

Electrooxidation of hydrazine by carminic acid as a mediator on a glassy carbon electrode

Mohammad MAZLOUM-ARDAKANI^{1,*}, Seyed Hossein MOOSAVIZADEH²
Ali SADEGHIANE², Mohammad Hossein MASHHADIZADEH³
Mohammad Ali KARIMI⁴

¹*Department of Chemistry, Faculty of Science, Yazd University, Yazd-IRAN
e-mail: mazloum@yazduni.ac.ir.*

²*Department of Chemistry, Payam Noor University, Ardakan Center, Ardakan-IRAN*

³*Department of Chemistry, Faculty of Science, Tarbiat Moalem University, Tehran-IRAN*

⁴*Department of Chemistry, Faculty of Science, Payam Noor University,
Sirjan Center, Sirjan-IRAN*

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Electrocatalytic oxidation of hydrazine on a glassy carbon electrode with carminic acid as a homogeneous mediator in 0.1 M phosphate buffer solution (pH 8.0) was studied. Cyclic voltammetry study showed that the catalytic current of the system depends on the concentration of hydrazine. The magnitude of the peak current obtained by linear sweep voltammetry for carminic acid increased sharply in the presence of hydrazine and proportional to the hydrazine concentration in the ranges of 5.0-800.0 μM and the detection limit was 3.0 μM by this technique. The detection limit was promoted by differential pulse voltammetry and decreased to 0.03 μM .

The diffusion coefficient of hydrazine was estimated using chronoamperometry. The chronoamperometry studies were also used to determine the rate constant for catalytic reaction of carminic acid with hydrazine. The experimental results showed that the peak current varied in the presence of different bivalence and more, metal cations, but these interferences were omitted in the alkaline media and in the presence of EDTA, while almost all anions and univalence metal cations had no effect on the peak current of hydrazine. The proposed method was used for analysis of hydrazine in real samples.

Key Words: Hydrazine; glassy carbon electrode; mediator; electrocatalytic; voltammetry.

*Corresponding author

Introduction

The detection of many compounds at conventional electrodes is hindered by the presence of large overpotentials, therefore a great deal of interest still exists in the development of materials capable of the catalytic electrooxidation of hydrazine, in order to diminish these typically large overpotentials encountered in its direct oxidation at most electrode surfaces.

Hydrazine is the base product of a well established fuel cell, due to its high capacity and the absence of contamination.¹ In addition, hydrazine and derivatives have found various applications such as catalysts, corrosion inhibitors, antioxidants, emulsifiers, reducing agents, pesticides, plant-growth regulators, dyes stuffs, and explosives. Hydrazine is commonly used in place of sulfite in boilers as an oxygen scavenger and removes dissolved oxygen. Because the products of this reaction are water and nitrogen, the reaction adds no solid to the boiler water.² Moreover, hydrazine is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance affecting the liver and brain glutathione. Consequently, drug regulatory authorities are becoming increasingly aware of the need to control the levels of hydrazones in isoniazid and other hydrazide drugs and in their formulations. Satisfactory techniques for the determination of special chemicals such as methods proposed for the determination of hydrazine must ideally be specified, reproducible, rapid, simple, and sensitive. These techniques include coulometry,³ titrimetry,⁴ amperometry,^{5,6} ion-selective electrode,^{7,8} and spectrophotometry.⁹ Various experimental hydrazine sensors have been reported based on the detection of resistance change due to heat generated by catalytic oxidation of hydrazine.¹⁰ Other methods such as spectrophotometric methods^{11–14} based on the reaction of hydrazine with dimethyl benzaldehyde and N-dimethyl aminobenzaldehyde^{12,13} have been reported. These methods have a high limit of detection and low precision. Furthermore, the mechanism and kinetics of hydrazine oxidation have been studied under a wide range of solution conditions² and at several electrodes including silver,¹⁵ gold,¹⁵ nickel,¹⁶ mercury,^{16–19} and platinum.^{17,19–22} The overpotential for electrooxidation of hydrazine depends on the electrode material,²³ the history of the electrode, and type of pretreatment employed.²⁴ Although metals such as Pt, Au, and Ag are very active in the anodic oxidation of hydrazine, they are too expensive for practical applications and, unfortunately, hydrazine compounds with a large oxidation overpotential at ordinary carbon electrodes are not suitable analytes for these electrodes. Electroanalytical techniques were proven to be relatively direct and effective for the detection of hydrazine.^{25–28} One approach for minimizing overpotential effects is through the use of an electrocatalytic process. Because it is simplified and reproducible and electrode preparation is not necessary, the homogeneous method is preferable to a modified one. We found a new mediator named carminic acid (7- α -D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid) that can catalyze the electrooxidation of hydrazine as a homogenous mediator. Then we evaluated the electrocatalytic parameters by some voltammetry methods.

