Addis Ababa University
Research and Graduate Programs
Department of Chemistry

Square wave anodic stripping voltammetric determination of Hg(II) with N-*p*-chlorophenylcinnamohydroxamic acid modified carbon paste electrode

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List of Abbreviations

AdSV	Adsorptive stripping voltammetry
ASV	Anodic stripping voltammetry
CMCPE	Chemically modified carbon paste electrode
CMEs	Chemically modified electrodes
CPCHA	N-*p*-chlorophenylcinnamohydroxamic acid
CPEs	Carbon paste electrodes
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
CVAAS	Cold vapor-atomic absorption spectrometry
DPASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
EDTA	Ethylenediaminetetraacetic acid
GCE	Glassy carbon electrode
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LOD	Limit of detection
MCPE	Modified carbon paste electrode
MWCNTs	Multiwall carbon nanotubes
NPV	Normal pulse voltammetry
PSV	Potentiometric stripping voltammetry
RSD	Relative standard deviation
SWASV	Square wave anodic stripping voltammetry
SWV	Square wave voltammetry
UMCPE	Unmodified carbon paste electrode
XRF	X-ray fluorescence spectrometry

Abstract

In this study a new method for the electrochemical determination of Hg(II) ions using N-*p*-chlorophenylcinnamohydroxamic acid (CPCHA) modified carbon paste electrode has been developed. The experiments were carried out using square wave anodic stripping voltammetry (SWASV). The Hg(II) was accumulated on the electrode surface by the formation of the complex in an open circuit and the resulting surface was characterized by medium exchange followed by electrochemical reduction and SWASV for the determination of Hg(II). Experimental parameters, including carbon paste composition, pH and concentration of accumulating and stripping solutions, preconcentration time, Hg(II) concentration and different instrumental parameters were investigated. The optimum voltammetric response was observed for a paste composition of 7.5% w/w (CPCHA to graphite powder in the carbon paste) and preconcentration time of 210 s in 0.1 M sodium acetate at pH 8 followed by electrochemical SWASV in 0.3 M ammonium chloride solution at pH 4 as supporting electrolyte, a reduction potential of -0.6 V with 60 s reduction time. Under these optimal experimental conditions, the voltammetric signals were linearly dependent on the Hg(II) concentration in the range of 1-25 µM with a detection limit of 12.9 nM at the signal noise ratio (S/N = 3). For six measurements, the voltammetric response was reproduced with 3.8% relative standard deviation (RSD) at 15 µM Hg(II). 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 Hg(II). Five "spiked" samples of water were evaluated by using the developed method giving recoveries of Hg(II) in the range 98-105%.

1. Introduction

Mercury is one of the most toxic heavy metals that occur in the environment mainly due to industrial applications such as electrical equipment, batteries, paints and extraction of gold from mines and rivers (Verestiuc *et al*., 2015). Because of its high reactivity, extreme volatility and relative solubility in water and living tissues, it can have several effects on human health and living organisms even at very low concentrations (Wang *et al*., 2009). Therefore, the determination of mercury is necessary particularly at trace levels.

The analytical techniques which are frequently used for the determination of mercury include inductively coupled plasma-mass spectrometry (ICP-MS) (Mekonnen *et al*., 2012), mercury analyzer (Mekonnen *et al*., 2012; 2014; 2015), spectrofluorimetry (Kim *et al*., 2016), cold vapor-atomic absorption spectrometry (CVAAS) (Almeida et al., 2016), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Lech, 2014), X-ray fluorescence spectrometry (XRF) (Brent *et al*., 2017) and graphite furnace atomic absorption spectrometry (GFAAS) (Moraes *et al*., 2013). Although these techniques are very reliable and accurate, they have some significant limitations, such as lengthy analysis times and the use of expensive instruments. Furthermore, several complex steps must be performed, and these require specially trained personnel (Martin-yerga *et al*., 2013).

Electrochemical techniques as alternative of spectrometric methods have been accepted as one of the most efficient tools for accurate quantification of trace metal ions due to its low cost, simplicity, speed, sensitivity and the ability to carry out speciation analysis (Wang *et al*., 2009). Among electrochemical techniques, stripping voltammetry provides a powerful tool for the determination of metal ions in environmental matrices (Mnyipika and Nomngongo, 2017). Its remarkable sensitivity and very low detection limit makes it suitable for determining trace metals.

Chemically modified electrodes (CMEs) have received great attention for they enhance the sensitivity and selectivity of the electrochemical techniques. Various CMEs have been used to determine heavy metal ions particularly chemically modified carbon paste electrode (CMCPE) could be used successfully, due to the electrode can be easily prepared, regenerated and modified by being mixed with various modifiers depending on the application (Afkhami *et al*., 2016). In this work a CPE modified with N-*p*-chlorophenylcinnamon- hydroxamic acid (CPCHA) as a modifier was used for the determination of Hg(II) by using square wave anodic stripping voltammetry (SWASV).

1.1. Objective of the study

1.1.1. General objective

The general objective of this study is the electrochemical determination of Hg(II)

1.1.2. Specific objectives

The specific objectives of this study are:

1. To investigate the performance of CMCPE for determination of Hg(II)
2. To establish the optimal electroanalytical parameters for the determination of Hg(II) at the CMCPE using SWASV
3. To establish the analytical performance characteristics (such as linear range, detection limit, reproducibility, stability) of the developed method
4. To carryout interference study on diverse ions
5. To study the analytical application of the method for the determination of Hg(II) in different types of water samples.

2. Literature Review

2.1. Mercury

Mercury is a naturally occurring transition metal found in air, water and soil. It is the only metal that is a liquid state at room temperature. Mercury got its name from the Roman god because its high surface tension causes it to form spheres that can roll and flow very quickly. For this reason, and because it is a silver-white metal, mercury is also called quicksilver. Mercury has been known for thousands of years. In many cultures, people learned to make mercury metal from its most important ore, cinnabar (HgS) which heated releases mercury as a vapor (gas) then the vapor is cooled and captured as liquid mercury (UNEP, 2002).

2.1.1. Occurrence of mercury

Mercury may exist in the environment as elemental mercury, inorganic mercury and organic mercury (Ziab *et al*., 2015).

2.1.1.1. Elemental mercury

The abundance of elemental mercury in the Earth's crust is estimated to be about 0.5 parts per million. That makes it one of the least common elements, which is more scarce than uranium but more plentiful than gold or silver. It very rarely occurs as an element. Instead, it is usually found as a compound mainly in cinnabar ore (HgS) (UNEP, 2002).

2.1.1.2. Inorganic mercury compounds

Inorganic mercury compounds occur when mercury combines with elements such as chlorine, sulfur, or oxygen. Most of these compounds are white powders or crystals, except for cinnabar (HgS), which is red and turns black after exposure to light (ATSDR, 1999). HgS is the most abundant naturally occurring inorganic mercury compound. It is stable and essentially insoluble in water. Mercuric chloride ($HgCl_2$) is a water soluble salt and relatively common in aquatic systems, the atmosphere, and in aerobic soils (ATSDR 1999). Water resources mainly consist of these mercury compounds in valence state of Hg(II) and Hg(I). Mainly Hg(II) is more common inorganic state due to its greater solubility in water (Ziab *et al*., 2015).

2.1.1.3. Organic mercury compounds

Organic mercury compounds contain mercury covalently bound to hydrocarbons (aliphatic or aromatic). There are several forms of organic mercury, including mercury acetate, methyl mercury, dimethyl mercury and phenyl mercury. Among these, methyl mercury is the most common and stable organic mercury compound found in the environment. (Suvarapu *et al*, 2013).

2.1.2. Uses of mercury

Elemental mercury is used in thermometers, barometers, and pressure-sensing devices. Its ease in amalgamating with gold is used in the recovery of gold from its ores. Industry uses mercury metal as a liquid electrode in the manufacture of chlorine and sodium hydroxide by electrolysis of brine. Mercury is still used in some electrical gear, such as switches and rectifiers, which need to be reliable, and for industrial catalysis. Much less mercury is now used in consumer batteries and fluorescent lighting, but it has not been entirely eliminated (ATSDR, 1999). Mercury compounds have various applications such as; calomel (Hg_2Cl_2) is used as a standard in electrochemical measurements and in medicine as a purgative, mercuric chloride ($HgCl_2$) is used as an insecticide, in rat poison, and as a disinfectant. Mercuric oxide (HgO) was used in skin ointments. Mercuric sulphate ($HgSO_4$) is used as a catalyst in organic chemistry, mercuric sulphide (HgS) used as a red pigment (vermilion) for paints (ATSDR, 1999).

2.1.3. Release of mercury in to the environment

Mercury is released to the environment by natural and anthropogenic activities. Naturally occurring mercury releases are mainly attributed to erosion and degassing of mineral deposits, volcanic emissions and forest fire. Anthropogenic emissions are mainly attributed to mining activities, agricultural materials, combustion of coal and oil, solid waste incineration, industrial discharges and mercury and gold production which contribute a major role to high levels of mercury in the environment. The major sources of mercury in aquatic environments include atmospheric deposition, erosion, urban discharges, agricultural materials, mining and combustion and industrial discharges (Wang *et al*., 2004). Water constitutes an important mercury transformation pathway, given the number and complexity of the transformations that take place. The most important transformation, in terms of environmental concern, is methylation which is the conversion of inorganic mercury to organic mercury particularly methyl mercury. When mercury reaches surface waters it is usually oxidized to Hg(II), which is either (a) methylated by sulfate-reducing bacteria or less frequently (b) reduced to elemental mercury, a process called demethylation, via biotic and abiotic (photochemical) pathways and then return to the atmosphere via volatilization (Kallithrakas-K and Foteinis, 2016). Hence microorganisms like bacteria can form methyl mercury in water which builds up in the tissues of fish; larger and older fishes may have high levels of methyl mercury (ATSDR, 1999). Mercury emissions from various sources in the environment are converted into methyl mercury, which are bio-accumulated in the food chain. The topmost predators in the food chain have higher concentrations of methyl mercury than the animals in the lower part of the food chain (Suvarapu *et al*, 2013).

2.1.4. Toxicity and health effects of mercury

There are several ways by which humans are exposed to mercury including eating fish with methyl mercury and breathing mercury vapors in air from the burning of mercury-containing fuels and incinerators. The most tragic incident in history regarding mercury toxicity of humans was first recognized at Minamata, Japan around 1960. The disease, named Minamata disease, induces symptoms such as numbness in the hands and feet, damage to hearing and speech, and even leads to death. Similar incidents occurred in Sweden where the population consumed fish contaminated with a pesticide having organic mercury compound, Iraq due to consumption of rice treated with mercury containing pesticide and China due to ethyl mercury toxicity (Ziab *et al*., 2015). These events helped in recognition of mercury and its compounds as environmental bio-accumulative (persistent) pollutant on global scale. With the passage of time, mercury and its compounds have attained a considerable attention from environment protection agencies in order to curtail emission sources and safeguard the environment (Ziab *et al*., 2015). At the United Nations Organization meeting of world environmental ministers held in Kenya during February 2009, more than 140 countries worldwide agreed to reduce global mercury emissions by 2013 (Suvarapu *et al*., 2013).

