic coordinating group in such a position so as to form a five membered ring on reaction with metal ions, (ii) they are available commercially at cheap coast or they are simple to synthesise in laboratories, and (iii) they are stable towards heat, light and air. As a result of these properties, these reagents have been used as analytical reagents for several metal ions. One of the analytically useful hydroxamic acid analogues is *N*-p-chlorophenylcinnamohydroxamic acid (**I**), which is abbreviated as CPCHA.



I

CPCHA has been used for extraction and spectrophotometric determination of V(V) [34], Ce(IV) [35] and Nb(V) [36]. However, the voltammetric behaviour of CPCHA and its metal complexes has not been reported so far. Furthermore, the complex formation reaction of CPCHA with Co(II) has not been studied. Hence, the design and behaviour of CPCHA modified CPE for the selective preconcentration and quantitation of Co(II) by differential pulse anodic stripping voltammetry have been studied. The selection of CPCHA modifier is based not only on some of the desirable properties of the reagent mentioned above but also on its low solubility in aqueous solution that avoids leaching of the electrode.

Therefore, the objectives of the present investigation are:

(i) to study the voltammetric behaviour of Co(II) at CPE modified with *N*-p-chlorophenyl-cinnamohydroxamic acid;

(ii) to establish the optimal experimental parameters for the determination of cobalt(II) at the electrode (i.e. to study the basic electroanalytical parameters of the modified electrode, such as effect of paste composition, pH of supporting electrolyte, depositon potential, deposition time, linear range, sensitivity, detection limit, etc.);

(iii) to carry out interference study on diverse ions (to study the selectivity of the electrode); and

(iv) to study the analytical application of modified CPE for the analysis of Co(II) in real sample.

2. Theoretical Background

2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is the most versatile electroanalytical technique for the study of electroactive species. The effectiveness of the technique resulted from its capability for rapidly observing redox behaviour over wide potential range [37-39]. CV is better suited for the identification of steps in the overall reaction of new species which appear in solution during electrolysis as a result of combined electrochemical and chemical steps [40].

CV consists of cycling the potential of an electrode which is immersed in an unstirred solution and measuring the resulting current. The controlling potential (excitation signal) is a linear potential scan with a triangular wave form. This triangular potential excitation signal sweeps the potential of the electrode between the initial and switching potential and the switching potential and final potential. Single or multiple cycles can be applied.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The important parameters that can be obtained from a cyclic voltammogram are the magnitudes of the anodic peak current (I_{pa}), cathodic peak current (I_{pc}), anodic peak potential (E_{pa}), and cathodic peak potential (E_{pc}).

A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The boundary condition at the electrode surface for the reversible cyclic voltammetric reduction of oxidized species is given by the Nernst equation:

$$E = E^0 - (RT/nF) \ln (a_o / a_R) \qquad (1)$$

where $E = E_{initial} - \nu t$, in which ν is the scan rate in volts/second and t is the elapsed time in seconds, a_o and a_R are activities of the of oxidized and reduced species, respectively, and n is the number of electrons transferred.

The formal reduction potential $E^{0'}$ for a reversible couple is centred between E_{pa} and E_{pc}:

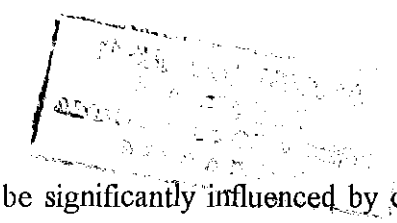
$$E^{0'} = \frac{Epa + Epc}{2} \qquad (2)$$

The expression obtained for the cathodic peak current under reversible condition is given by the Randles-Sevcik equation:

$$Ip = 0.4463\, nFAC^{\infty} (nF/RT)^{1/2} D^{1/2} \upsilon^{1/2} \qquad (3)$$

where Ip = peak current, A = electrode area, D = diffusion coefficient, C^{∞} = concentration of species in the bulk solution. Accordingly Ip, increases with $\upsilon^{1/2}$ and is directly proportional to concentration. The relationship of Ip to concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of I_{pa} and I_{pc} should be close for a simple reversible electrotransfer reaction. That is,

$$\frac{Ipa}{Ipc} \approx 1 \qquad (4)$$



However, the ratio of the peak current can be significantly influenced by chemical reaction coupled to electrode process. Furthermore, the potential of the two peaks are separated by a small increment for a reversible process as shown by the following relation:

$$\Delta E = Epa - Epc \approx \frac{0.059}{n} \qquad (5)$$

The number of electrons transferred in the electrode reaction for reversible couple can be determined from the separation between the peak potentials. Slow electron transfer at the electrode surface, "irreversibility" causes this peak separation to increase. Electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. In this case equations 1-5 are not applicable. Electrochemical irreversibility is characterized by a separation of peak potentials greater than indicated by equation 5.

2.2. Differential Pulse Voltammetry

Differential pulse voltammetry is the most widely used voltammetric technique.[41-46]. A potential pulse of a small constant amplitude is superimposed on a conventional rising linear dc voltage ramp. The current is measured in two intervals, the first is immediately prior to the application of the potential pulse and the second is during appliction but towards the end of the potential pulse. The final current signal displayed is the difference of these two current values.

The two current values represent the current at two potential values separated by about the pulse amplitude. The difference in current will be greatest on the steep rising part of the voltammetric wave around the half wave potential, where a small change in potential produces a large change in current. Although depletion occurs throughout the rising dc ramp, the jump of 10-100 mV occurring between the two current measurement pulses have very little effect on the capacitive current and other non-faradic sources of noise. On the other hand, the small potential jump will produce a large change in the faradaic current particularly at the peak potential. Thus the differential pulse mode allows the maximum differentiation of the faradaic or analytical signal from the back ground signal.

It is the change in current, on either side of the potential pulse, which differential pulse polarography records. Thus this technique in fact produces not a wave but a peak with the highest current signal at roughly the half wave potential of the classical dc voltammetry. Since the out put signal increases with the steepness or slope of the conventional current potential curve, this final curve approximates to a derivative or differential of the classical voltammetric current potential curve.