Experimental

Chemical reagents

All chemical reagents are used in this work like carminic acid (7- α -D-Glucopyranosyl-9, 10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid) and hydrazine were high purity and analytical

grade and were obtained from Merck and Fluka. All solutions were freshly prepared with doubly distilled water just prior to use and without further purification.

All experiments were carried out at ambient temperature. The phosphate buffer (pH 8.0) was used for optimum measurements and the pH of the buffer was adjusted with phosphoric acid and sodium hydroxide.

Apparatus

The electrochemical experiments were performed by using an AUTO LAB PGSTAT 302, potentiostat/galvanostat (ECO CHEMIE UTRECHT, NETHERLANDS) device connected to a 125 mL 3-electrode cell (ACE GLASS) and supported with GPES 4.9 software. A personal computer was used for processing data and potential control and also for electrochemical measurements.

The cell configuration contained a glassy carbon disk electrode as a working electrode, a Pt wire directly immersed in the solution, as auxiliary electrode, and an Ag/AgCl electrode as reference electrode. All reported potentials were measured based on this reference electrode. A Metrohm 781 pH/ion meter was also used for pH measurements.

Real samples

Samples of water arising from the boilers of power generation in the preserve condition were selected as real samples. The concentration of hydrazine for this condition must be 1 to 5 mg L⁻¹.

Recommended procedure

The glassy carbon electrode surface before each test was polished with slurry made of 0.05 μm alumina powder in water using a standard polishing surface until the electrode surfaces had a mirror-finish and then rinsed thoroughly with double distilled water. To prepare a blank solution, 4.0 mL of buffer solution and 1.0 mL of carminic acid were poured into a 10.0 mL volumetric flask and the solution was diluted to the mark with distilled 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 200 mV s⁻¹. The same experiment was repeated in 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 ($I_p = I_s - I_b$), was proportional to the hydrazine concentration. Calibration graphs were obtained by plotting the net peak current (I_p) against the standard concentration of hydrazine.

Results and discussion

Electrocatalytic oxidation of hydrazine

The cyclic voltammetric responses of a glassy carbon electrode in the phosphate buffer solution (pH 8.0) without and with hydrazine are shown in Figure 1(a) and (b), respectively. A small anodic current by the oxidation of hydrazine is observed but no cathodic peak is found, indicating an irreversible homogeneous charge transfer in the system.²⁵ Carminic acid has a reversible charge transfer as shown in Figure 1(c), but in the

presence of hydrazine a large irreversible anodic peak at lower potential than alone hydrazine is observed without a cathodic counterpart (Figure 1(d)), which showed the electrocatalytic behavior of carminic acid as a homogeneous mediator. The anodic peak potential for oxidation of hydrazine in the presence of carminic acid is near +200 mV vs. Ag/AgCl (Figure 1(c)), while hydrazine starts to oxidize at about +600 mV (Figure 1(b)) in the absence of mediator under identical conditions, and so a decrease in overpotential of 400 mV is observed.