Mercury and its compounds have several effects on human health and living organisms even at a very low concentration. They affect the central nervous system, kidneys, and liver and can disturb immune processes; cause tremors, impaired vision and hearing, paralysis, insomnia and emotional instability. During pregnancy, mercury compounds cross the placental barrier and can interfere with the development of the foetus, and cause attention deficit and developmental delays during childhood (Suvarapu *et al.*, 2013).

2.2. Electrochemical techniques

2.2.1. Voltammetry

The term voltammetry refers to a class of electrochemical techniques, and it is used to designate the current-voltage measurement obtained at a given electrode. The current is proportional to the analyte concentration in the sample (Strasunke, 2010). Voltammetry is typically performed by using a three electrode system which includes, a working electrode, at which the oxidation or reduction process of interest occurs, reference electrode, which maintains a constant potential throughout the experiments such as saturated calomel electrode (SCE) or silver-silver chloride electrode (Ag/AgCl) and the counter electrode, which complete the electrical circuit. The counter electrode also known as the auxiliary electrode, is often much larger than working electrode to minimize current density at the electrode surface. The working electrode can be solid (platinum, gold or glassy carbon). If the working electrode is formed by drop of mercury the analytical technique is called polarography (Lacourse, 1997). The common features of voltammetry is the measurement of a current response (i) at a working electrode as a function of the applied potential (E) with respect to a reference electrode by means of a potentiostat (Kounaves, 2008).

2.2.2. Cyclic voltammetry (CV)

CV has become important and widely used in many areas of electro-analytical chemistry. It is rarely used for quantitative determination but it is widely used for the study of redox reactions and provides information about the chemical reactions that occurs (Farghaly *et al.*, 2014). CV is carried out first, applying a linear sweep potential to the working electrode from an initial potential (E_i) to a final one (E_f) then, the sweep is reversed and the potential returns to E_i. It consists of scanning linearly the potential of a stationary working electrode, using a triangular potential waveform, in Figure 1. While the applied potential is scanned at the working electrode in both forward and reverse directions the resulting current is recorded. The resulting current *vs* potential plot is called a cyclic voltammogram, Figure 2 (Scholzs, 2015).

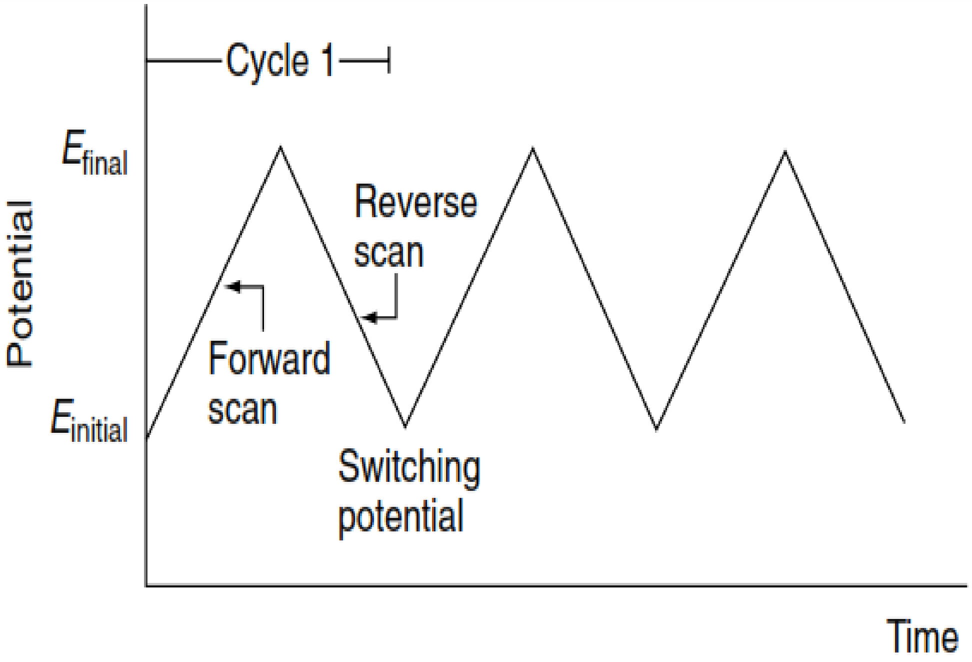

Figure 1. Excitation wave form of cyclic voltammetry

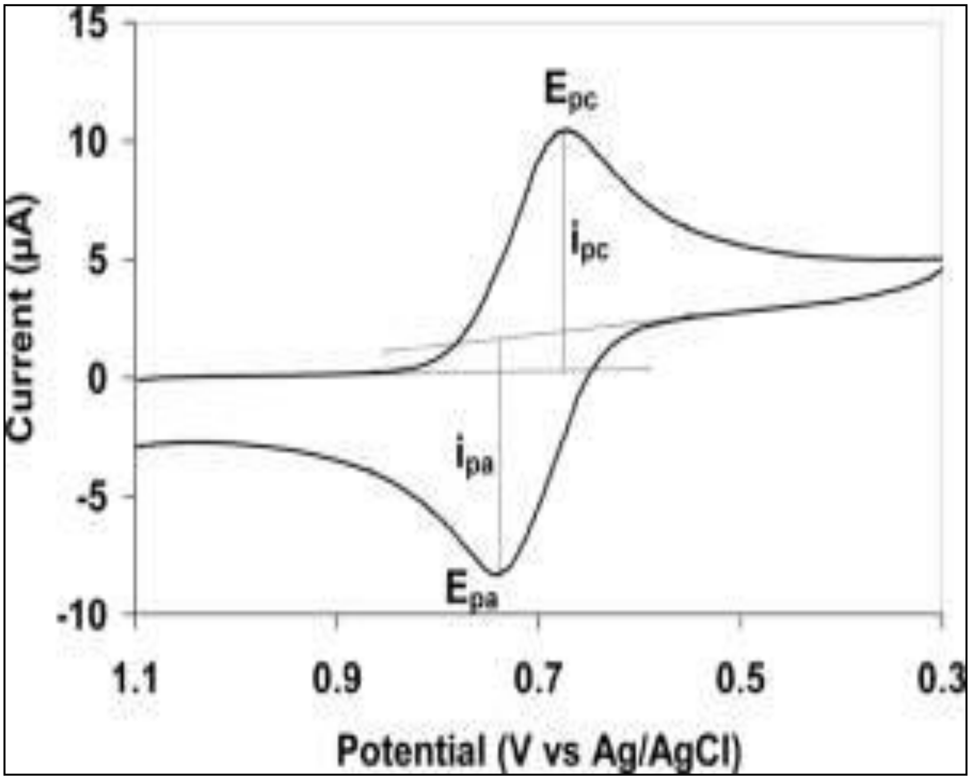

Figure 2. A cyclic voltammogram

The voltammogram is characterized by five main features: the cathodic and anodic peak potentials (E_{pc} and E_{pa} respectively) to which correspond the cathodic and anodic peak currents (i_{pc} and i_{pa}), the half-peak potential ($E_{p1/2}$) at which the cathodic and anodic currents reach half of their peak values. The values of these parameters and the relationship between them provide the basis for classifying cyclic voltammogram as reversible, irreversible or quasi-reversible systems (Alghamdi, 2010).

In a reversible electrode system, the electron transfer process is faster than mass transfer (diffusion). The peak current for a reversible couple is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} V^{1/2} \qquad (1)$$

where A is area of the electrode (cm^2), C is the concentration of analyte (mol cm^{-3}), D is the diffusion coefficient of analyte ($cm^{2}\ s^{-1}$) and v is the scan rate ($V\ s^{-1}$). The current is directly proportional to concentration. The current increase with the square root of the scan rate indicates the electrode reaction is controlled by mass transport. For a reversible couple, the reverse-to-forward peak current ratio is unity and the formal potential (E^0) is centered between E_{pa} and E_{pc}:

$$E° = \frac{E_{pa} + E_{pc}}{2} \tag{2}$$

The number of electrons (n) transferred in the electrode reaction for reversible couple can be determined from the separation between peak potentials:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n}\ V \tag{3}$$

where n is the number of electrons transferred, E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively.

For an irreversible electrode processes with sluggish (slow) electron exchange, the individual peaks are reduced in size and widely separated. The peak current for an irreversible system is given by:

$$i_p = (2.99 \times 10^5)n(\alpha n_a^{1/2}\ ACD^{1/2}\ V^{1/2} \tag{4}$$

where α is the transfer coefficient and n_a is the number of electrons involved in the charge transfer step.

For quasi-reversible systems the current is controlled by both the charge transfer and mass transport. Generally the voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potentials compared to a reversible system (Bard and Faulkner, 2001).

2.2.3. Pulse voltammetry

Pulse voltammetry is carried out with steps and sweep combinations that improve the speed and detection limits, it can be considered as a family of techniques with adjusted potential, the current is monitored after the potential has remained constant for a sufficient time, typically 40 milliseconds (Baron-Jaimez *et al.*, 2013). There are three types of pulse voltammetry.

2.2.3.1. Normal pulse voltammetry (NPV)

This technique consists of a series of potential pulses of increasing amplitude. The potential wave form for NPV is shown in Figure 3. The duration of the pulse, is usually 1 to 100 miliseconds and the interval between pulses is typically 0.1 to 5 second. The resulting voltammogram displays the sampled current on the vertical axis and the potential to which the pulse is stepped on the horizontal axis. The measurement of the peak current produced is usually carried out near the end of each pulse. In NPV at certain period, the resulting current is equal to zero (Baron-Jaimez *et al.*, 2013).

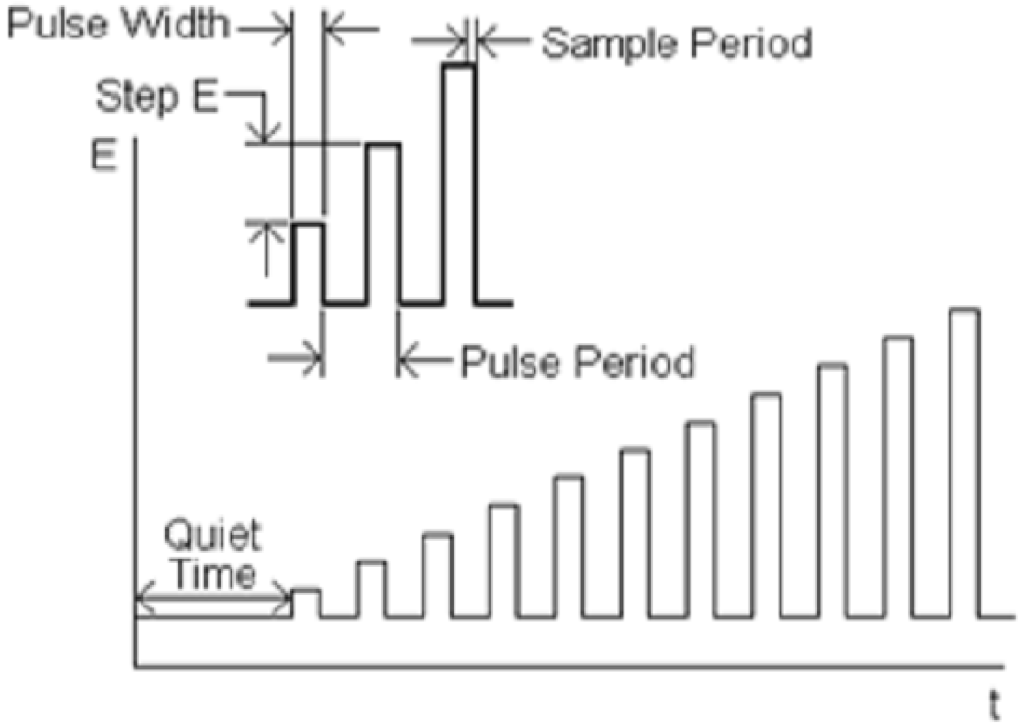

Figure 3. Excitation wave form of normal pulse voltammetry

2.2.3.2. Differential pulse voltammetry (DPV)

DPV is a very useful technique for measuring trace levels of organic and inorganic species (Strasunske, 2010). Comparison between NPV and DPV indicates that in DPV potential pulse is fixed. A potential wave form for DPV is shown in Figure 4, fixed magnitude pulses, superimposed on a slowly changing base potential, are applied to the working electrode. The current is measured at two points; before the application of the pulse, and at the end of the pulse. The first current is subtracted from the second, and the current difference is plotted versus the applied potential. The height of the produced peak current is proportional to the concentration of analyte (Baron-Jaimez *et al.*, 2013)

