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Application of 1,6-Hexanedithiol and 1-Hexanethiol Self Assembled Monolayers on Polycrystalline Gold Electrode for Determination of Fe(II) Using Square Wave Voltammetry

Tuğba TABANLIGİL CALAM[1,*], Erdoğan HASDEMİR[2]

[1] Gazi University, Vocational High School of Science, Department of Chemistry Technology, 06374, Ankara, Turkey

[2]Gazi University, Faculty of Science, Department of Chemistry, 06500, Ankara, Turkey

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Abstract

1,6-hexanedithiol and 1-hexanethiol monolayer films modified polycrystalline gold electrodes were fabricated by using self assembled monolayer method. Modified electrodes used for electro-catalytic oxidations of iron(II). The calibration curves were obtained in the range of 5.00×10^{-8} - 3.85×10^{-5} mol.L^{-1} and 1.00×10^{-7} - 2.56×10^{-5} mol.L^{-1} at the Au-HDT and Au-HT, respectively. Detection limit of 1.6×10^{-8} mol.L^{-1} and 3.2×10^{-8} mol.L^{-1} for iron(II) at the Au-HDT and Au-HT, respectively. Validity of the method and applicability of the sensors are successfully tested by determining of Fe(II) in real samples such as drinking water and carob syrup samples.

1. INTRODUCTION

Iron is widely distributed in nature and it is an essential nutrient and is abundant in many mineral oxides. Iron exchanges with surface and ground waters through dissolution and precipitation [1]. Additionally, iron is an significant element in medicals, human physiology, industrials, environmental, and in many other biological systems [2]. It is well known that the deficiency of iron is one of the most common causes of anemia in human. On the other hand, excess of iron can cause several health implications such as an increased risk for heart diseases, cancer and other illnesses like arthritis, endocrine problems, liver disease and diabetes. [3, 4]. According to World Health Organization (WHO) and European legislation, the permissible limits for iron in drinking water are 2 mg L^{-1} and 0.2 mg L^{-1} respectively [5]. Therefore, it is essential to develop sensitive methods for quantitative estimation of trace levels of Fe in various matrices. Analytical methods developed determination of iron (II) ion. Iron can be determined by several methods such as voltammetry [10–13], flow-injection analysis [6–8], chromatography [9,10], spectrophotometric methods [11,12], spectrofluorescence quenching [13], capillary electrophoresis [14], controlled potential coulometry [15] and potentiometry [16,17]. Particularly, electrochemical methods commonly have features such as better analytical performance, lower price and simplicity in instrument that cause have further role in the present and future analysis areas [18]. Electrochemical method [6,19,20] has been identified as an extremely sensitive technique for iron determination due to its advantages of low cost, fast analysis speed, quick detection, portable instruments, high sensitivity and selectivity [21,22]. Especially, the methods developed based on chemical modification of the electrode surface [23] are interesting. Gold thiol self-assembled monolayers (SAMs) functionalized with appropriate groups have become versatile model systems for electrochemists in the last decade as they make possible electrode surface to be modified in a well-defined and reproducible way [24]. These organic nanometric interfaces [25] can have selective interaction

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*Corresponding author, e-mail: ttabanligil@gazi.edu.tr

with the metal ions in solution phase, due to the functional groups designed at the monolayer–electrolyte interface [26].

Alkanethiol and/or alkanedithiol molecules are frequently used in the formation of self-assembled monolayers (SAMs) on a substrate surface [27]. For this purpose, a wide range of metal surfaces is used as a substrate and the most commonly used electrodes are gold, silver, platinum and copper. In addition to electrodes, non-metallic surfaces can be used, as well [28-30]. The self assembled monolayers have conformal ultra thin films and high tunable surfaces which display a better mass transport, electrocatalysis and surface area for well sensitivity, selectivity and high detection ability [31]. They are suitable for immobilization of receptors and chemical functionality of the resulting surface can be varied by using thiol molecules with different functional groups [32-34].