The peak potential Ep, is indicative of which species is involved. If the reduction (or oxidation) mechanisms is diffusion-controlled the concentration of the species controls the faradaic current. Since differential pulse polarography effectively displays the derivative of this current, theoretically it is the area under the peak which is proportional to the concentration. However, provided the shape of the peak does not change, the height of the peak is also proportional to the concentration.

2.3. Differential Pulse Stripping Voltammetry

The stripping method is the most commenly used electroanalytical technique for the

determination of trace elements [42]. In stripping analysis bulk electrolysis is used to preconcentrate a material in a small volume or on the surface of an electrode before a voltammetric analysis is made. It is the preconcentration step which allows the high sensitivity of stripping voltammetry. After the electrode deposition step the material is redissolved (stripped) from the electrode surface using differential pulse voltammety.

The much greater sensitivity of the differential pulse stripping step over the simpler linear sweep stripping step allows the use of much shorter pre-electrolysis or deposition times. The greater sensitivity of the differential pulse technique can some times even allow the use of a pre-electrolysis deposition step in unstirred solution, thus avoiding the problems associated with the non- reproducibility of the stirring [41].

2.4. Choice of Parameters in Differential Pulse Stripping Voltammetry

i. Choice of electrode type

The type of electrode to be employed is influenced mainly by the type of reaction which will be used for preconcentration. Some reactions (e.g. amalgam formation, formation of insoluble compound with the electrode material, adsorption of metal ions, etc.) can proceed only at a certain kind of electrode, and all other electrode parameters must be chosen with this in mind. However, some types of preconcentration reaction permit a free choice of the electrode; in these cases the type of species to be determined must be considered [45].

Metals which form too dilute amalgams or do not form amalgams at all, and those which react irreversibly or too slowly with mercury (Fe, Co, Ni, Mn, Cr, etc.) can be preconcentrated on solid electrodes either as metallic films or as suitable insoluble compounds with some component of the solution.

ii. Choice of the base electrolyte

Several factors must be considered when choosing the composition of the base electrolyte [45]. The solution must contain a sufficient concentration of conducting species in order that a large ohmic drop is prevented, migration currents are suppressed, and constancy of activity and diffusion coefficients is maintained. From this point of view, solutions of mineral acids, hydroxides, salts, etc. are most suitable. The components of the base electrolyte must be available

in sufficiently pure form, or the impurities must at least be removable. The base electrolyte composition must be chosen so that as high sensitivity and selectivity of the determination as possible are achieved. Non-complexing base electrolytes rarely allow sufficiently selective determinations. The selectivity of the method can often be substantially improved by using a suitable complexing agent, thus shifting along the potential axis the waves of the depolarizers present, depending on the stability of the complexes formed, their composition, and the concentration of complexing agent.

iii. Stirring the electrolyte solution

Stirring the solution during the deposition step increases the rate at which the analyte reaches the electrode to be deposited. Control of the stirring is vital. In unstirred solution the analyte reach the electrode for deposition by diffusion. This is much slower than transport in a stirred solution but it is also very reproducible [41].

iv. Deposition potential

Usually a potential is chosen a few hundred millivolts larger than the half wave potential of the analyte. The potential chosen allows a degree of selectivity. In the analysis of a solution containing a number of metal ions, each metal ion will have its own individual deposition potential. Thus only one metal or a group of metals can be deposited, avoiding the deposition of other metals which might interfere with the stripping step. When the deposition potential is higher, it is likely that more types of metal ions will be deposited which increases the interferences [45].

v. Deposition time

Long deposition times are not favourable due to various complications resulting in a loss of proportionality between the final signal and the concentration of the analyte. One problem can be reactions of the deposit or changes in its nature over a relatively prolonged time [44].

vi. Scan rate (mV/s)

With increasing scan rate the peak height increases and broadness. Fast scan rate results in poor resolution. The slowest scan rate gives the best results but a reasonable compromise with analysis time may be necessary.

vii. Pulse amplitude (ΔE) in mV

The peak current Ip for a thermodynamically reversible electrode process controlled by diffusion has been derived by Pary and Osteryoung [47]:

$$Ip = \frac{(n^2F^2AC)(D/\pi t)^{1/2}\Delta E}{4RT} \qquad (6)$$

where ΔE is the amplitude of the potential pulse; t is the time.

The Parry-Osteryoung equation shows that the height of the peak is proportional to the concentration as it is necessary for analytical use. It also shows that the peak height is directly proportional to the potential pulse amplitude. However, increase in the pulse amplitude results in broadening of the peaks and subsequent loss of resolution. For example, two close lying peaks will not be resolved unless the pulse amplitude is significantly smaller than the separation in the two peak potentials. Thus the choice of potential pulse amplitude must be a compromise between a high value for increased sensitivity and a lower amplitude for increased resolution. This is particularly true for electrochemically irreversible process which produce broader, lower, and less well formed peaks than do reversible processes [41].

viii. Choice for calibration and measurement between use of peak height or area under the peak

The measurement of peak height is much more convenient. The relation between peak height and area is only constant as long as the shape of the peak does not alter. But irreversible process produce lower broader peaks than reversible process. On the other hand, when two peaks partially overlap it is very difficult to separate the area under one from that under the other. The

ix. The stripping step

Anodic stripping voltammetry (ASV) is the most widely used form of stripping analysis [48]. For metal ions a cathodic deposition potential is set for the deposition time reducing the ions to metal. Then the anodic voltage is scanned for the reoxidation of the metal A typical scan rate would be 50-200 mV/s. Cathodic stripping voltammetry (CSV) is the ' mirror image' of anodic stripping voltammetry. The electrolysis step is anodic (oxidation) and the stripping step is a voltage scan to cathodic potentials (negative). Cathodic stripping voltammetry is often used to measure a wide range of organic and inorganic compounds capable of forming insoluble salts with the electrode material.