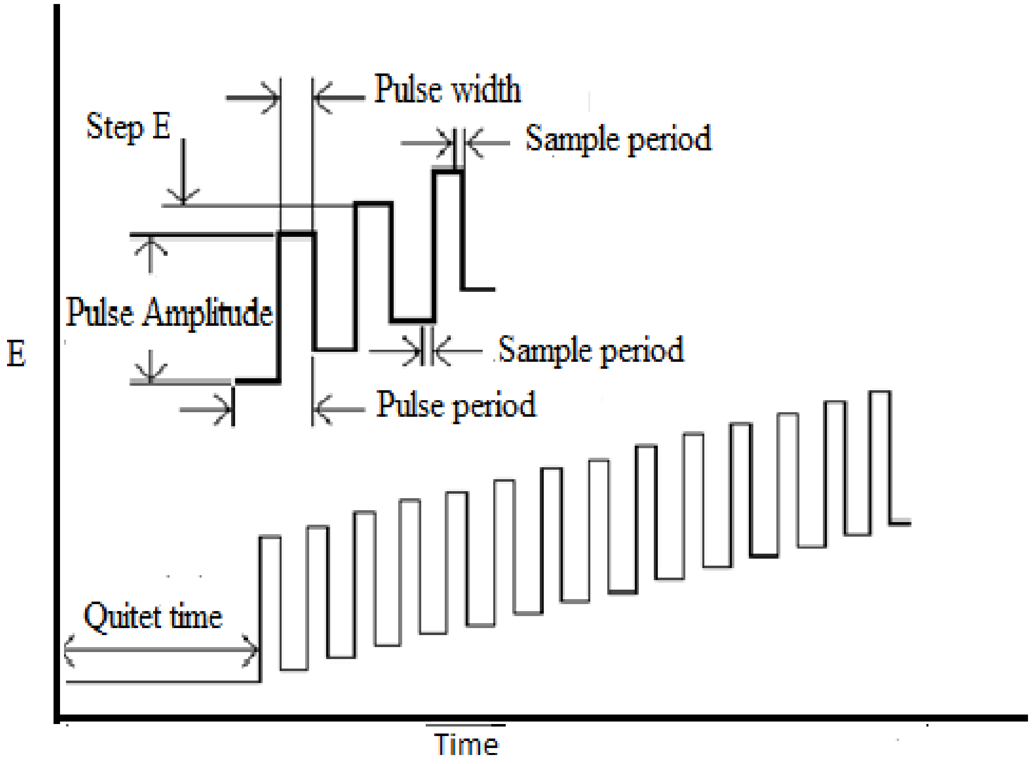

Figure 4. Excitation wave form of differential pulse voltammetry

2.2.3.3. Square wave voltammetry (SWV)

SWV is the most advanced and efficient voltammetric technique. A potential, consisting of symmetrical square-wave pulses shows in Figure 5, superimposed on a staircase-wave form is applied to the working electrode. The current is sampled during each square wave cycle, once at the end of the forward pulse and the other at the end of the reverse pulse. The current difference between the two measurements is plotted versus the base potential. The resulting peak current is proportional to the analyte concentration (Farghaly *et al*., 2014). SWV has several advantages such as excellent suppression of background currents and speed. This speed, coupled with computer control and signal averaging, allows for experiments to be performed repetitively and increases the signal to noise ratio. The major advantage of SWV over DPV is its speed (Baron-Jaimez *et al*., 2013).

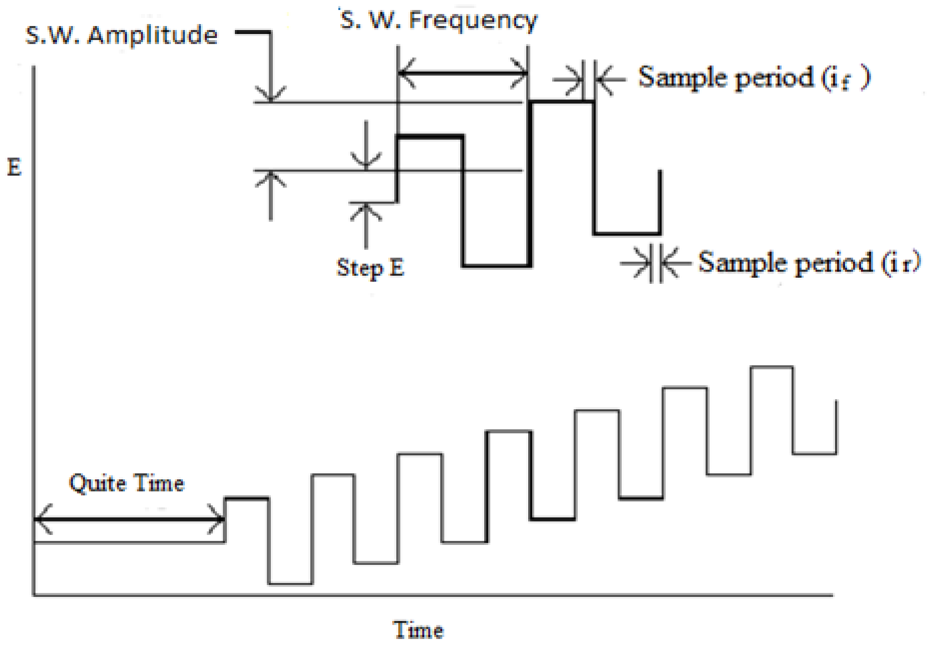

Figure 5. Excitation wave form of square wave voltammetry

2.2.4. Stripping voltammetry

Stripping voltammetry is a special branch of voltammetry used to determine very small concentrations of trace metals (subnanomolars); i.e. analysis of 10^{-10} M solution. Stripping voltammetry has two main steps. Preconcentration step, the accumulation of analyte on to the surface of the working electrode and striping step, electrochemical measurement of the deposited analyte by which it is stripped from the electrode surface by the application of a potential scan (voltammetry). The combination of the preconcentration step and the stripping step generates extremely favorable signal to background ratio. In addition, this technique offers a wide linear range and simultaneous determination of metal ions (Farghaly *et al*., 2014). There are different types of stripping voltammetric techniques; they can be classified according to the nature of the accumulation process and dissolution.

2.2.4.1. Anodic stripping voltammetry

ASV is one of the most widely used forms of stripping voltammetric analysis. It is an extremely sensitive technique available for determination of trace metals in water samples and has the advantage of simultaneous determination of metals at concentrations as low as 10^{-10} M (Florence, 1984). In this technique as shown in Figure 2(a), the metal is preconcentrated onto the electrode surface which is done by cathodic deposition at a controlled time and potential. After resting period, the potential is scanned anodically by using a more sensitive potential-time (pulse) wave form, called SWASV which discriminates against the charging background current. During the stripping step, as can be seen in Figure 6(b), the metal is re-oxidized, stripped out from the electrode surface. The voltammetric response shown in Figure 6(c), provides analytical information of interest. E_p serves to identify the analyte in the sample. The i_p depends upon various parameters of the preconcentration and stripping steps; as well as on the characteristics of the analyte and the electrode geometry; and it is proportional to the analyte concentration in the sample (Strasunske, 2010).

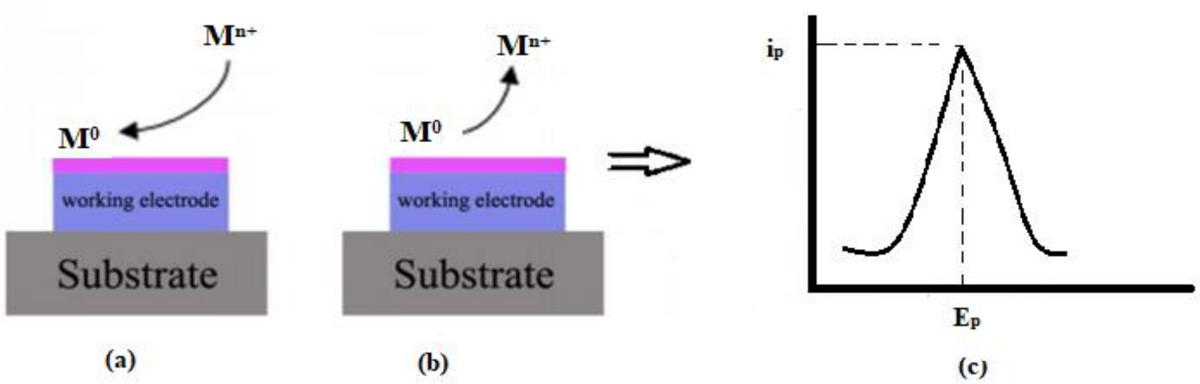

Figure 6. (a) preconcentration step, (b) stripping step and (c) the voltammetric result of anodic striping voltammetry

2.2.4.2. Cathodic stripping voltammetry (CSV)

CSV is used to determine many of organic and inorganic compounds that form insoluble salts with the electrode material. It can be considered as mirror image of ASV. It involves deposition of the analyte on the electrode when anodic potential is applied to the working electrode followed by stripping in a negative-going (cathodic) potential to reduce the deposited analyte back into the solution (Farghaly *et al*., 2014).

2.2.4.3. Adsorptive stripping voltammetry (AdSV)

AdSV is quite similar to ASV and CSV methods. The primary difference could be explained as using adsorption in the preconcentration step. The adsorption process plays an important role in the accumulation step. AdSV can be employed in trace analysis of organic and inorganic analyte species. In this method a metal ion reacts with a suitable ligand and forms a complex by being adsorbed on the electrode surface. Then the deposited complex form of the analyte is stripped by reduction or oxidation potential (Farghaly *et al*., 2014).

2.2.4.4. Potentiometric stripping voltammetry (PSV)

PSA is a technique where potentiostatic control is disconnected following preconcentration, and the preconcentrated analytes are reoxidized by an oxidizing agent present in the solution or an oxidizing current. A stirred solution during the stripping step is used in order to facilitate the transport of oxidant (Strasunske, 2010).

