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Traditio et Innovatio

**Investigation of deposition of some heavy
metals on heated gold-loop
electrode in comparison with gold
rotating disk electrode in various samples of
water**

Dissertation

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Department of Chemistry

Faculty of Mathematics and Natural Sciences

University of Rostock

Submitted by

Juhaina Abdulkhalek

Born in 25 Juli 1984

Aleppo-Syria

The present work was completed from 2012 to 2014

Supervisors:

1. Prof. Dr. Gerd-Uwe Flechsig

Institute of chemistry, University of Rostock

2. Prof. Dr. Peter Langer

Institute of chemistry, University of Rostock

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ABBREVIATIONS

AOPs	Advanced oxidation processes
Au-RDE	Gold-rotating disk electrode
Au-le	Gold-loop electrode
BiBE	Bismuth bulk electrode
Bi-film	Bismuth-film
°C	Degree centigrade
DAAD	Deutscher Akademischer Austausch Dienst
DNA	Deoxyribonucleic acid
DOCs	Dissolved organic compounds
DPV	Differential pulse voltammetry
DV	Direct voltammetry
EPA	Environmental protection agency
E	Potential
GPES	General Purpose electrochemical system
HMDE	Hanging Mercury Dropping Electrode
HF-thermalab	High Frequency-Thermalab
HDV	Hydrodynamic voltammetry
I	Current
ISO	International Organization for Standardization
K	Kelvin
LOD	Limit of Detection
LOQ	Limit of Quantitative
LSV	Linear Sweep Voltammetry
M	Mole per Liter
nm	Nanometer
NPV	Normal pulse voltammetry
ppb	Part per billion
ppm	Part per million
Ref	Reference electrode
rpm	Rotate per minute
SCE	Saturated Calomel electrode
SAM	Standard Addition Method
SMDE	Static mercury dropping electrode

SWV	Square Wave Voltammetry
UV	Ultraviolet
V	Voltage
VA	Voltammetry
V/s	Volt/second
μA	Micro ampere
μg/l	Micro gram per liter
μm	Micro meter
μM	Micro mole per liter
λ	Lambda(wavelength)
ν	nu (Frequency)

PREFACE

The temperature is considered as an important adjustable factor in the electrochemical experiments apart from concentration, potential, current, and time. Numerous applications and several general principles of the high-temperature electrochemistry have been accepted in the hot wire electrochemistry. Also few ways and different approaches have been used to heat the working electrode surface without causing the electrolysis solution to boil.

Several electrodes have been innovated to be heated directly and indirectly for the conduction of electrochemical experiments at a high temperature, among them:

- Electrically heated cylindrical microelectrode (1996), which was used to determine of lead Pb(II) at the platinum wire.
- Heated gold microelectrode was used to study the deposition and stripping of arsenic (V) (1998).
- Heated mercury-film electrode, which was used to determine mercury Hg(II) (2000).
- Heated bismuth-film electrode was used to measure the heavy metals (2002).
- Heated carbon paste electrode was used to analysis of DNA (from 2000 to 2004).

A new gold electrode has developed as a working electrode, which is heated directly by its connection with an electric power generator (HF Thermalab®system). This new electrode, which takes a shape of U, is called gold-loop electrode (Au-le) and it has been applied in our research to determine some heavy metals such as Cu(II), Pb(II), Hg(II), As(III), and As(V) in various water samples. In the current study, the negative as well as the positive aspects of the Au-loop electrode relative to the gold-rotating disk electrode (Au-RDE) will be described.

ABSTRACT

The experiments include deposition and stripping voltammetry of some heavy metals in aqueous solutions at Au-loop electrode at both temperatures 60 °C and room temperature. Au-loop electrode was heated directly by HF-Thermalb. The analytical signals at heated Au-loop electrode were much better than those obtained at room temperature and Au-RDE, where the sensitivity and selectivity were found to be higher at heated Au-loop electrode at unaffected signal-to-noise-ratio than at Au-RDE.

Bismuth-coated Au-loop electrode has been offered a significantly stripping voltammetry manner in all of the water samples studied, which enhances meaningfully the response of analytical signals upon heating the electrode. Additionally, the greatly enhanced analytical signals obtained at heated Au-loop electrode obviates the need for mechanical forced-convection transport.

Moreover, heated Au-loop electrode provides an attractive stripping voltammetry analytical signals response for analysis and determination of the concentration of some trace heavy metals in tap and river water samples obviating the need for application of UV-irradiation process, which is designed to digestion of dissolved organic compounds presented in a natural water.

These effects can be explained by assuming that a high temperature can be helpful for activating inhibited chemical reactions, for accelerating the mass transport process and increasing diffusion coefficient around the heated electrode surface, which improves the analytical signals response. As well as, heated Au-loop electrode work to achieve a high greatly self-cleaning effect, so it works to eliminate surface fouling effects. Furthermore, heated Au loop electrode produces microstirring within a thin solution layer near to the electrode surface.

1. INTRODUCTION

1.1. Hot wire electrochemistry

Hot wire electrochemistry is defined as an electrochemistry at which the electrode is directly heated, this means the temperature of the electrode is changing while the electrochemical experiment is taking place. Previously, the cell of electrolysis was heated by isothermal heating, which has been called as a hot-tube-voltammetry technique that was independent on the variation of temperature. This technique for heating was not useful till now. Therefore, it was found a more practically and applicably methods to heat the electrode surface by non-isothermal way. In the previous technique, it was possible to heat an electrode in two ways: the first way, continuous heating of an electrode surface, where the temperature of the electrode surface is kept stable under the boiling point causing an efficient microstirring effect, can be done directly or indirectly. By the direct heating, the body of the electrode surface itself is heated without any electrical isolating between the heater and the electrode. In (1966) Ducert and Cornet, the surface of an electrode was heated by means of laser beams [1]. In the advanced hot wire electrochemistry new techniques have been innovated to heat the working electrode directly by means of microwave, high frequency heating, and resistive heating by using an alternating current [2]. By indirect heating, which it was done by Harima and Aoyagui in (1976), a thin solution layer near to the electrode surface is heated. The second way is pulse heating, which was carried out through a directly heating of the working electrode surface, where the temperature of the electrode surface is increasing above the boiling point without causing any stirring, this means that the electrolysis solution is kept stable, quite, and unaffected. In pulse heating method several techniques were applied such as laser pulses, where the laser beams is concentrated on the electrode surface [3-6], joule heating of wire [7-8], electrically heated electrode by microwave heating [9], and joule heating of solution [10]. For hot wire electrochemistry, many species of the working electrode have been also innovated to be electrically heated and they have been used for different aims such as: ring electrode, sensors array, classic electrically heated wax coated wire electrode (25 μm), carbon printed band electrode, carbon paste electrode, indirectly heated gold electrode, array of electrically heated ring electrode, and polyethylene (PE) coated wire electrode (25 μm).

The advantages of electrically heated electrodes:

- Micro stirring consequence is achieved as a result of thermal convection in the surrounding area of the electrode due to improves the mass transport process.

- Increase the rate of slow reactions.
- Higher sensitivity and selectivity than rotating disk electrodes.
- Simple, small and cheap to manufacture.
- An enhanced and improved signal to noise ratio.

Electrochemical experiments using heated wire electrodes have been carried out simply for various applications such as analysis of DNA [10-18] and analysis of heavy metals [1926], where both ends of a metallic wire electrode is connected to a source of electric power to form with a reference and counter electrodes a complete unit of the electrolysis cell (potentiostat). These electrically heated electrodes have been developed by different ways as following: the electrically heated electrodes, which are in an asymmetric arrangement, get in touch with potentiostat by means of heating current invented by Prof. Dr. Gruendler [8], electrically heated electrodes, which are in contact with a potentiostat through a third touching base in the middle of the electrode, temperature pulse voltammetry [27-32], pulse heating which allow to heat the electrode surface above boiling point [1], heated carbon paste electrode [11], heated hybridization sensors [15], electrically heated electrode, which is connected to the potentiostat via bridge, and a compact and versatile instrument for radio frequency heating [33].

1.2. Concept and application of heated electrodes

The surface of electrodes which are used in electrochemical analytical experiments can be heated through two ways: either by light beams or by electric heating. The method of electric heating can be done by resistive heating or by inductive heating. Moreover heating of electrodes material can be done directly, where heater and active electrode surface are connected without any electrical isolation between them, or indirectly, where there is an insulating layer between heater and active electrode surface. In some approaches a thin solution layer near to the electrode surface is heated rather than the electrode surface itself. Heating a thin solution layer near to the electrode surface can be carried out by microwaves, where the electrode and its connections play as an antenna, or by AC current flowing in parallel to the electrolysis current, heating up portion of the solution.

1.2.1. Direct heating of the electrode surface

Direct heating of the electrode surface means there is not any electrical isolation between heated electrode and heater. Direct heating can be achieved using the following methods:

1.2.1.1. Light beams

This method was innovated by Miller and Valdes [4, 34] in which the electrode surface is heated by lightning with laser beams. It was prepared essentially to carry out the thermal modulation as an approach to study the different kinetic aspects of electrodes. Also for electrochemical researches laser beam heating was used to carry out the temperature jump method [34, 35]. Heating by light beams have been done by applying IR [36, 37] and tungsten light [38, 39].

1.2.1.2. Inductive heating by radio frequency

A radio frequency means a rate of oscillation in the range of around 3 to 300 KHz which corresponds to the frequency of radio waves. However, radio frequency refers to electrical rather than mechanical oscillations. Radio frequency heating is applied in an electrochemical cell [40]. The system includes a thin foil platinum electrode, placed inside a channel of a flow cell which is connected to two radio frequency coils that induce energy of 8 MHz generator. The electrode can be heated up quickly. Reference and counter electrodes are placed in flowing stream outside the heating region. The temperature can be controlled by using a thermocouple placed near to the electrode.

1.2.1.3. Joule heating by radio frequency

Heating an electrode wire inside an electrolyte solution was described [41], where a radio frequency current was applied to heat a thin platinum wire achieved a thermal stirring. It was already known that DC could not be applied to heat an electrode because of generating a voltage drop along the length of the electrode that would act as an additional polarization added to the value stabilized by a potentiostat. Also undesired polarization can be generated by using AC. Moreover, a huge distortion of voltametric signals can be formed with lower frequencies. Gabriel et al. [7, 42] offered the first results for ferro-/ferricyanide system gained at a platinum wire electrode (100 μm , diameter 2 cm length, and varnish isolation at both ends). Herewith, a radio frequency heating was applied and 250 KHz was used to get a maximum 6 $^{\circ}\text{C}$ temperature jump experiment. Alternating contribution to the overall signal could be separated to some degree by applying an appropriate electrical filtering. Gruendler et al. [8] has applied a similar arrangement in an initiative experiment, where a ferro-/ferricyanide were tested in a preparatory with the follow setup: a 35 μm platinum wire was used, which was

contacted by means of brass foil. The connections were isolated from the electrolyte by setting a silicon rubber, and then the whole assembly was preserved together by polytetrafluorethylene (PTFE) block. But with this simple order the results were not favorable. Moreover, the cell presented incorrect behavior with successful electrical filtering. It has been found that with modern potentiostat, it is possible to do correction against the AC even in radio frequency range. With microelectrodes, a temperature is rising rapidly in aqueous solution by means of direct radio frequency heating, where the temperature of the electrode can be made much higher than boiling point of the surrounding solution. Additionally, some kind of microstirring combined with a realistic stagnant layer can be made by heating electrodes permanently. Platinum wire electrode 25 μm in diameter are used in most direct heating experiments. Some of direct heating experiments were achieved with glassy carbon fibers of similar dimension [8], but they were not pleasing because of a high specific resistive of the carbon which due to cause a drop voltage along the fiber with amplitudes more than 10 Volt which cannot be compensated properly. Additionally, glassy carbon fibers can be distorted by chemical attack in aqueous solution by oxidation or hydrogenation if polarized with according potential. Also a thin metallic layers have been used for direct heating as alternative to metal wires.

Low temperature co-fired ceramic (LTCC) was the most successful electrode construction. This technique is applied in electronic manufacturing [29, 30]. Like these layers have appropriate value of resistance to be heated electrically.

An electrically heated carbon paste electrode has been developed to perform adsorptive stripping analysis of nucleic acids. Where carbon paste electrode consists of a piece of (PTFE) tube on an extended hole filled of carbon paste. Interesting features were offered by applying this approach among them elevated temperatures during the accumulation step which result in 4-32 fold enhancements of the stripping signals depending on the temperature and the kind of nucleic acid. Also the label-free DNA hybridization following a magnetic separation step was detected by using heated carbon paste electrodes [14].

To make a prelate heated mercury film electrode a screen-printed carbon layer on alumina substrate was used [24]. This electrode design was no danger by unfavorable of the heated iridium electrode. On heated mercury-carbon layer was determined cadmium Cd(II) and lead Pb(II) with an enhanced signal to noise ratio. It is important to mention that the screen printed carbon paste electrode offered a little bit instable temperature manner, so the temperature calibration would be repeated by open circuit potential frequently. In addition, an electrically heated carbon paste electrode was used to investigate a heated bismuth film electrode [25], where an electrode temperature of ca. 60 $^{\circ}\text{C}$ was obtained by using such as electrode. A heated

bismuth electrode was used to determine Zn(II), Cd(II) and Pb(II). The response was enhanced in ca. 10-16 fold of sensitivity combined with unaffected signal to noise ratio. Additionally, a good voltammetry signal with high reproducibility and linear calibration plots. Moreover, it has been studied the formation of a bismuth film on a carbon paste electrode by ex-situ atomic force microscopy [43]. However, in our research it has been investigated the effect of elevated temperature upon the bismuth film coated Au-loop electrode for determination of lead Pb(II) in various samples of water. The results will be discussed in the results and discussion section.

The effect of direct electrode heating upon redox process at self-assembled monolayer (SAM) modified electrode has been studied by Wang et al. [44]. For nucleic acids hybridization detection, electrically heated gold electrodes modified with DNA-SAMs have been applied to accelerate the hybridization and to carry out a thermal discrimination of mismatched target strands [45, 46]. Later it has been detected a DNA-hybridization at heated gold wire electrodes modified with a self-assembled monolayers of ss DNA [16]. The DNA-SAM strands have been formed a stable and constant surface coverage even at the highest temperature. Moreover, The DNA-SAM could be generated by middle heating of the electrode in distilled water.

A voltammetry determination of organic substances, which are characterized by weakness versus long time exposure to increased temperature [47] and by sluggish electrochemical response, was one of the first analytical applications of continuously heated wire electrodes. Additionally, it has been determined dissolved oxygen also at continuously heated wire electrodes [48]. At heated gold electrode it has been successfully determined different traces of heavy metals among them stripping voltammetry of arsenic (V) by direct electrochemical reduction [20] and stripping voltammetry of mercury traces [21]. At platinum electrode it has been effectively determined Pb(II) as PbO_2 [19]. After that, metallic traces have been effectively studied at heated mercury film electrodes [22, 24]. At heated carbon electrodes it has been studied a stripping determination of nucleic acids [11]. Determination at heated bismuth film electrode proved to be very great substitute for the traditional dropping mercury electrodes [25]. It has been demonstrated that bismuth film can be deposited on various electrode substrates offering well defined, undistorted and highly reproducible signals of heavy metals. In addition, greatly improved signal to noise background ratio, and high hydrogen overvoltage. Also, bismuth film is an environmentally, unharmed and non-toxic element. Mikkelsen and Schrøder have been proved that the electrode material can be improved with low hydrogen overvoltage by adding about 4 % of bismuth. Gold and silver electrodes are similar [49-52], they are less prone to corrosion. Also it has been found by Mikkelsen that the alloy made of gold and

4 % bismuth can be applicable in both the positive potential range (detection of mercury) and negative potential range (detection of cadmium and iron) [53].

1.2.2. Indirect electrical heating

In 1976 an indirectly electrically heated gold electrode was offered by Harrima et al. [54]. At this time, potentiometry was applied, where a thin gold foil was glued onto an isolator and heated by means of an aluminum layer. Later, it has been designed an indirectly heated electrode depending on the technology of LTCC that is based on involving an isolated resistance heater into the ceramic body completely underneath the screen-printed electrode layer. To study the effect of temperature on immobilized enzyme it has been applied LTCC-platinum electrodes. It was found by lau et al. that the hydrogen peroxide signal, which produced by immobilized glucose oxides, can be separated from the ascorbic acid oxidation signal, if the determination was carried out at two different temperatures. After that, the thermal discrimination for every analyte has been known from the different heat effect of both these analytes [55]. New innovated sensors of a heated double-enzyme, included amyloglucoseoxides, and a heated triple-enzyme contained additionally mutarotase. These sensors were able to detect maltose and glucose due to thermal discrimination [56]. Moreover, indirect electrically heated LTCC-platinum electrodes were used to detect nicotinamide adenosine dinucleotide [57], which can be formed fouling effects. Such effects can be hindered by means of electrode heating.

Yang et al. has been offered an array of indirectly heated platinum microelectrodes 100 μm diameter [58]. The single electrode of the array was completely thermally isolated from each other. These micro arrays order a very complicated multi-step silicon micro fabrication. The influence of the temperature was tested by open circuit potentiometry using hexacyanoferrat (II/III) redox couple. The built-in vacuum-sealed cavity under every electrode and its heater go ahead for rapid temperature settlement and low request for heating energy.

Recently, it has been innovated bismuth bulk electrodes (BiBE) [59]. These electrodes were used for the investigation of adsorptive stripping voltammetry of drug daunomycin. This analyte required a special cleaning operation after each measurement because of its strong adsorption. The effect of the elevated temperature has been tested upon indirectly heated BiBE, which result in a max 2-fold signal improvement.

1.2.3. Heating of a thin solution layer near to the electrode

The solution layer near to the electrode surface can be heated using different methods as following:

1.2.3.1. Resistive heating by radio frequency

A high frequency (0.1-2 GHz) electric current is applied to heat a thin solution layer near to the electrode surface. Baranski demonstrated that a high frequency electric current goes through electrode surface into the electrolyte in parallel to the faradic currents [60]. It was found that the distortion of the simultaneous electrochemical measurements was prevented by applying like this high frequency. Moreover, high steady state temperatures above the boiling point of the electrolyte can be achieved by this way. It is important to mention that a thin layer of the solution near to the electrode surface displays a high value of resistance compared to the surrounding bulk solution and the electrode body. Thus, only this area is joule heated.

1.2.3.2. Microwave heating

Compton et al. discovered a novel approach for heating by using adsorption of microwave energy [9]. One of the advantages of this method is that the solution layer near to the electrode is heated much faster than the bulk solution. In other words, if microwave pulses of 24 Watt were applied, the solution layer near to the electrode surface is heated up to 120 °C within 0.6 s, while the bulk solution changes its temperature at a rate of 1 K/s. The electrochemical cell together with the working electrode were put into the microwave, while the counter and reference electrodes stay outside connected to the cell by means of an electrolyte bridge. The voltammetry of methylene green has been studied using activation by means of microwave, laser, sound and ultrasound [61]. Anodic stripping voltammetry of Cd(II) at mercury film electrode on platinum micro disks was significantly improved by means of microwave radiation [62]. The effect of microwave radiations has been studied by Marken et al. [63]. It has been reported that up on applying microwave activation high temperatures can be reached in a thin solution layer near to the electrode surface, discarding was released from the electrode and the limiting current is ca. 10-fold higher compared to isothermal heating. These investigations assume the occurrence of a hot spot into the diffusion layer and connective of the mass transport. Electrodes that can be used to perform microwave activation are metal, glassy carbon and boron-doped diamond electrodes [64]. For example, the lead oxide modified boron doped diamond electrodes are useful for the electrocatalytic oxidation of ethylene glycol. Another example is lead determination in river sediment by mercury free anodic stripping voltammetry. It has been reported that by means of microwave activation the detection limit can be improved. Other examples are the reversible oxidation of ferrocene, the kinetically inactive reduction and dehalogenation of p, o, and m-bromonitrobenzene in organic solvents as dimethylformamide and acetonitrile [65]. Sur et al. tested the effect of microwave activation to heat glassy carbon

and boron-doped diamond electrodes [66]. (It has been mentioned that microwave absorption using the carbon materials lead to a superheating of the aqueous solution up to 400 K which is much more preferred rather than heating a thin layer of the solution method). In addition, small electrodes dimension were helpful.

Moreover, microwave activation was applied to micro electrodes in which it donates a very fast voltammetry in the sub-millisecond time range due to very thin Nernst diffusion layer that was formed at very high temperature of the electrode [67]. The voltammetric analytical signal of ferrocene at platinum microdisk electrodes was more than 100 fold improved even in ionic liquids by applying microwave irradiation [68]. Such self-focusing microwaves at the 25 μm platinum disk electrode can produce temperature of ca. 600 K. The effect of electro deposition of copper Cu(II) on gold, platinum and carbon electrodes has been studied by using microwave activation, where temperature of 400 K can be applied [69].

As a result, heated electrodes have been proved their strength with all previous mentioned analytical applications. In stripping determination the deposition process was enhanced. The nucleation overvoltage, which it can be occurred with solid electrodes, was decreased remarkably. Consequently low detection limits were found. An improvement of 10-fold sensitivity can be investigated in case of under potential deposition, if the electrode was heated during the accumulation step. The positive results of using heated electrodes could be attributed to the microstirring effect which due to accelerate the mass transport process replaced a mechanical stirrer effect. Inactive redox kinetics can be improved, especially for the determination of species that would upset if exposed to increased temperature for long term. On the other hand, temperature was not increased inside the solution, therefor no delicate or volatile substituents are decomposed. Moreover, it has been found that the microstirring effect can be useful if fluid compartments with a non-steady flow are monitored, where the natural stream is overlaid by the micro convection due to continuous flow in the neighborhood of the electrode surface, no substance what flow rate is in the bulk solution.

1.3. Measurement of the electrode temperature

Different methods were applied to measure the electrode temperature [48, 70]:

Metal thermometer method or resistance method: metallic wires can be considered as a resistance thermometer. Metals have known positive temperature coefficient of their specific resistance. In this method the electrode collectivity is heated in pure water with a punctually steady direct current of known quantity. It has been investigated that by calibrated precision

oscilloscope the direct current voltage drop at the metallic wire can be recorded. The resulting voltage-time diagrams were given by the change in resistance during the heating process. Every measured voltage value displayed one temperature value of the electrode metal by taking in consideration the temperature coefficient of the specific resistivity of metallic wire electrode. It has been assumed the homogenous temperature distribution into the heated wire or layer. This assumption was proved only for electrodes with micrometer dimensions, where thermal conductivity of metals is much greater than of electrolyte solution. It has been found that the conductivity of the solvent did not provide any detectable contribution to the results by measuring with low quantity currents. Moreover, it has been considered that the contribution of all parts of the electrode to the overall resistance make this method undesired. When a substantial part of the electrode wire was isolated by insulating material, then the isolated part can reach higher temperature than the exposed part due to heat dissipation inhibited by insulating material.

In the potentiometric method temperature values of heated wires, considered heated electrodes or layers, were measured through the temperature reliance of standard potential of reversible redox couple. Open circuit potential measurements in an electroanalytical cell containing an equivalent amounts of a reversible redox couple, for example ferro-/ferricyanide, allow continuously determination of the temperature. Such a reversible redox system has a temperature coefficient of standard potential equals to -1.56 mV/K . It has been found that by applying the potentiometric method only the surface temperature of the exposed electrode area was obtained. However, both previous mentioned methods offered only an average value of the temperature.

Temperature contribution in the space and time could be calculated by using digital simulation identical to the so called box method [71]. This method was used to solve diffusion problem in electrochemistry [27]. The solution surrounding the electrode wire was divided into individual cylindrical shells (boxes) with an equal thickness in area of $1 \text{ }\mu\text{m}$. During individual time steps Δt of $2.5 \text{ }\mu\text{s}$, a quantity of heat energy transferred from box to box into the solution can be calculated following the law of heat conduction (Fourier's law), while the heat energy transported to the electrode wire was considered as joule heating of a metallic cylinder. Consequently, for each time step temperature profiles were calculated. One point in these profiles was displayed as the electrode wire temperature. The actual temperature for every box was plotted as a function of square of heating current, which is proportional to electric power. It has been assumed that the actual surface temperature can be proportional to the square of heating current by assuming that the thermal distribution within a layer of constant thickness

equivalent to the Nernst diffusion layer. It was found that this calculation approach is the only to know how the temperature can be distributed on the solution side.

In our research a stationary temperature of Au-loop electrode is measured by applying open circuit potential measurements in an electrochemical cell containing an equivalent amount of reversible redox couple of potassium ferro- and ferrihexacyanide. More details will be discussed in the experimental chapter.

1.4. Objectives

Our research aims to the following goals:

- To develop a new, effective, and efficient method for deposition and stripping phenomena at Au-loop electrode in comparison with Au-rotating disk electrode.
- To prove the efficiency of Au-loop electrode to determine the concentration of some heavy metals in various samples of water (ultra-pure, tap, and river water).
- To investigate the applicability of more than one voltammetric analytical method as (LSV, DPV, and SWV), and the possibility of using different electrolytes with Au-loop electrode to analyze the degree of contamination of the tap and river water in respect to some heavy metals.
- To prove the ability of Au-loop electrode for deposition of some heavy metals in origin river water without treatment by UV/irradiation process.
- To investigate the possibility of bismuth-film formation on Au-loop electrode to determine the concentration of lead Pb(II) in ultra-pure water, tap water, and river water.

2. THEORETICAL BACKGROUND

2.1. Voltammetry techniques

A voltammetry is a class of electro-analytical methods in analytical chemistry that can be used in different industrial operations. This technique provides information about the analyte via measuring the current (amperes) along changing of the potential (volts). The response of the current is recorded as a function of the applied potential $I=f(E)$, the resulted curve of this measurement is called voltammogram.

The variation of the potential is either permanently or step by step, and the current value is measured as a dependent variable. The resulted curve shape is depending on whether the solution is stirred or not and on the variation rate of the potential [72].

To perform an electrochemical experiment at least two electrodes, working and reference electrodes are required. At working electrode, which is in contact with an analyte, a specific potential must be applied in a controlled way to facilitate the transfer of charges to and from the analyte. A reference electrode that has a known potential, controls the potential of working electrode potential. Other electrochemical experiments are carried out using three electrodes, in which the electrochemical analytical cell contains an auxiliary electrode additionally to the working and reference electrodes. The auxiliary electrode crosses all the current needed to balance the current observed at the working electrode, this could be achieved by swing the auxiliary electrode at an intense potential at the window edges, whereas a supporting electrolyte oxidizes or reduces. These three electrodes, working, reference, and auxiliary electrodes, are the modern three-electrode system.

A several well-known laws in voltammetry describe the effects of the applied potential and manner of the redox current. As described by the Nernst or Butler-volmer equations (1 and 2 respectively), the concentration of the redox species at the electrode surface (C_O^0 and C_R^0) and the reaction rate (K^0) are controlled by the applied potential. When the diffusion plays a controlling part, the resulted current (faradaic current) from the redox process is linked to the material flow at the electrode-solution interface and is described by Fick's law (equation 3). For a reversible electrochemical reactions, which can be described by $O + ne \leftrightarrow R$, the applications of potential (E) powers the respective concentrations of O and R at the electrode surface to a ratio in obedience with the Nernst equation (1):

$$E = E^0 - (RT / nF) (\ln C_R^0 / C_O^0).$$

Equation (1).

R is the molar gas constant ($8.3144 \text{ J. mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), n is the number of electrons transferred, F = Faraday constant ($96485 \text{ C/equivalent}$), and E^0 is the standard reduction potential for the redox couple. From the Nernst equation, if the potential is negative the ratio ($\ln C_R^0/C_O^0$) becomes large, which means that O is reduced, and if the potential completed is positive the ratio ($\ln C_R^0/C_O^0$) becomes smaller, which means that R is oxidized.

In some voltammetry techniques it is better to apply an equation that correlates the parameters of current, potential, and concentrations, this equation is described by Butler-Volmer equation (2):

$$I / n F A = K^0 \{C_O^0 \exp[-\alpha \theta] - C_R^0 \exp[1-\alpha] \theta\} \quad \text{Equation (2).}$$

$\theta = n F (E - E^0) / R T$, k^0 is the heterogeneous rate constant, α is known as the transfer coefficient, and A is the area of the electrode. This relationship allows us to obtain the values of the two analytically important parameters, i and k^0 .

Mostly the current flow is related to the material flow to the electrode surface. When the concentration of the studied material is increasing, it provides a power for its diffusion toward the bulk solution. This is taking place when R or O is established at the surface. When the concentration is decreasing, it promotes diffusion of new species from the bulk solution, this happens if R or O is broken. Fick's law (equation 3) describes the resulting concentration incline and mass transport, which states that the flow of matter (Φ) is immediately proportional to the concentration incline:

$$\Phi = -A D_O (\partial C_O / \partial x) \quad \text{Equation (3).}$$

D_O is the diffusion coefficient of O and x is the distance from the electrode surface. The same equation can be written for R.

The mass transport can be carried out through migration or convection. The migration process is a movement of a charged ion in the presence of an electric field. The convection process, is a movement of the electro active species by stirring the solution, rotating the electrode, or density gradient present in solution (concentration or by thermal gradient) [73, 74]. The mass transport must be controlled precisely to make a controlled transfer of the analyte to the electrode surface.

Historically, the voltammetry technique has been started in (1922) using the polarography that is innovated by Jaroslav Heyrovski. The first three-electrode potentiostat system has been built by Hickling in (1942) [75]. Many advances in the theory, instrumentation, and the introduction of computer added and controlled systems have been developed in (1960) and (1970), and several of new analytical methods have been improved and created by means of

these advancements. Additionally the production of a cheaper potentiostat, electrodes, and cells that can be effectively used in a routine analytical work was requested or needed by the industry. On the other hand, an enormous number of voltammetric systems have been invented for the study of specific species that are of interest in the scientific researches. These systems are sometimes called electrodes, but they are actually complete voltammetry cells better referred to as sensors, that are used for the analysis in several fields of organic and inorganic analytes under different conditions [76-84].

2.2. Voltammetric analytical methods

Currently, for several analytical purposes some common approaches of voltammetric techniques are in use. The individuality of each is beneficial and helpful depending on precise differences in the behavior and effectiveness, in which the potential is applied and the current is measured. Very varied chemical, electrochemical, and physical information can be provided by means of these differences such as electrons involved on the redox reactions, diffusion constants, rate constants for chemical reactions, and a highly quantitative analysis.

2.2.1. Pulse voltammetric analytical methods

They include the following techniques:

2.2.1.1. Normal Pulse Voltammetry (NPV)

In this technique the potential wave is a series of increasing amplitude pulses, in which the potential returning to the initial value after each pulse [72, 85-87].

2.2.1.2. Differential Pulse Voltammetry (DPV)

In this technique the form of the potential wave consists of small pulses of constant amplitude overlaid upon a stairway wave arrangement. In each pulse period the current is sampled twice, once before the pulse, and at the end of the pulse. The difference between these two current values is recorded and displayed [88-90]. There is no faradaic reaction in response to the pulse at a positive potential of the redox potential, so the difference current will be zero. The difference current reaches a maximum at a potential around the redox potential, and it

decreases to zero as soon as the current becomes diffusion-controlled. Therefore the current response is an asymmetric peak.

2.2.1.3. Square Wave Voltammetry (SWV)

The potential waveform in square wave voltammetry (SWV) is a square wave of constant amplitude overlaid on a stairs wave arrangement. The current is measured at each half-cycle. The current that is measured on the reverse half-cycle (i_r) is subtracted from the current that is measured on the forward half-cycle (i_f). The difference in current ($i_f - i_r$) is displayed as a function of applied potential [91-93]. The shape of the current response is a symmetric peak.

2.2.1.4. Cyclic Voltammetry (CV)

In a cyclic voltammetry the applied potential at a working electrode is ramped linearly versus time as in linear sweep voltammetry (LSV). This ramping is known as a scan rate (V/s) of the experiment. Between the reference electrode and working electrode, the potential is applied, and between the working electrode and auxiliary electrode, the current is measured and displayed a function of potential (E) [94].

2.2.2. Direct Voltammetry

In this technique that is including LSV, direct current voltammetry (DCV), and hydrodynamic voltammetry (HDV), the potential between the working electrode and reference electrode is swept linearly with time. The current at the working electrode is measured and recorded as a peak or trough at a potential, at which a species starts to be reduced or oxidized [95-97].

2.2.3. Pre-concentration and stripping techniques

These techniques that include anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV), have the lowest limit of detection compared to any commonly electro-analytical techniques, minimal sample preparation, and high greatly sensitivity and selectivity [98].

2.3. Heavy metals

There is more than one definition for heavy metal depends on density, atomic number or weight number, or depends on chemical properties and level of its toxicity. In general heavy metal is defined as toxic metal [99]. Naturally heavy metals exist with various concentrations in the environmental system [100]. Some heavy metals are needed in specific amounts for humans such as iron, cobalt, copper, manganese, molybdenum, and zinc, but their presence in excessive levels due to damage human organs. .Sever illnesses are caused by other heavy metals such as mercury, plutonium, and lead. These toxic metals accumulate over time in the organs of animals. Some of these diseases cause mental and central nervous problems. Also the accumulation inside the body due to damage of the blood composition, lungs, and kidneys is possible [101]. The most common sources for heavy metals are pollution resulted by purification of metals, preparation of nuclear fuels, melting of copper, electroplating of chromium and cadmium, and the dust from rubber tires where cadmium, lead, and zinc could be produced on the road surface. Small amounts of these toxic metals can be inhaled, or transported onto topsoil or edible plants via wind [102]. Heavy metals are pollutants for the environment as they can precipitate into the soil and mud. They are stable and not easy to degrade, it's very difficult to remove them.

It is possible to remove heavy metals such as mercury by using an electric field to induce electro osmosis (where the heavy metals are moved in an electro kinetic extraction). Some treatments of the mining tailings, which occurs where the vegetation is incinerated, can remove some heavy metals [103].

2.4. Heavy metals pollution of water and subsequent risks

Water is very important for all living organisms, humans, plants, and animals. Thus, water pollution is considered the biggest problem in the world and is a major cause for several and diverse diseases. Water can be naturally or chemically polluted by means of any chemical or physical change in the water bodies (lakes, rivers, oceans, aquifers, and ground water) [102-103]. The natural pollution can happen through any change in the natural properties of the water, for instance, a change of its temperature, its salinity, or increasing of organic suspended or inorganic solids in water [104-106]. The chemical water pollution can be as a result of existence of heavy metals such as mercury, arsenic, and lead or their compounds. Existences of the insecticides in water can also cause chemical pollution of water [107]. On the other hand, it is necessary to mention that some of heavy metals or their compounds are soluble in water but others are insoluble in water and they can accumulate in the living organisms that live in the

water bodies [108]. This accumulation is considered one of the main problems linked with the insistence of heavy metals that have a possibility for bioaccumulation and bio magnification producing heavier exposure for some organisms that exist in the environment [109]. The meaning of the bioaccumulation is increasing of concentration of a metallic element (any metallic element in the periodic table that is poisonous at low concentration and has relatively high density) or its compound in a biological organism over time. Existence of heavy metals or their compounds in water can be caused by means of industrial waste, consumer waste, or from acidic rain transgressing down soils and discharging heavy metals into water bodies (lakes, river, oceans, and groundwater) [110].

Examples about some heavy metals pollution of water:

- Copper(II): the ultimate source of copper in drinking water is pipes. Copper is an important element for living organisms, including humans, and it is with small-amount-necessary in our diet to safeguard good health. On the other hand, high concentration of copper can cause various health effects involving vomiting, diarrhea, stomach cramps, and nausea. It has been also related with liver damage and kidney diseases [111].
- Lead(II): a major source of lead in the tap water is old lead pipes and lead combining solder. Lead is a metal that has no apparent beneficial health for humans, a high concentration of lead can destroy diverse systems of the body including nervous reproductive system and kidneys. Lead can cause high blood pressure, and anemia in addition to its accumulation in the bones [112, 113].
- Mercury(II): specific bacterial organisms in the surface water produce organic mercury (primary methyl mercury) by converting of inorganic mercury into organic mercury. This is ingested by fish and bio-accumulated in tissues of fish and humans causing destroy of nervous system as well as teratogen. This form of the mercury (primary methyl mercury) is rarely in the drinking water while is very common in the surface water. Inorganic mercury is mostly common form in the drinking water but is not considered to be very harmful for human's health. Both organic and inorganic mercury have several of detrimental effect on children due to the fact that both forms are easily absorbed into their system [114].
- Arsenic: water contains usually very small amounts of natural arsenic salts. Arsenic is toxic metal with no known biological benefit for humans, where it can be entered in the water by means of industrial processes such as mining, metal refining, and timber treatment. A drinking arsenic-reach water over time due to diverse health effect involving skin problems such as color changing on the skin and hard patches on the palms and soles of the feet, skin cancer, cancer of the bladder, kidney, lung, diseases of the blood vessels in the legs and feet,

and it is possible also to cause a diabetes, a high blood pressure, and a reproductive disorders [115].

Therefore, the determination of heavy metals is very important in the context of environmental, food and agricultural chemistry. The major techniques for analysis of heavy metals are spectroscopic and inductivity coupled plasma mass transport (ICP-MS), voltammetric and chronoamperometric. In recent years, applications of chemically modified electrodes had great interest in various areas of research and development, such as material corrosion and inhibition, electrocatalysis, electronics, bio sensors and electroanalysis.

