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

A Thesis Presented to the School
of Graduate Studies of
Addis Ababa University

In Partial Fulfillment of the Requirements
for the Degree of Master of Science
In
Chemistry

By
Tesfaye Hailu Degefa

June, 1999

THIS ONE IS DEDICATED

To My Father and Mother
for
Their Deep Interest for Education
and
Let Their Children to Make it Possible

ACKNOWLEDGMENTS

I have the gratification of expressing my great appreciation to my advisor Dr. B.S. Chandravanshi for his constant and undeserved guidance, constructive criticisms, stimulating advice, friendly approach, and willing to open up discussions of any kind during the various stages in the realization of the research work as well as preparation of the thesis.

Prof. Theodros Solomon and Dr. B. Hundhammer, Department of Chemistry, Addis Ababa University, for their valuable comments, Prof. Alanah Fitch, Department of Chemistry, Loyola University Chicago, for sending reprint from which I have benefitted much, and the Ethiopian Institute of Geological Survey (EIGS) for allowing me to use their AAS and chemists in the soil and water section laboratories of the Institute for their valuable discussions and cooperation deserve due Appreciation.

I would like to express my sincere gratitude to Dr. Weridjniagegn Mammo, Head of Chemistry Department, Addis Ababa University, for his cooperation throughout the work. My gratitude is also extended to W/t Azeb Yigezu, W/t Woinshef Gehpyehu, and Ato Sahlemichael Deme for their valuable assistance. I should also have to mention my great pleasure in thanking colleagues at Bahr Dar Polytechnic Institute in particular, Ato Zerihun Ayalew, chief personnel, who has been at my back from the beginning of my M.Sc. studies.

May I express my thanks to the Department of Chemistry, Addis Ababa University, for providing me with every assistance and facilities to conduct the research work and the Addis Ababa University Science Library, Accusation Department for delivering reprints in time, which were very important for the work.

The Bahr Dar Polytechnic Institute, and the Swedish Agency for Research Cooperation with Developing Countries (SAREC) through Ethiopian Science and Technology Commission (ESTQ are highly acknowledged for sponsorship and financial assistance, respectively.

Finally, my cheerful thanks goes to my kind-hearted sisters and brother who have endured manuscripts and books on the reading-table for days on ends, and taught me the importance of not being out of patience in the route of any achievement.

CONTENTS

Page

Acknowledgments jv

Abstract x

1. Introduction 1

    1.1. Occurrence, and Uses of Lead 1

    1.2. General Chemistry of Lead 2

    1.3. Methods of Analysis 3

    1.4. Chemically Modified Carbon Paste Electrodes 5

        1.4.1. Reasons for Modification 6

        1.4.2. Methods of Modification 6

        1.4.3. Requirements for a Modifier 8

    1.5. Objectives of the Present Study 8

2. Theoretical Background 11

    2.1. Cyclic Voltammetry 11

    2.2. Differential Pulse Voltammetry 13

    2.3. Stripping Voltammetry 14

        2.3.1. Anodic Stripping Voltammetry 15

        2.3.2. Cathodic Stripping Voltammetry 15

        2.3.3. Adsorptive Stripping Voltammetry 15

    2.4. Choice of Operating Parameters in Differential Pulse Stripping Voltammetry 16

        2.4.1. Electrode Type 16

        2.4.2. Supporting Electrolyte 17

        2.4.3. To Stir or Not to Stir the Solution ? 17

        2.4.4. Preconcentration Time 18

        2.4.5. Deposition Time 18

2.4.6. Deposition Potential 18
2.4.7. Scan Rate 19
2.4.8. Pulse Amplitude 19
2.4.9. Peak Height or Area Under the Peak for Calibration and Measurement ? 20
3. Experimental 21
3.1. Reagents and Chemicals 21
3.2. Apparatus 21
3.3. Electrode Preparation 22
3.4. Procedures 23
3.5. Preparation of Sample Solution 24
4. Results and Discussion 25
4.1. Voltammetric Behavior of Lead(II) at CPCHA Modified Carbon Paste Electrode 25
4.2. Renewal of Electrode 29
4.3. Effect of Carbon Paste Composition 30
4.4. Effect of pH on the Preconcentration Solution and Supporting Electrolyte 31
4.5. Effect of Preconcentration Time 34
4.6. Effect of Reduction Potential and Time 35
4.7. Effect of Instrumental Parameters 37
4.8. Optimal Experimental Conditions 39
4.9. Calibration Curve, Detection Limit, and Precision 39
4.10. Effect of Other Ions 42
4.11. Analytical Application 45
5. Conclusion 47
6. References 48

List of Tables

Page

1. Effect of modifier composition in CPE 30
2. Effect of scan rate 38
3. Effect of pulse amplitude 38
4. Effect of pulse period 38
5. Optimum experimental conditions for the determination of Pb(II) by DPASV 39
6. Change in differential pulse anodic stripping voltammetric peak current of lead(II) in the presence of other ions 43
7. Determination of lead(II) in synthetic matrices 44

List of Figures

Page

1. Structure of N-p-chlorophenylcinnamohydroxamic acid (CPCHA) 9
2. Experimental set up for the study of voltammetric behavior of lead(II) at CPCHA modified carbon paste electrode 22
3. CPCHA modified carbon paste electrode 23
4. Cyclic voltammograms of CPCHA modified carbon paste electrode without and with lead(II) preconcentration 27
5. Cyclic voltammograms of CPCHA modified carbon paste electrode with lead(II) preconcentration with positive,and negative potential scans 28
6. Effect of preconcentration solution pH on the differential pulse anodic stripping voltammetric peak current 32
7. Effect of preconcentration time on the differential pulse anodic stripping voltammetric peak current at two different concentration of lead(II) 35
8. Effect of reduction potential on the differential pulse anodic stripping voltammetric peak current 36
9. Effect of reduction time on the differential pulse anodic stripping voltammetric peak current 37
10. Differential pulse anodic stripping voltammograms of lead(II) at CPCHA modified carbon paste electrode for lead(II) concentrations: 1.00 x 10^{-6} M - 2.40 x10^{-5} M 40
11. Differential pulse anodic stripping voltammograms of lead(II) at CPCHA modified carbon paste electrode for lead(II) concentrations: 2.00 x IO^ M - 1.00 x10^{-6} M 41
12. Differential pulse anodic stripping voltammograms for the determination of lead in potable water by standard addition method 46

Voltammetric Behavior of Lead(II) at N-p-Chlorophenylcinhamohydroxamic Acid Modified Carbon Paste Electrode

by Tesfaye Hailu Degefa

Advisor: Dr. B.S. Chandravanshi

Abstract

A sensitive and selective method for the determination of lead(II) with N-p-chlorophenylcinnamohydroxamic acid modified carbon paste electrode has been developed. The lead(II) is accumulated on the electrode surface by the formation of the complex in an open-circuit, and the resulting surface is characterized by medium exchange, potential reduction, and differential pulse anodic stripping voltammetry. The electrochemical response was evaluated with respect to carbon paste composition, pH and concentration of accumulating and stripping solutions, preconcentration time, lead(II) concentration, and other variables. Two linear ranges were obtained in the concentration ranges 1.00 x 10^{-6} - 2.40 x 10^{-5} M Pb(II) with 2 min preconcentration time and 2.00 x 10^{-8} - 1.00 x 10^{-6} M Pb(II) with 6 min preconcentration time. The detection limit was found to be 1.00 x 10^{-8} M with 6 min preconcentration time. For six preconcentration/medium exchange/voltammetric determination/renewal cycles, the differential pulse voltammetric response was reproduced with 5.3% and 4.9% relative standard deviations at 4.00 x 10^{-6} M and 8.00 x 104 M Pb(II), respectively. Rapid and convenient renewal allows the use of a single modified electrode surface in multiple analytical determinations over several weeks. Many coexisting metal ions had little or no effect on the determination of lead(II). The developed method was applied to lead determination in potable water.

1. Introduction

1.1. Occurrence, and Uses of Lead

Lead is one of the most widely distributed toxic and heavy metals in the environment. It is found in earth's crust, air, waters, soils, plants, and animals. It is rarely found in its elementary form. The most important ore of lead is the galena (PbS). Other ores of commercial importance are the anglesite ($PbSO_4$), cerossite ($PbCO_3$), pyromorphite ($PbCl_2.3Pb_3(PO_4)_2$), mimetesite ($PbCl_3.3Pb_3(AsO_4)_2$), crocite (or kallochrome, or red lead ore) ($PbCrO_4$), wulfenite (or molybdenium lead spar or yellow lead ore) ($PbMoO_4$), and stolizite ($PbWO_4$. These ores generally occur in nature in association with other metals, notably silver and zinc [1,2].

Industrially, the most important lead compounds are the lead oxides and tetraethyllead. Lead forms alloys with many metals and is generally employed in the form of alloys in most applications [3]. In addition, a considerable variety of lead compounds, such as silicates, and carbonates are used as heat and light stabilizers for polyvinyl chloride plastics. Lead silicates are also used for the manufacture of glass and ceramic frits. Lead azide and lead arsenates are used in large quantities as detonator for explosives and insecticides for crop protection, respectively. Among the newer uses of lead compounds, lead oxide is widely employed to improve the magnetic properties of barium ferrite ceramic magnets. Also, a calcined mixture of lead zirconate and lead titanate, known as PZT in trade, is finding increasing markets in piezoelectric materials [4].

Lead compounds are highly toxic when eaten or inhaled. Approximately two third of the total amount of lead assimilated by a healthy man is dietary in origin and the remainder is inhaled [2]. Most of lead retained by the body accumulates in the bones and the half life is estimated as 2-3 years. Since, the determination of the amount of lead in the bones of a living person is difficult, the level in the blood is felt to give a good indication of the amount present in the body. The average concentration of lead in human blood is about 0.25 ppm and acute lead poisoning is possible if the concentration in the blood rises above 0.80 ppm [5]. The symptoms of lead poisoning include loss of appetite, vomiting, dizziness, headaches, and brain damage. In acute cases there is usually stupor, which progresses to coma and terminate in death [4].

If the danger is known in time, lead intoxication can be cured and recovery is usually complete, leaving no disability. The most common clinical treatment involves the intravenous injection of sodium calcium salt of ethylenediaminetetraacetic acid, which results in an immediate ten to thirty fold increase in the urinary excretion of lead [1].

1.2. General Chemistry of Lead

Lead is located in group IVA of the periodic table and has electronic configuration [Xe] $4f^{14}5d^{10}6s^{2}6p^{2}$. It is relatively resistant to attack by sulfuric and hydrochloric acid but dissolves slowly in nitric acid. It forms many alloys, salts, oxides, and organometallic compounds. The principal oxidation states of lead are +2 and +4. Lead is present as Pb(II) in all of its simple compound, where as Pb(IV) compounds are not common. In acidic aqueous solution it is frequently present as the colorless aquo-lead(II) ion, in fairly alkaline medium lead(II) forms the colorless plumbate ion [4,6].

Lead(II) has co-ordination number 4 and yields stable planar complexes with ligands containing nitrogen, oxygen or sulphur as donors atom, and it may owe some of its physiological reactions to replacement of other metals in some enzymes. In masking procedure lead is most often converted into relatively stable complexes with acetate, tartrate, citrate or ethylenediaminetetraacetic acid (EDTA) [5,6].

