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

By

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To My Father, Mother, and Brother

for

Their Support, Encouragement, and Understanding

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

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Abstract

A sensitive voltammetric method has been developed for the determination of cadmium(II) utilizing a carbon paste electrode modified with *N*-p-chlorophenyl-cinnamohydroxamic acid. The analyte was accumulated at the modified electrode surface (via complexation) under open circuit and precisely controlled convective condition. It was then quantified electrochemically by differential pulse anodic stripping voltammetry in a different non-deaerated electrolyte solution following medium exchange. Detailed experiments were conducted to establish the optimal carbon paste composition, pH and concentration of accumulation and stripping solutions, preconcentration time, bulk cadmium(II) concentration, and instrumental parameters. Two good linearities were obtained between the voltammetric current and cadmium concentration employing different preconcentration times. One is acquired in the concentration range 2.00×10^{-7} - 3.20×10^{-6} M Cd(II) ($r=0.999$) and the other from 4.00×10^{-8} to 1.60×10^{-7} M Cd(II) ($r=0.999$) with 1 min and 2 min preconcentration time, respectively. The detection limit was found to be 9.80×10^{-9} M (1.1 ppb) Cd(II) with 2 min preconcentration time. For a series of six determinations of Cd(II) at 1×10^{-6} M and 8×10^{-8} M levels relative standard deviations of 2.6% and 5.5%, respectively, were achieved. Electrochemical cleaning was used to regenerate the surface rapidly and reproducibility; and this allows the use of a single modified electrode surface in multiple analytical determinations over several weeks. Many common metal ions had little or no effect on the determination of cadmium(II). The method was verified by the determination of trace cadmium(II) in municipal and mineral waters.

1. INTRODUCTION

1.1. Occurrence and Uses of Cadmium

Cadmium is a relatively rare element (about 0.2 g per ton in the earth's crust) [1]. It does not occur uncombined in nature and is nearly always found associated in small amounts with zinc. It is present in zinc sulfide ores, and in lesser concentrations in zinc carbonates and silicates, and in lead and copper sulfides. The rather uncommon true cadmium mineral, greenockite, is not a commercial source of the metal. Almost all of the cadmium produced is obtained as a by-product during various steps in the smelting and refining of zinc ores (which usually contain 0.2-0.4% cadmium); thus, its out put is directly linked to the out put of zinc [2-4].

A large amount of cadmium produced world wide is used in electroplating of steel, iron, copper, brass, and other metals to protect them from corrosion. Cadmium is often utilized in electrical parts because of its relatively low electrical conductivity and ease of soldering to it. Sizable amounts are used in low-melting-point alloys and relatively smaller uses are in brazing alloys, solders, and bearings. The low-melting point alloys are utilized for many purposes like in fusible elements in automatic sprinklers, forming and stretching dies, filler for thin-walled tubing that is being bent and, anchoring dies, punches, and parts being machined. A small portion is used to produce various pigments. CdS (cadmium yellow) and cadmium sulfoselenide (cadmium red) are permanent useful pigments. They provide the best yellow and red colours seen in many finishes including industrial enamels, and lacquers used for automobiles. Inorganic cadmium compounds are used as stabilizers in plastics and in the production of television picture tube phosphors. The metal is also used in the manufacture of cadmium-nickel alkaline rechargeable batteries which are used in buses and diesel

locomotives. Because of its great neutron-absorbing capacity cadmium is often used in control rods and shielding for nuclear reactors [3-5].

More recently, CdS is known to be an excellent heterojunction partner of p-type cadmium telluride (CdTe) or p-type copper indium diselenide ($CuInSe_2$). It is widely used as a window material in high-efficiency thin-film solar cells based on CdTe or $CuInSe_2$ owing to its transparency and photoconductivity among other properties [6]. Cadmium sulfide and cadmium sulfoselenide compounds exhibit strong photovoltaic response to visible light, and are becoming of interest in solar energy applications to convert low energy light into electricity [7]. Thus, in view of the changing worlds energy situation, uses of cadmium are anticipated in applications such as solar energy cells and energy storage systems.

1.2. Effect of Cadmium on Human Health and Its Sources of Pollution

The influence of metal toxicity on human affairs has a long and eventful history dating back at least 5000 years to the initial development of metal working. In more recent years, industrial effluents have been responsible for several episodes of chronic and acute poisonings of humans. Rapid industrial development has led to increased generation of waste materials that, if improperly dealt with, can threaten both public health and environment.

Cadmium is one of the most toxic heavy metals of prime environmental and health concern that has received widespread attention in recent years [4]. This is evidenced by its incorporation in the initial priority UK Red List [9] and other lists of "Priority Metals or Pollutants" established from the stand point of potential hazard to human health, like the U.S. Environmental Protection Agency (EPA) List of Priority Pollutants [10], and the

Black List of the European Economic Community [11]. These pollutants are not only highly toxic but also persistent and capable of bioaccumulation. Part of the concern was based on the manifestation of a disease called 'itai-itai' disease (translated literally as 'ouch-ouch' disease, from the cries of pain made by those suffering from it) in Japan in 1950s, for which the causative factor was high concentration of cadmium in locally grown rice. The symptoms of the disease include a yellow discolouration of the teeth, loss of the sense of smell, a reduction in red blood cell numbers, lumbar and leg pains, softening of the skeletal bones, and in severe cases skeletal deformation. Death is attributed to kidney failure [2,12,10].

Cadmium has never been demonstrated to be an integral part of natural product nor has shown any certain indication of being an essential trace element in biological processes [12-14]. It adversely affects several important enzymes; and can cause painful bone disease and kidney damage [15]. Cadmium concentrations were also correlated most closely and most frequently with the cancer death rate [16]. Although chronic poisoning traced back to cadmium in environment has been recorded [17,18], no effective chelates have yet been found for the treatment of chronic cadmium intoxication [12,17,18].

On chronic administration to man, cadmium accumulates in the liver and kidney. And, thus, the body burden of cadmium increases with age, as its half-life in the body is about 20-30 years. Normal dietary intakes are in the range of 0.21-0.42 mg per week which are close to the WHO recommended maximum (0.4-0.5 mg per week). The closeness between actual cadmium intakes and the suggested maxima is also one of the reasons for the considerable current interest over cadmium levels in soil, water and food. The average cadmium level in the general population is already between one-third and one-half of the toxic level. Smokers are especially at risk because of the cadmium content in tobacco [12,19,20].

Cadmium is considered by many to be the most dangerous heavy metal pollutant because it is widespread and poorly controlled. It reaches the general population through water and food supplies and to a lesser extent by air. Airborne emissions from zinc smelters are major sources of cadmium contamination in air, water, soil, and all crops including tobacco. Cadmium pollution can also originate from incineration of plastics and cadmium pigments, fossil fuels, electroplating, and metallurgical processes. Recently, use of phosphate fertilizer (which has an average concentration of about 7μg of cadmium per gram) and sewage sludge with a high concentration of cadmium as fertilizer has a high concern [2,3,13].

1.3. Methods of Analysis

Cadmium can be detected and identified by spot test, with either 4-nitronaphthalene-diazoamino-azo-benzene ('Cadion 2B') or bis(p-nitrophenyl) carbazide as colouring agents. The procedure in the former case involves adding a drop of the test solution onto a strip of filter paper to which an alcoholic solution of the reagent is applied. This is followed by making it acidic with acetic acid and then adding a drop of 10% KOH solution. A bright pink spot surrounded by a blue ring indicates the presence of cadmium. Bis(p-nitrophenyl) carbazide, on the other hand, forms a brown-coloured product with cadmium hydroxide, which turns greenish-blue with formaldehyde [22,23].

There are many insoluble salts of cadmium giving rise to the earliest known methods for determination of cadmium based on precipitation reactions. It can be determined gravimetrically by the sulphate method, which involves separation as CdS and quantitation by weighing as $CdSO_4$ following evaporation to dryness with excess sulfuric acid and ignition. Various other gravimetric methods are also applicable, such as precipitation as cadmium ammonium phosphate ($CdNH_4PO_4.H_2O$) and weighing,

either as such after drying in air or after ignition to pyrophosphate ($Cd_2P_2O_7$), or precipitation and weighing as the salt of 8-hydroxyquinoline, $Cd(C_9H_6ON)_2$, after cadmium has been isolated from nearly all other metallic elements [24,25].

Various titrimetric methods have been proposed, such as precipitation titration with ferrocyanide, bromometric titration after precipitation with anthranilic acid or with 8-hydroxyquinoline, complexometric titration with EDTA using Eriochrome Black T (EBT) as indicator [7,26], and iodometry of CdS with back titration of the iodide with thiosulphate [27]. Like most of the gravimetric methods, none of these are specific for cadmium and nearly all other metal ions interfere.

Cadmium selective electrode most useful as indicator electrode in the potentiometric titration of cadmium with such titrants like EDTA can be used for its quantitation [28,29].

Cadmium can also be determined colorimetrically. Dithizone provides the best means of separation and determination. This method involves extraction of cadmium-dithizone chelate from strongly basic tartarate medium containing cyanide ion to prevent extraction of other potentially interfering ions. Extraction methods for the separation of cadmium with thiocyanate and mercaptobenzothiazole were also reported. Though it is inferior to the dithizone method in sensitivity and specificity, moderately small amount of cadmium can be determined by formation of a colloidal suspension of CdS [30,31].

Since the commercial equipment became available in about 1960, the use of atomic absorption spectroscopy (AAS) in routine analysis has become widespread replacing many of traditional wet methods for estimation of metals in solution. Cadmium is one

of the most sensitive of all metals to be determined in various samples by this method. It is usually determined employing the sensitive absorption line at 228.8 nm with air/acetylene flame system [32-34].

More recently, separation and determinations of cadmium using high performance liquid chromatography (HPLC) via initial formation, off-line or on-line, of suitable chelate (mostly dithizone and EDTA) were done. However, these HPLC based methods are not among the most common or validated methods of cadmium determination [35].

By all odds, electroanalytical techniques are far superior to classical methods, both for separations and determinations of cadmium. When obtained by controlled potential electrolysis, the deposited cadmium from faintly alkaline cyanide solution can be weighed to provide an accurate electrogravimetric determination. If the amount of cadmium is too small for accurate weighing, the deposit can be dissolved from the cathode (either chemically or electrolytically), and the determination completed polarographically. The later constitutes electrochemical stripping analysis that is most useful for determination of low concentrations. Cadmium is very amendable to polarographic determination with the dropping mercury electrode [24,36].

Voltammetric techniques like stripping voltammetry are very suitable for decentralized analysis and quantitation of trace metals due to their speed, high analytical sensitivity, low detection limit, relatively compact and low-cost instrumentation with low maintenance costs, the possibility of employing inexpensive electrodes and, minimum (or none) sample pretreatment required prior to analysis. These attracting features have resulted in rapid development and wide spread application of the stripping voltammetry. Mercury-based electrodes, in their many forms, have been traditionally employed for achieving high sensitivity and reproducibility since the inception of polarography by

Heyrovisky. Accordingly, cadmium has been determined by anodic stripping at hanging mercury drop electrode (HMDE) in various samples [37,38]. A number of analytical determinations of cadmium based on adsorptive stripping voltammetry at HMDE have also been reported. Some of these have utilized ligands like 8-hydroxyquinoline [39], 2,5-dimercapto-1,3,4-thiadiazole [40] and 1-phenylpropane-1-pentylsulfonylhydrazone-2-oxime [41] as chelating agents. However, the toxicity of mercury and the growing interest for on-site environmental monitoring have prompted the search for new 'mercury free' electrodes.

In the past two decades chemically modified carbon paste electrodes have attracted a great deal of attention for trace metal analysis in view of eliminating mercury and its soluble salts from the analytical procedure and, their ability to enhance the sensitivity and selectivity of electrochemical techniques. Besides their non-toxicity and improving the performance of electrochemical techniques, these electrodes are endowed with so many other good qualities. In this direction few number of voltammetric determinations based on such CMCPEs were reported for cadmium [42,43].

1.4. Chemically Modified Carbon Paste Electrodes

Carbon paste electrode was invented by Adams at the end of the 1950s [44]. It is a mixture of an electrically conducting graphite powder and a pasting liquid that has been widely applied in electrochemistry mainly as a substitute for noble metals. Carbon paste electrode possesses many advantages. It has wider accessible potential window than useful metallic materials, which means more redox reactions can be observed at carbon paste electrode than at metallic electrodes. It is inexpensive and can be manipulated relatively easily (i.e. it is easy to prepare, pretreat, modify, and renew) [42,45,46].

The modification of carbon paste electrode began in 1964 with the fundamental studies of Kuwana and co-workers who dissolved electroactive organic compounds in the liquid component of the paste to investigate their electrochemical behaviours [47,48]. The expression 'Chemically Modified Electrode' was then introduced into the electrochemistry jargon a decade later by Murray *et al.* [49] in 1975 to designate an electrode with a chemically active species deliberately immobilized onto its surface. The aim of the modification is to introduce reactive group into the surface of the electrode in order to prompt an analytically exploitable effect on the analyte components in the bulk solution; mainly preconcentration and catalysis [50,51]. In 1981, Ravichandran and Baldwin [52] suggested direct mixing of the modifier into the plain carbon paste as a convenient way for modification which triggered the actual breakthrough for widespread application of chemically modified CPEs. Carbon paste is an electrode material that is particularly suitable for such modification due to the ease of handling and to its paste-like consistency which facilitates a direct mixing of modifiers [42].

CMCPEs are particularly attractive for analytical applications compared to other types of chemically modified electrodes [53]. The interest in using CMEs has increased, particularly to enhance sensitivity and selectivity of electrochemical techniques. They have been widely applied in voltammetric procedures involving an analyte preconcentration step prior to electrochemical measurement. In many cases the preconcentration is achieved by purely non-electrochemical (open-circuit) accumulation step based purely on physicochemical processes taking place between the analyte and the modifier; such as ion exchange, complexation, covalent attachment, or formation of insoluble salts. The collected analyte in this way is subsequently measured by its electrochemical response to a potential step or sweep after medium exchange to suitable electrolyte. This approach is an interesting analytical tool because it allows the construction of sensitive voltammetric sensors and development of novel analytical

procedures that are specific, or at least selective, for a particular analyte once a judicious choice of modifier and experimental conditions has been made [54,55].

1.4.1. Advantages of CMCPEs

Besides their non-toxicity, chemically modified electrodes carbon paste electrodes have many good characteristics including ease of fabrication, convenient renewability providing a fresh surface unaffected by the electrode story (with implied reproducibility of electrochemical response), low background current allowing the determination of low analyte concentrations, low cost, and wider useful electrochemical windows with applicability to anodic oxidations [42,43].

CMCPEs not only afford the possibility of low detection limits as a result of the preconcentration of the analyte but also provide an approach for improved selectivity as a result of the chemical constraints of the modifier-analyte binding reactions. There are broad range of materials and methodologies of electrode modification that can be employed for such purpose.

They can be used when sample dearation is not feasible and/or in conjunction with the medium exchange procedure as the accumulated species are rarely air sensitive [56]. The technique of medium exchange between accumulation and voltammetric measurements is particularly important in that it achieves two goals: first, components which are present in the sample solution and which may interfere with the voltammetric determination are separated off if they have no affinity for the modifier; second, accumulation and voltammetric measurement can take place under optimized conditions for each process that would lead to improved sensitivity and selectivity.

The experimental design of preconcentration/voltammetry at CMCPEs offers the potential for electrodes optimized for different analytes as the electrode can be tailor-made to exhibit desirable properties. It also provides effective means for extending the scope of stripping voltammetry toward analytes that can not be preconcentrated electrolytically or those requiring excessively negative deposition potentials. Thus, the range of applicability of CMCPE preconcentration is wider than those offered by the conventional stripping techniques.

1.4.2. Methods of modification

One of the merits of CMCPEs is their ability to be easily fabricated. A number of preparative methods are used to modify carbon paste electrodes, some of which are similar to those applied to other solid electrodes: direct mixing of particulate matter into the paste [42], solvent volatilization [42,57], dissolution of lipophilic substances into the pasting liquid [42,48], covalent binding of molecules [58,59], adsorption of modifier [42,59], and *in situ* modification [42]. The most common is the one involving direct mixing. In order to obtain reproducible and comparable results, the concentration of the modifier on the electrode surface must be similar in analogous experiments. For this reason thorough mixing of the two solid phases is essential to ensure that the same amount of modifier is always exposed to the analyte solution. As it is used in the method of solvent volatilization, admixing the modifier into the carbon powder with the aid of a solvent prior to adding the pasting liquid is particularly suitable if the modifier adsorbs to the carbon, which produces, after evaporation of the solvent, homogeneously covered graphite particles.

1.4.3. Nature of CPE modifier and pasting liquid

The great number and diversity of ion exchangers and organic reagents used in analytical chemistry are useful sources for the modification of CPE. Especially, complexing derivatives with high specificity for target analytes in different materials are of great interest. As a general rule, the modifier to be used with the direct mixing method should meet certain criteria. It should be insoluble in the analyte solution, or it should at least strongly adsorb to the paste components in order to avoid dissolution of the molecules from the electrode surface during measurement. Otherwise, its leaching causes modifier concentration gradients in the surroundings of the electrode surface as well as variable amounts in the interface itself. This, in turn, results in poor reproducibilty of the analytical signal. The other important requirement is that the modifier itself should not undergo electrochemical transformations around the redox potential of the analyzed species. If not so, the high background current would reduce or even impair the desired analytical properties of the electrode since the concentration of the modifier in the paste is rather high [56].

One selects immobilized modifier for a particular analysis on the basis of known and desired properties (such as functionalities which can strongly bind to the substance to be analyzed). The kinetics of the reaction between the analyte and the modifier should also be moderately fast both to shorten analysis time and avoid diffusion from the surface into the paste where it is not accessible for measurement.

The pasting liquid, on the other hand, should be electrochemically inactive and chemically inert, immiscible with the analyte solutions, minimally volatile, and free from electroactive impurities [42,59].

1.5. Objectives of the Present Study

The number of CMCPE reported for the voltammetric determination of cadmium in the past are very few when compared to those developed for other metals [42,43]. These are CPEs modified with a ion-exchange resin (Dowex 50W-X8) [60], Amberlite IRC 718 chelating resin [61], Zeolite [62], and tributyl phosphate [63]. However, Amberlite IRC 718 chelating resin modified CPE requires longer accumulation (10 min) and renewal time (4 min) [61]; Zeolite modified CPE necessitates longer accumulation time (4 min), has relatively higher detection limit (8.7×10^{-8} M), and demands deaeration of electrolyte solution for 5 min [62]; and the tributyl phosphate modified CPE requires longer accumulation time (6 min), longer renewal time (5 min) and the presence of another complexing agent (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) in the preconcentration solution [63]. Furthermore, no systematic interference studies have been made on some of these methods and have not been applied to the determination of cadmium in real samples [61,62]. Therefore, it is appropriate and valuable to develop a new CMCPE for reliable quantification of cadmium.

Very recently, *N*-p-chlorophenylcinnamohydroxamic acid (CPCHA) and its analog, *N*-phenylcinnamohydroxamic acid (PCHA), have been employed for the modification of carbon paste electrodes. These *N*-Arylhydroxamic acids have many attractive properties to be utilized as potential analytical reagents for the determination of metal ions. They contain an acid group with a replaceable hydrogen atom and a basic coordinating group in such appropriate positions that would allow formation of a five membered ring upon reaction with metal ions. They are commercially available at cheap price or they can simply be synthesized in laboratories. They are also stable towards heat, light and air. For these reasons they were utilized as analytical reagents for gravimetric and spectrophotometric determination of several metal ions [64-75].