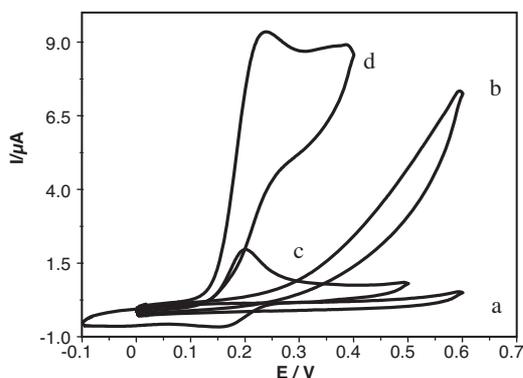
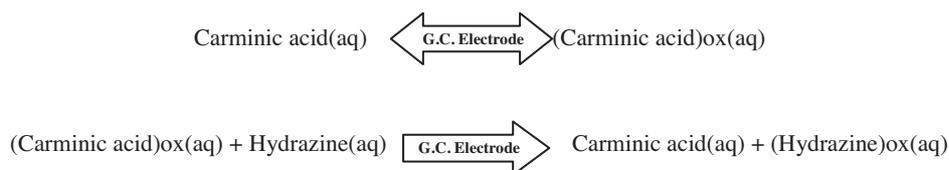
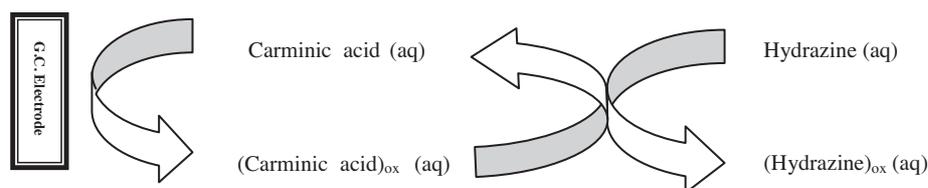


Figure 1. Cyclic voltammograms of a solution containing reactants on a glassy carbon electrode with a scan rate of 200 mV s^{-1} in 0.1 M phosphate buffer (pH 8.0), (a): in the absence of hydrazine; (b): in the presence of 0.20 mM hydrazine; (c): in the presence of 0.10 mM carminic acid; and (d): in the presence of 0.20 mM hydrazine and 0.10 mM carminic acid.

We found that carminic acid acts as a suitable mediator for electron transfer in the oxidation of hydrazine at the surface of a glassy carbon electrode. The carminic acid peak current increases sharply in the presence of hydrazine, and the peak potential of carminic acid is in lower potential than that of a hydrazine. Therefore, carminic acid was considered a suitable homogeneous electrocatalyst for hydrazine oxidation by electrochemical process. The proposed LSV method for the determination of hydrazine is based on the following sequence of reactions:

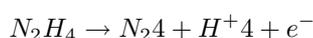


As can be seen in above diagram, in the first step carminic acid can be oxidized at the surface of the glassy carbon electrode reversibly; then in the presence of hydrazine the oxidized mediator can oxidize hydrazine and converts to its initial form, while the carminic acid itself can be oxidized further, so the peak current of carminic acid increases in the presence of hydrazine. 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 the intermediate in the oxidation process.²⁹ In aqueous solution the first intermediate of hydrazine oxidation has been identified as the radical ion $\text{N}_2\text{H}_4^{\circ+}$ by EPR^{30,31} and the formation of this radical ion is usually regarded as the rate determining step, because not all the proposed intermediates are stable.²⁹



In the presence of hydrazine, the oxidized carminic acid reacts with hydrazine presented in the solution and converts to its initial form. This reaction is an EC and because of relatively fast charge transfer between hydrazine and oxidized form of carminic acid the peak current depends on the diffusion of hydrazine to the diffused layer of the carminic acid and causes the carminic acid peak current to increase; therefore, ΔI_p depends on hydrazine concentration.