2.3. Working electrode materials

The performance of voltammetric analysis is strongly influenced by the material of the working electrode. The working electrode should be selected based on the following requirements: electrochemical inertness over a broad potential window, low back ground current, low ohmic resistance and the possibility of a sufficiently simple surface regeneration. All these factors provide; high accuracy, sensitivity and stability, good reproducibility and low detection limit

(Strasunske, 2010). The most common working electrodes including metal electrodes (platinum, gold, silver and bismuth), carbon based electrodes (glassy carbon, carbon paste, boron doped) have received great attentions in stripping analysis techniques (Akfhami, 2016).

2.3.1. Carbon paste electrodes (CPEs)

CPEs are among the most popular types of carbon electrodes which have been widely used in electroanalysis, mainly due to such interesting properties as chemical inertness, low cost, wide potential window and suitability for a variety of sensing and detection applications. The performance of the carbon paste electrodes depends on the properties of the modifier materials used to impart selectivity towards the target species (Aglan *et al*., 2012).

2.3.2. Chemically modified carbon paste electrodes (CMCPEs)

The modification of CPE begins in 1964 with the fundamental studies on the placement of a reagent onto the surface, to impart behavior of that reagent to the modified surface. Such deliberate alteration can thus meet the needs of solution to many electroanalytical problems. There are various ways in which the CMCPE can benefit analytical applications. These include the acceleration of electron transfer reactions, preferential accumulation or selective membrane permeation. Such steps can impart higher sensitivity, selectivity or stability (Strasunske, 2010).

CPE is chemically modified by means of various techniques. Some of the techniques include direct mixing, the modifier can be dissolved directly in the binder or admixed mechanically to the paste during its homogenization, soak graphite particles with a solution of a modifier, and after evaporating the solvent use the impregnated carbon powder (solvent volatilization) and the prepared pastes can be modified *in situ*. Whereas direct modifications obviously provide special sensors for one purpose use, but *in situ* approaches offer a possibility to employ the same carbon paste for repetitive modifications with different modifiers (Svancara *et al*., 2001).

2.3.3. N-*p*-chlorophenylcinnamohydroxamic acid (CPCHA)

CPCHA (Figure 7) contains an acid group with a replaceable hydrogen atom and basic coordinating group in such a position so as to form a five membered ring on reaction with metal ions. CPCHA is insoluble in water and it is stable towards heat, light and air.

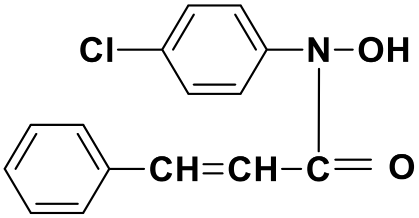

Figure 7. Structure of N-*p*-chlorophenylcinnamohydroxamic acid (CPCHA)

CPCHA has been used as an extracting agent for the spectrophotometric determination of Ce(IV) (Chandravanshi and Gupta, 1984) and Nb(V) (Wondimu and Chandravanshi, 1990) and as a modifier in carbon paste electrode for the voltammetric determination of Co(II) (Refera *et al.*, 1998), Pb(II) (Degefa *et al.*, 1999) and Cd(II) (Fanta and Chandravanschi, 2001) while its analogue N-phenylcinnamohydroxamic acid has been used for the voltammetric determination of Cu(II) (Alemu and Chandravanshi, 1998). However, the complex formation reaction and voltammetric behavior of Hg(II) by using CPCHA modified carbon paste electrode have not been investigated. Hence the voltammetric behavior of Hg(II) at CPCHA modified CPE was studied in the present investigation.

3. Experimental

3.1. Reagents and chemicals

All chemicals were of analytical grade. Graphite powder (spectroscopic grade) was from SGL Carbon (Ringsdorff, Germany) and parafin oil was supplied from (Uvasol, Merck). Anhydrous sodium acetate, acetic acid, sodium hydroxide, ammonium chloride, ammonium hydroxide, hydrochloric acid, sulfuric acid, potassium chloride, hydoxylammine hydrochloride ($NH_2OH.HCl$), sodium dihydrogen phosphate, phosphoric acid, sodium phosphate, sodium carbonate and ammonium chloride (NH_4Cl) were obtained from (BDH, England). Standard stock solution of Hg (1000 mg/L, atomic absorption standard) was purchased from Sigma-Aldrich (USA). Reagent grade nitrate, sulfate and chloride salts of other cations (Merck and Sigma-Aldrich) were used as received. Double distilled water was used throughout to prepare the solutions. The pH of sodium acetate solution was adjusted by adding acetic acid (0.1 M) or sodium hydroxide (0.1 M) and the pH of ammonium chloride buffer solution was adjusted to the desired value by using ammonia solution (0.1 M) or hydrochloric acid (0.1 M). The working standard solutions of different concentrations, for optimization studies, were prepared daily from the standard stock solution by suitable dilution with double distilled water.

The CPCHA was synthesized by the condensation of N-*p*-chlorophenylhydroxylamine with cinnamoyl chloride at low temperature in diethyl ether medium then making alkaline with a saturated solution of sodium bicarbonate (Bhura and Tandon, 1969).

3.2. Apparatus and instruments

All the voltammetric experiments for the determination of mercury were performed by using CHI 840C electrochemical analyzer (CHInstruments, USA) connected to IBM Personal computer 130100DX4 for recording of voltammograms and processing of data. All experiments were carried out using a conventional three electrode system as shown in Figure 7, with an unmodified CPE and CPCHA modified CPE as a working electrode, a platinum wire as an auxiliary electrode, and a silver/silver chloride (Ag/AgCl) as a reference electrode. Two different cells (10 mL each) were used for the preconcentration and stripping step. The pH measurements were carried out using a pH meter (sensION, SHA Snilu Instruments CO. LTD, China). A magnetic stirrer (STUART Scientific, Germany) with a Teflon coated stirring bar was used for stirring the solutions. A stop clock (Harris Digitimer, Japan) was employed for time measurement.

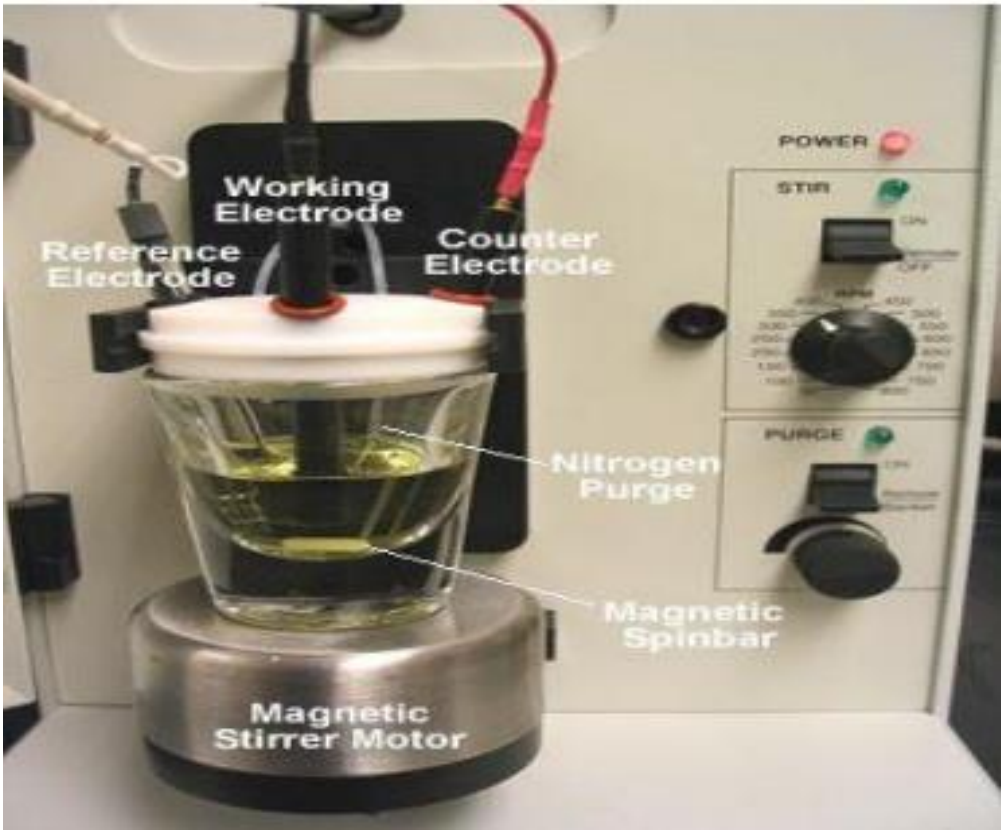

Figure 8. Typical electrochemical cell composed of three electrode system for voltammetry**.**

3.3. Electrode preparation

Unmodified carbon paste was prepared by adding 0.36 mL paraffin oil to 1 g graphite powder. Modified carbon pastes were prepared by substituting corresponding amounts of the graphite powder (5%, 7.5%, 10%, and 12.5% weight-to-weight ratio of the modifier (CPCHA) relative to the graphite powder) and adding the paraffin oil (0.36 mL) then manually homogenizing the mixture by using mortar and pestle. Both unmodified and modified pastes were finally pressed in to a cavity of the assembly made from 1 mL plastic syringe of 3 mm outer diameter with copper wire inserted at one end forming the external electric contact. The electrode surface was polished on clean paper until it had a shiny surface. Whenever regeneration of the electrode was required, a thin layer of the surface was removed and replaced by a fresh paste. The fresh electrode was pretreated by using CV (4-5 cycles) in the supporting electrolyte solution to get reproducible results.

3.4. Procedures

The CVs were performed at unmodified and modified carbon paste electrodes in the potential range of -1.0 to 1.0 V (at 100 mV/s scan rate). All the quantitative measurements were carried out by SWASV. The CMCPE was immersed in a preconcetration cell containing 0.1 M sodium acetate solution (pH 8) and a known amount of Hg(II) solution then preconcentration was done under open circuit for a preselected period of time with constant stirring. The electrode was then taken out from the pereconcetration cell, rinsed with distilled water and placed in to a stripping cell containing 0.1 M NH_4Cl solution (pH 4) as supporting electrolyte. Following the application of a deposition potential of -0.6 V (verses Ag/AgCl) for 60 s without stirring the electrode was scanned anodically from -0.6 V to 0.3 V after 10 s equilibration time with pulse amplitude 0.035 V; frequency 15 Hz and step potential of 0.004 V. After each voltammetric measurement, the electrode was renewed and pretreated by CV (4-5 cycles) in 0.1 M NH_4Cl solution. Fresh supporting electrolyte solution was used in each set of experiments to avoid potential build up of Hg(II) in the electrochemical cell. All electrochemical measurements were made at room temperature (25 ± 2 ^oC) under atmospheric conditions (without inert gas bubbling).

3.5. Analysis of real samples

In order to test its practical application, the Hg(II) content was determined in five different types of water samples (tap water, bottled water, well water, stream water and river water) by spiking method. The water samples were collected by using plastic container. Tap water was collected from Addis Ababa University, analytical chemistry laboratory. Bottled waters of three different types common in the Ethiopian market (Yes, Aquasafe and Fikir) were purchased from a supermarket, Addis Ababa. Well water and stream water were obtained from Akaki area and Ras Mekonnen bridge area respectively, Addis Ababa Ethiopia. River water was collected from Meki, Oromia region in Ethiopia. The samples were filtered before the analysis to remove suspended particles. Each water sample was spiked with 15 µM Hg(II) and placed in 10 mL of chemical cell containing 0.1 M of sodium acetate pH 8, preconcentrated for 3.5 min and followed by voltammetric measurements.