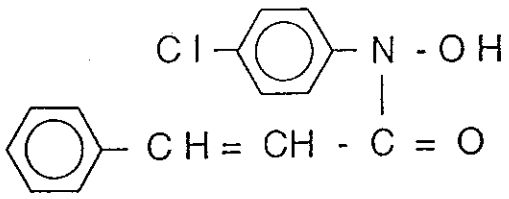

Figure 1. Structure of *N*-p-chlorophenyl-cinnamohydroxamic acid (CPCHA).

N-p-Chlorophenylcinnamohydroxamic acid (CPCHA) (Fig. 1), in particular, has been used for extraction and spectrophotometric determination of V(V) [73], Ce(IV)[74], and Nb(V)[75]. This potentially active reagent can also be used readily for the modification of CPE because of its such desirable properties as insolubility in aqueous solution, and substantial difference between its redox potentials and the redox potentials of most of its metal complexes, along with the other characteristics aforementioned. As a result of these desirable characteristics as modifier, it was used for the voltammetric determination of Cobalt(II) [76] and lead(II) [77]. However, the complex formation reaction and voltammetric behaviour of cadmium(II) at CPCHA and PCHA modified carbon paste electrodes have not been studied so far. This work is, thus, intended to extend the analytical utility of *N*-p-chlorophenylcinnamohydroaxmic acid modified carbon paste electrode to trace analysis of the toxic cadmium(II) ions.

The specific objectives of the present study are directed to:

(i) study the voltammetric behavior of cadmium(II) at carbon paste electrode modified with *N*-p-chlorophenylcinnamohydroaxmic acid,

(ii) establish the optimal experimental conditions for the determination of cadmium at the modified electrode (this involves studying the basic

electroanalytical parameters of the modified electrode, such as the effect of paste composition, pH and concentration of preconcentration and supporting electrolytes, preconcentration and deposition time, linear range, detection limit and so on),

(iii) carry out interference study on diverse ions (to assess the selectivity of the chemically modified electrode), and

(iv) study the analytical application of the modified electrode under optimized conditions for the determination of cadmium(II) in real samples.

2. THEORETICAL BACKGROUND

2.1. Analytical Behaviour of CMCPE

The experimental design of preconcentration/voltammetry at CMCPEs differs from the conventional electrochemical stripping technique. The deliberate modification of the electrode surface preestablishes and controls electrode/solution interface behaviour. Thus, the modified surface displays the electrochemical behaviour of the immobilized analyte without requiring the presence of the oxidized or reduced form of the immobilized analyte in the stripping medium. In the former case preconcentration is achieved by purely non-electrochemical means (rather than electrodeposition) via groups attached to the electrode surface. The preconcentration is also accompanied by medium exchange to the stripping solution, where electrochemical measurement is carried out.

The resulting effects caused by the changed physical and chemical properties of CPEs after modification were exploited for analytical purposes on empirical basis. Studies dealing with fundamental investigations on the ground of chemical laws are quite rare [55]. The following scheme is adopted from a model suggested to describe the analytical behaviour of CMCPE [55] with slight modifications to address the complexation process between CPCHA (HL) and divalent metal ions.

The accumulation process of a divalent ion on a chemically modified carbon paste electrode can be described by equation 1.

$$M^{2+}_{aq} + 2HL_{surf} \rightleftharpoons ML_{2,\,surf} + 2H^{+}_{aq} \qquad (1)$$

which can be simplified to approximation (equation 2), if the concentration of hydronium ion, H^+, is kept constant.

$$M^{2+}_{aq} + 2L^-_{surf} \rightleftharpoons ML_{2,\,surf} \qquad (2)$$

The indices (aq) and (surf) symbolize the bulk solution and the electrode surface, L^- designates the functional group of the modifier.

The equilibrium constant K_{eq} for the complexation process is defined by:

$$K_{eq} = \frac{[ML_2]_{surf}\,[H^+]_{aq}^2}{[M^{2+}]_{aq}\,[HL]_{surf}^2} \qquad (3)$$

If the concentration of H^+ is kept constant, it can be incorporated into K_{eq} yielding K_{eq}'.

$$K_{eq}' = \frac{[ML_2]_{surf}}{[M^{2+}]_{aq}\,[L^-]_{surf}^2} \qquad (4)$$

The concentration of the metal on the electrode surface is directly proportional to the voltammetric current registered during the scan (e.g. in the differential pulse mode) and can be expressed formally as moles per surface area:

$$[ML_2]_{surf} = [M^{2+}]_{surf} = f_{I\rightarrow c}\, I \qquad (5)$$

The factor $f_{I\rightarrow c}$ defines the conversion of measured current into the corresponding surface concentration of the electroactive species. The concentration of the free complexing group, $[L^-]_{surf}$, on the electrode surface can be calculated from its total concentration, $[L^-]_{surf,\,max}$, which can be obtained electrochemically as I_{max} by complete

saturation of the functional groups:

$$[L^-]_{surf} = [L^-]_{surf,\,max} - 2[M^{2+}]_{surf} \tag{6}$$

$$[L^-]_{surf} = 2f_{I\rightarrow C}(I_{max} - I) \tag{7}$$

Substituting entities of equations 5 and 7 into equation 4, considering equilibrium conditions, yields K_{eq}' expressed by voltammetric currents:

$$K_{eq}' = \frac{1}{4f_{I\rightarrow C}} \cdot \frac{1}{[M^{2+}]_{aq}} \cdot \frac{I_{eq}}{(I_{max} - I_{eq})^2} \tag{8}$$

To study the kinetics of the accumulation process and to obtain I_{eq} for different concentrations of $[M^{2+}]$, the following equation can be assumed to be valid:

$$\frac{d[ML_2]}{dt_{acc}} = k_v [M^{2+}]_{aq} ([L^-]_{surf,\,eff})^2 \tag{9}$$

The accumulation time is symbolized as t_{acc}, k_v represents the rate constant for the accumulation process, and $[L^-]_{surf,\,eff}$ corresponds to the effective surface concentration of functional groups available for preconcentration:

$$2[L^-]_{surf,\,eff} = [ML_2]_{surf,\,eq} - [ML_2]_{surf} \tag{10}$$

Substitution of concentrations by proper currents gives equation 11, which can be, in turn, integrated to express the voltammetric current I, after a certain period of accumulation t_{acc} (equation 12):

$$\frac{dI}{dt_{acc}} = 4f_{I\rightarrow c}k_v[M^{2+}]_{aq}(I_{eq} - I_t)^2 \quad (11)$$

$$I_t = I_{eq}[1 - \frac{1}{(4f_{I\rightarrow c}k_v[M^{2+}]_{aq}t_{acc} + 1)}] \quad (12)$$

Thus, the general plot of I_t versus t_{acc}, should give a hyperbolic-like curve with the current approaching I_{eq} for long accumulation time. This relation is found for many analytes when accumulated on CMCPEs [55].

2.2. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the first electroanalytical techniques reported in 1938 and described theoretically in 1948 by Randles and Sevcik. It has grown enormously in popularity over the past few decades, so much so that obtaining CV is often the first experiment performed by the electrochemist, giving invaluable information as to the presence of electroactive species in solution or at the electrode surface. The effectiveness of cyclic voltammetry results from its ability for rapidly observing redox behavior over the entire potential range available [51,59].

CV is an essential technique for initial electrochemical studies of new systems and has proven very useful in obtaining mechanistic information about fairly complicated electrode reactions. Although CV is particularly useful in qualitative studies of electrode processes, it is less well suited for quantitative measurement of potentials or currents. Its merits are, thus, largely in qualitative or diagnostic experiments. Quantitative measurements (of rates or concentrations) are best obtained by employing other (step or pulse) techniques [78-80].

It is common to find one or both members of an electrode couple adsorbed (confined) on an electrode surface, and CV is very helpful in studying the behaviour of such species. Suppose that O and R are both adsorbed on the electrode surface with surface concentrations Γ_O and Γ_R and, that the electrode process consists of complete reduction of O to R on the forward sweep and the oxidation of R to O on the reverse sweep. The current, then, is not diffusion limited but limited by the amount of adsorbed material. If the electron transfer process is reversible, the surface concentrations are related by the Nernst equation,

$$\frac{\Gamma_O(t)}{\Gamma_R(t)} = \exp\left(\frac{nF[E(t)-E_s^o]}{RT}\right) = \theta(t) \qquad (13)$$

where E_s^o is the formal potential of the adsorbed couple, n is the number of electrons transferred, and $E(t) = E_i - \upsilon t$, in which E_i and υ are initial potential and scan rate, respectively. If the total surface concentration (Γ^*) is constant,

$$\Gamma_O(t) + \Gamma_R(t) = \Gamma^* \qquad (14)$$

the individual surface concentrations are time (and potential) dependent and the current is given by

$$i = \frac{n^2F^2A\upsilon\Gamma^*}{RT} \cdot \frac{\theta}{(1+\theta)^2} \qquad (15)$$

The peak current of the i-E curve is given by

$$i_p = \frac{n^2F^2A\upsilon\Gamma^*}{4RT} \qquad (16)$$

Thus, the above equations predict the anodic wave on scan reversal as the mirror image of the cathodic wave reflected across the potential axis, with current peak at $E = E_s^o$ ($\theta = 1$) which is proportional to the number of moles of the adsorbed species and to the scan rate. The situation is more complicated when the redox species undergo coupled chemical reactions, the solution species participate in the electrode process, when only one member of the couple is adsorbed and/or when the electrode process is slow [79,80].

In contrast, the peak current for nernstian wave of diffusing species in a reversible system is given by the Randles-Sevcik equation:

$$I_p = (2.69 \times 10^5)\, n^{3/2} AcD^{1/2} v^{1/2} \qquad \text{at } 25\,^0C \qquad (17)$$

with the separation of the peak potentials given by:

$$\Delta E = E_{pa} - E_{pc} \approx 0.059/n \text{ V} \qquad (18)$$

where I_p = peak current (A), n = electron stoichiometry, A = electrode area (cm^2), D = diffusion coefficient (cm^2/s), c = concentration (mol/cm^3), and v = scan rate (V/s).

2.3. Differential Pulse Voltammetry

When the electrode background current is large and/or coverage of the attached redox species is low, greater sensitivity is needed to detect electroactivity of surface redox species. Differential pulse voltammetry (DPV) was introduced for such situations. Differential pulse voltammetry is one of the most important and versatile achievements for electrochemical trace analysis from the pioneering work of Barker, which is now

incorporated in every voltammetric device as the most significant function for analytical practice. Recording of the response from differential pulse mode applied in voltammetry is performed according to the principle introduced by Parry and Osteryoung [59,81].

In the differential pulse mode the test electrode is polarized essentially by a DC-voltage ramp on which at adjustable clock times a series of equal rectangular voltage pulses are superimposed. The current is sampled in two intervals, the first immediately prior to the application of the potential pulse and the second during but towards the end of the pulse life, when the charging current has decayed. In this manner the charging current of the double layer capacity, limiting the utility of voltammetry, can be efficiently separated from the faradaic component, which is due to the electrode process of the substance being analyzed and, thus, proportional to its concentration in the analyte. The resulting substantial improvement in signal-to-noise ratio has opened to voltammetry the area of trace, and in conjunction with electrochemical or chemical (open-circuit) preconcentration, ultra-trace analysis [51,80,82].

Differential pulse voltammetry produces a peak shaped output the important parameters of which are the peak potential (E_p) and the peak current (i_p). The position of the peak potential is a function of the half-wave potential, $E_{1/2}$, and the pulse amplitude, P.A.

$$E_p = E_{1/2} - \frac{(P.A.)}{2} \qquad (19)$$

Parry and Osteryoung [81] have derived an equation (equation 20) for the peak current of reversible system.

$$i_p = \frac{nFAcD^{1/2}\ (1\ -\ \Theta)}{\pi^{1/2}(\tau\ -\ \tau')^{1/2}\ (1\ +\ \Theta)} \qquad (20)$$

where τ' represents the first current sampling time immediately before the pulse and τ, the second current sampling time late in the pulse.

$$\Theta = \exp \frac{nF\ (P.A.)}{2RT} \qquad (21)$$

2.4. Stripping Voltammetry

Modern life makes very diverse demands on analytical chemistry. Present problems in technology, biology, environmental protection and medicine and other fields require determination of ever-decreasing amounts of substances in progressively more complex systems and so place increasing demands on the method of trace analysis. Among these methods voltammetric stripping analysis occupies a relatively important place [37]. It combines extraordinary determination sensitivity (especially when combined with DPV) with inherently high accuracy (i.e small tendency for systematic errors) and good precision [82]. Its analytical power originates from the unique coupling of an effective preoncentration step with an advanced measurement scheme of the deposited substance. The instrumentation is very compact and can, therefore, be easily used in field studies. The costs invested for instrumentation are also significantly lower than any of the other alternatives in trace metal analysis [37,82].

Conventionally, voltammetric stripping method employs a two-step approach consisting of an initial preconcentration step during which the analyte is electrodeposited at the

electrode surface under carefully controlled conditions and, a subsequent step in which the accumulated analyte is stripped off and quantified by either voltammetric or potentiometric means.

The voltammetric stripping method may be classified as anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV). Anodic stripping voltammetry is the most common version of stripping analysis. It involves the reduction of the metal ion in uncomplexed or complexed form to the metallic form, as the preconcentration (reduction) step followed by a positive-going potential scan to cause reoxidation of the species. Thus, the metals are stripped out of the electrode (in an order that is a function of each metal standard potential), and give rise to anodic peak current that is measured. Using CMEs the preconcentration step is carried out non-electrochemically at surfaces specifically designed for their ability to bind the target analyte followed by the usual electrochemical reduction and stripping schemes. Figure 2 shows the schematic representation of differential pulse anodic stripping voltammetry (DPASV) using CMCPE.

Cathodic stripping voltammetry (CSV) is the "mirror image" of anodic stripping voltammetry (ASV). Briefly, it involves anodic deposition of the analyte on the electrode; and subsequent stripping off during a negative-going potential scan. It is best suited for the determination of inorganic anions or organic compounds that are able to form insoluble salts with the electrode material.

Adsorptive stripping voltammetry (AdSV) is used for quantitation of numerous trace metals for which conventional (electrolytic) stripping procedures are complicated or not feasible [59,83] and many surface-active organic compounds that can be interfacially accumulated and measured [84,85]. Metal determination is based on formation of an

appropriate metal chelate, followed by its controlled accumulation onto the working electrode. The resulting adsorptive stripping current due to reduction of the adsorbed species during negative-going potential scan reflects the surface concentration of the analyte (which, in turn, is proportional to its bulk concentration).

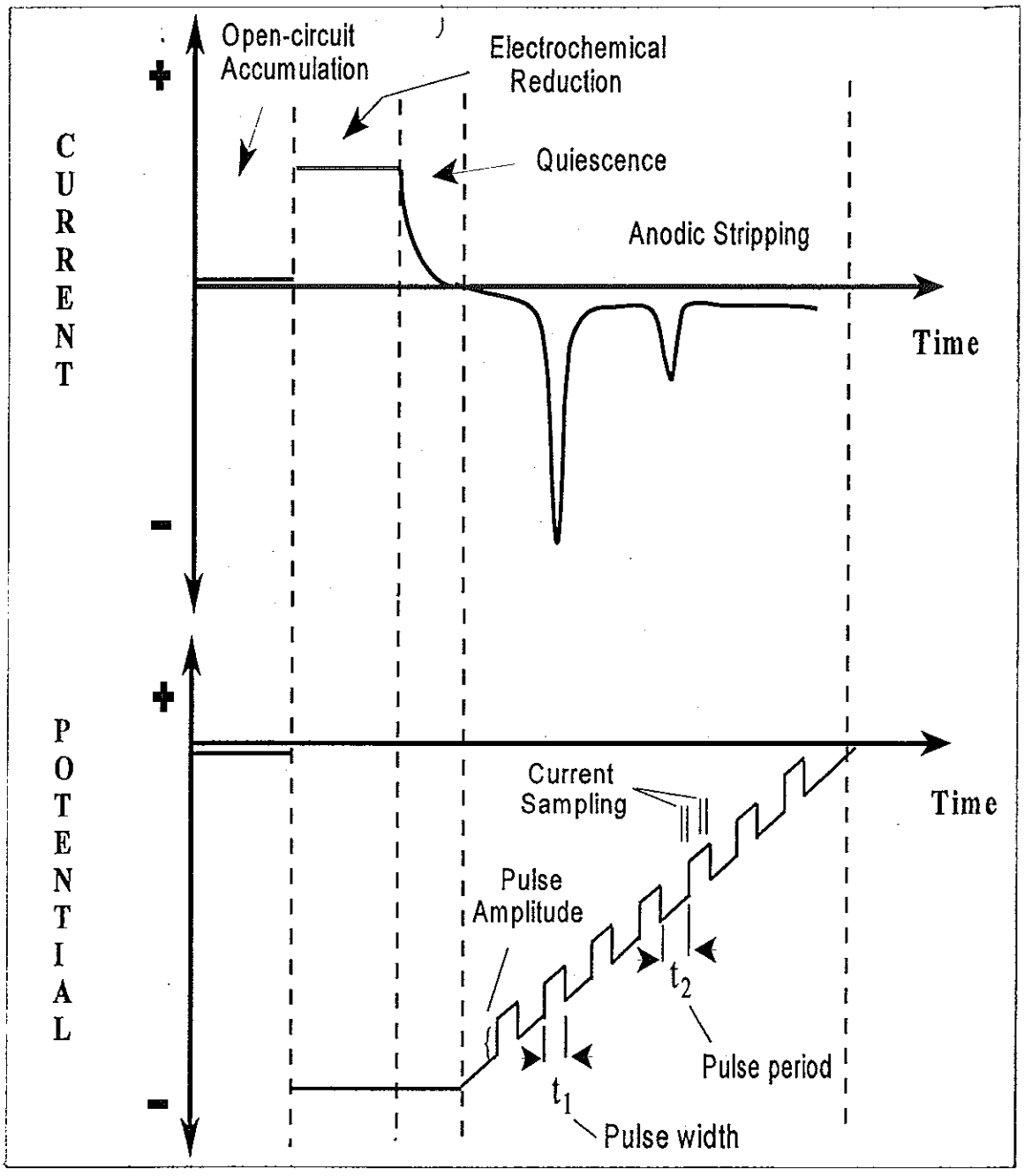

Figure 2. The principle of differential pulse anodic stripping voltammetry (DPASV) using chemically modified carbon paste electrode (CMCPE).

2.5. Choice of Operating Parameters in Differential Pulse Anodic Stripping Voltammetry

2.5.1. Electrode type

The analytical utility of a voltammetric procedure is strongly affected by the indicator electrode employed. Obviously to be of much use, the electrode ought to be stable in the medium used for analysis. It should provide a favorable signal to noise characteristics, as well as a reproducible response. It would be better if the electrode has wider potential range of utility, low resistance, and low background current. The suitability of an electrode for analytical application can also be dictated by electron transfer rate, mechanical properties, and type of reaction used for accumulation. The cost, availability, and stability during storage must be taken in account as well [37,86].

