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Simultaneous Determination of Phenylhydrazine, Hydrazine and Sulfite Using a Modified Carbon Nanotube Paste Electrode

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A sensitive and selective electrochemical method for the determination of phenylhydrazine (PH) was developed using a modified carbon nanotube paste electrode. It has been found that under the optimum condition (pH 5.0) in cyclic voltammetry, the oxidation of PH occurred at a potential of about 250 mV on the surface of the modified electrode. The linear range of 0.6 to 900.0 μM and a detection limit of 1.31×10^{-7} M were observed for PH in optimum conditions. The modified electrode showed an excellent character for electrocatalytic oxidization of PH, hydrazine (HZ) and sulfite (ST). Finally, this method was also examined as a selective, simple and precise electrochemical sensor for the determination of PH, HZ and ST in real samples such as urine and water samples.

Keywords: Phenylhydrazine, hydrazine, sulfite, carbon nanotube paste electrode, voltammetry

1. INTRODUCTION

Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrode consisting of mixture prepared from carbon powder (as graphite, glassy carbon and others carbonaceous materials) and a suitable water-immiscible or non-conducting binder [1-3]. The use of carbon paste as an electrode was initially reported by Adams [4]. In afterward researches a wide variety of modifiers including enzymes [5], polymers [6] and nanomaterials [7-11] have been used with these versatile electrodes. CPEs are widely applicable in both electrochemical studies and electroanalysis thank to their advantages such as very low background current (compared to solid graphite or noble metal electrodes), facility to prepare, low cost, large potential window, simple surface renewal process and easiness of miniaturization [12-15]. Besides the advantageous properties and characteristics listed before, the feasibility of incorporation different substances during the paste preparation (which resulting in the so-called modified carbon paste electrode), allow the fabrication of electrodes with desired composition, and hence, with pre-determined properties [16-17].

Since the discovery of carbon nanotubes (CNTs) [18], numerous investigations were focused on the studies of their properties and applications [19-21]. Because of the special tube structure, CNTs possess several unique properties such as good electrical conductivity, high chemical stability and extremely high mechanical strength [22, 23]. In addition, the subtle electronic behavior of CNTs reveals that they have the ability to promote electron-transfer reaction and have a high electrocatalytic effect when used as electrode materials [24, 25]. All these fascinating properties make CNTs as a suitable candidate for the modification of electrodes [26, 27].

Hydrazine (HZ) and its derivatives are widely used in agricultural chemicals (pesticides), chemical blowing agents, pharmaceutical intermediates, photography chemicals, and boiler water treatment in hot-water heating systems for corrosion control [28]. It is also employed as a starting material for many derivatives such as foaming agents for plastics, antioxidants, polymers, and plant-growth regulators. Moreover, HZ, its salts, and its methyl and dimethyl derivatives are used as rocket fuel, gas generators, and explosives [29]. HZ and its derivatives are industrial chemicals that enter the environment primarily by emissions from their uses as aerospace fuels and from industrial facilities that manufacture, process, or use these chemicals. HZ is volatile and toxic and is readily absorbed by oral, dermal, or inhalation routes of exposure [30]. Acute exposure can also damage the liver, kidneys, and central nervous system in humans [31]. The carcinogenic risks to humans of HZ and its derivatives have been considered on a number of occasions by the International Agency for Research on Cancer of the World Health Organization [32]. Environmental Protection Agency (EPA) has classified HZ as a group B_2 (human carcinogen) [32]. EPA and Agency for Toxic Substance and Disease Registry calculated an intermediate inhalation minimal risk level of 0.004 $\mu g\ ml^{-1}$ [31]. The National Institute for Occupational Safety and Health and the Occupational Safety and Health Administration recommended that the level of HZ in workplace air not exceed 0.03 $\mu g\ ml^{-1}$ for a 2-h period (National Institute for Occupational Safety and Health) [33]. Also the Food and Drug Administration has ruled that HZ cannot be added to water used for making steam which will contact food. Because of the environmental and toxicological significance of HZ compounds, sensitive and reliable analytical methods are necessary for preconcentration and determination of HZ in samples.