1.3. Methods of Analysis

Lead can be detected by spot test, mostly with either benzidine or sodium rhodizonates as coloring agents [7,8]. In basic medium, benzidine reacts with lead dioxide to form a deep blue fleck, commonly known as "benzidine blue". While sodium rhodizonate reacts with lead ion to produce colored precipitate of basic lead rhodizonates. In neutral solution, violet PbfQOΛ.PbfOHΛ.ΛO is formed, and from weakly acid solution the scarlet red $2Pb(C606).Pb(OH)_2.H20$ is formed.

There are also many insoluble salts of lead, leading to the time-honored methods for determination of lead: precipitation-based reactions. However, none of these are clearly the most satisfactory. Among the earliest known gravimetric precipitants for lead are sulphate, chromate, phosphate, oxalate, and oxinate [7,9].

Volumetric lead estimation involving titration with molybdate, chromate, phosphoric acid, ferrocyanide, fluoride, and iodide are all available, in addition to the most commonly used complexometric titration with reagents such as EDTA [1,4].

Lead can also be determined colorimetrically by means of its reaction with dithizone. In the usual procedure the dithizone is dissolved in either carbontetrachloride or chloroform. This is then shaken with the aqueous phase containing lead. Thus lead is extracted with the formation of a red colored complex which may be used for its spectrophotometric determination at Amax 555 nm, which lies in a deep valley between 450 and 620 nm absorption of the free dithizone [7,9].

Different absorption lines of lead are available for its determination by atomic absorption spectroscopy, AAS. Some of these are 217.0, 261.4, 283.3, and 405.8 nm. However, several investigators have conformed that the 217.0 nm line is the most sensitive [10].

Lead can be determined by atomic fluorescence which involves a similar process to atomic emission except that the excitation is obtained by an absorption event. Atomic fluorescence for lead is relatively a new method (since 1990) in which a lead atom in a gas is excited with a XeCl eximer that uses a second harmonic generation to lase with 3 kW power at the lead absorption line of 283.3 nm. After excitation, the atom emits at 405.8 nm. The intensity of the excitation beam leads to the high emission intensities allowing a very low limit of detection [7].

Success was also achieved in probing the Inner shell electrons both for qualitative and quantitative information. When a photon of angstrom wavelength strikes an atom it penetrates to the inner shell electrons. There the beam can be diffracted (X-ray diffraction) or it can cause the ejection of a photoelectron whose energy is less than that of the original photon by the binding energy of the shell. The absorption of the high energy beam is measured as absorbance. The loss of the photoelectron leaves behind a vacancy that can be filled by an electron from the outer shell with the release of an X-ray photon giving rise to X-ray fluorescence. Lead has three major X-ray fluorescence bands at 75(K), 10.5(L), and 2.3(M) keV. These bands are selective for lead [7].

Stripping voltammetry, which combines high analytical sensitivity with low cost for equipment, can also be used for effective determination of lead at very low concentration levels. Anodic stripping voltammetry at a hanging mercury drop electrode [11,12], adsorptive cathodic stripping voltammetry on a mercury film glassy carbon electrode, using catechol, 4-methylcatechol, 4-t-butylcatechol, and resorcinol as complexing ligands [13] have been reported for the determination of lead(II) in natural water, food, urine, and blood. Recently chemically modified carbon paste electrodes have been also reported to replace the toxic mercury electrodes in determination of lead at very low concentration levels [14-18].

1.4. Chemically Modified Carbon Paste Electrodes

Carbon paste electrode (CPE) has been widely applied in electroanalysis mainly as a substitute for noble metals because, depending on the supporting electrolyte, it can be used at both positive and negative potentials ranging from -1.4 to +1.3 V versus the saturated calomel electrode (SCE). In addition, CPE possesses many advantages: it is inexpensive, easy to prepare, easy to handle, easy to modify, and easily renewable [19,20].

The modification of carbon paste electrode began in 1964 with the fundamental studies ofKuwanaand co-workers [21,22] which was followed by different groups [23-25]. These work can be considered to be the first pioneering contribution to the forthcoming development of chemically modified carbon paste electrodes (CMCPEs) in the 1970s [20].

The actual breakthrough for widespread application of modified carbon paste electrode was triggered by the work of Ravichanrdan and Baldwin in 1981, who proposed a simple approach to the modification of carbon paste electrode [26].

Currently, CMCPEs represent a modern approach to electrode system [27]. They are characterized by deliberately altered surface with material which reacts selectively and reversibly with the target analyte [28]. Specific reactions at the modified surface represent an efficient way for accumulation of the target analyte, from dilute solution, onto the electrode surface prior to quantitation of the analyte by the usual voltammetric measurements. The rich chemistry that can be used for preconcentration at these molecularly tailored electrodes offers exciting prospects for trace analysis [29]. Hence, CMCPEs have attracted considerable attention for their application in analytical chemistry in recent years.

1.4.1. Reasons for Modification

The primary purpose behind modifying an electrode surface is to improve its analytical performance either by increasing its sensitivity and selectivity or by protecting the surface from unwanted reactions [19]. The accumulation step preceding the measurement can be performed with or without the application of a potential (closed or open-circuit condition, respectively) depending on the nature of the preconcentration. Whereas the first case may involve an electrochemical reaction (oxidation or reduction), the latter is based purely on physicochemical processes such as ion exchange, complexation or formation of an insoluble salts. With the open-circuit approach, it is possible to separate the species under consideration and eliminate interferences from other components by proceeding to a medium exchange step after the accumulation step. Thus, the preconcentrated substances are extracted from the test solution, and parameters such as acidity and ionic strength can be optimized separately for the analyte solution and the solution in which the electrode is polarized during the measurement.

1.4.2. Methods of Modification

CMCPEs are exceedingly easy to fabricate and can be generated rapidly and reproducibly in quantity. Some of the techniques used for the preparation of chemically modified carbon paste electrodes include:

Direct mixing. This method is most commonly used for preparing CMCPEs. The unique advantage of this approach is pronounced ease of modification, most simply done by admixing of a reagent (modifier) to the paste [19]. The disadvantage, however, lies in the difficulty in obtaining homogeneity, when using solid modifier as additives.

Solvent volatization. A special but very practical form of "direct mixing" is admixing the modifier into the carbon powder with the aid of a solvent prior to adding the pasting liquid [19,29]. This is particularly suitable if the modifier adsorbs to the carbon, which produce, after the evaporation of the solvent, rather homogeneously covered graphite particles.

Dissolving the modifiers in the paste. This approach is applicable only if the modifier possesses strongly lipophilic properties. Substances with tenside character are especially well suited because they orientate their hydrophilic ends, which normally represent the functional groups, to the aqueous buffer solution, thus promoting chemical reactivity with the bulk molecules of interest. This kind of electrode can be further modified by a dip-in treatment during which the effective agent is bound to the anchor molecule already dissolved in the paste [19].

Electrode coating. The basal plane of the carbon electrode is cleaned and polished. Then, the electrode coating modifier dissolved in a suitable solvent is transferred on the exposed area of the electrode and allowed to dry [29,30]. While this method is simple, it is difficult to control the amount of material that ends up on the electrode surface [29]. Hence, spin-coating is mostly used to yield uniform film thickness [30].

Covalent binding. Covalent binding of functional groups or fragments requires time-consuming, delicate pretreatment (e.g. oxidation, amidization) that often are not justified by the final results. Therefore, this kind of modification is not widely used with CPEs [19,30].

In situ modification. It is a special type of modification in which the product of a reaction with a modifier dissolved in the bulk solution adsorbs to the surface of the electrode [19]. This method requires frequent injection of the modifier.

1.4.3. Requirements for a Modifier

In general, the modifiers used with direct addition should meet the following criteria. First of all, they should be insoluble in the analyte solution, or they should at least strongly adsorb to the paste components in order to avoid dissolution of the molecules from the electrode surface during the measurement. The phenomenon of "bleeding" causes modifier concentration gradients in the surroundings of the electrode surface as well as variable amounts in the interface itself. This results in barely reproducible currents. The other important requirement is that the modifier itself should not undergo electrochemical transformations within the potential range of the voltammetric response of the analyzed species. Otherwise, the high background current would reduce or even impair the desired analytical properties of the electrode because the concentration of the modifier in the paste is rather high [19]. Of course the modifier's affinity and specifity for the species to be extracted and the value of the formation constant determine the quality of the analysis. The kinetics of the reaction should also be moderately fast both to shorten the time of analysis and to avoid diffusion from the surface into the paste where it is not accessible for the measurement.

1.5. Objectives of the Present Study

Voltammetric determination of lead(II) using CPEs modified with benzoin oxime [14], dibenzo-18-crown-6, and cryptand [15], moss [16], lichen [17], and 1-(2-pyridylazo)-2-naphthol and Nafion [18] have been reported for determination of lead at trace levels. Among these studies, some of the modified CPEs require additional steps for their preparation [16-18]. While the moss modified CPE requires longer accumulation time (15 min) [16], lichen modified CPE requires longer renewal time (5 min) and has high detection limit (2×10^{-5} M) [17], dibenzo-18-crown-6, and cryptand modified CPEs [15] have higher detection limits (1×10^{-6} and 0.5×10^{-6} M, respectively), and 1-(2-pyridylazo)-2-naphthol and Nafion modified CPE requires longer accumulation time

(8 min), suffers from leaching, and its regeneration requires recoating of the electrode surface [18]. Furthermore, no systematic interference studies have been made on some of these methods and have not been applied to the determination of lead in real samples [17,18]. Hence, it is rational to look for another modifier that can be used to prepare a new CMCPE for selective preconcentration and voltammetric determination of lead to overcome the problems mentioned above.

N-*p*-Chlorophenylcinnamohydroxamic acid (CPCHA) (Fig. 1) has a number of desirable properties as potential analytical reagent for the determination of metal ions:

(i) it contains an acid group with a replaceable hydrogen atom and a basic coordinating group in such a position so as to form a five membered ring on reaction with metal ions,
(ii) it is simple to synthesize in laboratories, and
(iii) it is stable towards heat, light and air.

As a result of these properties, this reagent has been used for extraction and spectrophotometric determination of V(V) [31], Ce(IV)[32], and Nb(V)[33].

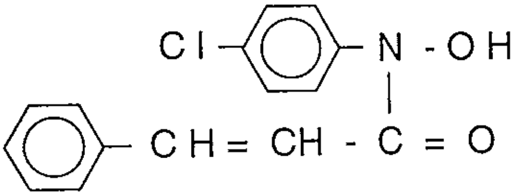

Figure 1. Structure of N-*p*-chlorophenylcinnamohydroxamic acid (CPCHA).

This potentially active reagent could also be used for the modification of CPE because of the following attractive properties:

(i) it is insoluble in aqueous solution, hence aviod leaching from the electrode, and

(ii) it does not undergo electrochemical transformations within the potential range of the voltammetric response of most metal ions.

Inspite of all these desirable characteristics, CPCHA has been only tested for voltammetric determination of Co(II) at CMCPE [34]. Except this trial, no attempt has been made to exploit the potential of CPCHA for modification of CPE, and no report appeared in the literature on the use of this reagent for voltammetric determination of lead at CPCHA modified carbon paste electrode, in particular. Hence, it is reasonable to use CPCHA for modification of CPE for voltammetric determination of lead.

