

*Full Paper*

## **Graphene Oxide Nano-sheets/Ferrocene Derivative Modified Carbon Paste Electrode as an Electrochemical Sensor for Determination of hydrazine**

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**Abstract-** A ferrocene-derivative compound, 2,7-bis (ferrocenyl ethynyl) fluoren-9-one (2,7-BFE), was synthesized and used to construct a modified-graphene oxide nano-sheets paste electrode. The electro-oxidation of hydrazine at the surface of the modified electrode was studied using electrochemical approaches. Under the optimized conditions, the square wave voltammetric peak current of hydrazine increased linearly with hydrazine concentrations in the range of  $2.2 \times 10^{-7}$  to  $3.0 \times 10^{-4}$  M and a detection limit of  $9.8 \times 10^{-8}$  M was obtained for hydrazine. Finally this modified electrode was used for determination of hydrazine in some water samples.

**Keywords-** Hydrazine, Graphene oxide nano-sheets, Chemically modified electrodes, Electrochemical sensors

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### **1. INTRODUCTION**

Hydrazine has been recognized as a neurotoxin, carcinogenic mutagenic [1] and hepatotoxic substance, which has adverse health effects such as liver, brain [2], DNA damage

[3], creation of blood abnormalities, and irreversible deterioration of the nervous system [1]. Moreover, hydrazine and its derivatives have been reported as environmental pollutants by Environmental Protection Agency (EPA) and the maximum recommended value of hydrazine in effluents is set to 1 ppm [4]. On the other hand, hydrazine and its derivatives have wide applications in industry and agriculture, as explosives, antioxidants, photographic developer, oxygen scavengers, insecticide, plant-growth regulators and propellants. Hydrazine is also considered as a base product in fuel cells [5]. Because of the great importance of hydrazine, its accurate and economical determination is still a challenging research in analytical chemistry [6,7]. Among several techniques that have been reported for the determination of hydrazine such as spectrophotometry, amperometry, potentiometry, titrimetry and chemiluminescence, electrochemical techniques offer the opportunity for portable, economical, sensitive and rapid methodologies [8,9].

The electrochemical behaviour of hydrazine is sensitive to the electrode surface structure. The direct oxidation of hydrazine at several electrodes has been investigated and large overpotentials have been reported. Although noble metals are active in the anodic oxidation of hydrazine, they are too expensive for practical applications and require a large overpotential for hydrazine oxidation. The electrooxidation of hydrazine on carbon electrodes are kinetically slow and are accompanied with large overpotentials. Modification of the electrode surface is an approach to enhance the rate of electron transfer and minimize overpotential [10-12].

The modification of the surface of electrodes by nanoparticles has long been a significant area of the theoretical and applied researches. The unique properties of nanoparticulate materials (e.g. enhanced mass transport, high surface area, improved signal-to-noise ratio) can often be advantageous in electroanalytical techniques. It is because of dependence of the electrochemical heterogeneous procedures on the properties of electrode surfaces, adsorption and diffusion mechanisms, and coatings applied on the electrode surface [13-26].

Since its discovery in 2004, graphene has attracted considerable attention because of its novel properties, such as thermal and chemical stability, superior biocompatibility, high carrier mobility, and electrical conductivity. Graphene is a superior electrode material for electrochemical sensor and biosensor applications [27-36].

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 [37]. The use of carbon paste as an electrode was initially reported in 1958 by Adams [38]. In afterward researches a wide variety of modifiers including enzymes, polymers (nafion, chitosan, etc.) and nanomaterials have been used with these versatile electrodes [38-42]. 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. 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 [43-47].

To our knowledge, no study has reported the electrocatalytic oxidation of hydrazine using 2, 7-bis (ferrocenyl ethynyl) fluoren-9-one (2,7-BFE) modified graphene oxide nano-sheets paste electrode (2,7-BFEGPE). Thus, in the present work, we described initially the preparation and suitability of a 2,7-BFEGPE as a new electrode in the electrocatalysis and determination of hydrazine in an aqueous buffer solution. Then, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of hydrazine in real samples, we examined this method for the voltammetric determination of hydrazine in water samples.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

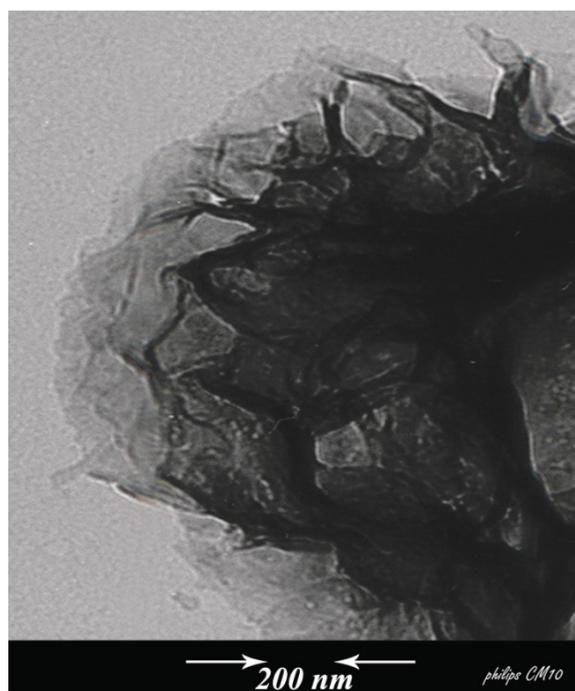
The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at  $25 \pm 1$  °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and 2,7-BFEGPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Hydrazine and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. 2,7-BFE was synthesized in our laboratory as reported previously [48].