It has been investigated intensively the basics of hot wire electrochemistry by Gruendler's group since 1993 [1, 2]. It has been found that it is possible to heat an electrode surface by using a high frequency alternating current of 100 KHz and simultaneously applying a direct current polarization for performing electroanalytical experiments including stripping analysis of heavy metals. Examples of stripping analysis of heavy metals at heated electrodes include the cathodic stripping voltammetric detection of Pb(II) on an electrically heated platinum wire described by Zerihun et al. [19], mercury Hg(II) at heated gold electrode by Wang et al. [21, 11], arsenic As(V) has been determined at a heated gold wire electrode by Gruendler et al. [20] and the comparison of a hot wire with rotating disk electrode for detection of Cu(II) by Flechsig et al. [23]. Different approaches have been described by Jasiski et al. for the determination of Pb(II) and Cd(II) at heated mercury film electrodes using iridium and screen-printed carbon substrates [22, 24]. Many of recent studies have been investigated the determination of some trace heavy metals at heated bismuth film-coated carbon electrodes, such as Pb(II), Cd(II) and zinc Zn(II), by Flechsig et al. and others [116].

2.5. Ultraviolet (UV) and ultraviolet sources

Violet is a color that has the shortest wavelength of visible spectrum, while the ultraviolet radiation has a wavelength shorter than visible light, but longer than x-ray, which is in the range from 10 to 400 nm. It is a type of electromagnetic radiations that is invisible by human's eyes. Ultraviolet was discovered by Johann Willhelm Ritter, German physicist, in (1801), who called it the oxidizing ray [117-120]. In (1893) the German physicist Victor Schumann has discovered an ultraviolet below 200 nm and he called it a vacuum ultraviolet, because it is absorbed strongly by air [121]. Ultraviolet radiations can be classified in corresponding to the ISO-standard on determining solar irradiances (ISO-21348) [122] as in the following table:

Table (1): Categories of the Ultraviolet radiations

Name	Abbreviation	Wavelength (nm)	Energy per photon (eV)
Ultraviolet	UV	400-100	3.10-12.4
Ultraviolet A	UVA	400-315	3.10-3.94
Ultraviolet B	UVB	315-280	3.94-4.43
Ultraviolet C	UVC	280-100	4.43-12.4
Near Ultraviolet	NUV	400-300	3.10-4.13
Middle Ultraviolet	MUV	300-200	4.13-6.20
Far Ultraviolet	FUV	200-122	6.20-10.16
Hydrogen Lyman-alpha	H Lyman- α	122-121	10.16-10.25
Extreme Ultraviolet	EUV	121-10	10.25-124
Vacuum Ultraviolet	VUV	200-10	6.20-124

The ultimate natural source for the ultraviolet radiation is the sun that radiates the ultraviolet beams at all wavelengths. Ultraviolet radiations can be also emitted proportionally more than the sun by means of the hot stars such stars seem blue-white rather than violet [123-124].

Several artificial sources for the ultraviolet radiations are:

- Black light lamps that emit long-wave radiation (UVA) and little of the visible light. These lamps are used to identify imitated money [124].
- Curing lamps that emit a required UV-light for treating certain types of dyes, stickers, and coatings [125].
- Germicidal lamps that are manufactured from mercury tubs which emit a long wavelength of the ultraviolet, and are used to kill microorganism in the air, on solid surface, and for disinfection of the workspaces, tools, and aquariums [125].
- Tanning booths are devices that emit UV-radiation to produce tanned skin. In this case many of the fluorescent lamps are designed to emit UV-radiation similar to the sun ray [125-126].

2.5.1. Ultraviolet irradiation

UV-light can be applied for the oxidation of micro pollutants or disinfection of water, air, food and industrial beverage. This oxidation or disinfection process can be performed by applying UV-radiation without the need to add any chemicals. UV-radiation can be combined with oxidants reagents like hydrogen peroxide to perform the oxidation process as well-known method of an advanced oxidation process (AOP). UV-radiation works to inactive pathogens by disrupting their DNA strands making them non-viable and non-infectious. UV-radiation is generated by flowing electrons from an electrical source through ionized mercury vapor. UV-lamps that are containing mercury are isolated from exposure to water by lamp wrapper and the surrounding lamp sleeves. For water treatment is commonly used UV lamps that can be classified as following:

- Low pressure lamps [LP]: the spectral radiation for LP-lamps is controlled by two ground state resonance lines at 23.7 nm and 185.0 nm. Radiation at 265.0 nm is deadly based on the doses. Direct UV disinfection can be performed optimally with an appropriate radiation at 254.0 nm, (AOPs) are mainly carried out with radiation at 185.0 nm obtained from LP-lamps. The preferred envelope material for standard LP-lamps is fused Quartz, which lead to the low wall temperature. Soft glass (sodium-barium glass) can be used also as envelope material for LP-lamps, but the UV-soft glass does not transmit at 185 nm, thus they are ozone free lamps. LP-lamps can be with standard output that are best appropriated for low flow applications not exceeding a flow rate of 350 gpm with an UV doses of 30,000 $\mu\text{Ws}/\text{cm}^2$, with high output (LP-HO) that are the best appropriated for moderate flow applications not exceeding a flow rate of 700 gpm with an UV doses of 30,000 $\mu\text{Ws}/\text{cm}^2$. LP-amalgam is the best for high flow applications of up to 3380 gpm of flow rate with an UV doses of 30,000 $\mu\text{Ws}/\text{cm}^2$.
- Medium pressure lamps (MP): they have much higher electrical power input compared to LP-lamps, due to continuous spectrum consists of broad and partly self-absorbed resonance lines. MP- lamps have specific UV-flux up to 35 W/cm which is considered as an advantage due to their very high UVC output and their compact design. However, they have extremely high wall temperature that covers the range of 500 °C to 950 °C and so they require complicated heating management and may cause problems to heat sensitive materials.
- Mercury free UV-lamps: is called the Excimer technology. The term Excimer refers to excited Dimer that can be excited Xe_2 molecule, which is formed in a dielectric barrier discharge. Excimer can be consisted of a rare gas and a halogen as for example, KrCl^* and

XeBr* radiating at 222.0 nm and 282.0 nm, respectively. Excimer lamps suffer until now from a low UVC efficiency additionally to the high investment costs for lamps and power suppliers.

The UV dose used for disinfection is a function of UV-irradiance and exposure time. The UV irradiance is defined by the rate at which UV energy is transported to the water and is described in terms of UV power per unit area (mW/cm^2). UV dose is amount of UV energy penetrating the water, multiplied by the amount of time at which the water is exposed to this energy. UV dose is mainly based on light intensity, water quality parameters such as turbidity and suspended solids as well as organic and inorganic compounds that can lower UV transmittance by absorbing UV light. Water quality parameters such as alkalinity, pH and temperature do not have a significant effect on the UV disinfection, but these parameters influence the scaling of UV-lamp sleeves. UV transmittance is a measured UV energy which is not absorbed by the water.

2.5.2. UV pre-treatment as a method of destruction of organic compounds in the investigated sample

Most of researches in chemical analysis work to determine heavy metals, nitrogen, phosphorus and carbon in natural samples like water, sewage, body fluid or beverage sample. All of the methods that can be applied to determine the metal concentration as atomic absorption spectroscopic (AAS), molecular spectrophotometric and electrochemical methods, require homogenous samples, which are free from organic compounds.

Dissolved organic compounds (DOCs) can hinder the determination of metals in electrochemical analysis process by interacting of organic ligands with metal ions due to form complexes that hinder the reduction of metal ions on the electrode surface, or shift their electrochemical reduction or oxidation potential to a more positive potential. Some of these complexes are unstable or convertible when they are acidified, where the metal ions can be replaced by hydrogen ions. Other complexes are stable toward such acid action.

On the other hand, (DOCs) can also interact with electrode material in the process of electrochemical analysis hindering the determination of metal ions.

Moreover, the presence of (DOCs) in the investigated samples of water makes easy application of electrochemical and (AAS) methods difficult or even impossible. Moreover, (DOCs) can be oxidized or reduced making measurements impossible by increasing background currents. Also their presence (DOCs) due to limit the active surface area of an electrode by its adsorption on the electrode surface, which allows to shift the peak potential and distort the

response analytical signal. These are some of problems that can be particularly caused by presence of (DOCs) in investigated samples.

So, it is very important for proper preparation of an investigated sample in analytical methods to avoid all of the above mentioned problems by eliminating organic compounds. A proper preparation of an investigated sample was carried out in some analytical methods by wet digestion, where an investigated sample is evaporated and then heated with concentrated acids, but this procedure may cause additional contamination.

An alternative procedure is mineralization with UV irradiation. In this way a small amount of oxidants is added to a studied sample which undergoes UV irradiation. It has been found that the mineralization with UV irradiation is friendly to the environment, does not contaminate a studied sample, giving the possibility of conducting the process at low temperature, eliminating the need for use of highly corrosive reagents like concentrated acids and preventing the production of injurious vapors and large amount of chemical wastes.

Applying of UV irradiation using mercury lamps for the destruction of organic compounds in many natural samples of water is known [127]. It has been described the mechanism and products of UV irradiation decomposition for many organic compounds among them: DDT (1, 1 (4, 4'-dichlorodiphenyl) 2, 2, 2-trichloroethane), HCB (hexa-chlorobenzene), PCP (pentachlorophenol), TNT (1, 3, 5-trinitrotoluene) [128], atrazine (an herbicide) [129] and others decompose following absorption of 180-250 nm radiation.

The UV-light action on dissolved organic and inorganic compounds in an investigated sample includes the formation of many intermediate compounds [130]: excited state of (DOC), hydrogen peroxide H_2O_2 , hydrated electrons, superoxide ions, singlet oxygen, hydroxyl radicals, halogen radicals and organoperoxy radicals. Additionally, it can be added some materials, which facilitate the oxidation process, to a studied sample such as: H_2O_2 , O_3 , $K_2S_2O_8$, $K_2Cr_2O_7$, HNO_3 and others.

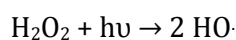
2.5.3. The Oxidation process by the Ultraviolet-radiation with Hydrogen peroxide

Through an oxidation process by means of ultraviolet radiation with hydrogen peroxide (H_2O_2) a highly reactive hydroxyl radical ($HO\cdot$) is generated by means of chain reactions, which it can attack and destroy a different of organic and inorganic compounds. This oxidation process by ultraviolet-irradiation activated hydrogen peroxide is applied for several applications including drinking water recycling, and ground water remediation, where at the same time UV-

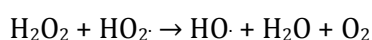
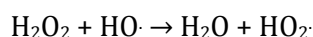
light is used to disinfect of water. This technique of the oxidation process is called as an advanced oxidation processes (AOPs) [131].

The chain reactions of H_2O_2 photolysis by UV-radiation are described through three steps as following:

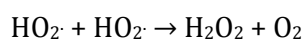
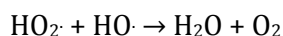
Initial reaction:



Propagation reactions:



Termination reactions:



The efficiency of the advanced oxidation process by means of the UV/ H_2O_2 depends on the hydrogen peroxide dose, UV-lamp type and its intensity, reactor contact time, acidity degree of the treated sample (pH), and the temperature. The excess of hydrogen peroxide (H_2O_2) is critical, because it can represent a scavenger, which limits the oxidation process effectiveness, thus it is necessary to optimize the added amount of the hydrogen peroxide (H_2O_2) to the treated sample under UV-light [132].

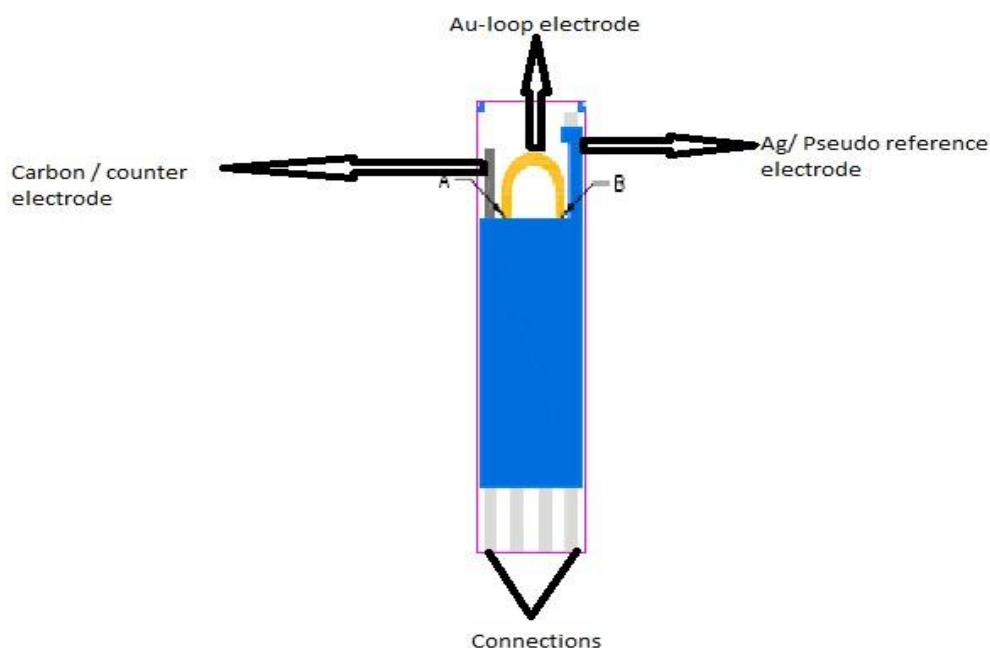
The generation of the hydroxyl radicals ($\text{HO}\cdot$) can be achieved by means of either low pressure (LP) or medium pressure (MP) UV-lamps. The low pressure lamps have lower working temperature and utilize less power than medium pressure ones. Using of the lamps sometimes depends on the type of the pollutants for example; when pollutants such as methyl tert-butyl ether (MTBE) and perchlorates a low pressure lamp is required [133], whereas a medium pressure lamp is used for a cyclic proceedings such as taste and odor or pesticides removal [134].

The advanced oxidation processes (AOPs) technique through UV/ H_2O_2 has been applied effectively and efficiently to destroy many of the micro pollutants that are presented in the ground water such as (MTBE, perchlorates, 1, 4 dioxan, etc.) [135], and in the surface water such as (pharmaceutical and personal care products, taste and odor compounds such as Geosmin (2, 6 dimethyl bicyclic [4. 4. 0] decan-1-ol), etc.) [136].

3. Experimental section

3.1. Instrument and operating Conditions

An Autolabpotentiostat (Ecochemie) with general purposes electrochemical system (GPES 4.9) software package connected to a faraday cage, which contains a stand electrolysis cell with three electrodes system consist of a Au-RDE as working electrode, a glassy carbon as counter electrode, and Ag/AgCl (3 M KCl) as reference electrode, was used for determination of the concentration of heavy metals Cu(II), Pb(II), Hg(II), As(III), and As(V) under cold stirred conditions in various samples of water. Whereas a Au-loop electrode was used as working electrode when the electrochemical experiments are conducted under hot and cold unstirred conditions figure (1). Au-loop electrode is a gold wire screen printed on a ceramic alumina substrate together with silver/pseudo reference electrode and carbon/counter electrode. It was heated by means of HF-thermalab®system with frequency of 50 KHz, which is heating generator (Gensoric, Rostock, Germany) with general purposes electrochemical system (PSTrace 3) software package in connection with a personal computer. Au-loop electrode has an active area of $0.67 \times 10^{-3} \text{ cm}^2$ and Au-RDE has an active area of 0.41 cm^2 . The electrochemical active surface area has been calculated by CV-measurements of the gold oxide reduction peak in pure 0.5 M H_2SO_4 . Numerous repetitive scans yielded $0.320 \mu\text{C}$ for Au-loop electrode and $196.8 \mu\text{C}$ for Au-RDE. A $480 \mu\text{C}/\text{cm}^2$ conversion factor has been used for these calculations [138].



Resistor value between A-B points -1-5 Ohms

Figure (1): Hot gold-loop electrode manufactured by DropSens Co. (Spain).

Pulse voltammetry technique was applied for the determination all of heavy metals in various samples of water (Ultra-pure, tap, and river water), where DPV method was applied for determination of Cu(II), Hg(II), As(III) and As(V) and SWV method was applied for determination of Pb(II). The parameters of the electrochemical experiments are shown in (table 2) and (table 3).

3.2. Reagents

All reagents, which were used for the conduction of the electrochemical experiments, were obtained from certified manufactures (Merck, Fluka, and Sigma Alderich) with ultra-pure grades. The stock solutions of Cu(II), Pb(II), and Hg(II) (1000 mg/L) were diluted with ultra-pure water ($>18.2 \text{ M}\Omega$, TOC $< 2 \text{ ppb}$) as needed. The Stock solutions of As(III) (1000 mg/L) were diluted with pure 0.02 M HCl and the stock solution of As(V) (1000 mg/L) were diluted with pure 0.1 M HCl. All dilutions were made with using ultra-pure water ($>18.2 \text{ M}\Omega$, TOC $< 2 \text{ ppb}$). Ultra-pure water, tap and Warnow river water samples were chosen as investigated samples, ultra-pure nitric acid (65%) was used to acidify the sample of river water to avoid adsorption of the metal ions at walls of the containers and to hinder biological activities, a required amount of ultra-pure hydrogen peroxide H_2O_2 (30%) was added to the river water sample as a supporting oxidizing

agent, ultra-pure hydrochloric acid 37% was used to prepare diluted solutions of it, ultra-pure sulfuric acid 98% was used also to prepare diluted solutions of it, and Argon stream.

As a supporting electrolyte of 0.05 M H_2SO_4 (sulfuric acid) was used to determine copper Cu(II) in all samples of water (ultra-pure, tap, and river water) with both working electrodes Au-loop electrode and Au-RDE. 0.1 M H_2SO_4 prepared in 0.01 M HCl was used as electrolyte to determine mercury Hg(II) in all samples of water on Au-loop electrode, and 0.2 M H_2SO_4 prepared in 0.002 M $\text{Na}_2\text{-EDTA}$ and 0.005 M NaCl was used as supporting electrolyte to determine of mercury Hg(II) on Au-RDE. A solution of 0.1 M Sodium acetate buffer containing 0.15 M KCl (PH=4.56) in the presence of 0.5 ppm Bi(III) was used as supporting electrolyte to determine lead Pb(II) in all samples of water with both working electrodes Au-loop electrode and Au-RDE. As supporting electrolyte of 0.1 M HCl was used to determine arsenic As(III) on Au-loop electrode and solution of 5 M HCl in the presence of ascorbic acid was used to determine of As(III) on Au-RDE in all samples of water. For determination of arsenic As(V) on Au-loop electrode 0.1 M HCl was used as supporting electrolyte.

3.3. Sample collection, Preparation and Preservation

Ultra-pure water ($>18.2 \text{ M}\Omega$, $\text{TOC} < 2 \text{ ppb}$) was analyzed directly without any treatment before. Tap water sample was taken from our laboratory in a bottle glass as container and analyzed directly without any treatment before. River water sample was taken from the downstream of Warnow river (Rostock, Germany) in a bottle glass as a sample container and acidified with ultra-pure HNO_3 65% to $\text{PH} = 2 \pm 0.2$ (1 ml of 65% HNO_3 per liter of water sample), after that it was filtered through pleated filter paper and divided to two aliquots designated as origin river water sample and river water UV-sample, which was transferred to a transparent quartz glass and irradiated by UV-lamp of 30 W at wavelength of 254 nm for six hours in the presence of hydrogen peroxide, where both samples were stored in refrigerator at 4 °C until determination take place.

Table (2): Instrument operating parameters for analysis of Cu(II), Hg(II), Pb(II), As(III); and As(V) on Au-loop electrode at both temperatures room temperature and 60 °C:

Metal	Cu(II)	Hg(II)	Pb(II)	As(III)	As(V)
Mode	DPV	DPV	SWV	DPV	DPV
Working electrode	Au-le	Au-le	Au-le	Au-le	Au-le
Calibration	St. add.	St. add.	St. add.	St. add.	St. add.
Purge time (s)	600	600	600	600	600
Start potential (V)	0	0.2	-0.8	-0.2	-0.2
End potential (V)	0.8	0.8	0.3	0.3	0.3
Step potential (V)	0.00244	0.006	0.00244	0.005	0.005
Pulse potential (V)	0.05	0.05		0.05	0.05
Potential amplitude (V)			0.03		
Conditioning potential (V)	0.8	0.7	0.8	0.5	0.5
Deposition potential (V)	0	0.2	-0.8	-0.4	-0.7
Conditioning time (s)	10	60	10	60	60
Deposition time (s)	60	120	120	30	30
Pulse time (s)	0.05	0.04		0.05	0.05
Scan rate (V/s)	0.024	0.06		0.024	0.024
Frequency (Hz)			30		
Equilibrating time (s)	3	5	3	3	3

(Notice: Potential amplitude and frequency are parameters that only belong to SWV-method. Pulse potential, pulse time and Scan rate are parameters that are not included in the SWV-method).

Table (3): Instrument operating parameters for analysis of Cu(II), Hg(II), Pb(II), As(III); and As(V) on Au-RDE:

Metal	Cu(II)	Hg(II)	Pb(II)	As(III)
Mode	DPV	DPV	SWV	DPV
Working electrode	Au-RDE	Au-RDE	Au-RDE	Au-RDE
Calibration	St. add.	St. add.	St. add.	St. add.
Purge time (s)	600	600	600	600
Start potential (V)	0	0.4	-0.8	-0.2
End potential (V)	0.8	0.7	0.3	0.3
Step potential (V)	0.00244	0.002	0.00244	0.005
Potential pulse (V)	0.05	0.05		0.05
Potential amplitude (V)			0.03	
Conditioning potential (V)	0.8	0.7	0.8	0.5
Deposition potential (V)	0	0.37	-0.8	-0.4
Conditioning time (s)	10	10	10	60
Deposition time (s)	60	180	120	30
Pulse time (s)	0.05	0.04		0.05
Scan rate (V/s)	0.024	0.02		0.024
Frequency (Hz)			30	
Equilibrating time (s)	3	5	3	3
Rotating rate (rpm)	500	3000	500	3000

Table (4): Instrument operating parameters for conditioning Au-RDE before analysis Hg(II):

Mode	DPV
Working electrode	Au-RDE
Purge time (s)	30
Start potential (V)	0
End potential (V)	0.8
Step potential (V)	0.006
Pulse potential (V)	0.05
Conditioning potential (V)	0
Deposition potential (V)	+1.5
Conditioning time (s)	10
Deposition time (s)	30
Pulse time (s)	0.04
Scan rate (V/s)	0.06
Equilibrating time (s)	5
Rotating rate (rpm)	2000
No. of replication	10
Supporting electrolyte	40 ml ultra-pure water containing 400 μ l HClO ₄ 70%

Table (5): Instrument operating parameters for the conditioning of Au-RDE before analysis As(III):

Mode	CV
Working electrode	Au-RDE
Purge time (s)	300
Potential vortex 1 (V)	-0.2
Potential vortex 2 (V)	+0.3
Start potential (V)	-0.2
Step potential (V)	0.006
Conditioning potential (V)	-1.5
Deposition potential (V)	+0.4
Conditioning time (s)	30
Deposition time (s)	60
No. of replication cycles	16
Scan rate (V/s)	0.02
Equilibrating time (s)	5
Rotating rate (rpm)	2000
Supporting electrolyte	40 ml ultra-pure water containing 400 μ l HClO_4 70%

3.4. Procedure

The electrochemical experiments for analysis of metals (Cu(II), Hg(II); Pb(II), As(III), and As(V)) on Au-loop electrode in all samples of (Ultra-pure, tap, and river water) were conducted after the experimental determination of the electrode temperature by applying an automatic temperature calibration technique. A maximum temperature can be obtained on Au-loop electrode is in the range (from 80 to 100 °C). All of metals (Cu(II), Hg(II), Pb(II), As(III), and As(V)) were analyzed under the given operating conditions. Three replicate measurements were taken for every added concentration of the analyzed metal ion. Standard addition method was

used to determine a concentration of metal ions in the investigated samples. Deaeration with Argon stream for 10 minutes was done after the filling the cell with a new electrolyte.

3.4.1. Determination of trace copper Cu(II)

For determination a concentration of copper Cu(II) at both working electrodes Au-loop electrode (at both temperatures 60 °C and room temperature) and Au-RDE, differential pulse voltammetry experiments were performed in a 50 ml electrochemical cell, containing the supporting electrolyte, 38 ml of water sample and 2 ml of 1 M H₂SO₄. Prior to the deposition step the working electrode was preconditioned for 10 s at 0.8 V. Deposition parameters were adjusted as described in tables (2) and (3). All steps proceeded in a quiescent solution, except when the Au-RDE is used and set to rotation.

3.4.2. Determination of trace mercury Hg(II)

For Hg(II) determination at both working electrodes Au-loop electrode (at both temperatures 60 °C and room temperature) and Au-RDE, differential pulse voltammetry experiments were performed in a 50 ml electrochemical cell, containing the supporting electrolyte. Prior to the deposition step the working electrode was preconditioned for 60 s at 0.7 V at Au-loop electrode and for 10 s at 0.7 V at Au-RDE. Deposition parameters were adjusted as described in tables (2) and (3). All steps proceeded in a quiescent solution, except when the Au-RDE is used. After the deposition period, the voltammogram current versus potential was recorded. All of the experiments for determination of Hg(II) on Au-RDE electrode in all samples of water (Ultra-pure, tap, and river water) were achieved after conditioning of Au-RDE surface in the conditioning solution: 40 ml of the ultra-pure water containing 400 µl HClO₄ 70%, by differential pulse voltammetry, Au-RDE was preconditioned for 10 s at 0 V. The deposition proceeded with rate of rotation 2000 rpm by applying a potential +1.5 V for 30 s. After the deposition period, the voltammogram was recorded with scan rate equal to 0.06 V/s, another parameters described in table (4).

3.4.3. Determination of trace lead Pb(II)

Square wave voltammetry measurements were performed for analysis of lead Pb(II) in all samples of water (ultra-pure, tap, and river water) on both working electrodes Au-loop electrode (at both temperatures 60 °C and room temperature) and Au-RDE in the presence of 0.5 ppm

Bismuth Bi(III) deposited along with the target of metal. The three electrodes were immersed in a 50 ml electrochemical cell containing 0.1 M acetate buffer solution (PH=4.56). Prior to each measurement, the working electrode was preconditioned by applying a conditioning potential of +0.8 V for 10 s followed by an accumulation step at -0.8 V for 120 s. After 3 s equilibrating period, the voltammogram was recorded positive going square-wave voltammetric potential scan with frequency of 30 Hz, potential step of 0.00244 V, and amplitude of 30 mV. All experiments were carried out in a quiescent solution, except when the Au-RDE is used.

3.4.4. Determination of traces arsenic As(III) and As(V)

For determination a concentration of As(III) on Au-RDE, differential pulse voltammetry experiments were done after conditioning the electrode surface with a conditioning solution of 5 M HCl (23.44 ml ultra-pure water and 16.56 ml HCl 37%), by applying cyclic voltammetry technique, Au-RDE was preconditioned for 30 s at -1.5 V. The deposition proceeded with rate of rotation 2000 rpm by applying a potential +0.4 V for 60 s. After the deposition period, the voltammogram was recorded with scan rate equal to 0.02 V/s, another parameters described in table (5). Differential Pulse Voltammetry experiments were performed in a 50 ml electrochemical cell, containing the supporting electrolyte (36 ml. of the investigated sample of water and 4 ml HCl 1 M) for determination of As(III) and As(V) on Au-loop electrode at both temperatures 60 °C and room temperature. Deposition parameters were adjusted as described in table (2), all steps proceeded in a quiescent solution. At Au-RDE for determination of As(III), an electrolysis cell was filled with supporting electrolyte of 5 M HCl (23 ml of the sample of water, 16.56 ml of HCl 37%) and 200 µl of ascorbic acid 1% that had here positive effect. Deposition parameters were adjusted as described in table (3). Ascorbic acid was used as reagent to stabilize As(III) ions at Au-RDE.

3.5. Definition and calculation of the standard addition, recovery rate and limit of detection

3.5.1. Standard addition method (SAM)

The standard addition method, which is a category of quantitative analysis, is utilized in analytical chemistry where the standard solution of the metal ion studied is added immediately to the analyzed sample solution. Before adding any concentration of the standard solution the

signal intensity of the sample solution is measured and recorded. After that a very small portions of the standard solution of the metal ion studied are added at a known concentrations to the sample solution. After each addition the signal intensity is measured and recorded. At the end of five addition (in our research) the signal intensities are plotted as a function of spiked concentrations. The found concentration is calculated from the point at which the extrapolated line crosses the concentrations axis (X-axis) at zero signal. The advantage of SAM is that to eliminate the matrix effect as little as possible [138-140]. Since the signal intensity of the metal ion studied is affected in many cases by the components of the sample solution.

3.5.2. Recovery rate

In our research, the classic recovery rate has been calculated for the analyzed samples to know how much is recovered of the substance studied.

$$\text{Recovery rate \%} = (\text{found concentration} / \text{known claimed concentration}) * 100$$

The found concentration is equal to the difference between a found concentration before adding any substance and a found concentration after adding a known concentration of the analyzed substance.

A modified recovery rate (MRR* %) will be calculated to discover a proportional systematic deviation, which is available when the deviation is depended on the concentration of the analyte. Therefore, more than three points-standard addition will be carried out. The obtained measure values of (Y_0, Y_1, \dots, Y_i) are used for the calculation of found concentrations equivalent ($X_{f0}, X_{f1}, \dots, X_{fi}$) by means of linear calibration function in pure water. Then it will be plotted a figure between the found concentrations (Y-axis) and the claimed concentration (X-axis). From the obtained linear calibration function $X_{\text{found}} = a X + b$, the MRR* % will be equal to $(a * 100)$. [W. Funk, „Statische Methoden in der Wasseranalytik“, VCH Weinheim, [1985] [141].

3.5.3. Limit of detection (LOD)

A detection limit is the minimum concentration of an analyte which can be observed in the absence of that analyte (a blind value) within stated confidence limit. The limit of detection is practically calculated from the blind value of the analyzed blank sample through the following equation: $\text{LOD} = b + n S$, in which b is the blind value of the analyzed sample, n is a practical number (here equal to 3), and S is the standard deviation of the blind value. A blank is a sample for analysis, which is presumably free of the components to be determined. The measured value

of a blank sample is called a blind value. A blank sample is prepared by the pure solvent, which is also used for the preparation of calibration solution; the complete analysis method is subjected, without addition an analyte to be examined. For the practical determination of the blind value it has been found two possibilities: the average blind value is determined from a large number of separately conducted blank samples analyzed or the blind value is constructed by extrapolating a calibration function of the concentration at $X = 0$. Thus the blind value is equal to the intercept of the calibration function at Y axis [141].

3.6. Automatic temperature calibration

Briefly, a stationary temperature of heated Au-loop electrode is measured by applying open circuit potentiometry measurements in an electrochemical cell containing an equivalent amount of a reversible redox couple using 5 mM equimolar ferro/ferricyanide solution prepared in 0.1 M KCl. After adjusting the pulse number, pulse duration and pulse interval the measurement is started automatically with open circuit potentiometry (OCP) technique as in the following flow chart in which n is number of pulses, P is electrical potential, k is pulse counter, dE is potential difference, i is pulse power in steps from 0–63, t is pulse duration in seconds, and m is interval between pulses.

Gensoric-flow chart-automated calibration: (It has been written by Martin Schoenhoff)

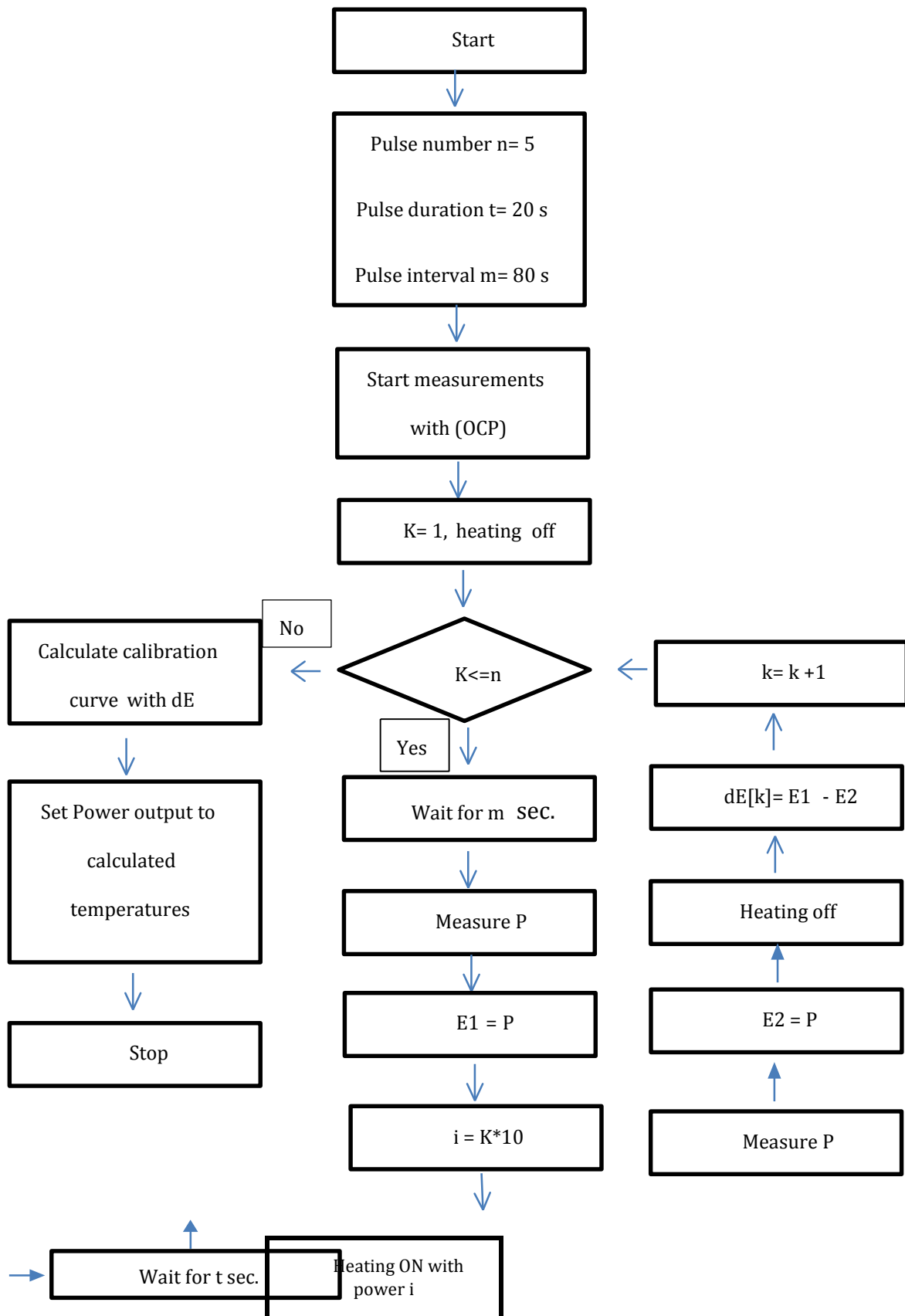


Figure (2) refers to (OCP) measurements with Au-loop electrode expressed about the changes of potential through time. Figure (3) display a set power output to calculated temperatures.

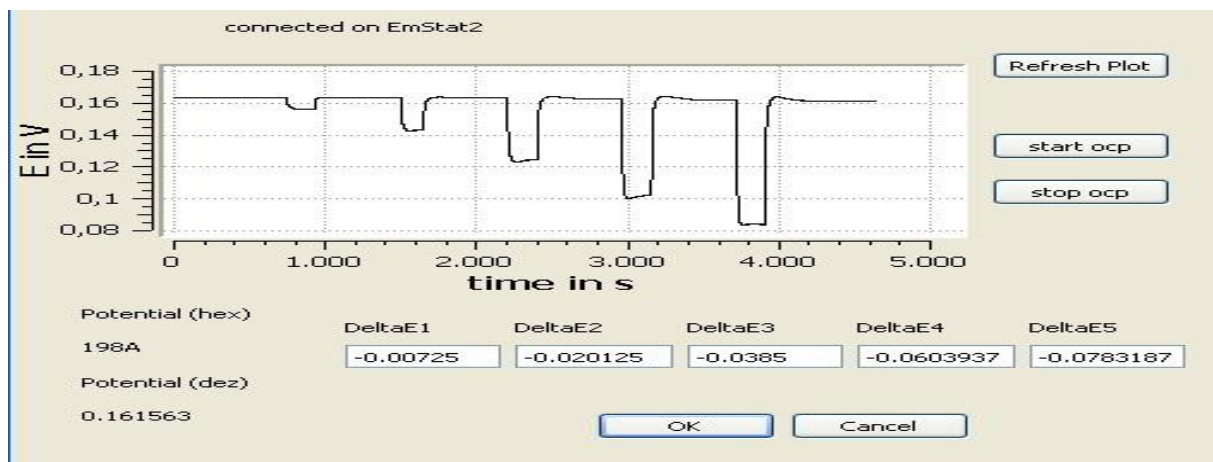


Figure (2): open circuit potentiometry measurement with Au-loop electrode impressed in a solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl at 22 °C bulk solution temperature by adjusting the electric power from 10 to 50 (from the left to the right).

