



JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

ELECTROCHEMICAL DETERMINATION OF THIOLYGLYCOLIC ACID
AT GOLD ELECTRODE

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JIMMA, ETHIOPIA

**ELECTROCHEMICAL DETERMINATION OF THIOGLYCOLIC
ACID AT GOLD ELECTRODE**

**A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
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Declaration

I declared that electrochemical determination of Thioglycolic acid at a gold electrode is my original work, except where reference is made, and has never been submitted anywhere for an award of any degree or diploma in any university.

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Abbreviations

| | |
|-------------------|--------------------------|
| A | Ampere |
| Au | Gold |
| BE | Bare Electrode |
| CA | Chronoamperometry |
| CE | Counter Electrodes |
| CPE | Carbon Paste Electrode |
| CV | Cyclic voltammetry |
| E_a | Anodic peak potential |
| E_c | Cathodic peak potential |
| EV | Electron volt |
| GC | Glassy carbon |
| I_a | Anodic peak current |
| I_c | Cathodic peak current |
| LOD | Limit of detection |
| LSV | Linear sweep voltammetry |
| mM | Milli molar |
| mVs^{-1} | Millivolt per second |
| RE | Reference Electrodes |
| TGA | Thioglycolic acid |
| TU | Thiourea |
| WE | Working Electrodes |
| μL | Microliter |
| μM | Micro Molar |

Abstract

Thioglycolic acid (TGA) is an organic compound widely used in cosmetics that cause various health problems when overexposed to it. So far many attempts have been made to develop methods for TGA determination. Therefore, a simple, cheap, and sensitive determination method of TGA is highly desired. In this work, the electrochemical determination of TGA is reported. The oxidation current response of TGA at the gold (Au) electrode is investigated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) methods. A comparison was made between the performance of glassy carbon (GC), Platinum (Pt), & Au electrodes toward the determination of TGA. Due to the different interactions of the TGA at the electrode surface, the Au electrode signal intensity of the developed method is much higher than GC and Pt electrodes in acetate buffer. Under the optimized experimental conditions, the electrode intensity has a direct relationship with the concentration of TGA in the range of 0.5 μM to 200 μM and a limit of detection (LOD) of 0.02 μM . The reported Au electrode has further been applied to determine TGA in hair perm with acceptable recoveries.

Keywords: Thioglycolic acid, Gold electrode, Cyclic Voltammetry, Linear sweep voltammetry, Cosmetics.

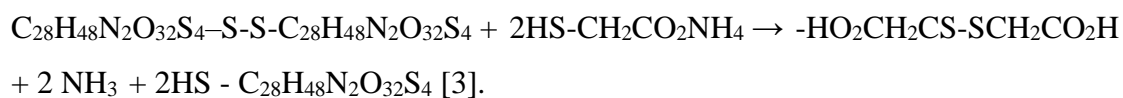
CHAPTER ONE

1. INTRODUCTION

1.1. Background of the Study

Thioglycolic acid (TGA, HSCH₂CO₂H) is a sulfur-containing organic compound that contains both thiol and carboxylic acid functional groups [1]. It is extensively used in the cosmetics and pharmaceutical industries, and its products are mainly used in hair perms and depilatory creams [1]. Human hair has an important role in society due to its value as a communication or signal device, and protective, sensory attractiveness functions. It is composed of approximately 90% proteins and follicle and shaft(1–9%) lipids [2].

TGA breaks the disulfide bonds (-S-S) in hair proteins by reacting with the keratin [3]. Disulfide bonds are made by the amino acid called cysteine. The cysteine of one keratin molecule forms a disulfide bond with the cysteine of the neighbouring keratin molecule. The more disulfide bonds there in strands of hair, the straighter it is. Ammonium thioglycolates (HSCH₂CO₂NH₄) is a compound that can break disulfide bonds [3]. This is because it contains a thiol group (-SH). The thiol group replaces one of the sulfur atoms in the disulfide bond,



When the disulfide bond is broken, the keratin bundles come apart, and hair is weakened. HSCH₂CO₂NH₄ is therefore used widely in beauty parlors when customers want their hair re-styled. However, if used too much of it, or if the reaction is left for too long, it causes bald. So do not, *ever*, try it at home [3].

TGA is used as a chemical depilatory and is still used as such, especially in salt forms, including calcium thioglycolates and sodium thioglycolates. It is the precursor to HSCH₂CO₂NH₄ is used for permanent. TGA and its derivatives break the disulfide bonds in the cortex of the hair. One form of these broken bonds is giving hair a "perm." Alternatively and more commonly, the process leads to depilation as is done commonly in leather processing [4].

It is a classical permanent hair-waving reducing agent. Permanent waves, and in particular thiols, affect hair keratin chemistry. The chemical aspects of the perm process are mainly considered to be a redistribution of disulfide bonds among the keratin chains [5].

In addition, it has wide industrial applications; for instance, it is used as a corrosion inhibitor, a stabilizer for polyvinyl chloride, in the treatment of wool, in leather processing, and in fabric dyeing [6]. On the other hand, excess TGA in turn has a potential impact on human health [7]. Excessive exposure to TGA through the skin, mouth, and ocular causes vomiting, diarrhea, allergic reaction, and hypoglycemia [8,9].

A cosmetic product is defined as a substance or preparation intended for placement in contact with any external part of the human body (this includes the mouth and teeth). The use of cosmetics to cleanse, perfume, protect, and change the appearance of human bodies or to change its odors [10].

Most cosmetic products are complex mixtures of chemical compounds that are directly applied to the skin. Products classified as Cosmetics are; Skin Creams, Lipstick, Foundation, Face powder, Mascara, Nail polish, False eyelashes, and Facial masks [10]. Specifically, there are seven categories of cosmetics and personal care products - oral care, skin care, sun care, hair care, decorative cosmetics, body care, and perfumes [11].

The extensive use of cosmetics at present has become one of the major problems related to social development. There are several ingredients that affect the safety of cosmetics [11]. The leading categories of cosmetics are personal care, beauty, hair care, and oral products. The chemical ingredients in cosmetics are added purposely with their use such as pigments, preservatives, antioxidants, and hair color [12].

Some harmful components probably exist in the end products which come from various causes, such as impurities from raw materials, degradation or chemical reaction of ingredients, and illegal addition [13,14].

Therefore, cosmetics must follow regulations based on the existing international guidelines. Since TGA is the main ingredient in hair perm agents, its simple and accurate detection will be necessary [15].

At present, the mainly used analytical techniques include ion chromatography (IC) [16], Calorimetric [17], high-performance liquid chromatography (HPLC) [18], Capillary electrophoresis [19], and spectrophotometry [20]. All of these methods have some limitations such as equipment cost, complex sample pretreatment, or sample matrix interferences, time consuming and required highly skilled technicians.

Interestingly, the electrochemical method has shown great or excellent potential in cosmetics analysis [21]. Therefore, effective and alternative analytical methods for the accurate determination of TGA are needed for attention purposes.

The aim of this study was to develop an effective and alternative analytical method for the determination of TGA in cosmetics.