Therefore, the objectives of the present study are:

(I) to study the voltammetric behavior of lead(II) at carbon paste electrode modified with CPCHA,

(ii) to establish the optimal experimental parameters for the determination of lead at the electrode (i.e. to study the basic electroanalytical parameters of the modified electrode, such as effect of paste composition, pH and concentration of accumulation solution and supporting electrolyte, accumulation and deposition time, linear range, detection limit, etc.),

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

(iv) to study the analytical application of the modified electrode for the determination of lead(II) in diverse samples.

2. Theoretical Background

Electrochemical transformation at chemically modified carbon paste electrodes as used in [14-18] and in this thesis diverges from the conventional electrochemical technique. The most essential difference is that one deliberately alteres the surface with material which reacts selectively (with out the application of potential) and reversibly with target analyte. Then the modified surface, therefore, will display the electrochemical behavior of the immobilized analyte. The electrochemical transformation, which follows the immobilization of the analyte, does not require the presence of the oxidized or reduced forms of the immobilized analyte in the solution contacting the modifier surface. Only inert supporting electrolyte are in the solution. Hence, the redox process doesn't involve semi-infinite diffusional mass transport, at least within a certain time frame, since these species (i.e., the oxidized and reduced forms of the analyte) are confined to the electrode surface. Having the above facts in mind the foregoing theoretical discussions are used in this thesis from analytical view point.

2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is the most effective electroanalytical technique available for acquiring information about electroactive species. The effectiveness of cyclic voltammetry results from its ability for rapidly observing redox behavior over the entire potential range available [27-29,35]. This technique is useful in the elucidation of mechanism particularly in respect of the identification of intermediates [28].

Cyclic voltammetry consists of scanning linearly the potential of a stationary electrode (in unstirred solution), using a triangular potential wave form. Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the triangular potential excitation signal causes the potential of the working electrode to sweep between two designated values, called the switching potentials. The resulting voltammogram is analogous to a conventional spectrum in that it coveys information as a function of an energy scan is termed as a cyclic voltammogram.

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

$$E = E^{o} - (RT/nF) \ln (a_O/a_R) \quad (1)$$

where $E = E_{intial} - vt$, in which v is the scan rate in volts/seconds and t is the elapsed time in seconds, a_O and a_R are activities of the oxidized and reduced species, respectively, and n is the number of electrons transferred.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (I_{pa}), cathodic peak current (I_{pc}), anodic peak potential (E_{pa}), and cathodic peak potential (E_{pc}) [35].

At 25 ^{0}C, the peak current for a reversible couple is given by the Randle-Sevick equation:

$$I_p = (2.69 \times 10^5)\, n^{3/2} A C D^{1/2} v^{1/2} \quad (2)$$

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). Accordingly, the peak current is directly proportional to the concentration and increases with square root of scan rate. The relation of I_p to concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of I_{pa} and I_{pc} are similar in magnitude for a simple reversible electron transfer reaction.

That is,

$$I_{pa}/I_{pc} \approx 1 \tag{3}$$

However, the ratio of the peak current can be significantly influenced by the chemical reactions coupled to the electrode process.

The separation between the peak potentials is given by:

$$\Delta E = E_{pa} - E_{pc} \tag{4}$$

$$\approx 0.059/n \text{ V}$$

Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior. Slow electron transfer at the electrode surface, electrochemical irreversibility, is characterized by separation of peak potentials that is greater than 0.059/n V.

2.2. Differential Pulse Voltammetry

Differential pulse voltammetry is an extremely useful technique for measuring trace levels of organic and inorganic species [27,28]. This technique is based on the effects of superimposing a series of equal wave impulses on a linear potential ramp. 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. The two current values represent the currents at two potential values separated by the pulse amplitude. The final current signal displayed is in fact the difference of these two current values.

This technique in fact produces not a wave but a peak with the highest current signal at roughly the half wave potential of the classical dc polarography. Since the output signal increases with the steepness or slope of the conventional current potential curve, this curve approximates to a derivative or differential of the classical polarographic current potential curve. The technique also allows the maximum differentiation of the faradaic or analytical signal from the background signal and an increased sensitivity [36].

The resulting differential pulse voltammogram consists of peak current plotted versus the applied potential. The peak potential, E_p, can be used to identify the species involved, as it occurs near the polarographic half-wave potential, $E_{1/2}$.

$$E_p = E_{1/2} - \Delta E/2 \qquad (5)$$

where ΔE is the pulse amplitude.

The peak shaped response of differential pulse voltammograms results also in improved resolution between two species with similar redox potentials [27].

2.3. Stripping Voltammetry

Stripping voltammetry is an extremely sensitive electrochemical technique for measuring trace level of analyte [27,37]. This technique involves two discrete steps: preconcentration step, and a stripping step. In the preconcentartion step, the target analyte is accumulated, from very dilute solution, onto the working electrode. It is this step which allows the great sensitivity of stripping voltammetry.

In the stripping step, the potential is scanned at a certain rate in a specific direction. At a characteristic potential the accumulated species is oxidized or reduced giving peak current, Ip, proportional to the concentration of that analyte on the electrode surface, which in turn reflects the concentration of the analyte in the sample solution.

2.3.1. Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) is the most common version of stripping analysis. It involves the reduction of the metal ion or its complex to the metal, as the preconcentration (reduction) step; preconcentration is 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 are measured.

2.3.2. Cathodic Stripping Voltammetry

Cathodic stripping voltammetry (CSV) is the "mirror image" of ASV. It involves anodic deposition of the analyte on the electrode; it is subsequently stripped off during a negative-going potential scan. The resulting reduction peak current provides the desired quantitative information.

CSV is best suited for the determination of inorganic anions (e.g. halides, cyanides) or organic sulfur compounds (e.g. pencillins, thiols) that form insoluble salts with the electrode material.

2.3.3. Adsorptive Stripping Voltammetry

Adsorptive stripping voltammetry (AdSV) has been demonstrated to be a very sensitive method for numerous trace metals, the quantitation of which by conventional (electrolytic) stripping procedures is complicated or not feasible [29,38]. This strategy involves the formation of an appropriate metal chelate, followed by its controlled interfacial accumulations onto the working electrode; then the adsorbed metal chelate is reduced by the application of a negative-going potential scan. The resulting adsorptive stripping reflects the corresponding adsorption isotherm, as the surface concentration of the analyte is proportional to its bulk concentration.

Short adsorption times (1-5 min) result in a very effective interfacial accumulations, allowing ultrasensitive measurements (down to 10^{-10} -10^{-11} M for some metals [27]). However, to attain such high sensitivity, it is essential to optimize operational variables (e.g. pH or accumulation potential) favoring strong adsorption.

All procedures of AdSV relay on judicious choice of the chelating agent. Usually the ligands used in AdSV are surface-active compound. Some of the ligands are electrochemically inactive, while other are electrochemically active. In the latter case, it is necessary that the redox potentials of the ligand and the complex differ substantially; these ligands are additionally very useful for the determination of elements which can not be easily reduced or oxidized electrochemically [38,39].

Besides trace metals, many surface-active organic compounds of biological, pharmaceutical, and environmental significance can be interfacial accumulated and measured at ultratrace levels [40-43].

2.4. Choice of Operating Parameters in Differential Pulse Stripping Voltammetry

2.4.1. Electrode Type

The performance of the voltammetric procedure is strongly influenced by the working electrode used. The working electrode should provide a favorable signal to noise characteristics, as well as a reproducible response. Its selection is dictated primarily by two factors: the type of the reaction which will be used for preconcentration [37], and useable potential range [44]. The cost, availability, and stability of the electrode must also be considered.

2.4.2. Supporting Electrolyte

Several factors must be considered when choosing the composition of the supporting electrolyte [37,44,45]. The solution must contain a sufficient concentration of conducting species in order that a large ohmic drop is prevented, migration currents are suppressed, and constancy of activity and diffusion coefficients is maintained. From this point of view, solutions of mineral acids, hydroxides, salts, etc. are most suitable. Buffer systems (such as acetate, phosphate or citrate) are used when pH control is essential. The components of the supporting electrolyte must be available in sufficiently pure form, or the impurities must at least be removable. All care must be taken 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). The electrolyte composition must be chosen so that as high sensitivity and selectivity of the determination as possible are achieved.

2.4.3. To Stir or Not to Stir the Solution ?

Stirring the solution during the accumulation step increases the rate at which the analyte reaches the electrode to be accumulated. However, the stirring must be uniform, gentle, and at controlled rate. The position of the electrode within the cell and hence in the solution must be reproducible. An alternative to stirring the solution is to rotate the electrode. In unstirred solution the analyte reaches the electrode for accumulation by diffusion. This is much slower than transport in a stirred solution but it is also very reproducible [36].

2.4.4. Preconcentration Time

The sensitivity of stripping determination can be increased by prolonging the preconcentartion time. The dependence of the signal response on the preconcentration time with a fixed composition of the analyte usually displays some linearity for short periods. Increasing the accumulation time causes deviation from linearity due to saturation of the binding sites and equilibrium effects of the modifier on the electrode [19]. The same relationship is found between the voltammetric signal and the concentration of the analyte for a constant accumulation time. Hence, if direct proportionality between the final signal and the accumulation time is to be maintained, the accumulation time must not be long.

2.4.5. Deposition Time

A further decision is how long to continue the deposition step. Eventhough the sensitivity of stripping determination can also be enhanced by carrying on the deposition process until all of the analyte would be deposited on the electrode, it is best to aviod long deposition times. Because this often leads to various complications resulting in a loss of proportionality between final signal and the concentration of the analyte. One problem can be reactions of the deposit or changes in its nature over a relatively prolonged time [36].

2.4.6. Deposition Potential

The final decision is the choice of the constant potential used in the deposition step. Usually a potential is chosen a few hundred millivolts larger than the half wave potential of the analyte. The potential chosen allows a degree of selectivity. In the analysis of a solution containing a number of metal ions, each metal ion will have its own individual deposition potential. Thus only one metal or a group of metals can be deposited, avoiding the deposition of other metals which might interfere with the stripping step. When the deposition potential is higher, it is likely that more types of metal ions will be deposited which increases the interferences [36,37].

2.4.7. Scan Rate

The scan rate must be chosen very carefully. Fast scan rate increases the height of the peak and broadness, hence results in poor resolution. On the other hand, the slowest scan rate gives the best results. In general, the selection of scan rate usually requires a trade-off among sensitivity, resolution, and speed [27].

2.4.8. Pulse Amplitude

The theoretical relation ship between the peak current, Ip, and pulse amplitude, ΔE, has been derived by Parry and Osteryoung [46,47]. For small pulse amplitude:

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

Consequently, it is clear that maximum sensitivity is obtained for larger values of pulse amplitude. In practice, however, it is also obvious that increasing the pulse amplitude increases the width of the peak (decreases the resolution), which is undesirable [47]. For example, two close laying peaks will not be resolved unless the pulse amplitude is significantly smaller than the separation in the two potentials [36]. Thus the choice of pulse amplitude must be a compromise between a high value for increased sensitivity and a lower amplitude for increased resolution .

