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ORIGINAL PAPER

Sensitive and selective determination of phenylhydrazine in the presence of hydrazine at a ferrocene-modified carbon nanotube paste electrode

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Abstract The determination of hydrazine derivatives is of special interest because they are toxic and widely used in industry, agriculture and explosives. Electrochemical analysis has become of growing importance in industrial process control, environmental monitoring, and different applications in medicine and biotechnology. In the present work, we used a carbon paste electrode modified by ferrocene and carbon nanotubes for simultaneous determination of phenylhydrazine and hydrazine. The modified electrode showed an excellent character for electrocatalytic oxidization of phenylhydrazine and hydrazine with a 310 mV separation of both peaks. Differential pulse voltammetric peak currents of phenylhydrazine and hydrazine increased linearly with their concentrations at the range of 0.85–700 and 16–800 μM, and the detection limits (3σ) were determined to be 0.6 and 14 μM, respectively. Here, we show that this electrode could be used as an electrochemical sensor for determination of phenylhydrazine and hydrazine in real samples (water and urine) with advantages such as short time of analysis, lack of pretreatment procedures and more cheaper in comparison with some routine analysis methods such as chromatography or spectroscopy. The modified electrode showed good reproducibility, remarkable long-term stability, and especially good surface renewability by simple mechanical polishing.

Keywords Phenylhydrazine · Hydrazine · Carbon nanotube · Electrocatalysis · Modified electrode · Ferrocene

Introduction

Hydrazine 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 (Schessl 1995). It is also employed as a starting material for many derivatives such as foaming agents for plastics, antioxidants, polymers, and plant-growth regulators. Moreover, hydrazine, its salts, and its methyl and dimethyl derivatives are used as rocket fuel, gas generators, and explosives (US Environmental protection Agency 1999). Hydrazine 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. Hydrazine is volatile and toxic and is readily absorbed by oral, dermal, or inhalation routes of exposure (Pingarron et al. 2001). Acute exposure can also damage the liver, kidneys, and central nervous system in humans (US Department of Health and Human Services 1993). The carcinogenic risks to humans of hydrazine and its derivatives have been considered on a number of occasions by the International Agency for Research on Cancer of the World Health Organization (World Health Organization 1987). Environmental Protection Agency (EPA) has classified hydrazine as a group B_2 (human carcinogen) (World Health Organization 1987). EPA and Agency for Toxic Substance and Disease Registry calculated an intermediate inhalation minimal risk level of 0.004 μg ml^{-1} (US Department of

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Health and Human Services 1993). The National Institute for Occupational Safety and Health and the Occupational Safety and Health Administration recommended that the level of hydrazine in workplace air not exceed 0.03 μg ml^{-1} for a 2-h period (National Institute for Occupational Safety and Health (NIOSH) 1997). Also the Food and Drug Administration has ruled that hydrazine cannot be added to water used for making steam which will contact food. Because of the environmental and toxicological significance of hydrazine compounds, sensitive and reliable analytical methods are necessary for preconcentration and determination of hydrazine in samples.

Several instrumental methods for determination of hydrazine by chromatography (Mori et al. 2004), spectrophotometry (Zarei 2007; Afkhami and Zarei 2004), flow injection with spectrophotometry (Ensafi and Naderi 1997), capillary electrophoresis (Siangproh et al. 2005), and fluorimetry (Safavi and Karimi 2002) have been reported.

Electroanalytical techniques seem to provide direct and efficient methods for the detection of hydrazine 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 (Richard Prabakar and Sriman Narayanan 2008; Jayasri and Sriman Narayanan 2007; Yang et al. 2007; Zheng et al. 2007; Yang and Li 2002).

Carbon nanotubes are a new kind of inorganic material with nanostructure, which is promising as an immobilization substance for different electron transfer mediators. The application of carbon nanotubes for fabrication of electrochemical sensors and biosensors is reviewed by many research groups. The electronic properties of these nanomaterials have been exploited as a mean of promoting the electron transfer reaction for a wide range of molecules and biological species (Lin et al. 2006; Balasubramanian and Burghard 2006; Shahrokhian and Amiri 2007; Beitollahi et al. 2008).