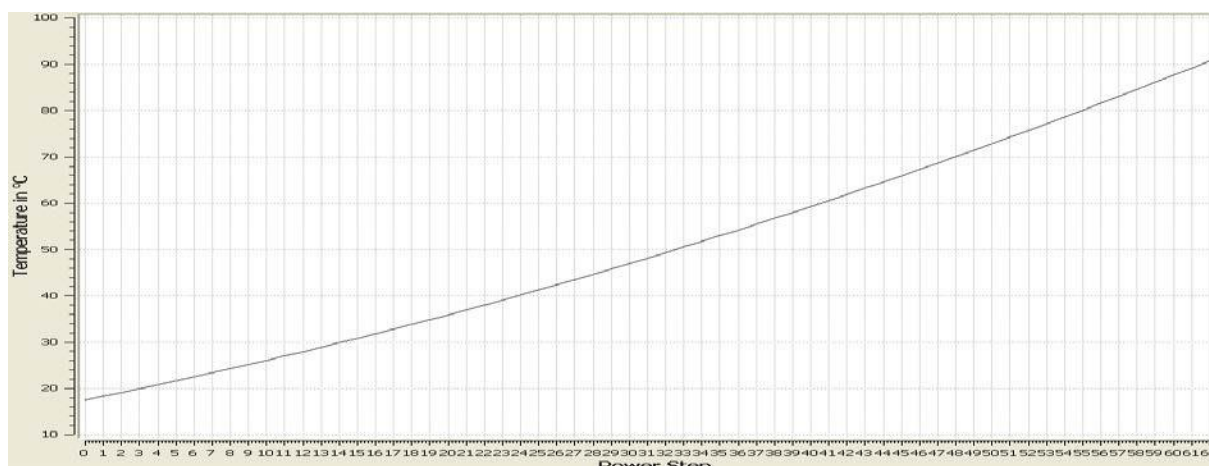


Figure (3): Temperature calibration plot for Au-loop electrode.

4. Results and discussion

Many methods have been proposed for the determination of heavy metals in various water samples, soil and food, most of them are based on atomic absorption spectrometry (AAS) [142, 143], inductivity coupled plasma mass spectroscopy (ICP-MS) [144-146], and inductivity coupled plasma optical emission spectrometry (ICP-OES) [147-149]. Other techniques include X-Ray florescence spectrometry [150], electromigration techniques [151, 152], and electrochemical techniques [153-155]. Each technique has its own advantages and disadvantages.

Our research aims to prove the efficiency and strength of Au-loop electrode to determine some heavy metals in various samples of water in comparison with Au-RDE. Au-loop electrode shows a different behavior with the studied heavy metals (Cu(II), Pb(II), Hg(II), As(III), and As(V)). On the other hand, our research also aims to check the ability of heated Au-loop electrode to replace a classic UV-irradiation process for determination some heavy metals in origin river water-sample.

4.1. Measurement of trace copper Cu(II)

It is essential in both community's health and environmental controlling to determine of trace heavy metals. Copper, as a typical heavy metal, acts a significant role in human lives, a vital constituent of several enzymes, and it helps the iron (Fe) transporting. However, excessive mange of Cu(II) can cause health dangers and also make large influence on the growth of plants. Therefore, determination of the concentration of trace copper Cu(II) is very significant in the environmental water-samples and food.

Many methods have been applied and developed for the determination of copper in many samples of natural water, food and human, among them being based on ICP-MS method which includes short time of analysis, high precision, low detection limit, and high accuracy. On the other hand, this method had some disadvantages included in a high risk of contamination due to the presence of some elements of interest in the environment, the cost of the equipment and the relatively delicate sample handling [156].

Also Atomic Absorption spectrometry (AAS) analysis method has been widely used for the determination of heavy metals such as copper in various water samples and food. AAS technique can be performed through two steps of atomization of the sample and the absorption of optical

radiation from light source by the free atoms in gaseous state. The main advantages of AAS technique are in high sample throughput, easy to use, high precision, and inexpensive. On the other hand, as the main disadvantage by applying AAS is a problem with refractory elements [157].

Electrochemical analytical methods have been successfully applied for the determination of copper. For example ASV technique was applied for the determination of copper on gold electrodes modified with disorganized monolayer films to prevent the deposition of surfactants on the electrode surface by LSASV of UPD. Such as disorganized monolayer gold electrodes have identified the most suitable modification reagent for the detection of copper by anodic stripping of UPD [158]. It has been found that the surfactants have no effect on detection of Cu(II) using mercaptoethansulfonate (MES)-modified gold electrodes, whereas with an unmodified gold electrodes a very harsh attenuation of the detection capability was established. On the other hand, analytical applications of UPD by stripping of such deposits from bare gold electrodes have been studied by Kirowa-Eisner and co-workers [159-164]. It has been found that the ability of such bare electrodes requires extensive sample preparation and, moreover, extremely sensitive analytical capabilities were demonstrated, which was referred to the adsorption of surfactants presented in a studied sample on the bare electrode surface.

Also copper has been determined at heated gold wire electrodes by stripping voltammetry [165]. Heated wire gold electrodes have been provided remarkable advantages compared to Au-RDEs, where the lowest detectable concentration of Cu(II) was 100 fold lower at the hot-wire electrode than at the RDE, that was caused by microelectrode behavior together with accelerated diffusion rate, which due to the existence of a constant diffusion layer thickness.

In our research, the concentration of Cu(II) will be determined by UPD at directly heated Au-loop electrode in various water samples of (ultra-pure, tap and river water).

4.1.1. Copper(II)-under potential deposition

Phenomenon of the under potential deposition is defined as an electrochemical deposition of an analyte (typically reduction a metal cation to a solid metal) at potential less negative than equilibrium potential for the reduction of this metal.

Under potential deposition has been applied as a description technique for numerous self-assembled monolayers (SAMs), it has been found that SAMs molded on UPD monolayer are more stable than on the substrate electrode and that UPD after construction of SAM consequences in metal monolayer actuality formed among the electrode substrate and the organic film [166-

170]. Additionally, UPD of metals such as copper has been studied at solid electrode modified with thiols [158, 171-174], it has been explained that the substantial features of the thiol adsorbed on the electrode surface effects significantly the form of the stripping peak and the amount of metal underpotentially deposited. Moreover, it has been applied of the copper-UPD stripping voltammetry at gold electrodes modified with mercaptoacetic acid for the analysis of soil extract sample [175] concluded that such these modified electrodes provided effective protection to prevent the adsorption of humic acid onto the gold electrode surface and that by using these modified gold electrodes more sensitivity for the detection of copper than bare gold electrodes was investigated.

Our aim in this experiment is detection and determination of copper by UPD of an electrochemical analytical method directly on bare Au-loop electrode in various water samples to examine the ability of such electrode for inhibition of humic acid adsorption on the surface of the Au-loop electrode. It will be found possibility for shortening of the electrochemical analysis of environmental samples, such as eliminating the need for extensive sample pre-treatment or digestion, if such manners can be protracted to natural surfactants present in environmental samples.

4.1.1.1. UPD of copper Cu(II) in ultra-pure water sample

Figure 4 shows stripping voltammetric analytical signals of 1 ppm copper(II) (deposition 120s) in pure 0.05 M H_2SO_4 on bare heated Au-loop electrode at 60 °C electrode temperature and at different deposition potentials. As depicted, the stripping voltammograms in figure 4 shows clearly the presence of two peaks and their relative intensities vary according to the deposition potential (E_{dep}) employed. The peak at ca. +250 mV is relatively insensitive to the (E_{dep}), while that at ca. +50 mV grows gradually with (E_{dep}) and reaches a maximum at the most negative value of (E_{dep}) employed. The peak at ca. +250 mV displays the typical characteristics of the UPD stripping process of copper on gold electrodes. In Accordance with previous investigations [159-164] and based on these analysis the peak at ca. +250 mV can be credited to the stripping of the copper UPD monolayer on the Au-loop electrode surface, whereas the stripping of the copper at ca. +50 mV referred to the stripping of a bulk deposited layer of copper. The maximum signal of the bulk stripping peak at +50 mV was obtained using a deposition potential of -100 mV. This peak response (90 μA) was much larger at 60 °C than at ambient deposition conditions, as depicted in Fig. 5, where the maximum signal of the bulk stripping peak response was 10 μA .

In contrast with another study on heated gold wire electrodes, that was carried out in 0.01

M HCl as supporting electrolyte [Electroanalysis 13 (2001) 786] [23], it has found to be no Cu-UPD stripping peak signal was observed, and the copper signal was located at +450 mV.at heated Au-wire electrode and +30 mV at RDE.

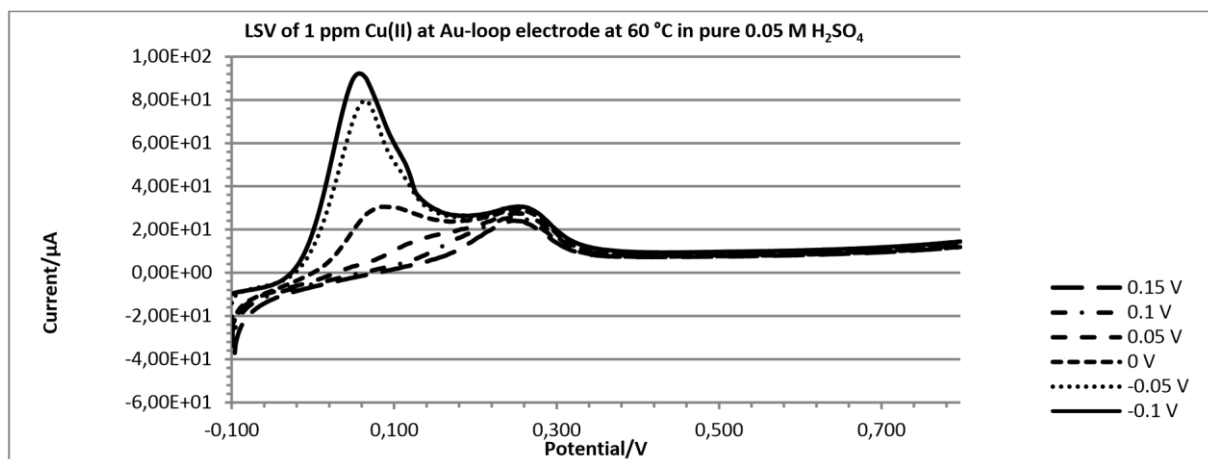


Figure (4): Linear sweep voltammetry of Cu(II) at Au-loop electrode at 60 °C in 0.05 M H₂SO₄ for 120 s deposition time at different deposition potential. Begin potential = -0.1 V, end potential = 0.8 V, scan rate = 0.1 V/s, and [Cu(II)] = 1 ppm.

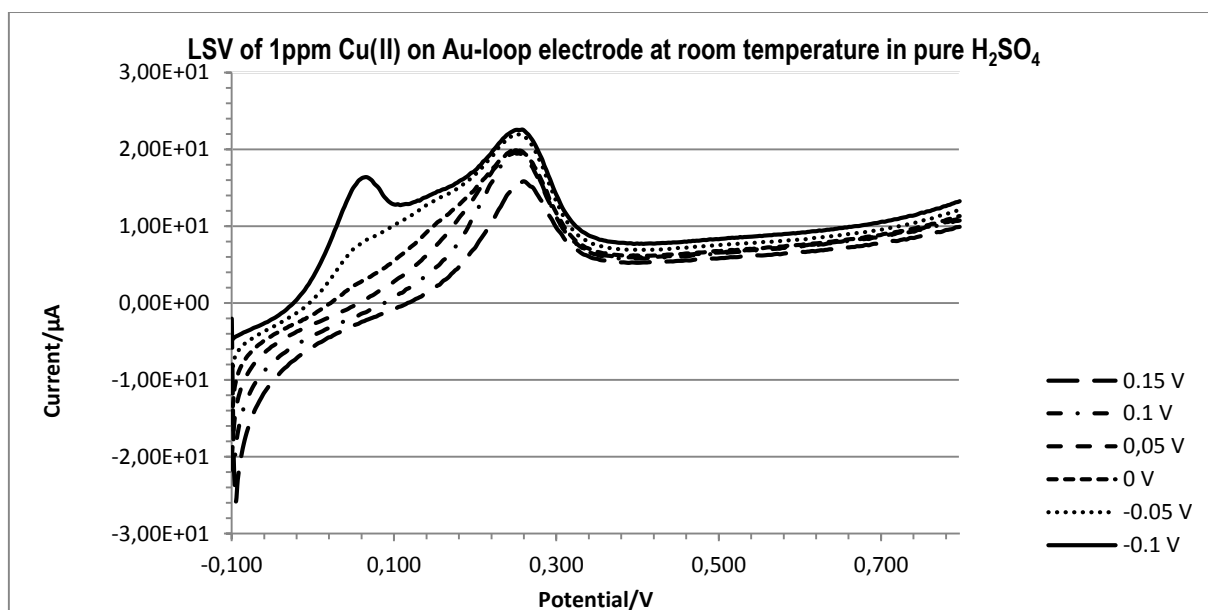


Figure (5): Linear sweep voltammetry of Cu(II) at Au-loop electrode at room temperature in 0.05 M H₂SO₄ for 120 s deposition time at different deposition potential. Begin potential = -0.1 V, end potential = 0.8 V, scan rate = 0.1 V/s, and [Cu(II)] = 1 ppm.

With the deposition potential of +100 mV the concentration of Cu(II)-UPD has been determined in ultra-pure water at Au-loop electrode to be 8.72 ppb with blind value equal to 1.11 ppb at 60 °C and 23.03 ppb at room temperature with blind value equal to 0.34 ppb (G. U. Flechsig and Zukas's measurements, see the attachment of the diss.)

4.1.1.2. UPD of copper Cu(II) in tap water sample

This experiment reports the possibility of the stripping of Cu(II)-UPD on bare heated Au-loop electrode at 60 °C in tap water containing 0.1 M H₂SO₄ for 120 s of deposition time by applying differential pulse voltammetry (DPV) method at -400 mV (E_{dep}). At this deposition potential, both bulk and UPD (monolayer) copper is expected, and the stripping voltammograms (Figure 6) show two processes, consistent with this.

It was shown (figure 6) that the large bulk stripping signals of Cu(II) of max. (1 mA) at ca. +50 mV was concentration-dependent, whereas the second Cu-UPD stripping peak was unchanged, consistent with a maximum of a single monolayer of copper deposited and stripped. This tendency held not quite true when deposition was performed at ambient conditions as depicted in Fig. 7. A bulk copper stripping signal was not observed in the tap water sample only after addition of 5 to 25 ppm Cu(II) did the bulk copper stripping peak appear and grow to a max. 120 μ A. In this case also the Cu-UPD stripping signal (+200 mV) was present in the absence of added copper, indicating the ability to detect copper by UPD stripping voltammetry in tap water. This UPD stripping peak increased gradually with added concentration but the current value gradually reached a plateau, suggestive of a monolayer formation. The linearity of the UPD peak was, however, better than at 60 °C deposition temperature. As it can be observed later, the concentration of copper UPD stripping has been successfully determined in the tap water at 0 V (E_{dep}).

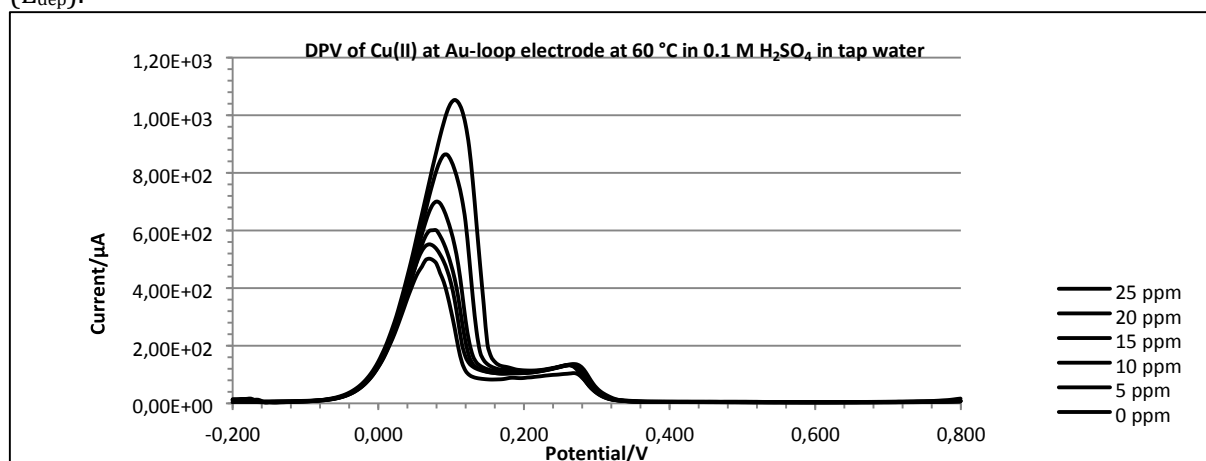


Figure (6): DPV of Cu(II) at Au-loop electrode at 60 °C in the tap water containing 0.1 M H₂SO₄. Concentration (0, 5, 10, 15, 20 und 25 ppm), deposition time = 60 s, deposition potential = -0.4 V, conditioning time= 0.8 V, conditioning time = 10 s, and equilibrating time = 3 s.

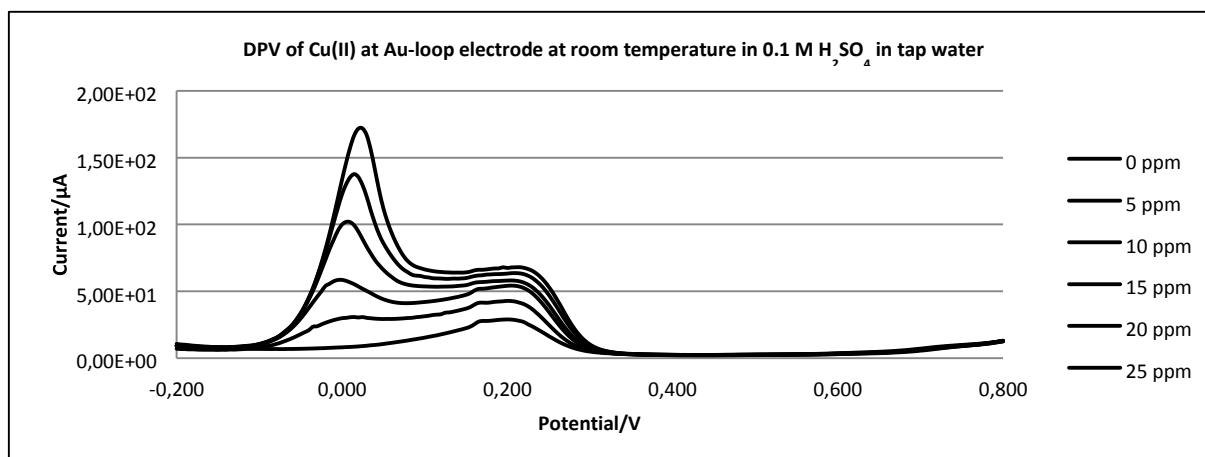


Figure (7): DPV of Cu(II) at Au-loop electrode at room temperature in the tap water containing 0.1 M H_2SO_4 . Concentration (0, 5, 10, 15, 20 und 25 ppm), deposition time = 60 s, deposition potential = -0.4 V, conditioning time = 0.8 V, conditioning time = 10 s, and equilibrating time = 3 s.

4.1.1.3. UPD of copper Cu(II) in river water sample

Figure 8 illustrates the Cu(II) UPD on heated bare Au-loop electrode at 60 °C in river water containing 0.05 M H_2SO_4 at deposition potential +50 mV for 120 s deposition time. At these conditions the Cu(II)-UPD was observed in the absence of copper at +177 mV and shifted to a more negative potential by Ca. -73 mV. The stripping peak of Cu(II)-UPD was gradually increased with the concentration added, but the current value gradually reached a plateau, suggesting the formation of copper monolayer and indicating the concentration of copper in this river water sample is too low. The bulk stripping signal of Cu(II) was not observed. This is in accordance with earlier investigations [171, 176-177]. This analysis held on quite when the deposition was performed at room temperature, as displayed in figure 9, Cu-UPD stripping can be observed in the range from 0 ppb to 100 ppb of Cu(II), indicating the ability to detect copper by UPD stripping voltammetry on Au-loop electrode in origin river water sample. The Cu-UPD was concentration-dependent.

However, as it will be depicted later, the concentration of Cu-UPD stripping has determined in origin river water sample at 150 mV of (E_{dep}).

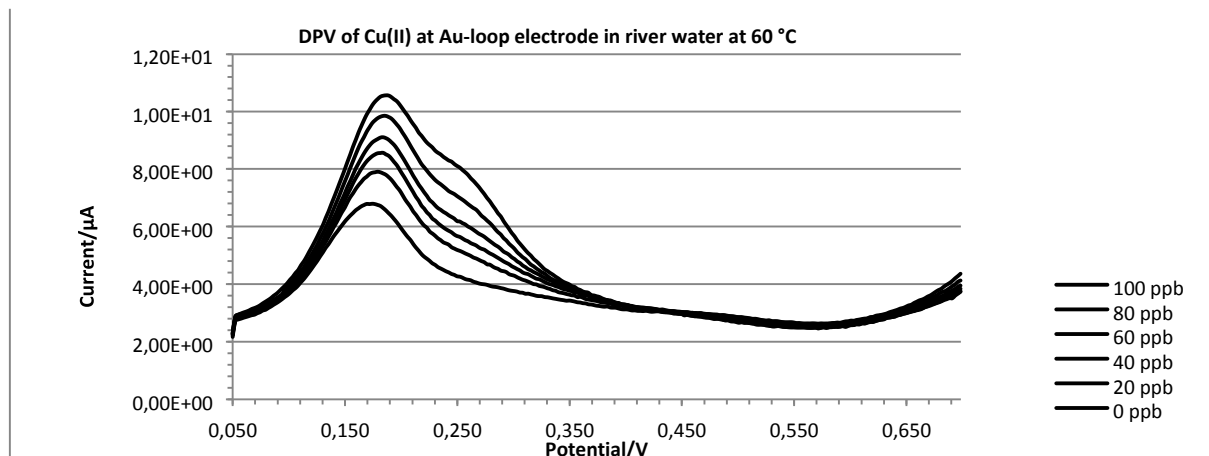


Figure (8): DPV of Cu(II) at heated Au-loop electrode at 60 °C in 0.05 M H₂SO₄ in river water. Deposition potential = 0.05 V, deposition time = 120 s, conditioning potential = 0.8 V, conditioning time = 10 s, initial potential = 0.05 V, end potential = 0.7 V, scan rate = 0.024 V/s, potential step = 0.00244 V, potential pulse = 0.05 V, time pulse = 0.05 s, time step = 0.1 s, and equilibrating time = 3 s.

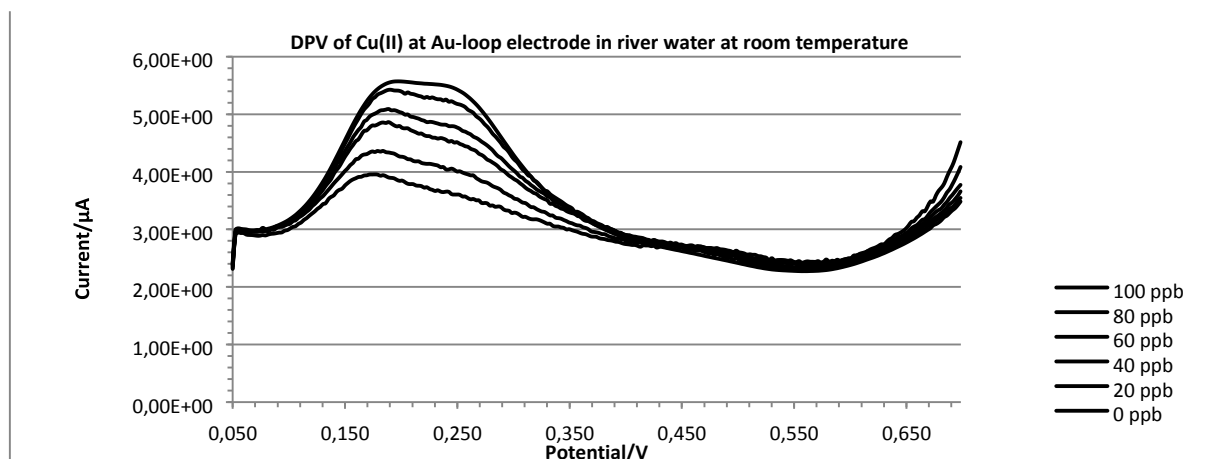


Figure (9): DPV of Cu(II) at Au-loop electrode at room temperature in 0.05 M H₂SO₄ in the river water. Deposition potential = 0.05 V, deposition time = 120 s, conditioning potential = 0.8 V, conditioning time = 10 s, initial potential = 0.05 V, end potential = 0.7 V, scan rate = 0.024 V/s, potential step = 0.00244 V, potential pulse = 0.05 V, time pulse = 0.05 s, time step = 0.1 s, and equilibrating time = 3 s.

As it can be concluded that this investigation at bare Au-loop electrode has identified the possibility for the detection of copper by stripping of underpotentially deposits in tap and river water samples. Moreover, the stripping peak current response of Cu-UPD on Au-loop electrode was varied linearly with the concentration added.

4.1.2. Concentration of Cu(II)-UPD in the tap water

Many analyzed natural samples are containing electrode-passivating composites that establish a challenge for analytical detection by applying electrochemical techniques. Heated working electrodes have received considerable attention because of toxicity and fouling of mercury electrodes and solid electrodes. Generally, heated working electrode enhances the selectivity and sensitivity of the electroanalytical method. In this experiment heated Au-loop electrode is combined with analytical stripping voltammetry technique to form a powerful and established method for the analysis of trace copper in tap water sample. Several methods are also used routinely such as AAS, X-ray florescence and ICP, but advantages of using heated electrodes combined with electroanalytical stripping voltammetry are successful, new, rapid, simple, selective and inexpensive for qualitative and quantitative determination of heavy metals.

In this study the concentration of copper Cu(II) underpotentially deposited has been successfully determined in the tap water sample investigated directly without any treatment before taking a measurement on Au-loop electrode at both temperatures 60 °C and room temperature (22 °C) in the comparison with Au-RDE. Figure (10) displays differential pulse stripping voltammetric analytical signals of copper in tap water sample containing 0.05 M H₂SO₄ for 60 sec. deposition time at 0 V deposition potential. The voltammograms shows the presence of one peak, where the stripping peak of a bulk deposited layer of copper was not observed at the same conditions employed. The stripping peak of Cu(II)-UPD was observed in the absence of copper added at 210 mV potential on heated and un heated Au-loop electrode and at 250 mV on Au-RDE, indicating the ability for detection of copper underpotentially deposited on bare Au-loop electrode in the tap water sample studied. This stripping peak was recorded to be increased gradually accordance to the concentrations added of copper with highsensitivity obtained on heated Au-loop electrode, where the stripping peak of 100 ppb added of Cu(II) was recorded to be higher in about 3-fold than that obtained on unheated Au-loop electrode and in about 2-fold than that obtained on Au-RDE. The concentration of the Cu(II) ions was determined by applying SAM as depicted in figure (11) to be 39.48 ppb, 86.04 ppb at 60 °C and room temperature respectively, and 43.34 ppb at the Au RDE. So it seems to be that the effect of heating during conditioning and deposition steps enhances the analytical signal at unaffected signal-to-noise ratio, this is actually in accordance with earlier studies [178], and helps to achieve the deposition and stripping processes more easily and quickly. So at Au-loop electrode was offered a good analytical signal response for stripping voltammetry of Cu-UPD in tap water. The recovery rate for copper was found to be 33.35 % at heated Au-loop electrode, 22.70 % at room temperature and 87.37 % at the Au-RDE. The results obtained in this experiment are given in table (6).

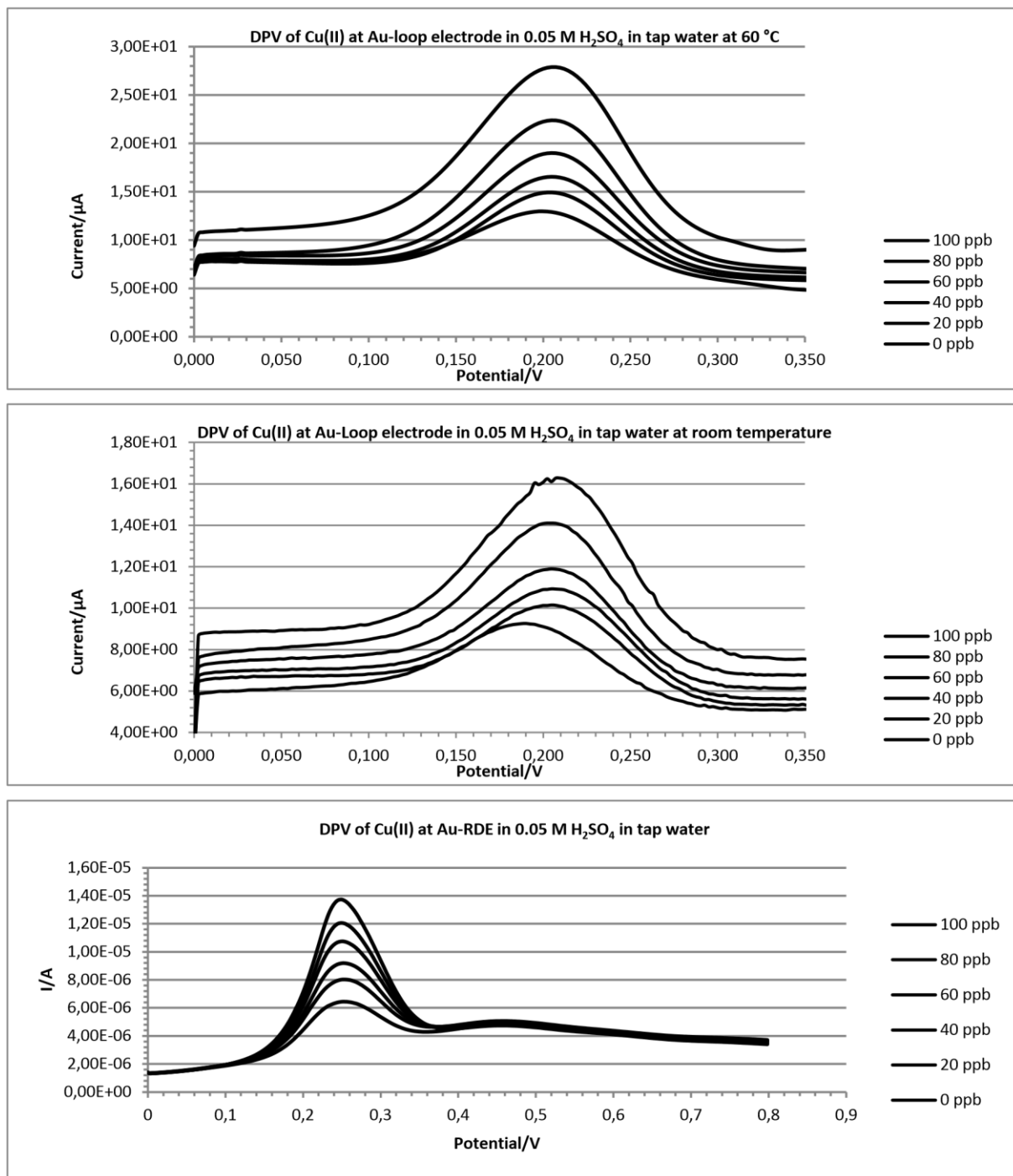


Figure (10): DPV of Cu(II) at Au-loop electrode at both temperatures of 60 °C and room temperature, and at Au-RDE in 0.05 M H_2SO_4 in the tap water at deposition potential 0 V for deposition time 60 s. Other conditions as in tables (1) and (2).

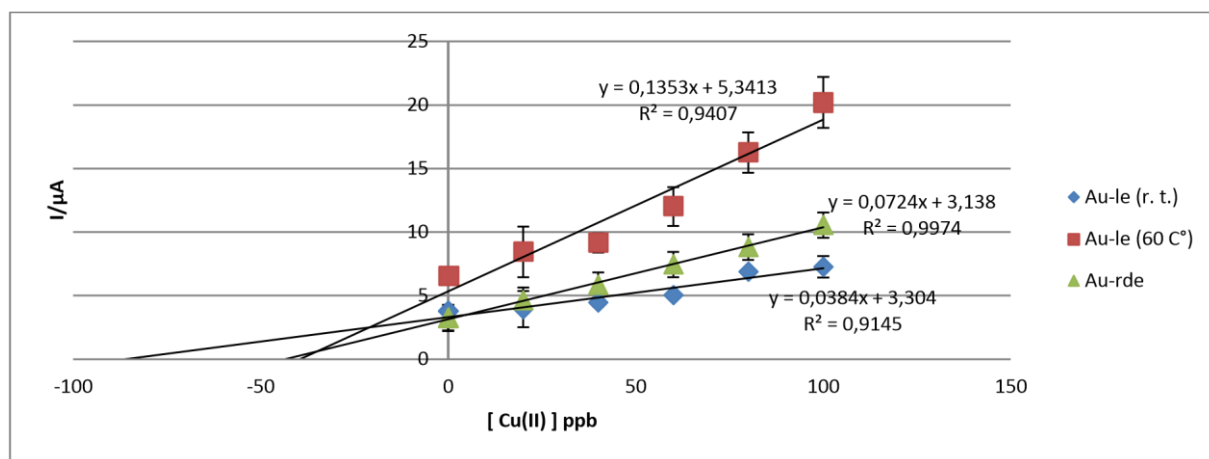


Figure (11): Calibration plots for deposition of copper(II) at Au-loop electrode at 60 °C and at room temperature in the Compare with Au-RDE in 0.05 M H₂SO₄ in tap water represent current peak versus the concentration of copper.

Table (6): concentration of Cu(II) and recovery rate Cu(II) in the tap water at both working electrodes of Au-loop electrode (at both of temperatures 60 °C and 22 °C) and Au-RDE.

Sample	Working electrode	[Cu(II)] ppb	Recovery rate %	MRR* %
Tap water	Au-le 60 °C	39.48	33.35	105.92
	Au-le 22 °C	86.04	22.70	263.28
	Au-RDE	43.34	87.37	254.00

4.1.3. Concentration of Cu(II)-UPD in river water sample

Stripping voltammetry technique has been widely applied for the determination of heavy metals such as copper, lead, mercury and cadmium in various samples like drink water, waste water, river water, sea water and urine. However, to overcome the problem of organic compounds present in natural samples, which adsorb onto the electrode surface and inhibit the electrochemical reactions, extensive sample preparation was required.

Humic acid as a natural matter is present in the aquatic environmental. Humic acid, which is water soluble at pH >2, offers numerous binding sites to metallic ions because of the large number of phenolic and carboxylic acid functions presented in the aquatic natural samples. The presence of natural surfactants in many natural samples such as humic acid makes the analytical detection therein using electrochemical technique more difficult [176]. It has been found to be

that a humic acid as a natural surfactant could be adsorbed under acidic conditions onto gold electrodes [177]. Moreover, other studies have been investigated that the adsorption of surfactants on bare electrode surface constitutes a challenge for stripping of a small amount of copper underpotentially and that the stripping peak is shifted to a more positive, which requires more energy to strip the copper, as well as it existences with low current and charge [98]. Labuda et al. investigated the anodic stripping voltammetry of heavy metals at a HMDE [179], where it has been found that the presence of 10 mg/L of humic acid in the studied sample resulted in a lowering of the sensitivity for the detection of copper in 0.01 M HCl. Moreover, Jeong et al. [180] reported that the optimal pH range for the detection of copper, by means of complexation with humic acid, was 3.5-7.5. The oxidation peak of copper was much smaller for $\text{pH} < 3.5$, indicating a limited complexation of copper with humic acid in such acidic conditions.

In our experiment, the concentration of copper-UPD in the river water sample has been successfully determined on Au-loop electrode at both temperatures 60 °C and room temperature in small concentration range (from 0 to 10 ppb). Bulk deposition does not occur under these conditions. The signals at 60 °C deposition temperature were 3-fold higher than at room temperature and appeared at the same potential. The concentration of copper was determined on Au-RDE in the range from 10 to 50 ppb. No analytical signals were observed and readable under 10 ppb of Cu(II) on Au-RDE for the same studied sample and under the same conditions.