1.2. Statement of the Problem

TGA is an organic compound used in a wide variety of consumer and industrial applications. TGA and its derivatives are used in the production of hair care products, pharmaceuticals [6]. On the other hand, excess TGA in turn has an impact on human health [8,22]. Excessive exposure to TGA through the skin, mouth, and ocular causes vomiting, diarrhea, allergic reaction, hypoglycemia, and cyanosis [8]. Many analytical methods can be used for determination of TGA. However, electrochemical methods offer good advantages in terms of quick analysis, lower concentrations simplicity, direct use in a point-of-care assay, and portability. Therefore, effective and alternative analytical methods for the accurate determination of TGA are needed for attention purposes.

In this work, we tried to develop a simple voltammetric method for the determination of TGA at gold electrodes. The oxidation of TGA was studied at different electrodes. Hence, this study may answer the following questions;

- i. Which electrode can give higher sensitivity for the determination of TGA?
- ii. What will be the reason for having a different response of electrodes?

1.3. Objective of the study

1.3.1. General Objective

- ✓ To develop an effective or alternative analytical method for determining Thioglycolic acid.

1.3.2. Specific objectives

- ❖ To investigate the electrochemical behavior of TGA at GC, Pt, and Au electrodes
- ❖ To optimize analytical parameters for the determination of TGA.
- ❖ To determine TGA under optimized conditions at the Au electrode.

1.4. Significance of the study

The previous analytical techniques for determining TGA were relatively time-consuming, lacked sensitivity, required expensive instruments, and were unavailable in most quality control laboratories. Developing a less expensive analytical method is important. Hence this work has the following significance;

- It serves as baseline information , and as reference materials for those who want to study TGA,
- To provide background information about gold electrodes.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Cosmetics

The word 'cosmetics' is taken from the Greek word "kosmeticos" which means to adorn (addition of something decorative to a thing or a person). It is defined as a substance that comes in contact with various parts of the human body, like skin, hair, nail, lips, teeth, mucous membranes, etc. Since the early day, materials used for beautification or appearance improvement have come under the category of cosmetics. People want to look beautiful, and the concept of cosmetics is a civilization [23].

A cosmetic product is a substance or preparation intended for placement in contact with any external part of the human body (this includes the hair, mouth, and teeth). Most cosmetic products are complex mixtures of chemical compounds that are directly applied to the skin [23]. It comprises a range of products such as toothpaste, shampoo, conditioners, creams, lotions, powders, perfumes, lipsticks, fingernail and toenail polish, eye and facial make-ups, hair wavers, hair dyes, hair sprays, and deodorants [23]. Among the complex mixture of chemical compounds, TGA plays an important role in cosmetics. Thioglycolates continue to be the most commonly used active ingredient in permanent waving, hair straightening lotions, and depilatory creams [12].

2.1.1. The Chemistry of TGA

2.1.2. Physical Properties

It is a clear, colorless liquid with an unpleasant odor and miscible with a polar solvent. It is also weak acid due to carboxylic acid function in the molecule [4]. TGA (2-mercaptoacetic acid, $\text{HSCH}_2\text{CO}_2\text{H}$, molecular weight 92.11, is the first member of the mercapto carboxylic acids series. Pure TGA is a water-white liquid that freezes at -16°C (3.2°F) and distills under reduced pressure. It was first developed commercially in the early 1940s in the field of cosmetology as an active material for cold wave permanents and depilatories [24].

TGA or its salts in aqueous solutions are rapidly oxidized by air or hydrogen peroxide to the disulfide, thioglycolic acid. It is a powerful reducing agent in neutral or alkaline solutions. One of the TGA most widely used reactions is the thiol-disulfide interchange reaction, particularly with the disulfide bond of cysteine in a protein material, e.g., wool, and hair, to form the amino acid cysteine [24].

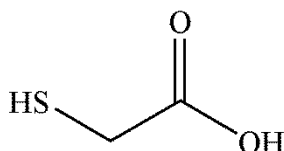


Figure 1: Structure of TGA

2.1.2.1. Chemical properties of TGA

It has two reactive centers: the mercapto group and the carboxyl group. The compound forms salts of the carboxyl and mercapto groups, esters, amides, anilides, thioethers, etc. Oxidation of mercaptoacetic acid, which occurs even on standing in the air, gives dithiodiglycolic acid $\text{HOOCCH}_2\text{SSCH}_2\text{COOH}$ [4].

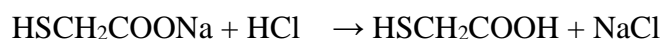
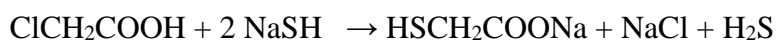
2.1.3. Manufacturing of TGA

TGA is manufactured by the reaction of mono chloroacetic acid or its salts with alkali hydrosulphide, e.g. NaSH or NH_4SH , in the aqueous medium, under controlled conditions of pressure, temperature, pH, and concentration, to give a higher yield of thioglycolate salt and minimize the formation of such by-products as thiodiglycolic and dithiodiglycolic acids [25]. Ammonium thioglycolate is produced by the reaction of thioglycolic acid with ammonia. Commercial monochloroacetic acid contains many other organic acids, particularly dichloroacetic acid, Cl_2CHCOOH , which has to be completely converted into sulfur derivatives to avoid residual chlorine compounds which are harmful to cosmetic applications. TGA, which has to meet cosmetic specifications, must be free of metal impurities and must be pure enough to avoid color and odor problems [25].

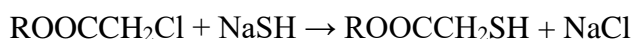
Many other routes to produce thioglycolic acid have been investigated. To try to minimize by-products, nucleophilic agents other than alkali sulfhydrates have been claimed e.g, thiosulfates, sodium disulfides, thiourea, and sodium trithiocarbonates. These alternative methods, which require the reduction of the disulfides or hydrolysis

of carboxymethylthioderivatives, seem less competitive than those using alkali sulfhydrates [25].

All the processes starting from chloroacetic acid are characterized by the formation of 1moles of salt per mole of thioglycolic acid produced:



Where thioglycolic acid is manufactured mainly as an intermediate for conversion to higher alkyl esters, the alcohol of the ester can be used as a solvent to extract thioglycolic acid. It is also convenient to manufacture the esters of thioglycolic acid directly and to use the ester of chloroacetic acid and alkali sulfhydrates as raw materials[25].



2.1.4. Use of TGA

TGA and its salts and esters modify hair fibers to facilitate changes to the structure of the fibers, such as with permanent waves or hair straightening. They are also used to chemically break down hair fibers so that unwanted hair can be removed by simply wiping it from the skin [24].

Cleaning Formulations: Due to their ability to form complexes with metals, TGA, and TGA salts are excellent additives in cleaning solutions, in particular for automotive applications including automotive wheel rim cleaners [26].

Leather Processing: In the leather industry, dehairing is a specific step in the treating animal skins, where the reducing properties of thioglycolic salts for the disulfide links of keratins are exploited alongside those of other reducing agents such as sodium sulfide and sodium hydrosulfide. TGA formulations have the advantage over simple sodium sulfide formulations regarding process safety issues, the better quality of the final leather, reduction of waste, and recovery of hair. Alkaline sodium thioglycolates are used in the removal of hair from leather hides. It minimizes wastewater treatment costs as compared to the more toxic and harmful sodium hydrosulfide [20].

Wool treatment by TGA improves elongation, elasticity, and strength properties of fibers, prevents shrinkage, and makes dyeing easier. These improvements result from the interchange reactions between disulfides and the HS group of thioglycolic acid observed on the fiber [25].