The anodic oxidation of hydrazine in aqueous solution has been studied extensively on several electrodes. In aqueous solution hydrazine is oxidized mainly through a 4-electron process with the final product N_2 :²⁵



In order to get information on the rate determining step, a Tafel plot was developed for the blank containing carminic acid. Figure 2 inset shows the linear sweep voltammogram for the blank containing carminic acid in 0.1 M phosphate buffer solution (pH 8.0), at scan rate of 5 mV s^{-1} . The points show the rising part of the voltammogram, which is known as a Tafel region, and is affected by electron transfer kinetics between hydrazine and carminic acid, assuming the deprotonation of hydrazine as a sufficiently fast step and follows one electron transfer in the rate determining step. In order to get information on the rate determining step a slope of $104.77 \text{ mV decade}^{-1}$ is obtained assuming a transfer coefficient of $\alpha = 0.43$.

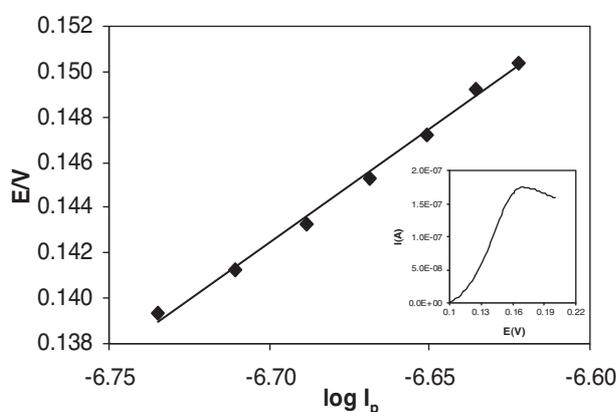


Figure 2. A Tafel plot at pH 8.0; 0.1 mM carminic acid, with a scan rate of 5 mV s^{-1} . Inset shows the linear sweep voltammogram.

Influence of variables

The influences of chemical variables such as pH, carminic acid concentration, and instrumental variables such as scan rate on the sensitivity were studied. The voltammetric behavior of the system was characterized at

various pH values. The results are shown in Figure 3. It can be seen that for the carminic acid solution when the pH was increased from 5.0 to 8.0 the carminic acid peak current increased and the peak current decreased from 8.0 to 10.0. When the pH was increased from 3.0 to 10.0 the peak potential shifted to lower values. Since the pK_a of hydrazine is 7.9, below this pH value hydrazine will be presented in its protonated form and it might be responsible for the observed effect.³¹ Figure 4 shows the effect of pH (phosphate buffer) on the electrocatalytic oxidation of hydrazine at the glassy carbon electrode in the presence of 0.1 mM carminic acid. The sensitivity increased with increasing pH from 6.0 to 8.0, and then decreased for higher pH values. However, better sensitivity obtained at pH 8.0 and it was suggested as the optimal pH value for this work.

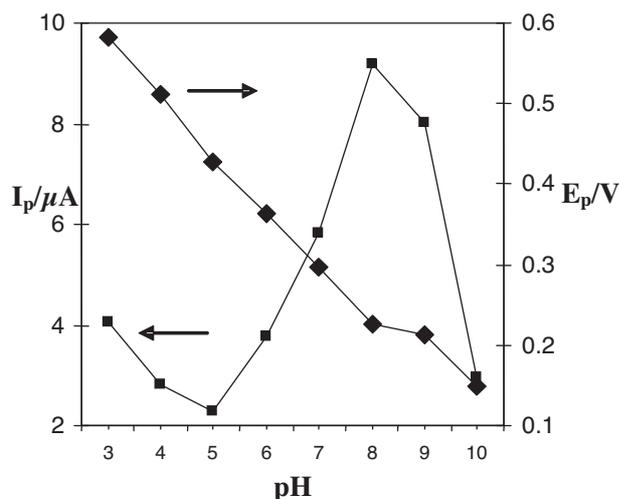


Figure 3. Effect of pH on the peak current and peak potential; conditions: 0.40 mM hydrazine with 0.10 mM carminic acid; scan rate of 200 mV s^{-1} ; potential range of 0.05 to 0.7 V vs. Ag/AgCl electrode.

