Investigation of Electrochemical Behavior of Hydrazine with Alizarin as a Mediator on Glassy Carbon Electrode

Mohammad Mazloum Ardakani [1,*], Mohammad Ali Karimi[2,3], Mohammad Mahdi Zare[2],
Sayed Mahdi Mirdehghan[2]

[1]Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran
[2]Department of Chemistry, Payam Noor University, Ardakan Center, Ardakan, Iran
[3]Department of Chemistry, Payam Noor University, Sirjan Center, Sirjan, Iran
[*]E-mail: mazloum@yazduni.ac.ir

The anodic oxidation of hydrazine has been studied on a glassy carbon electrode by electrocatalytic effect of alizarin as a homogenous mediator at 0.1 M concentration of phosphate buffer (pH=6). Using linear sweep voltammetry study showed that, the catalytic current of this system depends on the concentration of hydrazine. The catalytic peak current obtained, was linearly dependent on the hydrazine concentration in the ranges of 10-800 μM and the detection limit was 4.6 μM by linear sweep voltammetry. The magnitude of the peak current for alizarin increased severely in the presence of hydrazine, and proportional to concentration of hydrazine. The diffusion coefficient of hydrazine was estimated using chronoamperometry. This method also were used for determine the catalytic rate constant at catalytic reaction between alizarin and hydrazine. The experimental results showed that the peak current varied in the presence of different metal cations, but these effects were omitted in the presence of EDTA, while almost all of anions had no effect on the peak current of hydrazine. The importance of the technique is its ability to electrocatalytic determination of hydrazine with alizarin as homogenous electrocatalyst, while it does not need to prepare as for modified electrode. The independency of this method from the interferences, and its ability at removing the effect of most cationic interferences easily are the features of the technique.

Keywords: Hydrazine, modified electrodes, glassy carbon electrode, mediator

1. INTRODUCTION

Hydrazine is a highly reactive base and reducing agent. Its primary uses are as a high energy rocket propellant, as a reactant in military fuel cells, in nickel plating in the polymerization of urethane, for removal of halogens form waste water, as an oxygen scavenger in boiler feed water to inhibit corrosion, and in photographic development. Hydrazine was historically used experimentally as

a therapeutic agent in the treatment of tuberculosis, sickle cell anemia, and non-specific chronic illnesses [1].

Hydrazine is highly toxic and dangerously unstable, especially in the anhydrous form. Symptoms of acute exposure to high levels of hydrazine may include irritation of the eyes, nose, and throat, dizziness, headache, nausea, pulmonary edema, seizures, and coma in humans. Acute exposure can also damage the liver, kidneys, and central nervous system in humans. The liquid is corrosive and may produce dermatitis from skin contact in humans and animals. Effects to the lungs, liver, spleen, and thyroid have been reported in animals chronically exposed to hydrazine via inhalation. Increased incidences of lung, nasal cavity, and liver tumors have been observed in rodents exposed to hydrazine. Therefore, the determination of hydrazine is of practical importance [1-3].

Determination of hydrazine carried out by spectrophotometry [4], gas chromatography(GC) [5], coulometry [6], titrimetry [7], amperometry [8,9], voltammetry, and by some electrodes including, ion selective electrodes [10].

Hydrazine compound have a large oxidation overpotential at ordinary carbon electrodes and one approach for minimizing overvoltage effects is through the use of electrocatalytic process at chemically modified electrodes (CMEs) [11], electrochemically glassy carbon electrodes [12], carbon paste containing cobalt phthalocyanines [13], and inorganic mixed oxidation state Prussian blue [14,15].

In this paper, we described initially the response and suitability of an alizarin as a new homogenous mediator in the electrocatalysis and determination of hydrazine in an aqueous buffer solution, and then we evaluated the analytical performance of the homogenous electrocatalyst in quantification of hydrazine.

2. EXPERIMENTAL PART

2.1. Reagents

Alizarin (1, 2-dihydroxyanthraquinone, $C_{14} H_8 O_4$) and hydrazine were obtained from Merck and used as received. All solutions were prepared from analytical reagent grade chemicals and were used as received from the suppliers without further purification and by using doubly distilled water. Hydrazine and Alizarin solution were freshly prepared just prior to use and all experiments were carried out at ambient temperature. Phosphate buffer (0.1 M, pH = 6.0) was used for optimum measurements. Phosphoric acid and sodium hydroxide were used for increasing and decreasing the pH of the buffer.