Hair Perm: The salts of TGA are used to formulate hair treatments, specialty hair styling products, and the preparation of depilatory creams [26].

In wood industries, the addition of TGA to pulping liquor during the alkaline cooking of pinewood led to an increase in the degree of delignification of wood. It has facilitated the cleavage of lignins, gives higher pulp yields, and leads to lower alkali consumption [27].

2.1.5. Economic Aspects of TGA

Since its development in cosmetics in the 1940s, TGA has become a widespread thiochemical, used all over the world as an acid or in the form of its salts or esters. Because of the several derivatives of TGA used, the market size for this chemical is often expressed in terms of TGA equivalents. In 1994 the total world market was estimated at around 15,000 to 20,000 metric tons of thioglycolic acid equivalents [25].

The worldwide growth of TGA and its derivatives is primarily driven by the market growth of PVC, and more particularly by the demand for the tin stabilizers used in this thermoplastic [25]. The demand for cold wave permanents and chemical depilatories is the second driving force for the production of thioglycolic acid and its derivatives. The progress of TGA within this sector is closely linked to local hair fashion, changes in cultural habits, and the development of average purchasing power. The world market for TGA and its derivatives is thought to experience an average annual growth of 2% [25].

2.1.6. Determination of TGA

There are few reports in the literature concerning the determination of the TGA in cosmetic products [22, 14]. Gas chromatographic method is a common kind of chromatography used as a piece of analytical science for segregating and investigating exacerbates that can be vaporized without disintegration. It is a unique and versatile technique. In its initial stages of development it was applied to the analysis of gases and vapors from very volatile components. It is the analytical technique used for

product identification (under very controlled conditions) and must be directly coupled to a mass spectrometer when information other than a comparative fingerprint (program) is required, such as positive identification of peaks on the chromatogram [16]. The basic principle of gas chromatography is that greater the affinity of the compound for the stationary phase, more the compound will be retained by the column and longer it will be before it is eluted and detected. Thus the heart of the gas chromatograph is the column in which separation of the component takes place and to this must be added the source and control of the carrier gas flow through the column, a means of sample introduction and a means of detection of the components as they elute from the end of the column. GC is used widely in applications involving food analysis. Typical applications pertain to the quantitative and/or qualitative analysis of food composition, natural products, food additives, flavor and aroma components, a variety of transformation products, and contaminants, such as pesticides, fumigants, environmental pollutants, natural toxins, veterinary drugs, and packaging materials [16]. The advantages of GC performance optimum qualitative and quantitative GC analysis of complex mixtures presupposes: (1) good resolution, as shown by sharp and symmetric peaks; (2) high repeatability and reproducibility of retention times; (3) high precision, and accuracy in quantitation based on peak area measurements, i.e. no discrimination of components through volatility, polarity or concentration; (4) minimum thermal and catalytic decomposition of sensitive sample components [17]. The use of fused-silica capillary columns with improved surface inertness, thermal stability and resolution. It involves derivatization of TGA with diazomethane to Methyl ester and Methyl thioethers derivatives, respectively [25,28]. The HPLC is a method used to recognize and measure each part in a mixture. HPLC method involves a precolumn reaction of the TGA with ethacrynic acid to give TGA adduct [18]. HPLC relies up on directly to a packed liquid dissolvable containing the model mix through a portion stacked up with a solid adsorbent material. Principle of HPL is a separation technique that involves: The injection of a small volume of liquid sample into a tube packed with tiny particles (3 to 5 micron (μm) in diameter called the stationary phase) where individual components of the sample are moved down the packed tube (column) with a liquid (mobile phase) forced through the column by high pressure delivered by a pump. These components are separated from one another by the column packing that involves various chemical and/or physical interactions

between their molecules and the packing particles. These separated components are detected at the exit of this tube (column) by a flow-through device (detector) that measures their amount. Output from this detector is called an “HPLC” In principle, LC and HPLC work the same way except for the speed, and efficiency, sensitivity, and ease of operation of HPLC are vastly superior. Applications of HPLC ; the information that can be obtained using HPLC include the identification, quantification, and resolution of a compound. Preparative HPLC refers to the process of isolation and purification of compounds [18]. This differs from analytical HPLC, where the focus is to obtain information about the sample compound. The advantage of using HPLC is its relevance to different analyte types, from little natural atoms and particles to huge biomolecules and polymers. However, its main limitation is it can be a costly strategy, it required countless costly organics, needs a force supply and ordinary support is required, have low sensitivity for certain compounds, and some cannot be detected as they are irreversibly adsorbed [18].

The calorimetric method was used to detect TGA in hair perm. One of the calorimetric sensing mechanisms is catalytic oxidation such as the Fenton reaction based on the intrinsic peroxidase-like activity of Fe^{+3} ions, Fe_2O_3 . However, these systems for the detection of TGA relied on the enzyme-like activity of Fe^{+3} ions can only work properly over a pH range from 2.5 to 5.0 [17]. Fe^{3+} ions were first employed as a peroxidase mimic and different highly sensitive colorimetric sensor were developed for the detection of L-cysteine, organophosphorus and organochlorine pesticides successively [19, 20]. However, these systems for the detection of analytes relied on the enzyme-like activity of Fe^{3+} ions can only work well over a pH range from 2.5 to 5.0.

Ion chromatography (IC) is a part of high-performance liquid chromatography used to separate and determine anions and cations and also other substances after converting them into the ionic forms [16]. The most important ion chromatography advantages are; Simultaneous determination of several ions in a short time (< 10 minutes), using different detectors, simple sample preparation for analyses (liquid samples with simple matrices), simultaneous separation of anions and cations, or organic and inorganic ions. However, IC has some disadvantages such as limited to the separation of charged ions or polar molecules, the instrument is expensive and requires expensive chemicals such as buffers [16].

At present, the mainly used analytical techniques include ion chromatography (IC) [16], Calorimetric [17], high-performance liquid chromatography (HPLC) [18], Capillary electrophoresis [19], and spectrophotometry [20]. All of these methods have some limitations such as equipment cost, time consuming, complex sample pretreatment, or sample matrix interferences, and require highly skilled technicians.

Recently, special interest has been developed in the application of electrochemical methods to TGA determination. Because they have the advantage of sensitivity, and fastness, requiring simple and relatively inexpensive instrumentation, and small volumes of samples, with the improvement of research resources use [30,31].

2.1.6.1. Voltammetry

Voltammetry as a potentiodynamic assay is based on the recording of the current intensity at controlled potential variation and exploits the reducing ability of antioxidants or the reversibility of redox-active substances which are either single or part of a sample [32].

The confirmed analytical advantages of the various voltammetry techniques are; enhanced sensitivity, a broad concentration range (10^{-12} to 10^{-1} M), numerous applicable solvents and electrolytes, wide working temperature ranges, fast analysis, simultaneous determination of analytes (organic and inorganic), the facility of different potential waveforms generation yielding low current intensity values, these features being sustained by a strongly developed theoretical background [33].

An important consideration in this technique is the process by which species in solution move up to the surface of the electrode, where electro-active, they can be oxidized or reduced [33].