3. Experimental

3.1. Reagents and Chemicals

Spectral carbon powder (RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany), paraffin oil (Uvasol, Merck), anhydrous sodium acetate (BDH, AnalaR), acetic acid (Merck), sodium hydroxide (Bio-Lab), and cobalt(II) nitrate hexahydrate (Aldrich), were used as received. Sodium acetate solutions of various concentrations were prepared in water. The pH of the solutions were adjusted to the desired values by adding acetic acid or 1 M sodium hydroxide. Stock solution of 1.0×10^{-3} M cobalt(II) was prepared in water. Distilled water was used throughout.

CPCHA was prepared by the condensation of *N*-p-chlorophenylhydroxylamine with cinnamoyl chloride at low temperature in diethylether medium made alkaline with an aqueous suspension of sodium bicarbonate [49].

3.2. Apparatus

Cyclic voltammetry and differential pulse anodic stripping voltammetry were performed with BAS CV-50W Voltammetric Analyzer. The voltammograms were recorded on an IBM Personal Computer 130 100DX4. A one compartment PTFE electrochemical cell (30 mL) with a three electrodes (platinum disk counter electrode, Ag/AgCl reference electrode (BAS MF-2020), and the CPCHA modified carbon paste electrode as working electrode) was used for the measurements. An Oyster pH meter (EXTECH) was used for the measurement of pH. A magnetic stirrer (STUART Scientific) with a Teflon coated stirring bar was used for stirring the solutions. A stop clock (Harris Digitimer) was employed for time measurement. Figure 1 shows the experimental set up.

3.3. Electrode Preparation

Modified carbon paste was prepared by direct mixing of 0.90 g carbon powder, 0.10 g CPCHA, and 0.36 mL paraffin oil in mortar and pestle. The paste was packed into electrode

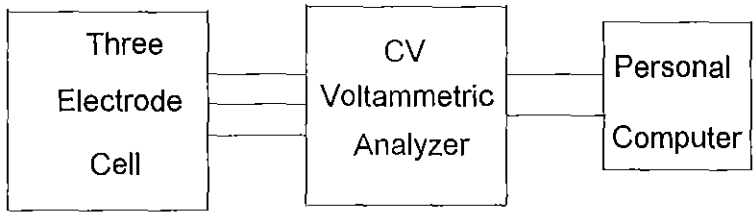


Figure 1. Experimental set up for the study of voltammetric behaviour of cobalt(II) at CPCHA modified carbon paste electrode

assemblies made from 1-mL plastic syringe (ONCE) of 3 mm outer diameter and smoothed off. Electrical contact was made with a copper wire through the syringe (Fig. 2). The unmodified carbon paste was prepared in a similar way, without adding CPCHA. Whenever regeneration of the electrode was required, a thin layer of the surface was removed with a spatula and replaced by a fresh paste.The fresh electrode was conditioned by dipping the electrode in 24 μM Co(II) solution and recording the differential pulse anodic striping voltammograms three times.The pretreated electrode gave reproducible results. The electrode was self-regenerated and was used for next run without cleaning after rinsing with water.

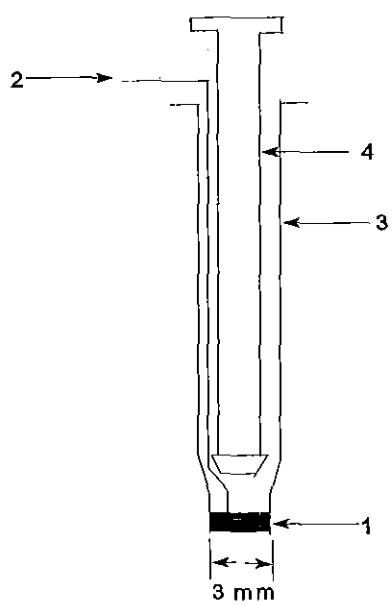


Figure 2. CPCHA modified carbon paste electrode: (1) paste, (2) copper wire, (3) syringe body and (4) piston

3.4. Procedures

Cyclic voltammograms (CVs) were run after purging the solutions for at least five min with argon (99.999% Merck-Schuchardt) *via* a Teflon tube. During the measurements argon was passed over the solution. The CVs were run starting from -1.4 to 0 V and back (with 100 mV/s scan rate).

For differential pulse anodic stripping voltammetry, 25 mL of the supporting electrolyte solution (0.2 M sodium acetate solution, pH 6) was transferred into the PTFE cell. A known amount (25 - 1000 µL of 1 mM) of Co(II) solution was spiked to it and the solution was stirred for 1 min. The modified carbon paste electrode was then immersed into the cell and a potential of -1.2 V was applied for 5 min (while stirrer was off). The differential pulse anodic stripping voltammogram was recorded (with 50 mV/s scan rate, 100 mV pulse amplitude, and 0.2 s pulse period). The scan was terminated at -0.1 V. All measurements were carried out at room temperature (22 ± 2 ^{0}C) using non dearated and unstirred solutions.

The effect of foreign ions were studied by adding known quantities of the desired ion to solution containing 16 µM of cobalt(II) and recording the differential pulse anodic stripping voltammogram according to the procedure described above.

3.5. Preparation of Sample Solution

The sample solution was prepared by wet acid digestion. A 1 mL vitamin B_{12} solution containing 1000 µg vitamin B_{12} (Laboratories STELLA, Belgium) was digested with a mixture of 4 mL nitric acid (65%, BDH) and 4 mL hydrogen peroxide (30%, Alvetra GmbH) and boiled to dryness. The residue was dissolved in 5 mL of water, diluted to 10 mL with water and kept in a plastic bottle. A suitable aliquot of the sample solution was used for the analysis.