Several instrumental methods for determination of HZ have been reported. Electroanalytical techniques seem to provide direct and efficient methods for the detection of HZ and its derivatives. Electrochemical techniques offer the opportunity for portable, cheap and rapid methodologies. However, electrochemical oxidations of hydrazines are kinetically sluggish and a relatively high overpotential is required at conventional electrodes. As such, several approaches have been investigated in an attempt to minimize this high overpotentials problem. One such approach included the application chemically modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode materials [34-37].

During the last years great attention has been drawn to the development of methods for sulfite (ST) determination. ST is used as a preservative in the food industry because its addition to several products (vegetables, fruits, and several beverages) prevents oxidation, inhibits bacterial growth and assists in preserving vitamin C. Despite these great advantages, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity. Therefore, the existence of methods allowing an accurate measurement of ST is very important for food industry in order to control product quality. Several instrumental methods such as titration, spectrofluorometry, chemiluminiscence, phosphorimetry, spectrophotometry and flow injection analysis (FIA) for determination of ST have been reported. However, the majority of these methods need extensive sample, pre-treatment and reagent preparation. Electroanalytical techniques seem to provide direct and efficient methods for the detection of ST [38-41].

In the present work, we described initially the preparation and suitability of a 1- (3, 4-dihydro-4-oxo-3-phenylquinazolin-2-yl)-4-phenylthiosemicarbazide modified carbon nanotube paste electrode as a new electrode in the electrocatalysis and determination of PH in an aqueous buffer solution. Then we evaluated the analytical performance of the modified electrode in quantification of PH in the presence of HZ and ST. Finally, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of PH, HZ and ST in real samples, we examined this method for the voltammetric determination of PH, HZ and ST in some real samples such as urine and water samples.

2. EXPERIMENTAL

2.1. Apparatus and reagents

All the cyclic voltammetric measurements were performed using a BHP 2063^+ Electrochemical Analysis System, Behpajooh, Iran potentiostat/galvanostat coupled with a Pentium IV personal computer connected to a HP laser jet 6L printer.

An Ag / AgCl / KCl 3 M, a platinum wire, and a MCNPE were used as reference, auxiliary and working electrodes, respectively. A digital pH/mV meter (Metrohm model 710) was applied for pH measurements. PH, HZ, ST, carbon nanotube, graphite powder, paraffin oil and reagents were analytical grade from Merck. The buffer solutions were prepared from ortho phosphoric acid and its salts in the pH range 2.0-12.0.

2.2. Preparation of the electrode

Modified carbon nanotube paste electrodes were prepared by dissolve 0.01 g of modifier in diethyl ether and hand mixing with 89-times its weight of graphite powder and 10-times its weight of carbon nanotube with a mortar and pestle. The solvent was evaporated by stirring. A 70:30 (w/w) mixture of modifier spiked carbon nanotube powder and paraffin oil was blended by hand mixing for 15 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (*ca.* 3.4 mm *i.d.* and 10 cm long). Electrical contact was made by inserting a copper wire into the glass tube at the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper. Unmodified carbon paste, prepared in the same way without adding modifier and carbon nanotube to the mixture and was used for comparison purposes.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of modified electrode

Cyclic voltammetry was employed for investigation the electrochemical properties of MCNPE in a pure buffered aqueous solution (pH 5.0). The cyclic voltammogram exhibits an anodic and corresponding cathodic peaks with E_{pa}=0.25 V and E_{pc}=0.19 V vs. Ag / AgCl / KCl 3 M. The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH from five separately prepared MCNPEs. The calculated RSDs for various parameters accepted as the criteria for a satisfactory surface reproducibility (1 – 4%). This degree of reproducibility is virtually the same as that expected for the renewal or ordinary carbon paste surface.

3.2. Catalytic Effect

The utility of the modified electrode for oxidation of PH was evaluated by cyclic voltammetry. The cyclic voltammetric responses of a bare carbon-paste electrode in 0.1M phosphate buffer (pH 5.0), without and with PH, are shown in Fig. 1 (curves c and d, respectively).