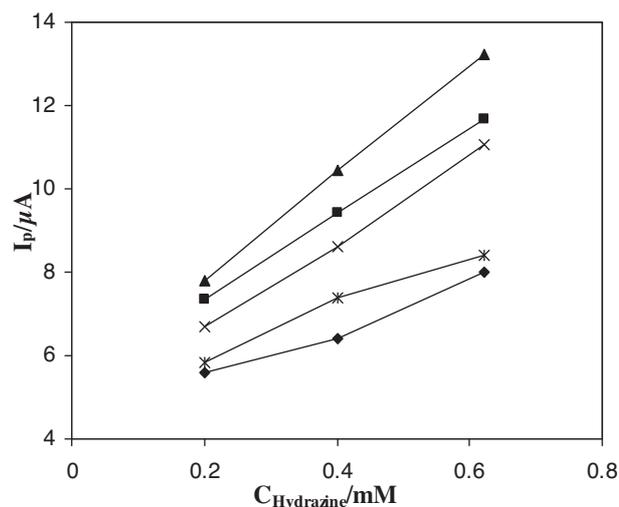


Figure 4. Influence of pH on the electrooxidation of different hydrazine concentrations (0.20, 0.40, and 0.60 mM) at a glassy carbon electrode. Conditions: 0.10 mM carminic acid; scan rate of 200 mV s^{-1} ; potential range of 0.05 to 0.7 V vs. Ag/AgCl electrode; pH values are (♦) 6.0, (■) 7.0, (▲) 8.0, (×) 9.0, (*)10.

The influence of concentration of carminic acid on the peak currents was studied for the range of 10.0-250.0 μM carminic acid, in the solutions containing different concentrations of hydrazine at pH 8.0. The results showed that by increasing carminic acid concentration up to 100.0 μM the peak current increased, whereas a higher concentration of carminic acid will not have a great effect in this case. Therefore, 100.0 μM carminic acid was selected as the optimal mediator concentration.

The peak potential for the system shifts slightly to a more positive potential with increasing scan rate, suggesting a kinetic limitation existing in the reaction between carminic acid and hydrazine. The cyclic voltammograms of the glassy carbon electrode in 0.1 M phosphate buffer solution containing 0.10 mM carminic acid and different concentrations of hydrazine at various scan rates (not shown) were used to get information about the rate determining step. Figure 5 shows that a plot of the anodic peak current versus the square root of the sweep rate is linear, indicating diffusion controlled mass transport. From the slope of the I_p versus $v^{1/2}$

plot, the number of electrons in the overall reaction can be obtained. According to the following equation for a totally irreversible diffusion controlled processes:^{25,32}

$$I_P = 3.01 \times 10^5 n[(1 - \alpha)]n_\alpha]^{1/2} AC_b D^{1/2} v^{1/2} \quad (1)$$

and considering $(1 - \alpha)]n_\alpha = 0.57$ and $D = 9.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (D was calculated by chronoamperometry), and $A = 0.0314 \text{ cm}^2$, it is estimated that the total number of electrons involved in the anodic oxidation of hydrazine is near 4 (the calculated values were 4.06 and 4.04). A plot of the sweep rate-normalized current ($I_P/v^{1/2}$) versus sweep rate exhibits the characteristic shape typical of an EC catalytic process.