In this work, polycrystalline gold electrodes modified with 1,6-hexanedithiol (HDT, $HS(CH_2)_6SH$) and 1-hexanethiol (HT, $CH_3(CH_2)_5SH$) were used in the fabrication of a sensitive voltammetric sensor (Au-HDT and Au-HT, respectively) for the determination of Fe(II). The detection limit of the electrode in determination of Fe(II) was able to reach nano-mole level by using square wave voltammetry (SWV). This current study aims to shed light on the redox behaviour of Fe(II) for its voltammetric analysis on the Au-HDT and Au-HT. Therefore, a simple, rapid, sensitive and validated procedure was examined and successfully used for the determination of Fe(II) in drinking water and carob syrup samples.

2. EXPERIMENTAL

2.1. Reagents and chemicals

1,6-hexanedithiol (96%), 1-hexanethiol (95%), $FeCl_2$ and absolute ethanol were purchased from Sigma Aldrich. All chemicals were analytical grade and were used as received. All the test solutions were deaerated by passing high purity argon (99.999%) before the electrochemical experiment. During the experiments, argon gas was passed over the surface of the test solutions in order to avoid the reentrance of oxygen into the solution. All experiments were carried out at room temperature (25±1 °C). Stock solutions of Fe(II) (1×10^{-3} M) was prepared daily by dissolving of $FeCl_2$ in 0.01 M hydrochloric acid solution.

2.2. Preparation of Au-HDT and Au-HT electrodes

Firstly, the bare gold electrodes were kept in Piranha solution (1:3, v/v; 30% H_2O_2 and concentrated H_2SO_4) for 10 minutes and rinsed carefully with pure water. Then, the electrodes were polished with 0.3 and 0.05 μm alumina slurry on a polishing cloth (Buehler®), rinsed with water and sonicated in water and ethanol each step 15 minutes, pespectively. The polished Au electrode was then electrochemically cleaned by cycling the potential between -0.2 and +1.6 V in 0.5 M H_2SO_4 at the scan rate of 100 mVs^{-1} for about 20 min or until the cyclic voltammogram characteristics for a clean gold electrode was obtained [35]. The monolayers of HDT and HT were prepared on Au electrodes by immersing a clean polycrystalline Au electrodes into 10 mM ethanolic solution, separately, for 3 h.

2.3. Electrochemical measurements

CV and SWV experiments were performed using an Electrochemical Work Station CHI 660B electroanalyzer. The measurements were performed in a three-electrode system that including a polycrystalline gold disc electrode (1.6 mm diameter, BAS MF-2014) as working electrode. A Pt wire counter electrode was used in all voltammetric measurements. The reference electrode was an Ag/AgCl/KCl (sat.) used in aqueous media. The measurements were performed at room temperature (25±1 °C).

3. RESULT AND DISCUSSION

3.1. Calibration and analytical application

3.1.1. Influences of the electrolyte solutions and pH

Various acidic electrolyte solutions were tested. Solutions including nitric, chloric, perchloric and sulphuric acid were tested as an electrolyte medium by using the SWV technique. The pH of the acidic mediums was adjusted to 2.0. The results showed that the utilisation of nitric acid and chloric acid was inconvenient due to the less sensitive and reproducible current responses. It was found that the peak shapes and heights in the sulphuric acid and perchloric acid solutions were better defined and slightly higher compared to nitric acid and chloric acid (Fig. 1). Among these solutions, the sulphuric acid and perchloric acid were found to be the best suited medium for Au-HDT and Au-HT, respectively.

It is well known that pH is one of the variables which commonly and strongly influence the shapes of voltammograms, and therefore it is very important to investigate the effect of pH on electrochemical systems [36]. The influence of pH on the detection of Fe(II) in the pH range from 1.0 to 4.0 (1.0, 2.0, 2.5, 3.0, 4.0) on the Au-HDT and Au-HT was also studied. The obtained results graphically were depicted in Fig. 2. The anodic peak currents of Fe(II) increased with decreasing pH of the solution, and reached the maximum value at pH 1.0 (Fig. 2). However, the resulting oxidation peak does not have a usable peak shape at pH 1.0. Because the optimum results for the Au-HDT and Au-HT electrodes were obtained at pH 2.0 in H_2SO_4 and at pH 2.0 in $HClO_4$, respectively. This medium was consequently selected for further analytical studies.