4. Results and Discussion

4.1. Voltammetric Behavior of Cobalt(II) at CPCHA-modified Carbon Paste Electrode

Cyclic voltammograms (CVs) were obtained at CPCHA modified and unmodified carbon paste electrodes in 0.2 M sodium acetate buffer of pH 6. Figure 3 shows the CVs of the unmodified and modified electrodes in the absence and presence of Co(II). The CVs of the unmodified (not shown) and the CPCHA modified (curve A) electrodes did not show any wave in the absence of cobalt(II) in the potential range used. When the potential range was extended up to 700 mV, the modified electrode showed characteristic anodic and cathodic waves for the ligand (*N*-p-chloro- phenylcinnamohydroxamic acid) which is similar to that of its analogue *N*-phenylcinnamohydro- xamic acid [50]. In the presence of Co(II), both electrodes give the characteristic anodic and cathodic waves. The unmodified electrode (curve B) shows the anodic and cathodic peaks at -326 mV and -1326 mV, respectively, while the modified electrode (curve C) exhibits the anodic and cathodic peaks at -368 mV and -1254 mV, respectively. The cathodic waves of both electrodes are due to the reduction of Co(II) to Co(0) while the corresponding anodic waves are due to the oxidation of Co(0) to Co(II). As can be seen from the curves, the anodic peak current of the modified electrode is more than twice that of the unmodified electrode. Thus there is a substantial enhancement in the cobalt oxidation peak current when CPCHA modified electrode is used. The proposed mechanism is shown below, where HL represents the modifier CPCHA.

Deposition step

$$\underset{\text{(solution)}}{Co^{2+}} + \underset{\text{(CPE surface)}}{2\,HL} \rightarrow \underset{\text{(CPE surface)}}{CoL_2} + \underset{\text{(solution)}}{2H^+}$$

$$\underset{\text{(CPE surface)}}{CoL_2} + \underset{\text{(solution)}}{2H^+ + 2\,e^-} \rightarrow \underset{\text{(CPE surface)}}{Co} + \underset{\text{(CPE surface)}}{2HL}$$

Stripping step

$$\underset{\text{(CPE surface)}}{Co} \rightarrow \underset{\text{(solution)}}{Co^{2+}} + 2e^-$$

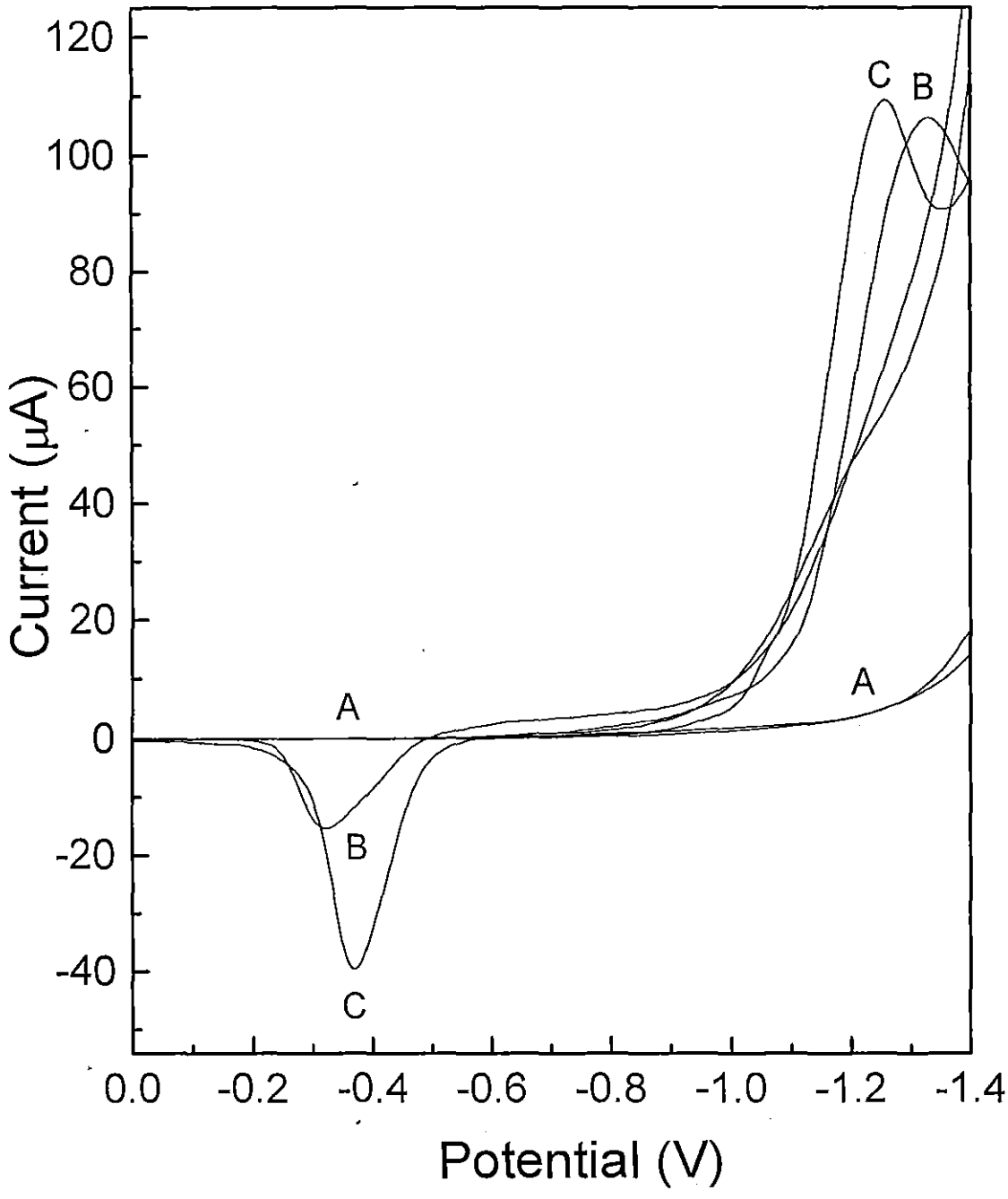


Figure 3. Cyclic voltammograms of (A) CPCHA modified carbon paste electrode in the absence of Co(II), (B) unmodified carbon paste electrode in the presence of 3.85 x 10^{-4} M, Co(II), and (C) CPCHA modified carbon paste electrode in the presence of 3.85 x 10^{-4} M, Co(II). Supporting electrolyte: 0.2 M sodium acetate of pH 6, scan rate: 100 mV/s, initial scan direction -1.4 to 0 V.