Comparison of the effect of the presence of DOCs on the voltammetric response of copper on Au-RDE and heated Au-loop electrode was researched fig. (12). At the Au-RDE the response observed for 10 ppb of Cu(II) has been too much low intensity and shifted to a more positive potential, that would explain by binding Cu(II) ions with DOCs presented in river water making a ligand is available on the electrode surface, consequently, it will be available in the matrix of the calibration plot. Whereas we cannot note such this result on heated Au-loop electrode. Voltammograms on Au-loop electrode and Au-RDE are displayed in figure (13). So it seems that the analytical signal response for 10 ppb Cu(II) on heated Au-loop electrode of max. (18 μA) is in 30-fold greater than that obtained on Au-RDE (0.60 μA) with unaffected signal-to-noise-ratio. Such results indicate the hindering or difficulty of the stripping voltammetry process of Cu(II)-UPD by the presence of DOCs on Au-RDE, which due finally to unsurely analysis results. So heated Au-loop electrode was offered a greater sensitivity and an improvement of the analytical response than Au-RDE. Based on this analysis, heated Au-loop electrode offers protection from the fouling activity of DOCs on the electrode surface compared with Au-RDE. The determined concentration for copper in the river water was found to be 1.48 ppb at 60 °C, 3.51 ppb at room temperature and 10.48 ppb on Au-RDE. The calculated recovery rates for the

detection of Cu(II) at Au-loop electrode were found to be 129.15 % at 60 °C and 429.31 % at room temperature.

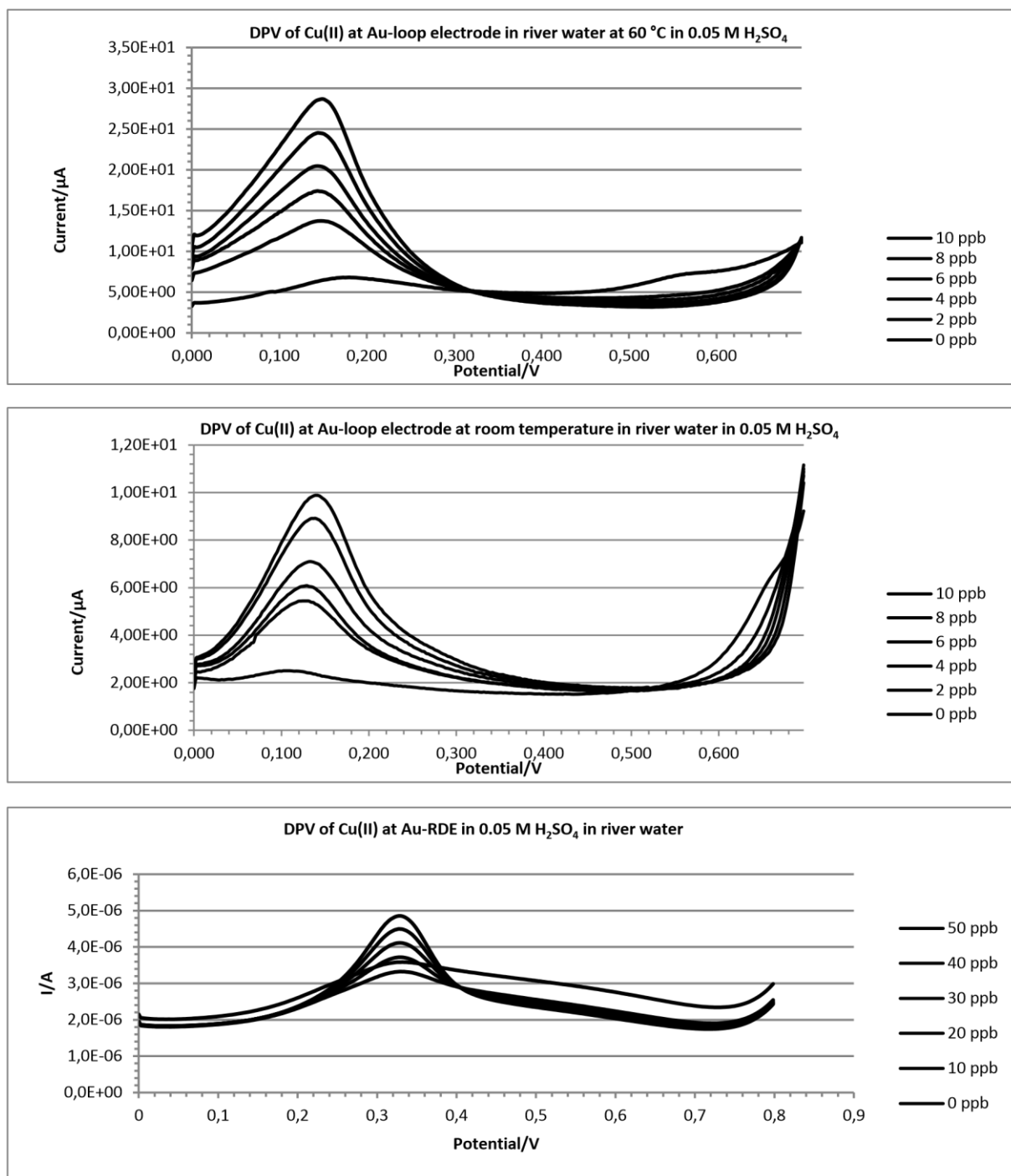


Figure (12): DPV of Cu(II) at Au-loop electrode at both temperatures of 60 °C and room temperature, and at Au-RDE in 0.05 M H₂SO₄ in river water at deposition potential 0.15 V for deposition time 120 s.

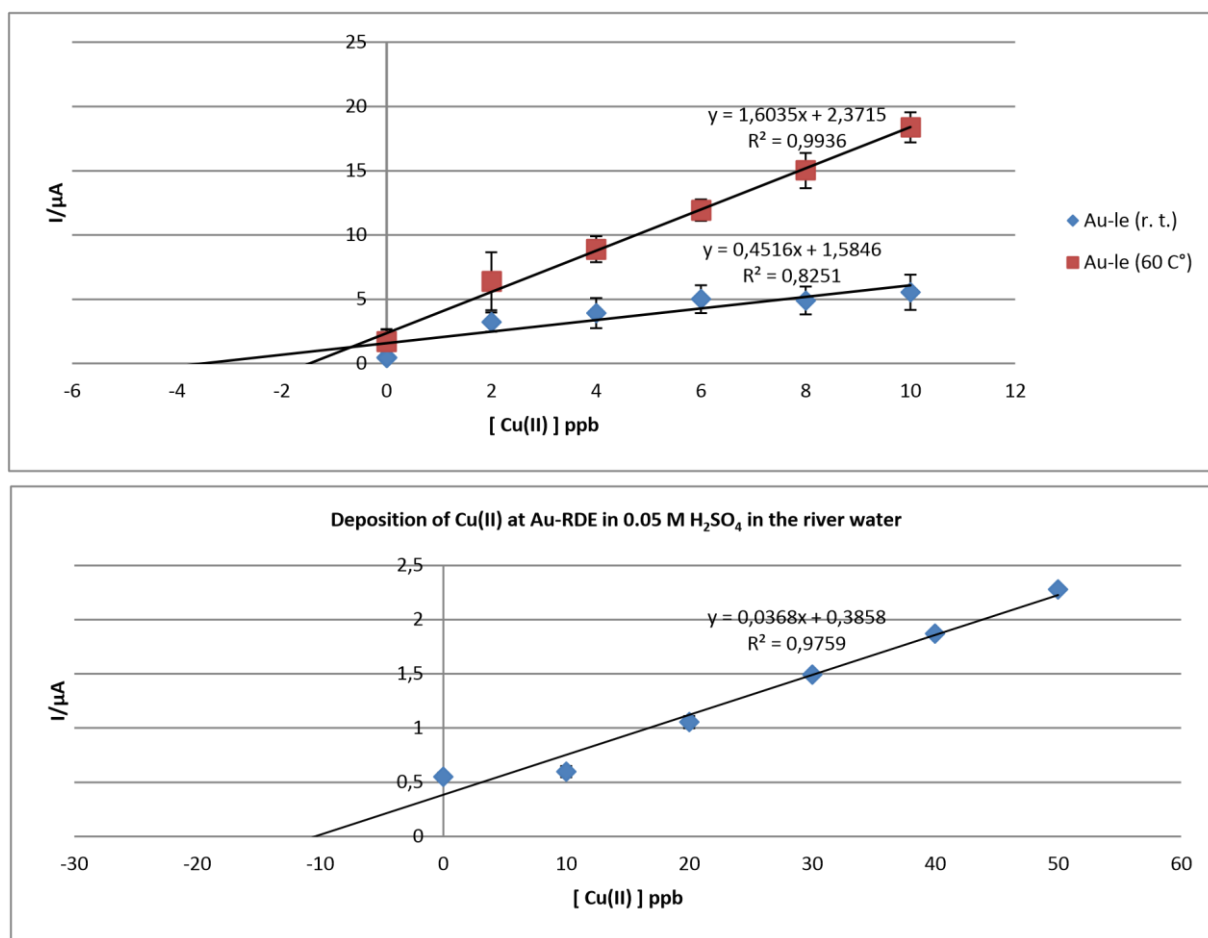


Figure (13): Calibration plots for DPV of copper(II) at Au-loop electrode at 60 °C, at room temperature, and at AuRDE in 0.05 M H₂SO₄ in river water represent current peak versus the copper concentration.

4.1.4. Concentration of Cu(II)-UPD in river water UV-sample

As it seems in figure (14), these responded analytical signals were achieved in our experiment after exposure a river water sample to UV-light for 6 hours in the presence of an oxidation reagent of hydrogen peroxide H₂O₂. On the other hand, no analytical stripping signals of Cu(II) were observed in the river water UV-sample on Au-RDE in the range concentration (2-10 ppb). Seemingly, the found concentration on heated Au-loop electrode before and after UV-irradiation was similar at both temperature of 60 °C and room temperature, indicating that the heated Au-loop electrode improves the conditions for copper determination in the presence of humic acid and can replace a classic UV-irradiation treatment for determination such as heavy metal in origin river water sample. This result is in agree with another study, it's found to be the determined concentration of Cu(II) in origin river water sample on heated Au-loop electrode (60 °C) fast equal to those were obtained at HMDE in river water-UV sample (G. U. Flechsig and Zukas's measurements, see the attachment of the diss.).

In Contrast with another study, copper was determined in river water at HMDE by DPV technique by G. U. Flechsig and G. Woldmichael, it has been found, the determined concentration of Cu(II) in origin river water was more little than that was found in river water UV-sample, indicating the fouling of the working electrode surface with organic river water matrix-complexed components.

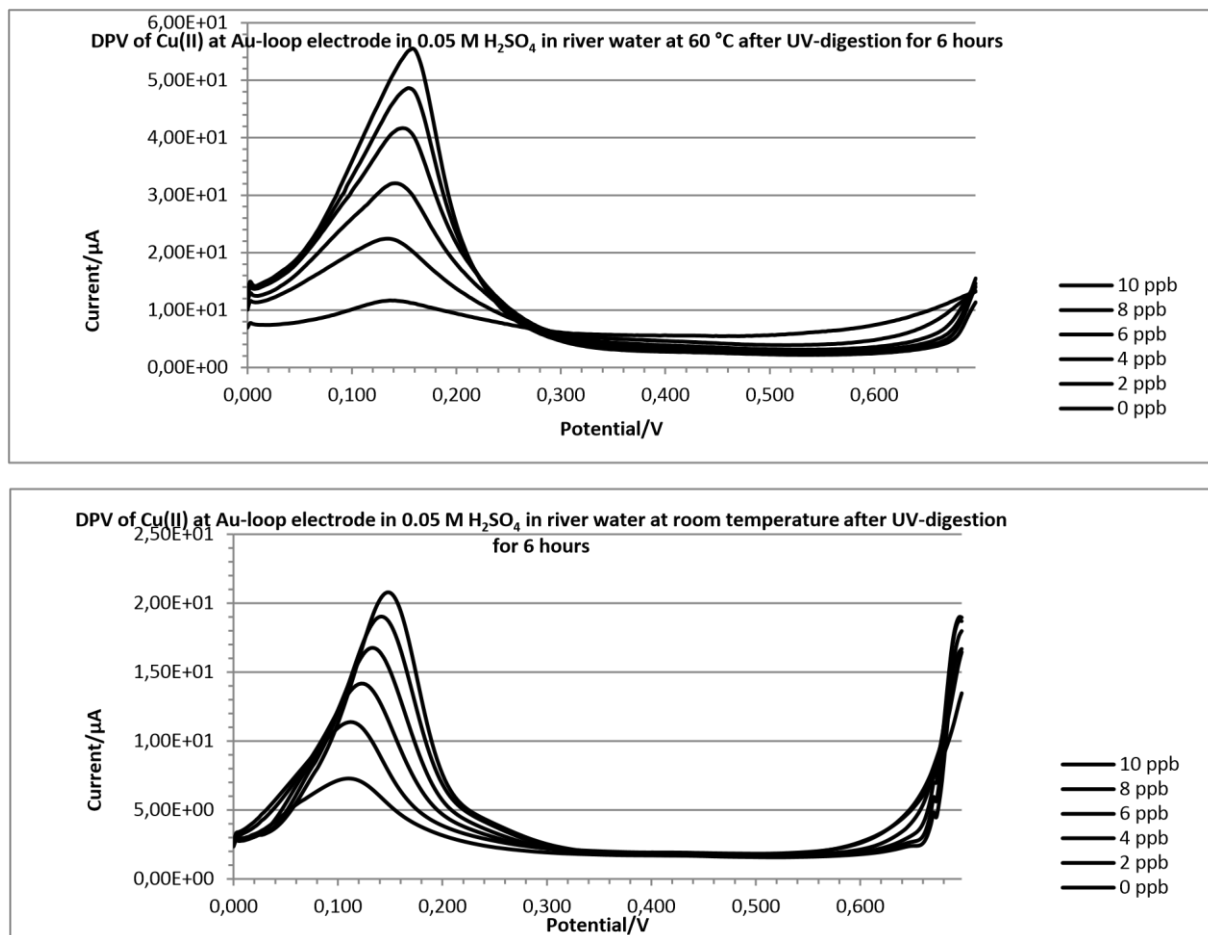


Figure (14): DPV of copper(II) at Au-loop electrode at 60 °C and at room temperature in 0.05 M H₂SO₄ in the river water UV-sample at deposition potential 0.15 V for 120 s deposition time.

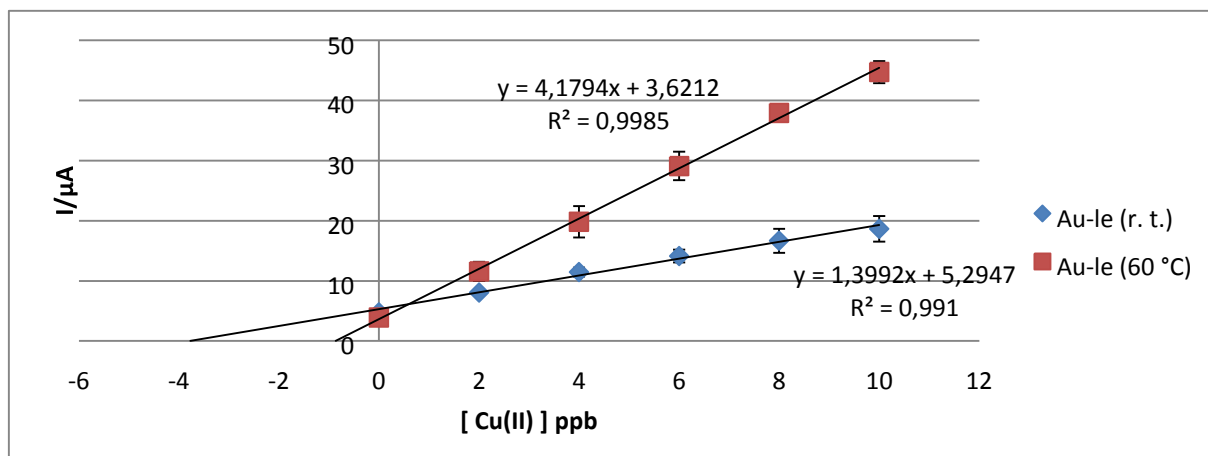


Figure (15): Calibration plots for DPV of copper(II) at the Au-loop electrode at 60 °C and at room temperature in 0.05 M H₂SO₄ in river water after UV-digestion for 6 hours represent current peak versus the copper concentration.

Figure (16), getting a higher analytical signals for Cu(II) in river water after UV-irradiation than those obtained before UV-irradiation, even though the determined concentration of Cu(II) stay the same can be explained by supposing that the UV-irradiation effect works to damage DOCs presented in the analyzed river water sample making a cupric ions move easier than before UV-irradiation and consequently teach to the working electrode surface more quickly.

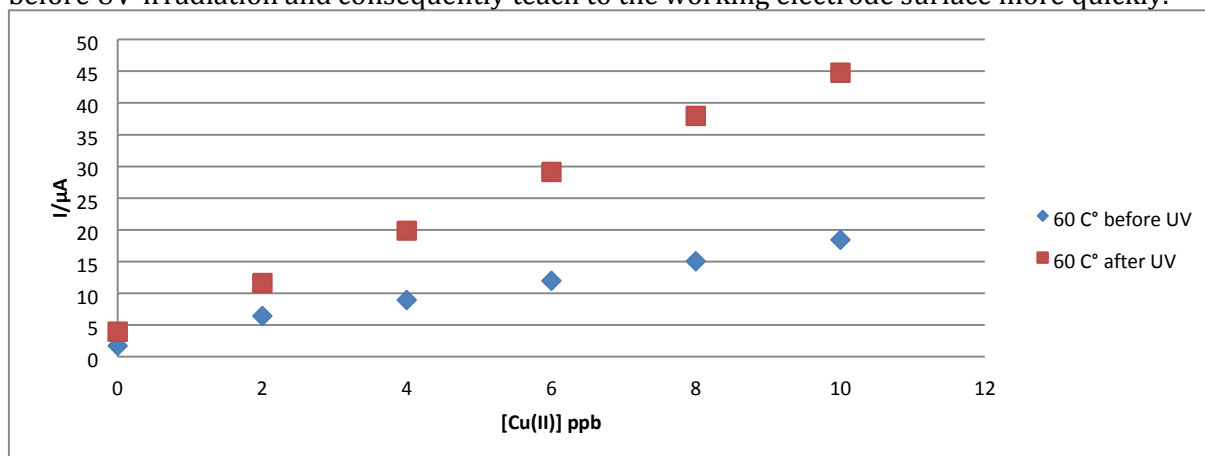


Figure (16): Calibration plot for DPV of copper(II) at Au-loop electrode at 60 °C in 0.05 M H₂SO₄ in river water before UV-digestion and after UV-digestion represent current peak versus the concentration of copper.

Table (7): concentration of and recovery rate of Cu(II) at both working electrodes of Au-loop electrode (at both of temperatures 60 °C and 22 °C) and Au-RDE.

Sample	Working electrode	[Cu(II)] ppb	Recovery rate %	MRR* %
River water	60 °C	1.48	129.15	1255.70
	22 °C	3.51	429.31	3093.00

	Au-RDE	10.48	44.22	129.24
River water-UV sample	60 °C	0.87	95.72	3272.80
	22 °C	3.78	134.14	9583.80

As result, the cupric ions can be underpotentially deposited on bare heated Au-loop electrode and detected by subsequent stripping. The concentration of copper-UPD was successfully determined in tap and river water samples on Au-loop electrode at both temperature 60 °C and room temperature compared with Au-RDE. So heated Au-loop electrode has offered good analytical signals for stripping voltammetry of Cu-UPD in tap and river water samples and good ability to prevent the adsorption of fouling organic compounds on the electrode surface replaced classic UV-irradiation process compared with Au-RDE. As these results can be explained by supposing that heated Au-loop electrode works strongly to achieve high greatly self-cleaning effect due to offer well-defined, undistorted and high reproducible stripping signals of heavy metals such Cu(II). Additionally to the efficiency and good behavior of Au-loop electrode, the deposition process at a high temperature helps to temperature to accelerate diffusion rate by generating an efficient micro stirring effect due to the presence of a constant diffusion layer thickness.

4.2. Measurement of trace lead Pb(II)

Lead has been determined before by applying different methods. For example, cyclic voltammetry and cathodic stripping voltammetry of lead oxide on an electrically heated platinum wire electrode, which has been pronounced by Zerihun [19]. Lead has been detected at heated mercury-coated electrode using iridium and screen-printed carbon substrates by Jasinski et al. [22, 24]. Recent studies have illustrated that bismuth-coated electrodes provide significant advantages of stripping voltammetry analytical signals for detection of trace heavy metals [25]. As we will see below that the Au-loop electrode has been positively acted as a suitable substrate for formation of Bi(III)-film for the determination of Pb(II) in varies samples of water (ultra-pure water, tap water, and river water). Obtained results were compared to those obtained on Au-RDE. Our aim in this work is to conjoin the positive features of electrically heated Au-loop electrode together with bismuth-coated electrode for improvement and enhancement the

stripping voltammetry analytical signals response of trace heavy metals like Pb(II) in varies water samples. Elevated temperature on Bi(III)-film coated Au-loop electrode provides high sensitivity and linearity of stripping voltammetric analytical signals of Pb(II) replaced the traditional mechanical stirring effect.

4.2.1. Lead Pb(II) in ultra-pure water sample

Au-loop electrode has been successfully applied to square wave voltammetric detection of lead Pb(II) in the presence of Bi(III)-film at both temperatures 60 °C and room temperature with an estimated detection limit of 1.9 ppb and 6.25 ppb, respectively. The voltammograms figure (17) display stripping voltammetric analytical signals of Pb(II) on heated and unheated Au-loop electrode in comparison with those obtained on Au-RDE in pure 0.1 acetate buffer solution in the presence of 0.5 ppm Bi(III) for 120 sec. deposition time at -800 mV deposition potential. As depicted from the calibration plots figure (18) that the analytical signals on heated Au-loop electrode have the highest analytical signals compared with those obtained on unheated Au-loop electrode and on Au-RDE, where the stripping peak of 50 ppb Pb(II) was recorded to be higher in about 14-fold than that obtained on Au-RDE and in about 3-fold compared to unheated Au-loop electrode. In comparison with another study, where Pb(II) was determined on electrically heated carbon paste electrode in the presence of bismuth film. It has been reported that the stripping analytical signal of 50 ppb Pb(II) was enhanced in about 5-fold compared to that obtained under cold stirred conditions [25]. So with simple, fast and quantitative method a heated Bi(III)-coated Au-loop electrode provides remarkable improved and enhanced analytical signals response after increasing the lead concentration from 10 to 50 ppb in 10 ppb addition, where the calibration plot fig. (18) under hot unstirred conditions offers a meaningfully higher slope in comparison to unheated Bi(III)-coated Au-loop electrode and to Bi(III)-coated Au-RDE at unaffected signal-to-noise ratio. The determined concentration of Pb(II) was found to be 0.024 ppb at 60 °C, 1.80 ppb at room temperature and 2.56 ppb on Au-RDE.

As result, we can illustrate that Au-loop electrode has shown to be an appropriate substrate for creation of bismuth film for determination of Pb(II) in both cases of heated and unheated. Additionally, an appealing micro stirring consequence at directly heated bismuth-coated Au-loop electrode has provided us possibility to replace of outdated motorized stirring as preferred for distant sensors.

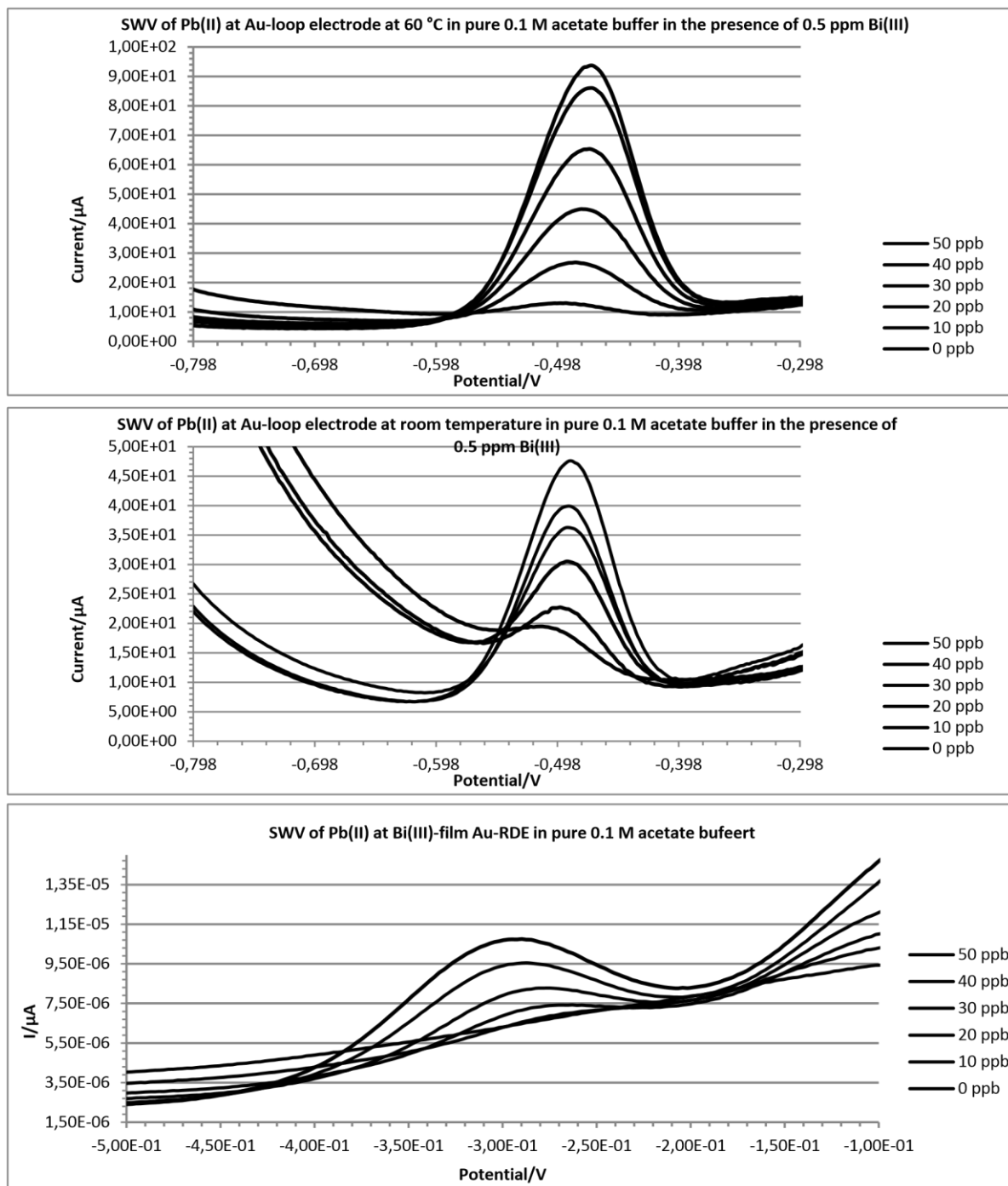


Figure (17): Square wave voltammetry signals of Pb(II) at Au-loop electrode at both temperatures of 60 °C and room temperature, and at Au-RDE (500 rpm) in 0.1 M acetate puffer containing 0.15 M KCl in the presence 0.5 ppm of Bi(III) film at deposition potential of -0.8 V for 120 s deposition time, another conditions as is described in tables (2 and 3).

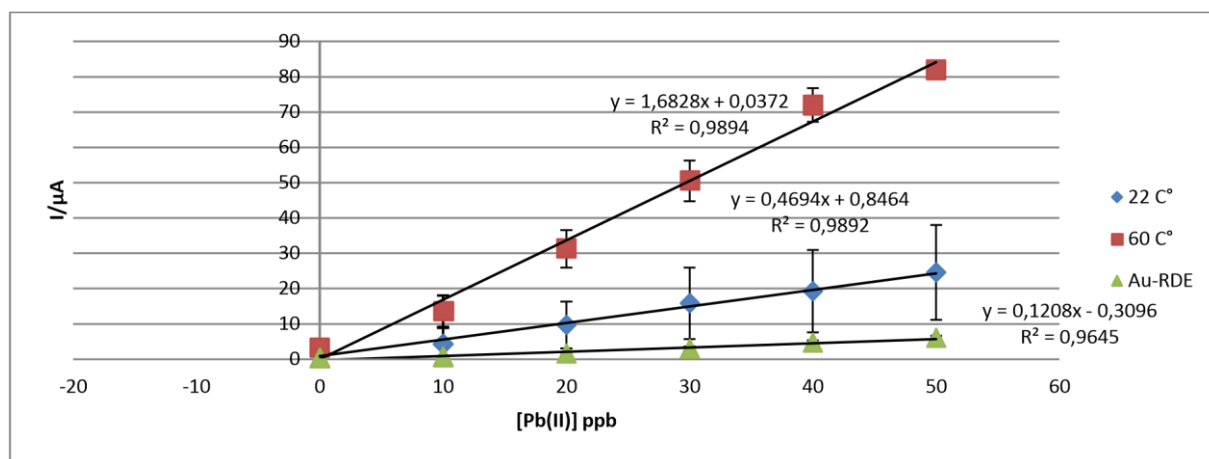


Figure (18): Calibration plots of deposition for trace lead $Pb(II)$ at Au-loop electrode at 60 °C, and at room temperature in the comparison with the Au-RDE with stirrer speed of 500 rpm in pure 0.1 M acetate buffer containing 0.15 M KCl in the presence of $Bi(III)$ -film 0.5 ppm at deposition potential -0.8 V for 120 s deposition time represent a current peak of $Pb(II)$ versus concentration of $Pb(II)$.

4.2.2. Lead $Pb(II)$ in tap water sample

It has been effectively determined the concentration of trace $Pb(II)$ on Au-loop electrode at both temperatures 60 °C and room temperature in an untreated tap water sample in the presence of $Bi(III)$ -film. Heated Au-loop electrode behave a linear response after increasing the lead concentration from 10 to 50 ppb in 10 ppb addition. Obtained stripping voltammetric analytical signals has been compared with those obtained on Au-RDE figure (19). As depicted from the calibration plots figure (20) the stripping analytical signal of 50 ppb added of $Pb(II)$ was recorded on heated Au-loop electrode to be higher in about 17-fold and 7fold compared to unheated Au-loop electrode and Au-RDE in, respectively, at unaffected signal to noise ratio. As depicted in the table (8), the found concentration of $Pb(II)$ was calculated by SAM to be 0.053 ppb on heated Au-loop electrode, 1.47 ppb on unheated Au-loop electrode and 2.03 ppb on Au-RDE with higher recovery rate obtained on heated bismuth Au-loop electrode of 70.08 %.

So a new, simple, fast and quantitative method has been innovated for determination of trace $Pb(II)$ on $Bi(III)$ -coated Au-loop electrode in the tap water sample investigated together with high sensitivity and linearity obtained on heated Au-loop electrode at unaffected signal-to noise ratio compared to those results obtained at ambient conditions and on Au-RDE.

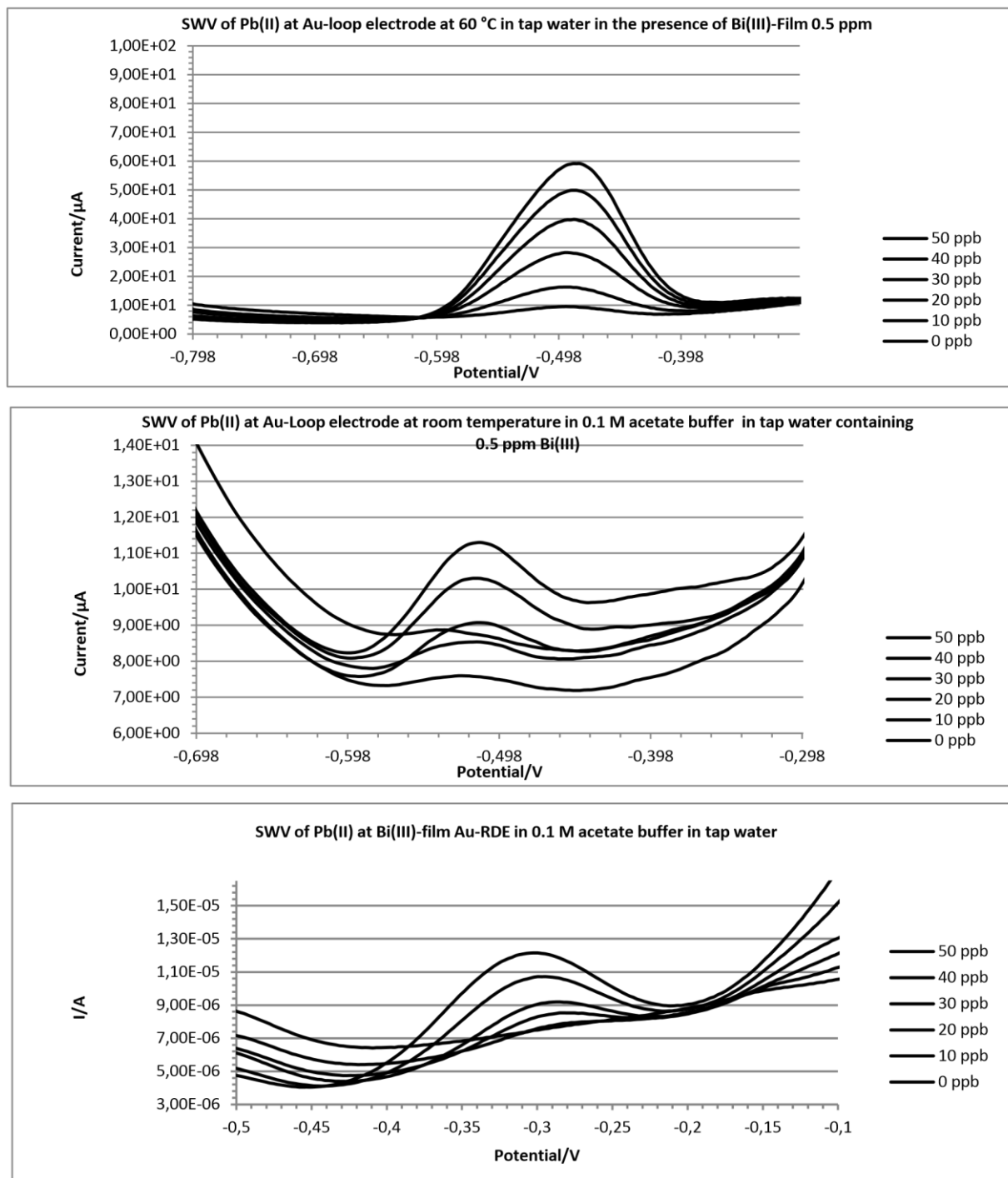


Figure (19): SWV signals of Pb(II) at both working electrodes of Au-loop electrode at both temperatures 60 °C and room temperature, and Au-RDE with rotating rate of 500 rpm in tap water containing 0.1 M acetate puffer with 0.15 M KCl in the presence of 0.5 ppm Bi(III)-film at deposition potential of -0.8 V for 120 s deposition time. Other conditions, as described in tables (1 and 2).

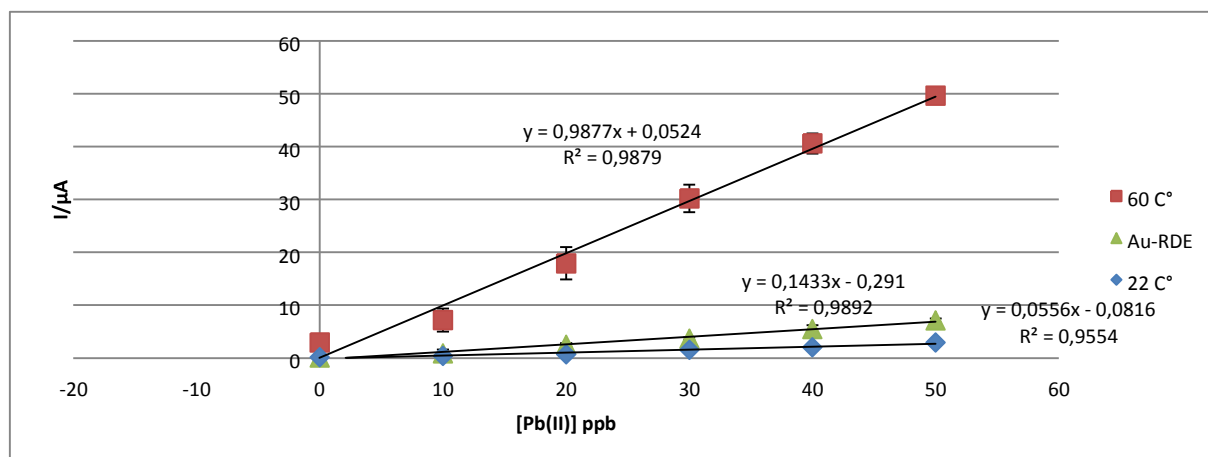


Figure (20): Calibration plots of the deposition Pb(II) at Au-loop electrode at 60 °C, and at room temperature in the comparison with Au-RDE (stirrer speed 500 rpm) in 0.1 M acetate buffer containing 0.15 M KCl in the presence of Bi(III)film 0.5 ppm in tap water at deposition potential -0.8 V for 120 s represent current peak of Pb(II) versus concentration of Pb(II).

Table (8): concentration of and recovery rate Pb(II) in tap water at both working electrodes of Au-loop electrode (at both of temperatures 60 °C and 22 °C) and Au-RDE.