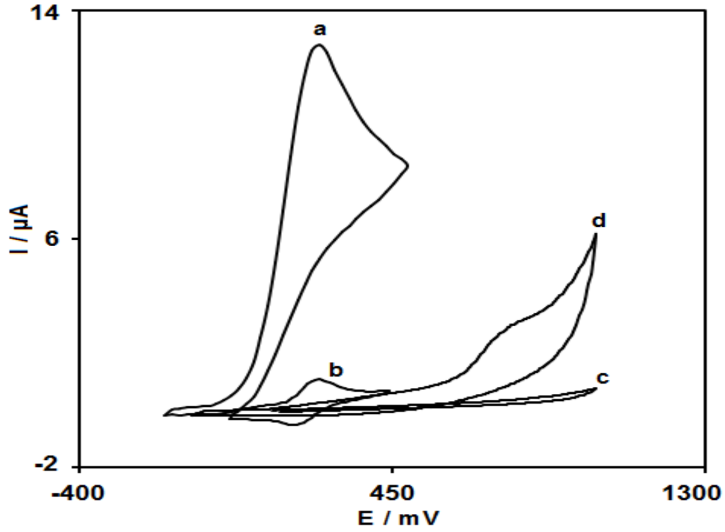

Figure 1. Cyclic voltammograms of MCNPE at 10 mV s^{-1} in 0.1M phosphate buffer (pH 5.0): (a) In the presence and (b) in the absence of 0.25 mM PH; (c) and (d) for an unmodified carbon-paste electrode in the absence and presence of 0.25 mM PH, respectively.

Figures 4a and b show cyclic voltammograms of modified electrode in the buffer solution with 250 μM of PH and without PH, respectively. The results show that the sensor produces a large anodic peak current in the presence of PH without a cathodic counterpart (Fig. 1, curve a). That the current observed is associated with PH oxidation and not the oxidation of modifier is demonstrated by comparing the current in Fig. 1 (curve b, without PH) with the one in the presence of PH in Fig. 1

(curve a). It is apparent that the anodic current associated with the surface-attached materials is significantly less than that obtained in the solution containing PH. At the surface of a bare electrode, PH was oxidized around 850 mV. As can be seen, the electroactivity of PH on the modified electrode was significant (Figs. 1 curve a), with strongly defined peak potential, around 250 mV vs. Ag/AgCl electrode. Thus, a decrease in overpotential and enhancement of peak current for PH oxidation are achieved with the modified electrodes. Such a behavior is indicative of an EC′ mechanism [42].

The effect of scan rate on the electrocatalytic oxidation of 250 µM PH at the modified electrode was investigated by linear sweep voltammetry (Fig.2).