2.2. Apparatus

The electrochemical experiments were performed using an AUTO LAB PGSTAT 302, potentiostat / galvanostat (Eco Chemie Utrecht, Netherlands) connected to a 125 mL three-electrode cell (from ACE glass incorporated), equipped with GPES 4.9.006 software. A personal computer for data acquisition and potential control also was used for electrochemical measurements.

The cell configuration contained a glassy carbon disk electrode (PINE AFE2M050) with a diameter of 5.0 mm as a working electrode, a Pt wire directly immersed in the solution, as auxiliary electrode and a silver / silver chloride electrode as reference electrode. All potentials were reported with respect to this reference electrode. A Metrohm 781 pH / ion meter was also used for pH measurements.
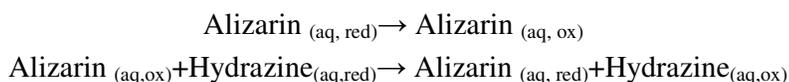
2.3. Procedure

The glassy carbon electrode surface was first polished with 0.05 µm alumina powder in a water slurry using a polishing cloth until the electrode surfaces had a mirror-finish and then rinsed thoroughly with double distilled water successively.

To prepare a blank solution, 4.0 mL of buffer solution, 1.0 mL of alizarin into a 10 mL volumetric flask. The solution was diluted to the mark with water. Then the solution was transferred into the electrochemical cell. The solution was diluted to the mark with water. Then the solution was transferred into the electrochemical cell. The initial and final potentials were adjusted to 0.0 V and +0.8 V vs. Ag / AgCl, respectively, with a scan rate of 250 mVs^{-1}. The same experiment was repeated with the presence of hydrazine as a sample. The cyclic voltammograms blank and sample solutions give the blank signal (I_b) and analytical signal (I_s). The difference between the blank and analytical signal ($\Delta I_p = I_s - I_b$), was proportional to hydrazine concentration. Calibration graphs were obtained by plotting the net peak current (ΔI_p) against standard concentration of hydrazine.

3. RESULTS AND DISCUSSION

The catalytic oxidation of hydrazine at the presence of alizarin can be seen clearly in Fig.1. The cyclic voltammetric responses of a bare glassy carbon electrode in a 0.1 M phosphate buffer solution (pH = 6.0), without and with hydrazine, are shown in Fig. 1 (curve a and curve b) respectively. At a bare glassy carbon electrode, the electrooxidation of hydrazine requires a large overpotential. The cyclic voltammetric behavior of alizarin on the glassy carbon electrode in a hydrazine free electrolyte is also shown in Fig.1 (curve c). However, the catalytic oxidation of hydrazine at the presence of alizarin can be seen clearly in Fig. 1 (curve d). The alizarin peak current increases sharply in the presence of hydrazine, and the peak potential of alizarin is in lower potential than that of a hydrazine. Therefore, alizarin was considered as a suitable homogenous electrocatalyst for hydrazine by electrochemical determination.

The electrochemical method for determination of hydrazine is based on the following sequence of reactions:
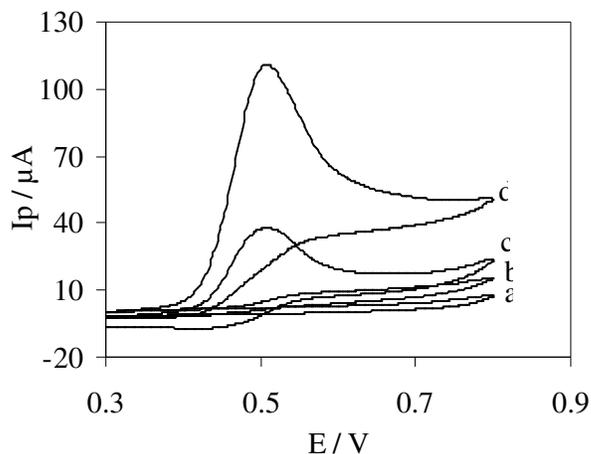
$$\text{Alizarin }_{(aq, red)} \rightarrow \text{Alizarin }_{(aq, ox)}$$
$$\text{Alizarin }_{(aq,ox)} + \text{Hydrazine}_{(aq,red)} \rightarrow \text{Alizarin }_{(aq, red)} + \text{Hydrazine}_{(aq,ox)}$$