Sample	Working electrode	[Pb(II)] ppb	Recovery rate %	MRR* %
Tap water	60 °C	0.053	70.08	58.69
	22 °C	1.47	26.40	11.85
	Au-RDE (500 rpm)	2.03	34.55	118.61

4.2.3. Lead Pb(II) in river water sample

It is known that a natural water samples like river water are including compounds like natural surfactants, which passivate the working electrode surface and constitute a challenge for analytical detection by using electrochemical methods. For example, humic acid as a natural surfactant was found to be adsorbed under acidic conditions onto bare gold electrodes, bismuth film, and mercury electrodes. It has been demonstrated that the voltammetric response of Pb(II) on bare Bi(III)-film electrodes was decreased when the humic acid concentration was increased. Obtaining like this adsorption onto the surface of the working electrode due to a more difficult stripping of a small amount of analyzed trace metal and reduces the active surface area of the

working electrode. So many studies have been worked to treat the analyzed natural water by applying UV-digestion, which designed to eliminate DOCs improved the quality of stripping voltammetry analytical signals of trace heavy metals. Other studies have been designed modified electrodes to prevent the electrode surface from the fouling activity. This experiment provide us possibility for determination a concentration of heavy metals like lead Pb(II) at Bi(III)-film coated Au-loop electrode at different temperature in river water under acidic conditions without the need to treat the analyzed water sample before and to the mechanical stirrer effect. The deposition at a high temperature can be useful for declining s the fouling effects on the electrode surface employed.

Voltammograms in figure (21) show the stripping analytical signals for trace lead in origin river water sample in the presence of 0.5 ppm Bi(III)-film on Au-loop electrode at both temperatures 60 °C and room temperature compared to the Au-RDE (rotating rate of 1500 rpm) in the concentration range of 10 to 50 ppb. It can be observed from the calibration plots figure (22) that the response of the analytical signal for 10 ppb Pb(II) is the same at both working electrodes of Au-loop electrode and Au-RDE. From 20 to 50 ppb Pb(II) the responded analytical signals become higher on heated Au-loop electrode, where the responded analytical signals of 50 ppb added of Pb(II) was recorded on heated Au-loop electrode to be higher in about 4-fold than that obtained on unheated and on Au-RDE. This result can be explained by supposing hat at the beginning of the measurement the presence of DOCs in origin river water sample make a challenge for stripping small concentrations added of Pb(II). So Heated Au-loop electrode works strongly to dissociate the metal ion complexed with DOCs. The equilibrium of the dissociation is as every equilibrium reaction depended on the temperature. It is known that with rising of the temperature the position of a complex equilibrium is shifted toward ions. For quantitative predication, the concentration of Pb(II) in origin river water sample was not calculated by means of SAM because of a non-linear response. The peak potential of Pb(II) on heated and unheated Au-loop electrode remained at the same as resulted in pure water, whereas the peak potential of Pb(II) on Au-RDE has been shifted to more positive potential by ca. +50 mV. On the other hand, the current peak for 50 ppb of lead on Au-RDE in origin river water was recorded to be (10.79 μ A) higher than that obtained in ultra-pure water (6.05 μ A), whereas the current peak for the unstirred 50 ppb lead solution on heated Au-loop electrode was found to be lower (41.86 μ A) in origin river water sample compared to that was found in ultra-pure water (82.04 μ A). So that means, the selectivity and sensitivity of Bi(III)-coated Au-loop electrode at both temperature 60 °C and room temperature for the determination of trace lead Pb(II) in origin river water is too much better than on Bi(III)-coated Au-RDE and that the Au-RDE is affected in the presence of complicated organic compounds, which can be deposited on the electrode

surface caused an increased analytical signals and shifting for the peak potential, which leads to the incorrect analysis results. Moreover, such a new novel heated electrode offers protection of the electrode surface from the fouling effects of DOCs on the electrode surface by means of elevated temperature and its self-cleaning effect. In another study, Pb(II) has been determined at a HMDE in river water sample (Warnow river, Germany, Rostock) by G. U. Flechsig and G. woldmichael, it has been reported that HMDE was affected in the presence of DOCs depending on the determined concentration before and after UV-irradiation, where the determined concentration of Pb(II) was increased after UV-irradiation (6 hours).

As conclusion and based on the prior mentioned analysis results, it has been successfully proved that it is possible to determine a concentration of trace lead Pb(II) on Bi(III)-coated Au-loop electrode at both temperatures 60 °C and room temperature (22 °C) in various samples of water, where Au-loop electrode has been acted an appropriate substrate for creation of Bi(III)-film electrode. Obtained results were compared to those obtained on Bi(III) coated Au-RDE. Bismuth-coated Au-loop electrodes behave an attractive stripping voltammetry manner, where well defined and undistorted stripping voltammetry analytical signals were obtained for Pb(II) on heated Bi(III)-coated Au-loop electrode at unaffected signal-to-noise ratio. A low detection limit of 1.90 ppb Pb(II) was observed together with a linear calibration plot over to 50 ppb Pb(II). So an attractive micro stirring effect generated on a directly heated Bi(III)-film coated Au-loop electrode as a result of the thermal convection around the electrode surface due to replace a mechanical stirring effect. Moreover, possibility for determination of trace lead Pb(II) on heated Bi(III)-coated Au-loop electrode progresses the possibility for determination some heavy metals such as cadmium and zinc on heated Bi(III)-coated Au-loop electrode in various samples of water.

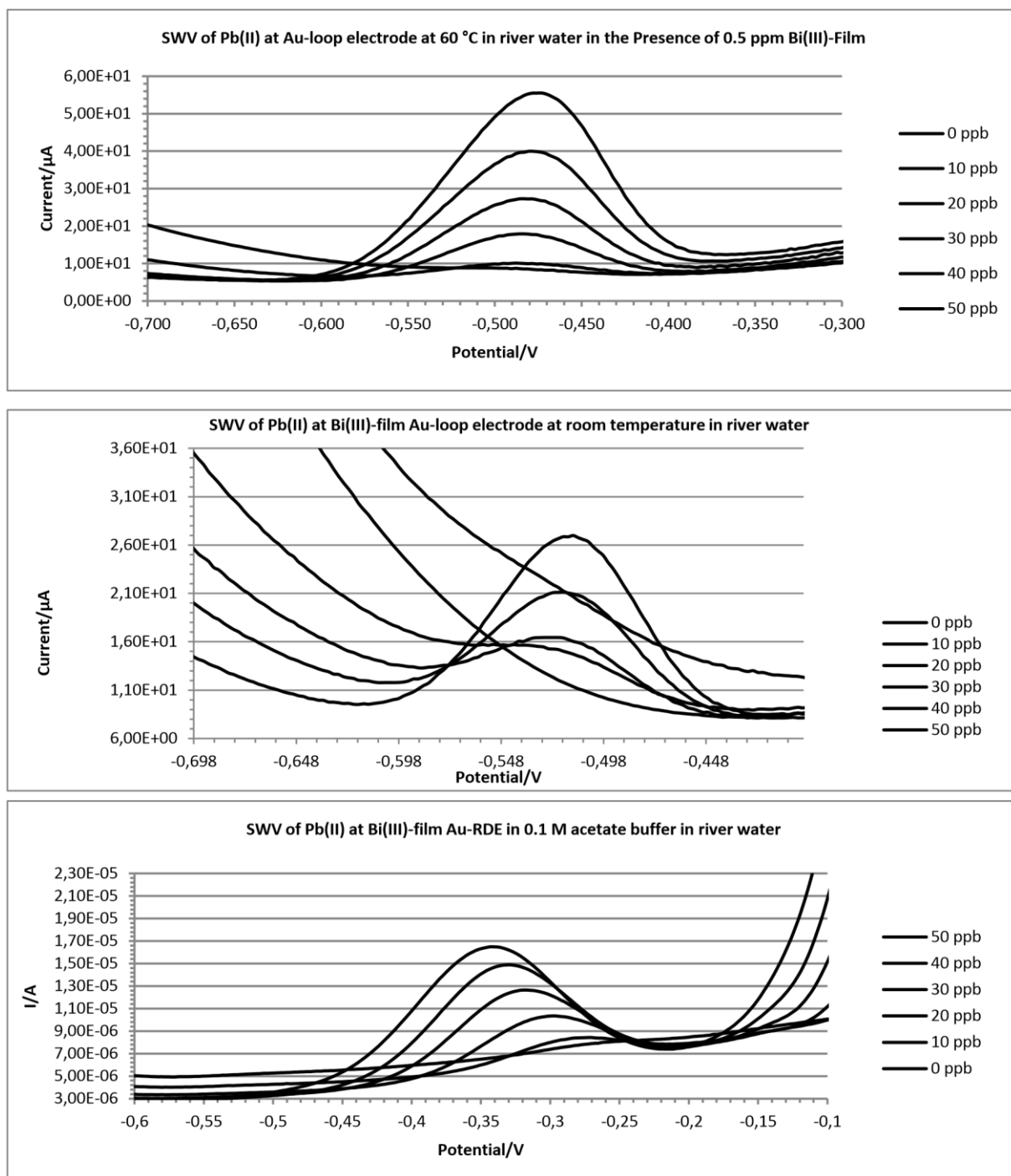


Figure (21): SWV signals of Pb(II) at both working electrodes of Au-loop electrode at both temperatures of 60 °C and room temperature, and Au-RDE (rotating rate of 1500 rpm) in 0.1 M acetate buffer containing 0.15 M KCl in the presence of 0.5 ppm Bi(III)-film in river water at deposition potential of -0.8 V for 120 s deposition time, another conditions as described in tables (1 and 2).

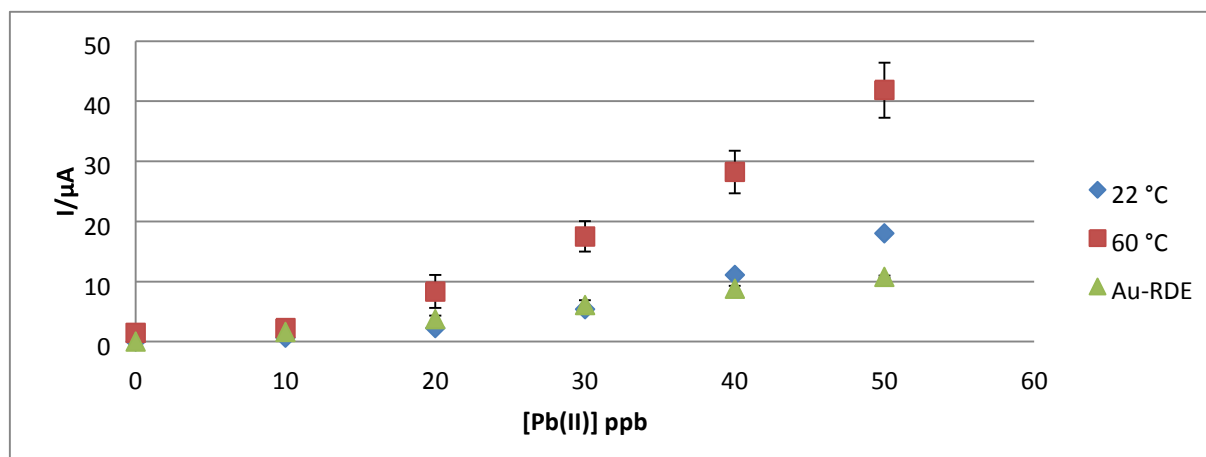


Figure (22): Calibration plots of the deposition of Pb(II) at the Au-loop electrode at 60 °C (red), and at room temperature (blue) in the comparison with Au-RDE (green) with stirrer speed 1500 rpm in 0.1 M acetate buffer containing 0.15 M KCl in the presence of Bi (III)-film 0.5 ppm in the river water at deposition potential -0.8 V for 120 s represent current peak of Pb (II) versus concentration of Pb (II).

4.3. Measurement of trace mercury Hg(II)

Several analytical methods have been developed for the determination of highly toxic mercury trace. The determination has been performed commonly by applying either cold vapor fluorescence or ICP-MS. Cold vapor fluorescence technique was developed by Thompson and Godden [181] in 1975, and further refined by others including Godden and Stockwell [182]. But this technique has disadvantage that the studied sample of mercury has to be separately prepared and analyzed, away from the other metals determination which is usually performed by ICP technique. On the other hand, several challenges represent by applying ICP-MS technique, among them loss of mercury onto the materials of the sample delivery system of the ICP-MS instrument. There is also possibility to keep the loss of mercury onto these materials gradually over time due to contamination of subsequent samples and poor calibration. It has been found that this technique was not satisfied and that some of stabilizing preserving agent would be used to make this method of analysis successful [183]. Trace of mercury has been determined on Au-RDE [184] or flow-through gold electrode [185]. In 1999 the mechanical forced-convection transport has been replaced with thermal convection for determination of trace mercury by using hot gold wire electrode (two wires 25 μm diameter, 1 cm long) [21]. In the following experiments we will illustrate the features obtained from the combining of heated Au-loop electrode with stripping voltammetry of mercury Hg(II).

Significantly improved stripping voltammetry analytical signals have been obtained for trace Hg(II) on heated Au-loop electrode at 60 °C and in a quiescent solution. The response was from 2 to 10 ppb tested for 2 minutes deposition time.

4.3.1. Mercury Hg(II) in the ultra-pure water

Figure (23) displays voltammograms that were resulted from the measure of trace mercury on Au-loop electrode at both temperatures 60 °C and room temperature in a quiescent solution in the range of concentrations (2 ppb-10 ppb) at deposition potential of 0.2 V for 120 s deposition time. The analytical signal response of 10 ppb mercury on heated the Au-loop electrode was enhanced in about 10-fold upon deposition at room temperature with a projected detection limit of 2.64 ppb mercury at 60 °C and 3.36 ppb at room temperature. Figure (24) displays voltammograms of increased concentrations of Hg(II) in the range of (2 ppb-10 ppb) on Au-RDE (3000 rpm) at deposition potential of 0.37 V for 180 s deposition time. Figure (25) shows the calibration plots of mercury (2 ppb-10 ppb) under hot and cold unstirred conditions compared to the Au-RDE, which demonstrate that the high of the analytical signals obtained on heated Au-loop electrode are similar to those obtained on Au-RDE for. In another study, trace mercury has been determined with stripping potentiometry at a hot-wire electrode at 60 °C. It has been reported that the responded analytical signals on a hot-wire electrode were similar to that obtained for 600 rpm stirred solution at room temperature [21].

Significantly, it is essential to mention that Au-RDE has been conditioned by recording a series of ten successive voltammograms of a 0.12 M perchloric acid (HClO_4) under differential pulse voltammetry (DPV) method at deposition potential of 1.5 V for 30 s deposition time (another conditions in table 4) to obtain reproducible curve progressions, whereas the voltammograms for trace mercury on Au-loop electrode at both temperatures 60 °C and room temperature are recorded directly without doing any conditioning for the electrode surface before. So we can say that the sensitivity of Au-loop electrode is more sufficient for the analysis of low concentration ppb mercury solutions than Au-RDE.

Improved and enhanced stripping voltammetry of trace mercury were obtained on heated Au-loop electrode together with improved signal-to-noise ratio compared to those obtained on Au- RDE. As it seems from table (9), the concentration of trace mercury was found to be 0.52 ppb, 0.66 ppb, and 0.27 ppb on heated and unheated Au-loop electrode on Au-RDE in ultra-pure water respectively.

As a result indicate that using of heated Au-loop electrode for determination of trace Hg(II) due to avoid the need for a mechanical forced convective transport mode, decrease the effect of changes in the typical convection, and improve the sensitivity without disturbing the noise level.

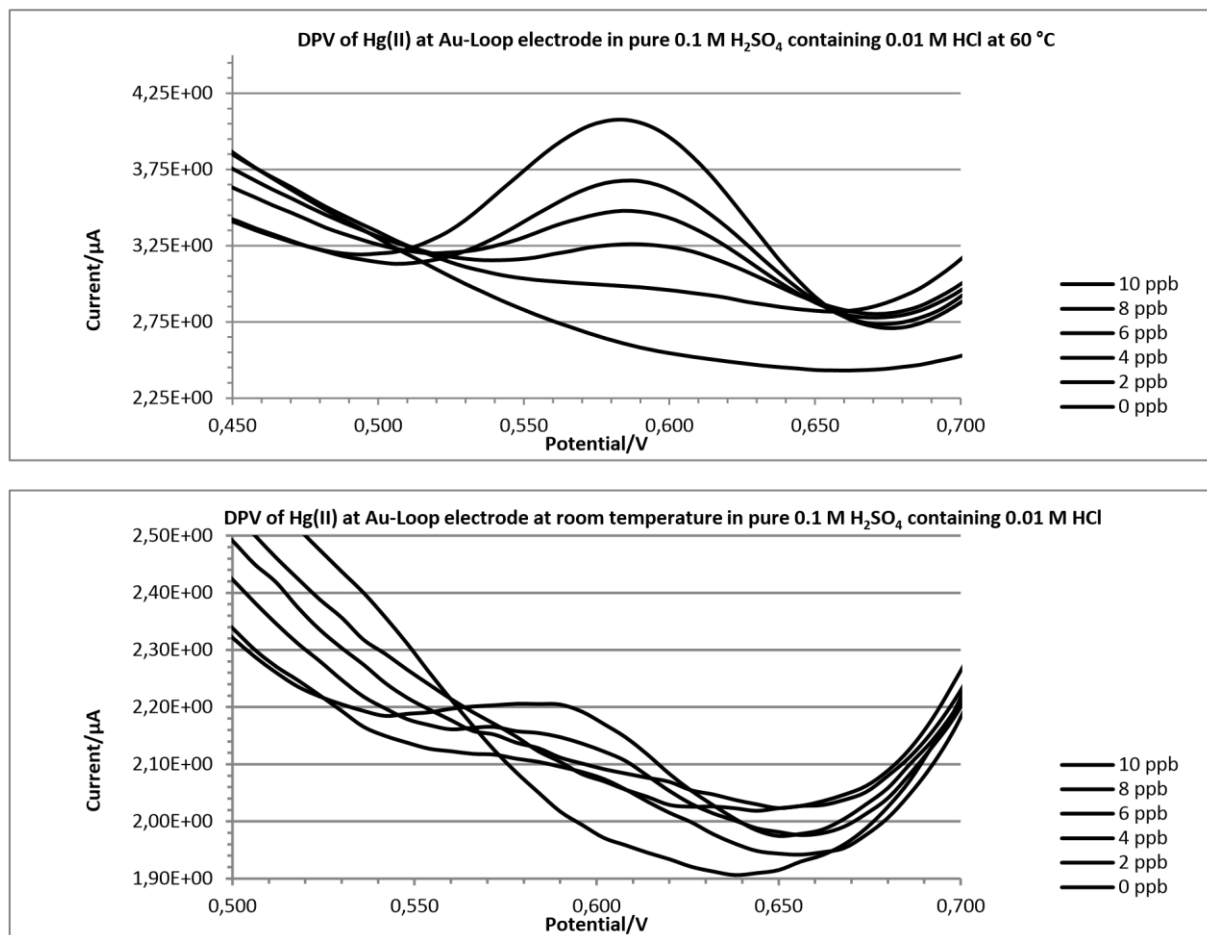


Figure (23): DPV of Hg(II) at Au-loop electrode at 60 °C and at room temperature in 0.1 M H₂SO₄ containing 0.01 M HCl. Deposition potential = 0.2 V, deposition time = 120 s, conditioning potential = 0.7 V, conditioning time = 60 s, initial potential = 0.2 V, end potential = 0.7 V, scan rate = 0.06 V/s, potential step = 0.006 V, potential pulse = 0.05 V, time pulse = 0.04 s and equilibrating time = 5 s.

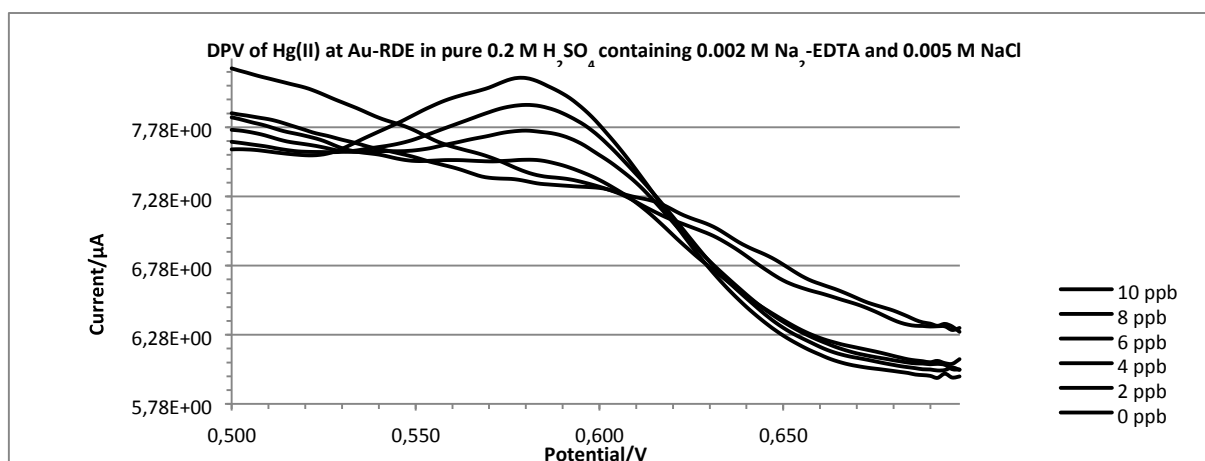


Figure (24): DPV of Hg(II) at Au-RDE in pure 0.2 M H₂SO₄ containing 0.002 M EDTA-Na₂ and 0.005 M NaCl. Deposition potential = 0.37 V, deposition time = 180 s, conditioning potential = 0.7 V, conditioning time = 10 s, initial potential = 0.4 V, end potential = 0.7 V, scan rate = 0.02 V/s, potential step = 0.002 V, potential pulse = 0.05 V, time pulse = 0.04 s and equilibrating time = 5 s and the rate of Rotating (ω) = 3000 rpm.

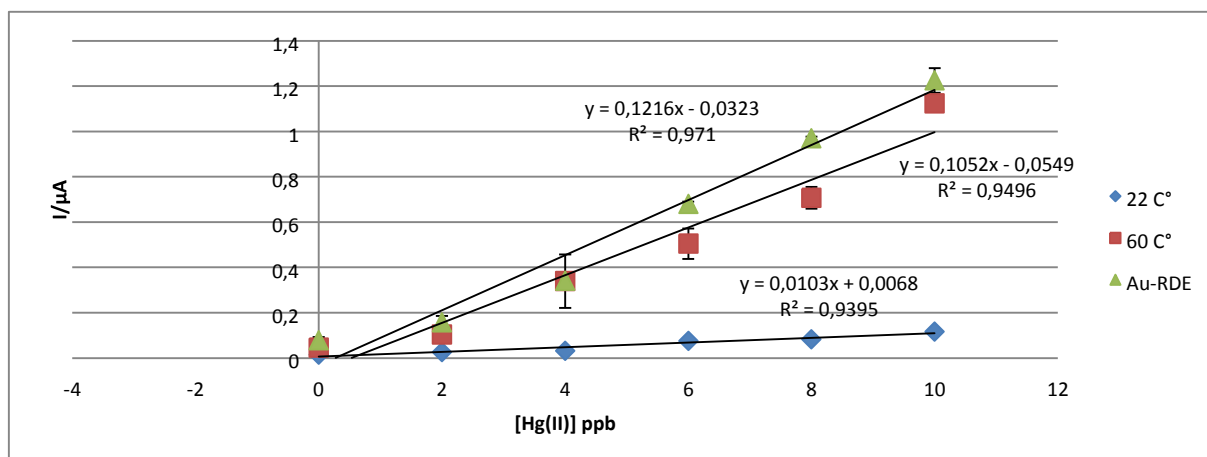


Figure (25): Calibration plots of the deposition Hg(II) at the Au-RDE in 0.2 M H₂SO₄ in the presence of 0.002 M EDTANa₂ and 0.005 M NaCl at 0.37 V for 180 s with stirrer speed 3000 rpm (green) in the comparison with the Au-loop electrode at both temperatures of 60 °C (red) and 22 °C (blue) in 0.1 M H₂SO₄ containing 0.01 M HCl at 0.2 V for 120 s represent current peak of the mercury versus the concentration of mercury.

Figure (26) illustrates the effect of Au-loop electrode temperature (during condition and deposition steps) upon the voltammetric response of 10 ppb mercury Hg(II). The analytical signal of 10 ppb mercury rises fast upon raising the temperature when going from room temperature (22 °C) to 60 °C, and falls quickly above 60 °C. The effect of the deposition time was tested at the unheated Au-loop electrode (room temperature) for 10 ppb mercury solution.

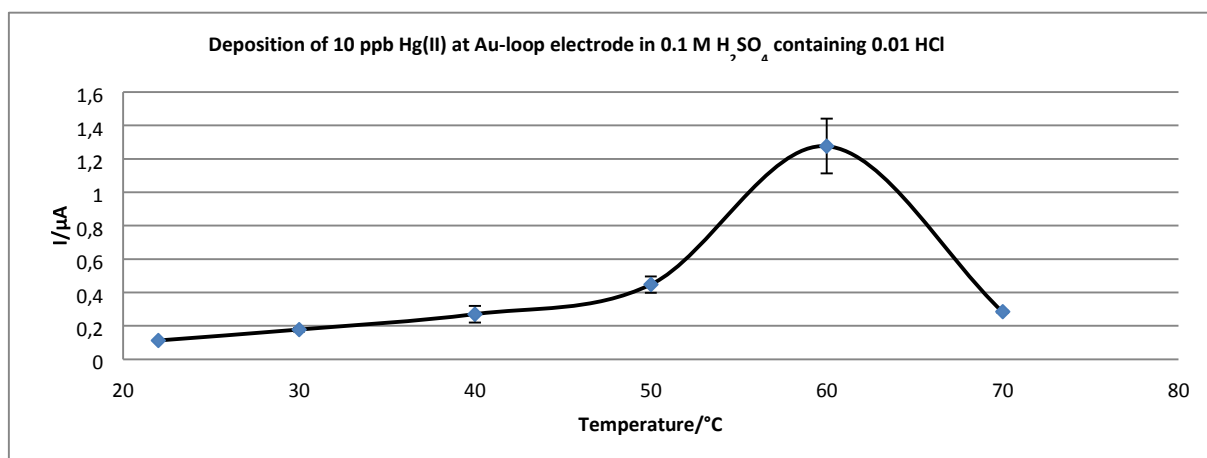


Figure (26): Calibration plot of the deposition 10 ppb Hg(II) at the Au-loop at different temperature in 0.1 M H₂SO₄ in the presence of 0.01 M HCl represent current peak of the mercury versus the temperature.

As it can be observed figure (27), the response was increased upon raising the time deposition between 2 and 6 minutes, and decreased slightly above 6 minute.

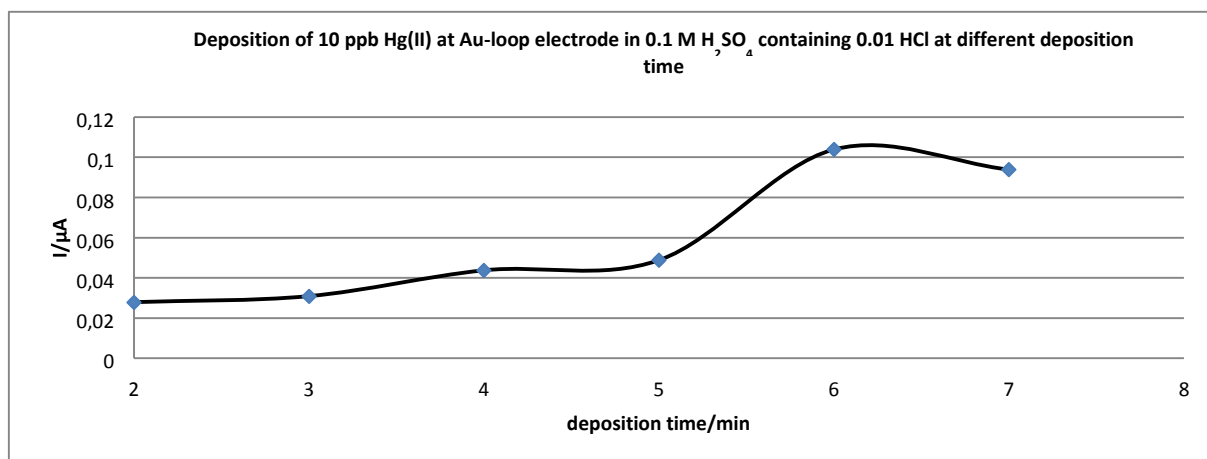


Figure (27): Calibration plot of the differential pulse voltammetry of 10 ppb Hg(II) at the Au-loop at room temperature in 0.1 M H₂SO₄ containing 0.01 M HCl represent current peak of the mercury versus the time of the deposition.

4.3.2. Mercury Hg(II) in tap water sample

Figure (28) shows the analytical signals that have been recorded for trace Hg(II) of quiescent solutions in tap water sample on Au-loop electrode at both temperatures 60 °C and room temperature by DPV measurements. The responded analytical signals are similar to those obtained by analyzing of ultra-pure water. The response was greatly enhanced on heated Au-loop electrode (60 °C) compared with unheated Au-loop electrode (room temperature), where the analytical signal started to be observed after spiking 4 ppb of mercury. The analytical signal for 10 ppb trace Hg(II) on heated Au-loop electrode was found to be higher than that recorded on unheated Au-loop electrode (room temperature) in about 7-fold together with improved and enhanced signal-to-noise-ratio, as it seems from figure (30).

On the other hand, the high of the resulted analytical signals on heated Au-loop electrode for quiescent solutions of the Hg(II) with 2 min. deposition time are a bit lower than those obtained on Au-RDE for a 3000 rpm stirred solutions with 3 min. deposition time. On the other hand, the recorded analytical signals of Hg(II) on Au-RDE are larger than those responded by analyzing of ultra-pure water even though the determined concentration of Hg(II) was lower in tap water, indicating that the deposition and stripping of mercury under hot unstirred conditions are more easily than under cold stirred conditions. So a hot deposition on Au-loop electrode due to highly reproducible stripping analytical signals of the metal ion studied.

So it has been successfully determined quiescent solutions of trace Hg(II) from 2 to 10 ppb in an untreated tap water sample on heated Au-loop electrode. Significantly, it was observed an

improved sensitivity deprived of disturbing the noise level and replace the need to the mechanical stirring effect.

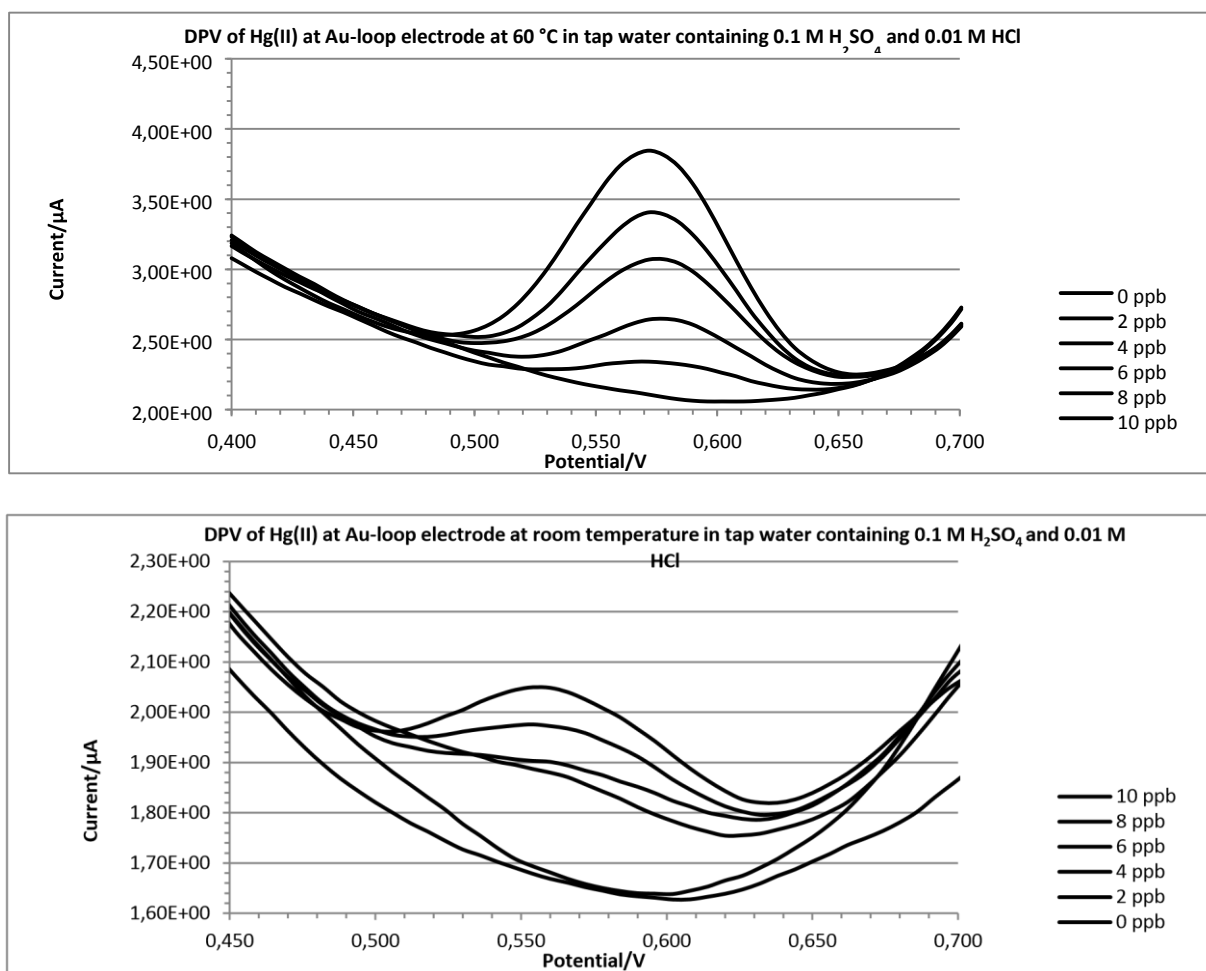


Figure (28): DPV of Hg(II) at Au-loop electrode at 60 °C and at room temperature in 0.1 M H₂SO₄ containing 0.01 M HCl in the tap water. Deposition potential = 0.2 V, deposition time = 120 s, conditioning potential = 0.7 V, conditioning time = 60 s, initial potential = 0.2 V, end potential = 0.7 V, scan rate = 0.06 V/s, potential step = 0.006 V, potential pulse = 0.05 V, time pulse = 0.04 s and equilibrating time = 5 s.

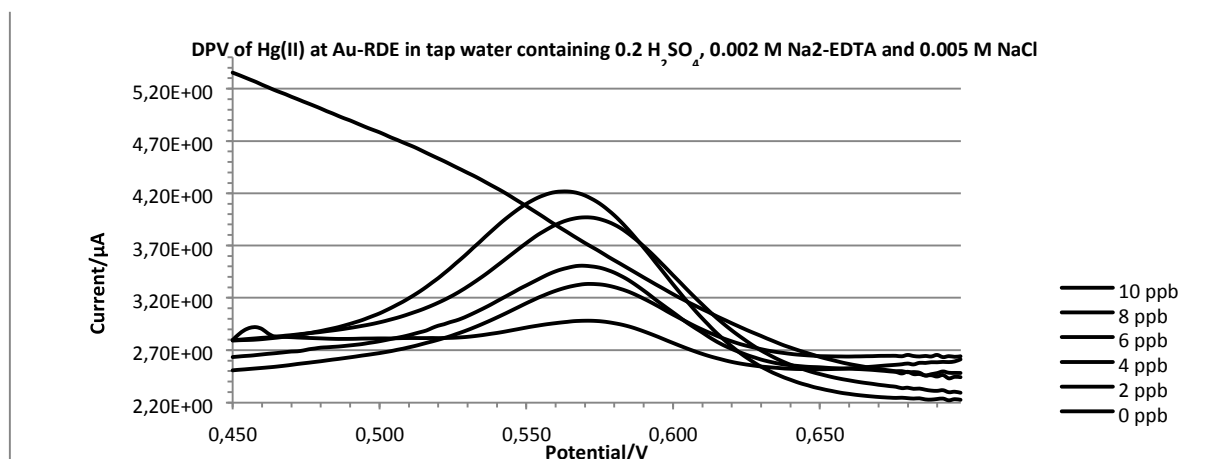


Figure (29): DPV of Hg(II) at the Au-RDE in 0.2 M H_2SO_4 containing 0.002 M $EDTA-Na_2$ and 0.005 M $NaCl$ in the tap water. Deposition potential = 0.37 V, deposition time = 180 s, conditioning potential = 0.7 V, conditioning time = 10 s, initial potential = 0.4 V, end potential = 0.7 V, scan rate = 0.02 V/s, potential step = 0.002 V, potential pulse = 0.05 V, time pulse = 0.04 s and equilibrating time = 5 s and the rate of Rotating (ω) = 3000 rpm.