An important factor in using solid electrode is the dependence of the response on the surface state of the electrode. Accordingly, the use of such electrodes usually require precise electrode pretreatment and polishing to obtain reproducible results. Regarding chemically modified carbon paste electrodes, it is possible that not all the accumulated ions are contributing to the voltammetric response. Only the trapped ions with direct access to the active graphite particles would participate in the redox reaction. Thus, effective mixing of the various components is desirable when preparing the chemically modified carbon paste electrode.

2.5.2. Choice of supporting electrolyte and preconcentration medium

The main role of supporting electrolyte in an electrochemical cell is to provide the source of ions to conduct current across the cell and to dissolve the electroactive

species. Although the supporting electrolyte does not take part in the electrode reaction, the ionic composition of the electrolyte may influence the electrode kinetics due to the presence of anions and cations in the double layer and due to adsorption at the electrode of many anions [87].

The supporting electrolyte is subjected to much considerations with regard to stability towards electrolysis and chemical inertness. Electrolytic media of high conductivity are desirable since they prevent internal heating due to I^2R power dissipation and permit relatively error-free control of electrode potential. In some cases the electrolyte may be chosen to serve as buffer when acids or bases are formed during the redox process [88].

Several factors must be considered when choosing the composition of the supporting electrolyte. 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. Buffer systems (such as acetate, phosphate or citrate) are used when pH control is essential. The components of the supporting electrolyte must also be available in sufficiently pure form, or the impurities must at least be removable. Care must be taken in that the electrolyte chosen is truly inert in the potential range of the experiment, not reacting with the electrode or the products of the electrode reaction (except when desired) [37,80,86].

The preconcentration electrolytes are usually solutions of simple inorganic acids and salts or buffers. Solution conditions, in particular pH and concentration of the medium, have profound effects. In the presence of complexing agents some components of the sample can be masked and, thus, selectivity of the determination can be improved. The presence of these weakly complexing species in the preconcentration medium also

helps to prevent hydrolysis of the metal ion of interest at those high pH's where the complexation with the modifier may be maximum. However, the concentrations of such species should not be high to the extent of affecting the complexation of the metal ion with the modifier. In general, the electrolyte composition must be chosen in such a way that high sensitivity and selectivity of determination are achieved.

2.5.3. Agitation

Because electrolysis and open-circuit accumulation are heterogeneous reactions, mass transport of material toward and away from the electrode is an important consideration. Though the transport in unstirred solution (via diffusion) is very reproducible, it is much slower than that of convection. Therefore, in most cases it will be desirable to agitate the solution in order to speed up mass transport during accumulation and cleaning . However, the stirring must be uniform, gentle, and at controlled rate. The position of the electrode within the cell and hence in the solution should also be reproducible [88].

2.5.4. Preconcentration time

If direct proportionality between the final signal and the accumulation time is to be maintained, the accumulation time must not be too long. Otherwise, deviation from linearity due to saturation of the binding sites or attainment of equilibrium may occur. It is advisable to use a relatively short preconcentration time for higher analyte concentrations in order to avoid saturation and the subsequent nonlinearity between concentration and analytical signal. On the other hand, it is possible to enhance the sensitivity of the stripping determination by employing prolonged preconcentration periods for lower concentrations. Short accumulation time is also important in reducing the total analysis time [42].

2.5.5. Electrolytic deposition and stripping

Electrolytic processes characteristically are controlled and affected by many variables, some of which are mechanical, electrical, and chemical as well as combinations of thereof. The effect and relative importance of these factors depend on the particular situation at hand. It is only by understanding and considering their possible effects that electrolytic reactions can be controlled and optimized effectively [88].

The efficiency of electrodeposition of trace amounts of metals as a preconcentration technique for analysis is significantly influenced by the presence of oxidizing agents in the electrolyte solution and such factors as solution pH, deposition potential, deposition time, electrode size, nature of electrode, and stirring [89]

Deposition Potential used in the deposition step is the most important variable, since it essentially controls the type of reaction and its rate. When the deposition potential is extremely negative, it is likely that more types of metal ions will be deposited leading to increased interferences. Provided a special choice of the potential is not dictated by the selectivity requirements, the preelectrolysis potential is usually selected in the region of sufficiently negative potential where steady state current can be achieved [37,88].

The sensitivity of stripping determination can also be enhanced by carrying out the deposition process for sufficiently long time until all of the analyte deposits on the electrode. It is best, however, to avoid long deposition times since this often results in various complications including loss of proportionality between final signal and the concentration of the analyte. One cause can be reactions undergone by the deposit or changes in its nature over a relatively prolonged time [90].

The peak height from voltammetric stripping depends on the amount of substance deposited and is the function of may parameters. In order to be able to correlate the peak height with the original concentration of the test substance in the solution, the deposited fraction of the substance must be constant in all measurements that are to be compared. This can be ensured by maintaining constant the preelectrolysis time and potential, the convection conditions (cell geometry, stirring), the electrode properties (surface area, material, pretreatment), temperature, solution composition and the stripping conditions (scan rate, pulse amplitude, etc.)[91].

2.5.6. Pulse amplitude

It can be seen from equation 20 that i_p increases as pulse amplitude, P.A., increases because $[(1 - \Theta) / (1 + \Theta)]$ approaches unity as P.A. increases. However, the peak width also increases with increasing pulse amplitude. It can also increase residual current ending up in peaks deformation. Therefore, the optimum pulse amplitude must be found to maximize both sensitivity, ip, and resolution (small peak width).

2.5.7. Scan rate

The choice of scan rate is one of the most important instrumental variable that requires due consideration. Just like pulse amplitude, fast scan rate increases the peak height accompanied by the undesirable peak broadening. On the other hand, very slow scan rates give low but narrow signals and, increase the total analysis time. Hence, selection of scan rate usually requires a compromise among sensitivity, resolution, and speed [81].

2.5.8. Other variables

Normally temperature should have little effect on the electron-transfer part of the electrode reaction. However, electrode potentials (including reference electrode) can shift with temperature, but are not major problems with moderate fluctuations. Most important would be consideration of the effect of temperature on the course of follow-up chemical reactions. The conductivity of most electrolytes usually increases with increasing temperature by 1 to 2% per °C. The solubility of various species in the medium may also be a function of temperature. Therefore, the solution temperature should be maintained within at least ± 1 °C, as the voltammetric current depends on it.

Since differential pulse voltammetry is a differential technique, it is the area under the peak which is proportional to the charge passed and hence to the concentration of the analyte. The measurement of peak height is much more convenient and generally yields results with sufficient precision. Thus, peak height can be used instead of area as long as the shape of the peak does not alter. Especially when two peaks partially overlap, making area separation very difficult, it would be much easier to measure the well-defined peak heights. [79,91].

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 (BDH), sodium hydroxide (Bio-Lab), ammonium chloride (BDH, AnalaR), ammonia solution (AR, Bio-Lab), hydrochloric acid (Riedel-deHaen), and cadmium nitrate (BDH, AnalaR) were used as received. Sodium acetate and ammonium chloride solutions of various concentrations were prepared in water. The pH of sodium acetate and ammonium chloride solutions were adjusted to the desired values by adding acetic acid or 1 M sodium hydroxide and, 1 M ammonia or 1 M hydrochloric acid, respectively. Stock solution of 10 mM cadmium(II) was prepared in water. Working standard solutions of lower concentrations were prepared freshly by dilution. Double distilled water was used throughout to prepare all solutions.

N-p-Chlorophenylcinnamohydroxamic acid was prepared by the condensation of *N*-p-chlorophenylhydroxylamine with cinnamoyl chloride at low temperature in diethyl ether medium made alkaline with an aqueous suspension of sodium bicarbonate [92].

3.2. Apparatus

The electrochemical behavior of cadmium(II) at *N*-p-chlorophenylcinnamohydroxamic acid modified carbon paste electrode has been studied by voltammetric methods. Monitoring of experimentation, recording of voltammograms and data processing were made by BAS CV-50W Voltammetric Analyzer connected to an IBM Personal Computer 130 100DX4. A one-compartment PTFE electrochemical cell (30 mL) with three

electrodes (platinum disk counter electrode, Ag/AgCl reference electrode (BAS MF-2020), and CMCPE as working electrode) served as the measurement cell. Two different cells (30 mL) were used for the preconcentration and stripping steps. pH measurements were made on an Oyster pH meter (EXTECH). A magnetic stirrer (STUART Scientific) with a Teflon-coating stirring bar was used in the preconcentration, cleaning and rinsing steps to provide convective transport. A stop clock (Harris Digitimer) was employed for time measurement. Standard solutions were added to the preconcentration cell with adjustable volume micropipette (GILSON) with disposable tips. Figure 3 shows the experimental set up schematically.

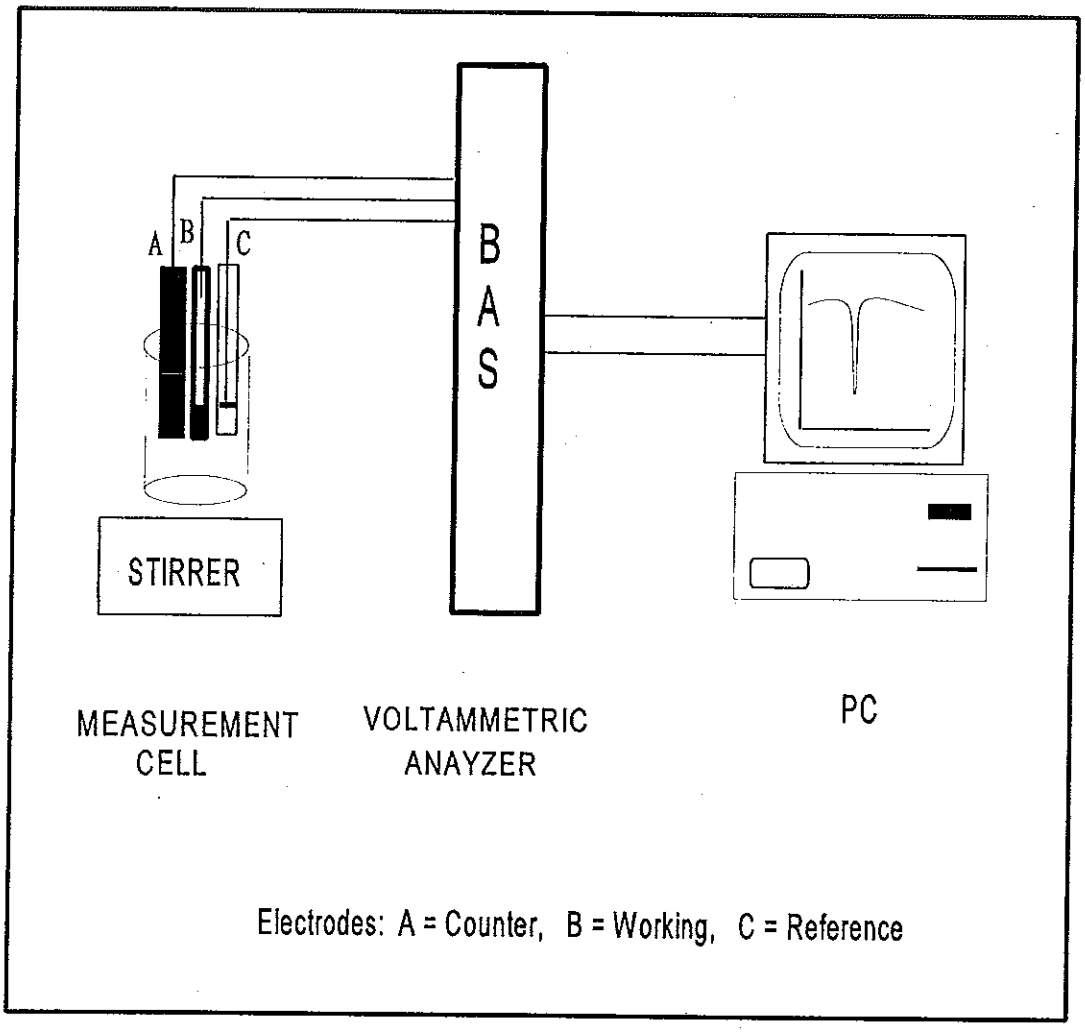

Figure 3. Experimental set up for the study of voltammetric behaviour of cadmium(II) at CPCHA modified carbon paste electrode.

3.3. Electrode Preparation and Pretreatment

Unmodified carbon paste was prepared by adding 0.36 mL paraffin oil to 1 g carbon powder. Modified carbon pastes were prepared by substituting corresponding amounts of the carbon powder (5%, 10%, 15%, 20%, and 25% weight-to-weight ratio) by CPCHA and then adding the paraffin oil and thoroughly hand-mixing in a mortar and pestle. The pastes were packed into electrode assemblies made from 1-mL plastic syringes (B/BRAUN) of 3 mm outer diameter and smoothed off until a shiny surface emerged. A copper wire was inserted along the plunger of the syringe to establish electrical contact as shown in Figure 4. The freshly assembled and polished chemically modified electrode surface was conditioned by subjecting it to few cyclic scans in the supporting electrolyte followed by open circuit accumulation of cadmium(II) from the preconcentration medium and the subsequent electrochemical stripping and renewal schemes (usually 3-4 cycles) to improve its performance. The preconditioned electrode has good stability, sensitivity, and reproducibility. A single conditioned CME surface could always be used for hours of continuous operation with no signs of fatigue. The modified electrodes were stored at room temperature in open air.

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 cyclic voltammograms were run starting from -1.4 to 0 V and back (at 100 mV/s scan rate).

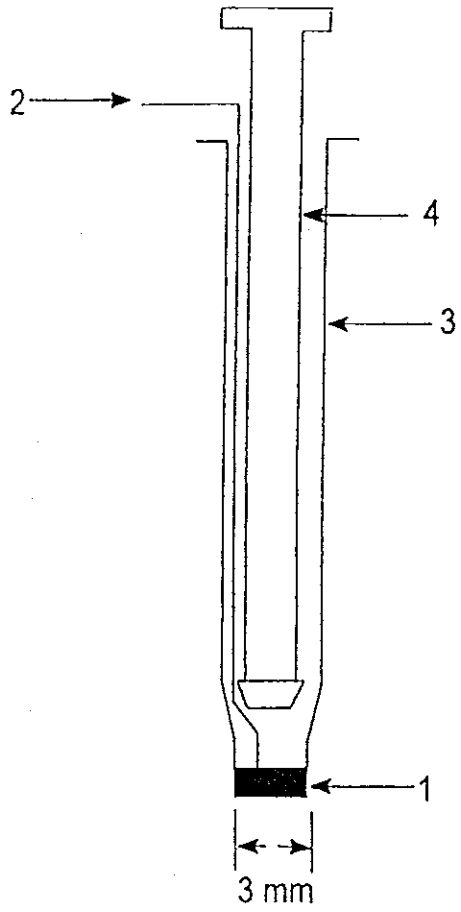

Figure 4. CPCHA modified carbon paste electrode: (1) paste, (2) copper wire, (3) syringe body, and (4) piston/plunger.

All quantitative measurements were performed using differential pulse anodic stripping voltammetry to achieve the required sensitivity for trace analysis. The analytical procedure involved chemical deposition of cadmium(II), transfer of the electrode to the electrochemical cell, voltammetric determination and eventually regeneration of the electrode surface. For the preconcentration step, the modified carbon paste electrode was exposed for a preselected period of time to 25 mL of 0.1 M sodium acetate solution (pH 10) containing a known amount of cadmium(II) under open-circuit and stirred conditions. Subsequently, the electrode was removed from the preconcentration cell, rinsed thoroughly with water, and placed in quiescent blank of 25 mL of 0.3 M NH_4Cl

electrolyte solution (pH 5). Following the application of an initial potential of -1.1 V for 60 s, the electrode was then scanned anodically at a rate of 30 mV/s with pulse amplitude of 100 mV and pulse period of 0.2 s. The scan was terminated at -0.4 V. After each scan, the electrode was cleaned by keeping the electrode in stirred supporting electrolyte under application of +100 mV for 60 s followed by rinsing with distilled water. The electrode was, thus, ready for the succeeding preconcentration step. The stripping solution was replaced by a fresh one for every set of experiment to avoid potential buildup of cadmium(II) in the electrochemical cell. All measurements were carried out at room temperature ($22 \pm 2\ ^{0}C$) using non-deaerated solutions.

3.5. Analysis of Samples

3.5.1. Analysis of drinking water

Drinking water was collected from a municipal water supply pipeline in Kolfe residential area, Addis Ababa, Ethiopia. It was sampled after allowing water to flow out in full stream through the open pipe for a while before collection. Three water samples were collected at interval of one week in March 2000. All the samples were stored in polyethylene bottles.

The water samples were spiked with cadmium(II) to concentrations of 5×10^{-7} M and 1×10^{-6} M (0.056 and 0.112 μg mL^{-1}). A 0.1 M sodium acetate solution, pH 10, was then prepared in 500 mL of the spiked water samples. A 25 mL aliquot of this solution was transferred into the accumulation cell for preconcentration and subsequent voltammetric measurement. The amount of cadmium in the water sample was quantified by standard addition method.

3.5.2. Analysis of mineral water

Three bottles of Ambo (Ethiopia) Natural Mineral water were purchased from the market and used for the analysis. The water sample from each bottle was subjected to same treatment. A 500 mL aliquot of the mineral water sample spiked with cadmium(II) to concentration of 1 x 10^{-6} M (0.112 μg mL^{-1}) was mixed with 2.5 mL each of concentrated hydrochloric and nitric acids and heated to dryness. The residue was dissolved in 500 mL of distilled water. To this solution was added appropriate amount (4.1 g) of sodium acetate to bring the acetate concentration to 0.1 M and then adjusted to pH 10. The amount of cadmium in the water sample was quantified by standard addition method.

3.5.3. Analysis of water samples by Atomic Absorption Spectroscopy (AAS)

The concentration of Cd(II) in both types of water samples were also determined with a Varian atomic absorption spectrometer Model SpectrAA 220 equipped with a Varian SIPS sample introduction pump system using air-C_2H_2 flame system. The cadmium spiked-municipal water was directly analysed, while cadmium spiked-mineral water was treated in identical manner as in section 3.5.2. except addition of sodium acetate and pH adjustment.

4. RESULTS AND DISCUSSION

4.1. Voltammetric Behaviour of Cadmium(II) at CPCHA-modified Carbon Paste Electrode

Cyclic voltammograms (CVs) were obtained at unmodified and CPCHA modified CPEs in 0.3 M NH_4Cl of pH 5. The CVs of the unmodified and CPCHA modified electrodes were run with and without chemical accumulation of cadmium(II) from 0.1 M sodium acetate solution of pH 10 at open circuit condition. The CVs of CPCHA modified carbon paste electrode with and without Cd(II) preconcentration are shown in Figure 5. The CV of the unmodified electrode (not shown) with and without Cd(II) preconcentration and the CPCHA modified electrode without Cd(II) preconcentration (curve 1) did not show any wave in the potential range (-1.4 to 0 V) used. Whereas the CV of the modified electrode with Cd(II) preconcentration (curve 2) revealed an anodic peak at - 0.74 V and a broad cathodic peak at about -0.95 V. The appearance of anodic and cathodic peaks in the CV obtained after open circuit accumulation of Cd(II) proved qualitatively the ability of the CPCHA modified electrode to preconcentrate Cd(II) ions from aqueous solutions. The redox potentials seen at the CPCHA modified electrode closely matched that of the cadmium which had been electrodeposited at an unmodified CPE from 0.3 M ammonium chloride solution of pH 5 (curve 3). Hence, the peaks were assigned to the oxidation of the surface-bound cadmium (which was chemically accumulated as Cd(II)-CPCHA complex on the electrode surface and reduced to Cd(0) during the initial potential scan) and reduction of the Cd(II) (as CPCHA complex) to Cd(0) on the electrode surface during the reverse scan. The CV of CPCHA modified carbon paste electrode was also obtained by scanning the potential from 0 to -1400 mV and back with 100 mV/s scan rate (fig. 6). However no significant changes were observed in changing the direction of the potential scan.