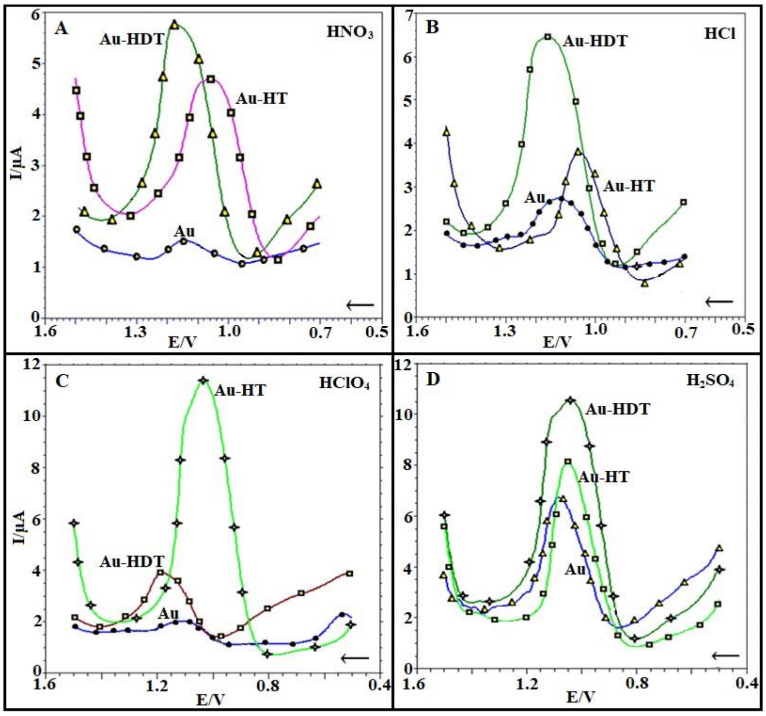

Figure 1. *Square wave voltammograms of bare Au, Au-HDT and Au-HT electrodes at pH 2 in (A) HNO_3, (B) HCl, (C) $HClO_4$ and (D) H_2SO_4 solutions containing $1.5x10^{-5}$ M Fe(II).*

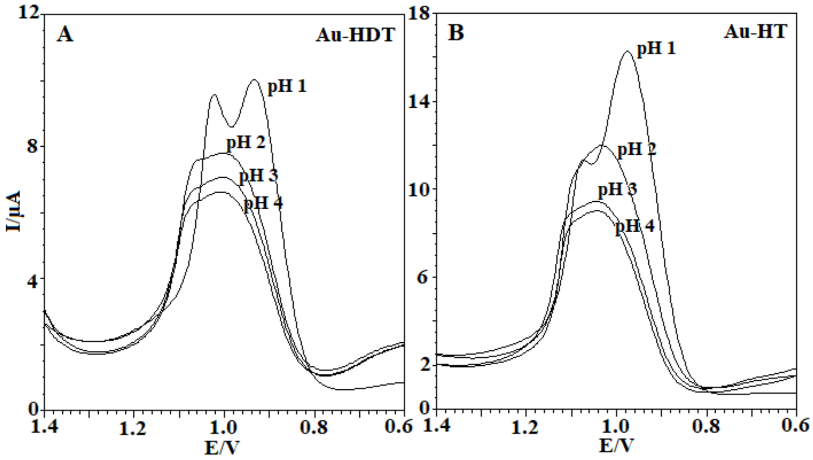

Figure 2. Square wave voltammograms of (A) show that Au-HDT electrode at pH 1.0, 2.0, 3.0, 4.0 in H_2SO_4 *and (B) show that Au-HT electrode* $HClO_4$ *at pH 1.0, 2.0, 3.0, 4.0.*