There are three general processes by which ions move in solution: diffusion, convection, and electrostatic migration. Diffusion involves the random motion of species in solution. Convection is a physical movement created by something like a magnetic stir bar. Electrostatic migration results from the attraction of a positive species toward a negatively charged electrode or alternatively the attraction of a negative species toward a positively charged electrode. Diffusion will always occur in a solution [33].

Therefore, voltammetry has distinguished itself among the methods applied for both qualitative analysis and quantitation of molecules, such as TGA, even when present in trace amounts [32].

2.1.6.2. Cyclic Voltammetry (CV)

Cyclic voltammetry is an electrochemical method carried out by scanning the potential at a controlled rate and measuring the current during oxidations or reductions. The potential is altered linearly with time, in a system composed of three electrodes: a counter, working, and reference electrode [34].

The important parameters obtained from a voltammogram are I_a (anodic peak current), I_c (cathodic peak current), E_a (anodic peak potential), and E_c (cathodic peak potential). According to the Randles-Sevcik equation, the peak current, I , for an electrochemically reversible system, is described as follows:

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

Where I is the peak current in Amperes, n is the electron stoichiometry in equivalents per mole, A is the electrode area in square centimeters, D is the diffusion coefficient in square centimeters per second, C is the concentration in moles per cubic centimeter and ν is the Potential scan rate in volts per second [35].

For a well-behaved system, the anodic and cathodic peak currents are equal, and the ratio i_{p_a}/i_{p_c} is 1.00. The half-wave potential, $E_{1/2}$, is midway between the anodic and Cathodic peak potentials [36].

$$E_{1/2} = \frac{E_{p_a} + E_{p_c}}{2}$$

Scanning the potential in both directions provides us with the opportunity to explore the electrochemical behavior of species generated at the electrode. This is a distinct advantage of cyclic voltammetry over other voltammetric techniques [36].

A CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl) [37].

The controlling potential which is applied across these two electrodes is considered an excitation signal. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal [39].

The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). Because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This helps understand the fundamentals of the technique [39].

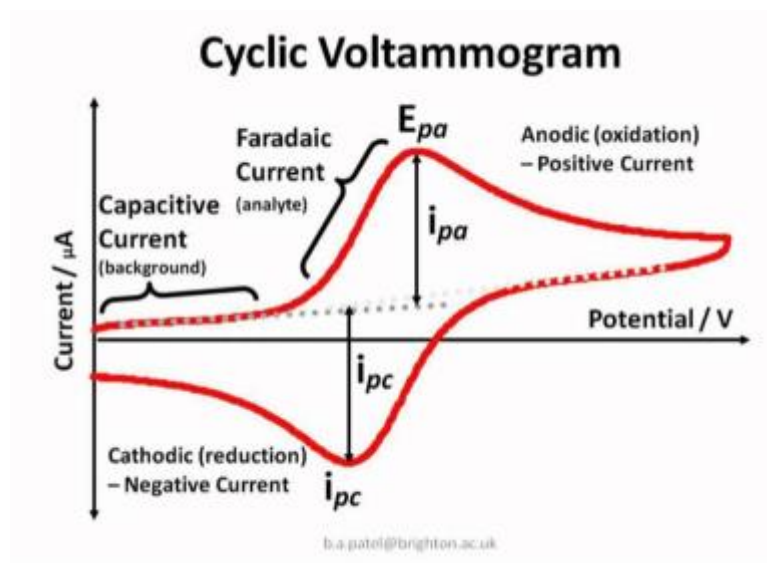


Figure 2: Cyclic Voltammogram for the reversible process [39].

Where E_{pa} is anodic peak potential, E_{pc} is cathodic peak potential, I_{pa} is anodic peak current, and I_{pc} is cathodic peak current.

Three electrode system

Three electrodes that are used in voltammetric studies are the working (indicator) electrode, reference electrode, and counter (auxiliary electrode) [40].

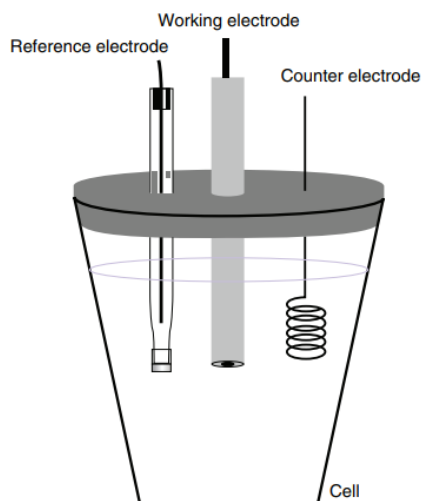


Figure 3: Schematic presentation of an electrochemical cell for voltammetric study [40].

The three type's electrode has a different function.

- i. Working electrodes(WE): The working electrode carries out the electrochemical event of interest. The most important aspect of the working electrode is that it is composed of redox-inert material in the potential range of interest. It is the place where oxidation or reduction of analytes occurs. The working electrode is the electrode where the potential is controlled and where the current is measured.

Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathode or anode, respectively. It is an inert material such as gold, platinum or inert carbon such as glassy carbon and mercury drop and film electrodes. Chemically modified electrodes are also used for the analysis of both organic and inorganic samples [41].

- ii. Reference Electrodes (RE): A reference electrode has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell. It is thus typically reported as "vs" a specific reference [41].

There are a few commonly used (and usually commercially available) electrode assemblies that have an electrode potential independent of the electrolyte used in the cell. Some common reference electrodes used in aqueous media include the saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the Ag/AgCl electrode. The reference electrode is used to measure the working electrode potential; hence the potential of the electrode remains constant. Therefore in this work Ag/AgCl was used as RE [41].

- iii. Counter Electrode (CE): When a potential is applied to the working electrode such that oxidation or reduction of the electroactive species can occur, current begins to flow. The purpose of this electrode is to complete the electrical circuit. The current was recorded as electron flow between the working electrode and counter electrode. In this work, Platinum wire is used as a CE electrode [41].

2.1.6.3. Linear Swept Voltammetry (LSV)

LSV is the simplest voltammetric technique [42]. In LSV the current at a working electrode is measured while the potential between the working electrode and a reference electrode is scanned from a lower limit to an upper limit linearly in time [33].

Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced. The characteristics of the linear sweep voltammogram recorded depend on several factors including the rate of the electron transfer reaction(s), chemical reactivity of the electroactive species, and voltage scan rate [41].

2.1.7. Electrode Materials

Electrodes and electrode materials are metals and other substances used as the makeup of electrical components. They are used to make contact with a nonmetallic part of a circuit, and are the materials in a system through which an electrical current is transferred [43]. As well as optimizing the applied current density or potential difference across a cell, electrochemical reactions can be performed in either batch or flow cells, or divided or undivided cells. However, it is the electrodes that constitute the most important difference, as the success or selectivity of a particular transformation is highly dependent on the material [43].

Not only does, the electrode material itself determine the mechanism of electron transfer, but the electrode separation distance, shape, and size determine the submerged surface area, the field homogeneity, and the resulting current density; all of which can affect the reaction outcome. While the electrode material is an additional parameter that requires optimization, it can be reactivity through electrode-catalysis, mediator-modified or chemically-modified electro-catalysis [43].

The ability of specific materials to give unique outcomes and be exploited to control and change the selectivity of a reaction, and provides opportunities to vary and determine the selectivity for synthetic electrochemical reactions has long been recognized [44].