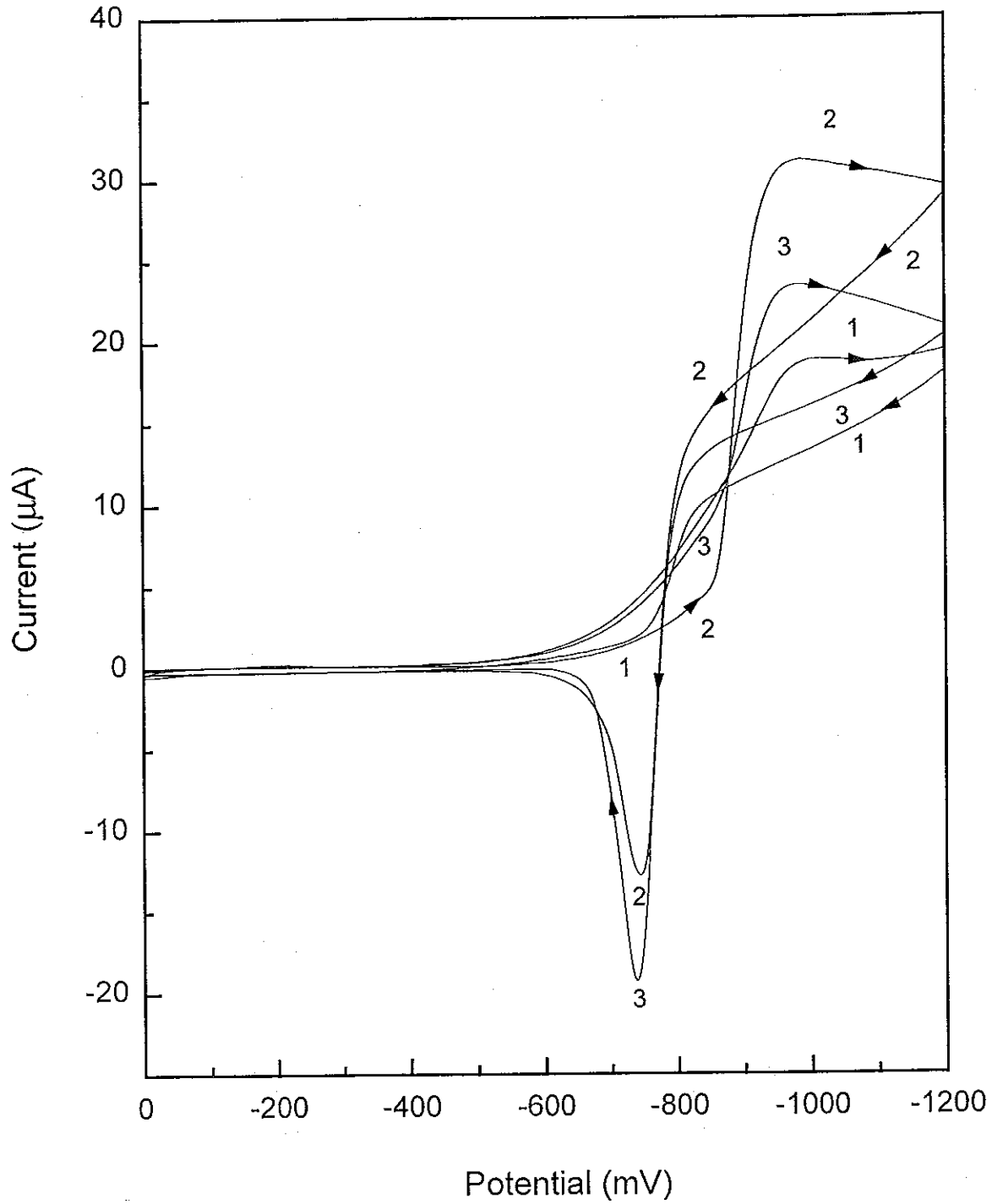

Figure 5. Cyclic voltammograms of: CPCHA-modified CPE (1) without cadmium(II) preconcentration and (2) with cadmium(II) preconcentration from 0.1 M NaAc solution of pH 10; preconcentration time: 2 min, and unmodified CPE (3) with cadmium(II) electrodeposition; cadmium(II) concentration: 8.0×10^{-5} M; supporting electrolyte: 0.3 M NH_4Cl solution of pH 5; scanned from -1.4 to 0 V and back at scan rate: 100 mV/s.

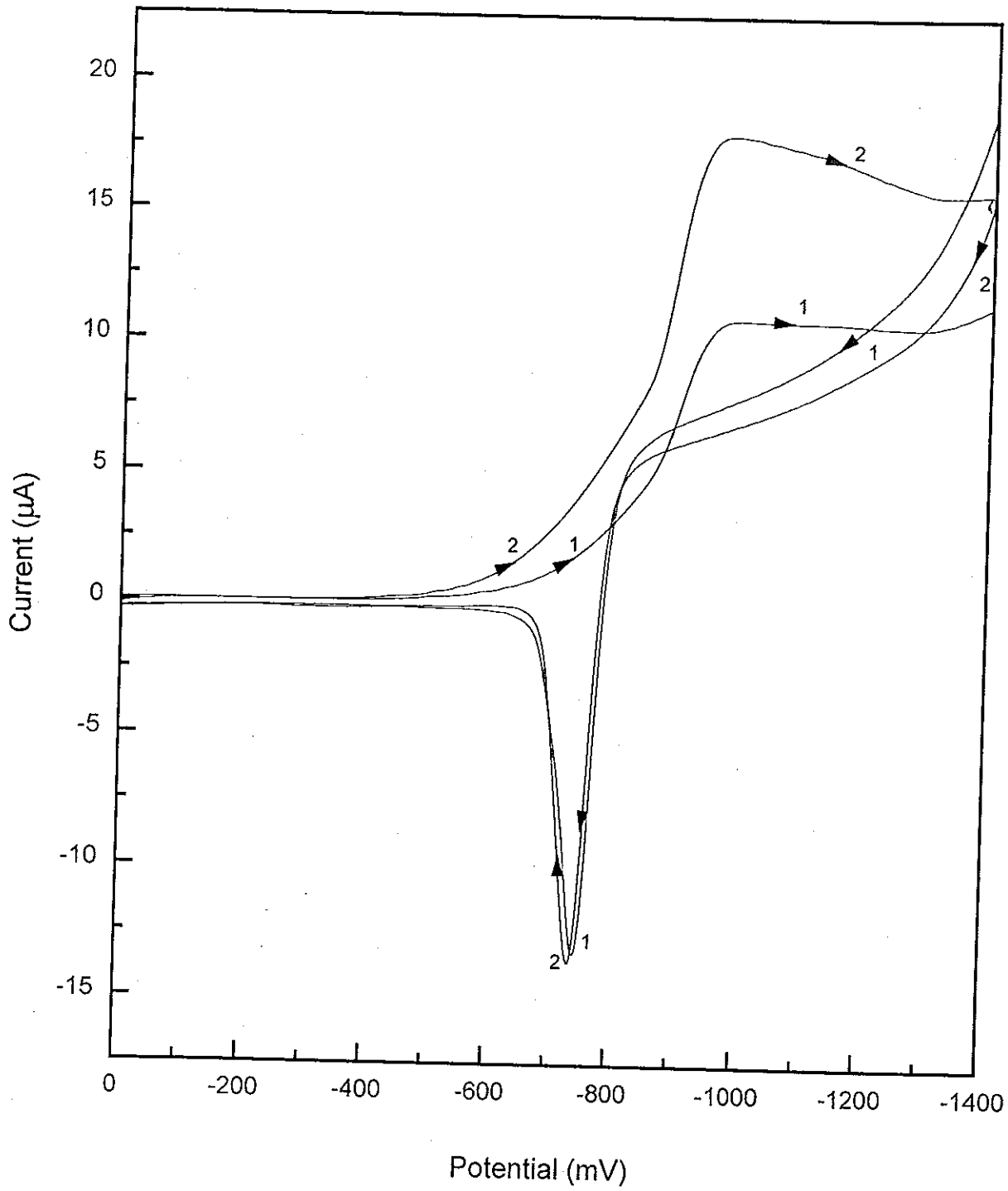

Figure 6. Cyclic voltammograms of CPCHA modified CPE after cadmium (II) open-circuit preconcentration and scanning (1) from -1400 to 0 mV and back at scan rate of 100 mV/s (2) from 0 to -1400 mV and back at scan rate of 100 mV/s; other conditions are as in Figure 5.

The mechanism of CPCHA modified electrode reactions is attributed to the following steps (where HL represents CPCHA):

1. Preconcentration step (open circuit cell, 0.1 M NaAc, pH 10):

$$\underset{\text{(Solution)}}{Cd^{2+}} + \underset{\text{(CPE surface)}}{2HL} \rightarrow \underset{\text{(CPE surface)}}{CdL_2} + \underset{\text{(Solution)}}{2H^+}$$

2. Reduction step (closed circuit cell, 0.3 M NH_4Cl, pH 5, -1.1 V):

$$\underset{\text{(CPE surface)}}{CdL_2} + \underset{\text{(Solution)}}{2H^+} + 2e \rightarrow \underset{\text{(CPE surface)}}{Cd} + \underset{\text{(CPE surface)}}{2HL}$$

3. Stripping step (closed-circuit cell, 0.3 M NH_4Cl, pH 5, positive scan: -1.1 to -0.4 V):

$$\underset{\text{(CPE surface)}}{Cd} + \underset{\text{(CPE surface)}}{2HL} \rightarrow \underset{\text{(CPE surface)}}{CdL_2} + \underset{\text{(Solution)}}{2H^+} + 2e$$

Evaluation of the analytical performance of CPCHA modified CPE for Cd(II) analysis requires optimization of many aspects of the chemically modified electrode, and the associated preconcentration and stripping procedures. These include modifier loading, solution condition during open-circuit accumulation and electrochemical measurement (nature of electrolyte, concentration, pH), preconcentration and electrodeposition times, instrumental parameters (deposition potential, scan rate, pulse amplitude, pulse period), and so on. Accordingly, this study covered a series of experiments in which suitable experimental conditions for the determination of Cd(II) were established. The effect of a particular variable was studied by the procedure described in section 3.4. under identical conditions keeping all the variables constant except the one under study.

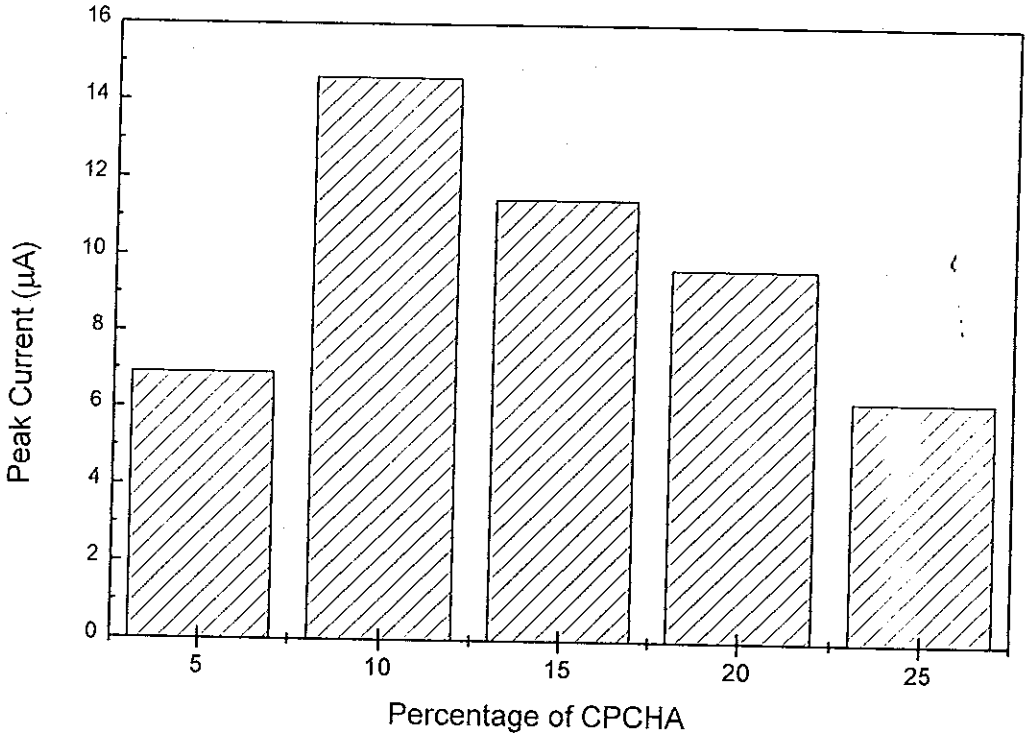

Figure 7. Effect of modifier composition in CPE: Cd(II) concentration: 2 x 10^{-6} M; reduction potential: -1.1 V; reduction time: 1 min; scan rate: 30 mV/s; pulse amplitude: 100 mV; pulse period: 0.2 s. Other conditions are as in Figure 5.

4.2. Effect of Carbon Paste Composition

The quantity of CPCHA in the carbon paste is expected to significantly influence the height of the voltammetric signal. There was no peak observed with unmodified carbon paste electrode. The anodic peak of cadmium was obtained only with CPCHA modified CPE. This obviously indicates that the voltammetric response results from the accumulation of Cd(II) at the CPCHA modified CPE by means of the complex formation reaction between the metal ion, Cd(II) and the modifier, CPCHA. The effect of carbon paste composition on the peak current was tested using chemically modified electrodes prepared from 5%, 10%, 15%, 20% and 25% weight-to-weight ratio of CPCHA and

carbon powder-contained pastes under identical conditions (Fig. 7). Electrodes containing either lower or higher modifier loadings gave smaller voltammetric signals for cadmium. Optimum paste composition was found to be 10% CPCHA with respect to the analytical performance of the electrode. The decrease in the peak current at higher compositions (>10% of CPCHA) might be ascribed to the reduction of conductive area (carbon particles) at the electrode surface. While the decrease in the peak current at lower percentages (<10% of CPCHA) is due to lower extent of complexation because of smaller coverage of the modifier on the electrode surface. Hence an electrode containing 10% CPCHA was used for all subsequent experiments.

4.3. Effects of Preconcentration Solution and Supporting Electrolyte

Nature and conditions (such as pH and concentration) of the media used for the purpose of accumulation as well as stripping measurement have profound effect on the voltammetric response. These can exert their influences either directly or indirectly on the complexation equilibria during preconcentration and in the electrochemical measurement after medium exchange.

4.3.1. Effect of composition and concentration of preconcentration solution

The extent of complexation of Cd(II) with the modifier at the electrode surface could vary with the composition of the preconcentration solution. With this view, various media, including NH_4Cl, NaAc, $NaClO_4$, and Na_2CO_3 (each 0.1 M, pH=10), were evaluated for their suitability in accumulating cadmium(II) at the electrode surface. Among the tested ones, NaAc was found to be the best for the purpose. While $NaClO_4$ medium gave results comparable to that of NaAc solution, the reproducibility was poor. This might be attributed to changes in pH during the accumulation process as the ions

of the salt do not participate in equilibrium involving hydrogen ion. The peak current was slightly smaller with Na_2CO_3 compared to that of NaAc. This might be due to the likelihood of precipitation of Cd(II) as $CdCO_3$ at pH 10. Much smaller peak current was obtained when NH_4Cl solution was used for preconcentration since the complex formation of Cd(II) with NH_3 and chloride [22,23] hindered the accumulation of Cd(II) on the electrode surface.

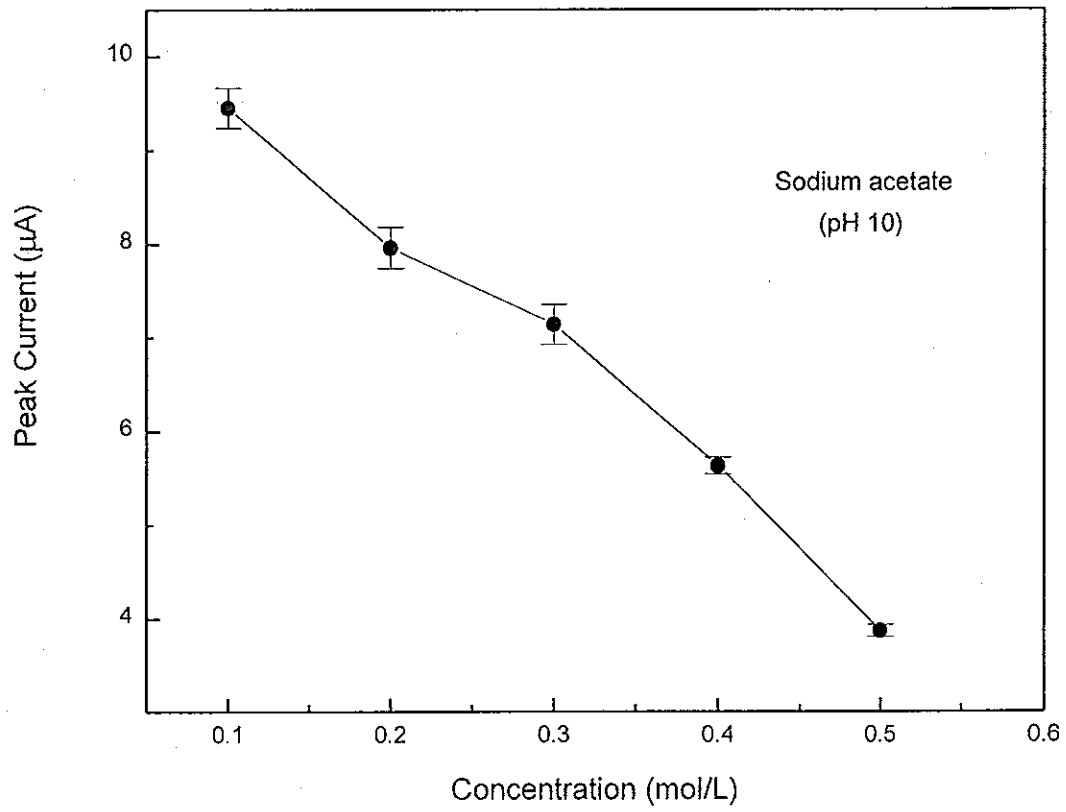

Figure 8. Effect of concentration of preconcentration solution. Each bar represents mean ± 3 standard deviation. Cadmium(II) concentration : 8.0×10^{-6} M; Other conditions are as in Figure 7.

The effect of sodium acetate concentration was examined in the range of 0.1-0.5 M (Fig. 8). The peak current decreased with increasing concentration of sodium acetate due to weak complexation of cadmium(II) with acetate. Maximum peak current was observed with 0.1 M solution. On the other hand, the study of the influence of ionic

strength on Cd(II) accumulation revealed that the analytical signal was not influenced by ionic strength up to 0.3 M when adjusted with sodium perchlorate. Thus, 0.1 M sodium acetate was utilized as preconcentration solution during the whole study.