3.1.2. SWV of behavior of Fe(II)

A SWV was used to investigate the oxidation behavior of Fe(II). Fig. 3 shows the electrochemical responses obtained at the surface of bare Au, Au-HDT and Au-HT at pH 2 in H_2SO_4 and at pH 2 in $HClO_4$ solutions. As shown in Fig. 3, the anodic peak potentials of Fe(II) were observed at about +1.08, +1.16, +1.06 V at bare Au, Au-HDT and Au-HT at pH 2 in H_2SO_4, respectively. Additionally, the anodic peak potentials of Fe(II) were observed at about +1.10, +1.17, +1.03 V at bare Au, Au-HDT and Au-HT at pH 2 in $HClO_4$, respectively. According to the anodic peak currents of Fe(II) at the bare Au, Au-HDT and Au-HT, the highest peak current in the H_2SO_4 solution was observed at the Au-HDT electrode. The highest peak current in the $HClO_4$ solution was observed at the Au-HT electrode.

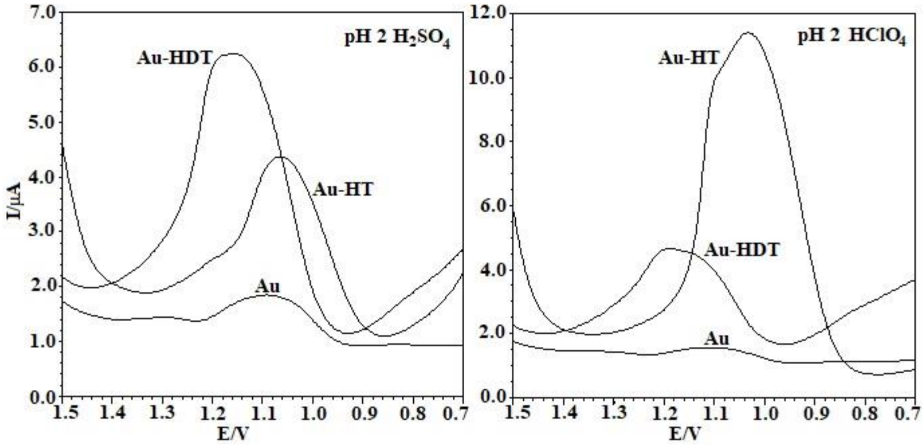

Figure 3. Square wave voltammograms of bare Au, Au-HDT and Au-HT electrodes at pH 2 in H_2SO_4 *and at pH 2 in* $HClO_4$ *solutions containing 1.5x*10^{-4} *M Fe(II). SWV conditions: pulse amplitude, 25 mV, frequency, 5 Hz, step potential, 4mV.*

3.1.3. The effect of scan rates on oxidation of Fe(II) on Au-HTs SAMs electrodes

The effect of scan rates (ν) on oxidation peak currents of 4.0×10^{-4} M Fe(II) on the Au-HDT and Au-HT surfaces were investigated in the range of 10 to 1000 mV s^{-1} (Fig. 4). It was noticed that the oxidation peak became wider at higher scan rates. Furthermore it was found that the peak potential shifted to more positive values.