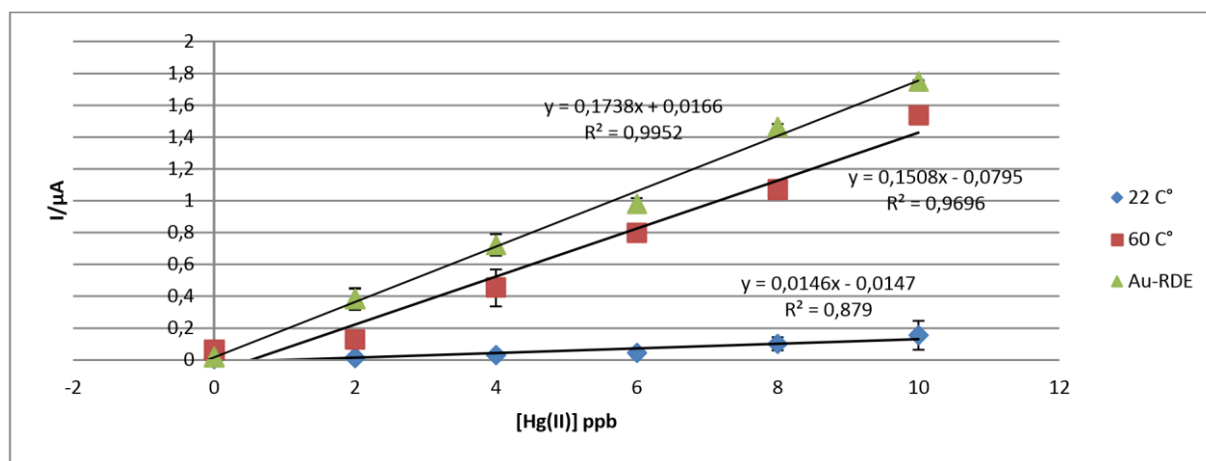


Figure (30): Calibration plots of the deposition Hg(II) at the Au-RDE in 0.2 M H_2SO_4 in the presence of 0.002 M $EDTA-Na_2$ and 0.005 M $NaCl$ in the tap water at 0.37 V for 180 s with stirrer speed 3000 rpm (green) in the comparison with the Au-loop electrode at both temperatures 60 °C (red) and 22 °C (blue) in 0.1 M H_2SO_4 containing 0.01 M HCl at 0.2 V for 120 s represent current peak of the mercury versus the concentration.

4.3.3. Mercury Hg(II) in river water sample

The major types of interferences in stripping analysis are overlapping peaks, which produced by similarity in the oxidation potentials of the metals, the presence of organic surface active compounds that adsorb on the electrode surface due to hinder the metal deposition and create of intermetallic compounds. The most important organic ligands in natural waters are humic substances washed out from soils, which are strongly able to bind with trace metal cations. So the Mineral surfaces are often coated by humic substances to a large content in natural waters

make direct determinations for heavy metals rather difficult or impossible. Our current research is to develop methods that would make it easy and possible.

A Au-loop electrode was suitable effectively to determine the concentration of mercury in origin river water sample in the range of concentrations from 2 to 10 ppb resulted in good distinct voltammetric stripping peaks following 2 minutes deposition time at 60 °C. The voltammograms obtained by using Au-loop electrode are displayed in figure (31) at both temperature 60 °C and room temperature. Calibration plots are displayed in figure (33), at both temperatures of 60 °C and room temperature compared to the Au-RDE. Accordance to these measurements the concentration of mercury was found to be 0.56 ppb and 0.66 ppb on Au-loop electrode at 60 °C and room temperature (22 °C) respectively and 0.64 ppb on Au-RDE. In contrast to our study in ultra-pure water, the analytical signals that were recorded on Au-RDE look to be higher than those recorded on Au-loop electrode at both temperature 60 °C and room temperature. That means the Au-RDE was affected in the presence of complicated organic compounds in origin river water due to increase the analytical signals, which due to incorrect analysis results. On the other hand, the responded analytical signals on heated Au-loop electrode were found to have the same form to those obtained by analyzing of ultra-pure water. So Heated Au-loop electrode was unaffected by the presence of DOCs in origin river water offered a great high sensitivity and selectivity caused by elevated temperature which due to achieve an efficient parallel self-cleaning without any manual intervention, which in its turn works to eliminate bio-fouling deposits on the electrode surface.

Based on the obtained analysis results, it has been successfully determined quiescent solutions of environmental samples for trace mercury on heated Au-loop electrode. In comparison with earlier study, mercury has been analyzed at hot-gold wire electrode under potentiometry method by J. Wang [21], but no mercury signals were observed in the origin sample of river water.

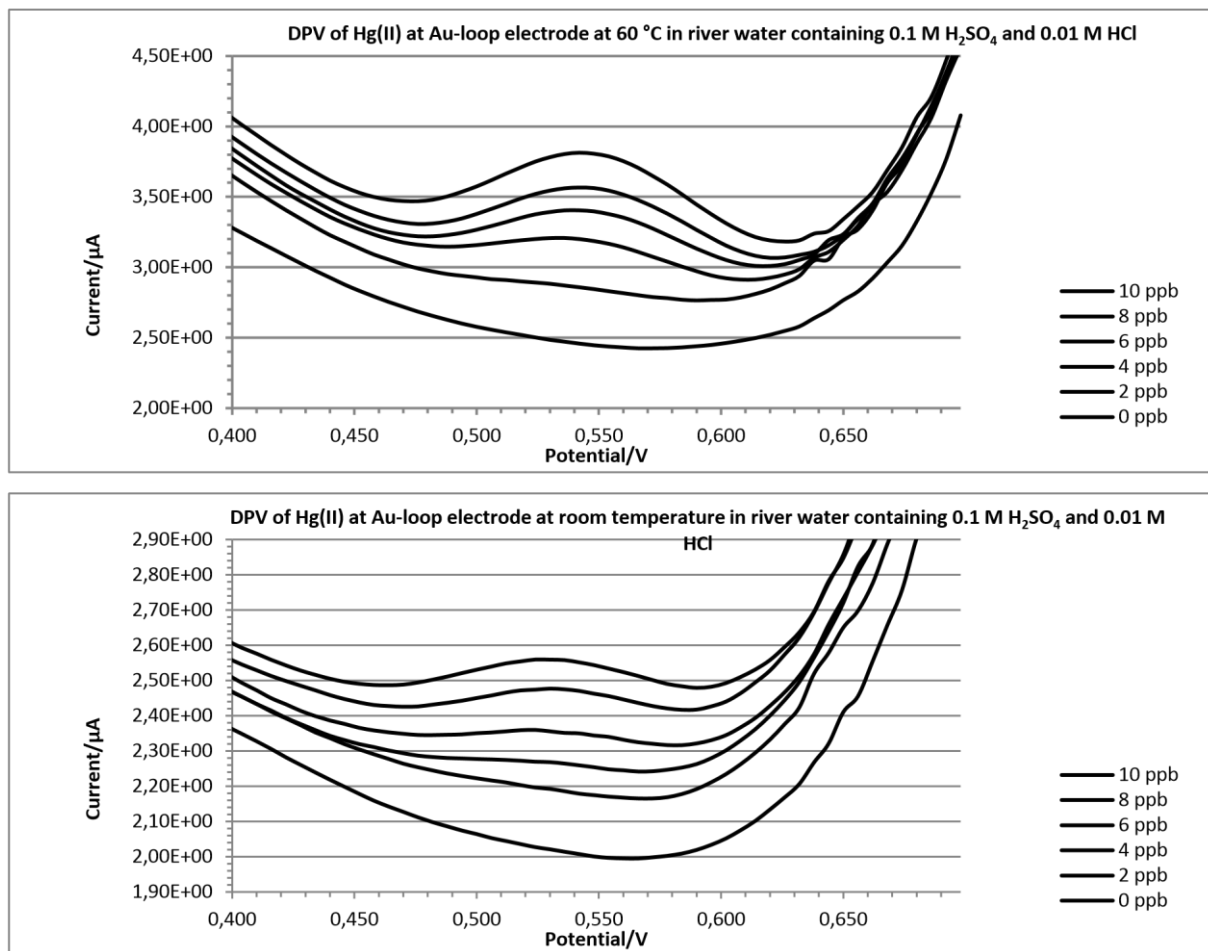


Figure (31): DPV of Hg(II) at Au-loop electrode at 60 °C and at room temperature in 0.1 M H₂SO₄ containing 0.01 M HCl in river water. Deposition potential = 0.2 V, deposition time = 120 s, conditioning potential = 0.7 V, conditioning time = 60 s, initial potential = 0.2 V, end potential = 0.7 V, scan rate = 0.06 V/s, potential step = 0.006 V, potential pulse = 0.05 V, time pulse = 0.04 s, and equilibrating time = 5 s.

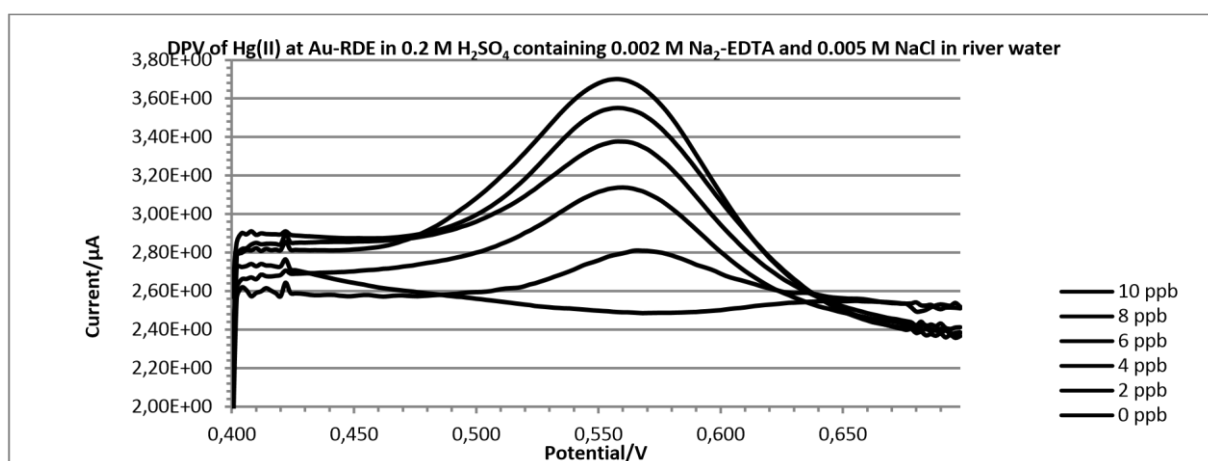


Figure (32): DPV of Hg(II) at Au-RDE in 0.2 M H₂SO₄ containing 0.002 M EDTA-Na₂ and 0.005 M NaCl in river water. Deposition potential = 0.37 V, deposition time = 180 s, conditioning potential = 0.7 V, conditioning time = 10 s, initial potential = 0.4 V, end potential = 0.7 V, scan rate = 0.02 V/s, potential step = 0.002 V, potential pulse = 0.05 V, time pulse = 0.04 s, equilibrating time = 5 s, and the rate of Rotating (ω) = 3000 rpm.

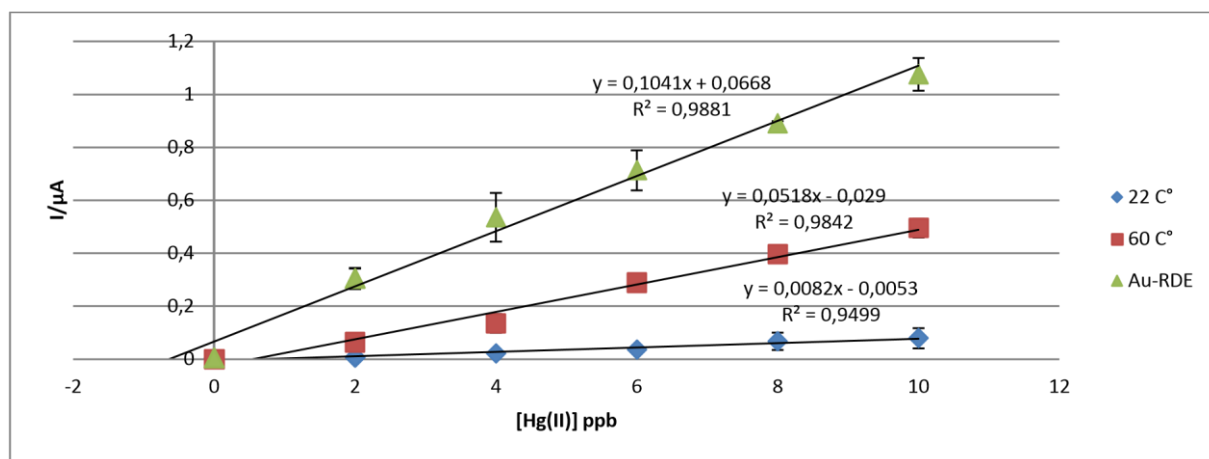


Figure (33): Calibration plots of the deposition pulse voltammetry for trace mercury Hg(II) at Au-RDE in 0.2 M H₂SO₄ containing 0.002 M EDTA-Na₂ and 0.005 M NaCl in river water at 0.37 V for 180 s with stirrer speed 3000 rpm in the comparison with Au-loop electrode at both temperatures of 60 °C and 22 °C in 0.1 M H₂SO₄ containing 0.01 M HCl at 0.2 V for 120 s represent current peak versus the concentration of mercury.

4.3.4. Mercury Hg(II) in river water UV-sample

Generally, the main goal of treatment of the river water-origin sample with UV-light in the presence of an oxidant reagent is to get an enhanced significant analytical signals of the trace metal studied in the river water sample investigated by eliminating the natural surfactants presented in this water sample. UV-light helps to damage the complicated organic compounds existed in a natural water. Consequently, more metal ions will be available for the reduction during the deposition step. In our experiment, origin river water sample has been exposed to the UV-light for 6 hours in the presence of hydrogen peroxide H₂O₂ to determine of trace mercury Hg(II). The obtained results on heated Au-loop electrode after UV-irradiation fig. (37) are compared with those obtained on heated Au-loop electrode before UV-irradiation fig. (31).

Figure (34) and (35) display the voltammograms for trace Hg(II) in river water UV-sample on both working electrodes of Au-loop electrode and Au-RDE. The calibration plots are displayed in figure (36). As it seems and in contrast with the resulted analytical signals in origin river water sample, the high of the resulted analytical signals on heated Au-loop electrode are approximately similar to those resulted on Au-RDE for a 3000 rpm stirred solution with 3 min. deposition time. This result can prove again that Au-RDE was affected by presence of DOCs in origin river water sample. Anyway, an improved and enhanced stripping analytical signals obtained on heated Au-loop electrode replace the need to a mechanical stirrer effect.

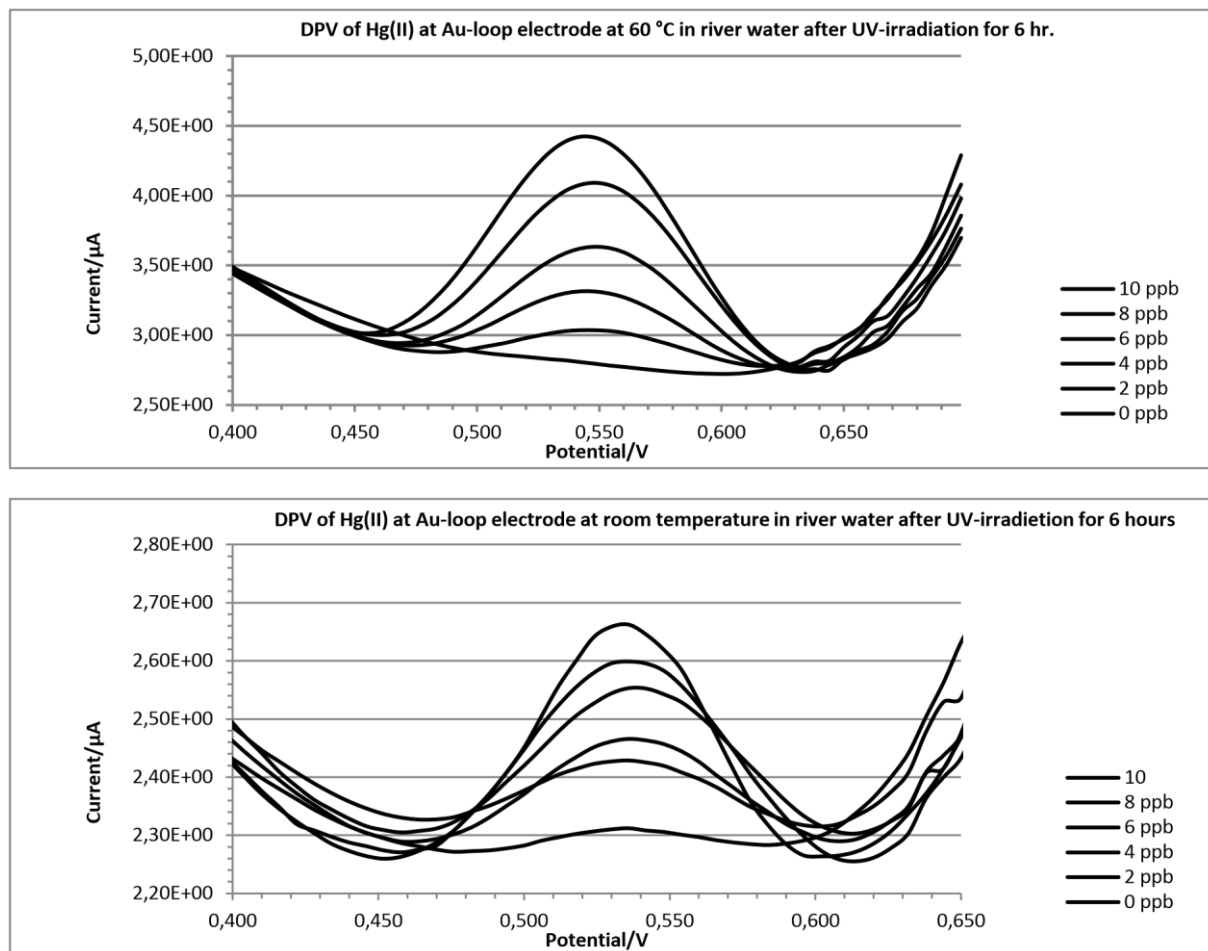


Figure (34): DPV of mercury Hg(II) at Au-loop electrode at 60 °C and at room temperature in 0.1 M H₂SO₄ containing 0.01 M HCl in river water after UV-irradiation for 6 hours. Deposition potential = 0.2 V, deposition time = 120 s, conditioning potential = 0.7 V, conditioning time = 60 s, initial potential = 0.2 V, end potential = 0.7 V, scan rate = 0.06 V/s, potential step = 0.006 V, potential pulse = 0.05 V, time pulse = 0.04 s, and equilibrating time = 5 s.

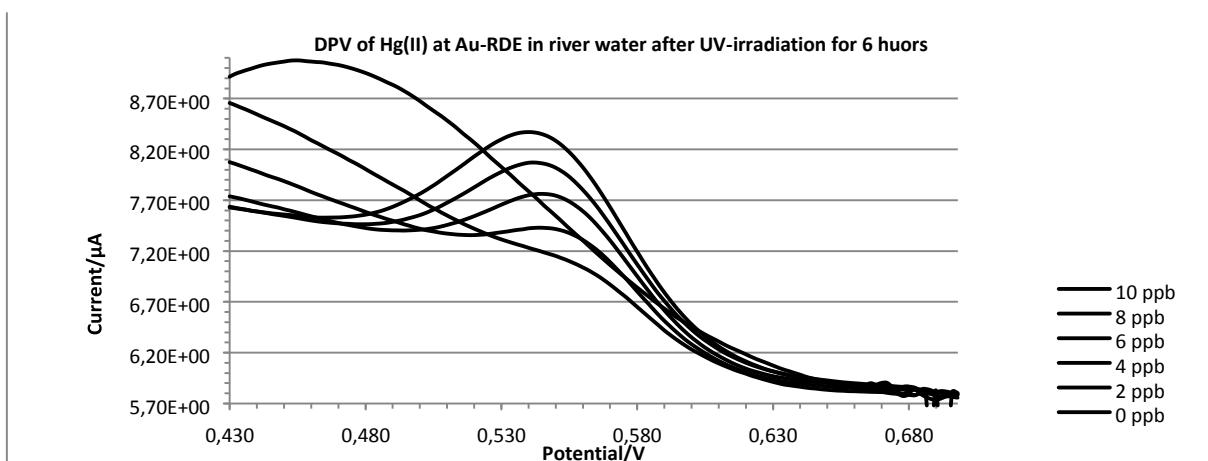


Figure (35): DPV of Hg(II) at Au-RDE in 0.2 M H₂SO₄ containing 0.002 M EDTA-Na₂ and 0.005 M NaCl in river water after UV-irradiation for 6 hours. Deposition potential = 0.37 V, deposition time = 180 s, conditioning potential = 0.7 V, conditioning time = 10 s, initial potential = 0.4 V, end potential = 0.7 V, scan rate = 0.02 V/s, potential step = 0.002 V, potential pulse = 0.05 V, time pulse = 0.04 s, equilibrating time = 5 s, and the rate of Rotating (ω) = 3000 rpm.

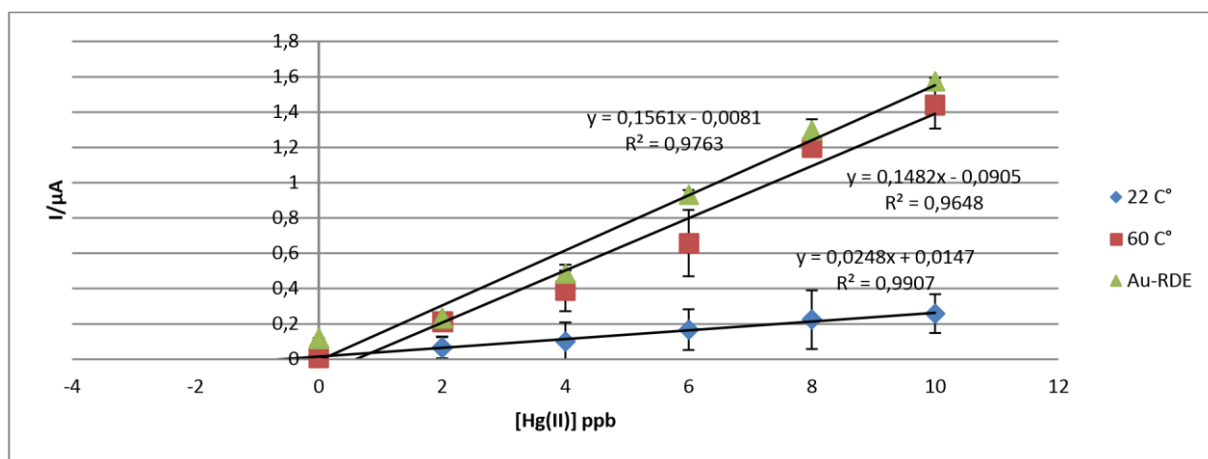


Figure (36): Calibration plots of the deposition Hg(II) at Au-RDE in 0.2 M H_2SO_4 containing 0.002 M EDTA- Na_2 and 0.005 M NaCl in river water after UV-irradiation for 6 hours at 0.37 V for 180 s with stirrer speed 3000 rpm in the comparison with the Au-loop electrode at both temperatures of 60 °C and 22 °C in 0.1 M H_2SO_4 containing 0.01 M HCl at 0.2 V for 120 s represent current peak versus the concentration of mercury.

Figure (37) shows the comparison between the analytical signals for trace mercury in river water on Au-loop electrode at 60 °C before UV-irradiation and after UV-irradiation. Seemingly, the responded analytical signals after UV-irradiation are higher than those responded before UV-irradiation. On the other hand, the calculated concentration of Hg(II) in river water UV-sample (0.61 ppb) is approximately equal to the calculated concentration in origin river water (0.56 ppb). Such result indicates that the adsorption of DOCs on the heated Au-loop electrode in the origin river water sample was totally prevented. So as a result, heated Au-loop electrode prevents the complexation between the metal ion studied and DOCs presented in origin river water sample due to replace a classic UV-irradiation process for determination of Hg(II). Meaning, UV-irradiation effect on the responded analytical signals on heated Au-loop electrode can be explained by supposing that UV-irradiation works to damage DOCs presented in the analyzed river water sample making Hg(II) ions move faster than before UV-irradiation and consequently reach to the working electrode surface more quickly making the responded analytical signal higher.

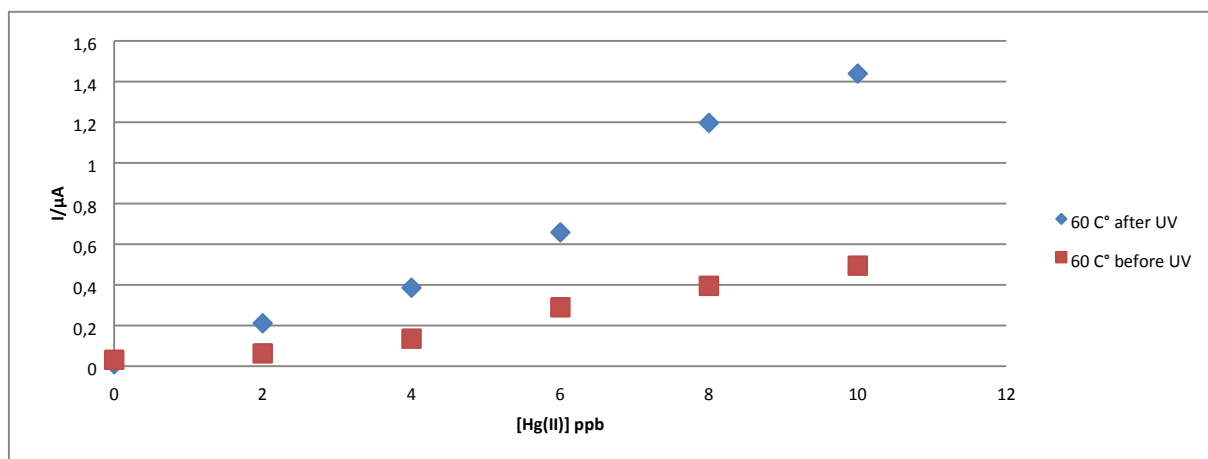


Figure (37): Calibration plots of the deposition Hg(II) at Au-Loop electrode at 60 °C before UV-digestion and at 60 °C after UV-digestion for 6 hours in 0.1 M H₂SO₄ containing 0.01 M HCl in the river water represent current peak versus the concentration of mercury.

Table (9): concentration of and recovery rate Hg(II) in the samples of water at both working electrodes Au-loop electrode (at both of temperatures 60 °C and 22 °C) and Au-RDE.

Sample	Working electrode	[Hg(II)] ppb	Recovery rate %	MRR* %
Tap water	60 °C	0.52	5.45	143.36
	22 °C	1.01	43.48	141.58
	Au-RDE (3000 rpm)	0.10	99.66	142.96
River water	60 °C	0.56	17.81	49.20
	22 °C	0.66	12.47	79.46
	Au-RDE (3000 rpm)	0.64	156.25	85.64
River water UV-sample	60 °C	0.61	7.95	140.83
	22 °C	0.59	87.89	241.12
	Au-RDE (3000 rpm)	0.05	56.07	128.35

As conclusion and based on the prior mentioned analysis results, the ability of the heated Au-loop electrode to achieve high greatly self-cleaning effect due to offer easy and fast method to determine the concentration of trace mercury Hg(II) in the tap and origin river water sample on heated Au-loop electrode compared with the Au-RDE. In the comparison with river water UV-sample, the adsorption of the DOCs onto heated Au-loop electrode surface in origin river water sample was totally prevented. So heated Au-loop electrode protects the electrode surface from the fouling activity of DOCs. The UV-irradiation treatment together with heated Au-loop electrode donate an enhancement of the voltammetric analytical signals response.

4.4. Measurement of trace Arsenic As(III)

Indeed, the trace metal of arsenic is naturally occurring element in the environmental in both formulas of organic and inorganic. The most toxic form is measured to be inorganic arsenic, which is found in natural water plus in many types of nourishment. It is of concern the presence of arsenic in the surface and ground water because of possible carcinogenic activity, its toxicity, and by means of its oxidation state plus its complexation with organic components make the biotic special effects of arsenic changed. Arsenic can be existed as As(III) and As(V) in the natural water, but As(V) is thermodynamically chosen because of its ability to form complexes with specific coenzymes, whereas As(III) is more toxic to plants and animals than As(V). Hence, the determination of trace arsenic is very important for understanding its manner of both the biological and geochemical.

Arsenic exists as anions in aquatic systems. When anions of arsenic would be formed in an aquatic media then they form bond with organic sulphur, nitrogen and carbon. The complexes of arsenic anions act as ligands in water due to, consequently, increase the arsenic flexibility in environmental samples [186].

For the determination of trace arsenic several methods have been used involving some spectrometer techniques [187-189], such as graphite furnace atomic absorption spectrometry (GF-AAS), hydride generation atomic absorption spectrometry (HG-AAS), inductive coupled plasma atomic emission spectrometry (ICP-AES) [190, 191], (ICP-MS) can be also applied [192] and radioactivity-based methods [193]. But electrochemical analytical techniques have been recently proposed, especially stripping voltammetry techniques [194-200], they offer more economical approach. For example, cathodic stripping voltammetry is most applied for arsenic determination in water, where arsenic is pre-concentrated on a HMDE in the form of intermetallic compound with copper or selenium added to analyzed solution [199, 201-204]. Differential pulse anodic stripping voltammetry (DPASV) has also been applied for determination of arsenic in natural water [205, 206]. Anodic voltammetry is applied in combination with platinum, gold or gold film electrodes [207-209]. DPASV offers higher sensitivity than linear scan anodic stripping voltammetry. The using of heated gold wire electrodes was a way for improvement of the sensitivity of the anodic stripping technique [23] or use of RDEs [210]. It has also been reported for arsenic determination in natural water a constant-current in stripping step [211]. Glassy carbon was rarely used as an inert support for gold deposition when constant-current stripping potentiometry is used [212]. By Adeloju et al. [213], it has been also reported for the determination of trace arsenic onto the mercury film electrodes in the presence of copper by using constant-current cathodic stripping potentiometry

method. Copper addition is necessary because of arsenic has low solubility in mercury. Moreover, for direct determination of arsenic in water chronopotentiometry stripping analysis technique was developed [214].

A straightforward, prompt and quantitative method is developed for the direct determination of As(III) and As(V) in tap and river water sample by using differential pulse voltammetry method (DPV) on Au-loop electrode at both temperatures 60 °C and room temperature (22 °C), where the experiments were carried out on Au-loop electrode from a quiescent solution of 0.1 M HCl. The analytical results were compared with those results obtained in pure 0.1 M HCl.

4.4.1. Arsenic As(III) in ultra-pure water sample

The concentration of trace arsenic As(III) has been successfully determined in pure 0.1 M HCl on Au-loop electrode at both temperatures 60 °C and room temperature (22 °C) by DPV method with an estimated detection limit of 2.99 ppb and 0.28 ppb respectively. The concentration of As(III) was found to be 0.35 ppb and 1.64 ppb at 60 °C and 22 °C respectively for 30 s deposition time at -0.4 V deposition potential. The response was recorded in the range of the concentration from 1 to 5 ppb. The analytical signals have been shown in figure (38) that are recorded as current peak (μA) versus potential (V), where the peak potential of As(III) was practically at (0.13 V) at 60 °C and at (0.24) at room temperature. Heated Au-loop electrode offers a remarkable improvement of the sensitivity together with unaffected signal-to-noise ratio features. Calibration plots displayed in figure (40). In comparison with the earlier studies [178], As(III) was determined at 25 μm diameter hot wire electrode heated by using a laboratory-made sine-wave power generator connected to the assembly via a high frequency transformer, preconditioning for 120 s at 0.6 V was applied with 0.2 V/s scan rate. It had been found that the maximum peak response of As(III) was recorded by applying the heat only during condition and deposition step. Moreover, the second and third analytical signal of As(III) did not appear at all after one deposition step.

Figure (39) shows the voltammogram of As(III) on Au-RDE in the range of concentrations from 1 to 5 ppb of 1 ppb addition in the presence of ascorbic acid, which was used to stabilize the As(III) ions, with the rotating rate of 3000 rpm during the conditioning and deposition step. The measurements have been done on Au-RDE after conditioning the electrode surface in 5 M HCl for 30 s conditioning time at -1.5 V conditioning potential (another conditions show in the table 5) by cyclic voltammetry method. The concentration of As(III) on Au-RDE was found to be 1.05 ppb. So a low concentration of the supporting electrolyte (0.1 M HCl) was used and no ascorbic acid was added for determination of As(III) on Au-loop electrode. So that would mean

the selectivity and sensitivity on heated Au-loop electrode (60 °C) are much better than on Au-RDE (3000 rpm).

Figure (40) shows the calibration plots for trace As(III) on Au-loop electrode at both temperatures 60 °C and room temperature compared to Au-RDE. Seemly, the resulted analytical signals heated Au-loop electrode are greatly improved at unaffected signal-to-noise ratio, where the stripping peak of 5 ppb added of As(III) was recorded to be higher in about 4-fold than that obtained on Au-RDE.

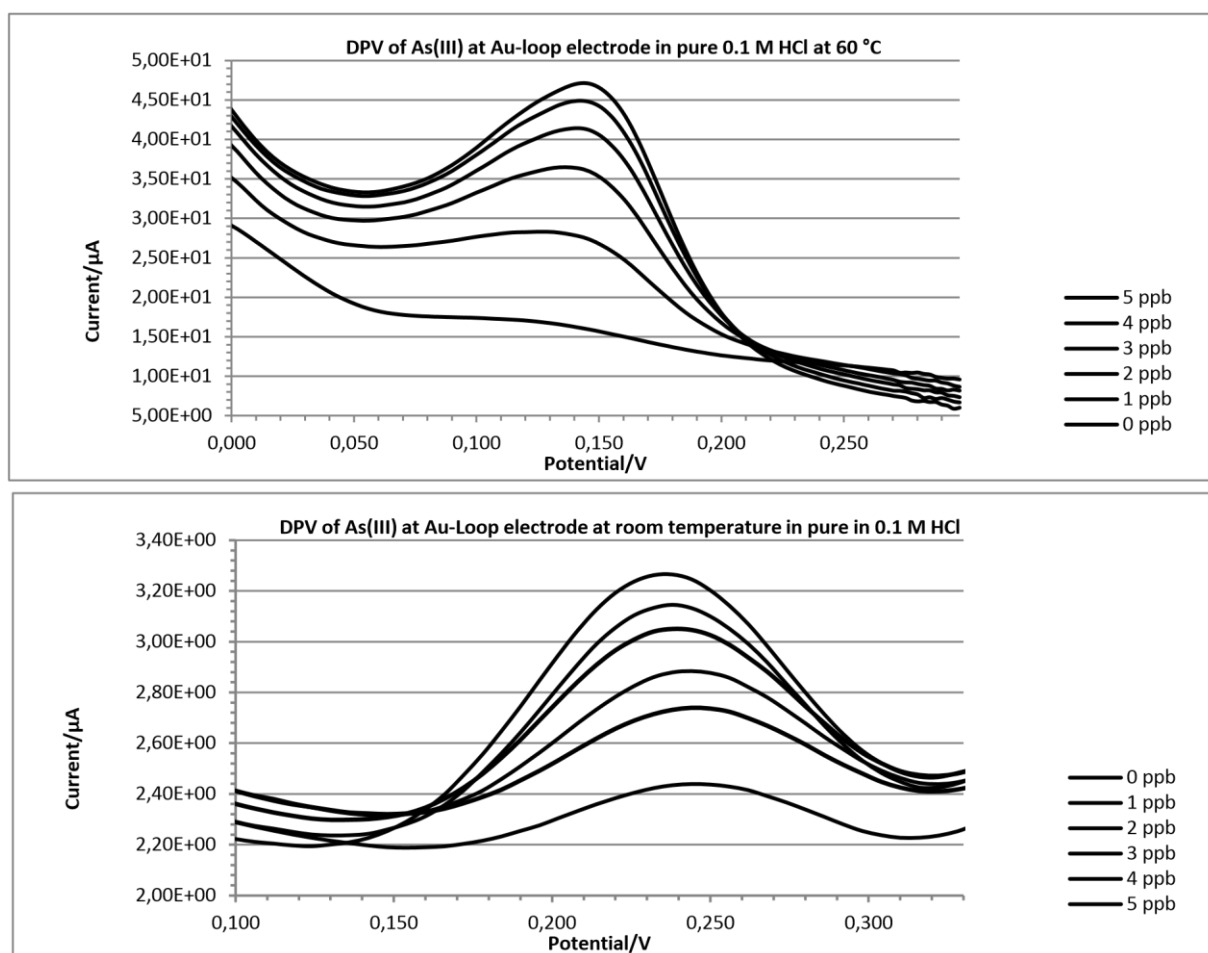


Figure (38): DPV of As(III) at the Au-loop electrode at 60 °C and at room temperature in pure 0.1 M HCl. Deposition potential = -0.4 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 120 s, initial potential = 0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

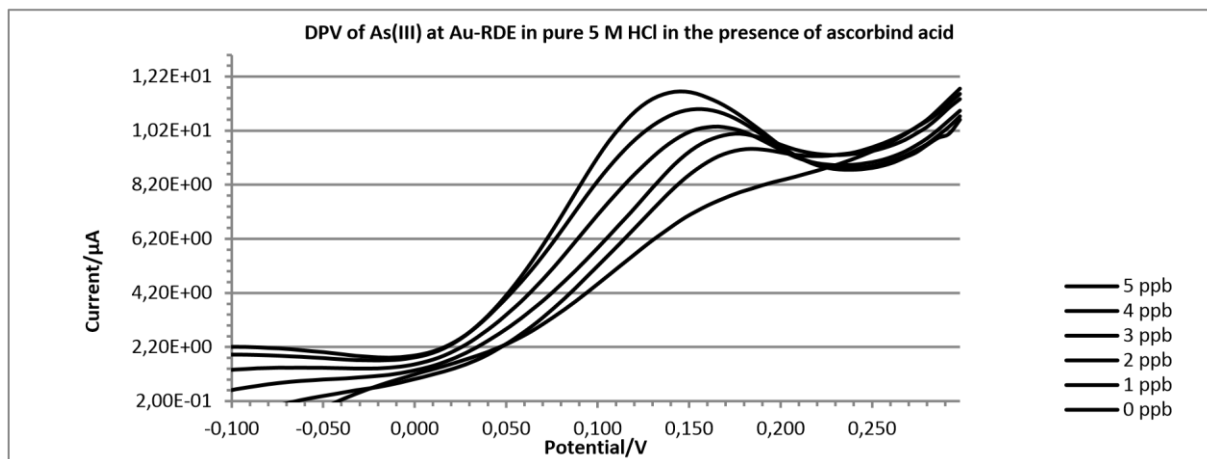


Figure (39): DPV for trace As(III) at the Au-RDE in 5 M HCl in the presence of ascorbic acid. Deposition potential = 0.4 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 120 s, initial potential = -0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s and equilibrating time = 3 s and the rate of the rotating = 3000 rpm.