Hence, the anodic wave of Co(II) was systematically studied using differential pulse anodic stripping voltammetry for analytical applications. Open circiut accumulation was tried in different media at different pH but it was not succesful. Therefore, closed circuit deposition was employed for further work.

4.2. Effect of Carbon Paste Composition

Six different modified carbon paste electrodes (2.5%, 5%, 7.5%, 10%, 15%, 20% CPCHA) were examined for voltammetric signals (Table 1). The maximum peak current was obtained for 10% CPCHA in the carbon paste. Further increase in the concentration of CPCHA (≥ 10%) showed a decrease in the peak current. This may be due to the reduction of conductive area (carbon particles) at the electrode surface. Hence an electrode containing 10% CPCHA was used for all subsequent measurements.

Table 1. Effect of modifier composition in CPE (supprting electrolyte is 0.2 M sodium acetate; pH of supporting electrolyte is 6; deposition potential is -1.2 V; deposition time is 5 min; scan rate is 50 mV/s; pulse amplitude is 100 mV; and pulse period is 200 ms)

% CPCHA	Ip (- μA)	
	8 μM Co(II)	16 μM Co(II)
2.5	4.588	8.980
5	6.020	10.547
7.5	6.299	11.31
10	7.279	13.703
15	5.622	11.03
20	5.2385	11.637

4.3. Effect of pH of the Supporting Electrolyte

The effect of pH of the supporting electrolyte (0.2 M sodium acetate) was studied in the pH range 3 to 9 (Table 2). The optimum pH range was found to be 5.5 - 6.5. Accumulation of

cobalt(II) from more acidic or alkaline medium caused a drastic decrease in the differential pulse anodic stripping peak current. This happened due to the fact that at low pH the ligand may have been protonated whereas at higher pH the hydrolysis of cobalt(II) ion may interfere in the adsorption of cobalt at the electrode surface. Cobalt(II) is precipitated as hydroxide from oxygen-free aqueous solutions at a pH of 6.8. It was also found that there was no significant change in the peak current when the concentration of the supporting electrolyte was varied from 0.1 to 0.5 M. Hence, 0.2 M sodium acetate solution of pH 6 was selected for all subsequent studies.

Table 2. Effect of pH of supporting electrolyte (other conditions are as in Table 1)

pH	Ip (-μA)	
	2×10^{-5} M Co(II)	4×10^{-5} M Co(II)
3	2.1955	25.28
4	1.4403	10.257
5	14.275	31.507
5.5	12.053	21.84
6	9.7185	18.385
6.5	5.726	10.82
7	0.462	1.781
9	0.7619	0.726

4.4. Effect of Deposition Time

The effect of deposition time on the peak current was studied for two different Co(II) concentrations (Fig. 4). The peak current increased with increasing accumulation time, indicating an enhancement of cobalt(II) concentration at the surface of the electrode. At the lower concentration (curve 1), the peak current increased linearly with time up to 10 min without attaining a limiting value. For the higher concentration (curve 2), the peak current increased

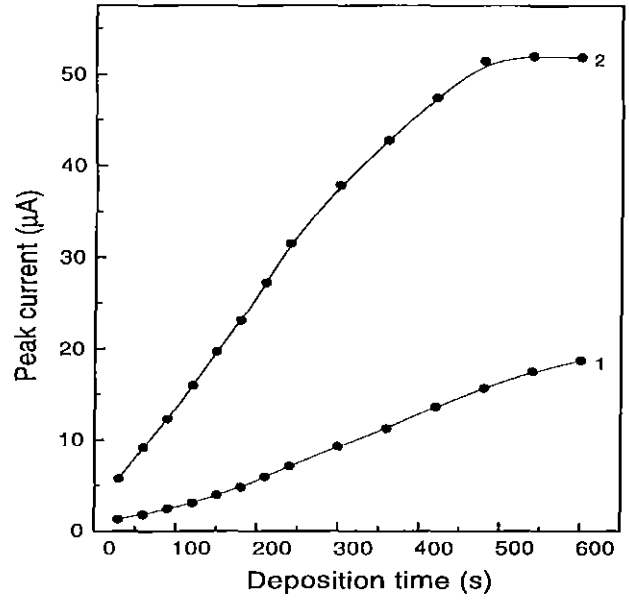


Figure 4. Effect of deposition time on the differential pulse anodic stripping voltammetric peak current. Co(II) concentrations (1) 8 μM and (2) 32 μM. Supporting electrolyte: 0.2 M sodium acetate of pH 6, deposition potential: -1.2 V, deposition time: 5 min, scan rate: 50 mV/s, pulse amplitude: 100 mV, and pulse period: 200 ms.

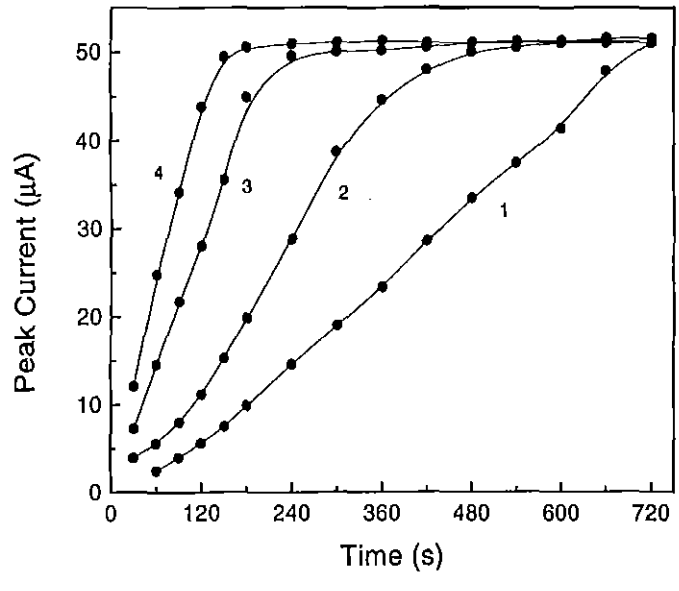


Figure 5. Effect of stirring on deposition time on differential pulse anodic stripping voltammetric peak current. Co(II) concentration (1) 2 μM, (2) 4 μM, (3) 8 μM, and (4) 16 μM. Other conditions are as in Figure 3.