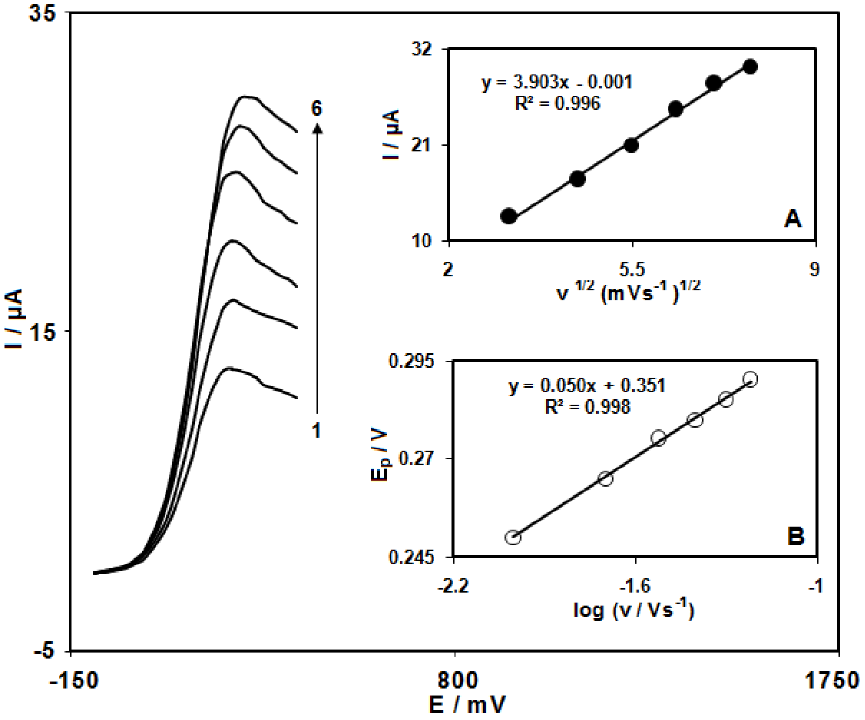

Figure 2. Linear sweep voltammograms of the MCNPE in the presence of 250 µM PH at various scan rates; The numbers 1-6 correspond to 10, 20, 30, 40, 50 and 60 mVs^{-1} scan rates, respectively Insets:(A) The variation of the anodic peak currents vs. $v^{1/2}$. (B) the variation of the anodic peak potential vs. log v.

The oxidation peak potential shifts with increasing scan rates toward a more positive potential, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height (Ip) against square root of scan rate ($v^{1/2}$), in range of 10– 60 mVs^{-1}, was constructed, which was found to be linear, suggesting that at sufficient overpotential the process is diffusion rather than surface-controlled(Fig.2 A).

In order to get the information on the rate determining step, Tafel slope (b) determinates using the following equation for a totally irreversible diffusion controlled process [43]:

Ep=(b/2) log v+constant (1)

Based on Eq. 1, the slope of Ep versus log v is b/2, where b indicates theTafel slope. The slope of Ep versus log v plot was found to be 0.05 V in this work (Fig. 2B), thus, b=2×0.05= 0.1 V. This slope value indicated an electron transfer process, which is the rate-limiting step by assumption of a transfer coefficient (a) equal to 0.41.

3.3. Chronoamperometric studies

The catalytic oxidation of PH by a modified electrode was also studied by chronoamperometry (Fig. 3).

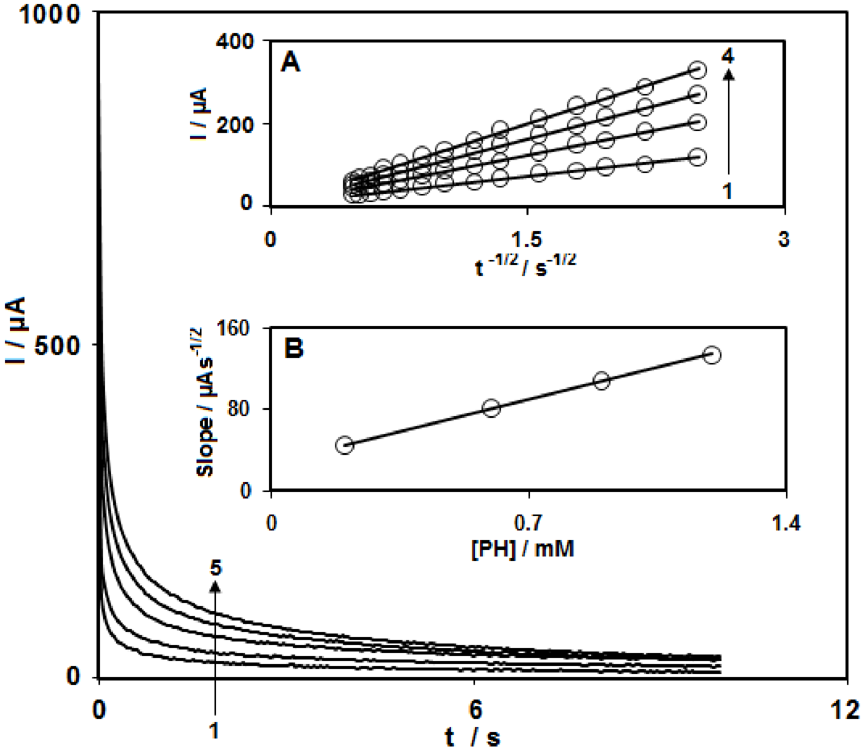

Figure 3. Chronoamperograms obtained at MCNPE in 0.1 M phosphate buffer solution (pH 5.0) for different concentration of PH. The numbers 1–5 correspond to 0.0, 0.2, 0.6, 0.9 and 1.2 mM of PH. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamprograms 2–5 and (B) plot of the slope of the straight lines against the PH concentration.