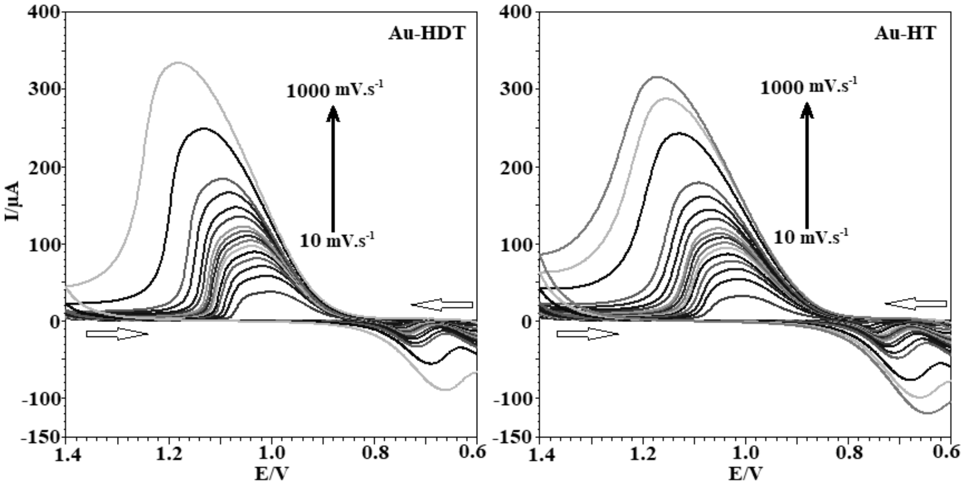

Figure 4. *Cyclic voltammograms of* 4.0×10^{-4} *M Fe(II) on Au-HDT electrode at pH 2.0 in* H_2SO_4 *and Au-HT electrode at pH 2.0 in* $HClO_4$ *with different scan rates. (1)–(18) were 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 200, 250, 500, 750 and 1000 mV s-*^{1}.

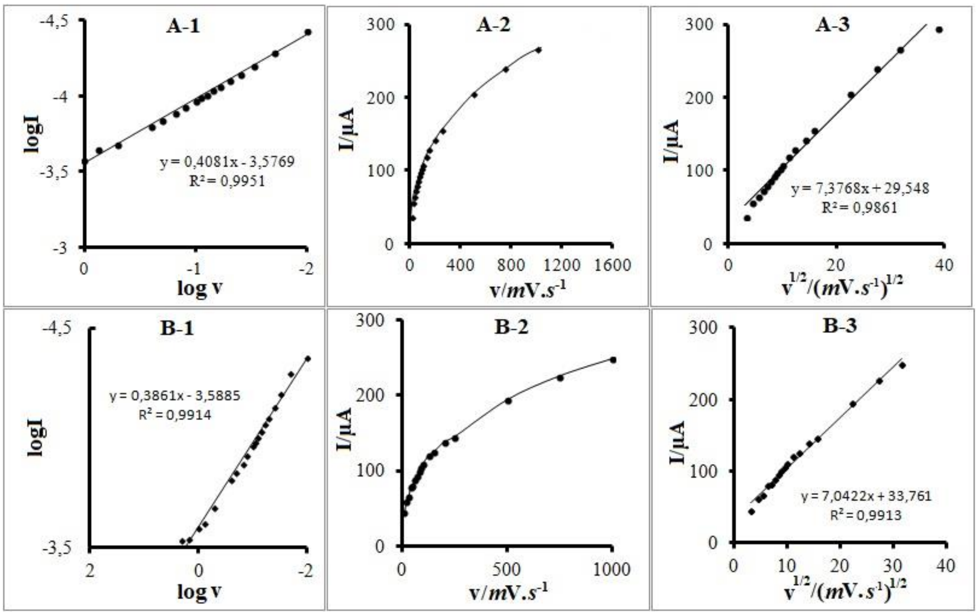

Figure 5. *CVs of* 4.0×10^{-4} *M Fe(II) at pH 2.0 in* H_2SO_4 *and at pH 2.0 in* $HClO_4$ *with different scan rates. (1)–(18) were 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 200, 250, 500, 750 and 1000 mV.s-*^{1}*, respectively. A and B demonstrate graphics of Au-HDT and Au-HT, respectively.*
A-1 and B-1 show the plots of log I vs. log v.
A-2 and B-2 show the plots of I vs. v.
A-3 and B-3show thep plot of I vs $v^{1/2}$.

The effect of scan rate on the electrochemical responses of 4.0×10^{-4} M Fe(II) at the Au-HDT was studied by CV (Fig. 5A). In the case of the slopes of the curve logI versus log*v* are 0.4081 and 0.3861 at the Au-HDT and Au-HT modified electrodes in Fig. 5A-1 and Fig. 5.B-1 respectively. Because slope values were found close to the theoretical value of 0.5, which is expected for an ideal reaction of solution species, the oxidation reaction of Fe(II) at the modified electrodes is a typical diffusion-controlled process. [37, 38]. If the plot of log I versus log v yielded a slope value which was between the theoretical value of 0.5 and 1, this situation indicate that the electrode reaction might be a mixed adsorption-diffusion control electrode process.

Fig. 5A-2 and Fig. 5B-2 show a nonlinear dependence of anodic peak current of the oxidation reaction of Fe(II) at the Au-HDT and Au-HT electrodes, respectively on the scan rates. This behavior suggests a diffusion-controlled process [39].