2.4.9. Peak Height or of Area Under the Peak for Calibration and Measurement ?

Since differential pulse Voltammetry is a differential or derivative technique it is the area under the peak which is proportional to the current recorded and hence to the concentration. The measurement of their height is much more convenient and generally yields results with sufficient precision. However, the relationship between peak height and area is only constant as long as the shape of the peak does not alter. But irreversible process produce lower broader peaks than reversible process, therefore, any change in thermodynamic reversibility will alter the relative peak height. On the other hand, when two peaks partially overlap it is very difficult to separate the area under one from that under the other. The two peak heights may be well defined, and provided the tail of the other peak would effectively be zero at this potential, then the peak heights can be used with much greater precision than the areas under the peaks [36,37].

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), ethylenediaminetetraacetic acid disodium salt (BDH, AnalaR), and lead nitrate (BDH, AnalaR) were used as received. Sodium acetate solutions of various concentrations were prepared in water. The pH of the solutions were adjusted to the desired values by adding acetic acid or 1 M sodium hydroxide. Stock solution of 1 mM lead(II) was prepared in water. Distilled water was used throughout.

CPCHA was prepared by the condensation of N-*p*-chlorophenylhydroxylamine with cinnamoyl chloride at low temperature in diethylether medium made alkaline with an aqueous suspension of sodium bicarbonate [48].

3.2. Apparatus

Cyclic voltammetry and differential pulse anodic stripping voltammetry were performed with a BAS CV-50W Voltammetric Analyzer. The recording of voltammograms and processing of data were done with 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 CPCHA modified carbon paste electrode as working electrode) served as the measurement cell. Three different cells (30 mL) were used for the preconcentation, renewal (cleaning), and rinsing step. An oyster pH meter (EXTECH) was used for the measurement of pH. A magnetic stirrer (Philip Harris) with a Teflon-coating stirring bar was used in the preconcentration, renewal, and rinsing steps. A stop clock (Harris Digitimer) was employed for time measurement. Figure 2 shows the experimental set up schematically.

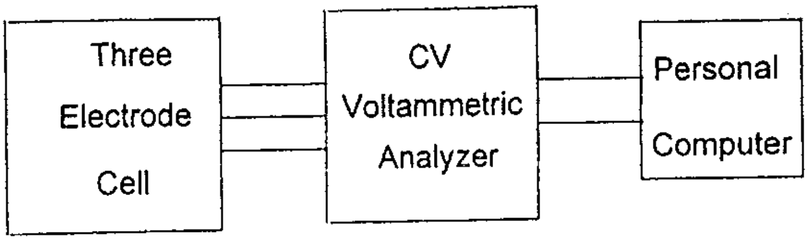

Figure 2. Experimental set up for the study of voltammetric behavior of lead(II) at CPCHA modified carbon paste electrode.

3.3. Electrode Preparation

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%, 7.5%, 10%, 12.5%, 15%, and 20% weight-to-weight ratio) by CPCHA and then adding the paraffin oil and thoroughly hand-mixing in a mortar and pestle. A portion of the paste was packed into the tip of electrode assembly made from 1-mL plastic syringe (B/BRAUN) of 3 mm outer diameter and smoothed off. Electrical contact was made with a copper wire through the syringe as shown Figure 3. Whenever regeneration of the electrode was required, a thin layer of the surface was removed with a spatula and replaced by a fresh paste. The fresh electrode was conditioned by dipping the electrode in 10 μM Pb(II) solution and recording the differential pulse anodic striping voltammograms three times. The pretreated electrode gave reproducible results.

A 25 % benzoin oxime-modified CPE [14] was also prepared using the above procedure. The fresh electrode was preconditioned at 1.0 V by exposure to a stirred sodium acetate buffer (pH 2.9) solution for 1 minute. The electrode was used for the determination of Pb(II) in potable water by differential pulse anodic striping voltammetry as a reference method.

cell, rinsed thoroughly with water and placed in a quiescent blank 25 mL of 0.3 M sodium acetate buffer solution (pH 6) at -1.2 V for 1 min. The differential pulse anodic stripping voltammogram was recorded (with 30 mV/s scan rate, 100 mV pulse amplitude, and 0.2 s pulse period). The scan was terminated at 0 V. After each cycle, the electrode was cleaned by dipping in a stirred 10 mM ethylenediaminetetraacetic acid disodium salt, EDTA, solution (pH 9) for $\geq 10^{-6}$ M Pb(II) and 1 mM EDTA solution (pH 9) for $\leq 10^{-6}$ M Pb(II) for 1 min. Then the electrode was washed by dipping it in a stirred 25 mL of water for 1 min. The electrode was then ready for the ensuring preconcentration step. All measurements were carried out at room temperature (22 ± 2 °C) using nondearated solutions.

The same cycle was also used for determination of Pb(II) in potable water using benzoin oxime-modified CPE with preconcentration solution 25 mL of 0.1 M NH_3-NH_4Cl buffer (pH 8.5), preconcentration time 10 min, supporting electrolyte 25 mL of 0.1 M sodium acetate buffer (pH 2.9) solution, and reduction potential at -1.0 V for 45 s. The differential pulse anodic stripping voltammogram was recorded (with 20 mV/s scan rate, 50 mV pulse amplitude, and 0.5 s pulse period). The electrode was cleaned electrochemically at 1.0 V for 60 s in 0.1 M sodium acetate buffer (pH 2.9) solution while stirring.

3.5. Preparation of Sample Solution

A 0.1 M sodium acetate, pH 9, was prepared in 500 mL potable water. A 25 mL aliquot was transferred into the cell for preconcentration and subsequent voltammetric measurement. This was then followed by spiking known amounts of Pb(II) solution into fresh aliquots of the sodium acetate solution in potable water. The sample was also analysed by differential pulse anodic stripping voltammetry using a benzoin oxime-modified CPE [14].

4. Results and Discussion

4.1. Voltammetric Behavior of Lead(II) at CPCHA Modified Carbon Paste Electrode

Cyclic voltammograms (CVs) were obtained at freshly prepared unmodified and CPCHA modified carbon paste electrodes in 0.3 M sodium acetate buffer of pH 6. The CV of unmodified CPE with Pb(II) preconcentration from 0.1 M sodium acetate solution (pH 9) on the electrode surface at open-circuit condition did not show any wave, indicating that Pb(II) is not accumulated on surface of unmodified CPE. Figure 4 shows the CVs of CPCHA modified carbon paste electrode with and without Pb(II) preconcentration from 0.1 M sodium acetate solution (pH 9) on the electrode surface at open-circuit condition. The CV of the CPCHA modified electrode without Pb(II) preconcentration (curve 1) did not show any wave in the potential range used, -1400 to 0 mV (however, when the potential was extended up to 700 mV, the modified electrode showed characteristic anodic and cathodic waves for the ligand N-*p*-chlorophenylcinnamohydroxamic acid which is similar to that of its analogue N-phenylcinnamohydroxamic acid [39]). The principal changes resulting from the Pb(II) preconcentration (curve 2) was the appearance of anodic and cathodic peaks at -518 mV and -802 mV, respectively. The CVs were run starting from -1400 to 0 mV and back with 100 mV/s scan rate. During the initial potential scan (positive direction) the accumulated Pb(II) (as CPCHA complex) on the electrode surface was reduced to Pb(o) and susequently oxidized back to Pb(II) showing the anodic peak at -518 mV. The cathodic peak observed at -802 mV during the return scan (negative direction), clearly corresponds to the reduction of Pb(II) to Pb(0). This observation is in accordance with the results of CVs of other CMCPEs based on open circuit Pb(II) accumulation [14,16]. 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. 5). However no significant changes were observed in changing the direction of the potential scan.

The anodic peak current observed was substantially larger and sharper than the corresponding cathodic peak. Hence, it was systematically studied by differential pulse anodic stripping voltammetry for analytical determination of lead(II). The mechanism involved in the study of Pb(II) at the CPCHA modified carbon paste electrode by differential pulse anodic stripping voltammetry is attributed to the following steps (where HL represents CPCHA):

1. Preconcentration step (open-circuit cell, 0.1 M NaAc, pH 9.0):

$$\underset{\text{solution}}{Pb^{2+}} + \underset{\text{CPE surface}}{2HL} \rightarrow \underset{\text{CPE surface}}{PbL_2} + \underset{\text{solution}}{2H^+}$$

2. Reduction step (closed-circuit cell, 0.3 M NaAc, pH 6, -1.2 V):

$$\underset{\text{CPE surface}}{Pb^{II}L_2} + \underset{\text{solution}}{2H^+} + 2e \rightarrow \underset{\text{CPE surface}}{Pb^0 + 2HL}$$

3. Stripping step (closed-circuit cell, 0.3 M NaAc, pH 6, positive scan: -1.2 V to 0 V):

$$\underset{\text{CPE surface}}{Pb^0} \rightarrow \underset{\text{solution}}{Pb^{2+}} + 2e$$

and

$$\underset{\text{CPE surface}}{Pb^{2+} + 2HL} \rightarrow \underset{\text{CPE surface}}{PbL_2} + \underset{\text{solution}}{2H^+}$$

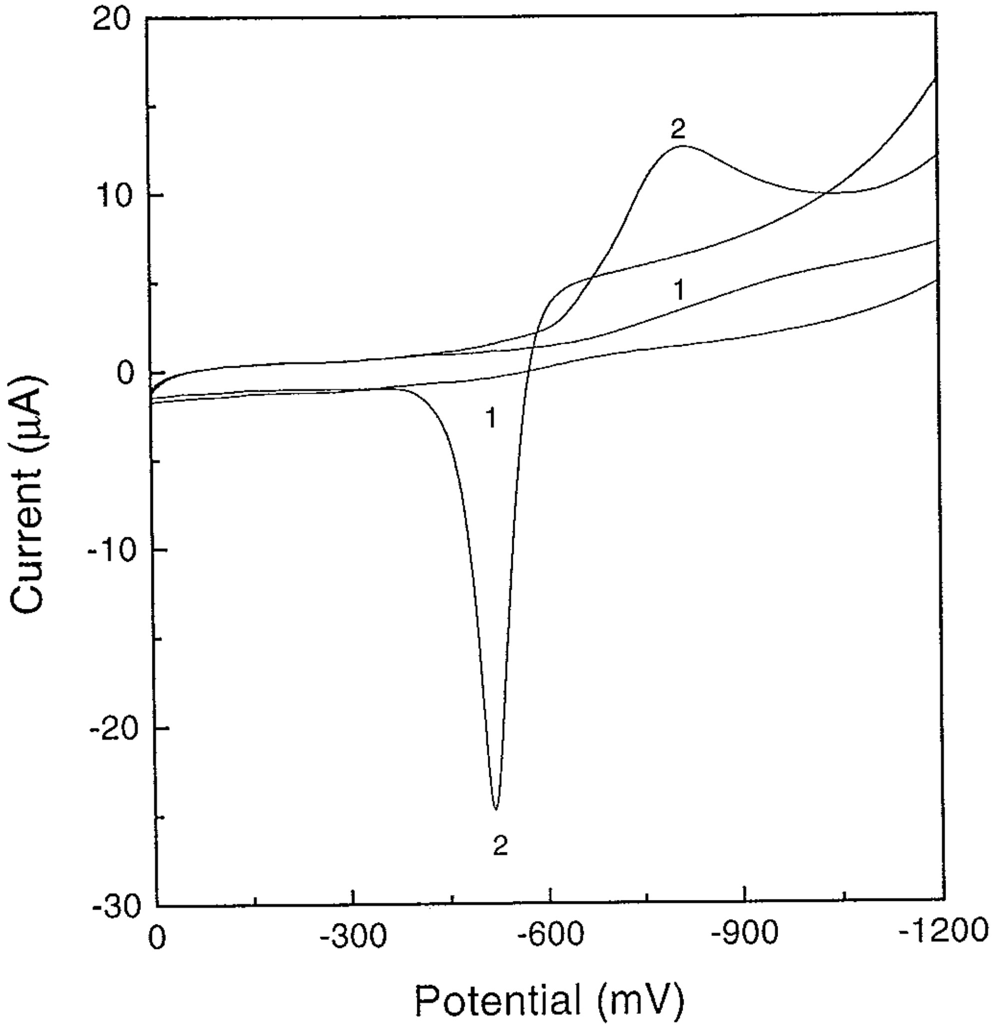

Figure 4. Cyclic voltammograms of CPCHA modified carbon paste electrode (1) without lead(II) preconcentration and (2) with lead(II) preconcentration. Lead(II) concentration: 4.0 x 10^{-5} M; preconcentration pH 9 (0.1 M sodium acetate); preconcentration time: 2 min; supporting electrolyte: 0.3 M sodium acetate buffer of pH 6; from -1400 to 0 mV and back at scan rate: 100 mV/s.