To our knowledge, no study has reported the electrocatalytic and simultaneous determination of phenylhydrazine and hydrazine by using carbon nanotube paste electrodes. Also, no paper has reported ferrocene as catalyst for electrocatalysis of phenylhydrazine. Thus, in continuation of our studies concerning the preparation of chemically modified electrodes (Mirmomtaz et al. 2008; Raoof et al. 2008; Karimi-Maleh et al. 2010), in the present work, we described initially the preparation and suitability of a ferrocene-modified carbon nanotube paste electrode as a new electrode in the electrocatalysis and determination of phenylhydrazine in an aqueous buffer solution, then we evaluated the analytical performance of the modified electrode in quantification of phenylhydrazine in the presence of hydrazine. Finally, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of phenylhydrazine and hydrazine in real samples, we examined this method for the voltammetric determination of phenylhydrazine and hydrazine in human urine and water samples.

Experimental

Apparatus and reagents

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

An Ag/AgCl/KCl 3 M, a platinum wire, and a ferrocene-modified carbon nanotube paste electrode were used as reference, auxiliary, and working electrodes, respectively. A digital pH/mV meter (Metrohm model 710) was applied for pH measurements. Graphite fine powder, paraffin oil, and reagents were analytical grade from Merck. Phenylhydrazine and hydrazine were purchased from Merck. Multi-walled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 0.5 to 200 nm were prepared from Nanostruc-tured & Amorphous Materials (USA). The buffer solutions were prepared from ortho phosphoric acid and its salts in the pH range 2.0–11.0.

Preparation of the electrode

Modified carbon nanotube paste electrodes were prepared by dissolve 0.01 g of ferrocene 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 ferrocene-spiked carbon nanotube powder and paraffin oil was blended by hand mixing for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 2 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 ferrocene and carbon nanotube to the mixture and was used for comparison purposes.

Results and discussion

Electrochemical behavior of modified electrode

Cyclic voltammetry was employed for investigation the electrochemical properties of modified electrode in a pure buffered aqueous solution (pH 7.0). The cyclic voltammogram (Fig. 1) exhibits an anodic and corresponding cathodic peaks with $E_{pa} = 0.370$ Vand $E_{pc} = 0.265$ V vs. Ag/AgCl/KCl 3 M. The experimental results show well-defined and reproducible anodic and cathodic peaks related to ferrocene/ferricenium redox couple with quasireversible behavior, because of the peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$, is greater than that of $59/n$ mV expected for a reversible system. Also, the obtained result from cyclic voltammetry of this modified electrode in various buffered solutions does not show any shift in the anodic and cathodic peak potentials. Therefore, the electrochemical behavior of the redox process of ferrocene/ferricenium couple in modified electrode is independent on the pH of aqueous solution.

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 modified electrodes (Table 1). The calculated RSD 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.

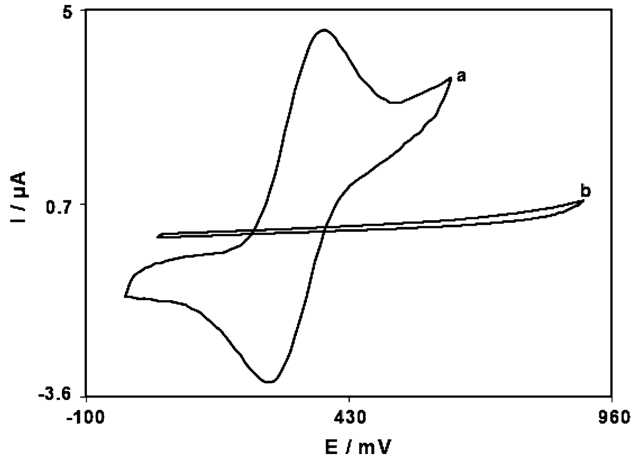

Fig. 1 The cyclic voltammograms of **a** modified electrode and **b** bare carbon paste electrode in 0.1 M phosphate buffer solution (pH 7.0) containing at a scan rate 20 mV s^{-1}

In addition, the long-term stability of the modified electrode was tested over a 3-week period. The cyclic voltammetry of phenylhydrazine at the surface of modified electrode after the modified electrode was stored in an atmosphere at room temperature shows the oxidation peak potential of phenylhydrazine was unchanged, and the anodic peak current was only decreased less than 2.43% of the initial oxidation peak current. The antifouling properties of modified electrode toward phenylhydrazine and its oxidation product were investigated by recording the cyclic voltammograms of this modified electrode before and after using in the presence of phenylhydrazine.