2.1.7.1. Properties of Electrode materials

Important properties of electrode materials are conductivity, corrosion resistance, hardness, current load, form, and size. Many of these are determined by the inherent characteristics of the material [43].

Conductivity is the measure of a material's ability to carry or conduct an electric current. It is often given as a percent of the copper standard, which is 100% IACS, (International Annealed Copper Standard). Silver has an IACS of 105 and has the highest conductivity [43].

Corrosion resistance is the material's ability to resist chemical decay. A material that has little corrosion resistance will degrade rapidly in corrosive environments; resulting in a shorter lifespan. Platinum group metals are known for their high resistance to corrosion [43].

Hardness is the measure of how resistant the material is to various kinds of permanent deformations resulting from an applied force. It is depend on a material's ductility, elasticity, plasticity, tensile strength, and toughness [44].

Form refers to the shape an electrical material must fit in order to carry out its operation. Some shapes include contact tips, pins, sockets, stampings, sheets, wires, and wheels. Size relates to the thickness, length, and width or outer diameter of the form a material takes [44].

2.1.7.2. Inert Metal as Working Electrodes

A broad alternative of solid metal electrodes exists for use in electro analysis such as gold, platinum, nickel, and palladium, which are of the least reactive metals. Of these metals, gold and platinum are the most widely used metallic solid electrodes. In most cases, metal electrodes show fast electron-transfer kinetics for many redox reactions and possess a wide anodic potential window [45].

The cathodic window for some solid metal electrodes, such as platinum, is more limited due to evolution of hydrogen. Platinum has extremely small overpotentials for

hydrogen evolution. Gold has significantly larger overpotential for hydrogen evolution and it does not adsorb hydrogen and this factor together with its larger overpotential for hydrogen evolution makes gold the metal of choice for the study of cathodic process [45].

Usually the background of the voltammograms (*i.e.* voltammetric $i-E$ curve) for metals have larger overall current per geometric area than that for carbon electrodes and exhibit features or peaks related with the oxidation and reduction of surface oxides, and the adsorption and removal of H^+ and other ions. Metals possess a larger double-layer capacitance than most carbon electrodes and this gives them a larger background current. Some of the draw backs of metal electrodes are the presence of the surface oxides, that can hinder the electrode reaction kinetics and mechanism for certain redox systems and this can lead to inconsistency in the electroanalytical measurement [46].

Gold is a commonly used material in electrochemistry. Due to its chemical inertness and resistance to oxide formation within the stability potential window of water, gold is a material of choice for many electrode reactions [46].

2.1.7.3. Glassy Carbon Electrode

In 1962, starting from phenolic resins, Yamada and Sato prepared a gas-impermeable carbon which they called glassy carbon. This glassy carbon has interesting physical properties in comparison with other carbons such as impregnated carbon. Due to its physical and chemical properties, glassy carbon has become an interesting and widely applied electrode material. It exhibits low oxidation rate and high chemical inertness, its small pore sizes and a small gas and liquid permeability, make glassy carbon a suitable inert electrode. The starting polymer and the temperature of the carbonization have a great influence on physico-chemical properties of glassy carbons. GCE is made up of aromatic ribbon molecules, randomly oriented and twisted in a complicated manner. It is one of the widely used electrode materials for making working electrodes [47].

It is an electrically conductive and gas impermeable material, high resistant to chemical attack and obtain in pure state. Some of the advantages of glassy carbon over other inert metal electrodes are low cost, of high-temperature resistance, hardness, low density, extremely resistant to chemical attack , very high thermal

stability ,and low electrical resistance, pretreatment by polishing with metallographic paper, larger overpotential.for generation of hydrogen and dissolved oxygen, increasing reversibility for several redox couples, wide applicability for trace toxic heavy metals by stripping analysis [47].

2.1.7.4. Mercury Electrodes

Mercury has been widely used in electrochemistry as a working electrode for the electrochemical study of inorganic and organic species due to its unique electrochemical properties [48].

The species to be determined on the mercury electrode should exhibit electroactivity within the available potential range or catalytic activity or the ability to be adsorbed on mercury. The electroactive species must be soluble in a conductive solvent free of other interfering materials. Mercury electrodes enable negative potentials up to -2.5 V versus SCE since they have high over potential for evolution of hydrogen, but the positive potential is limited to +0.4 V due to the oxidation of mercury beyond this potential, limits the mercury electrodes to measure less easily oxidized species [48].

There are several types of mercury electrodes, such as, dropped mercury electrode (DME), hanging mercury drop electrode (HMDE), static mercury drop electrode (SMDE), and etc. DME is the most representative mercury electrode in polarography. The DME exhibits the advantages of simplicity, reliability, and renewable surface, which is suitable for many cases of electroanalysis [48].

Despite the fact that , the DME is less frequently used now a days, due to the limitations such as high consumption of mercury and higher charging current, when dropping mercury as an anode, the mercury itself will be oxidized, there is a charging current on the mercury drop electrode, which limits the detection limit of polarography, Produce a lot of waste mercury [48].

2.2. Electrode selection

1. Practical aspects

The primary judgment of candidate materials was based on their performance in the reaction, i.e., yields and selectivity, but current efficiencies, obvious signs of corrosion, cost, availability, and machinability are other critical factors, the relative importance of which will vary according to the specific process [43]. In principle, the

electrode can be made from any conductive material, in order to make an appropriate choice there are several mechanical and electrochemical properties to consider. An idealized electrode material must be inexpensive, non-toxic, and stable to a wide range of temperatures, pressures, and solvents, yet able to be manipulated into forms for electrode construction, such as rods, wires, plates, foams, and meshes. Most electrodes consist of a single material, but a support material combined with an electroactive coating, such as Pt, can also be used [43].

An electrode should be stable and resist corrosion. An exception to this is when the electrode is sacrificial, for example when metal ionization is intended as a counter-electrode process, or when the metal ions are used to stabilize a product, such as in a carboxylation reaction [43].

2. Reactivity aspects

The mechanism for electron transfer at an electrode occurs between two limiting scenarios. In the first limiting case (Figure A), the electrode surface is intimately involved in the mechanism of electron transfer and acts as a catalyst in the reaction; i.e., electro-catalysis. In the second limiting case (Figure B), the electrode is completely inert and provides a source or sink of electrons that are transferred in an outer-sphere manner between the substrate and electrode. The identity of the products formed, and the mechanism and kinetics of their formation should be independent of the material [49].

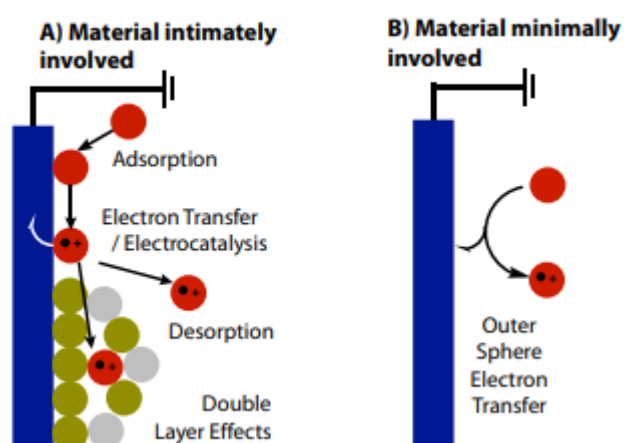


Figure 4: The two limiting cases for electron transfer [49].