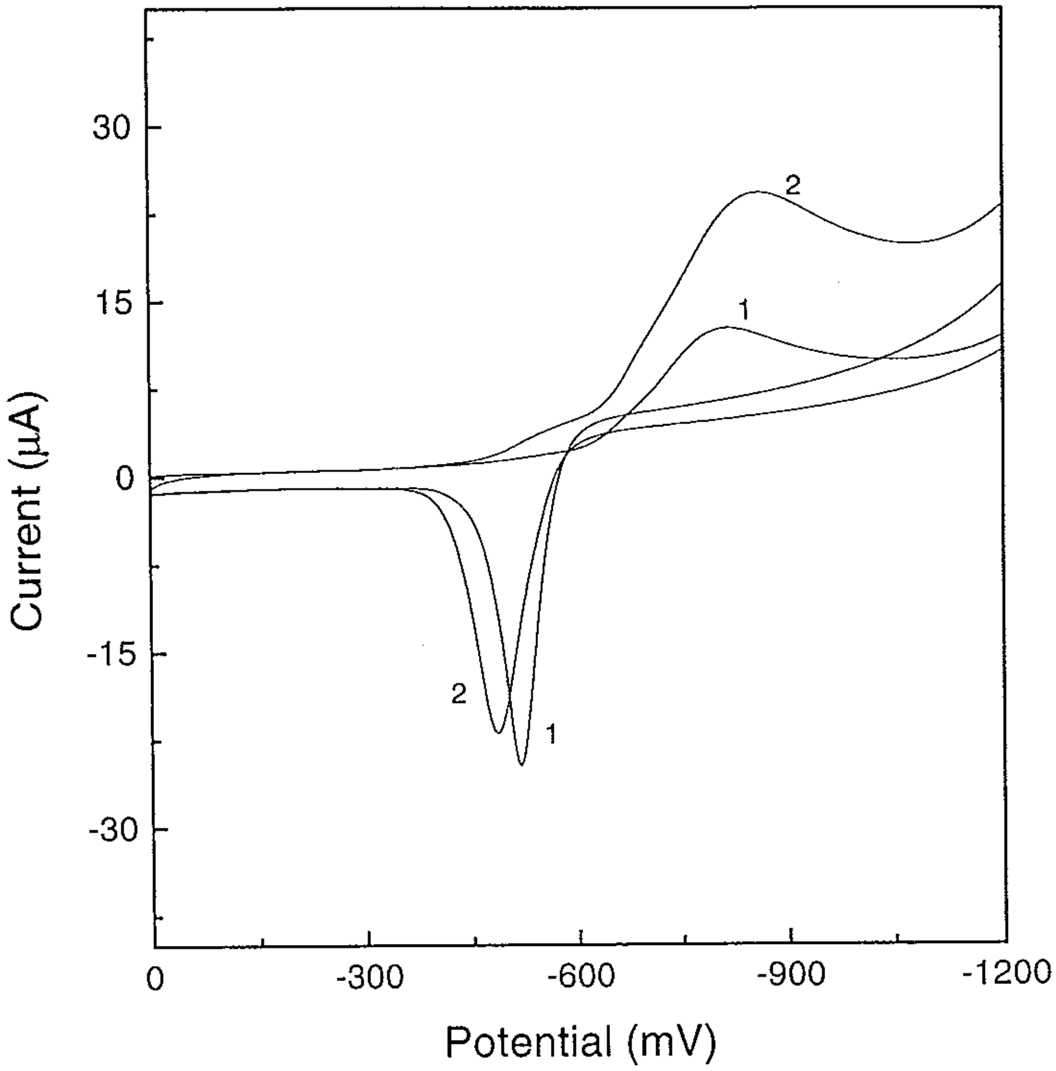

Figure 5. Cyclic voltammograms of CPCHA modified CPE with lead(II) preconcentration (1) from -1400 to 0 mV and back at scan rate: 100 mV/s (2) from 0 to -1400 mV and back at scan rate: 100 mV/s; other conditions are as in Figure 4.

4.2. Renewal of Electrode

During the stripping step as indicated above the complex is re-formed on the modified surface. Hence, in order to use a single surface repetitive and get reproducible results, regeneration of the reactive functional groups on the surface was very important after each electrochemical measurement. Acetic acid (1 M) and sodium acetate buffer (0.3 M, pH 3) were effective in cleaning the electrode surface without memory effect. However, there was a gradual decrease in the electrode response which was probably due to protonation of CPCHA at the surface of the electrode. Best cleaning efficiency and reproducibility were obtained with ethylenediaminetetraacetic acid disodium salt, EDTA, solutions (pH 9) without any memory effect. This is due to the formation of stable water soluble EDTA-lead(II) complex [49,50] that easily removes any Pb(II) complexed with CPCHA on the electrode surface. However for $\leq 10^{-6}$ M Pb(II) there was a gradual decrease in the electrode response which was probably caused by adsorption of EDTA molecules on the surface of the electrode. Consequently when the electrode was dipped into the lead(II) solution for preconcentration, a water soluble Pb(II)-EDTA complex was formed at the electrode surface. This was overcome by using 1 mM EDTA solutions (pH 9) for $\leq 10^{-6}$ M Pb(II) and 10 mM EDTA solutions (pH 9) for $\geq 10^{-6}$ M Pb(II). Whenever physical damage (such as cracking or scratching) of the electrode surface occurred or when an interfering species was accumulated (that can not be removed by cleaning solution), a thin layer of the electrode surface was removed with spatula and replaced by fresh paste. Under normal conditions, a single electrode surface can be used for multiples of analytical determinations over several weeks. The mechanism of renewing the modified surface after each electrochemical measurement by EDTA is attributed to the following reaction:

$$\underset{\text{CPE surface}}{PbL_2} + \underset{\text{solution}}{H_2Y^{2-}} \rightarrow \underset{\text{solution}}{PbY^{2-}} + \underset{\text{CPE surface}}{2HL}$$

4.3. Effect of Carbon Paste Composition

The accumulation of Pb(II) at the CPCHA modified CPE was based on the complex formation reaction between the metal ion, Pb(II) and the modifier, CPCHA. Therefore the concentration of CPCHA in the carbon paste had significant influence on the voltammetric response of the modified electrode. Six different electrodes prepared from 5%, 7.5%, 10%, 12.5%, 15%, and 20% weight-to-weight ratio CPCHA contained carbon pastes were examined for their voltammetric signals under identical conditions (Table 1). The maximum peak current was obtained for 15% CPCHA in the paste. Higher concentrations (> 15%) showed a decrease in the peak current. This is presumably due to the reduction of conductive area (carbon particles) at the electrode surface [16,34] . Hence an electrode containing 15% CPCHA was employed for all subsequent experiments.

Table 1. Effect of modifier composition in CPE (preconcentration solution : 0.1 M sodium acetate buffer of pH 9; preconcentration time: 2 min; supporting electrolyte: 0.3 M sodium acetate buffer of pH 6; reduction potential: -1.2 V; reduction time: 1 min; scan rate: 30 mV/s; pulse amplitude: 100 mV; and pulse period: 0.2 s)

% CPCHA in the paste	Ip (-μA)	
	8 μM Pb(II)	16 μM Pb(II)
5	3.229	5.633
7.5	4.604	6.668
10	6.944	8.669
12.5	9.315	14.34
15	9.912	16.04
20	6.587	10.16

4.4. Effect of pH of Preconcentration Solution and Supporting Electrolyte

The complex formation reaction of lead(II) with CPCHA modified electrode (as shown in the above mechanism) is affected by factors that influence the up take of lead(II) from the solution on the electrode surface. Hence, different preconcentration media with different pH were studied in order to obtain conditions that favor the up take of lead(II) by the CPCHA modified electrode from the preconcentration solution.

Ammonium chloride buffer (0.1 M, pH 9) and sodium acetate buffer (0.1 M, pH 9) were evaluated as a media for the accumulation. In view of the results obtained, sodium acetate buffer was found to be more effective in favoring the accumulation of lead(II) on the electrode surface, and thus employed as a preconcentration solution throughout the study. The effect of pH of the preconcentration solution (0.1 M sodium acetate) on the accumulation of lead(II) was studied in the pH range 5-10. The Pb(II) peak current as a function of pH is shown in Figure 6. It was found that the peak current increased sharply with increasing pH up to 9 and then remained constant. This is due to the increasing complex formation of lead(II) with CPCHA at the electrode surface with increasing pH and the completion of complex formation at higher pH (≥ 9). One would expect the precipitation of Pb(II) as $Pb(OH)_2$ at such higher pH. However, this was not observed in this investigation due to the fact that the Pb(II) solution was spiked into the preconcentration cell just before dipping the electrode in the cell and subsequent stable complex formation of Pb(II) with CPCHA at the electrode surface. It should also be noted that the acetate ions form weak complexes with Pb(II) [49,50] that prevent the precipitation of $Pb(OH)_2$.

The effect of sodium acetate concentration was also studied in the range 0.1- 0.5 M at constant pH. The maximum peak current was observed for 0.1 M solution. It was found that increasing the concentration of sodium acetate decreased the peak current. This is due the fact that acetate ions form weak complexes with Pb(II) [49,50] and hence increasing the concentration of acetate ions decreases the accumulation of Pb(II) as CPCHA complex at the electrode surface.