The cyclic voltammetry of phenylhydrazine at the surface of modified electrode after 15 repetition cycles at a scan rate 20 mVs^{-1} shows the oxidation peak potential of phenylhydrazine was not changed, and the anodic peak current was decreased by less than 3.35%. However, we regenerated the surface of modified electrode before each experiment.

Electrochemistry of phenylhydrazine at modified electrode

Figure 2 depicts the cyclic voltammetric responses from the electrochemical oxidation of 200 μM phenylhydrazine at ferrocene-modified carbon nanotube paste electrode (curve f), ferrocene-modified carbon paste electrode (curve e), carbon nanotube paste electrode (curve d), and bare carbon paste electrode (curve a). As can be seen, the anodic peak potential for the oxidation of phenylhydrazine at ferrocene-modified carbon nanotube paste electrode (curve f) and ferrocene-modified carbon paste electrode (curve e) is about 370 mV, while at the CNPE (curve d) peak potential is about 700 mV, and at the bare carbon paste electrode (curve b) peak potential is about 755 mV for phenylhydrazine. From these results, it is concluded that the best electrocatalytic effect for phenylhydrazine oxidation is observed at ferrocene-modified carbon nanotube paste electrode (curve f). For example, the results are shown that the peak potential of phenylhydrazine oxidation at ferrocene-modified carbon nanotube paste electrode (curve f) shifted by about 330 and 385 mV toward the negative values compared with that at a carbon nanotube paste electrode (curve d) and bare carbon paste electrode (curve b), respectively. Similarly, when we compared the oxidation of phenylhydrazine at the ferrocene-modified carbon paste electrode (curve e) and ferrocene-modified carbon nanotube paste electrode (curve f), there is a dramatic enhancement of the anodic peak current at ferrocene-modified carbon nanotube paste electrode relative to the value obtained at the ferrocene-modified carbon nanotube paste electrode. In the other words, the data obtained clearly show that the combination of carbon nanotube and

Table 1 Cyclic voltammetric data obtained for constructed ferrocene-modified carbon nanotube paste electrode in 0.1 phosphate buffer solution (pH 7.0) at 20 mVs^{-1}

E_{pa} (V)[a]	E_{pc} (V)[a]	$E_{1/2}$ (V)[a]	ΔE_{pa} (V)[a]	I_{pa} (μA)	I_{pc} (μA)	Γ_a (mol cm^{-2})	Γ_c (mol cm^{-2})
0.370 (0.75)[b]	0.265 (0.67)[b]	0.3175 (0.78)[b]	0.105 (0.81)[b]	4.55 (2.45)[b]	3.27 (2.12)[b]	1.85×10^{-9} (3.4)[b]	1.45×10^{-9} (2.8)[b]

[a] Versus Ag/AgCl/KCl 3 M as reference electrode

[b] The values in parenthesis indicate the calculated RSD

mediator (ferrocene) definitely improve the characteristics of phenylhydrazine oxidation. The ferrocene-modified carbon nanotube paste electrode in 0.1 M phosphate buffer (pH 7.0), without phenylhydrazine in solution, exhibits a well-behaved redox reaction (curve c) upon the addition of 200 μM phenylhydrazine, the anodic peak current of mediator was greatly increased, while the corresponding cathodic peak was disappear on the reverse scan of the potential (curve f). This behavior is typical of that expected for electrocatalysis at chemically modified electrodes (Bard and Faulkner 2001).

The effect of scan rate on the electrocatalytic oxidation of 200 μM phenylhydrazine at the modified electrode was investigated by cyclic voltammetry. 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.