4.3.2. Effect of pH of preconcentration solution

Throughout the process of accumulation the pH of the solution plays crucial role because of its direct effect on modifier-cadmium complexation equilibrium. This important variable was studied for 0.1 M NaAc solution in the pH range 6.0 - 11.5. The voltammetric peak current as a function of pH is shown in Figure 9.

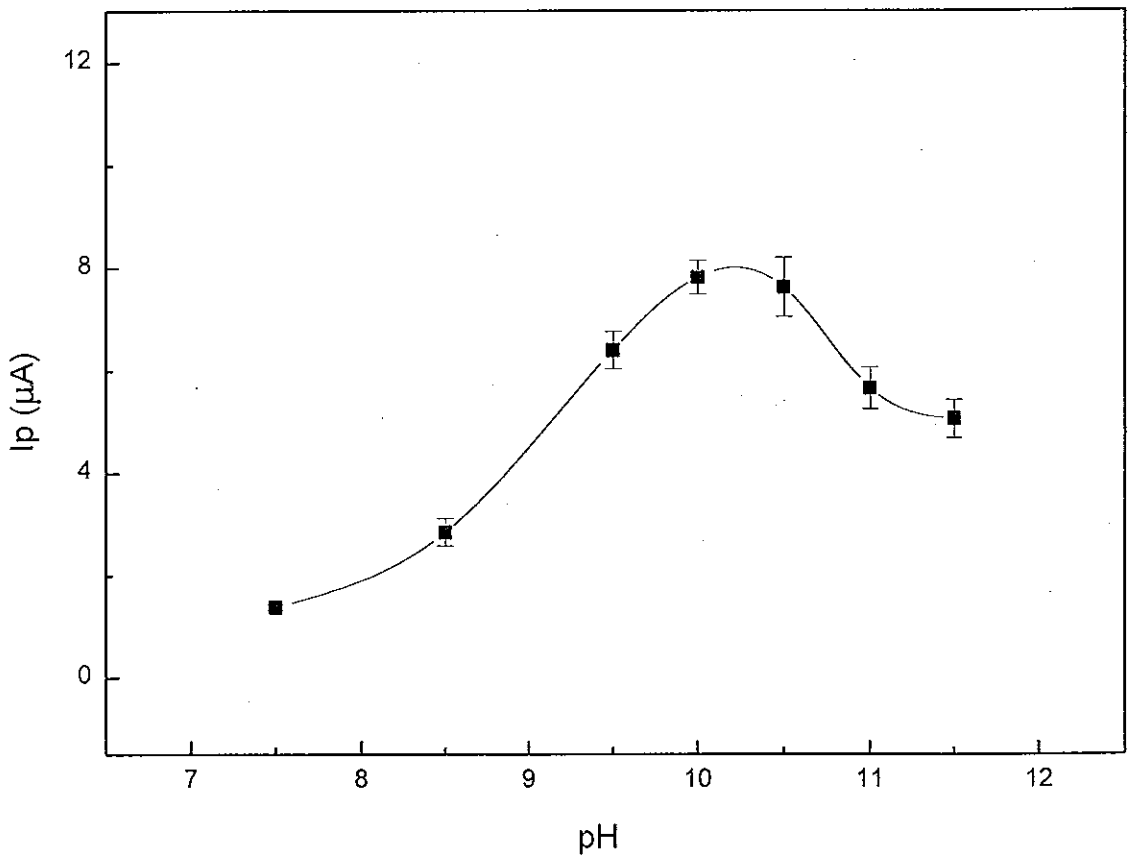

Figure 9. Effect of pH of preconcentration solution on DPASV peak current. Each bar represents mean ± 3 standard deviation. Cadmium(II) concentration: 2×10^{-6} M. Other conditions are as in Figure 7.

Maximum retention was observed at pH 10. Attempts to preconcentrate in more acidic or alkaline media caused a drastic decrease in the voltammetric response. This can readily be explained in terms of the increasing complex formation of cadmium(II) with CPCHA at the electrode surface with increasing pH until the optimum value and the competition of hydroxide formation at exceedingly high pHs (> 10). As a consequence of these observations the remaining study was carried out with pH 10.

One would expect the precipitation of Cd(II) as $Cd(OH)_2$ at such high pH as 10. However, this was not observed in this investigation due to the fact that the Cd(II) solution was spiked into the preconcentration cell just before dipping the electrode in the cell and subsequent stable complex formation of Cd(II) with CPCHA at the electrode surface. It should also be noted that the acetate ions form weak complexes with Cd(II) [93,94] that also prevent the precipitation of $Cd(OH)_2$.

4.3.3. Effect of composition and concentration of supporting electrolyte

The effect of the composition of the supporting electrolyte on the voltammetric measurement of cadmium(II) was investigated using sodium acetate, sodium citrate, ammonium chloride, sodium perchlorate and potassium nitrate solutions of similar pH and concentration (each 0.3 M). The peak current was found in the order: ammonium chloride > sodium acetate > sodium citrate > sodium perchlorate > potassium nitrate. The response was very low in sodium perchlorate and potassium nitrate solutions. This might be explained in terms of unability of the ions of the two salts to supply hydrogen ions required during the electrochemical measurement steps (as shown in the mechanism given in page 41).

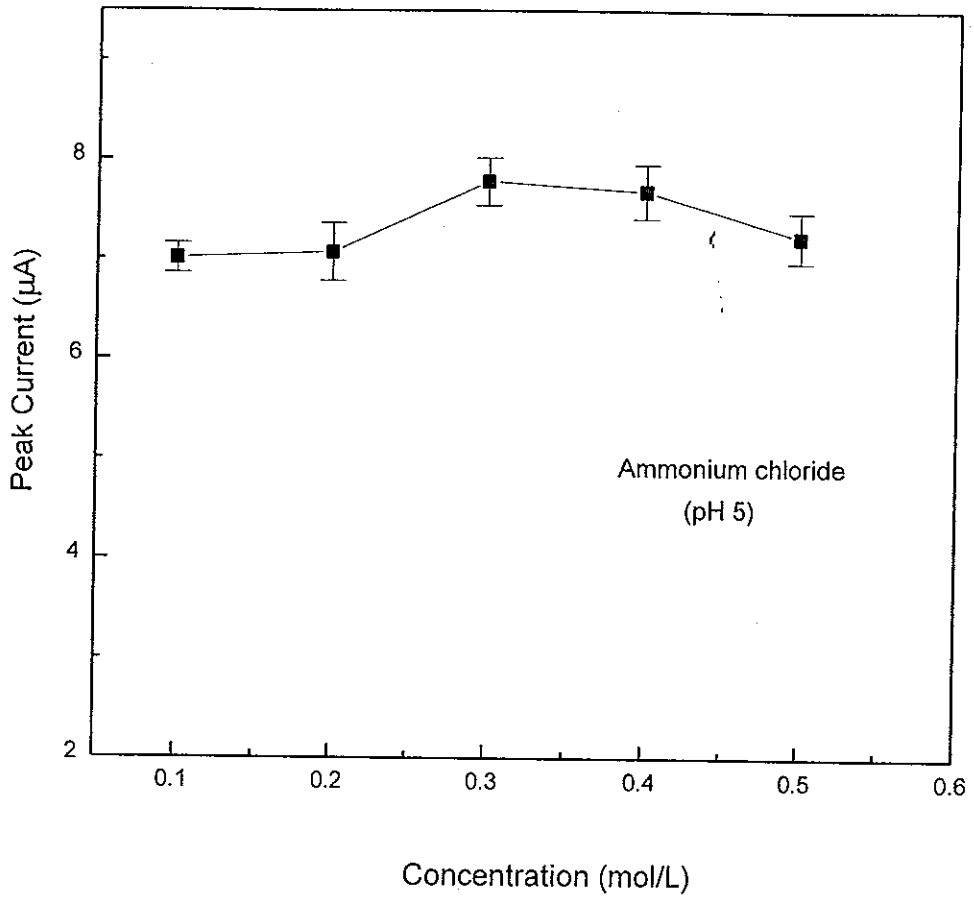

Figure 10. Effect of concentration supporting electrolyte on the voltammetric response. Each bar represents mean ± 3 standard deviation. Other conditions are as in Figure 8.

While the voltammetric response was better in sodium citrate than the former two salts it was lower than that obtained in NaAc and NH_4Cl. This is presumably due to the stable complex forming ability of the citrate ion with Cd(II) [93,94] which would result in leaching of the Cd(II) complexed with CPCHA at the electrode surface before the completion of the reduction step. The peak current observed in NaAc was slightly smaller and some what poor in reproducibility than that in NH_4Cl. This is presumably due to differences in the extent of providing hydrogen ions required for the reduction step (as shown in the above mechanism) and consequently favoring the proceeding stripping step. Ammonium chloride was found to be the most suitable in the stripping

measurement with respect to signal enhancement and reproducibility, peak shape, background stability as well as rapid cadmium removal during surface regeneration. Hence, NH_4Cl solution was chosen as supporting electrolyte in the measurement cell.

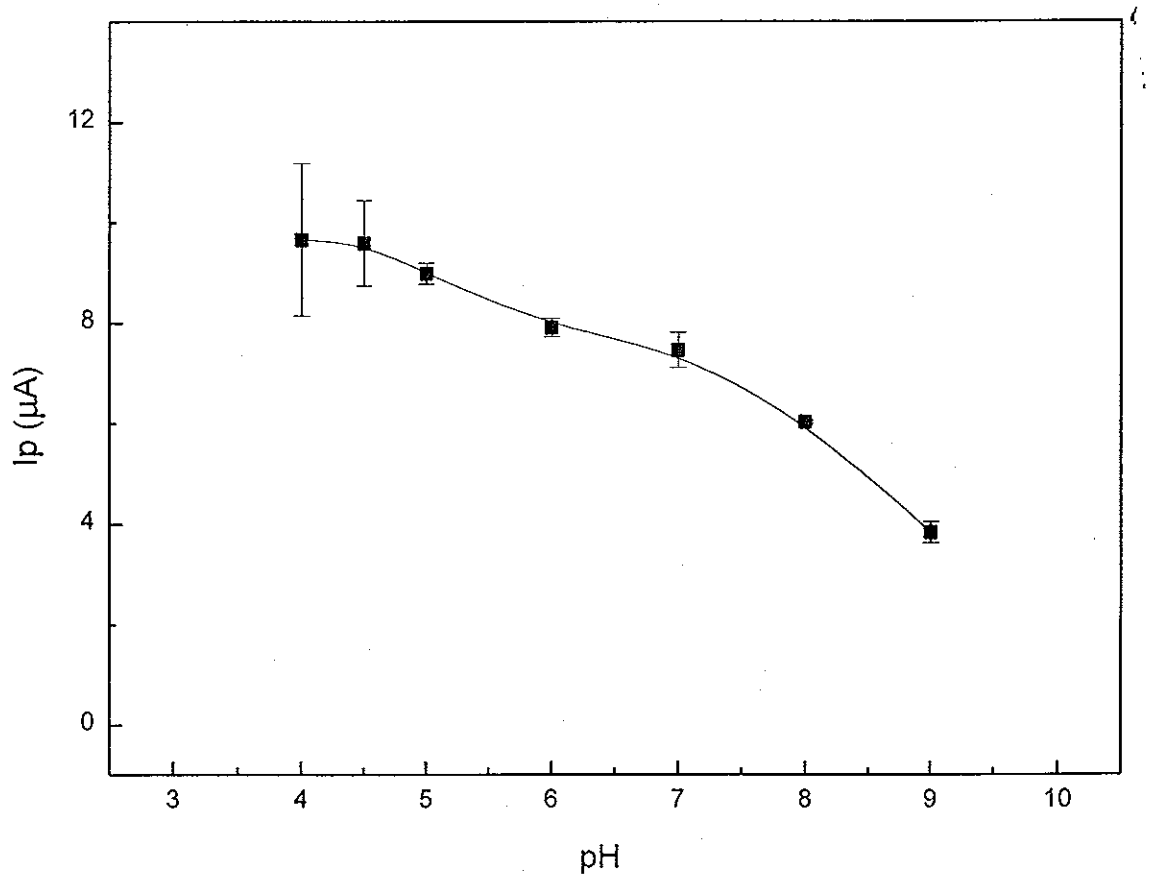

Figure 11. Effect of pH of supporting electrolyte solution on the differential pulse anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Other conditions are as in Figure 9.

The effect of concentration of supporting electrolyte was studied by varying the concentration of NH_4Cl solution between 0.1-0.5 M at constant pH. As shown in Figure 10, concentration of the supporting electrolyte was observed not to have much effect on the current response. A 0.3 M NH_4Cl solution was selected as supporting electrolyte since it gave slightly larger and reproducible peak current.

4.3.4. Effect of pH of supporting electrolyte

The Cd(II) oxidation peak signal also depended on the pH of 0.3 M NH_4Cl solution as evidenced by the results obtained from variation of the pH in the range 4-9. The Cd(II) peak current as a function of pH is shown in Figure 11. Maximum peak currents were observed for pH 4 and 4.5. However, the reproducibility of the signal at these pHs was poor due to the favourable condition for leaching of the accumulated Cd(II) from cadmium(II)-CPCHA complex at the surface of the electrode as soon as medium is exchanged. A relatively higher pH, pH 5, was thus selected as a compromise between sensitivity and reproducibility. The peak current decreased with increasing pH. This is due the fact that the reduction step of Cd(II) at the CME surface involves hydrogen ions (as shown in the mechanism) and thus increasing pH hinders the reduction reaction.

It is evident from the above discussion that the preconcentration and the electrochemical measurement steps require sodium acetate and ammonium chloride solutions of different concentrations and different pH. This clearly shows the necessity to carry out the preconcentration and the electrochemical measurement separately. Accordingly, 0.1 M sodium acetate solution of pH 10 and 0.3 M ammonium chloride solution of pH 5 were used for open-circuit accumulation and voltammetric measurement, respectively.

4.4. Effect of Preconcentration Time

The accumulation time is a decisive factor in any technique dealing with a preconcentration step. The dependence of peak current on the preconcentration time was studied for three different concentrations of Cd(II) under carefully controlled convective conditions. As would be expected, rapid convectional transport during the

accumulation process was essential for a sensitive determination. Figure 12 shows the relation between peak current and accumulation time for three different concentrations of cadmium(II) under identical conditions.

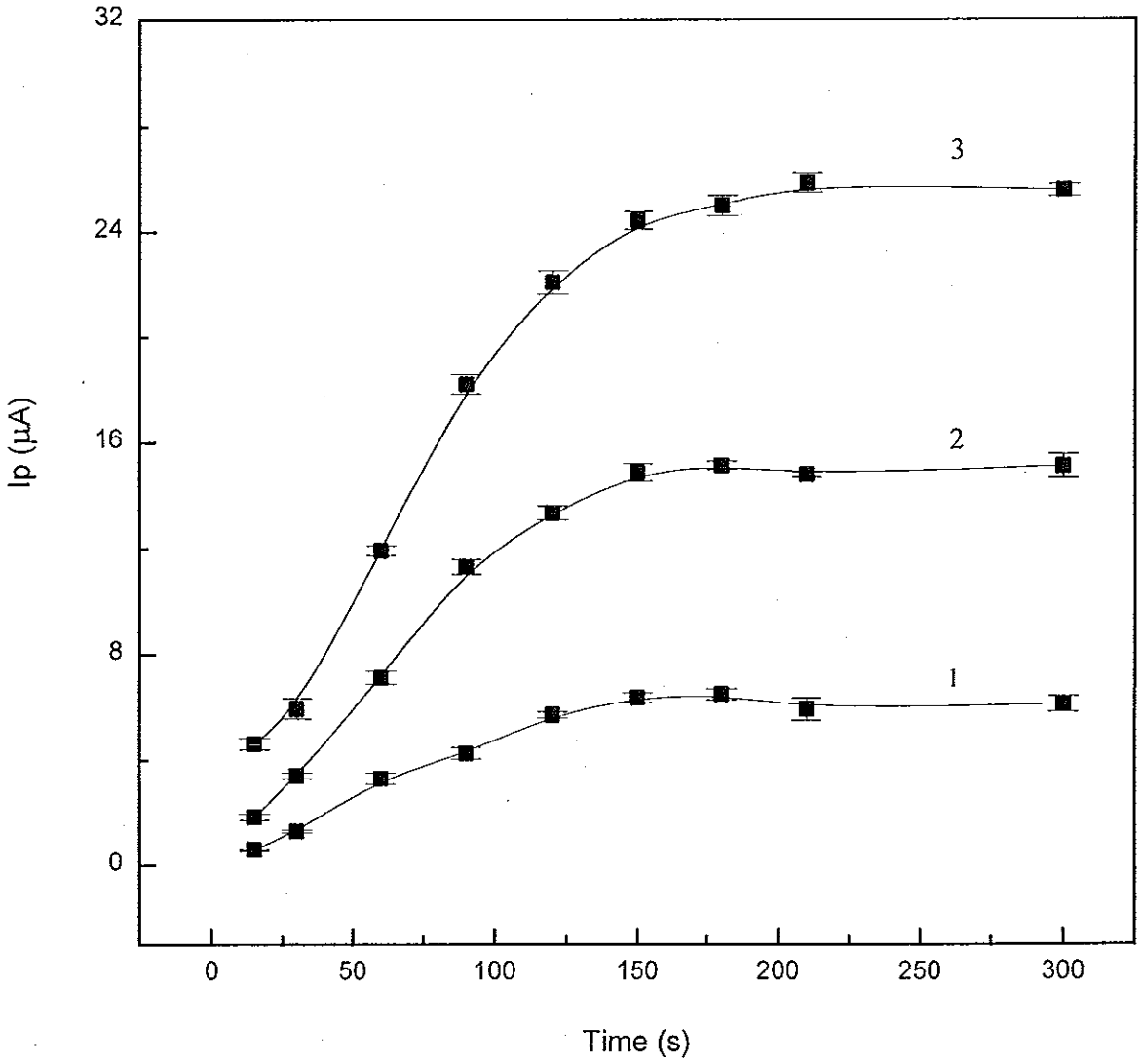

Figure 12. Effect of preconcentration time on the differential pulse anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Cadmium(II) concentration: (1) 2 x 10^{-6} M; (2) 4 x 10^{-6} M; (3) 8 x 10^{-6} M; other conditions are as in Figure 7.

In all cases short preconcentration periods (up to 120 s) yield a quasi-linear and rapid increase in the peak current with an increase in time. Beyond 2 min accumulation

period, the linear portion of the curves soon become leveled off approaching a limiting value. The manifestation of this limiting (steady state) value for the current at longer accumulation periods could originate from attainment of complexation equilibrium between CPCHA at the surface and Cd(II) in solution or saturation of the binding sites (if sufficiently high Cd(II) concentration is used). For each of the concentration employed the steady state peak current value was different; larger values being obtained for higher concentrations of Cd(II). This is due to the fact that the maximum amount of Cd(II)-CPCHA complex that can be accumulated in such prolonged accumulation time is determined by the equilibrium constant for the complexation process.

These profiles of cadmium uptake obtained at different concentrations are well in accord with profiles of similar shapes obtained with a model developed to describe the kinetics and equilibria of the accumulation process in chemically modified carbon paste electrodes [55]. The theoretical relation between the voltammetric current and accumulation time obtained based on such model is given in equation 12.