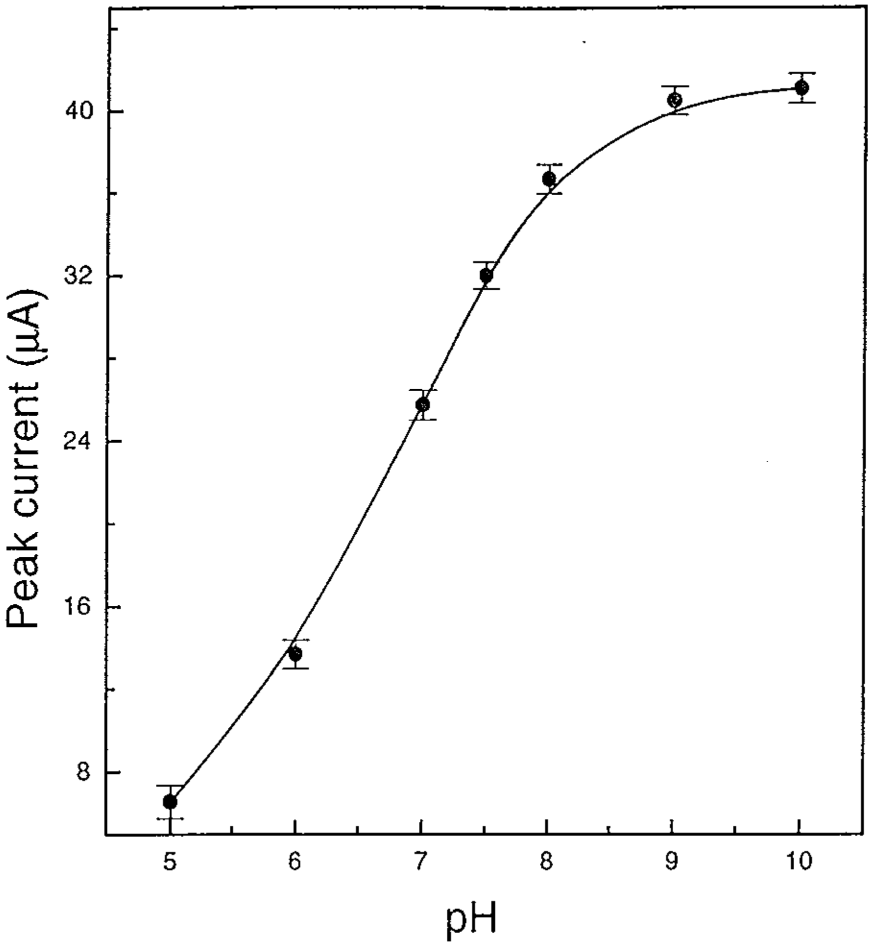

Figure 6. Effect of preconcentration solution pH on the differential pulse anodic stripping voltammetric peak current. Each bar represents mean±3 standard deviation. Lead(II) concentration: 4.0 x 10^{-5} M; reduction potential: -1.2 V; reduction time: 1 min; scan rate: 30 mV/s; pulse amplitude: 100 mV; pulse period: 0.2 s. Other conditions are as in Figure 4.

The effect of the composition of the supporting electrolyte on voltammetric measurement of lead(II) was also studied. Solutions of sodium acetate, sodium perchlorate, and potassium nitrate (each 0.3 M) were examined as supporting electrolyte for the voltammetric measurements. In view of the results obtained, sodium acetate buffer was chosen as supporting electrolyte in the measurement cell, in order to obtain the highest analytical signal.

The effect of pH of the supporting electrolyte (0.3 M sodium acetate) was also studied by varying the pH in the range 3-8. Maximum peak current was obtained at pH 6. The reduction step of Pb(II) at the CME surface involves hydrogen ions (as shown in the above mechanism), consequently the reduction reaction is hindered as the pH is increased. On the other hand, at lower pH the lead(II)-CPCHA complex starts to dissociate as a result the accumulated Pb(II) ions leach from the surface of the electrode. As a consequence, in both cases a drastic decrease in the differential pulse anodic stripping peak current was observed. The effect of concentration of the supporting electrolyte on the voltammetric signal of Pb(II) was also studied by varying the concentration of sodium acetate in the range 0.05-0.5 M. Maximum and reproducible peak current was obtained at 0.3 M sodium acetate buffer solution in the measurement cell.

It is evident from the above discussion that the preconcentration and the electrochemical measurement steps require sodium acetate solutions of different concentrations and different pH. Hence, it was necessary to carry out the preconcentration and the electrochemical measurement separately. Furthermore, the exchange of medium between accumulation and measurement offers some advantages: components of the analyte solution, which are electroactive but do not have an affinity for the electrode modifier, CPCHA, will not interfere with voltammetric determination of the analyte, additionally optimum parameters for both media, analyte, and measurement solutions, can be optimized independently leading to improved sensitivity [19]. Therefore, 0.1 M sodium acetate of pH 9 and 0.3 M sodium acetate of pH 6 were used for an open-circuit preconcentration and voltammetric measurements, respectively.

4.5. Effect of Preconcentration Time

The final parameter of major importance is the length of time allowed for the accumulation of lead(II) from the preconcentration solution at the electrode surface. The dependence of the differential pulse anodic stripping voltammetric peak current on the preconcentration time for two different Pb(II) concentrations is shown in Figure 7. The peak current increases with increasing preconcentration time, indicating an enhancement of Pb(II) up take at the electrode surface. Normally, the increase in the response continues until a maximum signal level, presumably corresponding to either a saturation or an equilibrium surface coverage, is attained. The results obtained indicated attainment of steady-state accumulation levels of Pb(II) at the electrode surface requiring exposure times of 6 min for 8 μM Pb(II) (curve 1) and 4 min for 16 μM Pb(II) (curve 2). In general, it was found that the peak current depends on the preconcentration time for a short period. However, with longer period of preconcentration time gradual change in the peak current was observed.

This observation is in accordance with the results of other stripping methods based on open-circuit accumulation [14-18]. Thus, in order to obtain linear relationship between Pb(II) concentration and peak current a relatively shorter and longer preconcentration times must be employed for higher and lower concentrations of Pb(II), respectively, in order to avoid saturation. Hence, 2 min and 6 min preconcentration times were employed for $\geq 10^{-6}$ M Pb(II) and $\leq 10^{-6}$ M Pb(II), respectively, in all subsequent experiments.

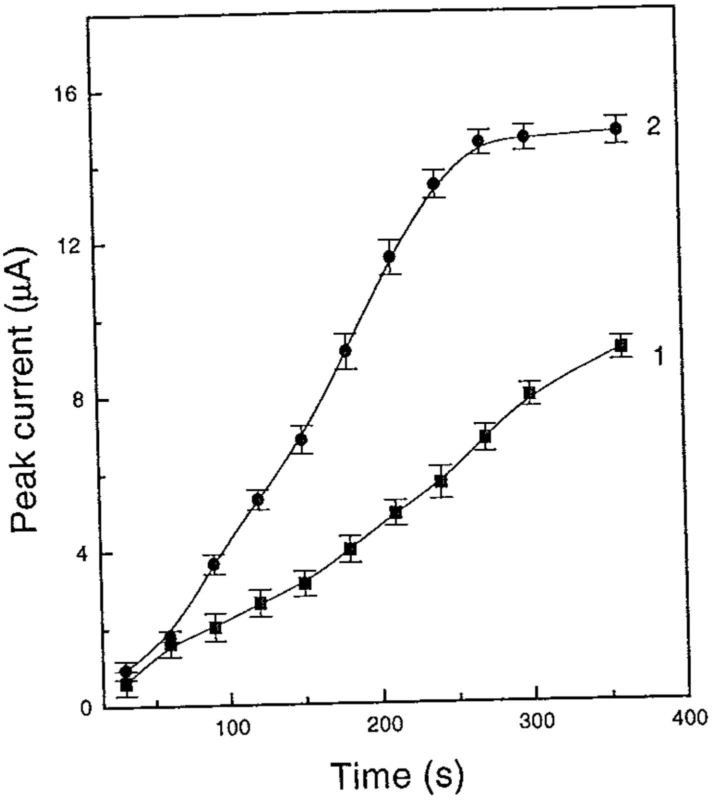

Figure 7. Effect of preconcentration time on the differential pulse anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Lead(II) concentration: (1) 8.0 x 10^{-6} M; (2) 1.6 x 10^{-5} M; other conditions are as in Figure 6.

4.6. Effect of Reduction Potential and Reduction Time

The effect of the reduction potential on the anodic peak current of lead(II) was studied by varying the initial potential from -0.7 to -1.3 V. The anodic peak began to appear only at an applied potential of -0.9 V. When the potential was increased to -1.2 V, the highest peak current was obtained. Further increasing the reduction potential from -1.2

to -1.3 V led to a steady-state current (Fig. 8). Hence -1.2 V was employed as a reduction potential in all subsequent experiments.

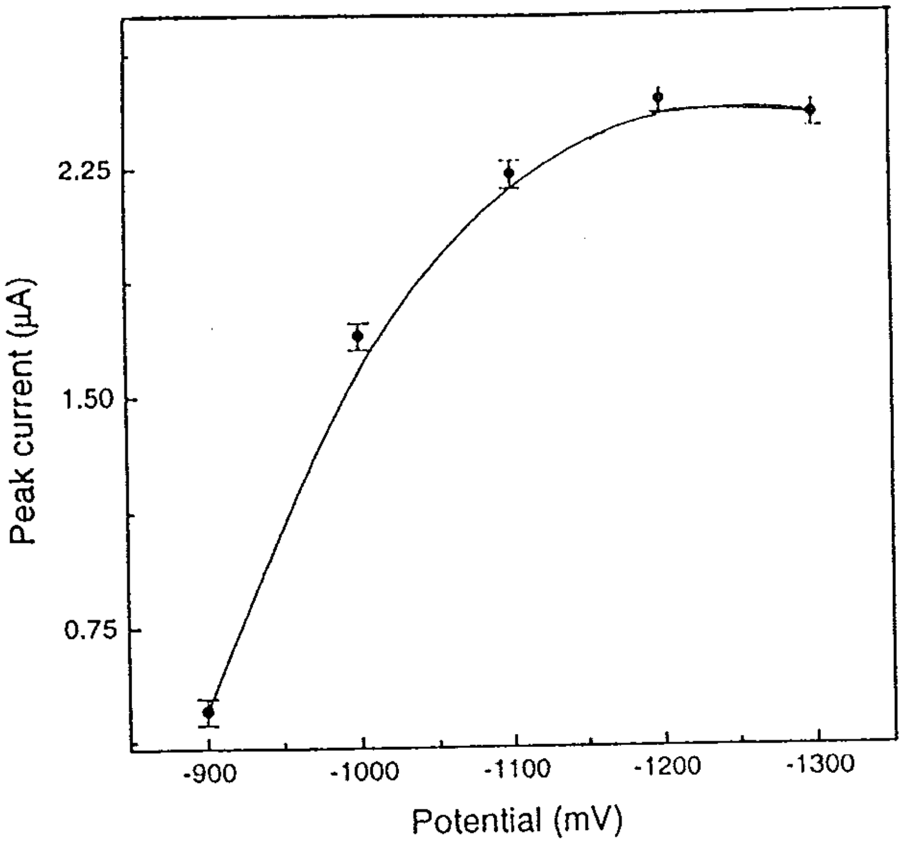

Figure 8. Effect of reduction potential on the differential pulse anodic stripping voltammetric peak current. Lead(II) concentration: 8.0 x 10^{-6} M; other conditions are as in Figure 6.

The effect of the reduction time on the anodic peak current of lead(II) was also examined. The peak current was found to increase linearly with increasing reduction time up to 60 s and then remained constant (Fig. 9). Therefore 1 min reduction time was used for all subsequent measurements.