Tafel plot that was drawn from data of the rising part of the current–voltage curve recorded at a scan rate of 20 mVs^{-1}. This part of voltammogram, known as Tafel region, is affected by electron transfer kinetics between substrate (phenylhydrazine) and surface confined ferrocene, assuming the deprotonation of substrate as a sufficiently fast step. In this condition, the number of electron involved in the rate determining step can be estimated from the slope of Tafel plot. A slope 0.114 V $decade^{-1}$ is obtained indicating a one electron transfer to be rate limiting assuming a transfer coefficient of $\alpha = 0.48$.

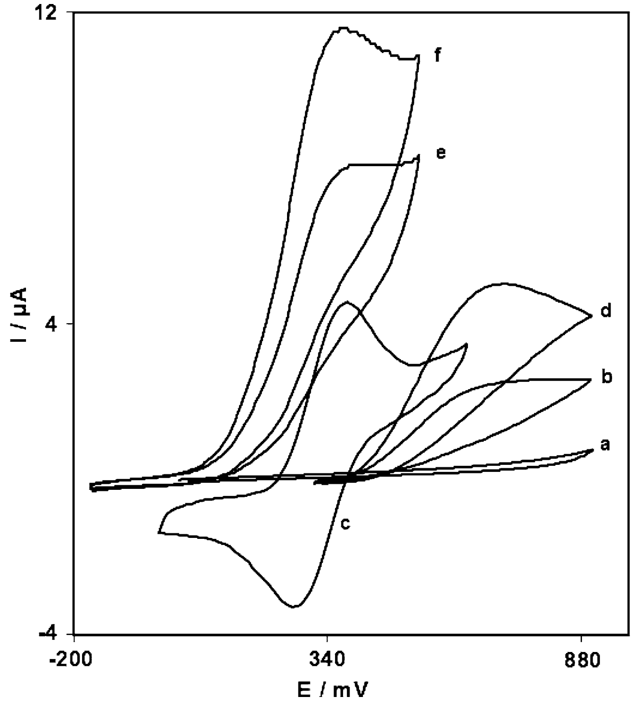

Fig. 2 Cyclic voltammograms of **a** carbon paste electrode in 0.1 M PBS (pH 7.0) at scan rate 20 mV s^{-1} and **b** as (**a**) + 200 μM phenylhydrazine; (**c**) as (**a**) and (**d**) as (**b**) at the surface of ferrocene-modified carbon paste electrode and carbon nanotube paste electrode, respectively. Also, (**e**) and (**f**) as (**b**) at the surface of ferrocene-modified paste electrode and ferrocene-modified carbon nanotube paste electrode, respectively

Chronoamperometric studies

The catalytic oxidation of phenylhydrazine by a modified electrode was also studied by chronoamperometry. Chronoamperometric measurements of different concentrations of phenylhydrazine at modified electrode were done by setting the working electrode potential at 450 mV. In chronoamperometric studies, we have determined the diffusion coefficient, *D*, of phenylhydrazine. The experimental plots of *I* versus $t^{-1/2}$ with the best fits for different concentrations of phenylhydrazine were employed. The slopes of the resulting straight lines were then plotted versus the phenylhydrazine—concentrations, from whose slope and using the Cottrell equation (Bard and Faulkner 2001):

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \tag{1}$$

we calculated a diffusion coefficient of 1.97×10^{-6} cm^2 s^{-1} for phenylhydrazine.

Calibration plot and limit of detection

Differential pulse voltammetry was used to determine the concentration of phenylhydrazine. Responses were linear with phenylhydrazine concentrations ranging from 8.5×10^{-7} to 7.0×10^{-4} M and a current sensitivity of 0.0389 μA/μM. The detection limit (3σ) was 0.6 μM.