3. Trends

The factors that contribute to the choice of electrode material vary and can be very specific. The number of electrode materials available has increased over time and trends of use have changed and evolved. For example, lead and mercury were previously preferred due to their high hydrogen overpotential (η_{H}) and stability to acidic media [43].

With mercury being in the liquid state, the surface is constantly renewed and can remain clean and free of impurities. However, concern over the high toxicity of these metals has limited more recent wide-spread use and hence other materials have attracted greater attention [45].

The modern organic electrochemical methodology relies more heavily on platinum, which is robust, easy to clean, and redox stable, as well as carbon-based electrodes that are more inexpensive and thus appropriate when the scale of a reaction renders the cost of platinum prohibitive [43].

Glassy carbon is the most commonly used carbon material, which is the fullerene allotrope of carbon and includes a high-surface area [50].

CHAPTER THREE

3.1. MATERIALS AND METHODS

3.1.1. Chemicals

TGA, sodium acetate anhydrous ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$), acetic acid (CH_3COOH), potassium hydrogen phosphate (K_2HPO_4 98%, (Finkem), potassium dihydrogen phosphate (KH_2PO_4 , 98% (Finkem), Sodium hydrogen phosphate (Na_2HPO_4), Sodium hydroxide (NaOH), TU, FeS , Na_2CO_3 , were used. Distilled water was used during experimental work.

3.1.2. Apparatus /Instrument

A three-electrode assembled cell was employed, consisting of the GC, Pt, and Au electrodes (3.0 mm diameter) as the working electrode, a platinum wire as a counter electrode, and Ag/AgCl electrode as a reference electrode. Electrochemical techniques were performed using Epsilon EC-Ver 1.40.67 voltammetry analyzer (Bioanalytical Systems, USA). All experiments were conducted at room temperature. pH meter (pH -016 pH METER, China), analytical balance (WANT Balance Instrument Co., Ltd, China), used.

3.2. Methods

3.2.1. Electrode preparation

GC, Pt, and Au electrodes were mechanically polished with 0.3 μm alumina slurry. After polishing, the electrodes were carefully rinsed with distilled water. The electrode should be further cleaned electrochemically. The electrode was conditioned by potential scanning from -0.5 to 1.4V.

A simple way to polish electrodes is with figure-eight motions on the polishing pad in water–alumina slurry as shown in (figure 5).

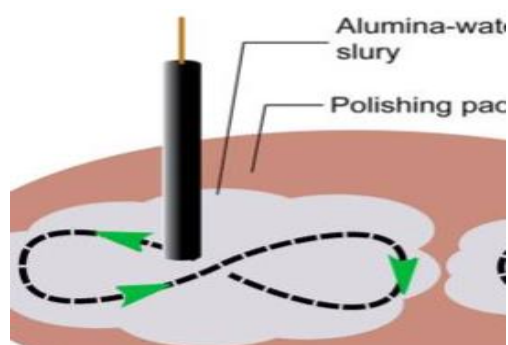


Figure 5: Simple way of polishing electrode

3.2.2. Standard Solution Preparation

A stock solution of 10 mM was prepared by dissolving 72 μL of TGA in 100 mL of 0.1 M acetate buffer at an optimum pH solution. From the stock solution, working solutions of various concentrations were prepared through serial dilution using an acetate buffer of pH 6 each day.

3.2.3. Buffer preparation

Supporting electrolyte of 0.1M of (Sodium acetate and Acetic acid) in pH range 4 - 6.5 was Prepared from 0.1 M $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ (2.72 g) and 0.1 M CH_3COOH (60 μL) in distilled water and mix in 100 mL of volumetric flask. The drops of 0.1 M NaOH Solution were used to adjust the pH of the buffer solution. Distilled water was used to prepare all aqueous electrolyte solutions throughout the analysis.

3.2. Optimization of Experimental Parameters

3.2.1. Optimization of pH

The effect of pH on the voltammetric determination TGA at the Au electrode was studied. 1 μM of TGA was prepared in 0.1 M acetate buffer with different pH values (4 - 6.5) and the potential is scanned using CV with a scan rate of 100 mVs^{-1} and the oxidation currents of TGA were measured. The pH with the highest oxidation peak current was chosen for the subsequent electrochemical measurements.

3.2.2. Interference study

The utilization of the Au electrode for the determination of TGA was evaluated by studying the selectivity of the method for the determination of TGA. Various possible interfering species such as (0.1 mM of Thiourea (TU), 0.1 mM of sulfide (S^{2-}), and 0.1 mM SO_3^-) were added to the solution containing 10 μ M of TGA were added. Then the percent change in the oxidation current of TGA was calculated upon the addition of these interfering substances.

3.2.3. Real Sample preparation and Analysis

The practical application of the proposed sensor was evaluated by testing the TGA concentration in hair perm and hair conditioners. The concentration of TGA in the hair perm and hair conditioners was determined by LSV using the standard addition method. Hair perm and conditioners were purchased from a local cosmetics store and it was weighed. 0.25 g of the hair perm and shampoo was dissolved into a 25 mL volumetric flask separately, and diluted with acetate buffer then centrifuged. 5 μ L of the supernatant solution from each sample solution was taken to determine TGA under optimized conditions. The Triplicate of LSV was measured and the mean values were recorded.

Then electrochemical measurements were performed at the Au electrode. The recovery was also studied based on the formula in (equation). All samples and experiments were conducted at room temperature.

$$\% \text{Recovery} = \frac{\text{Concentration of spiked} - \text{Concentration of Un spiked}}{\text{Concentration of added amount}} \times 100$$

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.2. Electrochemical Behavior of TGA at GC, Pt, and Au Electrodes

The electrochemical behavior of 1 μM TGA was studied using CV in acetate buffer (pH-6) at bare GC, Pt, and Au electrodes and as shown in Figure 6. The oxidation peak of TGA was observed at about 1 V at the Au electrode and no clear oxidation peak is observed at both bare GC and Pt electrodes. The oxidation current response of TGA is much higher at the Au electrode than Pt and GC electrodes. This was because the immobilization of the thiol groups on the surface (Au-S bonding formation) can catalyze the oxidation of TGA at the Au electrode surface [51]. The inset Figure shows a comparison of Pt, GC & Au electrodes in Acetate buffer (in the blank) and no peak was observed at Pt and GC electrodes, but a small peak was observed at the Au electrodes, this is due to Au electrode has by nature the ability to form oxidation itself.