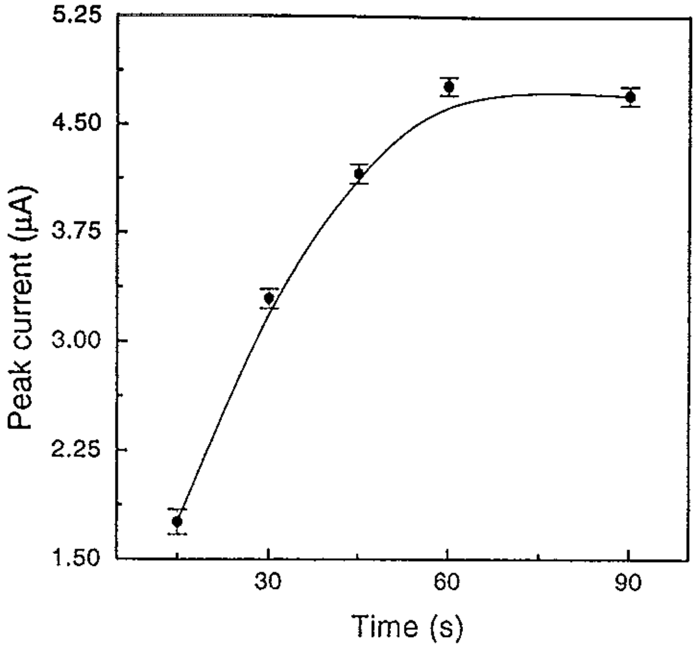

Figure 9. Effect of reduction time on the differential pulse anodic stripping voltammetric peak current. Each bar represents mean±3 standard deviation. Lead(II) concentration: 8.0 x 10^{-6} M; other conditions are as in Figure 6.

4.7. Effect of Instrumental Parameters

The scan rate was varied from 5 to 75 mV/s. The peak current increased and become broader on increasing the scan rate. A scan rate of 30 mV/s was used for the further studies. A similar pattern of the peak current was obtained with increasing the pulse amplitude from 25 to 125 mV. A pulse amplitude of 100 mV was chosen for further work. Variation of the pulse period from 100 to 200 ms increased the peak current and from 200 to 400 ms pulse period the peak current remained constant. Hence a pulse period of 200 ms was used. The scan rate, pulse amplitude, and pulse period were selected on the consideration of both the peak-height and half-peak width [27]. The results are given in Tables 2-4.

Table 2. Effect of scan rate (other conditions ar as in Table 1)

Scan rate (mV/s)	Ip (-μA) for 8 μM Pb(II)
5	1.005
10	1.464
20	2.327
30	2.949
50	3.289
75	3.679

Table 3. Effect of pulse amplitude (other conditions ar as in Table 1)

Pulse amplitude (mV)	Ip (-μA) for 8 μM Pb(II)
25	1.402
50	2.275
75	3.439
100	5.096
125	5.948

Table 4. Effect of pulse period (other conditions ar as in Table 1)

Pulse period (ms)	Ip (-μA) for 8 μM Pb(II)
100	2.039
200	4.318
300	4.452
400	4.565

4.8. Optimal 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 lead(II) at CPCHA modified CPE. The results are summarized in Table 5.

Table 5. Optimum experimental conditions for the determination of Pb(II) by DPASV

Parameters studied	Optimum value obtained
Composition of modifier in CPE	15%
pH of preconcentration solution	9
Concentration of preconcentation solution	0.1 M
Preconcentration time	2 min for ≥10^{-6} M Pb(II) and 6 min for ≤10^{-6} M Pb(II)
pH of supporting electrolyte	6
Concentration of supporting electrolyte	0.3 M
Reduction potential	-1.2 V
Reduction time	1 min
Scan rate	30 mV/s
Pulse amplitude	100 mV
Pulse period	200 ms

4.9. Calibration Curve, Detection Limit, and Precision

The differential pulse anodic stripping voltammograms at different concentrations of Pb(II) are shown in Figure 10 and 11. The peak potential was found to shift towards more positive with increasing concentration of Pb(II). The peak current increased with increasing Pb(II) concentration and two linear ranges were obtained. The response was

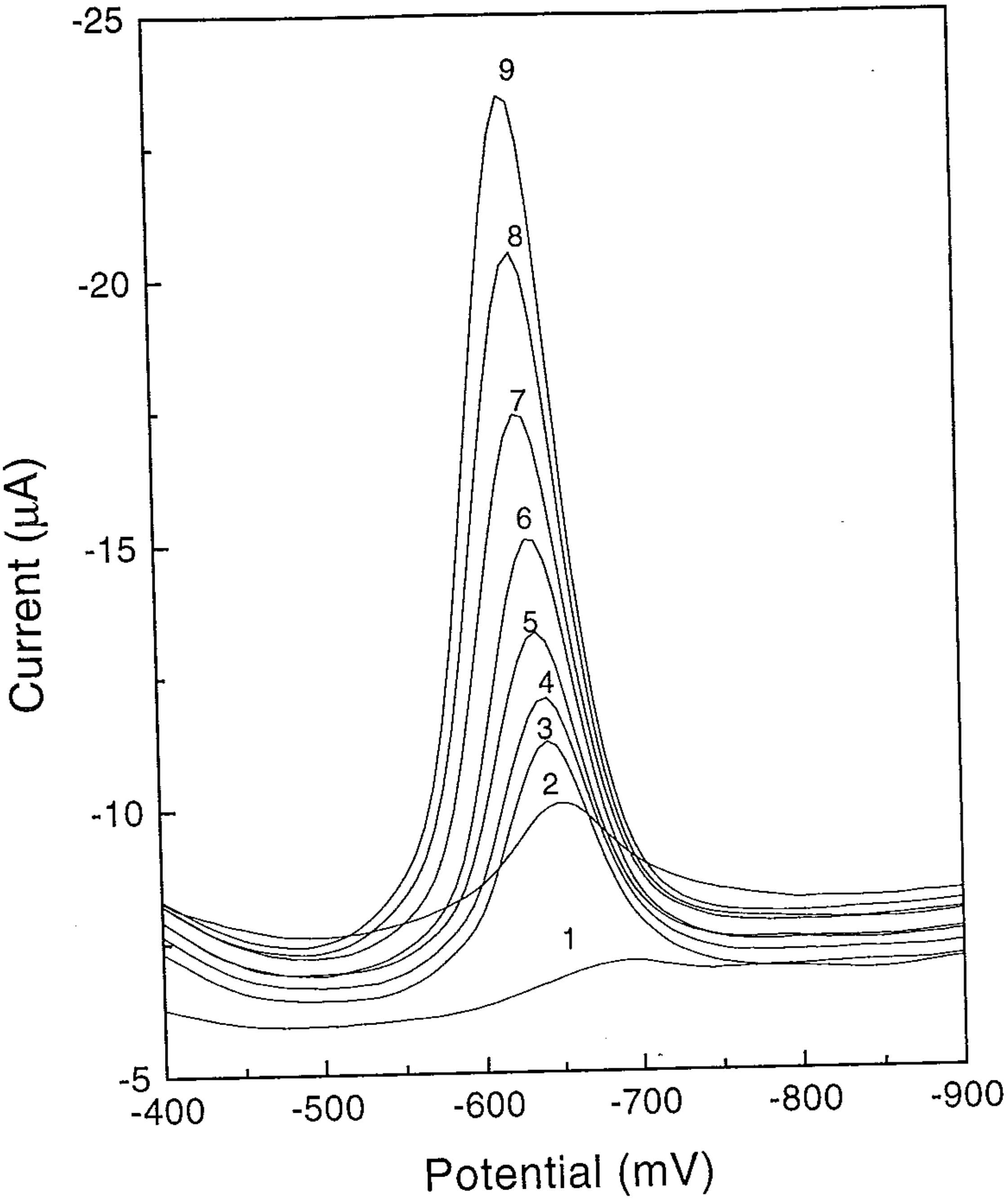

Figure 11. Differential pulse anodic stripping voltammograms of lead(II) accumulated at CPCHA modified carbon paste electrode. Lead(II) concentration: (1) 0.0 M; (2) 2.0 x 10^{-8} M; (3) 5.0 x 10^{-8} M; (4) 1.0 x 10^{-7} M; (5) 2.0 x 10^{-7} M; (6) 4.0 x 10 $^{-7}$ M; (7) 6.0 x 10^{-7} M; (8) 8.0 x 10^{-7} M; (9) 1.0 x 10^{-6} M; preconcentration time: 6 min; other conditions are as in Figure 6.

4.10. Effect of Other Ions

Chemically modified CPEs not only have significant analytical potential to enhance sensitivity but also provide an avenue for improved selectivity which is determined by the chemical reactivity of the modifier with the analyte. Hence, the use of selective or specific modifier helps to overcome interferences from coexisting ions. But those metal ions which compete for complexation with the modifier and binding sites on the modified electrode surface would interfere significantly in the determination of the analyte. Anions which form stable complexation with the metal ion to be determined can also interfere.

The effect of other ions were studied by adding known quantities of the desired ion to solution containing 10 μM of lead(II) and recording the differential pulse anodic stripping voltammogram according to the procedure described above. The influence of other ions, present in the analyte solution on the current response of Pb(II) is shown in Table 6 (concentrations shown are the highest assayed). As can be seen from Table 6, several ions such as K^+, Li^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+},Tl^+, Mn^{2+}, F^-, SO_4^{2-}, I^-, ClO_4^-, SCN^-, Cl^-, and Ag^+ (up to 100-fold molar excess); Co^{2+} and $C_2O_4^{2-}$(up to 20-fold molar excess); Cd^{2+} and CO_3^{2-} (10-fold molar excess); Cr^{3+} (5-fold molar excess); Hg^{2+}, Bi^{3+}, Sn^{2+}, Zn^{2+}, and Fe^{3+} (2-fold molar excess); Al^{3+} and Au^{3+} (equi-molar) have only negligible effect on the determination of Pb(II). However, equi-molar amount of Cu^{2+} and Ni^{2+} interfere significantly by decreasing the Pb(II) signal, because they form complexes with CPCHA and prevent the complex formation and accumulation of Pb(II) at the electrode surface.

The influence of weakly interfering ions can easily be eliminated by applying the standard addition method for the evaluation of the concentration of Pb(II). This has been examined by determining Pb(II) in four different synthetic matrices composed of weakly interfering ions. These matrices are of similar compositions to that of water samples [5]

Table 6. (Continued)

Interfering ion	Concentration (M)	Change in current (%)
CO_3^{2-}	1×10^{-4}	-3.0
Cr^{3+}	5×10^{-5}	-6.4
Hg^{2+}	2×10^{-5}	-7.9
Bi^{3+}	2×10^{-5}	-5.0
Sn^{2+}	2×10^{-5}	+6.6
Zn^{2+}	2×10^{-5}	-8.6
*Fe^{3+}	2×10^{-5}	-4.0
*Al^{3+}	1×10^{-5}	-4.2
Au^{3+}	1×10^{-5}	-4.6
Ni^{2+}	1×10^{-5}	-20.4
Cu^{2+}	1×10^{-5}	-36.2

* In the presence of 0.01 M NaF.