Chronoamperometric measurements of different concentrations of PH at modified electrode were done by setting the working electrode potential at 280 mV. In chronoamperometric studies, we have determined the diffusion coefficient, D, of PH. The experimental plots of I versus $t^{-1/2}$ with the best fits for different concentrations of PH were employed (Fig. 3A). The slopes of the resulting straight lines were then plotted versus the phenylhydrazine – concentrations (Fig. 3B), from whose slope and using the Cottrell equation [42]

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

we calculated a diffusion coefficient of 1.83×10^{-6} cm^2 s^{-1} for PH .

3.4. Electrocatalytic Determination of PH

The electrocatalytic peak current of PH oxidation at the surface of the modified electrode can be used for determination of PH in solution. Therefore, differential pulse voltammetry experiments were performed using modified electrode in phosphate buffer solution containing various concentration of PH. The results show the electrocatalytic peak current of PH oxidation at the surface of modified electrode was linearly dependent on the PH concentrations. The mediated oxidation peak currents of PH at the surface of a modified electrode were proportional to the concentration of the PH within the ranges 6.0×10^{-7} M– 9.0×10^{-4} M (with a correlation coefficient of 0.9991) in the differential pulse voltammetry. The detection limits (3σ) wad 1.31×10^{-7} M.

3.5. Simultaneous determination of PH, HZ and ST at MCNPE

One of the main objectives of the present study was the development of a modified electrode capable of the electro-catalytic oxidation of PH and separation of the electrochemical responses of PH, HZ and ST.

The utilization of the modified electrode for the simultaneous determination of PH, HZ and ST was demonstrated by simultaneously changing the concentrations of PH, HZ and ST. The differential pulse voltammetric results show three-well-defined anodic peaks (Fig. 4), while the bare carbon paste electrode only gave an overlapped and broad oxidation peak. Fig. 4 insets A, B and C show the dependence of differential pulse voltammetric peak currents on the concentration of PH, HZ and ST respectively. The sensitivity towards PH in the absence and presence of HZ and ST was found to be 0.030 (absence of HZ and ST) and 0.029 (presence of HZ and ST) μA.μM^{-1}. It is very interesting to note that the sensitivities of the modified electrode towards PH in the absence and presence of HZ and ST, are virtually the same, which indicate the fact that the oxidation processes of PH, HZ and ST, at the modified electrode are independent and therefore simultaneous or independent measurements of the three analytes are possible without any interference. If the PH signal was affected by the HZ and ST, the above-mentioned slopes would be different.

3.6. Determination of PH, HZ and ST in real samples

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of PH, HZ and ST in urine and water samples. The samples tested were found to be free from PH, HZ and ST, and thus synthetic samples were prepared by adding known amounts of PH, HZ and ST to urine and water samples. The results are given in Table 1.