4. Results and Discussion

4.1. Voltammetric behavior of Hg(II) at CPCHA modified carbon paste electrode

The cyclic voltammetry of unmodified and modified carbon paste electrodes were run without and with Hg(II) preconcentration in 0.1 M sodium acetate solution (pH 10) on the electrode surface at open circuit. Figure 9 shows the CVs of CPCHA with and without Hg(II) preconcentration. The voltammograms of the unmodified electrode (curve a) with and without Hg(II) preconcentration and the CPCHA modified electrode without Hg(II) preconcentration did not show any significant peak in the potential range -1 V to 1 V, where as the CV of the modified electrode with Hg(II) preconcentration (curve b) shows a well-defined an anodic peak at 0.11 V and a broad cathodic peak at about -0.64 V. The anodic peak is due to the oxidation of Hg(0) to Hg(II), formed by complexation with the CPCHA modifier from the preconcentrating solution while the cathodic peak is due to the reduction of Hg(II) to Hg(0). The modified carbon paste electrode also shows a small anodic peak at about 0.69 V due to the CPCHA modifier. The anodic peak current of Hg(II) at the CPCHA modified electrode is substantially larger and sharper than the corresponding cathodic peak current. Hence the anodic peak of Hg(II) was systematically studied by square wave anodic stripping voltammetry for analytical applications.

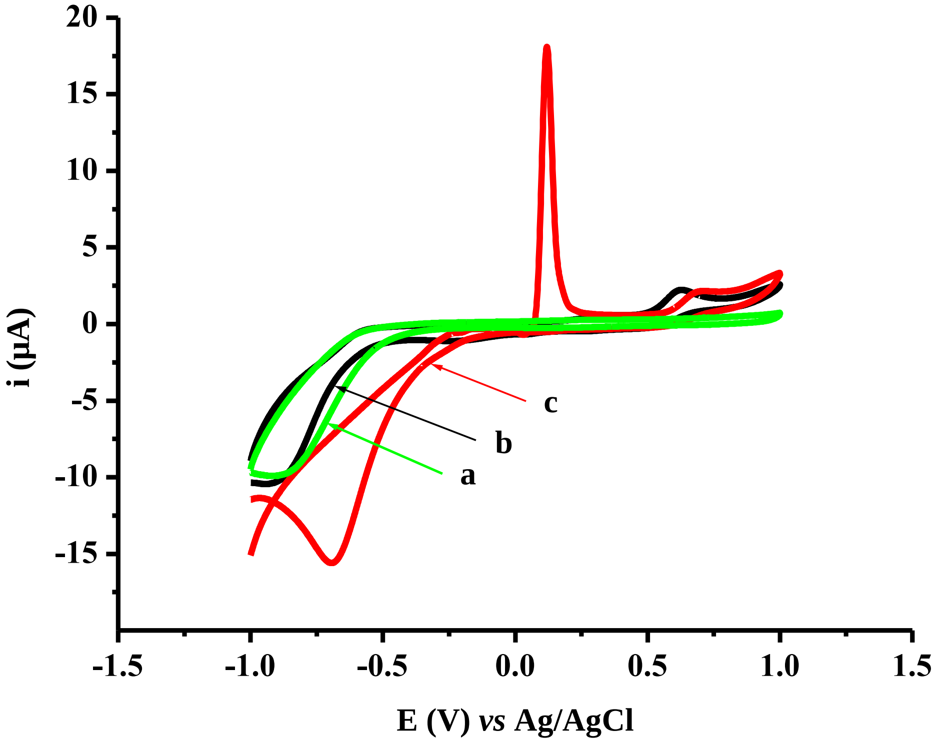

Figure 9. Cyclic voltammograms: (a) bare CPE without Hg(II) preconcentration, (b) MCPE without Hg(II) preconcentration and (c) MCPE with Hg(II) preconcentration from 0.1 M sodium acetate solution pH 10; preconcentration time: 5 min; Hg(II) concentration: 100 µM; supporting electrolyte: 0.3 M NH_4Cl pH 5; scanned from -1 to 1 V and back at scan rate: 0.1 V/s

The square wave voltammetry of the unmodified and modified carbon paste electrodes were run in the presence of 80 µM Hg(II). As observed in the voltammogram shown in Figure 10, the anodic peak current of Hg(II) at the CPCHA modified electrode is larger than that of the unmodified electrode. Therefore, the use of the CPCHA made it possible to significantly improve the analytical signal of the electrode.

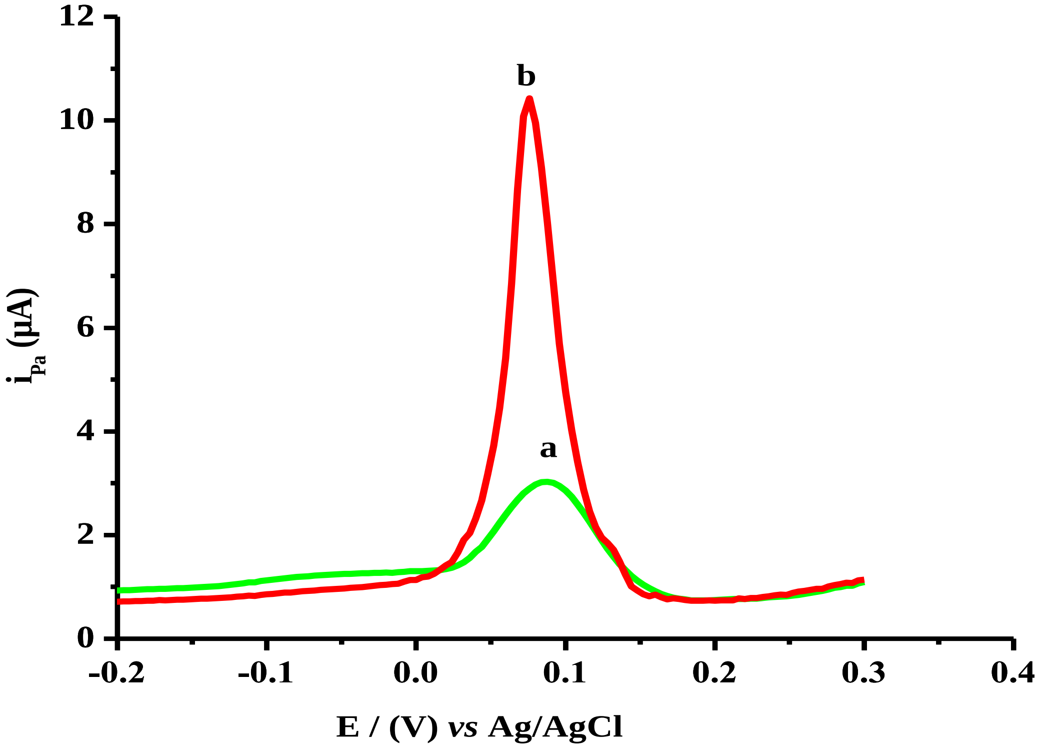

Figure 10. Square wave voltammograms of 80 µM Hg(II) in 0.3 M NH_4Cl pH 4 at (a) unmodified carbon paste electrode and (b) CPCHA modified carbon paste electrode: preconcentration time 5 min. in 0.1 M NaAc; deposition potential -0.6 V; deposition time; 60 s and potential scan from -0.6 V to 0.3 V after 10 s equilibration time with pulse amplitude 0.025 V, frequency 15 Hz and step potential 0.004 V

Mechanism of the method

The possible mechanism for the reaction of Hg^{2+} at CPCHA modified electrode can be described by the following steps (where HL represents CPCHA) based on the similar studies reported in the literature (Alemu and Chandravanshi, 1998; Degefa *et al.*, 1999; Fanta and Chandravanshi, 2001)

1) Preconcentration step (open circuit cell, 0.1 M NaAc, pH 8):

$$\underset{\text{Solution}}{Hg^{2+}} + \underset{\text{CPE surface}}{2HL} \rightarrow \underset{\text{CPE surface}}{HgL_2} + \ddagger \underset{\text{Solution}}{2H^{+}}\ddagger \qquad (5)$$

2) Reduction step (closed circuit cell, 0.3 M NH_4Cl, pH 4, -0.6 V):

(i) HgL_2 + $2H^+$ + → Hg^{2+} +‡ 2HL (6)
CPE surface Solution Solution CPE surface

(ii) Hg^{2+} + 2e → Hg^0 (7)
Solution CPE surface CPE surface

3) Stripping step (closed circuit cell, 0.3 M NH_4Cl, pH 4, positive scan: -0.6 V to 0.3V):

Hg^0 + $2H^+$ → Hg^{+2} + 2HL + 2e (8)
CPE surface Solution Solution CPE surface

4.2. Effect of amount of the CPCHA in the carbon paste

The accumulation of Hg(II) at the CPCHA modified CPE was based on the complex formation reaction between the metal ion, Hg(II) and the modifier, CPCHA. Therefore the amount of CPCHA in the carbon paste had significant influence on the voltammetric response of the modified electrode. The effect of the amount of CPCHA in the modified carbon paste electrode was investigated by preparing five different modified carbon paste electrodes (2.5%, 5%, 7.5%, 10%, 12.5% and 15% weight-to-weight ratio of CPCHA to graphite powder in the carbon paste) under identical conditions. Maximum peak current was obtained for 7.5% CPCHA in the CPE as shown in Figure 11. CPCHA above 7.5% in the CPEs resulted in a decrease in the peak current which is presumably due to the decrease in the carbon content of the paste and, consequently, reduction of the conductive electrode area (carbon particles) hampering the electron transfer at the electrode surface. On the other hand the decrease in the peak current for CPEs containing below 7.5% of CPCHA is due to lower extent of complex formation because of smaller coverage of the modifier on the electrode surface. Hence an electrode containing 7.5% CPCHA was applied for all subsequent experiments.

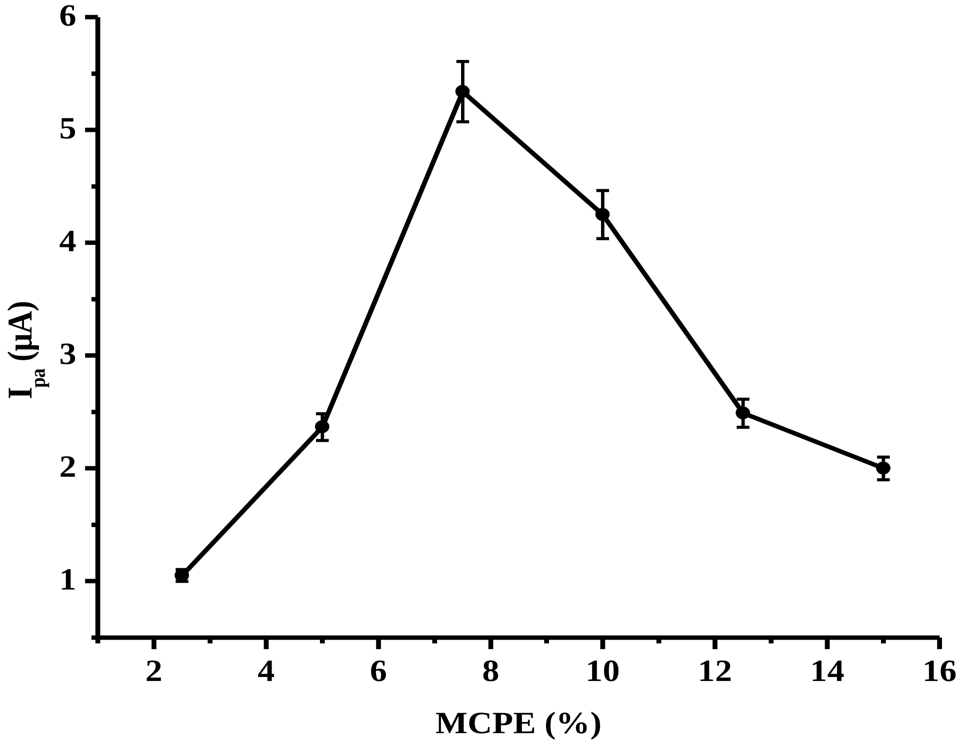

Figure 11. Effect of amount of modifier in the CPE on the square wave anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Hg(II) concentration: 80 µM and other conditions are as in Figure 10

4.3. Effects of preconcentration solution and supporting electrolyte

In stripping voltammetric analysis, carbon paste composition, pH and concentration of the preconcentration solution and supporting electrolyte can significantly affect the voltammetric response. Therefore the effect of these solutions with different concentration and pH were studied.