Table 2 Determination of phenylhydrazine and hydrazine in real samples

Sample	phenylhydrazine Added (μM)	phenylhydrazine Found(μM)[a]	Recovery (%)	RSD (%)	hydrazine Added (μM)	hydrazine Found(M)[a]	Recovery (%)	RSD (%)
Drinking water	0	0	–	–	0	0	–	–
	50	51.3	102.6	2.7	50	51.6	103.2	2.3
	100	101.4	101.4	1.8	100	98.3	98.2	1.6
	200	198.2	99.1	3.2	200	202.4	101.2	3.3
River water	0	0	–	–	0	0	–	–
	50	51.6	103.2	3.1	50	49.3	98.6	1.6
	100	98.6	98.6	1.5	100	98.5	98.5	3.2
	200	203.7	101.8	2.1	200	205.6	102.8	1.5
Urine	0	0	–	–	0	0	–	–
	50	48.8	97.6	2.9	50	48.8	97.6	2.5
	100	103.2	103.2	1.7	100	97.8	97.8	1.3
	200	204.7	102.3	2.2	200	202.7	101.3	2.8

[a] Average of five replicate measurement

Simultaneous determination of phenylhydrazine and hydrazine at modified electrode

One of the main objectives of the present study was the development of a modified electrode capable of the electrocatalytic oxidation of phenylhydrazine and separation of the electrochemical responses of phenylhydrazine and hydrazine. Also, using modified electrode as the working electrode, the analytical experiments were carried out by varying either the hydrazine concentration in the presence of 350 μM phenylhydrazine in 0.1 M phosphate buffer (pH 7.0) and slope was 0.0253 μA μM^{-1} (Fig. 3). From the analysis of data, we estimate that the lower limit of detection of hydrazine is approximately 14 μM. Results show that an increase in the peak current of hydrazine is observed with increasing hydrazine concentration, and the voltammetric peak of phenylhydrazine is almost unchanged during the oxidation of hydrazine.

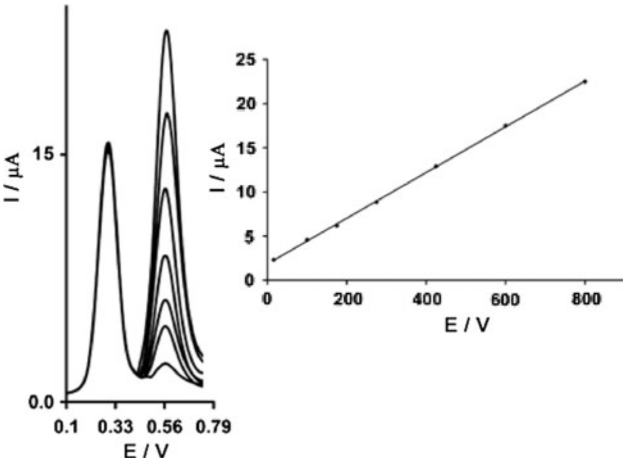

Fig. 3 Differential pulse voltammograms of modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing 350 μM phenylhydrazine and different concentrations of hydrazine (from inner to outer): 16, 100, 175, 275, 425, 600, and 800 μM. *Inset*: plot of the electrocatalytic peak current as a function of hydrazine concentration

The utilization of the modified electrode for the simultaneous determination of phenylhydrazine and hydrazine was demonstrated by simultaneously changing the concentrations of phenylhydrazine and hydrazine. The differential pulse voltammetric results show two-well-defined anodic peaks with a 310 mV separation of both peaks (Fig. 4), while the bare carbon paste electrode only gave an overlapped and broad oxidation peak. Figure 4 insets a and b show the dependence of differential pulse voltammetric peak currents on the concentration of phenylhydrazine and hydrazine, respectively. The sensitivity toward phenylhydrazine in the absence and presence of hydrazine was found to be 0.0375 (absence of hydrazine) and 0.0380 (presence of hydrazine) μA μM^{-1}. It is very interesting to note that the sensitivities of the modified electrode toward phenylhydrazine in the absence and presence of hydrazine are virtually the same, which indicate the fact that the oxidation processes of phenylhydrazine and hydrazine, at the modified electrode are independent and therefore simultaneous or independent measurements of the two analytes are possible without any interference. If the phenylhydrazine signal was affected by the hydrazine, the above-mentioned slopes would be different.