As demonstrated in Fig. 5A-3, the anodic peak current of Fe(II) increases linearly with the square root of scan rate ($v^{1/2}$) over the range of 10–1000 mV.s^{-1} (I(µA)= 7.3768 $v^{1/2}$ + 29.5480, R^2 = 0.9861). The anodic peak current of Fe(II) increases linearly with the square root of scan rate ($v^{1/2}$) over the range of 10–1000 mV s^{-1} (I(µA)= 7.0422 $v^{1/2}$ + 33.761, R^2 = 0.9913) at the Au-HT in Fig. 5B-3.

All these results indicate that the oxidation reaction of Fe(II) on the Au-HDT and Au-HT SAM modified electrodes are diffusion-controlled processes [40].

3.1.4. Calibration curve and detection limit

Calibration was performed for the determination of Fe(II) at pH 2.0 in H_2SO_4 and at pH 2.0 in $HClO_4$ at the Au-HDT and Au-HT, respectively, containing 5x10^{-3} M KCl solution. Fig. 6 presents square wave voltammograms obtained by successive additions of Fe(II) over the 0.05–38.50 µM concentration range at the Au-HDT modified electrode. The peak current at a potential of +0.95V increased proportionally with the Fe(II) concentration (Fig. 6, inset) to yield a highly linear calibration plot, I(µA) = 8.0391C(µM)–0.0255 (R^2 = 0.9998). At the Au-HT electrode, the SWV responses (Fig. 7) at a potential of +0.94 V showed that the dependence of peak currents on the Fe(II) concentration was linear, in the range of concentration from 0.10 to 25.60 µM. The linear regression equations was expressed as I(µA) = 9.3732C(µM)–2.0525 (R^2 = 0.9954).

The sensitivity of the proposed method was evaluated both the limit of detection (LOD) and limit of quantification (LOQ) values. The LOD and LOQ were calculated using the following equations [41]:

$$LOD = \frac{3s}{m}; \quad LOQ = \frac{10s}{m}$$

where s is the standard deviation of the peak current (five runs) of the lowest concentration of the linearity range (0.05 µM) and m is the slope of the related calibration equation. Using Au-HDT modified electrodes, LOD and LOQ were calculated as 0.016 µM and 0.053 µM, respectively. In addition, LOD and LOQ were calculated as 0.032 µM and 0.107 µM by using Au-HT electrodes, respectively. Table 1 shows the analysis results of the statistical analysis of the experimental data.

Table 1. *Analysis results for Fe(II) obtained by SWV method Au-HDT and Au-HT modified electrodes.*

Parameters	Values	
	Au-HDT	Au-HT
Concentration range (µmol L^{-1})	0.05-38.50	0.10-25.60
LOD (µmol L^{-1})	0.016	0.032
LOQ (µmol L^{-1})	0.053	0.107
Slope (µA L µmol^{-1})	8.0391	9.3732
R.S.D. %	1.01	4.38
Correlation coefficient (r)	0.9998	0.9954
Number of measurements	5	5

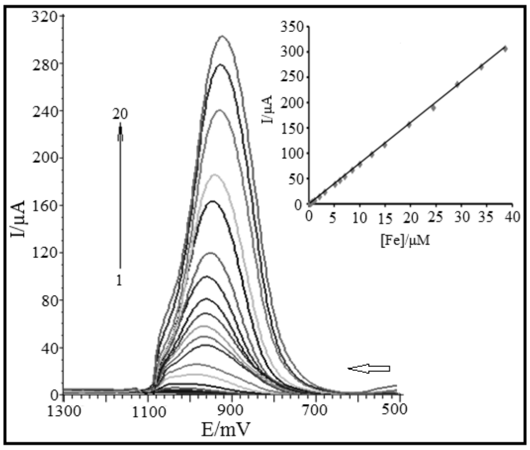

Figure 6. *(A) Square wave voltammograms of Fe(II) at the Au-HDT SAM electrode at pH 2 in H_2SO_4 solution. Fe(II) concentration (1 to 20) 0.00, 0.05, 0.20, 0.35, 0.60, 1.00, 2.00, 3.00, 5.00, 5.96, 6.95, 8.43, 9.90, 12.30, 14.30, 19.60, 24.40, 29.10, 33.80, 38.50 μmol.L^{-1} Fe(II). (B) The calibration curves are also given for lower and upper ranges. The signals are corrected for background (blank) currents.*