For higher concentrations a relatively short preconcentration time must be employed to avoid saturation and the subsequent nonlinearity between Cd(II) concentration and peak current. On the other hand, it is possible to enhance the sensitivity of the method by employing extended preconcentration periods for lower concentrations of cadmium(II). As it is evident from the three curves, the accumulation process was relatively rapid, with 80-90% of the equilibrium response generated within the first 2 minutes of exposure. This behaviour is important as it helps to shorten the total analysis time required to determine low concentrations. Based on the kinetics of cadmium uptake observed, 60 and 120 second preconcentration periods were chosen for relatively high ($\geq 2 \times 10^{-7}$ M) and low ($\leq 2 \times 10^{-7}$ M) cadmium(II) concentrations, respectively, as compromise between sufficiently measurable peak current and analysis time.

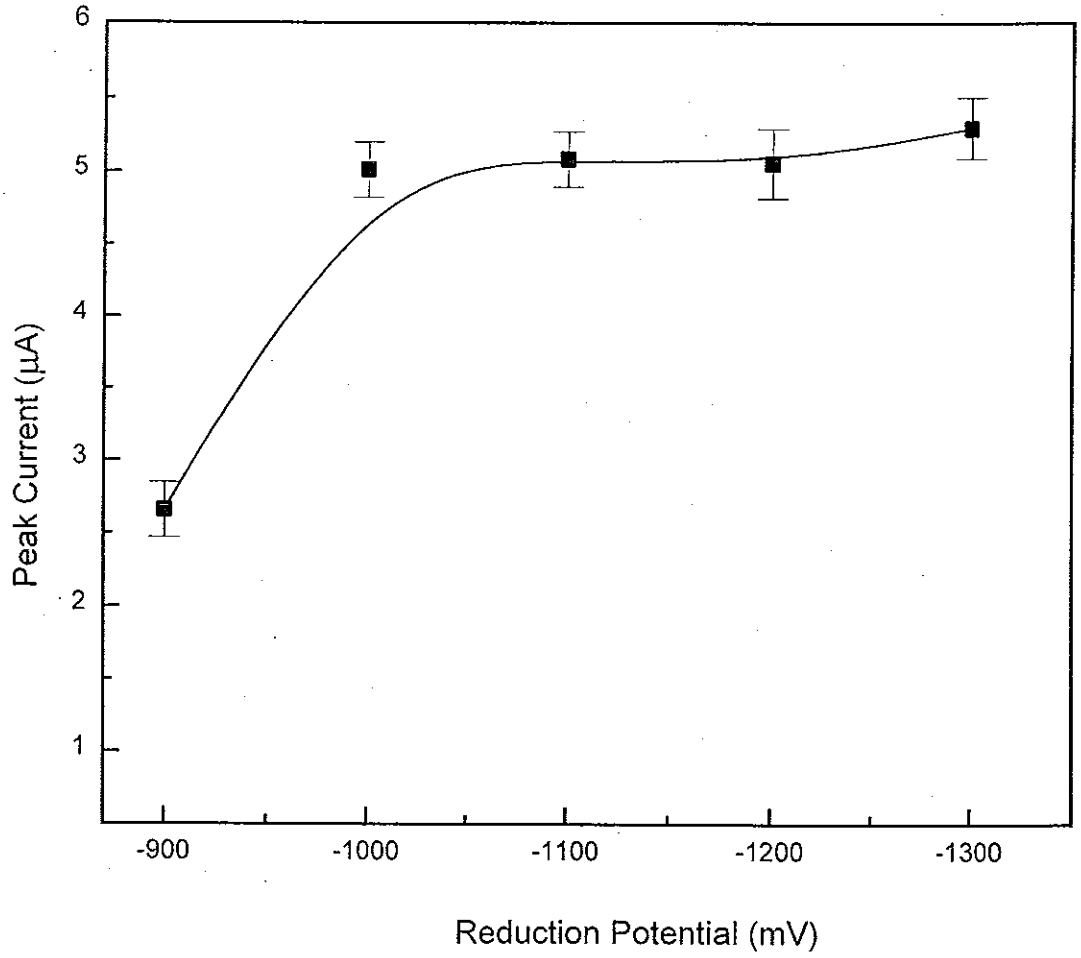

Figure 13. Effect of reduction potential on the voltammetric response. Each bar represents mean ± 3 standard deviation. Cadmium(II) concentration: 4.0×10^{-6} M; Other conditions are as in Figure 7.

4.5. Effect of Instrumental Parameters

4.5.1. Effect of reduction potential and time

The reduction potential (pre-electrolysis potential) is an essential parameter that determines the magnitude of peak height and, thus, the analytical sensitivity. It should have to be sufficiently negative to ensure fast and quantitative reduction of the Cd(II)-CPCHA complex on the electrode surface with only small amount being lost from the

surface by diffusion. The effect of reduction potential on the peak current was investigated in the range -0.9 to -1.3 V (Fig. 13). The peak current appeared starting even from an applied potential of -0.9 V. The peak increased with the reduction potential and reached maximum after -1.0 V. Increasing the reduction potential beyond -1.0 V (in negative sense) led to a steady-state current. Potentials less negative than -1.0 V were incapable of effecting complete reduction of the accumulated Cd(II) as Cd(II)-CPCHA complex. Hence, a reduction potential of -1.1 V was chosen for all subsequent experiments to allow a difference of about 200 mV from the observed peak potential.

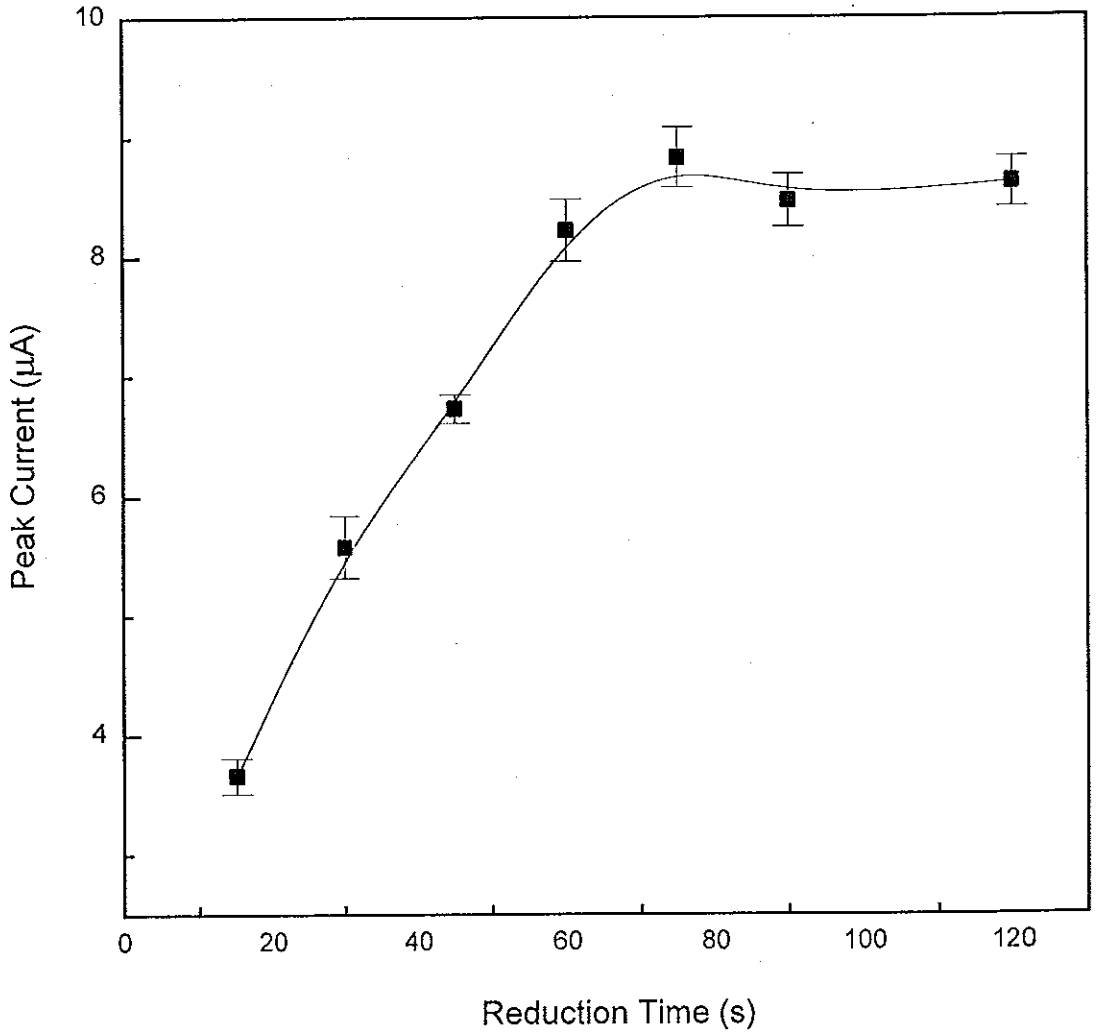

Figure 14. Effect of reduction time on the voltammetric response. Each bar represents mean ± 3 standard deviation. Other conditions are as those given in Figure 13.

The effect of the reduction time on the peak current was studied at fixed reduction potential. The peak current increased at first, and eventually, the steady-state current was reached at the reduction time of 60 s (Fig. 14). No signal enhancement resulted when the deposition time was extended to more than 60 s. Accordingly, a reduction period of 60 s was selected as it is long enough to bring about exhaustive reduction of the Cd(II) taken up in the accumulation step.

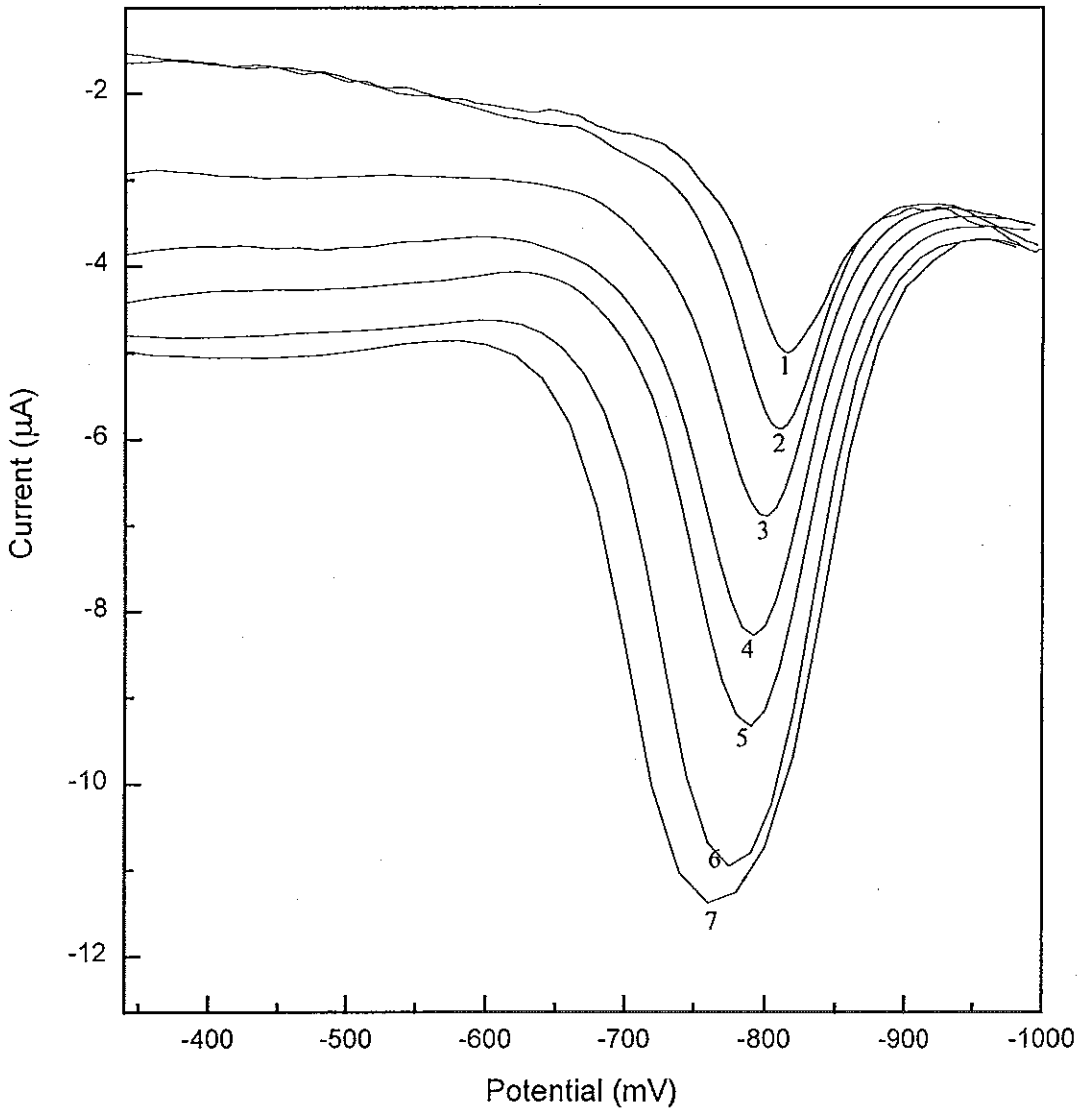

Figure 15. Effect of scan rate on the DPASV response. Scan rate(mV/s): (1) 10 (2) 20 (3) 30 (4) 40 (5) 50 (6) 75 (7) 100. Each bar represents mean $\pm$ 3 standard deviation. Cadmium concentration : 4.0 x 10^{-6} M; Other conditions are as in Figure 7.

4.5.2. Effect of scan rate, pulse amplitude, and pulse period

The effect of scan rate, pulse amplitude and pulse period on the peak current were studied by varying each of them at a time keeping any two of the three parameters constant. The scan rate was varied from 10 to 100 mV/s. The peak current increased and became broader with increasing scan rate (as shown in Fig. 15). A scan rate of 30 mV/s was, thus, chosen for subsequent experiments taking the peak broadening and background distortion into account.

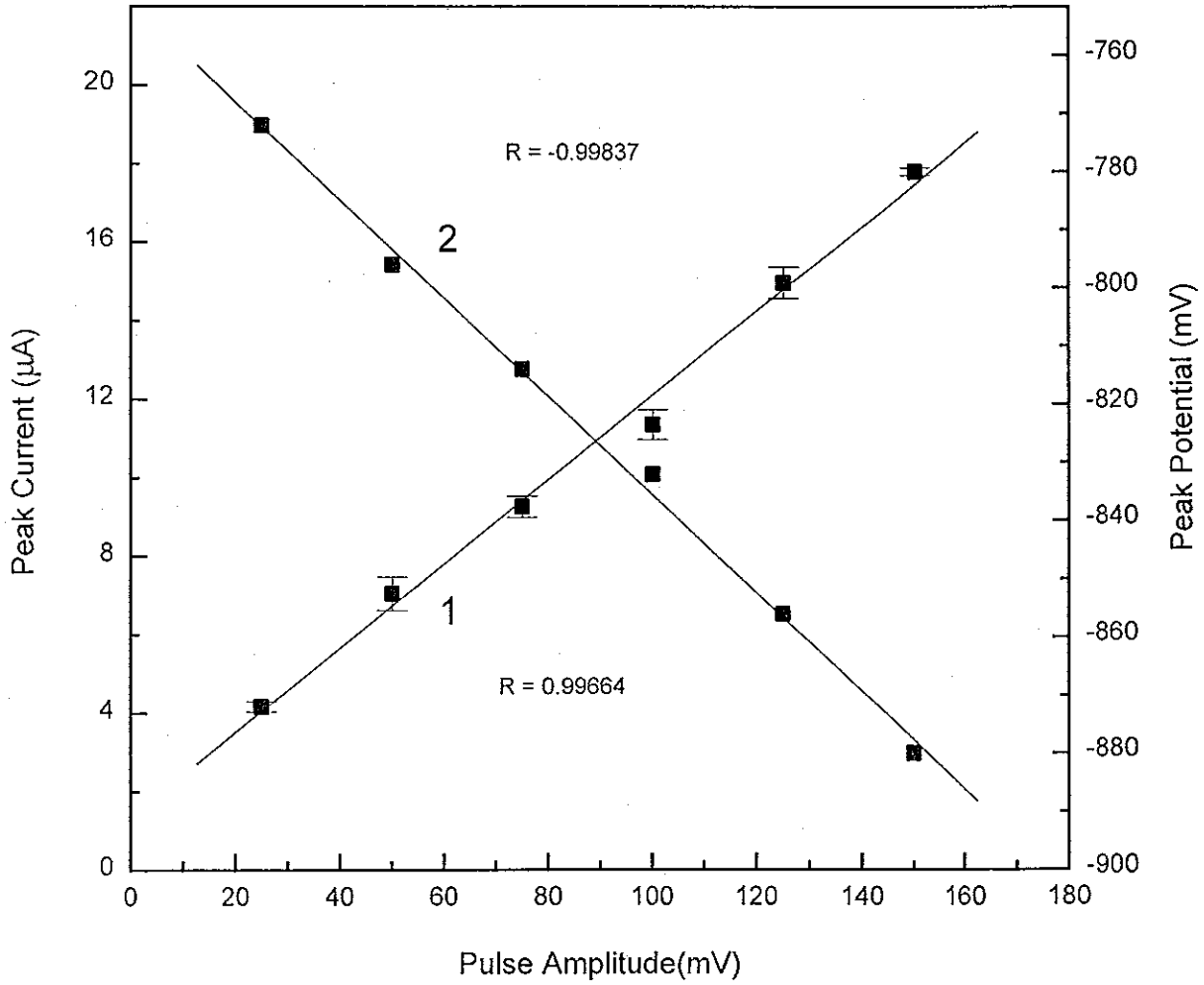

Figure 16. Effect of pulse amplitude on peak current (1) and peak potential (2). Each bar represents mean ± 3 standard deviation. Cd(II) concentration: 4.0×10^{-6} M. Other conditions are as in Figure 7.

A similar pattern of peak current was observed upon increasing the pulse amplitude from 25 to 150 mV, in which the peak current increased linearly accompanied by peak broadening (Fig. 16). A pulse amplitude of 100 mV was chosen for subsequent experiments as a compromise between peak broadening and signal enhancement [51]. Another feature evident from Figure 16 is the effect of pulse amplitude on the peak potential. The peak potential underwent shift towards more negative potentials (cathodic shift) in a linear fashion as the amplitude of the applied pulse increased. This observation is in accord with the relation given in equation 19.

The effect of pulse period on the response obtained is shown in Table 1. The pulse period was varied from 100 to 500 ms. Variation of the pulse period from 100 to 400 ms increased the peak current along with broadening of the peak. At 500 ms the peak was too broad to be defined. Hence, a pulse period of 200 ms was used in all subsequent experiments since it yielded sufficiently high and narrower peak.

Table 1. Effect of Pulse period (other conditions are as in Figure 7)

Pulse period (ms)	Ip ($-\mu$A) for 8×10^{-6} M Cd(II)
100	4.13
200	5.60
300	8.27
400	9.40
500	Too broad to be defined

4.6. Renewal of Electrode

To utilize the electrode for multiple and long-term operation, the regeneration of the reactive functional groups on the electrode surface in reproducible manner is very important. Different chemical and electrochemical cleaning techniques were tested to restore the electrode surface to its pre-accumulation state after each differential pulse voltammetric determination. A 0.01 M EDTA (pH 9) was tested and the observed cleaning efficiency and reproducibility were not that much promising. Repeated and long-term exposure of the electrode were required to remove a significant amount of the cadmium remaining after accumulation and stripping steps. Moreover, there was a gradual decrease in the electrode response on successive runs which was probably caused by adsorption of EDTA molecules on the surface of the electrode. Consequently when the electrode was dipped into the cadmium(II) solution for preconcentration, a water soluble Cd(II)-EDTA complex was formed at the electrode surface.