Interference studies

The influence of various substances as compounds potentially interfering with the determination of phenylhydrazine

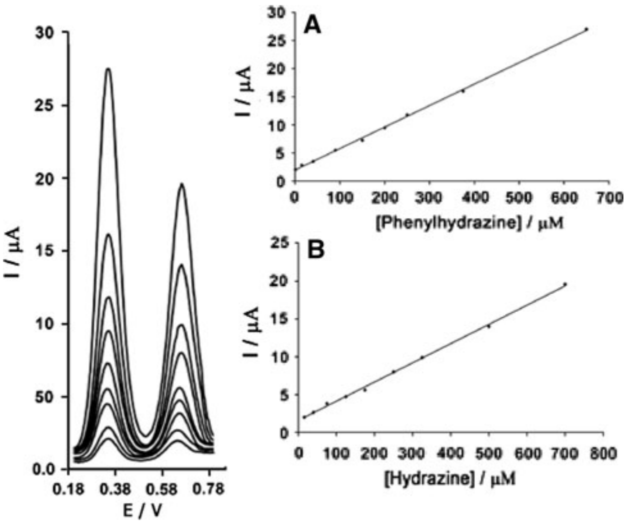

Fig. 4 Differential pulse voltammograms of modified electrode in 0.1 M PBS (pH 7.0) containing different concentrations of phenylhydrazine and hydrazine. (from inner to outer) mixed solutions of 1.0 + 16, 15 + 40, 40 + 75, 90 + 125, 150 + 175, 200 + 250, 250 + 325, 375 + 500, and 650 + 700, respectively, in which the first value is concentration of phenylhydrazine in µM, and the second value is concentration of hydrazine in µM. **a** Plots of the peak currents as a function of phenylhydrazine concentration and **b** Plot of the peak currents as a function of hydrazine concentration

and hydrazine was studied under optimum conditions with 20 µM phenylhydrazine and hydrazine at pH 7.0. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±5% in the determination of phenylhydrazine and hydrazine. According to the results, neither an 600-fold excess of glucose, sucrose, lactose, fructose, or citric acid nor a 500-fold excess of methanol, ethanol, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, SO_4^{2-}, SO_3^{2-}, Al^{3+}, As^{3+}, NH_4^+, Fe^{2+}, Fe^{3+}, CO_3^{2-}, Sn^{4+}, NO^{3-}, Cl^-, Br^-, or F^-nor a 150-fold excess of alanine, methionine, phenylalanine, glycine, or folic acid (vitamin B_9) affected the selectivity. In addition, neither a saturated starch solution nor a 50-fold excess of urea interfered with the determination of phenylhydrazine and hydrazine. Although ascorbic acid showed interference. This interference could be minimized, if necessary, by using ascorbic oxidase enzyme, which exhibits a high selectivity to the oxidation of ascorbic acid.

Determination of phenylhydrazine and hydrazine in real samples

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of phenylhydrazine and hydrazine in water and human urine samples.

The samples tested were found to be free from phenylhydrazine and hydrazine and thus, synthetic samples were prepared by adding known amounts of phenylhydrazine and hydrazine to water samples. The results are given in Table 2.

Conclusion

This work demonstrates the construction of a carbon nanotube paste electrode chemically modified by incorporation of ferrocene. The peak separation potential obtained for the ferrocene/ferricenium redox couple suggests that the couple can act as a quasi-reversible system in the carbon nanotube paste matrix. The carbon nanotube paste electrode modified with ferrocene was quite stable. This electrode is simple to prepare, and surface renewal is easy. The electrochemical behavior of ferrocene has been studied by cyclic voltammetry and chronoamperometry in both the absence and presence of phenylhydrazine. The results show that the oxidation of phenylhydrazine is catalyzed at pH 7.0, where the peak potential of phenylhydrazine is shifted by −385 mV at the surface of the modified electrode. The modified electrode displays improved selectivity for voltammetric measurement of phenylhydrazine and hydrazine in solutions containing both analytes. The oxidation peak potentials for phenylhydrazine and hydrazine in differential pulse voltammetry are separated by approximately 310 mV.

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