rapidly at first, then gradually up to about 8 min, and reached a limiting value. This is presumably due to attainment of steady-state equilibrium of adsorption/complex formation. This observation is in accordance with other stripping methods based on adsorptive accumulation [23, 51-54]. Thus, to obtain a linear relationship between Co(II) concentration and peak current, a relatively short preconcentration time must be employed to avoid saturation effect. Therefore, 5 min preconcentration time was chosen as a compromise between peak current and the length of time required for analysis.

The effect of stirring on the deposition time was studied for four different concentrations (2, 4, 8, and 16 μM) of Co(II). In general, stirring decreased the deposition times of all the four concentrations of Co(II). However, the limiting peak currents for the different concentrations of Co(II) were obtained at different deposition times (Fig.5). For lower concentrations of Co(II) longer deposition time was required to attain the saturation limit while for higher concentrations the saturation limit was attained at shorter deposition time. Different concentrations of Co(II) were measured at 1 min, 2 min, and 5 min deposition times and calibration curves were constructed. However, very narrow linear response ranges were obtained for each deposition time that limit practical applications. Therefore, the deposition of Co(II) and the differential pulse anodic stripping voltammetric measurements were carried out using unstirred solutions.

4.5. Effect of Instrumental Parameters

The effect of deposition potential (reduction potential) on the anodic peak current of Co(II) was studied by varying the deposition potential in the range -0.8 to -1.4 V. The anodic peak of Co(II) began to appear only at a deposition potential of -1.1 V. Maximum peak current was obtained at a deposition potential of -1.2 V. Hence a reduction potential of -1.2 V was used for all subsequent measurements. The effects of scan rate, pulse amplitude, and pulse period on the differential pulse anodic stripping voltammetric behavior of Co(II) were studied. The scan rate was varied from 10 - 100 mV/s, the peak current increased and became broader with increasing scan rate. A similar pattern of the peak current was obtained with increasing pulse amplitude from 25 to 150 mV. But as both the half height peak width and back ground current must be considered a scan rate of 50 mV/s and a pulse amplitude of 100 mV were chosen for further work.

Table 5. Effect of pulse amplitude (other conditions are as in Table 1)

Pulse amplitude (mV)	Ip (-μ A) for 1.6 x 10^{-5}M Co(II)
25	2.9025
50	6.38
75	8.951
100	9.7195
125	10.985
150	10.685

Table 6. Effect of pulse period (other conditions are as in Table 1)

Pulse period (ms)	Ip(-μA) for 1.6 x 10^{-5}M Co(II)
100	9.38
200	13.17
300	13.63
400	13.62
500	very broad and undefined

Table 7. Optimum experimental conditions for the determination of Co(II) by DPASV

Parameter	Optimum value
Composition of the modifier in CPE	10%
pH of supporting electrolyte	6
Concentration of supporting electrolyte	0.2 M
Deposition potential	-1.2 V
Deposition time	5 min
Scan rate	50 mV/s
Pulse amplitude	100 mV
Pulse period	200 ms

4.7. Calibration Curve, Detection Limit, and Precision

The differential pulse anodic stripping voltammograms at different concentrations of Co(II) are shown in Figure 6. The peak current increased with increasing Co(II) concentration. The response was found to be linear in the concentration range 1 - 40 μM Co(II) (r = 0.996). The detection limit (concentration equal to three times the standard deviation of peak current for six determinations of 1 μM Co(II) with 5 min deposition time [55]) was found to be 0.33 μM Co(II). The relative standard deviations were found to be 8%, 3.1%, and 6.9% for eight successive determinations of 2, 10, and 30 μM Co(II), respectively.

4.8. Effect of Other Ions

Chemically modified electrodes have significant analytical potential to enhance sensitivity and selectivity of a determination because of the modifier-analyte interaction. The use of selective or specific modifier helps to overcome interferences from coexisting ions. But those metal ions which compete for complexation with the modifier and binding sites on the modified electrode surface would interfere significantly in the determination of the analyte. Anions which form stable complexes with the metal ion to be determined can also interfere.

The influence of other ions, present in the analyte solution, on the current response of cobalt(II) is shown in Table 8. As can be seen from Table 8, several ions such as Cl^-, F^-, NO_3^-, ClO_4^- SO_4^{2-}, $C_2O_4^{2-}$, NH_4^+, Li^+, K^+, Ca^{2+}, and La^{3+} (up to 100-fold molar excess); Mg^{2+}, Sr^{2+}, Al^{3+}, Bi^{3+}, and Ce^{4+} (up to 50-fold molar excess); Ba^{2+}, Ag^+, and Y^{3+} (up to 25-fold molar excess); Nb(V) and Mn^{2+} (up to 10-fold molar excess); W(VI), Ta(V), and Fe^{3+} (up to 5-fold molar excess); As^{3+} and Th^{4+} (up to 2-fold molar excess); V(V) and Sn^{2+} (equi-molar); have only negligible effect on the determination of Co(II). However, Hg^{2+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, UO_2^{2+}, Au^{3+}, Cd^{2+}, Pb^{2+}, Pd^{2+}, and Tl^+ interfere significantly by decreasing the Co(II) signal, presumably because they form complexes with CPCHA and prevent the adsorption/complex formation and accumulation of Co(II) at the electrode surface. In the presence of metal ions Pd^{2+}, Ni^{2+} and Hg^{2+} it was not possible to observe the Co(II) peak.