To decrease the extent of adsorption and in view of better complexation at lower pH [93,94], 0.001 M EDTA (pH 4 and 9) were tried. Though the efficiency was improved, it did not work to the extent needed. On the other hand, electrochemical cleaning via anodizing the electrode at +100 mV for 1 min in the supporting electrolyte (0.3 M NH_4Cl of pH 5) under convective condition was successful in renewing the electrode in that it provided the best cleaning efficiency and reproducibility. After such cleaning, the subsequent voltammetric run gives no peak within the potential range of interest indicating complete removal of any cadmium(II) remaining at the surface after the stripping scan. In case of high concentration ($> 10^{-5}$ M of Cadmium(II)), the regeneration step may be repeated.

Even keeping the electrode in more acidic electrolyte (0.3 M ammonium chloride or sodium acetate of pH 4) was found effective for cleaning the electrode surface but failed to provide reproducible results presumably due to protonation of the modifying ligand at the electrode surface.

Manual resurfacing, that involves removal of thin layer of the surface with spatula and replacement by fresh paste, was applied in cases of physical damage (like cracking or scratching) and electrode spoilage by an interfering species that can not be removed by the usual cleaning scheme. Under normal conditions, a single electrode surface can be used for multiple analytical determinations over several weeks. The electrode with fresh surface gave signals with approximately the same degree of precision (about 5%) as that obtained with the electrode with used surface.

4.7. Optimum Experimental Conditions

The effects of several experimental parameters have been studied to obtain optimum conditions for the differential pulse anodic stripping voltammetric (DPASV) determination of cadmium(II) at *N*-p-chlorophenylcinnamohydroxamic acid modified carbon paste electrode. The selected optimum conditions are summarized in Table 2.

4.8. Analytical Figures of Merit: Linear Range, Detection Limit, and Precision

The analytical utility of a given procedure depends on achieving a well defined concentration dependence. The dependence of the signal on concentration of Cd(II) and inherent sensitivity of the method are illustrated by the differential pulse anodic stripping voltammograms at different concentrations of Cd(II) (Fig. 17 and 18). The peak current was found to be directly proportional to the bulk concentration of cadmium(II).

Table 2. Optimum experimental conditions for the determination of Cd(II) by DPASV.

Parameters studied	Optimum values obtained
Composition of modifier in CPE	10%
pH of preconcentration solution	10
Conc. of preconcentration solution	0.1 M NaAc
Preconcentration time	120 s for $< 2 \times 10^{-7}$ M and 60 s for $> 2 \times 10^{-7}$ M $[Cd^{2+}]$
pH of supporting electrolyte	5
Concentration of supporting electrolyte	0.3 M NH_4Cl
Reduction potential	- 1.1 V
Reduction time	60 s
Scan rate	30 mV/s
Pulse amplitude	100 mV
Pulse period	200 ms

Under the optimum experimental conditions two linear ranges were found using two different accumulation times. The response was found to be linear in the concentration ranges 2×10^{-7} - 3.2×10^{-6} M Cd(II) ($r = 0.999$) at 1 min preconcentration and 4×10^{-8} - 1.6×10^{-7} M Cd(II) ($r = 0.999$) at 2 min preconcentration. Linearity prevails as long as linear isotherm conditions (i.e. low surface coverage by Cd(II)) exists. At higher concentrations ($> 4.0 \times 10^{-6}$ M Cd(II) and/or longer preconcentration times > 2 min) deviations from linearity were observed as expected from the nature of the preconcentration process (i.e. saturation of the accessible binding sites on the electrode surface). This saturation effect is typical for chemically modified electrodes where limited number of functional groups are available at the surface.

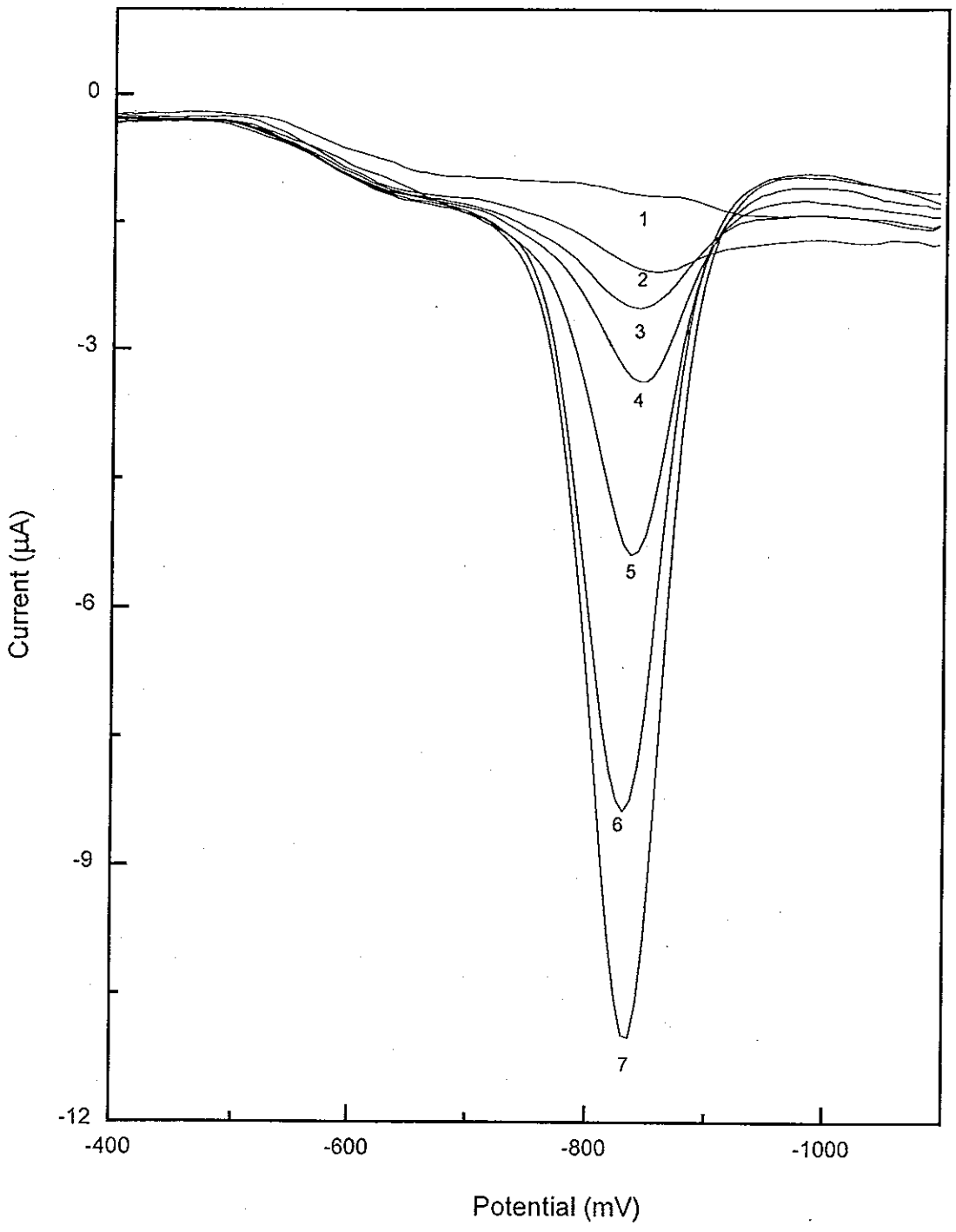

Figure 17. Differential pulse anodic stripping voltammograms of cadmium(II) accumulated at CPCHA modified CPE. Cadmium(II) concentration: (1) 0.0 M; (2) 1.0 x 10^{-7} M; (3) 4.0 x 10^{-7} M; (4) 8 x 10^{-7} M; (5) 1.6 x 10^{-6} M; (6) 3.2 x 10^{-6} M, (7) 4 x 10^{-6} M; preconcentration time: 1 min; other conditions are as in Figure 7.

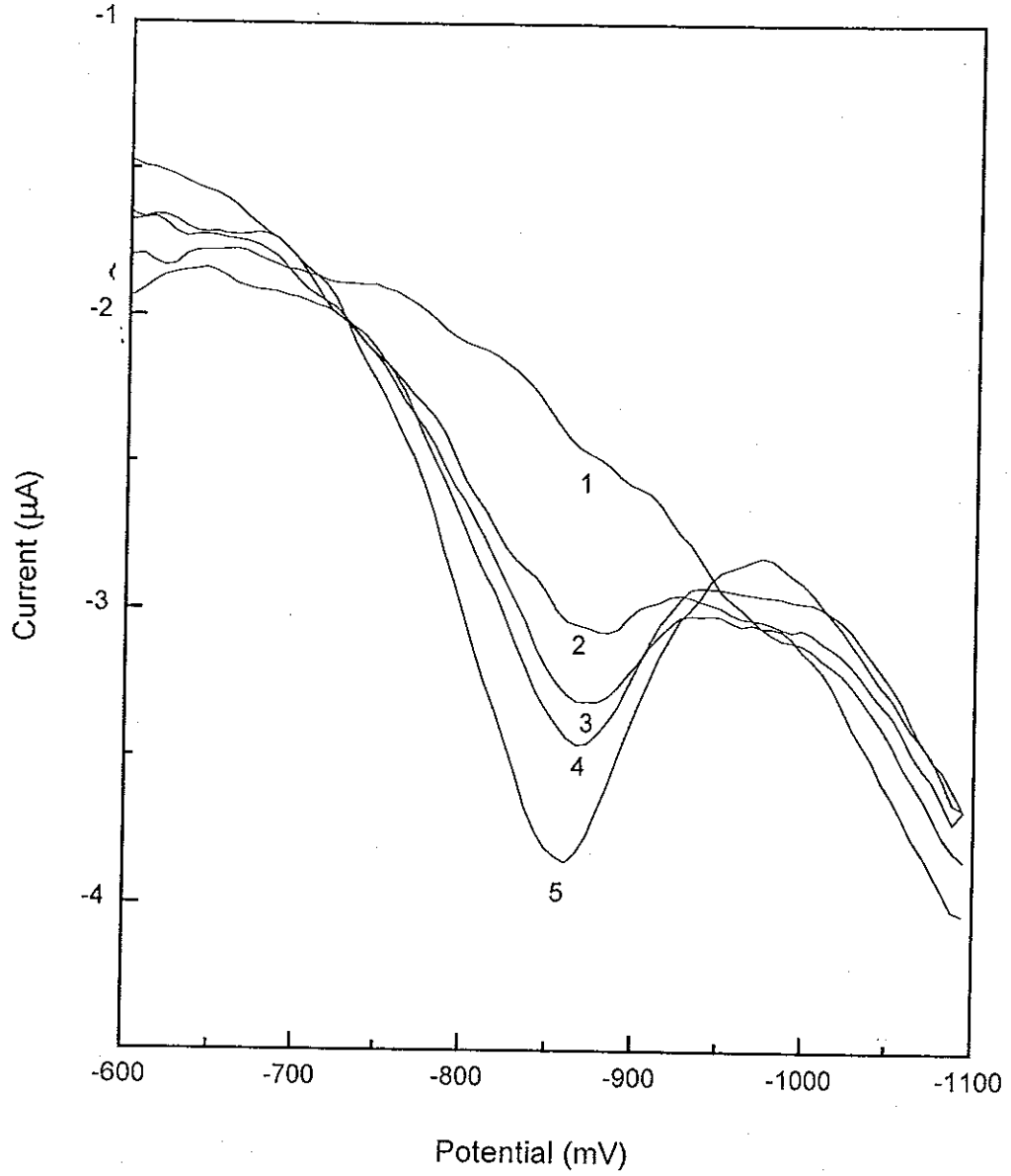

Figure 18. Differential pulse anodic stripping voltammograms of cadmium(II) accumulated at CPCHA modified carbon paste electrode. Cd(II) concentration: (1) 0.0 M; (2) 4.0 x 10^{-8} M; (3) 8.0 x 10^{-8} M; (4) 1.0 x 10^{-7} M; (5) 2.0 x 10^{-7} M; preconcentration time: 2 min; other conditions are as in Figure 7.

The detection limit (concentration equal to three times the standard deviation of peak current for six determination of 4 x 10^{-8} M Cd(II) with 2 min preconcentration time [95]) was found to be 9.8 x 10^{-9} M Cd(II), which corresponds to 1.1 ppb of cadmium.

The effective cleaning and reproducible preconcentration were illustrated by the precision obtained during repetitive determinations with two representative concentrations. The relative standard deviations were found to be 5.50% and 2.58% for six successive determinations of 8×10^{-8} M and 1×10^{-6} M Cd(II), respectively. The initial preconditioning scheme is also essential for achieving such precision. Slight variations in the peak current (about 5%) were observed for different batches of the electrode containing the same amount of CPCHA modified carbon paste. Thus, the preparation of new calibration curves is recommended each time a new surface is used.

Upon examination of the performance of the chemically modified electrode over several cycles of cadmium determination it became apparent that virgin chemically modified electrode surfaces were somewhat less efficient for cadmium uptake than surfaces that had been previously exposed to cadmium. The reason for this behaviour has not yet been determined with certainty. However it was hypothesized that, given the preference of geometry of the complex formed, one of the functions of the early accumulation cycles might be to assist the ligand molecules (initially oriented randomly in the carbon paste) attain a degree of ordering on the surface thereby facilitating complexation with the specific metal ion of interest.

4.9. Effects of Other Ions

Although high sensitivity is the dominant requirement for any analytical method it must be accompanied by high selectivity as well. The most significant capability of CMCPE is the possibility that the modifier-analyte interaction can be used to enhance selectivity. The selectivity achieved in this manner is also further strengthened by the medium exchange following the accumulation of analyte at open circuit condition. In general, the voltammetric signal may be affected by overlapping response of the analyte and

interferant or by competition between the two for binding sites, or by both phenomena. Non accumulated ions will have no effect on the determination because of the use of medium exchange procedure.

Table 3. Change in DPASV peak current of 2 x 10^{-6} M Cd(II) in presence of other ions (optimum conditions)

Interfering ion	Added as	Concentration (M)	Change in current (%)
F^-	NaF	2 x 10^{-3}	-1.69
ClO_4^-	$NaClO_4$	2 x 10^{-3}	-2.23
NO_3^-	$NaNO_3$	2 x 10^{-3}	+7.45
K^+	KNO_3	2 x 10^{-4}	-4.23
Li^+	$LiNO_3$	2 x 10^{-4}	-7.78
NH_4^+	NH_4NO_3	2 x 10^{-4}	-1.36
Mg^{2+}	$Mg(NO_3)_2$	2 x 10^{-4}	+4.64
Ca^{2+}	$Ca(NO_3)_2$	2 x 10^{-4}	+7.80
Sr^{2+}	$Sr(NO_3)_2$	2 x 10^{-4}	-1.59
Ba^{2+}	$Ba(NO_3)_2$	2 x 10^{-4}	-5.14
Tl^+	$TlNO_3$	2 x 10^{-4}	-4.56
As^{3+}	$As(NO_3)_3$	2 x 10^{-4}	-5.26
VO_3^-	NH_4VO_3	2 x 10^{-4}	+3.00
WO_4^{2-}	Na_2WO_4	2 x 10^{-4}	-2.28
SO_4^{2-}	Na_2SO_4	2 x 10^{-4}	-2.14
Cl^-	NaCl	2 x 10^{-4}	-4.10
I^-	NaI	2 x 10^{-4}	-3.28
CO_3^{2-}	K_2CO_3	2 x 10^{-4}	-2.02
$C_2O_4^{2-}$	$Na_2C_2O_4$	2 x 10^{-4}	-0.75
SCN^-	NH_4SCN	4 x 10^{-5}	-2.18
Al^{3+}	$Al(NO_3)_3$	2 x 10^{-5}	+2.75

Hg^{2+}	$HgSO_4$	2×10^{-5}	+1.90
Sn^{2+}	$SnCl_2$	2×10^{-5}	-4.46
MoO_4^{2-}	$(NH_4)_2MoO_4$	2×10^{-5}	-3.53
Bi^{3+}	$Bi(NO_3)_3$	1×10^{-5}	-7.72
Mn^{2+}	$MnSO_4$	1×10^{-5}	-2.16
PO_4^{3-}	NaH_2PO_4	1×10^{-5}	-4.19
Ce^{4+}	$Ce(SO_4)_2$	4×10^{-6}	-6.33
La^{3+}	$La(NO_3)_3$	4×10^{-6}	-6.25
Y^{3+}	$Y(NO_3)_3$	4×10^{-6}	-0.20
UO_2^{2+}	$UO_2(NO_3)_2$	4×10^{-6}	-0.51
Au^{3+}	$AuCl_3$	2×10^{-6}	-9.31
Zn^{2+}	$Zn(NO_3)_2$	2×10^{-6}	-6.88
Fe^{3+}	$Fe(NO_3)_3$	2×10^{-6}	-1.97
Co^{2+}	$Co(NO_3)_2$	2×10^{-6}	-11.70
Ni^{2+}	$Ni(NO_3)_2$	1×10^{-6}	-3.07
Cu^{2+}	$Cu(NO_3)_2$	1×10^{-6}	-20.40
Pb^{2+}	$Pb(NO_3)_2$	2×10^{-6}	-24.51

Coexisting metal ions (whether electroactive or not) can interfere with the determination of Cd(II) if they are capable of competing for the binding sites on the electrode surface. Anions which are capable of forming sufficiently stable complexes with the metal ion of interest can interfere as well. In this view, the effect of various common ions were evaluated with respect to their interference in the determination of cadmium(II) by adding appropriate amounts of metal ions and anions to 25 mL of solution containing 2×10^{-6} M Cd(II) sample solutions during preconcentration.

The influence of ions, present in the analyte solution at different concentrations, on the current response of Cd(II) is shown in Table 3. Most of the ions studied have only little

effect on the determination of Cd(II). As can be seen from the table, several ions such as F^-, ClO_4^-, and NO_3^- (up to 1000-fold molar excess); K^+, Li^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+},Tl^+, As^{3+}, VO_3^-, WO_4^{2-}, SO_4^{2-}, Cl^-, I^-, CO_3^{2-}, and $C_2O_4^{2-}$, (up to 100-fold molar excess); SCN^- (up to 20-fold molar excess); Al^{3+}, Hg^{2+}, Sn^{2+}, and MoO_4^{2-} (10-fold molar excess); Bi^{3+}, Mn^{2+}, and PO_4^{3-} (5-fold molar excess); Ce^{4+}, La^{3+}, Y^{3+}, and UO_2^{2+} (2-fold molar excess); Au^{3+}, Zn^{2+}, Fe^{3+}, and Co^{2+} (equi-molar) have only negligible effect on the determination of Cd(II). However, equal amount of Cr(III), Pb(II), and Cu(II) interfere significantly by suppressing the Cd(II) signal, because they form complexes with CPCHA and prevent the complex formation and accumulation of Cd(II) at the electrode surface. These interferences are expected on the basis of the previous selectivity studies [76.77], as the mentioned metal ions were observed to preferentially bound over cadmium(II) and might in fact displaced any Cd(II) that had already been complexed to CPCHA at the electrode surface. Although these ions interfered in the determination of cadmium(II), they did not spoil the electrode at all (the electrode was regenerated by the normal cleaning procedure).