Figure 1. Cyclic Voltammograms of a solution containing reactants of a glassy carbon electrode with a scan rate of 250 mVs^{-1} in 0.1M phosphate buffer (pH 6.0); the buffer solution (a): in the absence of hydrazine; (b): in the presence of 0.10 mM hydrazine; (c): in the presence of 0.20 mM alizarin; and (d): in the presence of 0.10 mM hydrazine and 0.10 mM alizarin.
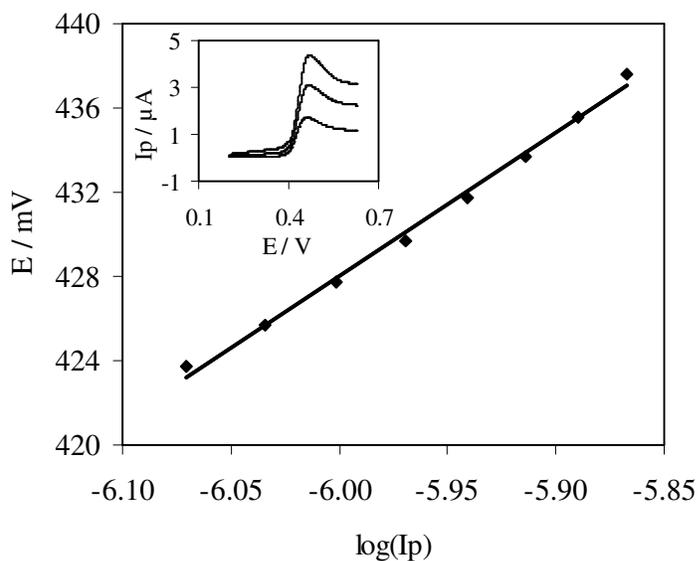

Figure 2. A Tafel plot at pH 6.0; 0.2 mM alizarin, with a scan rate of 1 mV/s. Inset show the linear sweep voltammogram.

The mechanism of hydrazine depends mainly on the condition of the electrolyte solution and the nature of the electrodes. The main difficulty in determining the exact mechanism is identification of intermediate in the oxidation process [16]. The anodic oxidation of hydrazine in aqueous solution

has been studied extensively on several electrodes. In aqueous solution hydrazine is oxidized mainly through a four-electron process with the final product N_2 [16]:

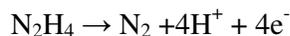$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^-$$

Fig.2 inset shows the linear sweep voltammogram for the blank containing alizarin only in 0.1 M phosphate buffer solution (pH=6.0), at scan rate of 1 mVs[-1]. The points show the rising part of voltammogram which is known as Tafel region and is affected by electron transfer kinetics between hydrazine and alizarin, assuming the deprotonation of hydrazine as a sufficiently fast step. In order to get information on the rate determining step a slope of 67.98 mV decade[-1] is obtained indicating that the process follow one electron transfer in rate determining step assuming a transfer coefficient of $\alpha = 0.6$ [17].

3.1. Influence of variables

The influence of chemical variables such as pH, alizarin concentration, and scan rate on sensitivity was studied.

The results showed that the pH affects the electrochemical behavior of alizarin and also hydrazine activity. From Fig.3, it can be seen that the pH value of buffer medium has an important effect on the efficiency of the electrocatalytic oxidation of hydrazine. We found that in the pH 6.0, the best results were obtained, so this medium was chosen for the following experiments.
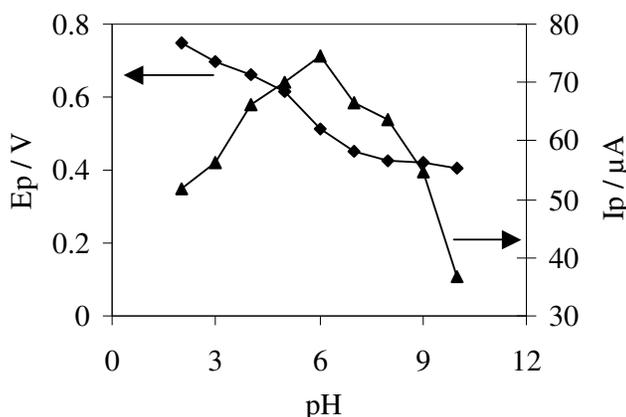

Figure 3. Effect of pH on the peak current and peak potential; conditions: 0.10 mM hydrazine; 0.20 mM alizarin; scan rate of 250 mV/s; potential range of +0.30 to +0.74 V vs. silver-silver chloride electrode.