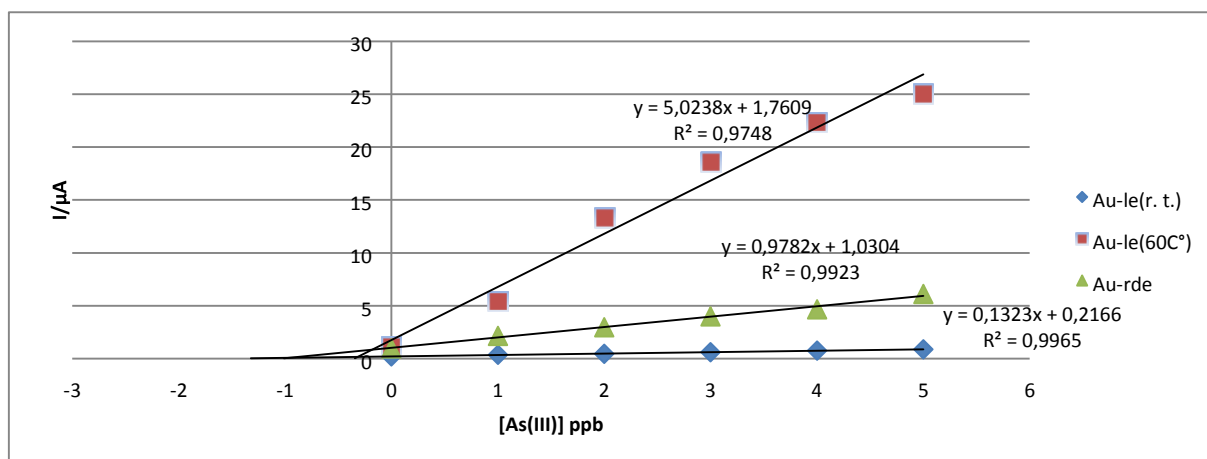


Figure (40): calibration plots of the differential pulse voltammetry for the trace As(III) at the Au-loop electrode at 60 °C (red) and at room temperature (22 °C) (blue), which it was tested in 0.1 M HCl at -0.4 V deposition potential for 30 s deposition time, in the comparison to that obtained at the Au-RDE (green), which was tested in 5 M HCl at -0.4 V deposition time for 30 s deposition time and a 3000 rpm, represent current peak (μA) versus concentration ($\mu\text{g/l}$).

Figure (41) demonstrates the effect of the Au-loop electrode temperature during the deposition and condition steps upon the stripping response. Observably, that the recorded analytical signal of 5 ppb trace arsenic As(III) was increased promptly upon the raising temperature between room temperature (22 °C) and 80 °C, and after that was decreased slightly. The recorded analytical signal of 5 ppb As(III) was enhanced in about 14-fold when going from 22 °C to 80 °C.

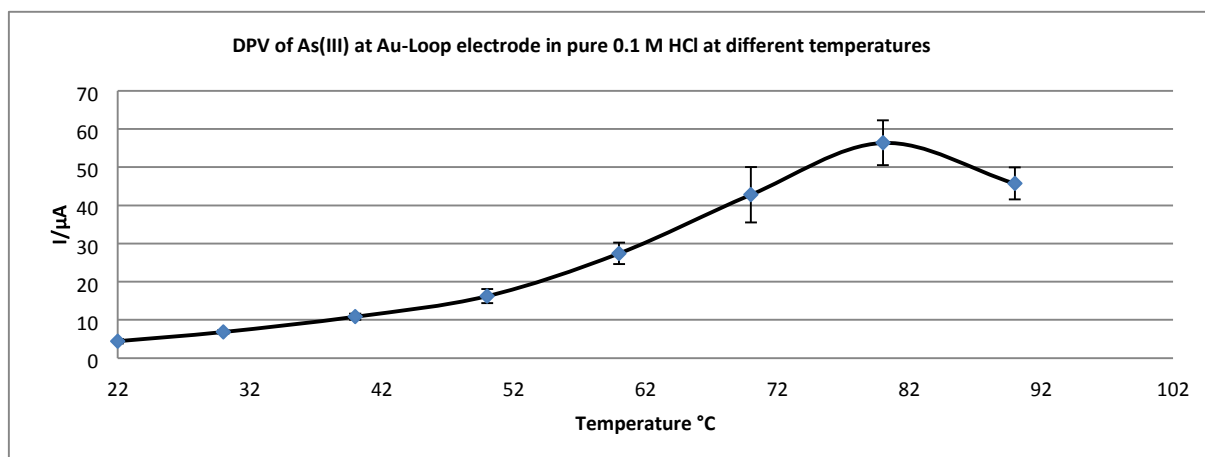


Figure (41): DPV of 5 ppb As(III) at the Au-loop electrode at different temperature in pure 0.1 M HCl. Deposition potential = -0.4 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 120 s, initial potential = 0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

The effect of the accumulation time has been examined at the Au-loop electrode at room temperature in figure (42) upon the stripping response of 5 ppb trace arsenic As(III). As it depicts the responded analytical signal for 5 ppb As(III) was increased linearly upon the raising time at first (up to 10 s), and leveled off above 3 min at room temperature, whereas the response at 60 °C fig. (43), was increased linearly upon the raising time at first (up to 10 s) and after 6 minutes begin to appear shoulder at left side of the peak. So heated Au-loop electrode can be cleaned effortlessly and simply from adsorbed coatings, and dissolved trace metals can be removed more speedily.

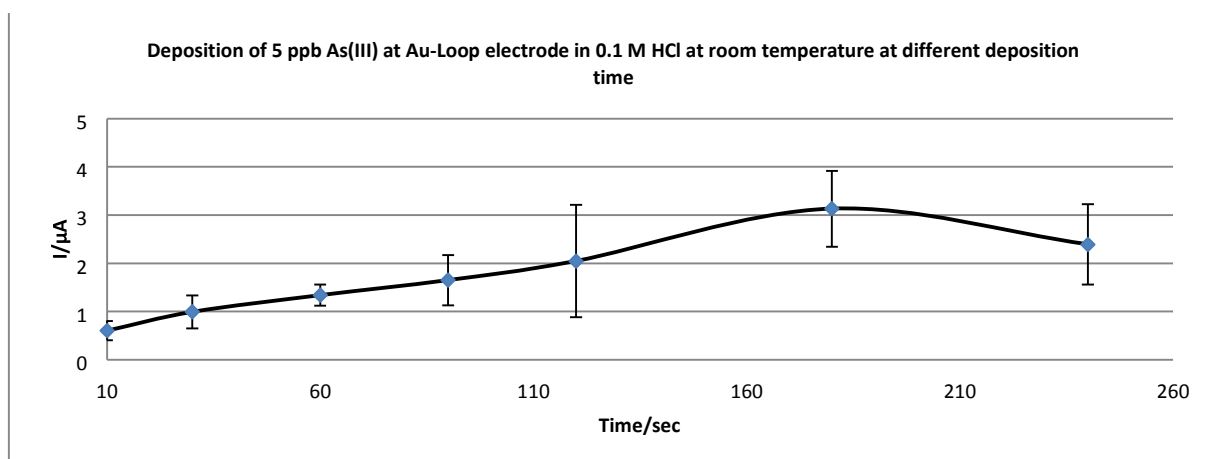


Figure (42): DPV of 5 ppb As(III) at the Au-loop electrode at room temperature at different deposition time in pure 0.1 M HCl. Deposition potential = -0.4 V, conditioning potential = 0.5 V, conditioning time = 120 s, initial potential = 0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

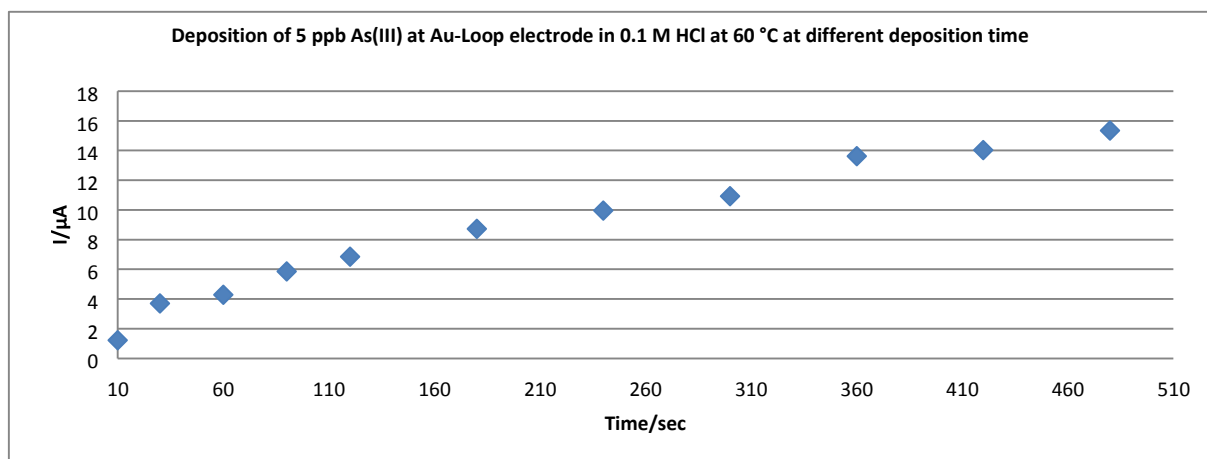


Figure (43): DPV of 5 ppb As(III) at the Au-loop electrode at 60 °C at different deposition time in pure 0.1 M HCl. Deposition potential=-0.4 V, conditioning potential=0.5 V, conditioning time=120 s, initial potential=-0.2 V, end potential=0.4 V, scan rate=0.024 V/s, potential step=0.005 V, potential pulse 0.05 V, time pulse=0.05 s, and equilibrating time= 3 s.

4.4.2. Arsenic As(III) in tap water sample

A working electrode such as Au-loop electrode shows an attractive stripping voltammetry behavior, which recovers significantly high linearity and sensitivity upon heating the electrode during the condition and deposition steps. Such hot-deposition process produced on Au-loop electrode due to a dramatic enhancement of the stripping peaks of As(III) in the tap water sample studied. Highly calibration plot is observed over the (from 1 to 5 ppb) As(III) range on heated Au-loop electrode at unaffected signal-to-noise ratio compared to the unheated-Au-loop electrode at 22 °C for 30 s deposition time at deposition potential of -0.6 V and for 60 s conditioning time at 0.5 V conditioning potential. The voltammograms for the response are displayed in figure (44) at both temperatures 60 °C and room temperature. Results obtained on heated Au-loop electrode are compared to those obtained on Au-RDE figure (45). As it shows from the calibration plots figure (46), a high sensitivity and selectivity are found to be higher on heated Au-loop electrode, where the response analytical signal of 5 ppb As(III) on Au-loop electrode at 60 °C was improved in about 2-fold compared to the Au-RDE (3000 rpm) at unaffected signal to noise ratio. The determined concentration for trace As(III) was found to be 3.07 and 0.79 ppb on heated Au-loop electrode and Au-RDE respectively. On the other hand, the responded analytical signals on heated Au-loop electrode in the tap water sample are approximately similar to those obtained in ultra-pure water, whereas they are not in case of the Au-RDE.

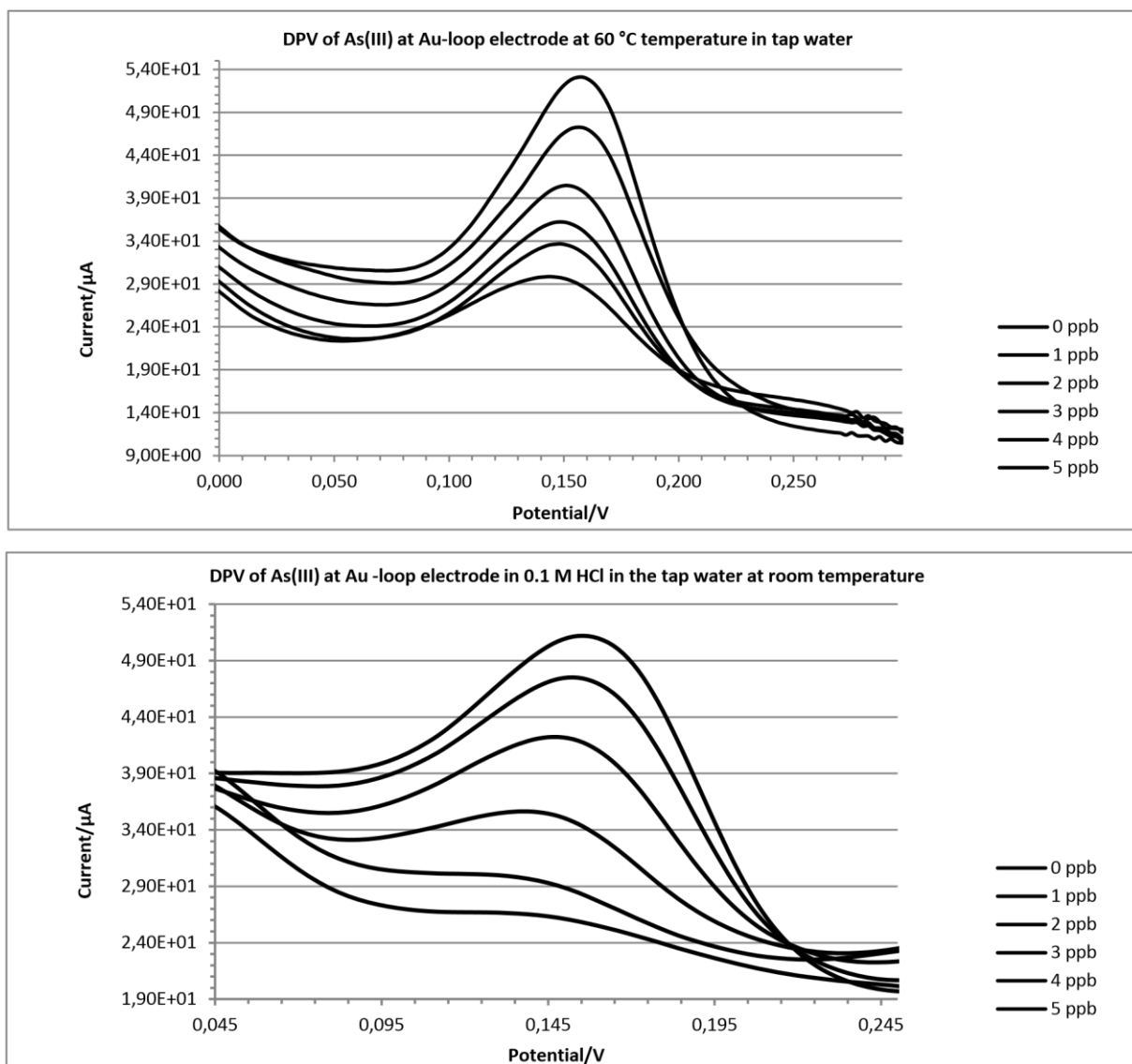


Figure (44): DPV of As(III) at the Au-loop electrode at 60 °C and at room temperature in 0.1 M HCl in the tap water. Deposition potential = -0.6 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

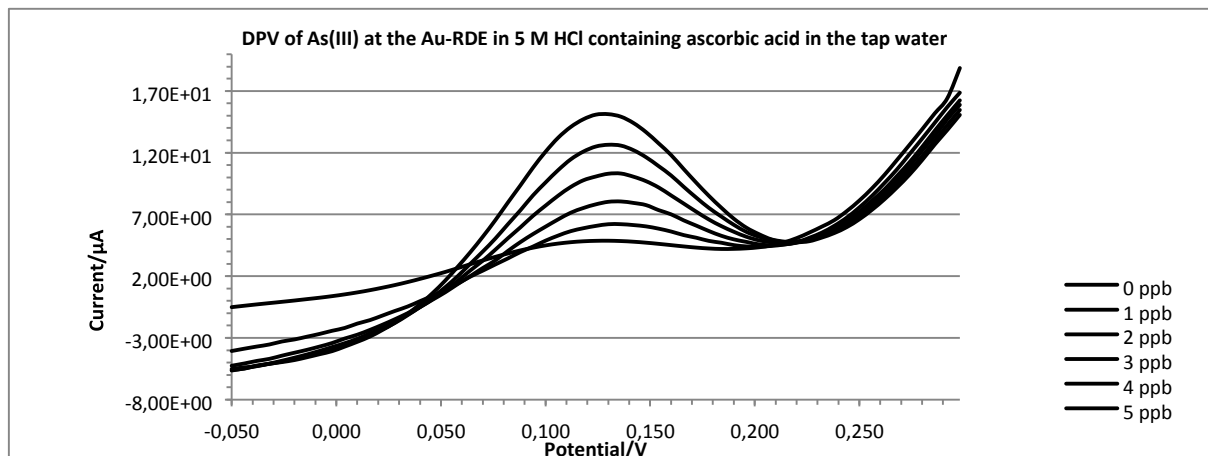


Figure (45): DPV of As(III) at the Au-RDE in 5 M HCl in the tap water in the presence of ascorbic acid. Deposition potential = -0.6 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 540 s, initial potential = 0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, equilibrating time = 3 s, and the rotating rate = 3000 rpm.

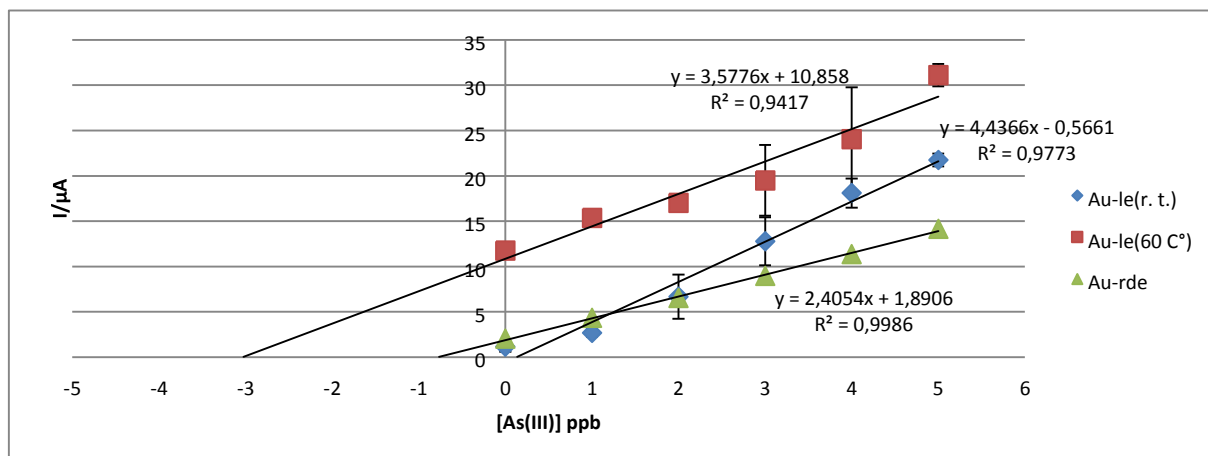


Figure (46): Calibration plots of the deposition As(III) at the Au-RDE in 5 M HCl containing ascorbic acid in the tap water at conditioning potential 0.5 V for 540 s with stirrer speed of 3000 rpm in the comparison with the Au-loop electrode at both temperatures 60 °C and 22 °C in 0.1 M HCl at conditioning potential 0.5 V for 60 s represent current peak of the As(III) versus the concentration.

Table (10): concentration and recovery rate of As(III) in the tap water at both of working electrodes of Au-loop electrode (at both of temperatures 60 °C and 22 °C) and Au-RDE.

Sample	Working electrode	[As(III)] ppb	Recovery rate %	MRR* %
Tap water	60 °C	3.07	49.08	182.50
	22 °C	0.13	37.02	3353.40
	Au-RDE (3000 rpm)	0.79	91.45	245.90

4.4.3. Arsenic As(III) in river water sample

In this experiment, As(III) is determined in origin river water sample (Rostock, Germany) by means of DPV measurements using Au-loop electrode at both temperatures 60 °C and room temperature (22 °C). The developed method is simple, with no need to long time for the conditioning of the electrode surface, since using of heated Au-loop electrode work to achieve a high greatly self-cleaning effect due to an effortlessly and basically strip the metal ion deposited on the electrode surface. Figure (47) shows the voltammograms for trace As(III) in quiescent solutions in the range from 1 to 5 ppb As(III) for 30 s deposition time at -0.6 V deposition potential and for 60 s conditioning time at 0.5 V conditioning potential. Au-loop electrode behave a linear response after increasing the As(III) concentrations with high sensitivity and linearity obtained under hot unstirred conditions, as depicted from the calibration plots figure (48), where the stripping analytical signal of 5-ppb As(III) was higher in about 5-fold than that obtained room temperature (22 °C) at unaffected signal-to-noise ratio. A determined concentration for trace As(III) was calculated by means of SAM to be 2.33 ppb and 0.32 ppb on heated and unheated Au-loop electrode. However, no stripping voltammetric analytical signals of As(III) were obtained on Au-RDE in the same river water sample investigated under the same conditions employed.

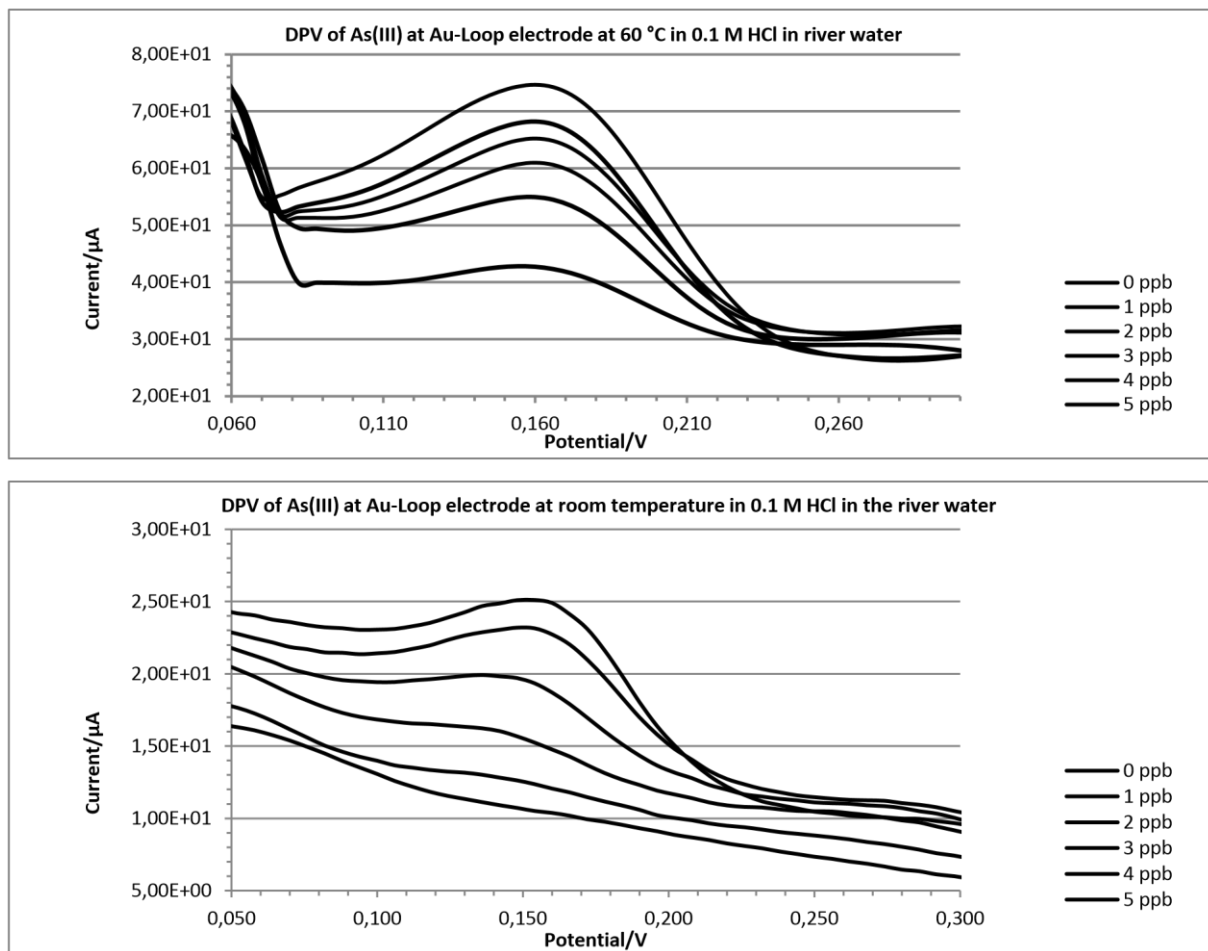


Figure (47): DPV of As(III) at the Au-loop electrode at 60 °C and at room temperature in 0.1 M HCl in the river water. Deposition potential = -0.6 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.4 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

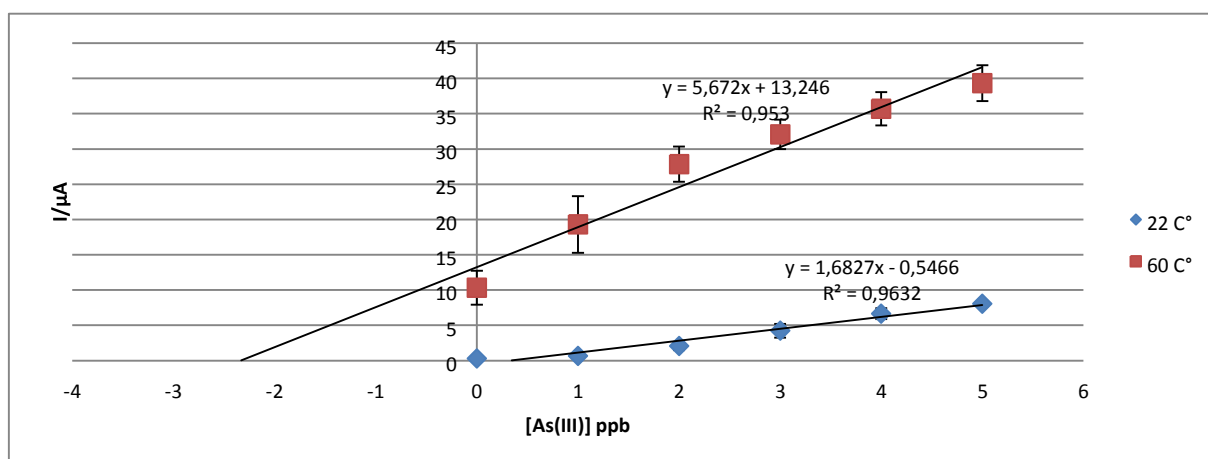


Figure (48): Calibration plots of the deposition As(III) at the Au-loop electrode at room temperature and 60 °C in 0.1 M HCl in the river water at deposition potential of -0.6 V for 30 s represent current peak versus concentration.

Table (11): the concentration of and recovery rate As(III) in the river water at Au-loop electrode (at both of temperatures 60 °C and 22 °C).

Sample	Au-loop electrode	[As(III)] ppb	Recovery rate %	MRR* %
River water	60 °C	2.33	210.55	112.90
	22 °C	0.32	9.17	1271.90

4.5. Measurement of trace arsenic As(V)

Generally, the determination of trace As(V) at solid electrodes is connected with many problems, among them a memory effects, because solid electrodes are matter to pollution by adsorbed compounds, run-down correctness and limited sensitivity, because deposited metal ion cannot be stripped always effortlessly and simply, because of the diffusion process of metal in metal is sluggish, and the problem of nucleation overvoltage is forced in deposition of metal oxides on metals or with deposition of metals at a carbon surface. So in an effortless to avoid these difficulties, stripping voltammetry at the heated Au-loop electrode is applied to determine of trace As(V) in the studied samples of water in this work.

A trace metal of arsenic has been chosen to add more positive advantages by using Au-loop electrode for various another possible analytical applications.

4.5.1. Arsenic As(V) in ultra-pure water sample

It has been successfully determined trace metal of As(V) on Au-loop electrode at both temperatures 60 °C and room temperature (22 °C) in pure 0.1 M HCl with a detection limit of 38.08 ppb and 8.12 ppb respectively. The voltammograms are depicted in figure (49) and the calibration plots are shown in figure (50). The resulted analytical signal of 2.5 ppb As(V) at the heated Au-loop electrode at 60 °C was enhanced and improved at deposition potential -0.7 V for 30 s deposition time. A concentration for trace As(V) was found to be 3.09 ppb on heated A-loop electrode. All of the effects on heated Au-loop electrode are caused by means of heating the working electrode, which works to accelerate the mass transport process of studied metal to the electrode surface and to motivate the blocked chemical reactions. Heating of the Au-loop electrode generates a highly reproducible micro stirring effect caused by thermal convection near to the electrode surface and dues to achieve a high greatly self-cleaning effect. In previous studies [20], it was shown the determination of As(V) in 0.1 M HCl containing Au(III) ions, which

had positive effect, at a heated 25 μm gold wire electrode at -0.7 V deposition potential for 240 s deposition time required 300 s pre-conditioning time at 60 $^{\circ}\text{C}$ and 600 s at room temperature at 0.5 V conditioning potential, so an advanced detection limit by factor of 14 was obtained, while going from room temperature to 60 $^{\circ}\text{C}$.

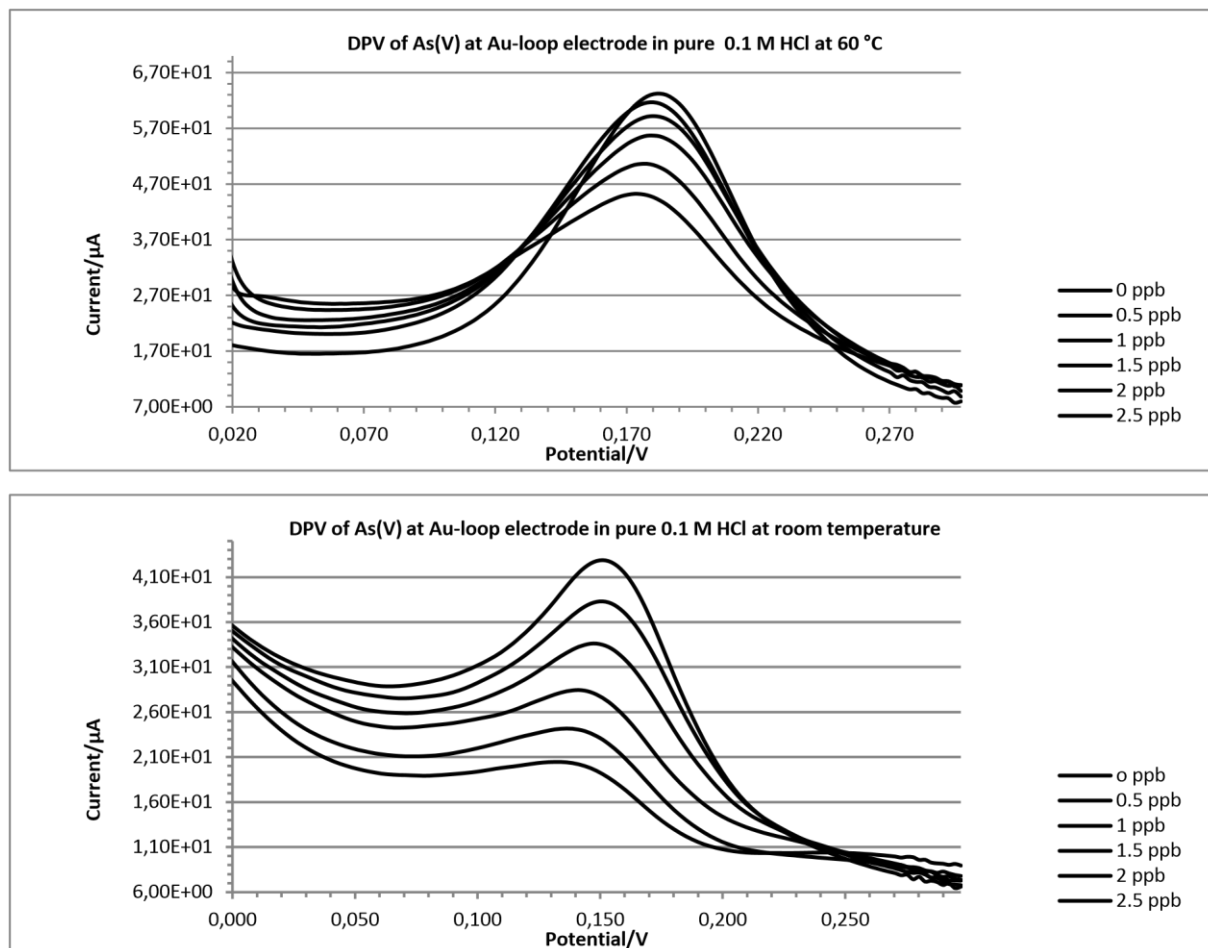


Figure (49): DPV of As(V) at the Au-loop electrode at 60 $^{\circ}\text{C}$ and at room temperature in pure 0.1 M HCl. Deposition potential = -0.7 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.3 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

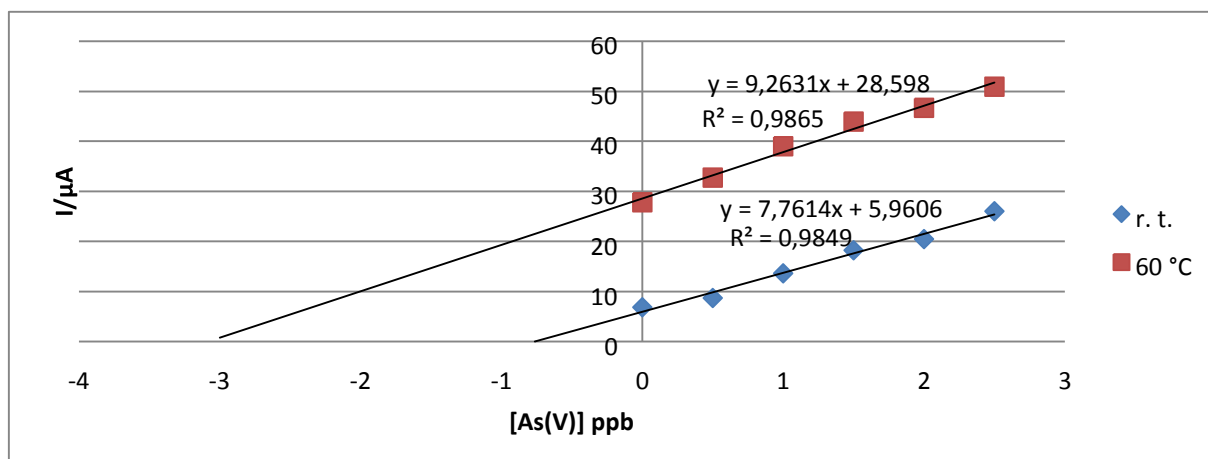


Figure (50): Calibration plots of the deposition As(V) at the Au-loop electrode at room temperature and at 60 °C in pure 0.1 M HCl represent current peak (μA) of As(V) versus concentration.

Figure (51) shows the effect of increased temperature of a heated Au-loop electrode upon the response of 2.5 ppb As(V) in 0.1 M HCl. Seemly, the resulted analytical signal was enhanced by a factor of 3 when going from room temperature to 80 °C. This effect can be explained by assuming that the thermal convection near to the working electrode surface is accelerated as a result of the temperature rise, high diffusion coefficient is achieved, the deposition process of As(V) is more quickly, and mass transport is improved. This result is in accordance with earlier study [20].