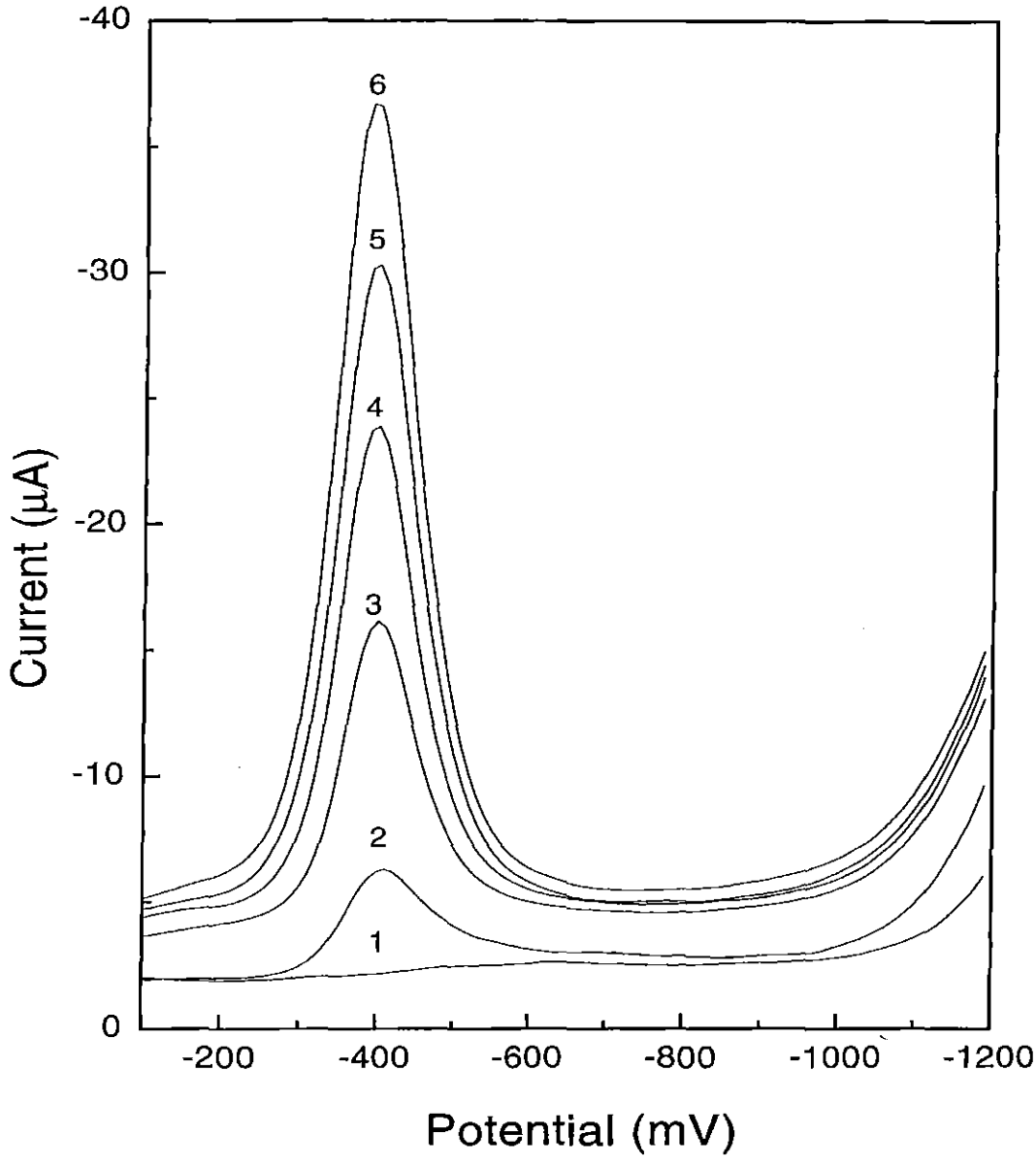


Figure 6. Differential pulse anodic stripping voltammograms of cobalt(II) at CPCHA modified carbon paste electrode at different concentrations (1) 0.0, (2) 4.0, (3) 12, (4) 20, (5) 28, and (6) 36 μM Co(II) in 0.2 M sodium acetate of pH 6, other conditions are as in Figure 3.

Table 8. Change in differential pulse anodic stripping voltammetric peak current of 1.6×10^{-5} M cobalt(II) in the presence of other ions (5 min deposition time)

Interfering ion	Concentration, M	Change of current(%)
F^-	1.6×10^{-3}	+6.2
Cl^-	1.6×10^{-3}	-6.1
NO_3^-	1.6×10^{-3}	-5.2
SO_4^{2-}	1.6×10^{-3}	-5.1
ClO_4^-	1.6×10^{-3}	+2.4
$C_2O_4^{2-}$	1.6×10^{-3}	-6.3
Li^+	1.6×10^{-3}	+5.7
K^+	1.6×10^{-3}	-5.2
NH_4^+	1.6×10^{-3}	-5.1
La^{3+}	1.6×10^{-3}	-2.8
Ca^{2+}	1.6×10^{-3}	+1.7
Sr^{2+}	8×10^{-4}	-0.2
Mg^{2+}	8×10^{-4}	-8.1
Al^{3+}	8×10^{-4}	+3.7
Bi^{3+}	8×10^{-4}	+2.8
Ce^{4+}	8×10^{-4}	-1.1
Ba^{2+}	4×10^{-4}	-3.8
Ag^+	4×10^{-4}	-5.6
Y^{3+}	4×10^{-4}	-2.2
Nb(V)	1.6×10^{-4}	+4.9
Mn^{2+}	1.6×10^{-4}	-8.1
Er^{3+}	8×10^{-5}	-7.3
W(VI)	8×10^{-5}	-5.2
Ta(V)	8×10^{-5}	+6.3
Fe^{3+}	8×10^{-5}	+5.1
As^{3+}	3.2×10^{-5}	-3.7
Th(IV)	3.2×10^{-5}	-6.2

Table 8. (Continued)

Interfering	Concentration, M	Change of current(%)
Sn^{2+}	1.6×10^{-5}	-1.9
V(V)	1.6×10^{-5}	-1.2
Mo(VI)	1.6×10^{-5}	-12.4
Pb^{2+}	1.6×10^{-5}	-20.2
Cr^{3+}	1.6×10^{-5}	-35.4
Tl^{+}	1.6×10^{-5}	-65.3
Au^{3+}	1.6×10^{-5}	-74.7
U(VI)	1.6×10^{-5}	-84
Cd^{2+}	1.6×10^{-5}	-59
Cu^{2+}	1.6×10^{-5}	-90
Pd^{2+}	1.6×10^{-5}	*
Ni^{2+}	1.6×10^{-5}	*
Hg^{2+}	1.6×10^{-5}	*

*No Co(II) peak was observed in the presence of interfering ion.