Fig.4 shows the effect of pH on the electrocatalytic oxidation of hydrazine at glassy carbon electrode in the presence of 0.2 mmol L^{-1} alizarin. The peak current increased with increasing pH from 3.0 to 7.0, and then decreased for higher pH values. However the higher peak current and better shape of the voltammogram of the peak at pH 6.0 suggested it as optimal pH value for the purpose.
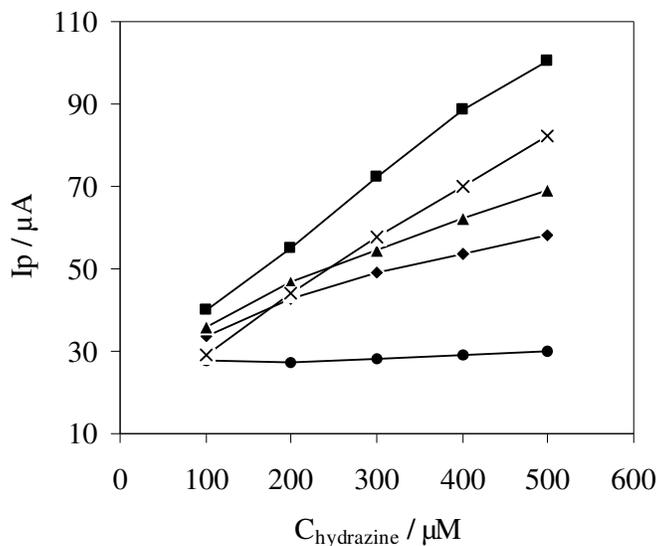
Figure 4. Influence of pH on the electrooxidation of different hydrazine concentrations (0.10, 0.20, 0.30, 0.40, 0.50 mM) at a glassy carbon electrode. Conditions: 0.20 mM alizarin red s; scan rate of 250 mVs^{-1}; potential range of +0.30 to +0.74 V vs. silver-silver chloride electrode; pH values are ($\bullet$) 3.0, ($\blacklozenge$) 4.0, ($\blacktriangle$) 5.0, ($\blacksquare$) 6.0 and ($\times$) 7.0.

The influence of alizarin concentration on the peak currents was studied for the range of 10.0 to 600 µM alizarin concentration, in the solutions containing different concentrations of hydrazine at pH 6.0 (Fig. 5). The results showed that by increasing alizarin concentration up to 200 µM the peak current increased, whereas higher concentration of alizarin caused a slight decrease on the magnitude of peak current, due to the formation of alizarin aggregation. Therefore, 200 µM alizarin concentrations were selected as the optimal mediator concentration.
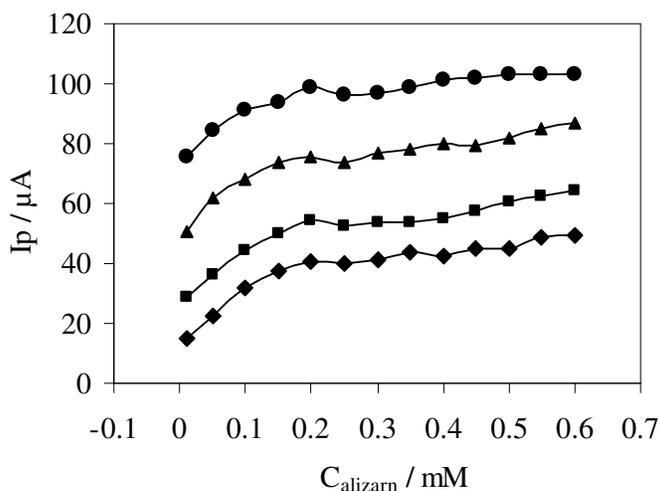

Figure 5. Effect of alizarin concentration on the peak current. Conditions: Hydrazine concentration ($\bullet$) 0.1, ($\blacklozenge$) 0.2, ($\blacktriangle$) 0.3 and ($\blacksquare$) 0.4 mM; pH of 6.0; at 250 mV s^{-1}.