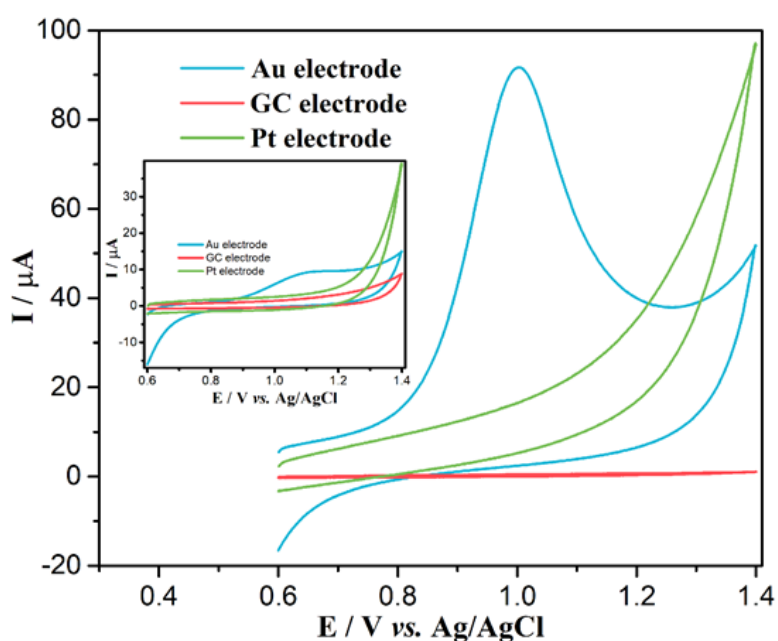


Figure 6: A CV response of TGA at GC, Pt, and Au electrodes in 0.1 M pH 6 acetate buffer. (The inset: CVs of GC, Pt, and Au electrodes in blank acetate buffer).

4.3. Optimization of Parameters for Determination of TGA

4.3.1. Optimization of pH of the supporting electrolyte

The pH of the supporting electrolyte is an important parameter that could have a significant influence on the response of the electrode in electro-analysis [52]. It was studied in the pH range of 4 to 6.5 in 0.1 M acetate buffer. As seen in Figure 7, the oxidation current of TGA was increased as the pH of the acetate buffer solution increased from pH 4 to 6. But further increase pH values after 6.5, the oxidation current of TGA decreased. Therefore, pH - 6 was taken as the optimal pH for the electro-analysis of TGA in acetate buffer.

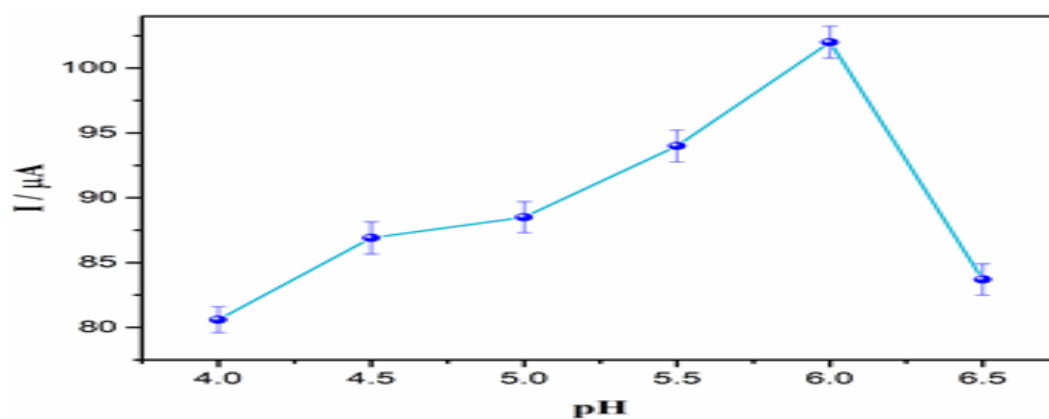


Figure 7: Effect of pH

4.3.2. Effect of scan rate

The scan rate of the experiment controls how fast the applied potential is scanned. It shows the reaction process at the electrode surface was either diffusion or not. The effect of scan rate on the electrochemical behavior of TGA was also investigated at different scan rates. A positive shifts of the peak potentials increases as the oxidation peak current increases with an increase in scan rate. LSVs corresponding to TGA oxidation was recorded at various scan rates ranging from 10 to 250 mVs^{-1} using $1\mu\text{M}$ TGA in acetate buffer (pH-6) at the Au electrode as shown in Figure 8. The anodic peak currents increase with increasing scan rates and are linearly correlated to the square root of scan rates with a regression equation of $I = 12 v^{1/2} - 22.7$ and correlation coefficient of ($R^2 = 0.988$), implying that the electrochemical process is diffusion controlled process [51-54], hence oxidation peak current was directly proportional to $v^{1/2}$.

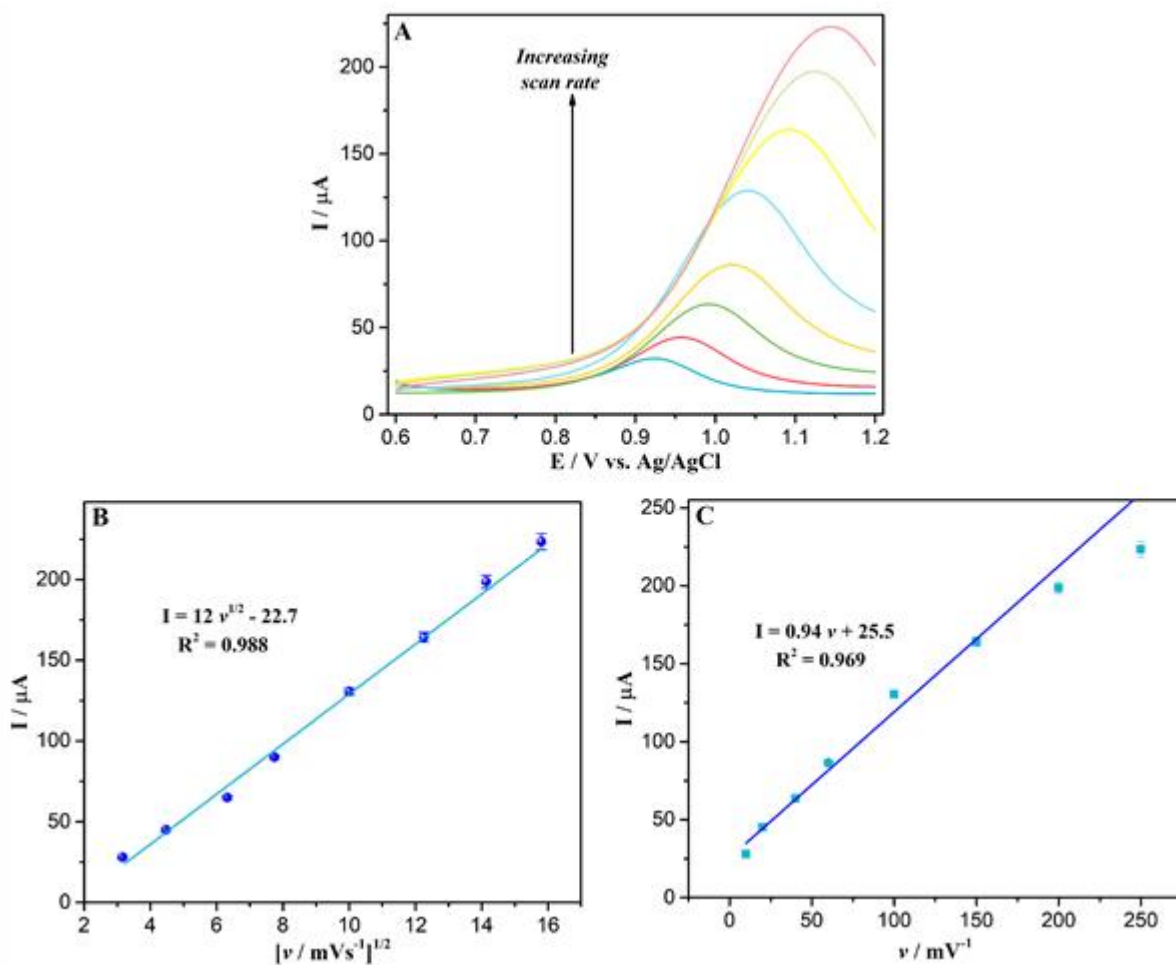


Figure 8:(A) LSVs of 1 μM TGA recorded at Au electrode in 0.1 M pH 6 acetate buffer with different scan rates (10,20,40,50,100,150,200 and 250 mV/s); (B) plot of I (μA) vs $v^{1/2}$ [mV/s] ; (C) plot of I (μA) vs v [mV/s].