4.3.1. Effect of composition and concentration of preconcentration solution

The complex formation reaction of Hg(II) with CPCHA at the electrode surface could vary with different preconcentration solutions. The anodic stripping voltammetric properties of Hg(II) preconcentration in NH_4Cl, NaAc and Na_2CO_3 buffer solutions (each one 0.1 M, pH 8), were investigated. The peak current of Na_2CO_3 was slightly smaller than NaAc. This could be due to precipitate formation of Hg(II) as $HgCO_3$ at pH 8. In NH_4Cl solution a much smaller peak current was obtained. This is due to complex formation Hg(II) with ammonia and chloride at high concentration that can hinder the accumulation of Hg(II) on the electrode surface. Among these, best voltammetric result was obtained in NaAc preconcentration solution.

The effect of NaAc concentration was also tested in the range 0.1- 0.5 M at pH 8. The maximum peak current was obtained for 0.1 M NaAc solution. It was observed that increasing the concentration of NaAc decreased the peak current. This is due to the formation of a weak complex between acetate ions and Hg(II). Hence, increasing the concentration of acetate ions decreases the accumulation of Hg(II) that complexes with CPCHA at the electrode surface. Thus 0.1 M sodium acetate solution was used as a pre concentration throughout the study.

4.3.2. Effect of pH of preconcentration solution

The pH of the preconcentration solution (Equation 5) has a direct effect on the complex formation reaction of Hg(II) with CPCHA. Hence the effect of pH of the preconcentration solution (0.1 M NaAc) on the accumulation of Hg(II) was investigated in the pH range 5-11. The Hg(II) peak current as a function of pH is shown in Figure 12. It was observed that the peak current increased sharply with increasing pH from 5 to 8 and then decreased from 9-11. This is due to the increased complex formation of Hg(II) with CPCHA at the electrode surface with increasing pH and the completion of complex formation at higher (pH > 8). Hence 0.1 M sodium acetate pH 8 was used for all subsequent experiments.

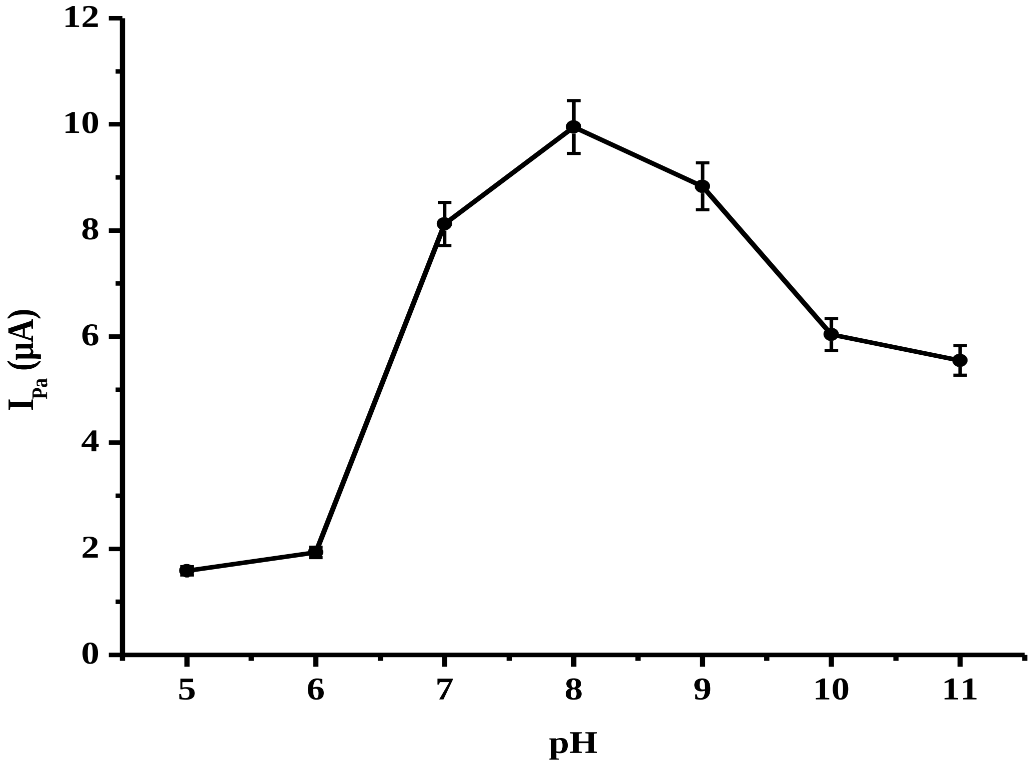

Figure 12. Effect of pH of preconcentration solution on the square wave anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Hg(II) concentration: 80 μM and other conditions are as in Figure 10

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

4.3.3. Effects of composition and concentration of supporting electrolyte

The effect of composition of supporting electrolytes, including, (H_2SO_4 and KCl), $NH_2OH.HCl$, NaH_2PO_4 and NH_4Cl buffer solution (each 0.3 M, pH 4) were examined. The results showed, Figure 13, voltammetric peaks were observed in all these solutions. The peak currents were very low in (H_2SO_4 and KCl) and NaH_2PO_4 buffer solutions. This might be due to the inability of the ions of the two salts to supply hydrogen ions required during the stripping steps (Equation 8). While the peak current for $NH_2OH.HCl$ was comparable with that of NH_4Cl, it has unstable background current. Among these, the electrochemical response in NH_4Cl solution had the best peak shape, largest stripping peak current, higher reproducibility and stable background current. This might be due to the differences in the extent of providing hydrogen ions required for the reduction step (Equation 6) and consequently favoring the proceeding stripping step. Hence NH_4Cl buffer solution was selected throughout this study.

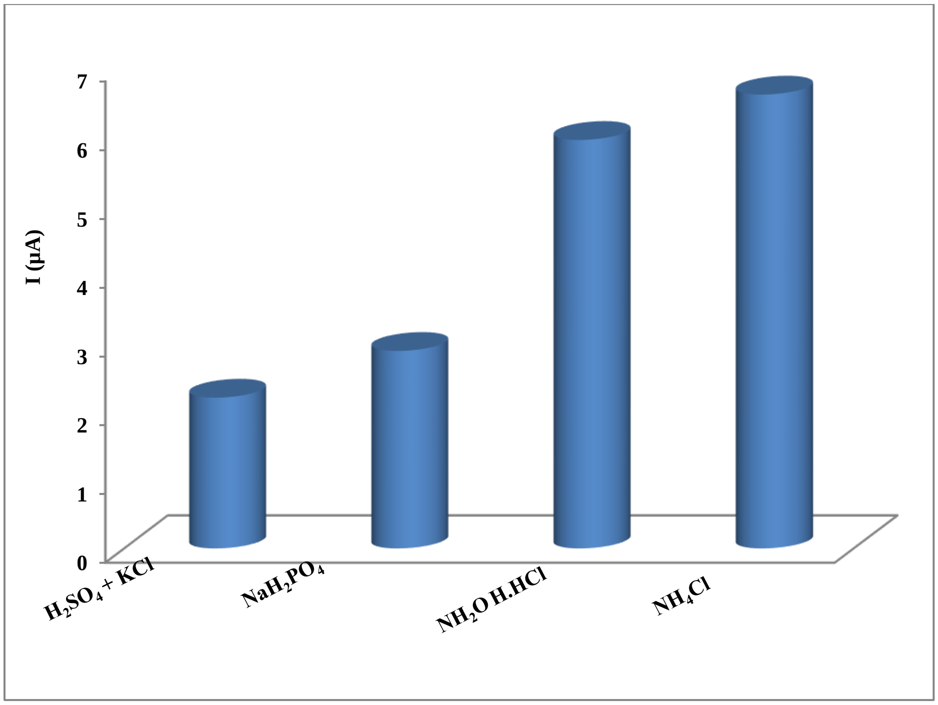

Figure 13. Effect of composition of supporting electrolytes each 0.3 M pH 5 for 80 µM Hg(II) at CPCHA modified CPE and other conditions as Figure 10

The effect of concentration of NH_4Cl was also studied in the range 0.1-0.5 M at pH 8. Although the concentration of the supporting electrolyte did not have significant effect on the current response, maximum and reproducible peak current was obtained in 0.3 M NH_4Cl solution and thus was selected for the subsequent experiments.

4.3.4. Effect of pH of supporting electrolyte

The effect of pH of the supporting electrolyte (0.3 M NH_4Cl) was also studied by varying the pH in the range 3-8. Peak current increased with increasing pH up to pH 4. This is due to reduction of Hg(II) at the CME surface involves hydrogen ions (Equation 6 and 7). The peak current decreased with further increase in the pH beyond 4. The increasing pH hinders the reduction reaction. Maximum peak current was observed at pH 4.