Table 7. Determination of lead(II) in synthetic matrices

Matrix	Composition	Pb(II) found*
A	1×10^{-5} M Pb(II) + 1×10^{-3} M Mg(II) + 1×10^{-3} M Ca(II) + 1×10^{-3} M Sr(II) + 1×10^{-3} M Ba(II) + 1×10^{-3} M K(I) + 1×10^{-3} M Li(I)	$(0.99 \pm 0.04) \times 10^{-5}$ M
B	1×10^{-5} M Pb(II) + 2×10^{-5} M Zn(II) + 5×10^{-4} M Mn(II) + 4×10^{-5} M Cr(III) + 1×10^{-3} M Ca(II)	$(1.02 \pm 0.07) \times 10^{-5}$ M
C	1×10^{-5} M Pb(II) + 9.2×10^{-6} M Cd(II) + 8.7×10^{-6} M Sn(II) + 1.9×10^{-5} M Bi(III)	$(0.98 \pm 0.05) \times 10^{-5}$ M
D	1×10^{-5} M Pb(II) + 1×10^{-5} M Sn(II) + 1.6×10^{-5} M Bi(III)	$(0.99 \pm 0.04) \times 10^{-5}$ M

*Mean ± 95% confidence limits of triplicate analysis.

4.11. Analytical Application

In order to evaluate the performance of CPCHA modified carbon paste electrode in practical analytical work, quantitation of lead in potable water was attempted. The water sample showed a distinct peak of lead(II). Hence, the concentration of lead in the water sample was determined by standard addition method. Known concentrations (2.00×10^{-6}, 4.00×10^{-6}, 6.00×10^{-6}, and 8.00×10^{-6} M) of Pb(II) solution were added to the water sample. The differential pulse anodic stripping voltammograms were recorded after each addition. The voltammograms are shown in Figure 12. Three determinations were made on each addition. The plot of peak current against lead concentration was linear ($r = 0.998$). The concentration of lead in the water was found to be $(2.60 \pm 0.05) \times 10^{-7}$ M. This is in a good agreement with the value from the reference method (differential pulse anodic stripping voltammetry with benzoin oxime modified carbon paste electrode [14]), which gave $(2.51 \pm 0.07) \times 10^{-7}$ M lead in the water sample.

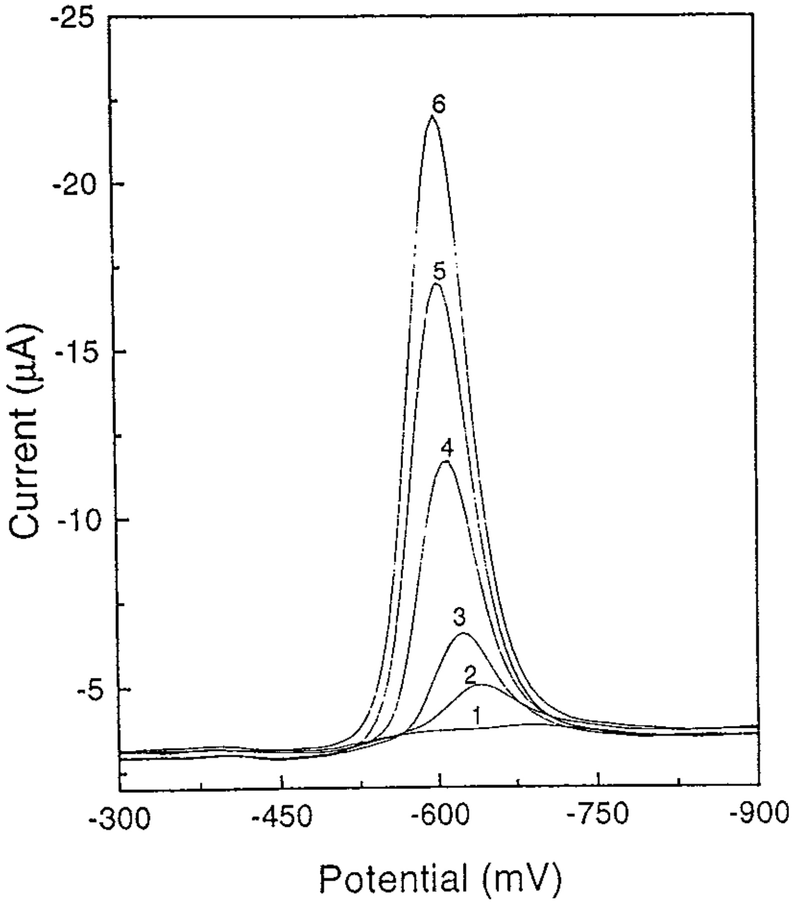

Figure 12. Differential pulse anodic stripping voltammograms for the determination of lead in potable water by standard addition method. (1) 0.1 M sodium acetate buffer (pH 9); (2) 0.1 M sodium acetate buffer (pH 9) prepared in potable water; and after the addition of: (3) 2.0×10^{-6} M ; (4) 4.0×10^{-6} M; (5) 6.0×10^{-6} M; and (6) 8.0×10^{-6} M Pb(II) to 0.1 M sodium acetate buffer (pH 9) prepared in potable water; other conditions are as in Figure 6.

5. Conclusion

A new chemically modified carbon paste electrode has been developed using N-*p*-chlorophenylcinnamohydroxamic acid for the determination of lead(II) at trace levels by differential pulse anodic stripping voltammetry. The electrode offers attractive properties compared to the pervious studies [15-18] such as simplicity of electrode preparation, high stability, and the use of nondearated solution. Also there is no leaching of the electrode because of the low solubility of CPCHA in aqueous solution and hence a single electrode surface can be used for multiple analytical determinations over several weeks. The method presented here has wider linear range and a lower detection limit than some of the reported methods [15,17] and is not interfered so strongly by other metals, which are normally associated with lead in alloys and complex materials. The linear range, detection limit, and selectivity of the proposed method are comparable to other stripping voltammetric methods for the determination of lead(II) using chemically modified carbon paste electrodes [14,16,18].

6. References

1. J.C. Bailor, H.J. Emeleus, R. Nyholm, A.F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon, Oxford, 1975, pp 105-112.
2. V. Valkovic, *Trace Element Analysis*, Taylor and Francis, London, 1975, p 114.
3. P.L. Soni, *Text Book of Inorganic Chemistry*, 6th Ed., Sultan Chand and Sons, Delhi, 1971, p 506.
4. S.P. Parker, *McGraw-Hill Encyclopedia of Chemistry*, 2nd Ed., McGraw-Hill, New York, 1993, pp 585-587.
5. P. Oneill, *Environmental Chemistry*, 2nd Ed., Chapman and Hall, London, 1993.
6. F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., John Wiley, 1988, pp 297-298.
7. A. Fitch, *Critical Reviews in Analytical Chemistry*, **1998**, 28, 267.
8. F. Feigel, V. Anger, R. Oesper, *Spot Tests in Inorganic Analysis*, Elsevier, New York, 1972, p 283.
9. T.W. Gilbert, in *Treatise on Analytical Chemistry*, Part II, Vol. 6, I.M. Kolthoff and P.J. Elving, eds., Intersicence, New York, 1966.
10. G.D. Christian, F.J. Feldman, *Atomic Absorption Spectroscopy Applications in Agriculture, Biology, and Medicine*, Robert E. Krieger publishing Company, New York, 1979, p 409.
11. D. Sancho, M. Vega, L. Deban, R. Parod, G. Gonzalez, *Analyst*, **1998**, 122, 727.
12. P. Barberia, N. Stadiotto,*Talanta*, **1997**, 44, 185.
13. J. Limson, T. Nyokons, *Anal. Chim. Acta*, **1997**, 344, 87.
14. P. Tuzhi, T. Zhe, W. Guoshun, S. Baoen, *Electroanalysis*, **1994**, 6, 597.
15. S.V. Prahu. R.P. Baldwin, L. Kryger, *Electroanalysis*, **1989**, 1, 13.
16. J.A. Ramos, E. Bermejo, A. Zapardiel, J.A. Perez, L. Hernandez, *Anal. Chim.*

Acta, **1993**, 273, 219.

17. M. Connor, E. Dempsey, M.R. Smyth, B. Fleet, H. Gunasingham, *Electroanalysis*, **1991**, 3, 331.
18. Z.M. Hu, C.J. Selisker, W.R. Heineman, *Anal. Chim. Acta*, **1998**, 369, 93.
19. K. Kalcher, *Electroanalysis*, **1990**, 2, 419.
20. K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, *Electroanalysis*, **1995**, 7, 5.
21. T. Kuwana, W.G. French, *Anal. Chem.* **1964**, 36, 241.
22. F.A. Schultz, T. Kuwana, *J. Electroanal. Chem.*, **1965**,10, 95.
23. D. Bauer, M.P. Gaillochet, *Electrochim. Acta*, **1974**,19, 597.
24. M. Lamache, D. Bauer, *J. Electroanal. Chem.*, **1977**, 79, 359.
25. M. Lamache, *Electrochim. Acta*, **1979**, 24, 79.
26. K. Ravichandran, R.P. Baldwin, *J. Electroanal. Chem.*, **1981**, 126, 293.
27. J. Wang, *Analytical Electrochemistry*, VCH Publisher, New York, 1994.
28. D.R. Crown, *Principles and Applications of Electrochemistry*, 4th Ed., Blackie Academic and Professional, Glasgow, 1994.
29. P.T. Kissinger, W.R. Heimeman, *Laboratory Techniques In Electroanalytical Chemistry*, 2nd Ed., Marcel Dekker, New York, 1996.
30. R.W. Murray, in *Electroanalytical Chemistry*, Vol. 13, A.J. Bard, ed., Marcel Dekker, New York, 1984.
31. D.C. Bhura, S.G. Tandon, *Anal. Chim. Acta*, **1971**, 53, 379.
32. B.S. Chandravanshi, V.K. Gupta, *Croat. Chem. Acta*, **1984**, 57, 243.
33. T. Wondimu, B.S. Chandravanshi, *Bull. Chem. Soc. Ethiop.*, **1990**, 4, 1.
34. T. Refera, B.S. Chandravanshi, H. Alemu, *Electroanalysis*, **1998**, 10, 1038.
35. D.T. Sawyer, W.R. Heineman, J.M. Beebe, *Chemistry Experiments for Instrumental Methods*, John Wiely, New York, 1984.
36. T. Riley, A. Watson, *Polarography and Other Voltammetric Methods*, A.M. James, ed., John Wiley, Chichester, 1987.

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

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

39. H. Alemu, B.S. Chandravanshi, *Electroanalysis*, **1998**, 10, 116.

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

41. D.B. Luo, *Anal. Chim. Acta*, **1986**, 189, 277.

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

43. N.K. Lam, M. Kopanica, *Anal. Chim. Acta*, **1984**,161, 315.

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

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

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

47. A.M. Bond, *Modern Polarographic Methods in Analytical Chemistry,* Marcell Dekker, New York, 1980.

48. D.C. Bhura, S.G. Tandon, *J. Chem. Eng. Data*, **1969**, 14, 278.

49. J. Inczedy, *Analytical Application of Complex Equilibria*, Ellis Horwood, Chichester, 1976.

50. Z. Holzbecher, L. Davis, M. Kral, L. Sucha, F. Vlacil, *Handbook of Organic Reagents in Inorganic Analysis*, Ellis Horwood, Chichester, 1976.