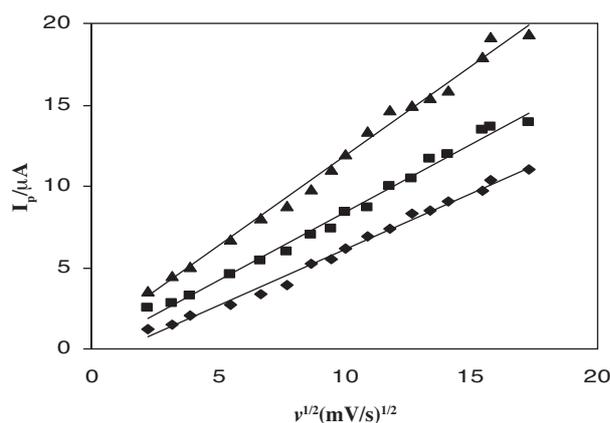


Figure 5. Variation in the electrocatalytic current (I_p) with the square root of scan rate. Conditions: hydrazine concentrations are (◆) 0.20, (■) 0.30 ,and (▲) 0.40 mM; at pH 8.0 and 0.1 mM carminic acid.

Determination of the diffusion coefficient by chronoamperometry

The electrocatalytic oxidation of hydrazine with carminic acid at a glassy carbon electrode was studied by chronoamperometry. The chronoamperograms show that an increase in hydrazine concentration is accompanied by an increase in anodic peak currents of carminic acid for a potential step of 300 mV vs. Ag/AgCl.

In the presence of hydrazine at long experimental times ($t > 4 \text{ s}$), the carminic acid oxidation is completed and the rate of electrocatalyzed hydrazine oxidation exceeds that of hydrazine diffusion from the bulk to the carminic acid (formerly diffused to the electrode surface) and therefore the current has a diffusional nature, and so D is calculated by the Cottrell equation:²¹

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

where D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) and C_b is the bulk concentration (mol cm^{-3}). The level of the Cottrell current, measured for 50 s, increased with increasing hydrazine concentration. In accordance with the Cottrell equation, the plot of I vs. $t^{-1/2}$ at various hydrazine concentrations is linear. We performed these studies at various hydrazine concentrations at a glassy carbon electrode with carminic acid. The slopes of the resulting straight lines were then plotted vs. the hydrazine concentration. We can calculate the value of D for hydrazine as $9.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is in good agreement with values reported in the literature.^{31,33,34}

Kinetics of the electrocatalytic oxidation of hydrazine

Chronoamperometry studies can be used to evaluate the catalytic rate constant. At intermediate time (0.2-1.0 s in the present work) the catalytic current (I_{cat}) is dominated by the rate of electrocatalyzed oxidation of hydrazine. Therefore, the rate constant for the chemical reaction between hydrazine and the oxidized form of carminic acid is determined according to the method described in the literature.^{21,33,34}

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

where I_{cat} and I_L are the currents of carminic acid in the presence and in the absence of hydrazine, respectively. $\gamma = kC_b t$ (C_b 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 carminic acid; in addition, where γ exceeds 2, the error function is almost equal to 1 and the above equation can be considered as follows:

$$I_{cat.}/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kC_b t)^{1/2} \quad (4)$$

The slope of $I_{cat.}/I_L$ vs. $t^{1/2}$ for 0.40 mM hydrazine was determined and k was calculated to be $6.9 \times 10^4 M^{-1} s^{-1}$.

Calibration curve studies

Linear sweep voltammetry was used under the optimum conditions selected as follows: pH 8.0 (phosphate buffer) and 100.0 μM carminic acid with a scan rate of 200 $mV s^{-1}$, for hydrazine concentration range of 5.0 to 700.0 μM , the regression equation is: $I_p (\mu A) = (4.7033 \pm 0.0079) + (0.0264 \pm 0.0002) C_{Hydrazine}$ with $r^2 = 0.9961$ ($n = 11$), while $C_{Hydrazine}$ is hydrazine concentration in μM . In addition, under the optimum conditions with the scan rate of 400 $mV s^{-1}$ and hydrazine concentration between 5.0 and 800.0 μM , a regression equation is $I_p (\mu A) = (9.6991 \pm 0.0808) + (0.0297 \pm 0.0002) C_{Hydrazine}$ with $r^2 = 0.9972$ ($n = 11$). The results are shown in Figures 6 and 7, respectively. The relative standard deviation (%RSD) for 5 replicated analyses of 100 and 200 μM hydrazine at 200 $mV s^{-1}$ was 3.4% and 3.6%, respectively. In the identical conditions at a scan rate of 400 $mV s^{-1}$ the %RSD for 100 and 200 μM hydrazine was 0.4% and 1%, respectively. The limit of detection (LOD) 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 ($n = 11$) at 200 and 400 $mV s^{-1}$ it is 4.5 and 3.0 μM hydrazine, respectively.