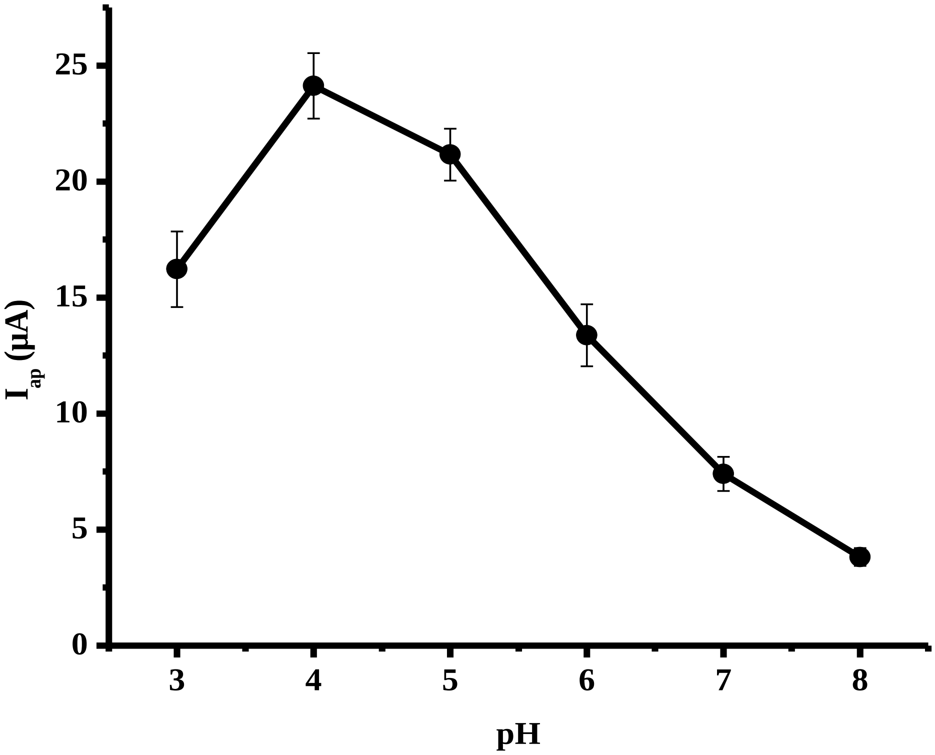

Figure 14. Effect of pH of supporting electrolyte solution on the square wave anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Hg(II) concentration: 80 µM and other conditions are as in Figure 10

It is evident from the above discussion that the preconcentration and the voltammetric measurement steps require NaAc and NH_4Cl solutions of different concentrations and different pH. Hence it was necessary to carry out the preconcentration and the voltammetric measurement separately. Therefore, 0.1 M NaAc solution pH 8 and 0.3 M NH_4Cl solution pH 4 were used for an open-circuit preconcentration and voltammetric measurements, respectively.

4.4. Effect of preconcentration time

The other important parameter that affects the voltammetric response is the time allowed for the accumulation of the Hg(II) from the preconcentration solution at the electrode surface. The effect of accumulation time on the peak current was studied from 30 s to 240 s. The time effect on the anodic peak current of the modified electrode is shown in Figure 15. The peak current increases with increasing preconcentration time, indicating an enhancement of Hg(II) up take at the electrode surface. Normally, the increase in the response continues until a maximum peak current, presumably corresponding to either saturation or an equilibrium surface coverage, is attained. The results obtained indicated attainment of steady-state accumulation levels of Hg(II) at the electrode surface at exposure times of 5 min. 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. Thus, to obtain a linear relationship between Hg(II) concentration and the peak current, a relatively short preconcentration time must be employed to avoid saturation effect. Therefore, 3.5 min preconcentration time was selected throughout this study.

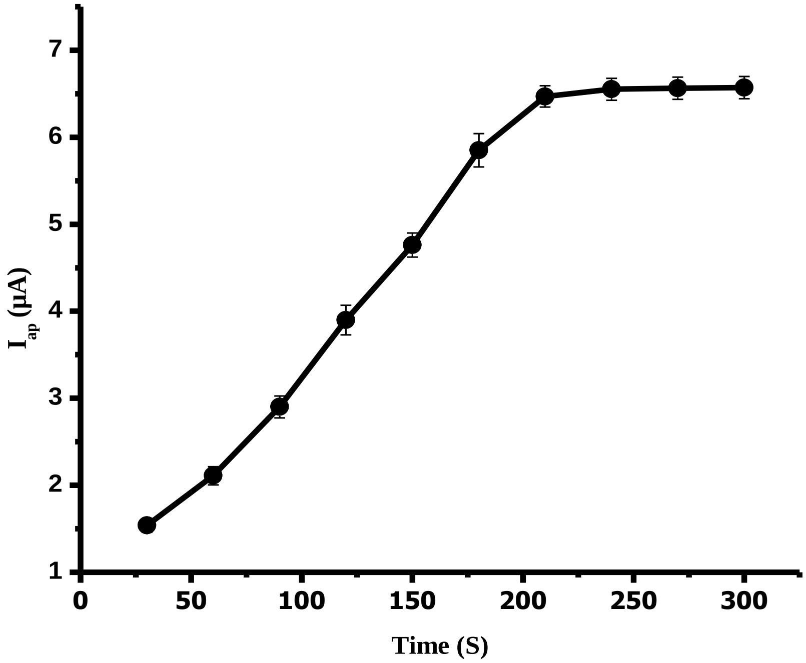

Figure 15. Effect of preconcentration time on the square wave anodic stripping voltammetric peak current. Each bar represents mean ± 3 standard deviation. Hg(II) concentration: 80 µM and other conditions are as in Figure 10.

4.5. Effect of instrumental parameters

4.5.1. Effect of reduction potential

The effect of the reduction potential on the anodic peak current of Hg(II) was investigated in the range from -0.2 V to -0.8 V. The effect of the reduction potential on the anodic peak current of the modified electrode is shown in Figure 16. At more negative reduction potentials, Hg(II) is reduced more completely, thus increasing the peak current. The peak current increased as the reduction potential became more negative up to -0.6 V and then decreased. At more positive potentials a decrease in the anodic peak current was caused by an inefficient reduction of Hg(II) to Hg(0) at the electrode surface. The maximum peak current was obtained at a potential of -0.6 V, providing maximum analytical signal for Hg(II) determination.

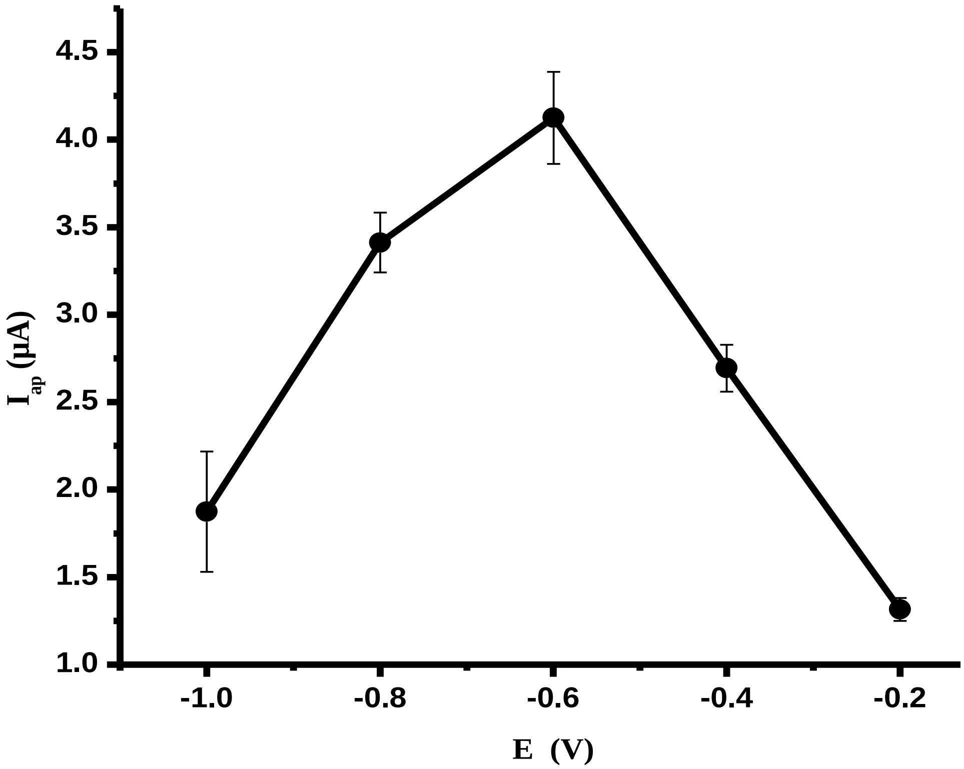

Figure 16. Effect of reduction potential on the SWASV peak current. Each bar represents mean ± 3 standard deviation. Hg(II) concentration 80 µM and other conditions as in Figure 10.

4.5.2. Effect of reduction time

Reduction time is also the most important factor for determination of the detection limit in stripping voltammetric analysis. At the same reduction potential, a longer reduction time will cause Hg(II) to be reduced completely and consequently lead to a higher peak current. However, when the reduction time is too long the reduced Hg(0) covers the entire effective electrode surface, and the peak current does not change with increasing reduction time. The effect of the reduction time on the anodic peak current of Hg(II) was performed at constant reduction potential with different reduction times from 20-80 s. The reduction time effect on the anodic peak current of the modified electrode is shown in Figure 17. The peak current was found to increase linearly with increasing reduction time up to 60 s and then remained constant. Therefore 60 s reduction time was used for all subsequent measurements.

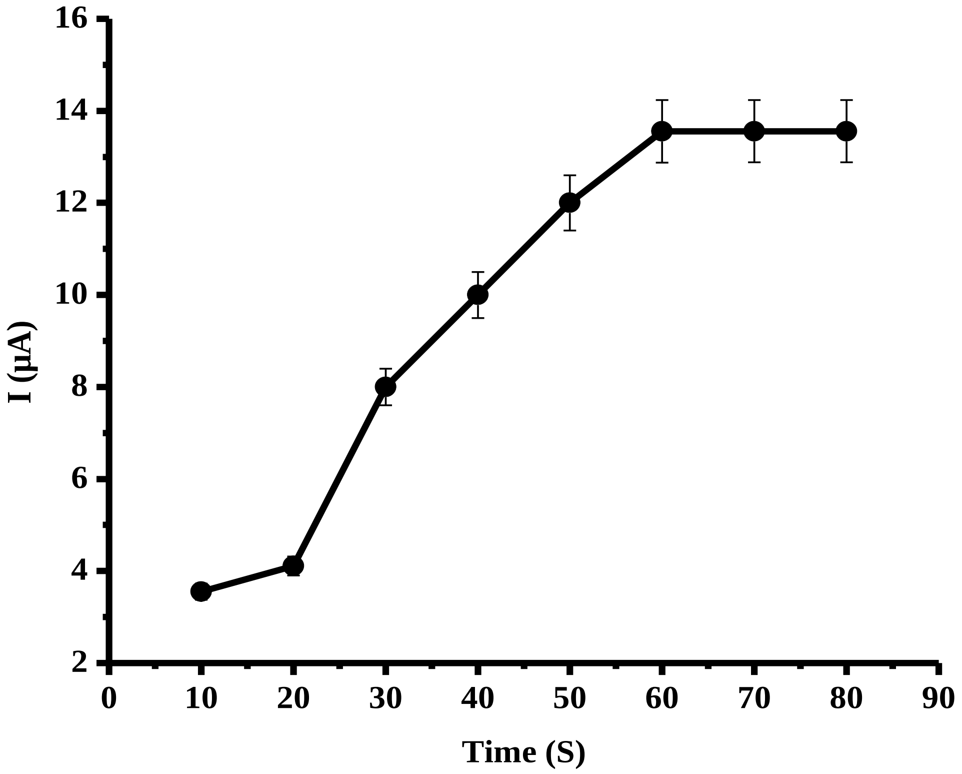

Figure 17. Effect of reduction time on anodic peak current at -0.6 V reduction potential and other conditions as in Figure 10

4.5.3. Effect of frequency and amplitude

In SWASV amplitude and frequency are the most important parameters affecting the shape and sensitivity of the peak current. Effect of amplitude was studied by varying the value from 20 to 50 mV. The peak current increased and became broader with increasing amplitude, maximum amplitude of 35 mV was chosen for the study. A similar pattern of the peak current was obtained with increasing the frequency (from 15 to 35 Hz). Frequency of 25 Hz was selected for this work

4.6. Calibration plot, detection limit and reproducibility

Under the above optimized conditions, the relationship between the anodic peak current and the Hg(II) concentration was studied. Well-defined peaks were observed following a 210 s preconcentration time and reduction potential of -0.6 V. Stripping voltammograms and calibration plot for Hg(II) concentration in the range 1.0 µM to 25 µM are shown in Figure 18 and 19, respectively. The peak current increased with increasing Hg(II) concentration and a linear calibration plot was obtained with I_P (µA) = 0.334 [Hg] (µM) + 0.845 and a correlation coefficient of 0.998. The detection limit (S/N = 3) was found to be 12.9 nM and a relative standard deviation (RSD) 3.83% was obtained for six repeated measurements of 15 µM Hg(II) solution.