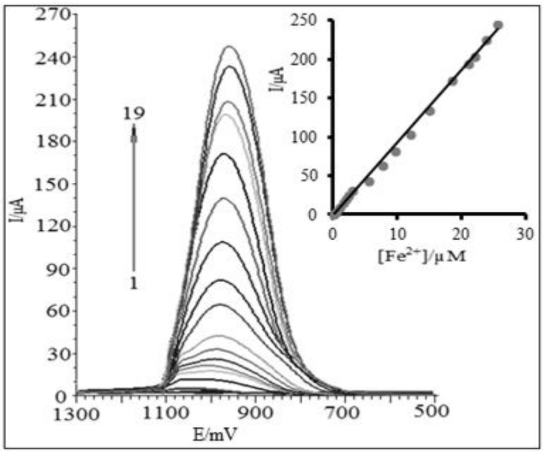

Figure 7. *(A) Square wave voltammograms of Fe(II) at the Au-HT SAM electrode at pH 2 in $HClO_4$ solution. Fe(II) concentration (1 to 19) 0.00, 0.10, 0.30, 0.40, 1.00, 1.48, 1.96, 2.44, 2.91, 6.77, 8.69, 10.06, 12.50, 15.34, 19.1, 20.97, 21.90, 23.76, 25.62 μmol.L^{-1} Fe(II). (B) The calibration curves are also given for lower and upper ranges. The signals are corrected for background (blank) currents.*

3.1.5. Influence of some coexistent ions

In order to evaluate the selectivity of the modified electrode, some common heavy metal cations were tested under optimized conditions. The effects of Ni^{2+}, Cu^{2+}, Hg^{2+}, Ag^{+}, Co^{2+}, Mn^{2+}, Sn^{2+} were studied by recording the current responses of 5 μM Fe(II) using SWV technique. In the presence of Fe(II), the results show that the tolerable concentration ratios with respect to 5 μM Fe(II) are 200-fold for Hg^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Ag^{+}, 5-fold Cu^{2+} and 10-fold Sn^{2+} the determination gives an error less than ±5.0% at pH 2 in H_2SO_4 solution on the Au-HDT modified electrode and 200-fold for Hg^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, 50-fold for Ag^{+}, 3-fold Cu^{2+} and 5-fold Sn^{2+} the determination gives an error less than ±5.0% at pH 2 in $HClO_4$ solution on the Au-HT modified electrode.

3.1.6. Repeatability and Reproducibility

The repeatability and reproducibility of Au-HDT and Au-HT were measured to evaluate this electrode's sensing performance. The repeatability of the modified electrode was evaluated by measuring the Fe(II) ($6.95x10^{-6}$ M) in H_2SO_4 and $HClO_4$ (pH 2) solutions at the same electrode on the same day, respectively [42]. The relative standard deviation (RSD) of the five repeated measurements were 1.01% and 4.38%. The reproducibility of the Au-HDT and Au-HT were calculated for the Fe(II) ($6.95x10^{-6}$ M) signal obtained by five different electrodes on the same day. The RSD value of reproducibility were calculated to be 2.14% indicating that the fabrication procedure was reliable.