For differential pulse voltammetry used under the optimum conditions for hydrazine concentration range of 0.1 to 5.0 μM the regression equation is $I_p (\mu A) = (3.3776 \pm 0.0500) + (1.5576 \pm 0.0090) C_{Hydrazine}$ with $r^2 = 0.9958$ ($n = 11$), where $C_{Hydrazine}$ 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 ($n = 11$) LOD was 0.03 μM . The results are shown in Figure 8.

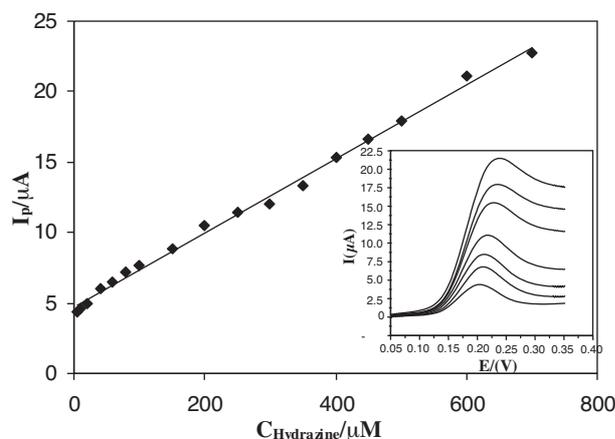


Figure 6. Calibration curve for determination of hydrazine, with a scan rate of 200 mV s^{-1} ; at the optimum conditions. Inset shows the linear sweep voltammogram.

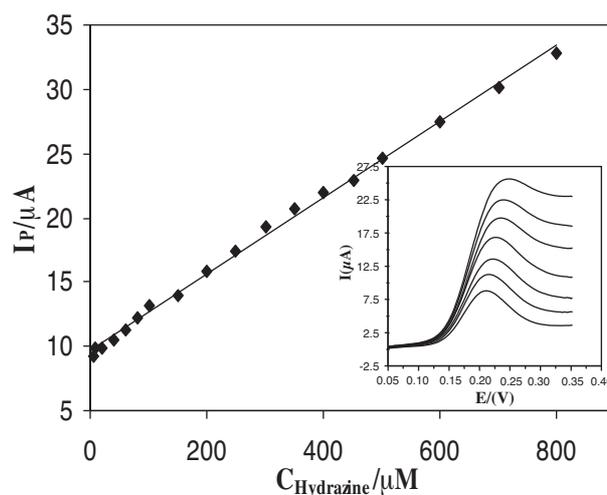


Figure 7. Calibration curve for determination of hydrazine, with a scan rate of 400 mV s^{-1} ; at the optimum conditions. Inset shows the linear sweep voltammogram.

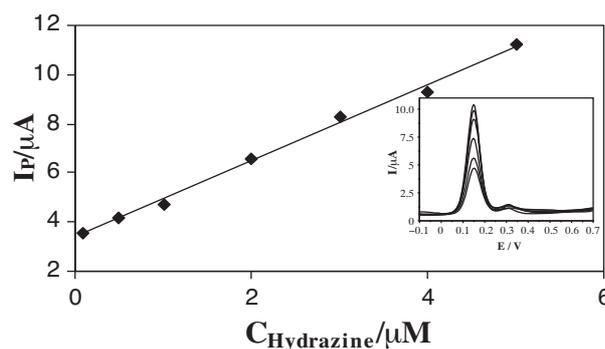


Figure 8. Calibration curve for determination of hydrazine, with differential pulse voltammetry; at the optimum conditions.