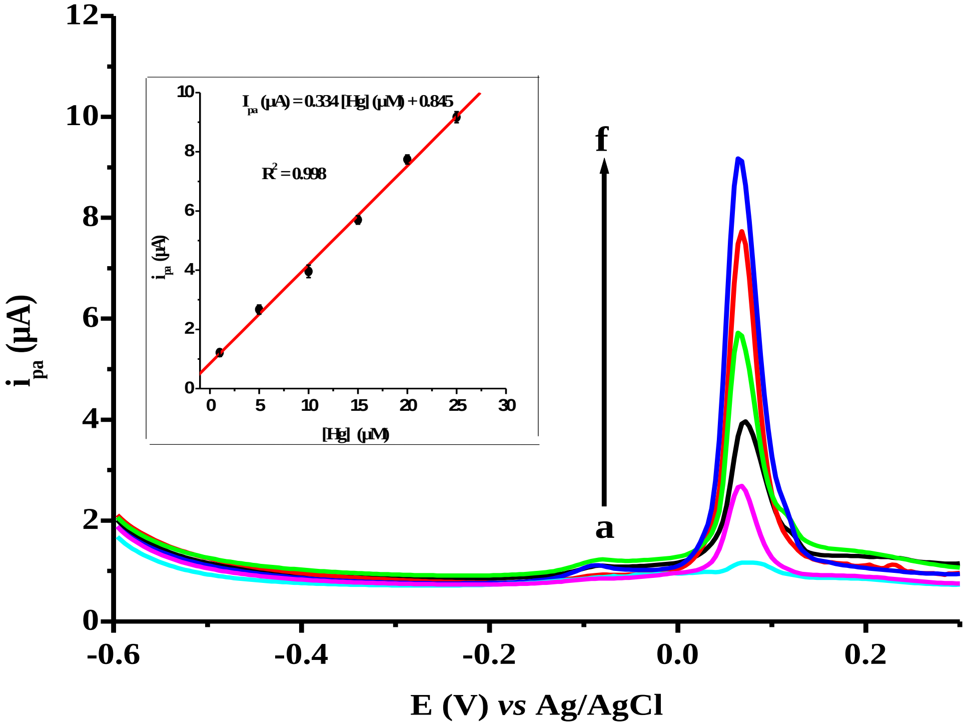

Figure 18. Anodic stripping voltammograms for different concentrations of Hg(II) (a) 1; (b) 5; (c) 10; (d) 15; (e) 20 and (f) 25 µM in 0.3 M NH_4Cl solution pH 4, preconcentration time 3.5 min with pulse amplitude 0.035 V, frequency 25 Hz and step potential 0.004 V and other conditions as in Figure 10

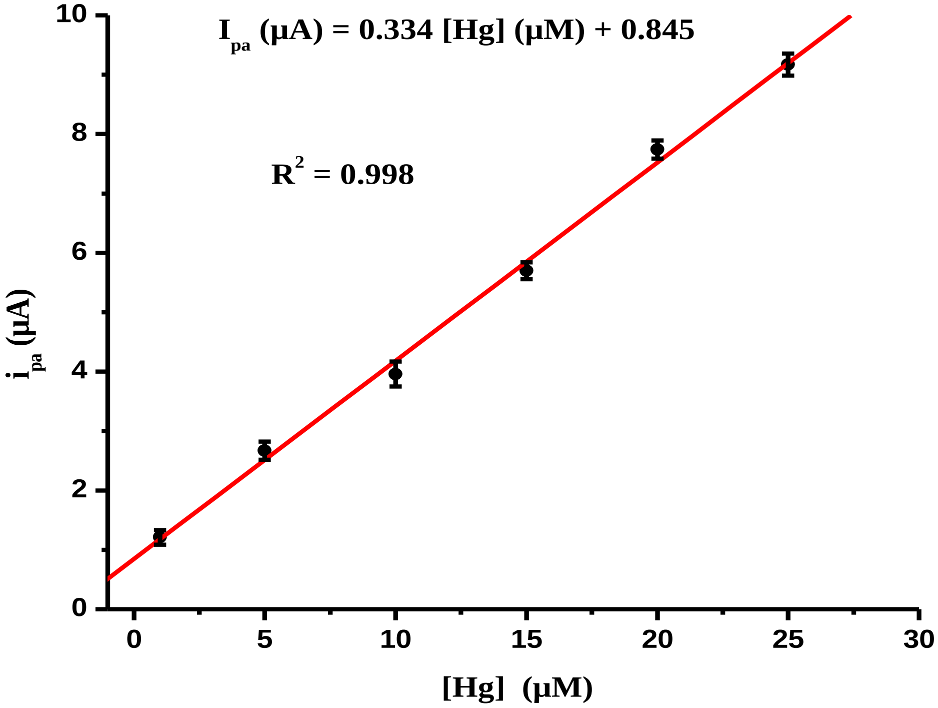

Figure 19. Calibration plot of peak current *versus* concentrations of Hg(II) at CPCHA/CPE

4.7. Comparison of the performance of CPCHA modified CPE with other electrodes

The analytical performance of the proposed method was compared with several reported methods in the literature and the results are summarized in Table 1. The results show that the limit of detection obtained in this study was lower or comparable to those reported by other authors in the literature. Some reported methods achieved lower detection limits of Hg(II), having preconcentration times which are several times longer than that of the present study (3.5 min). A shorter accumulation time enables faster measurements, therefore in the same duration more analyses can be made. The proposed method also has good linear range. Thus the proposed method is able to detect the presence of Hg(II) at trace levels.

Table 1. Comparison of the analytical performance obtained at CPCHA/CPE with different electrodes reported in the literature for the electrochemical determination of Hg(II)

Electrode type	Technique	Preconcentration time (min)	Linear range (μM)	LOD (nM)	Reference
[a]HA-NP/GCE	SWASV	-	0.20–210	141	(Kanchana *et al*., 2015)
[b]NG/GCE	DPASV	-	0.99–8.90	50	(Xing *et al*., 2016)
[c]PdO-NP/CPE	DPASV	3	0.25–100	19.3	(El Aroui *et al*., 2014)
[d]WBM/CPE	DPASV	10	1.98–3.96	965	(Rajawat *et al*., 2012)
[e]TCA/GCE	SWASV	5	0.008–3	5.0	(Wang *et al*., 2009)
[f]MTTZ-MSU-2 /CPE	DPASV	5	0.1–1	99	(Sanchez *et al*., 2012)
[g]EDTA/CPE	SWASV	5	50 –350	8.6	(Moutcine and Chtaini, 2018)
[h]MWCNT/CPE	Potentiometry	-	0.1- 100000	100	(Ali and Mohamed, 2015)
[i] Schiff baseL/CPE	DPV	-	0.005–5	0.38	(Nourifard and Payehghadr, 2016)
CPCHA/CPE	SWASV	3.5	1–25	12.9	Present work

[a]*Hydroxyapatite nanoparticles;* [b]*N-doped grapheme;* [c]*Palladium oxide supported onto natural phosphate;* [d]*Water hyacinth biomass;* [e]*4-tertbutyl-1-(ethoxycarbonylmethoxy)thiacalix[4]arene;* [f]*Mesostructured silica nanoparticles functionalized with a 5-mercapto-1-methyltetrazole derivative;* [g]*Etylene diamine tetra acetic acid* ; [h]*multi-wall carbon nanotubes nanosilca;* [i] *2,2-((pyridine-2,6-diylbis(azanylylidene))bis(methanylylidene))diphenol schiff base ligand.*

4.8. Effects of other ions

CMCPE has significant capability to enhance selectivity because of the modifier-analyte interaction. The selectivity of the CMCPE was evaluated by adding different solutions of other ions into known concentration of Hg(II) solutions during the preconcentration step, and the results are shown in Table 2. Alkali and alkaline earth metal ions, NH_4^+, Cl^- and NO_3^- (up to 100-

fold molar excess); Ni^{2+} and SO_4^{2-} (up to 10-fold molar excess); Cd^{2+} and Co^{2+} (up to 5-fold molar excess) and Cu^{2+} (up to 2 fold) have no significant effect on the determination of Hg(II). However, equal molar amounts of Pb^{2+} and Fe^{3+} interfere significantly by decreasing the Hg(II) signal, because they form complexes with CPCHA and prevent the complex formation and accumulation of Hg(II) at the electrode surface.

Table 2. Change in SWASV peak current of 15 µM Hg(II) in the presence of other ions (preconcentration time 3.5 min)

Interfering ion	Concentration (M)	Change in peak current (%)
Alkali and alkaline earth metal ions	15×10^{-4}	< ± 5
NH_4^+	15×10^{-4}	-1.4
Cd^{2+}	7.5×10^{-5}	1.6
Co^{2+}	7.5×10^{-5}	3.1
Cu^{2+}	3.0×10^{-5}	-4.2
Ni^{2+}	1.5×10^{-3}	2.2
Pb^{2+}	15×10^{-6}	-42
Fe^{3+}	15×10^{-6}	-7.3
Cl^-	15×10^{-4}	-3.5
SO_4^{2-}	1.5×10^{-4}	1.2
NO_3-	15×10^{-4}	-2.1

4.9. Analytical application

The applicability and feasibility of the proposed method for the analysis of real samples was assessed by its application for the determination of Hg(II) in various type of water samples. Ground water, river water, stream water, tap water and bottle water samples were employed. The concentrations of Hg(II) in water samples were determined by the spiking method. The recovery results are summarized in Table 3. The percentage recoveries were found in the range 98-105%

these are within the acceptable range. Thus the proposed method is precise and reliable that can be used for the determination of Hg(II) in environmental water samples.

Table 3. Percentage recovery of Hg(II) in water samples (N = 3)

Sample	Original (μM)	Added (μM)	Found (μM)	Recovery (%)
Tap water	[*]Nd	15	14.7 ± 0.17	98.0
Bottled water	Nd	15	14.9 ± 0.12	99.5
Well water	Nd	15	14.8 ± 0.48	98.6
Stream water	Nd	15	15.3 ± 0.22	102
River water	1.8	15	17.6 ± 0.86	105

[*] Not detected

5. Conclusion

A new method has been developed for the square wave anodic stripping voltammetric determination of Hg(II) using N-*p*-chlorophenylcinnamohydroxamic acid modified carbon paste electrode. The method is relatively cheap and easy, and has proved to be selective for the determination of Hg(II) at trace level in water samples. The method offers attractive properties compared to the previous studies such as simplicity of electrode preparation, high stability, short preconcentration time, and the use of non-de-aerated solution. The proposed method has a good linear range and a lower detection limit than most of the reported methods and not interfered strongly by other metals, which are normally associated with mercury in environmental waters and other complex materials.

6. References

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