3.1.7. Application to real sample

The possibility of using Au-HTs SAMs electrodes for the determination of Fe(II) in real samples, drinking water and carob syrup samples were tested. Here, the SWV technique was used in the experiments. The possibility of using Au-HTs SAMs electrodes for the determination of Fe(II) in the real samples, drinking water and carob syrup samples were tested and the results werelisted in the Table 2. From these results, it shows that the Au-HTs SAMs electrode shows good catalytic activity for real sample analysis and the obtained recoveries were satisfactory. Additionally, Statistical evaluations of the level of the significance difference were shown in Table 2, in which the calculated t values are all less than the critical value of t (the confidence coefficient 95%). The results of the statistical evaluations indicated that the proposed method showed a good agreement with label values. For real samples analysis, intra-day and inter-day precisions were given. The RSD (n = 5, intra-day) for 8.52 × 10^{-6} mol L^{-1} Fe(II) were calculated as 1.31% and 2.66%, and inter-day precision (n = 5) was also calculated as 1.56% and 4.15% for 8.52 × 10^{-6} mol L^{-1} Fe(II) in drinking water at Au-HDT and Au-HT, respectively. For carob syrup, the RSD (n = 5, intra-day) for 4.60 × 10^{-6} mol L^{-1} Fe(II) was calculated as 0.88% and 1.76%, and inter-day precision (n = 5) was also calculated as 3.57% and 3.33% for 4.60 × 10^{-6} mol L^{-1} Fe(II) at Au-HDT and Au-HT, respectively. Which shows that the proposed method has good precision.

Table 2. *Determination results and statistical evaluation of Fe(II) in drinking water and carob syrup by the Au-HDT and Au-HT SAM electrodes*

Samples		Added (µM)	Found[a] (µM)		RSD%		Critical value of t[b]	Calculated value of t	
			Au-HDT	Au-HT	Au-HDT	Au-HT		Au-HDT	Au-HT
Drinking water	intra-day	8.52	8.40±0.11	8.65±0.23	1.31	2.66	2.78	-1.68	1.16
	Inter-day	8.52	8.36±0.13	8.68±0.36	1.56	4.15	2.78	-2.75	0.99
Carob syrup	intra-day	4.60	4.54±0.04	4.55±0.08	0.88	1.76	2.78	-2.24	-1.24
	Inter-day	4.60	4.48±0.16	4.50±0.15	3.57	3.33	2.78	-1.68	-1.49

[a] n=5

[b] The confidence coefficient 95%.

To reveal the performance of the present method on the basis of its working concentration ranges and detection limit, it was compared with some other methods reported in the literature for Fe(II) determination, and the results were presented in Table 3. The electrochemical methods showed relatively superior performances, such as cheap instrument, simple procedure, low testing cost, a good working concentration range and relatively lower detection limit without using chelating agents. Above all, the Au-HDT and Au-HT SAM electrodes may be a good choice for Fe(II) determination.

Table 3. *Comparison of proposed method with the reported data for Fe(II) determination.*

Reference No.	Detection limit (µmol L^{-1})	Working concentration range of Fe(II) (µmol L^{-1})	Methodes	Electrodes
43	0.270	0.89-895	DPV*	Hanging mercury drop electrode
44	0.036	0.10-1.6	DPV*	Carbon paste electrode
45	0.039	0.078-1.4	CV	Multiwalled carbon nanotubes

46	0.0005	0.001-10	ASDPV**	Carbon paste electrode
47	0.027	1-100	ASDPV**	Glassy carbon electrode
This work:	0.016	0.05-38.50	SWV	Au-HDT
This work:	0.032	0.10-25.60	SWV	Au-HT

*Differential pulse voltammetry

**Anodic stripping differential pulse voltammetry

4. CONCLUSIONS

The Au-HDT and Au-HT modified electrodes were fabricated and employed for determination of Fe(II) by using SWV. The analytical conditions such as pH and type of electrolyte were studied. The SWV oxidation peak potential of the iron ion was found around +1.0 V enabling the quantitative determination of Fe(II) in the range of 5×10^{-8} mol L^{-1} to 3.85×10^{-5} mol L^{-1} and 1×10^{-7} mol L^{-1} to 2.56×10^{-5} mol L^{-1} of Fe(II) at the Au-HDT and Au-HT modified electrodes, respectively. The proposed electrode was evaluated by RSD in drinking water and carob syrup samples for Fe(II). The intra-day and inter-day precisions of the DPV method were analyzed and showed relative standard deviations lower than 5%. These modified electrodes were proved to be of high sensitivity and fabrication reproducibility in real analyses.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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