Interference studies

The influence of various substances as potential interference compounds on the determination of hydrazine was studied under the optimum conditions with $50.0 \mu\text{M}$ of hydrazine concentration. The tolerance limit was dependent as the maximum concentration of the potential interfering substance causes an error less than 3% for determination of $50.0 \mu\text{M}$ of hydrazine concentration. The results are given in Table 1; which shows that the peak potential and peak current vary with different bivalence, but these interferences were omitted in the alkaline media after sedimentation by OH^- effect (the modified pH was 8.0 and isolated of cationic hydroxide in this pH) and in the presence excess amount of EDTA, while almost all the anions and univalence metal cations had no effect on the peak current.

Table 1. Interference study for the determination of 50.0 μM hydrazine under optimized conditions.

Species	Tolerance limits ($W_{\text{Species}}/W_{\text{Hydrazine}}$)
F^- , Cl^- , Br^- , I^- , IO_4^- , ClO_4^- , NO_2^- , NO_3^- , CH_3CO_2^- , SO_4^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, NH_4^+ , Na^+ , K^+ , Citrate, Tartrate, Bicarbonate, EDTA, Glucose, Fructose, Sucrose, Lactose	1000 ^a
Mg^{2+} , Ca^{2+} , Ba^{2+} , Mn^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Co^{3+} , Cr^{3+} , Al^{3+}	1000 ^b
Cu^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+}	500 ^b
NH_2OH	1.5

^aMaximum amount tested.^bAfter sedimentation in the alkaline media and addition of excess EDTA solution.

Real sample

This developed method was applied for determination of hydrazine in boilers' water as real samples. The concentration of these samples was between 1 and 5 ppm. The determination of hydrazine was carried out by applying the standard additions method to avoid matrix effects, and the results were compared with the reported amounts found by spectrophotometry as a standard method. Then the t-test was implemented for comparing these 2 methods and indicated that there is no meaningful difference between them; thus the method is suitable for the determination of hydrazine in this type of sample.

The applicability of the proposed method was evaluated, which is potentially useful for monitoring concentration levels of hydrazine in synthesized water samples in the presence of some interferences, and the results showed good recovery. The results are presented in Table 2.

Table 2. Comparison of the efficiency some modified electrodes used in the electrocatalysis of Hydrazine.

Type	Modified pH	α	k ($\text{M}^{-1} \text{s}^{-1}$)	D (cm^2/s)	Detection Limit (μM)	Dynamic range (μM)	References
Heterogeneous	2.0	0.64	4.83×10^3	1.1×10^{-6}	0.14	0.2-1.0 & 2.0-10.0	25
Heterogeneous	-	0.65	2.2×10^3	3.2×10^{-6}	-	200-800	33
Homogeneous	9.0	0.59	2.33×10^3	3.39×10^{-6}	1.98	5-500	35
Homogeneous	6.0	0.6	2.42×10^3	2.37×10^{-5}	0.02 & 4.6	0.05-4 & 10-800	36
Homogeneous	8.0	0.43	6.9×10^4	9.2×10^{-6}	0.03 & 3.0	0.1-5.0 & 5.0-800.0	This work

Conclusions

The homogeneous electrocatalytic process for the determination of hydrazine is very rapid, reproducible, selective, and sensitive and can be used for real sample analysis. The importance of the technique is its ability for electrocatalytic determination of hydrazine with carminic acid as a homogeneous process, while a modified electrode does not need to be prepared. The independency of the system from interferences, and the ability to eliminate the effect of most cationic interferences easily are the key features of the technique. On the

other hand, the kinetic parameters of the system were calculated from the experimental results, which are in good agreement with the literature.

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