The scan rate dependence of cyclic voltammograms for the glassy carbon electrode in 0.1 M phosphate buffer solution containing 0.20 mM alizarin and different concentrations of hydrazine (not shown) was used to get the information about the rate determining step. Fig.6, curves a-c, shows that a plot of the anodic peak current versus the square root of the sweep rate is linear. From the slope of the I_p versus $\upsilon^{1/2}$ plot, can be obtained the number of electrons in the overall reaction. According to the following equation for a totally irreversible diffusion controlled processes [18]:

$$I_p = 3.01 \times 10^5 \, n[(1-\alpha)]n_\alpha]^{1/2} \, AC_bD^{1/2}\upsilon^{1/2} \qquad (1)$$

and considering $[(1-\alpha)]n = 0.4$, $D = 2.37 \times 10^{-5}$ cm^{2}s^{-1} (D was calculated by chronoampeometry), and A=0.196 cm^2, it is estimated that the total number of electrons involved in the anodic oxidation of hydrazine is n=3.5.

A plot of the sweep rate-normalized current $(Ip/\upsilon^{1/2})$ versus sweep rate exhibits the characteristics shape typical of an EC′ catalytic process.
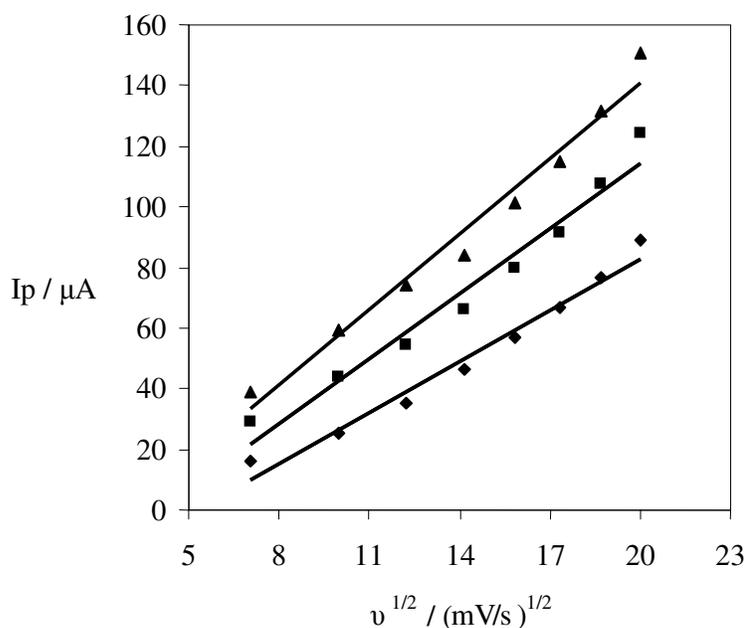

Figure 6. Variation of the electrocatalytic current (ΔIp) with the square root of scan rate. Conditions: hydrazine concentrations are (◆) 0.10, (■) 0.20 and (▲) 0.30 mM; at pH 6.0 and 200.0 µM alizarin.

3.2. Chronoamperometric Measurements

The electrocatalytic oxidation of hydrazine with alizarin was studied by chronoamperometry. The chronoamperograms obtained for a series of hydrazine solutions with various concentrations are illustrated in Fig.7. From Fig.7 it can be seen that an increase in concentration of hydrazine was accompanied by an increase in anodic currents obtained for a potential step of 600 mV vs. Ag / AgCl

reference electrode. In the presence of hydrazine at long experimental times (t > 4s), the alizarin oxidation is completed and the rate of electrocatalyzed oxidation hydrazine exceeds that of hydrazine diffusion from the bulk to the alizarin (formerly diffused to the electrode surface), and therefore the current has diffusional nature. In chronoamperometric studies, the diffusion coefficient of hydrazine can be determined. The relationship between diffusion coefficient and bulk concentration can be describe by the Cottrell equation [17]:

$$I = nFAD^{1/2} C_b / \pi^{1/2} t^{1/2} \qquad (2)$$

Where D and C_b are diffusion coefficients (cm^2 s^{-1}) and the bulk concentration (mol / cm^3), respectively. The level of Cottrell current measured for 60 s, increased with increasing hydrazine concentration. From the Cottrell equation it can be seen the plot of I vs. $t^{-1/2}$ under diffusion control is linear (Fig.7 Inset), and from the slope, the value of D can be obtained. Fig. 8 shows the experimental plots for different concentrations of hydrazine employed. The slopes of the resulting straight line from Fig.7 inset were then plotted vs. the concentration of hydrazine, from which we calculated a diffusion coefficient of 2.37 × 10^{-5} cm^2 s^{-1} for hydrazine, which is in good agreement with values reported in literature [8, 19, and 20].
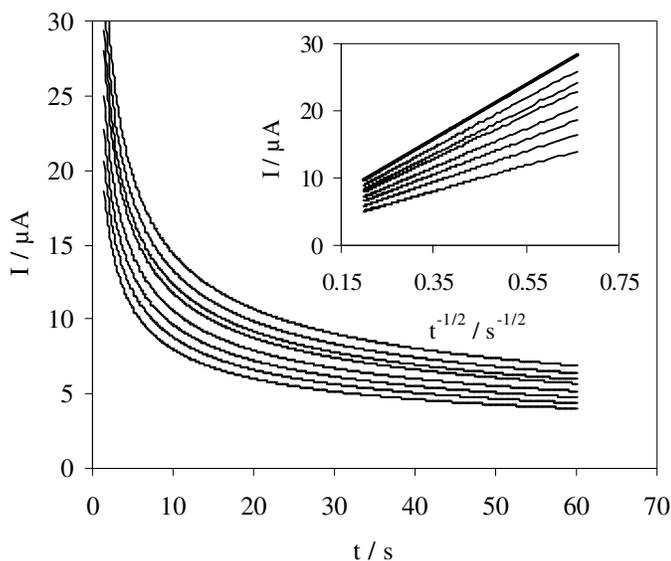

Figure 7. Chronoamperograms for different hydrazine concentrations; at the optimum conditions with 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0 and 80.0 µM of hydrazine (from bottom to top). Inset shows plot of I vs. $t^{-1/2}$ from the data of chronoamperograms for different concentration of hydrazine at the optimum conditions.

Chronoamperometry studies can be done to evaluate the catalytic rate constant. At intermediate time (0.2-1 s in present work) the catalytic current ($I_{cat.}$) is dominated by the rate of electrocatalyzed
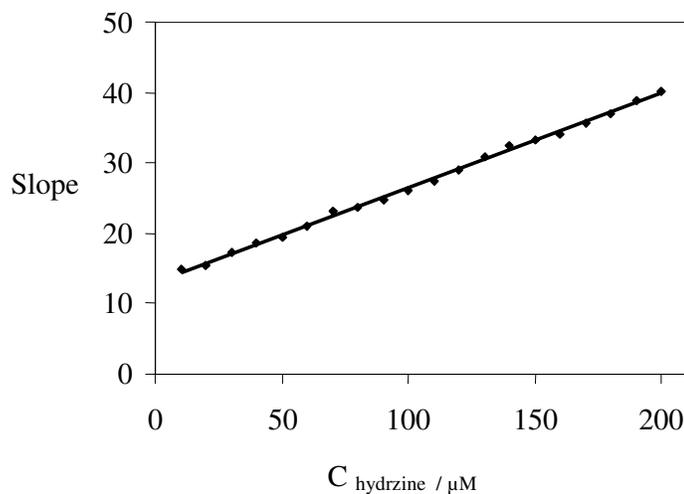
Figure 8. The slopes of resulting straight lines from (Fig.7 inset) vs. the hydrazine concentration to evaluate D.
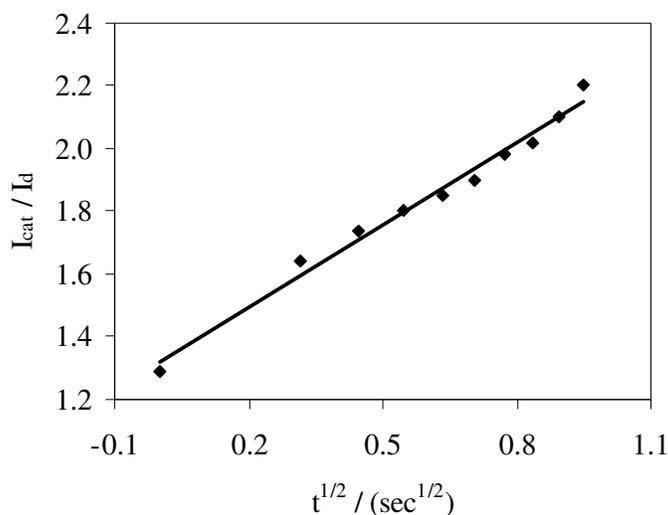