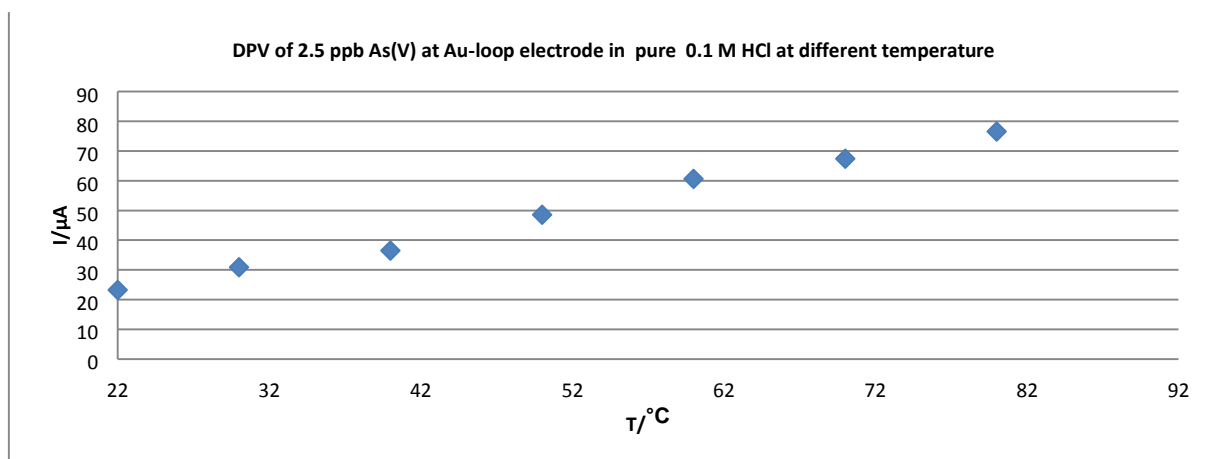


Figure (51): DPV of 2.5 ppb As(V) at Au-loop electrode at different temperature in pure 0.1 M HCl. Deposition potential = -0.7 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.3 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

Figure (52) depicts the effect of the deposition time for the determination of 2.5 ppb As(V) on Au-loop electrode at room temperature. As it can be observed that the resulted analytical signal

was increased with increasing the deposition time when going from 10 to 90 seconds. With more deposition times, the resulted analytical signal keeps constant.

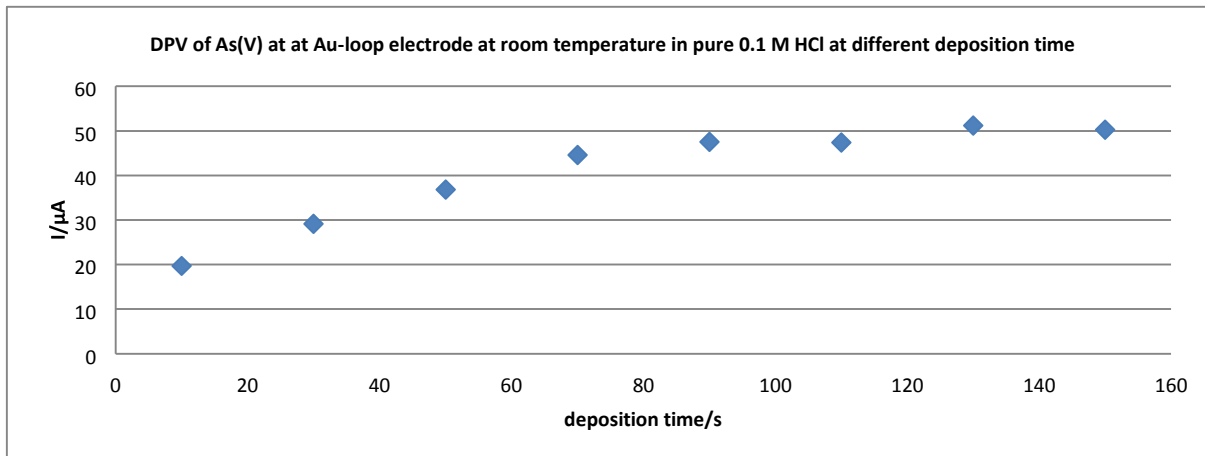


Figure (52): DPV of 2.5 ppb As(V) at Au-loop electrode at room temperature at different deposition time in pure 0.1 M HCl. Deposition potential = -0.7 V, conditioning potential = 0.5 V, conditioning time = 60, initial potential = -0.2 V, end potential = 0.3 V, Scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

Arsenious hydride can be produced at a very negative potential, where extreme hydrogen evolution takes place. This would decrease the deposited amount of the analyzed material, consequently, more negative deposition potential values due to slowly decreasing peak current as depicted in figure (53).

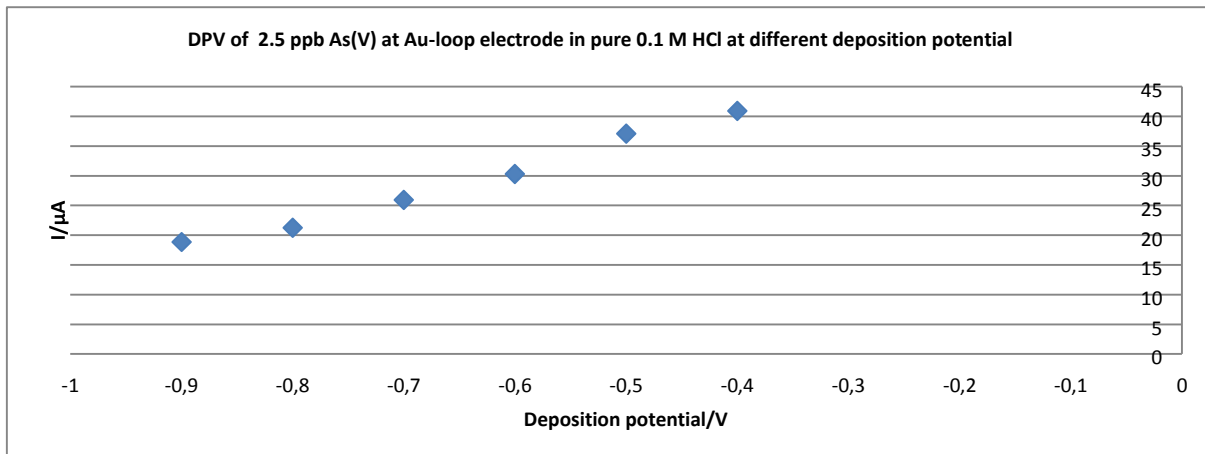


Figure (53): DPV of 2.5 ppb As(V) at Au-loop electrode at room temperature at different deposition potential in pure 0.1 M HCl. Deposition time = 30 s, conditioning potential = 0.5, conditioning time = 60, initial potential = -0.2 V, end potential = 0.3 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

Accordance to the earlier studies [20], the presence of Au(III) ions in the supporting electrolyte for determination of trace As(V) had a positive effect on the resulted analytical

signals, as depicted in figure (54), where an increased analytical signals of 2.5 ppb As(V) were achieved by increasing the concentration of Au(III) ions. The end of this response growth is reached at 5 μM of Au(III) ions.

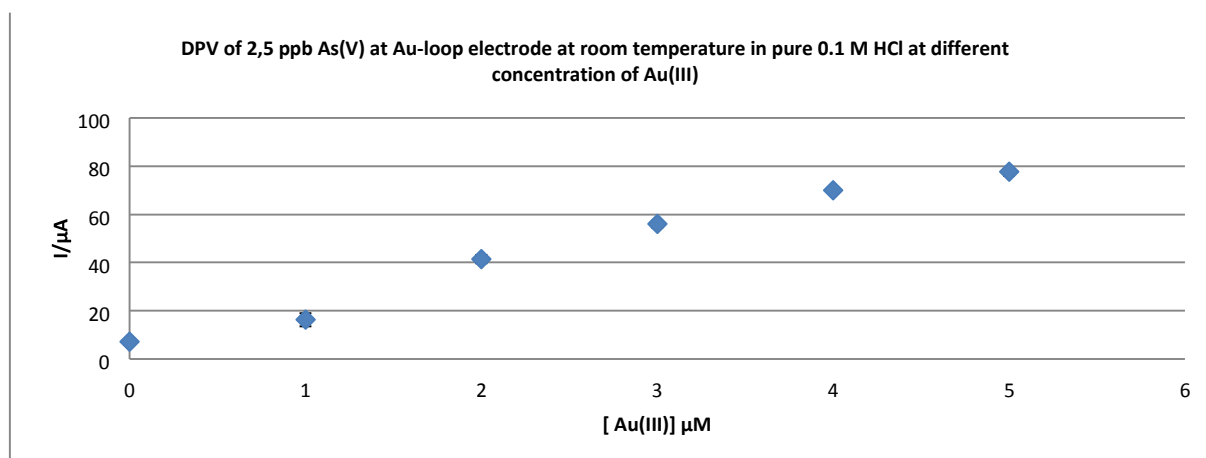


Figure (54): Calibration plot of deposition 2.5 ppb As(V) at Au-loop at room temperature at different concentration of Au(III) in pure 0.1 M HCl represent current peak versus the concentration of Au(III) ions. Deposition potential = -0.7 V for 30 s deposition time, conditioning potential = 0.5 for 60 s conditioning time.

4.5.2. Arsenic As(V) in tap water sample

The determination of the concentration of heavy metals such as As(V) in natural waters like tap and river waters requires homogenous sample which are free of DOCs that might adsorb on the electrode surface decreasing the active surface area of the electrode. As it discussed prior, DOCs complexes with metal ions cause increased background current or shift the peak potential disturbing the signal and making the determination very difficult or impossible. So for homogenous of the studied water sample many methods were applied, among them wet digestion and dry ash that have been offered long ago for the mineralization of DOCs, but it has been found that the application of these methods is combined with high danger of pollution of the studied sample. Therefore, an alternative clean and efficient method has been developed by using UV-irradiation treatment to avoid the problem of contamination of the analyzed sample. Many applications were reported for the determination of heavy metals in UV-digested natural waters. The irradiation process with powerful UV lamps is until now considered essential to guarantee complete digestion of the DOCs.

Our research offers a new approach for the determination of As(V) in tap and river water sample onto a novel type of direct heated Au-loop electrode, which make the analysis process effortless and easily as well as can substitute UV-sample preparation and the mechanical stirring effect.

In this work the chemical conditions and the instrumental variables optimized for the determination of As(V) in a quiescent untreated tap water solution containing 0.1 M HCl directly without prior reduction on Au-loop electrode at both temperatures 60 °C and 22 °C. Figure (55) shows stripping signals of As(V) at different temperatures, where the peak potential of the responded analytical signals on Au-loop electrode is at the same potential in ultra-pure water. From figure (56) can be noticed a higher sensitivity obtained on heated Au-loop electrode by a factor of 3 in the case of the highest concentration at unaffected signal-to-noise ratio.

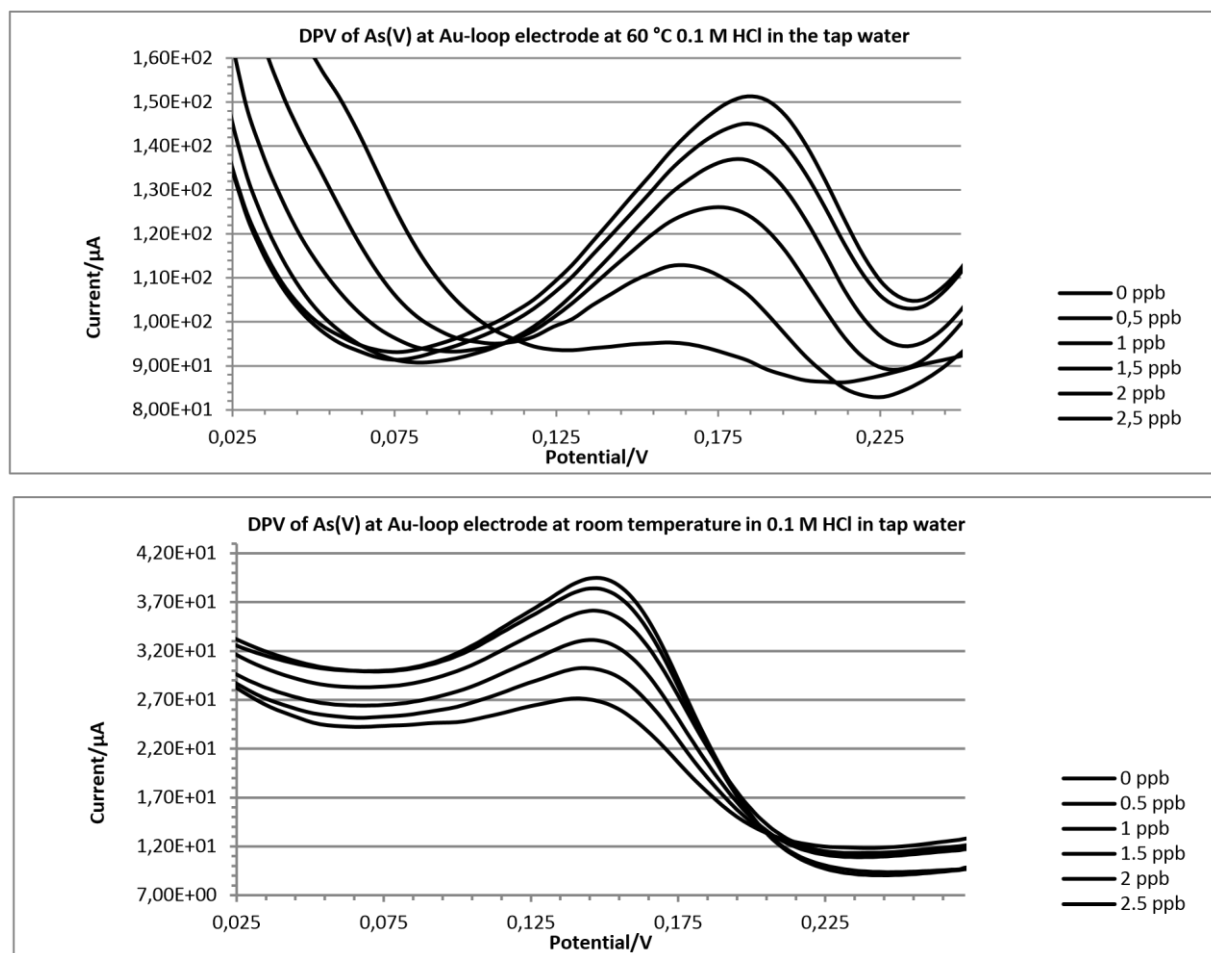


Figure (55): DPV of trace As(V) at Au-loop electrode at 60 °C and at room temperature (22 °C) in 0.1 M HCl in the tap water. Deposition potential = -0.8 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.3 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

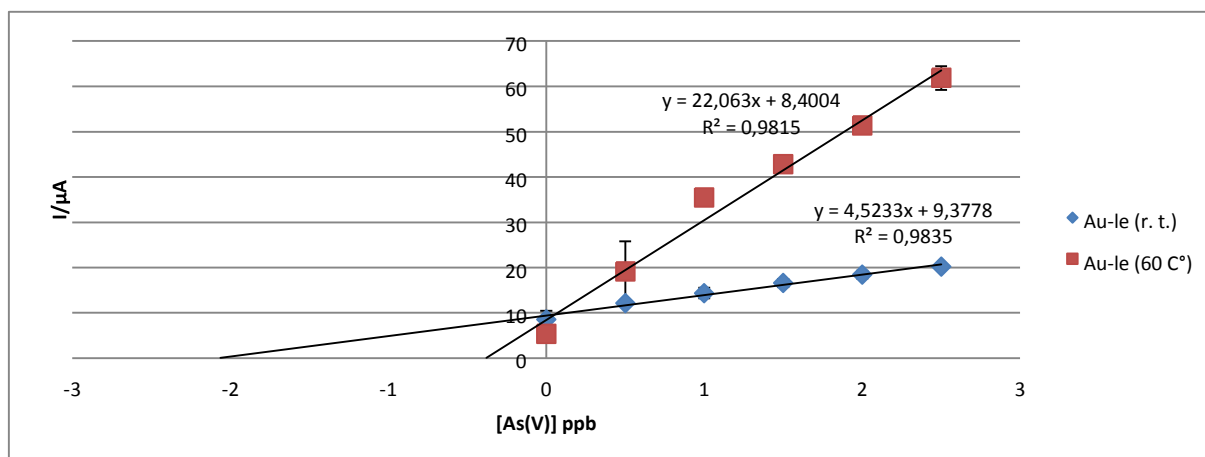


Figure (56): Calibration plots of the deposition As(V) at the Au-loop electrode at room temperature and at 60 °C in 0.1 M HCl in tap water represent current peak (μA) of arsenic versus concentration.

Table (12): concentration and recovery rate of trace As(V) at Au-loop electrode at both temperatures 60 °C and 22 °C in tap water.

Sample	Au-loop electrode	[As(V)] ppb	Recovery rate %	MRR* %
Tap water	60 °C	0.38	139.69	229.26
	22 °C	2.09	200.50	58.14

4.5.3. Arsenic As(V) in river water sample

For the determination of As(V) in origin river water sample a simple, fast and quantitative method was developed by applying DPV measurements directly on heated Au-loop electrode. River water was collected from the downstream of Warnow river (Rostock, Germany) and acidified with ultra-pure 65% nitric acid (HNO_3) to PH of 2 ± 0.2 . Figure (57) illustrates analytical signals of As(V) on Au-loop electrode in origin river water ample containing 0.1 M HCl at 60 °C and at room temperature. The stripping peak potential of the responded analytical signals is at the same stripping potential in ultra-pure water. Figure (58) displays the calibration graphs, clearly, the sensitivity is improved by a factor of 11 in the case of the highest concentration by heating the electrode surface with unaffected signal-to-noise ratio.

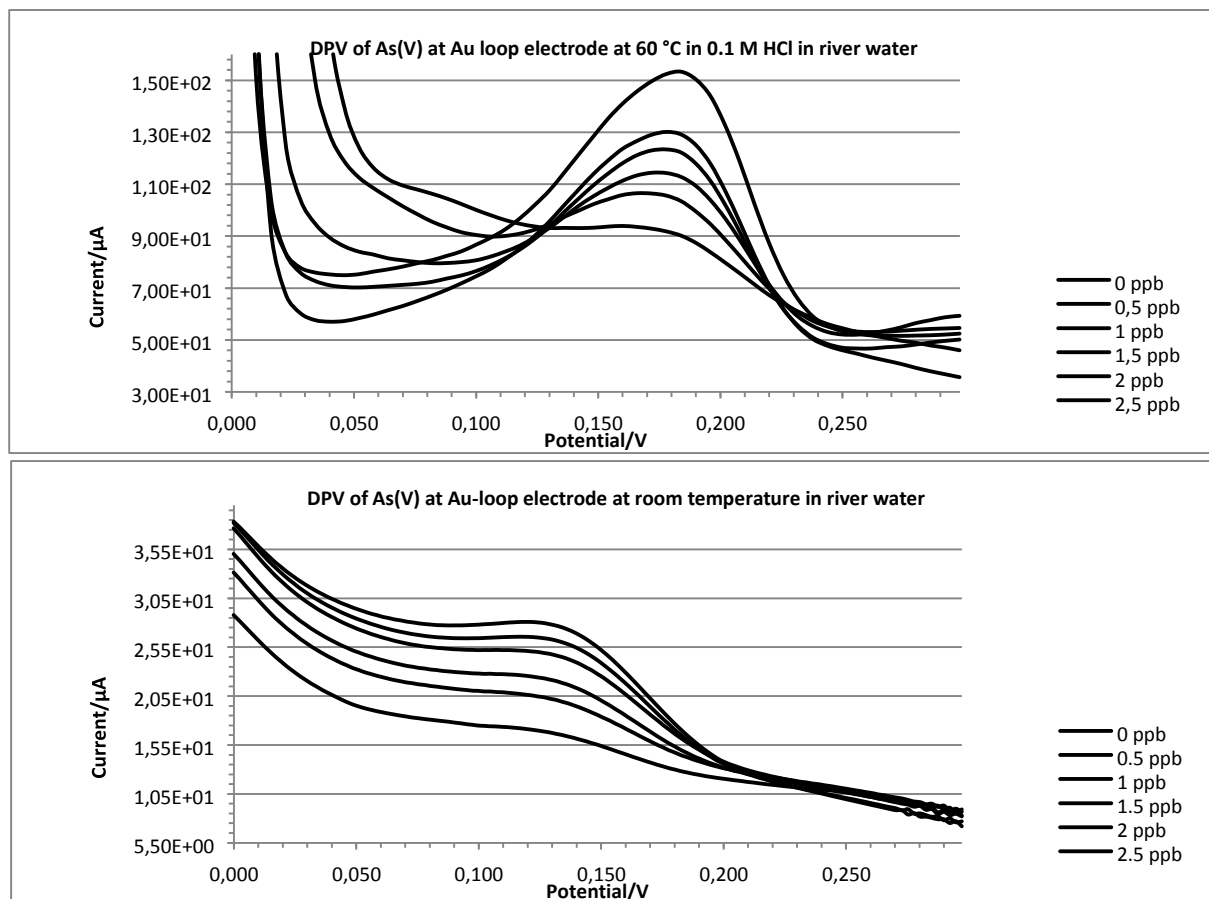


Figure (57): DPV of trace As(V) at Au-loop electrode at 60 °C and at room temperature in 0.1 M HCl in river water. Deposition potential = -0.8 V, deposition time = 30 s, conditioning potential = 0.5 V, conditioning time = 60 s, initial potential = -0.2 V, end potential = 0.3 V, scan rate = 0.024 V/s, potential step = 0.005 V, potential pulse = 0.05 V, time pulse = 0.05 s, and equilibrating time = 3 s.

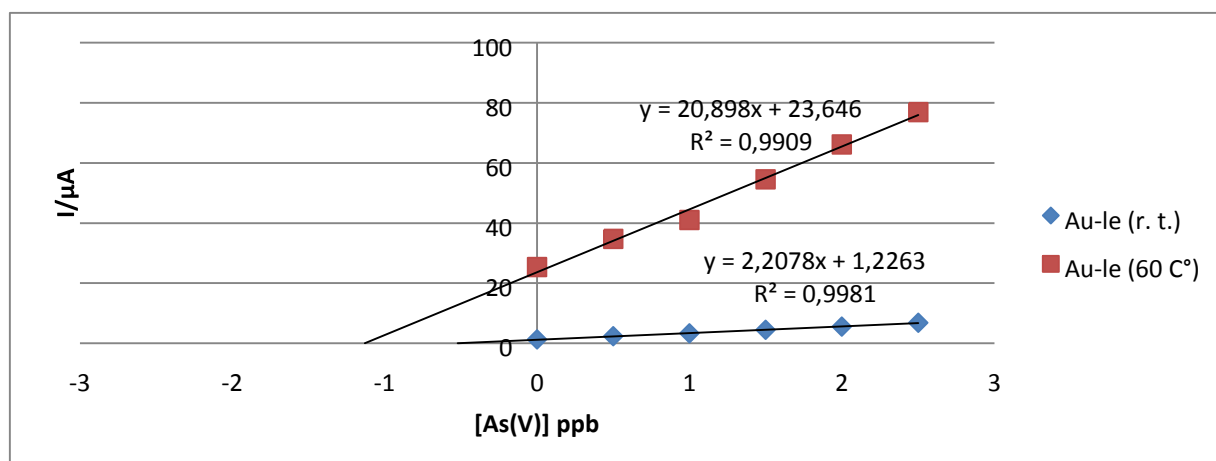


Figure (58): Calibration plots of the deposition As(V) at Au-Loop electrode at room temperature and at 60 °C in 0.1 M HCl river water represent current peak (μA) of arsenic versus concentration.

Table (13): concentration and recovery rate of As(V) in river water at Au-loop electrode (at both of temperatures 60 °C and 22 °C).

Sample	Working electrode	[As(V)] ppb	Recovery rate %	MRR* %
River water	60 °C	1.13	72.94	217.16
	22 °C	0.56	91.58	28.45

It can be concluded based on our analysis results that trace of Arsenic in both oxidation state As(III) and As(V) can be determined by applying of (DPV) measurements directly on Au-loop electrode at 60 °C and room temperature in a quiescent solution of 0.1 M HCl. The response was tested at 60 °C and room temperature for 30 s deposition time. Stripping voltammetry on heated Au-loop electrode offers a simple, fast and quantitative method and prove the strength of the heated Au-loop electrode for the determination of As(III) and As(V), the deposition process was enhanced, no nucleation overvoltage was remarkable, which it can be produced with solid electrodes, and an improvement of the sensitivity with an unaffected signal-to-noise ratio was achieved. Such results can be attributed to the self-cleaning effect offered by means of heated Au-loop electrode due to well-defined, undistorted and highly reproducible stripping signals of heavy metals, as well as micro stirring effect generated by means of the elevated temperature due to produce an increased mass transport and consequently replaced a mechanical stirrer effect. Additionally, Possibility to work with increased temperature beside the electrode surface without affecting the bulk solution. However, no stripping voltammetric analytical signals of As(V) were recorded on Au-RDE in the same samples of water analyzed under the same conditions employed.

5. Summary and outlook

It has been published that hot-wire electrochemistry offers several advantages for electro-analytical work. In our research hot-wire electrochemistry has been combined with a new kind of directly heated Au-loop electrode for the determination of some heavy metals in various samples of water by applying pulse voltammetry technique (DPV, SWV). As can be concluded, Au-loop electrode combined with high temperature work strongly to achieve a high greatly self-cleaning effect due to well-defined, undistorted and high producible stripping voltammetric analytical signals for all of the heavy metals studied in all of the samples of water investigated. Additionally, heated Au-loop electrode, like other heated electrodes are studied before, generates an efficient microstirring effect as a result of a thermal convection around the electrode surface due to accelerate the mass transport process of the metal ions studied to and from the electrode surface. Moreover, Heated Au-loop electrode work strongly to prevent the complexation between the metal ion studied and DOCs presented in origin river water sample due to replace a classic UV-irradiation processes. Heated Au-loop electrode hinders the fouling effect of DOCs on the electrode surface making the electrochemical experiments more easily and effortless. A high sensitivity, selectivity and linearity was obtained on Heated Au-loop electrode in comparison with Au-RDE at unaffected signal-to-noise ratio.

In this work has been demonstrated that some heavy metals such as copper Cu(II), lead Pb(II), mercury Hg(II), arsenic As(III), and As(V) have been successfully determined on directly Au-loop electrode at both temperatures of 60 °C and room temperature. Obtained results on Au-loop electrode were compared to those obtained on Au-RDE. For example, Au-loop electrode combined with pulse voltammetry technique represents an easy tool to use for the determination of As(III) and As(V) as heavy metals in tap and origin river water sample upon small concentrations for short deposition time with high sensitivity and linearity obtained under hot unstirred conditions. Moreover, using of heated Au-loop electrode due to replace a classic UV-irradiation process for determination of Cu(II) as heavy metals in origin river water sample investigated. Heated Au-loop electrode offers greatly enhanced stripping signals of Hg(II) due to replace the need for mechanical stirring effect. Cu(II)-UPD has been successfully carried out on bare Au-loop electrode under hot and cold unstirred conditions with high sensitivity obtained on heated Au-loop electrode, where the stripping peak of Cu(II)-UPD was recorded to be increased gradually accordance to the concentration added of copper.

Additionally, Au-loop electrode displays a suitable substrate for creation of Bi(III)-film at both temperature 60 °C and room temperature, where Pb(II) has been successfully determined as

heavy metals Bi(III)-coated Au-loop electrode in all of the water samples investigated with high sensitivity and linearity was obtained under hot unstirred conditions in comparison with cold unstirred and stirred conditions. As this investigation indicates a great analytical performance of the described hot bismuth stripping protocol.

So Au-loop electrode has been offered an easy, simple and effortless electrochemical method for determination all of the heavy metal studied in various samples of water.

Attachment

(Amy Zukas works in working group of Prof. Dr. Flechsig, University at Albany, SUNY):

Zukas's measurements of Cu(II) were done at Au-loop electrode at both temperatures of 60 and 23 °C at 0.01 V deposition potential for 120 s deposition time. 0.05 M H₂SO₄ was used as supporting electrolyte. Fig. (1) displays the calibration plots of Cu(II) at heated and unheated Au-loop electrode in ultra-pure water. The concentration of Cu(II) was found to be 8.72 ppb and 23.03 ppb at 60 and 23 °C respectively.

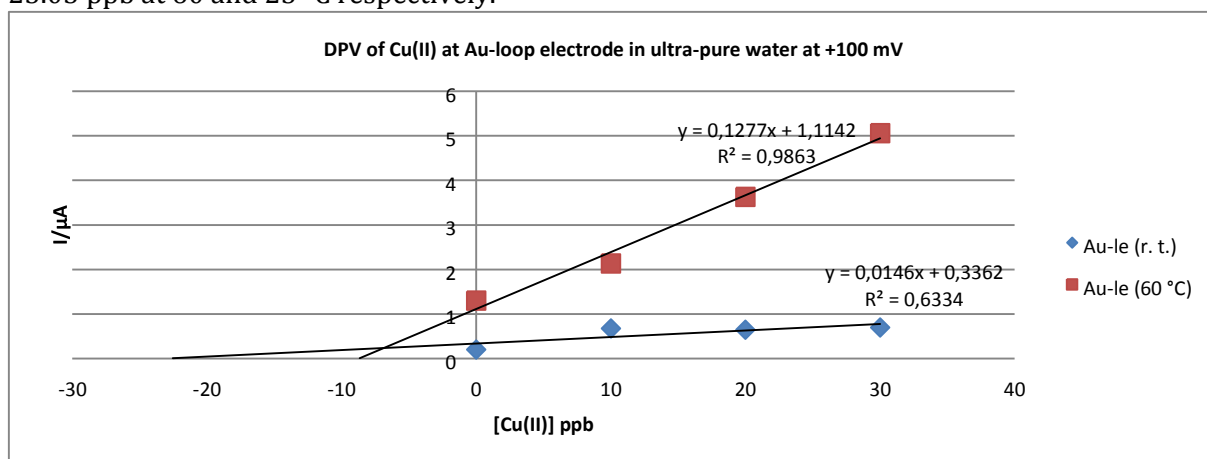


Figure (1): DPV of Cu(II) in pure 0.05 M H₂SO₄ at +100 mV deposition potential for 120 s deposition time.

Figure (2) shows the responded analytical signals of Cu(II) at heated and unheated Auloop electrode in origin river water sample. The concentration of Cu(II) was found to be 21.20 ppb and [-964.07] ppb at 60 and 23 °C respectively.

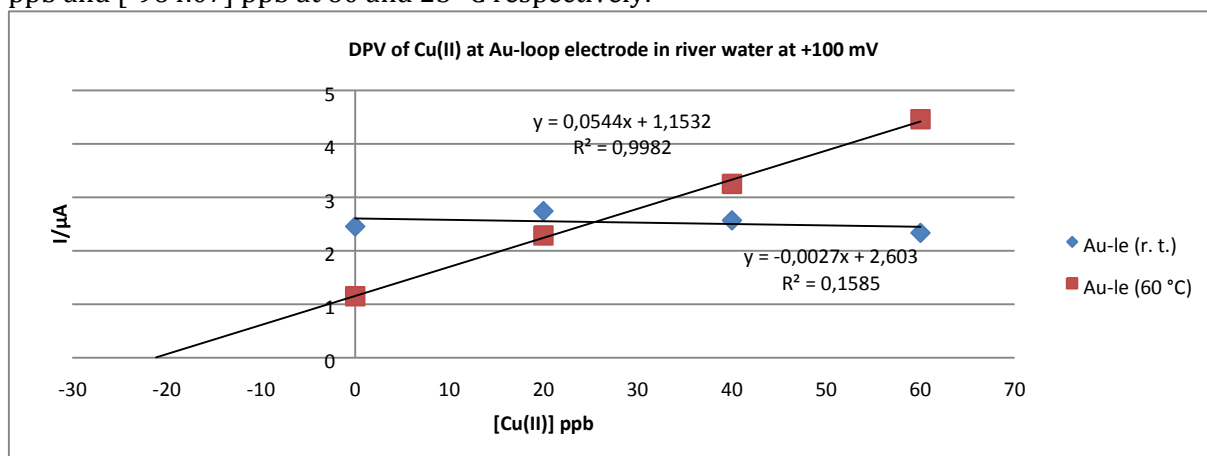


Figure (2): DPV of Cu(II) at heated and unheated Au-loop electrode in origin river water sample at 100 mV deposition potential for 120 s deposition time.

As reference measurement of the same Warnow river water was done with Metrohm HMDE after classic UV-irradiation. The buffer for HMDE ref-measurement was made using TraceSelect HOAc, NaOH, KCl. UV was done using TraceSelect HNO₃ and H₂O₂. Figure (3) shows the calibration plots of Cu(II) at HMDE in distilled water. The concentration of Cu(II) was found to be 3.65 ppb copper. Whereas the calibration plots of Cu(II) at HMDE in river water UV-sample is displayed in figure (4).

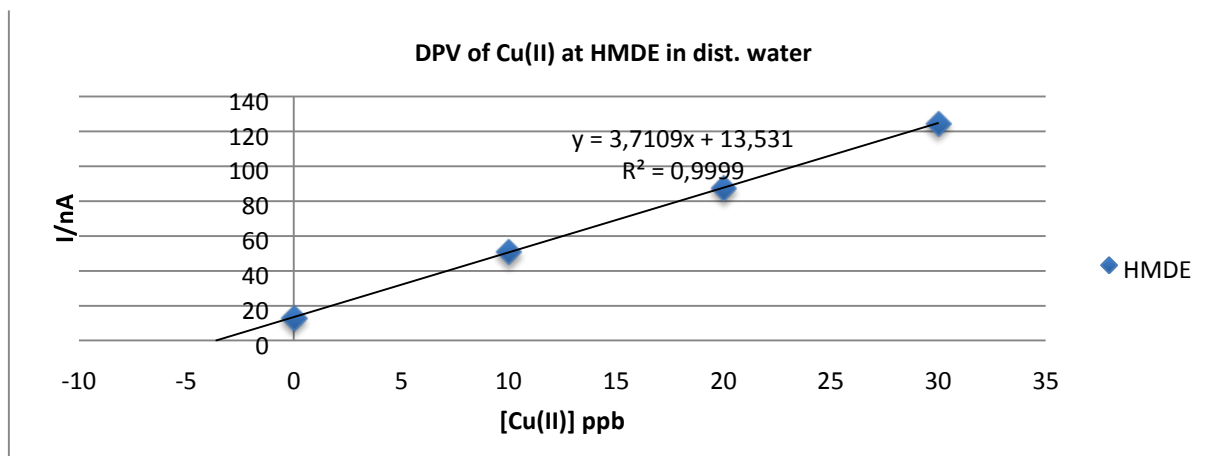


Figure (3): DPV of Cu(II) at HMDE in distilled water.

The calibration plots of Cu(II) at HMDE in river water UV-sample is displayed in figure (4). The concentration of Cu(II) was found to be 11.41 ppb copper.

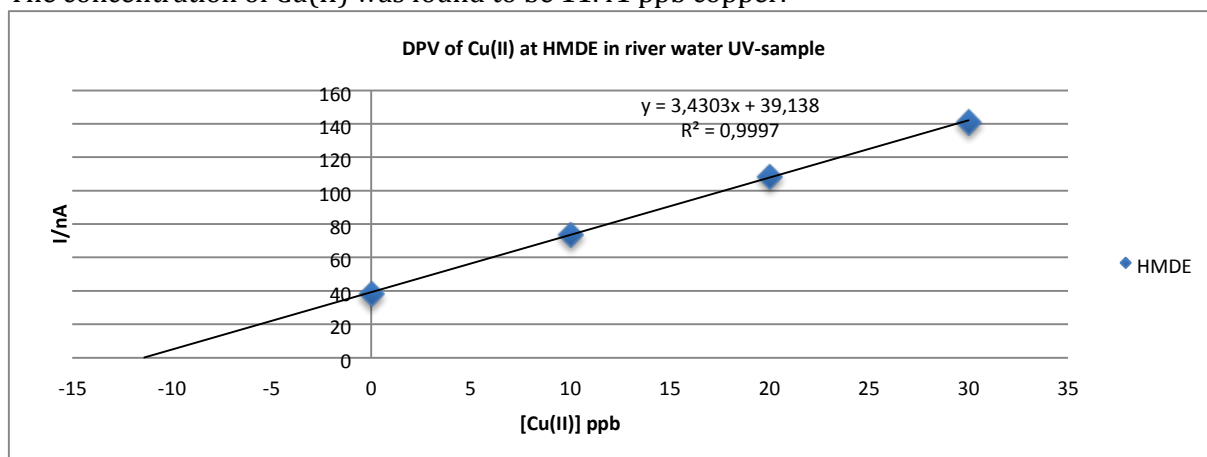


Figure (4): DPV of Cu(II) at HMDE in river water after classic UV-irradiation.

So the determined concentration of Cu(II) at HMDE in river water UV-sample = 11.41.

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Statement

I declare that the present doctoral thesis entitled:

“Investigation of deposition of some heavy metals on heated Au-loop electrode in comparison with Au-rotating disk electrode in various samples of water”

have written self-employed and without the use of other than the indicated sources and aids.