The influence of weakly interfering ions can easily be eliminated by applying the standard addition method for evaluation of the concentration of cadmium(II) within the range of linear proportionality as it is a convenient way to avoid such matrix effect. This has been examined by determining cadmium(II) in three different synthetic matrices composed of weakly interfering ions. Matrix A is of similar compositions to that of water samples [12] and matrices B and C represent mixed oxides of cadmium (and their mixtures) used as semiconductors [14]. The results are given in Table 4. These results, which show good correlation between the added and found concentration of cadmium(II), clearly demonstrate that cadmium(II) can be determined reliably in the presence of weakly interfering ions.

Table 4. Determination of cadmium(II) in synthetic matrices

Matrix	Composition	Cd(II) found*
A	2×10^{-6} M Cd(II) + 2×10^{-4} M Mg(II) + 2×10^{-4} M Ca(II) + 2×10^{-4} M Sr(II) + 2×10^{-4} M Ba(II) + 2×10^{-4} M K(I) + 2×10^{-4} M Li(I)	$(1.92 \pm 0.09) \times 10^{-6}$ M
B	1×10^{-6} M Cd(II) + 2×10^{-6} M Fe(III) + 2×10^{-6} M Al(III) + 2×10^{-6} M As(III) + 2×10^{-6} M Mn(II)	$(0.94 \pm 0.10) \times 10^{-6}$ M
C	1×10^{-6} M Cd(II) + 2×10^{-5} M W(VI) + 2×10^{-5} M Mo(VI) + 2×10^{-5} M Ba(II) + 2×10^{-5} M Sn(II)	$(0.96 \pm 0.08) \times 10^{-6}$ M

*Mean ± 95% confidence limits of triplicate analysis.

4.10. Analytical Applications

The adequacy of the analytical procedure described above for the determination of trace amount of cadmium was assessed by the determination of cadmium in municipal drinking water from Addis Ababa (Ethiopia) and natural mineral water from Ambo (Ethiopia). Both water samples did not show any peak of cadmium(II). Hence the water samples were spiked with known concentrations of cadmium(II) at trace levels. The concentrations of cadmium in the water samples were determined by standard addition method. The differential pulse anodic stripping voltammograms that were recorded after each addition and the standard addition curve are shown in Figure 19. To certify the reliability of the analytical method, the cadmium(II) spiked water samples were also

analyzed by flame atomic absorption spectrometry. The results obtained with the voltammetric method and atomic absorption spectrometry are given in Table 5. The agreement between the two independent methods confirms the validity of the proposed method for cadmium analysis in water samples.

Table 5. Determination of cadmium(II) in water samples

Water sample	Cd(II) added to water sample (mg/L)	Cd(II) found* by DPASV (mg/L)	Cd(II) found* by AAS (mg/L)
Municipal water	0.112	0.110 ± 0.017	0.104 ± 0.018
Municipal water	0.056	0.056 ± 0.028	0.057 ± 0.022
Mineral water	0.112	0.119 ± 0.016	0.106 ± 0.024

*Mean ± 95% confidence limits of triplicate analysis.

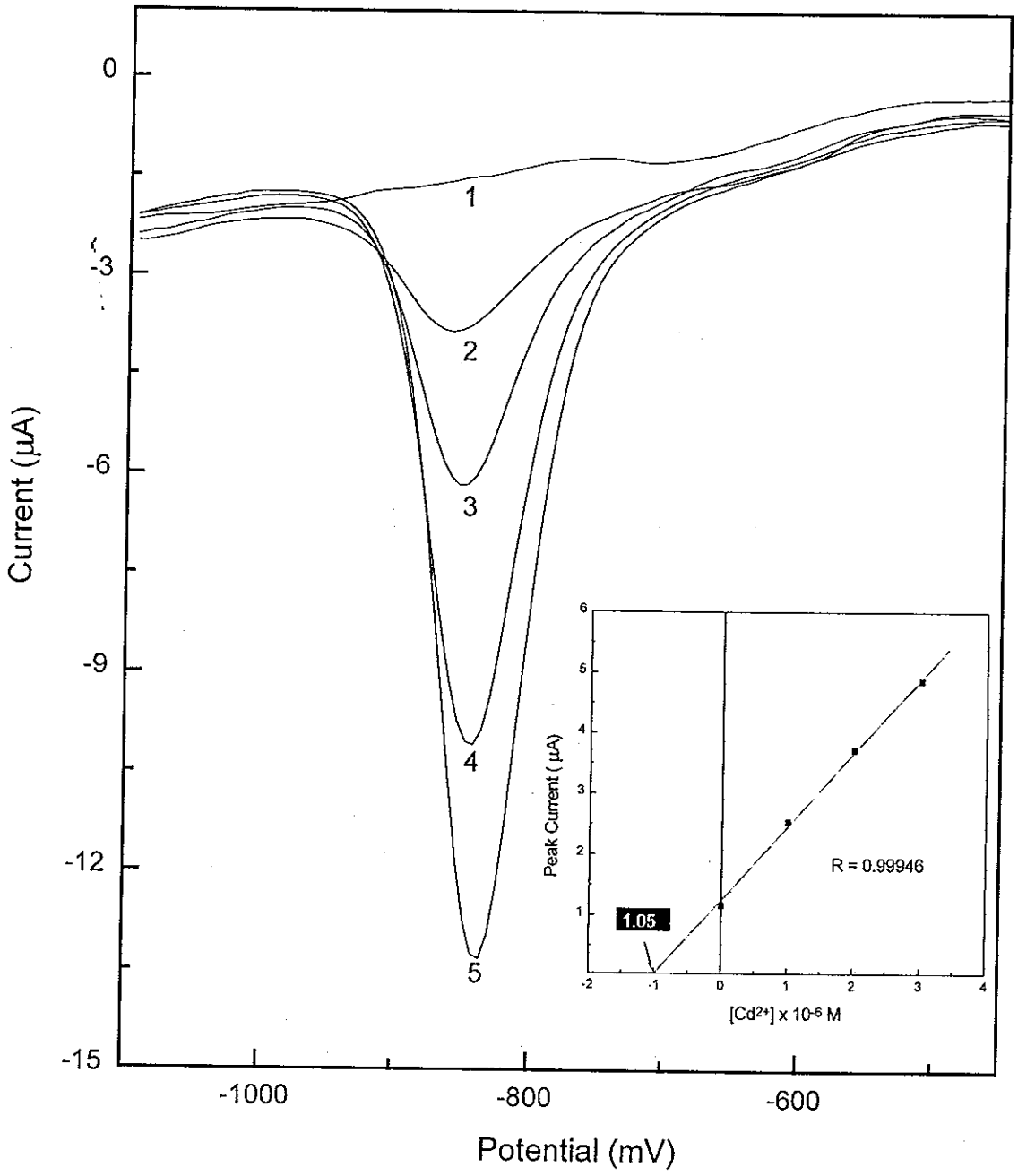

Figure 19. Differential pulse anodic stripping voltammograms and standard addition curve for the determination of cadmium in Ambo mineral water. (1) 0.1 M sodium acetate prepared in Ambo; (2) 0.1 M sodium acetate prepared in Ambo water spiked with known concentration of cadmium(II) to make its concentration 1.0 x 10^{-6} M; and after addition of: (3) 1 x 10^{-6} M; (4) 2 x 10^{-6} M; and (5) 3 x 10^{-6} M cadmium(II) to the simulated unknown described in (2). Other conditions are as of the optimal conditions.

5. CONCLUSION

This work demonstrates that *N*-p- chlorophenylcinnamohydroxamic acid (CPCHA) is an appropriate carbon paste electrode modifier for use in conjunction with the preconcentration/voltammetric measurement technique for the determination of cadmium(II). The CMCPE showed good stability, sensitivity, reasonable selectivity, and ability to be easily generated. The method provides attractive features compared to those reported earlier [60-63] such as capability to be easily generated, simplicity of electrode preparation, high stability, shorter analysis time, and the use of nondearated solution. As there is no leaching of the electrode, a single electrode surface can be used for multiple analytical determinations over several weeks. Therefore, the method presented can be considered as a reasonable alternative to other electroanalytical and AAS methods to determine Cd(II) at trace levels. The proposed is reliable and the method can be applied for on-site analysis of municipal and mineral water samples for cadmium.

6. REFERENCES

1. *The New Encyclopedia Britannica*, 15th Ed., Vol 2, Encyclopedia Britannica, Chicago, **1995**.
2. A. Wild, *Soils and the Environment*, Cambridge University Press, Cambridge, **1995**.
3. A. Steinberger, in *Handbook of Hazardous Materials* , M. Corn, ed., Academic Press, San Diego, **1993**.
4. W. Hague, in *McGraw-Hill Encyclopedia of Science and Technology*, 7th Ed., McGraw-Hill, New York, **1992**.
5. G.F. Liptrot, *Modern Inorganic Chemistry*, 4th Ed., CollinsEducational, London, **1983**.
6. I.O, Oladeji, L. Chow, *J. Electrochem. Soc.* ,**1997**, 144, 2342-46.
7. *Encyclopedia of Inorganic Chemistry*, R. B. King , ed., John Wiley, Chichester, **1995**.
8. P.J. Craig, *Organometallic Compounds in the Environment: Principles and Reactions*, Wiley, New York, **1986**.
9. R.M., Harrison, *Pollution: Causes, Effects and Control*, 2nd Ed., The Royal Society of Chemistry, Cambridge, **1995**.
10. D.J.H. Phillips, P.S. Rainbow, *Biomonitoring of Trace Aquatic Contaminants*, Chapman and Hall, London, **1994**.
11. P.H. Walton, in *Chemistry of Waste Minimization*, Chapter 14, J. Clark, ed., Blackie, London, **1995**.
12. P. O'Neill, *Environmental Chemistry*, 2nd Ed., Chapman and Hall, London, **1995**.
13. M.B. McBride, *Environmental Chemistry of Soils*, Oxford University Press, New York, **1994**.

14. J.C. Bailor, H.J. Emeleus, R. Nyholm, A.F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon, Oxford, **1975.**

15. S.E. Manhahan, *Hazardous Waste Chemistry, Toxicology and Treatment*, Lewis Publishers, Michigan, **1990.**

16. V. Valković, *Trace Analysis*, Taylor and Francis, London, **1975.**

17. T.P. Coultate, *Food: The Chemistry of Its Components*, 2nd Ed., The Royal Society of Chemistry, Cambridge, **1990.**

18. A. Avdeef, F. Hartenstein, A.R. Chemotti, Jr., J.A. Brown, *J. Inorg. Chem.*, **1992,** 31, 3701.

19. S.R. Radel, *Chemistry*, 2nd Ed., M.H.Navidi, West minneapolis/St. Paul, **1994.**

20. W.N. Aldridge in *Experimental Toxicology, The Basic Issues*, 2nd Ed., Chapter 5, D. Anderson, D.M. Conning, Eds., Royal Society of Chemistry, Cambridge, **1993.**

21. R.M. Harrison, S.J. deMora, *Introductory Chemistry for Environmental Sciences*, 2nd Ed., Cambridge University Press, Cambridge, **1996.**

22. G. Svehla, *Vogel's Quantitative Inorganic Analysis*, 7th Ed., Longman, **1996.**

23. F. Feigl, V. Anger, R. Oesper, *Spot Tests in Inorganic Analysis*, Elsevier, New York, **1972.**

24. J.J. Lingane, *Analytical Chemistry of Selected Metallic Elements*, Reinhold, New York, **1966.**

25. L. Erdey, *Gravimetric Analysis*, Part II, Pergamon, Oxford, **1965.**

26. H.A. Flaschka, *EDTA TItrations, An Introduction to Theory and Practice*, 2nd Ed., Pergamon, Oxford, **1967.**

27. G. Charlot, D. Bézier, *Quantitative Inorganic Analysis*, Methuen, New York, **1957.**

28. P.L. Bailey, *Analysis with Ion-Selective Electrodes*, Heyden, London, **1980.**

29. J.W. Ross, M.S. Frant, *Anal Chem.*, **1969**,41,1900.

30. E.B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, London, **1959**.

31. I. Vogel, *A Text-Book of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, Green, **1961**.

32. G.D. Christian, F.J. Feldman, R.E. Krieger, *Atomic absorption Spectroscopy, Applications in Agriculture, Biology, and Medicine*, New York, **1979**.

33. J.C. Van Loon, *Analytical Atomic Absorption Spectroscopy*, Academic Press, **1980**.

34. B. Welz, *Atomic Absorption Spectroscopy*, Verlag Chemie, Weinheim, **1976**.

35. I.S. Krull, in *Liquid Chromatography in Environmental Analysis*, Chapter 5, J.F. Lawrence, ed., Humana, Clifton, **1984**.

36. J. Heyrovský, P. Zuman, *Practical Polarography*, Academic Press, London, **1968**.

37. F. Vydra, K. Stulik, E. Julakova, *Electrochemical Stripping Analysis*, Ellis Horwood, Chichester, **1976**.

38. G.D. Christian, *J. Electroanal.Chem.* **1969**, 23,1.

39. C.M.G. Van den Berg, *J. Electroanal. Chem.*, **1986**, 215, 111.

40. C. Li, B.D. James, J. Rumble, R.J. Magee, *Mickrochim. Acta (Wien)*, **1988**, III, 175.

41. E.N. Iliadou, S.T. Girousi, U.Dietze, M. Otto, A.N. Voulgaropoulos, C.G. Papadopoulos, , *Analyst*, **1997**, 122, 597.

42. K. Kalcher, *Electroanalysis*, **1990**, 2, 419.

43. K. Kalcher, J.M. Kauffmann, J. Wang, I. Švancara, K. Vytřas, C. Neuhold, Z. Yang, *Electroanalysis*, **1995**, 7, 5.

44. R.N. Adams, *Anal Chem.* **1958**, 30, 1576.

45. C. Urbaniczky, K. Lundstrom, *J. Electroanal. Chem.*, **1984**, 176, 169.

46. M. Rice, Z. Galus, R.N. Adams, *J. Electroanal. Chem.*, **1983**, 143, 89.

47. T. Kuwana, W.G. French, *Anal. Chem.* **1964**, 36, 241.

48. F.A. Schultz, T. Kuwana, *J. Electroanal. Chem.*, **1965**,10, 95.

49. P.R. Moses, P. Wier, R.W. Murray, *Anal. Chem*, **1975**, 47, 1882.

50. C. Talaber, K. Kalcher, G. Golbl, G. Raber, X.Cai, *Sci.Int. (Lahore)*, **1992**, 4(4), 347.

51. J. Wang, *Analytical Electrochemistry*, VCH Publishers, New York, **1994**.

52. K. Ravichandran, R.P. Baldwin, *J. Electroanal. Chem.*, **1981**, 126, 293.

53. Z. Gao, P. Li, Z. Zhao, *F. J. Anal. Chem.*, **1991**, 339, 137.

54. M.F.B., Sousa, R. Bertazzol, *Anal. Chem.*, **1996**, 68, 1258.

55. K. Kalcher, I. Grabec, G. Raber, X. Cai, G. Tavcar, B. Ogorevc, *J. Electroanal. Chem.*, **1995**, 386, 149.

56. J.C. C. Villar, A.C. Garcia, P.T. Blanko, *Talanta*, **1993**, 40, 325-31.

57. J. Wang, J. Lu, D.D. Larson, K. Olsen, *Electroanalysis*, **1995**, 7, 247.

58. R.W. Murray, in *Electroanalytical Chemistry*, Vol. 13, A.J. Bard, ed., Marcel Dekker, New York, **1984**.

59. P.T. Kissinger, W.R. Heimeman, *Laboratory Techniques In Electroanalytical Chemistry*, 2nd Ed., Marcel Dekker, New York, **1996**.

60. L. Hernandez, P. Hernandez, M.H. Blanco, M. Sanchez, *Analyst*, **1989**, 114, 397.

61. R. Agraz, M.T. Sevilla, J.M. Pinilla, L. Hernandez, *Electroanalysis*, **1991**, 3, 393.

62. C. Bing, L. Kryger, *Talanta*, **1996**, 43, 153.

63. S.-S. Huang, Y.-D Cheng, B.-F. Li, G.-D. Liu, *Mickrochim. Acta*, **1998**, 130, 97.

64. A.K. Majumdar, *N-Benzoylphenylhydroxylamine and its Analogues*, Pergamon, Oxford, **1972**.

65. M. Assefa and B.S. Chandravanshi, *Mikrochim. Acta*, **1983**, I, 255.

66. B.S. Chandravanshi, A. Yenesew and Z. Kebede, *Anal. Chim. Acta*, **1985**, 172, 175.

67 A. Abebaw and B.S. Chandravanshi, *Bull. Chem. Soc. Ethiop.*, **1996**, 10, 121.

68 B.S. Chandravanshi and B. Temesgen, *Ann. Chim. (Rome)*, **1996**, 86, 401.

69 B.S. Chandravanshi and A. Amsalu, *Mikrochim. Acta*, **1984**, II, 7.

70 S. Afeworki and B.S. Chandravanshi, *Bull. Chem. Soc. Ethiop.*, **1987**, 1, 1.

71 S. Afeworki and B.S. Chandravanshi, *Mikrochim. Acta*, **1987**, II, 143.

72 B.S. Chandravanshi and T. Juhar, *J. Radioanal. Nucl. Chem.*, **1996**, 210, 171.

73. D.C. Bhura, S.G. Tandon, *Anal. Chim. Acta*, **1971**, 53, 379.

74. B.S. Chandravanshi, V.K. Gupta, *Croat. Chem. Acta*, **1984**, 57, 243.

75. T. Wondimu, B.S. Chandravanshi, *Bull. Chem. Soc. Ethiop.*, **1990**, 4, 1.

76. T. Refera, B.S. Chandravanshi, H. Alemu, *Electroanalysis*, **1998**, 10, 1038.

77. T.H. Degefa, B.S. Chandravanshi, H. Alemu, *Electroanalysis*, **1999**, 11, 1305.

78. P. A. Christensen, A. Hamnett, *Techniques and Mechanisms in Electrochemistry*, Blackie Academic, London, **1994**.

79. A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, John Wiley, New York, **1980**.

80. P.H. Rieger, *Electrochemistry*, 2nd ed., Prentice-Hall International, New Jersey, **1994**.

81. E.P. Parry, R.A. Osteryoung, *Anal. Chem.*, **1965**, 37, 1634.

82. H.W. Nürnberg, in *Electrochemistry in Research and Development*, R. Kalvoda, R. Parsons, eds., Plenum Press, New York, **1985**.

83. M.G. Paneli, A. Voulgaropulos, *Electroanalysis*, **1993**, 5, 355.

84. R. Kalvoda, *Anal. Chim. Acta*, **1984**, 162, 197.

85. J. Wang, J.S. Mahmoud, *Anal. Chim. Acta*, **1986**, 186, 31.

86. C.M.A. Brett, A.M.O. Brett, *Electrochemistry Principles, Methods, and Applications*, Oxford University Press, New York, **1994**.

87. H.-A. Kozlowska, *Comprehensive Treatise of Electrochemistry*, Vol. 9, E. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapanic,eds., Plenum Press, New York, **1984**.