Figure 9. The plot of I_{cat}/I_L vs. $t^{1/2}$ for 0.1 mM hydrazine at optimum condition to evaluate k ($k=2.42\times10^3$ ($M^{-1} S^{-1}$).

oxidation of hydrazine. So the rate constant for the chemical reaction between hydrazine and oxidized form of alizarin is determined according to the method described in the literature [17-19]:

$$I_{cat.} / I_L = \gamma^{1/2}[\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \qquad (3)$$

Where $I_{cat.}$ and I_L is the currents of alizarin in the presence and in the absence of hydrazine, respectively. $\gamma = kC_0t$ (C_0 is the bulk concentration of hydrazine (M), k is the catalytic rate constant ($M^{-1} S^{-1}$) and t is time elapsed (s)), and erf ($\gamma^{1/2}$) is the argument of error function. In treatments, it is

assumed that hydrazine is present in large excess rather than alizarin, in addition where γ exceed 2, the error function is almost equal to 1 and the above equation can be considered as follows:

$$I_{cat.} / I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0t)^{1/2} \tag{4}$$

The slopes of $I_{cat.} / I_L$ vs. $t^{1/2}$ for 0.10 mM hydrazine was determined and k was calculated to be $2.42\times10^{+3}$ ($M^{-1} S^{-1}$) (Fig. 9).

3.3. Calibration curve

Linear sweep voltammetry is suitable for determination of hydrazine in the rang of 10-800 μM with detection limit of 4.6μM, and differential pulse voltammetry too so suitable for determination in the range of 0.05-4 μM with detection limit of 0.0208 μM.

In initial method, linear sweep voltammetry used under the optimum conditions with scan rate 250 mVs^{-1}, for hydrazine concentration range of 10 to 800 μM, the regression equation is: ΔI_p (μA) = (31.64±1.6) + (0.242 ± 0.0002)$C_{hydrazine}$ with $r^2=0.9972$ (n=20), while $C_{hydrazine}$ is hydrazine concentration in μM. The results are given in Fig. 10.
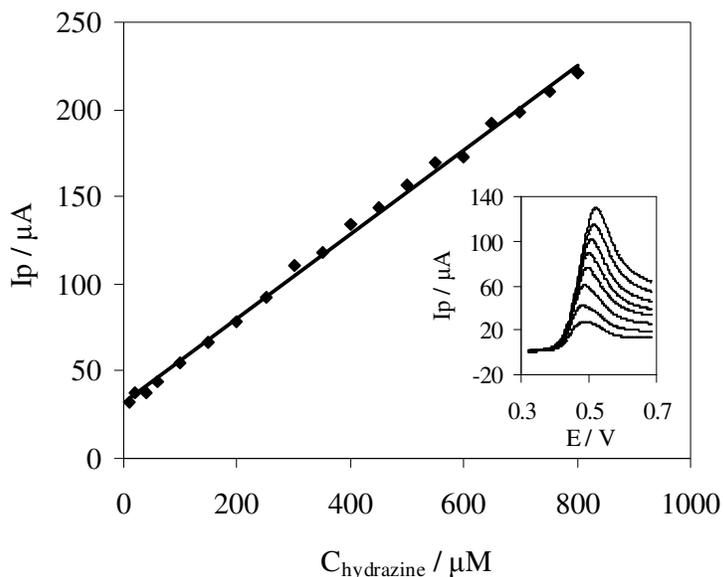

Figure 10. Calibration curves for determination of hydrazine, with a scan rate of 250 mVs^{-1} ; at the optimum conditions. Inset show the raw voltammogram.