4.3.3. Determination of TGA

The Au electrode exhibited a well-defined peak with reproducible peak current values for repetitive measurements using vary the concentration of TGA. As the concentration of TGA increased, the obtained oxidation peak of current was also increased [55]. The result revealed a linear relationship in ranges between 0.5 μM to 200 μM as shown in Figure 6. The obtained linear regression equation for TGA was I (μA) = 0.81 C_{TGA} (μM) + 12.5 ($R^2 = 0.997$). The detection limit was found to be 0.02 μM ($3\sigma/m$).

This shows the confirmation of Randles Sevcik equations means that peak current has a linear relationship with the concentration of the analytes.

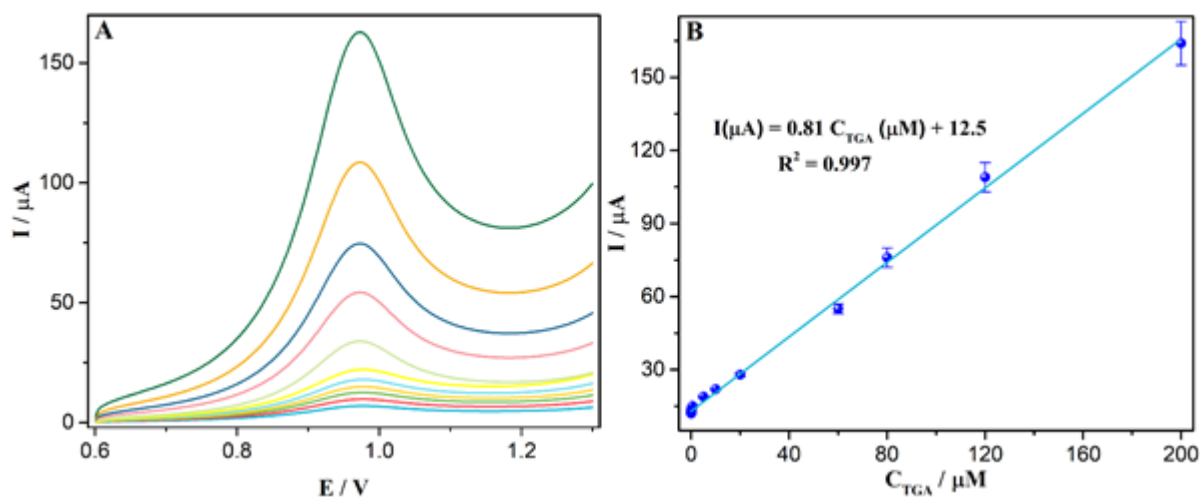


Figure 9: (A) LSVs recorded for the determination of the different concentration of TGA (from 0.5 μM- 200 μM); (B) the calibration curve (plots of I_{pa} vs C_{TGA})

4.4. Interference Study

To evaluate the applicability of the developed method the selectivity of the Au electrode for the determination of TGA, and the effect of possible interfering substances was studied under optimum conditions. Different interfering species (0.1 mM of Thiourea (TU), 0.1 mM of sulfide (S^{2-}), and 0.1 mM SO_3^-) were added to the solution containing 10 μM of TGA. The selected interfering species did not show significant interference for TGA determination (Figure 10). These indicate the high selectivity of the gold electrodes for the determination of TGA.

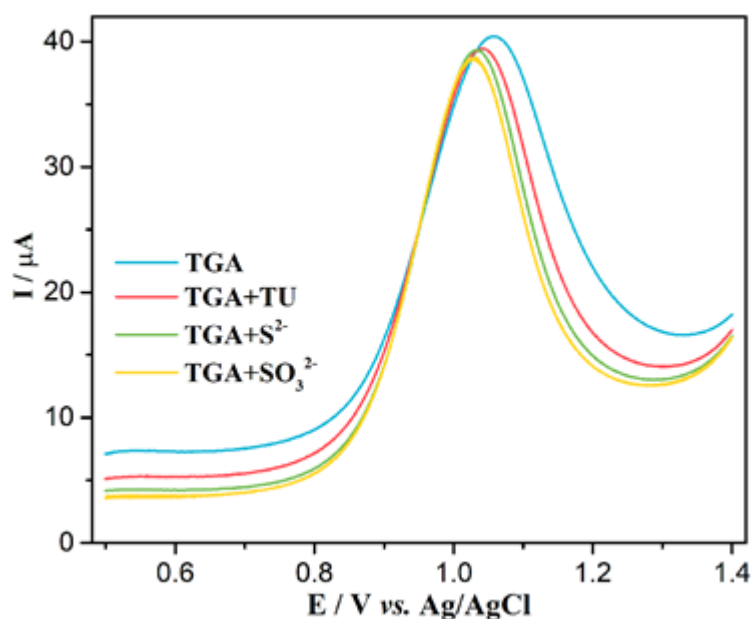


Figure 10: Effect of Interference

4.5. Real sample analysis

For the recovery studies, 5 μL of perm real samples were transferred into the electrochemical cell. The recovery was performed by spiking three different concentrations of TGA (5, 10, and 20 μM) to each sample. The resultant current peak of CV was obtained using the Au electrode. Table 1, shows the respective good recovery percentage for the determination of TGA in perm sample extracts in the range of 90 - 114% demonstrating the selectivity for the detection of TGA from complex sample matrices using an Au electrode.

Table 1: Determination Results of TGA in Real Sample.

| TGA added (μM) | TGA found (μM) | RSD % n=3 | % Recovery |
|-----------------------------|-----------------------------|--------------|------------|
| 0 | 0.09 | - | - |
| 5 | 4.5 | 6.3 | 90 |
| 10 | 11.4 | 6.8 | 114 |
| 20 | 19.43 | 3.18 | 97.15 |

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

In this work, the electrochemical determination of TGA was studied at the Au electrode for the first time. Under the optimized experimental conditions, the oxidation peak current of TGA at the Au electrode shows a good relationship with the concentration of TGA in the range of 0.5 μM to 200 μM and a limit of detection of 0.02 μM ($3\sigma/m$) than Pt and GCE. The electrode process is diffusion-controlled (hence, the square root of the scan rate has a linear relationship with the current). The method has exhibited very good electro-analytical properties such as high sensitivity, and a lower limit of detection. It was shown that the treatment procedure GC enhanced the oxidation peak current of TGA compared with the bare GC and Pt. This method was successfully applied to the determination of TGA in perm samples. Furthermore, the detection of TGA in hair perm agents and hair conditioners was accomplished with acceptable recoveries.

5.2. RECOMMENDATION

For further work to determining TGA; different analytical method development was necessary by using different parameters.

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