The influence of weakly interfering ions can easily be eliminated by applying the standard addition method for the evaluation of the concentration of Co(II). This has been examined by determining Co(II) in several synthetic matrices composed of weakly interfering ions corresponding to ores and alloys of cobalt. The results are given in Table 9. The results obtained clearly demonstrate that Co(II) can be determined reliably in the presence of weakly interfering ions.

4.9. Analytical Application

The proposed method was used for the determination of cobalt in vitamin B_{12} using the standard addition method (Fig. 7). The concentration of cobalt in vitamin B_{12} was found to be 4.44% which is in good agreement with the percentage calculated from the molecular weight of vitamin B_{12} (4.35%) [3].

Table 9. Determination of cobalt(II) in synthetic matrices

Matrix	Composition	Co(II) found*
A	1.38×10^{-5} M Co(II) + 3.34×10^{-4} M Li(I) + 1.67×10^{-4} M Mg(II) + 3.34×10^{-4} M Ca(II) + 1.67×10^{-4} M Sr(II) + 1.67×10^{-4} M, Ba(II)	$(1.39 \pm 0.08) \times 10^{-5}$ M
B	1.39×10^{-5} M, Co(II) +6.97×10^{-4} M, La(III) + 3.14×10^{-4} M, Ce(IV) + 6.97×10^{-5} M Y(III) + 6.97×10^{-5} Er(III)	$(1.39 \pm 0.06) \times 10^{-5}$ M
C	1.47×10^{-5} M Co(II) +1.45×10^{-4} M Bi(III) + 2.89×10^{-4} M Al(III) + 2.85×10^{-5} M Ta(V) + 7.24×10^{-5} M Nb(V)	$(1.51 \pm 0.09) \times 10^{-5}$ M
D	1.56×10^{-5} M, Co(II) + 3.01×10^{-5} M Mn(II) + 3.01×10^{-5} M W(V) + 7.53×10^{-5} M Ag(I) + 1.56×10^{-5} M V(V)	$(1.56 \pm 0.06) \times 10^{-5}$ M
E	1.6×10^{-5} M Co(II) + 3.2×10^{-5} M Fe(III) + 2×10^{-6} M V(V) representing *Supermendurs* an alloy which contain 49% Co, 49% Fe and 2% V	$(1.61 \pm 0.07) \times 10^{-5}$ M
F	1.6×10^{-5} M Co(II) + 1.6×10^{-5} M Fe(III) +1.6×10^{-5} M W(VI) + 1.0×10^{-6} M Cr(III) representing *Stellite* alloys contain around 50% Co, and 3% Cr, the rest being made up from tungsten, iron, carbon and silicon.	$(1.54 \pm 0.06) \times 10^{-5}$ M
G	1.6×10^{-5} M Co(II) + 3.2×10^{-5} M Fe(III) + 8×10^{-5} M Mn(II) The "oxidized" cobalt minerals, as the oxides are called, include *Asbolite*, a cobaltiferous mixture of manganese and iron oxides having a very variable cobalt content	$(1.61 \pm 0.03) \times 10^{-5}$ M

*Mean ± 95% confidence limits of triplicate analysis.

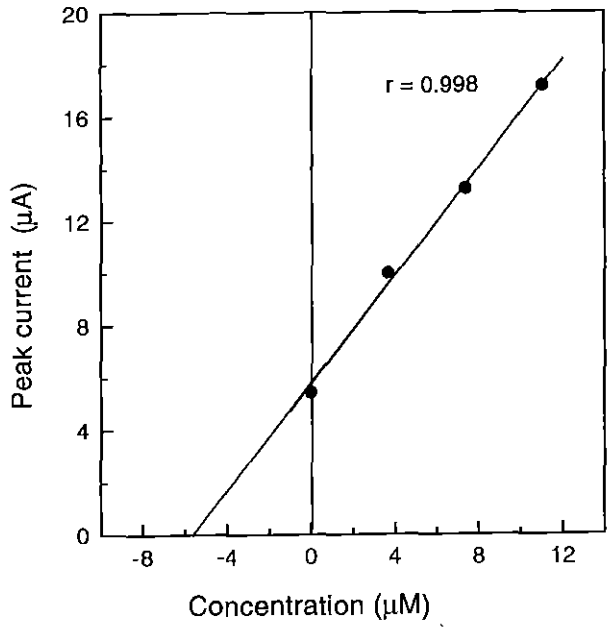


Figure 7. The standard addition curve for the determination of cobalt in vitamin B_{12}.

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Addis Ababa,ETHIOPIA

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Date June 19/1998

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Ref.No. CD/92/3-12a/98

To: **Prof Theodros Solomon**
Dean, SGS

From: **Wendimagegn Mammo**
Chairman, Department of Chemistry

Subject: **MSc Theses**

The following MSc Candidates in Chemistry have successfully defended their MSc theses between June 8 and 12, 1998.

1. Tesfaye Refera
2. Abi Tadesse
3. Derib Shewangizaw
4. Yohannes Ali
5. Kahsay G/Medhn
6. Kasim Ahmed

The research supervisors of all have testified that they have incorporated all comments made by the examining panel in their final versions of their theses.

Thank You

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