The limit of detection equals $3s_b/m$, where s_b is the standard deviation of the blank signal and m is the slope of the calibration curve for the proposed method (n=10) at 250 mVs^{-1}.

The relative standard deviation (%RSD) for 10 replicated analysis of 0.10 and 0.25 μM hydrazine at 250 mVs^{-1} were 3.3% and 3.9%, respectively.

Then differential pulse voltammetry used under the optimum conditions for hydrazine concentration range of 0.05 to 4 µM, the regression equation is: ΔI_p (µA) = (14.13±0.05)+ (15.98±.0.009)$C_{hydrazine}$ with r^2=0.9636 (n=10), while $C_{hydrazine}$ is hydrazine concentration in µM. The limit of detection equals $3s_b/m$, where s_b is the standard deviation of the blank signal and m is the slope of the calibration curve for the proposed method (n=10). The results are given in Fig. 11.
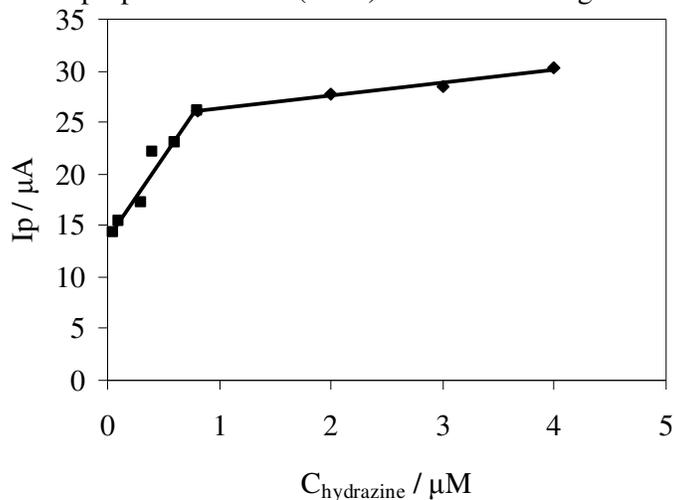

Figure 11. Calibration curves for determination of hydrazine, with differential pulse voltammetry; at the optimum conditions.

3.4. Interference studies

The effect of various substances as potential interference compounds on the determination of hydrazine was studied under the optimum conditions with 0.1 M of hydrazine concentration. The limit of the potential interferent substances was defined error less than 3% in determination of 0.1 mM of hydrazine concentration. The results are given in Table 1, the effects of the cations such as Ca^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+} have been omitted in the presence of excess amount of EDTA (0.05 M), after sedimentation by OH^- effect (isolated of cationic hydroxide by increase of pH with NaOH, addition, then tested on fine solution), while almost all of anions have no effect on the peak current [20].

Table 1. Interference study for the determination of 100.0 µM hydrazine under optimized conditions

Species	Tolerance limits ($W_{species}/W_{Hydrazine}$)
Cl^-, NO_3^-, F^-, CH_3COO^-, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, Br^-, NH_4^+, Na^+, K^+, Mg^{2+}, Citrate, Tartarate, EDTA, Glucose , Fructose, Sucrose, Lactose	1000[a]
Ca^{2+}, Ba^{2+}, Mn^{2+}, Co^{3+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Cd^{2+},	100[b]
NH_2OH	1

a Maximum amount tested.
b After addition of 50mM EDTA solution

3.5. Real sample

To evaluate the applicability of the proposed method, makes their potentially useful for monitoring concentration levels of hydrazine in water samples. Standard addition method was used for the analysis in different water samples. The results are presented in Table 2 indicate good recovery.

Table 2. Determination of hydrazine in water samples

Sample	Hydrazine Added(μM)	Hydrazine Found(μM)[a]	Recovery (%)
well Water	-	<Detection limit	-
well Water	10.0	9.75±0.67	97.5
well Water	20.0	19.85±0.46	99.25
well Water	30.0	30.67±0.22	102.23
well Water	40.0	38.95	97.45
well Water	50.0	51	102

a: Average of five determinations

4. CONCLUSIONS

This technique offers certain advantages over conventional modified glassy carbon electrodes especially in its simplicity because it doesn't need prepare as for modified electrodes. The independency of these methods from the interferences, and its ability at removing the effect of most cationic interferences easily are the features of the technique.

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