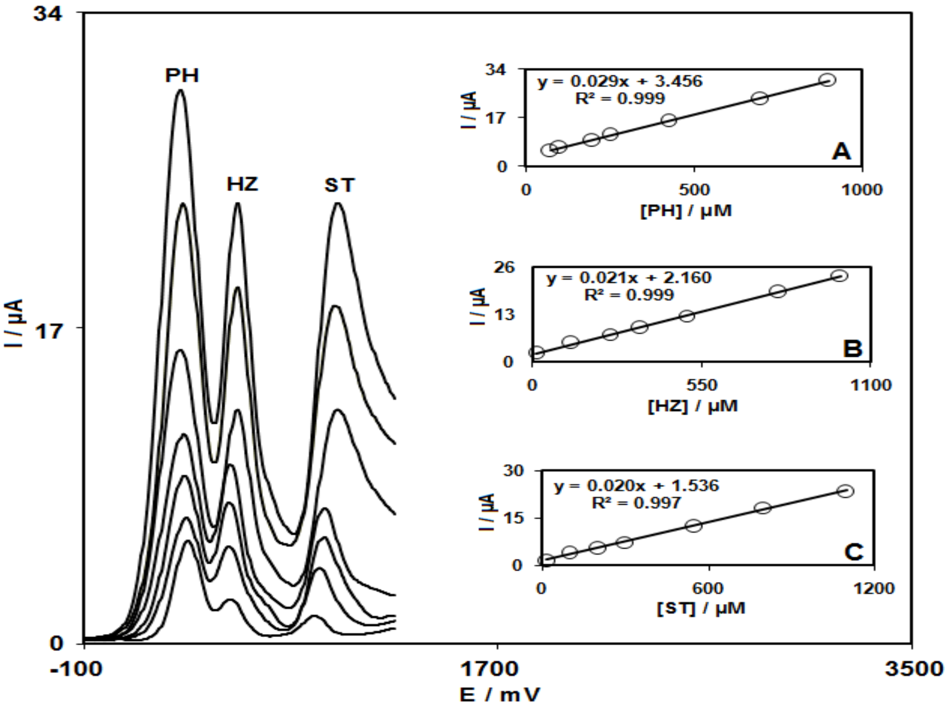

Figure 4. Differential pulse voltammograms of MCNPE in 0.1M PBS (pH 5.0) containing different concentrations of PH, HZ and ST (from inner to outer) mixed solutions of 75+10+15, 100+125+100, 200+250+200, 250+350+300, 425+500+550, 700+800+800 and 900+1000+1100 respectively, in which the first value is concentration of PH in µM, the second value is concentration of HZ in µM and the third value is concentration of ST in µM. Insets: (A) Plot of the peak currents as a function of PH, (B) HZ and (C) ST concentrations respectively.

4. CONCLUSION

A modified carbon nanotube paste electrode has been fabricated and the results demonstrated that the electrooxidation of PH at the surface of modifies electrode occurs at a potential about 250 mV. The modified electrode has been shown to be promising for PH detection with many desirable properties including high sensitivity, excellent catalytic activity and low detection limit. The kinetic parameters of the electrocatalytic process and the diffusion coefficients of PH were determined. The electrocatalytic oxidation currents of PH at the surface of modified electrode were linear to concentration of PH. The modified electrode displays improved selectivity for voltammetric measurement of PH, HZ and ST in solutions containing three analytes. This method was also used for the determination of PH, HZ and ST in urine and water samples using standard addition method.

Table 1. The application of MCNPE for simultaneous determination of PH, HZ and ST in urine and water samples.

Sample	PH Added (μM)	PH Found (μM)	Rec. (%)	RSD (%)	HZ Added (μM)	HZ Found (M)	Rec. (%)	RSD (%)	ST Added (μM)	ST Found (μM)	Rec. (%)	RSD (%)
Urine	0	0	-	-	0	0	-	-	0	0	-	-
	10	9.91	99.1	3.4	20	20.71	103.55	1.7	25	25.6	102.4	2.3
	15	15.41	102.7	1.3	25	24.4	97.6	2.2	30	31.1	103.67	3.1
	20	19.57	97.85	2.3	30	30.42	101.4	3.2	35	34.5	98.57	1.9
River Water	0	0	-	-	0	0	-	-	0	0	-	-
	10	10.25	102.5	1.5	20	19.73	98.65	2.6	25	25.3	101.2	3.2
	15	14.79	98.6	3.1	25	25.8	103.2	1.9	30	29.3	97.67	2.6
	20	20.61	103.1	2.1	30	29.19	97.3	2.3	35	35.9	102.57	3.3
Drink Water	0	0	-	-	0	0	-	-	0	0	-	-
	10	10.12	101.2	2.9	20	20.56	102.8	1.8	25	24.3	97.2	2.4
	15	14.58	97.2	1.6	25	25.32	101.28	2.8	30	30.4	101.33	2.2
	20	19.82	99.1	2.4	30	29.45	98.17	3.3	35	36.1	103.14	1.8

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