### 2.2. Synthesis of graphene oxide nano-sheets

Graphene oxide nano-sheets were synthesized from natural graphite flakes based on the modified Hummers and Offeman's method [49]. In a typical synthesis process, 1.0 g of pristine graphite flakes was immersed in 50 mL of formic acid, and then sonicated for 2 h at room temperature. These resulting graphite plates were washed with acetone, and then dried in an oven at 95 °C for 12 h. Then, 100 mL H<sub>2</sub>SO<sub>4</sub> (95%) was added into a 500 mL flask, and cooled by immersion in an ice bath followed by stirring. About 1.0 g treated graphite powder and 0.5 g NaNO<sub>3</sub> were added under vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed, 3 g KMnO<sub>4</sub> was added gradually under stirring and cooling so that the temperature of the mixture was maintained below 10 °C. The mixture was stirred for 2 h and diluted with deionised double distilled water (in an ice bath). After that, 25

ml 15%  $\text{H}_2\text{O}_2$  was slowly added to the mixture until the colour of the mixture changed to brilliant yellow, indicating fully oxidised graphite. The as-obtained graphite oxide slurry was re-dispersed in deionised double distilled water and then exfoliated to generate graphene oxide nano-sheets by sonication for 2 h. Then, the solution was filtered and washed with diluted HCl solution to remove metal ions. Finally, the product was washed with deionised double distilled water until the solution became acid free, and dried under vacuum at 50 °C. A typical TEM for synthesized graphene nano-sheets is shown in Fig. 1.



**Fig. 1.** TEM image of synthesized graphene oxide nano-sheets

### 2.3. Preparation of the electrode

The 2,7-BFEGPEs were prepared by hand mixing 0.01 g of 2,7-BFE with 0.89 g graphite powder and 0.1 g G with a mortar and pestle. Then, ~0.7 mL of paraffin was added to the above mixture and mixed for 20 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). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, 2,7-BFE modified CPE electrode (2,7-BFECPE) without G, G paste electrode (GPE) without 2,7-BFE, and unmodified CPE in the absence of both 2,7-BFE and G were also prepared in the same way.

### 3. RESULT AND DISCUSSION

#### 3.1. Electrochemical Behavior of 2,7-BFEGPE

2,7-BFEGPE was constructed and its electrochemical properties were studied in a 0.1 M PBS (pH 7.0) using CV. The experimental results show well-defined and reproducible anodic and cathodic peaks related to 2,7-bis(ferrocenyl ethynyl)fluoren-9-one/2,7-bis(ferricenium ethynyl)fluoren-9-one redox system, with  $E_{pa}$ ,  $E_{pc}$  and  $E^{\circ'}$  of 460, 290 and 375 mV vs. Ag/AgCl/KCl (3.0 M) respectively. The observed peak separation potential,  $\Delta E_p = (E_{pa} - E_{pc})$  of 170 mV, was greater than the value of  $59/n$  mV expected for a reversible system [50] suggesting that the redox couple of 2,7-BFE in 2,7-BFEGPE has a quasi-reversible behavior in aqueous medium.

In addition, the long term stability of the 2,7-BFEGPE was tested over a 2-week period. When CVs were recorded after the modified electrode was stored in atmosphere at room temperature, the peak potential for hydrazine oxidation was unchanged and the current signals showed less than 2.5% decrease relative to the initial response. The antifouling properties of the modified electrode toward hydrazine oxidation and its oxidation products were investigated by recording the CVs of the modified electrode before and after use in the presence of hydrazine. CVs were recorded in the presence of hydrazine after having cycled the potential 15 times at a scan rate of  $10 \text{ mV s}^{-1}$ . The peak potentials were unchanged and the currents decreased by less than 2.4%. Therefore, at the surface of 2,7-BFEGPE, not only the sensitivity increase, but the fouling effect of the analyte and its oxidation product also decreases.

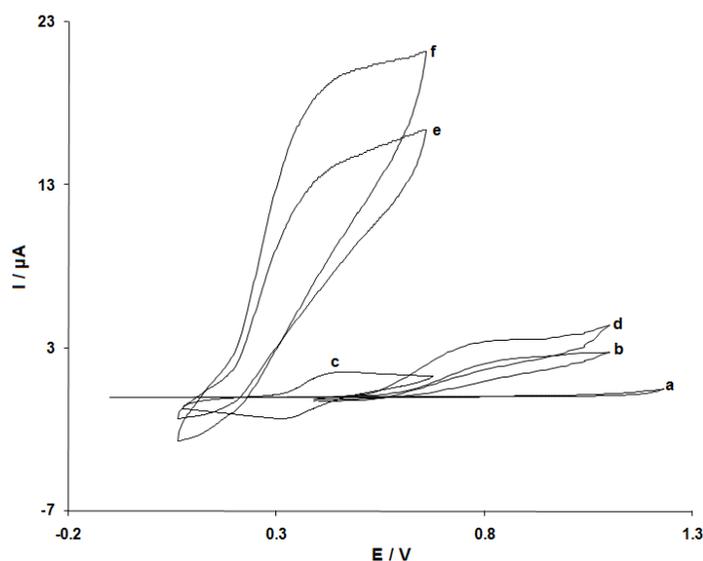
#### 3.2. Influence of pH

The electrochemical behavior of hydrazine is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of 2,7-bis(ferrocenyl ethynyl)fluoren-9-one / 2,7-bis(ferricenium ethynyl)fluoren-9-one ( $\text{Fc}/\text{Fc}^+$ ) redox couple are independent on pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of hydrazine. Thus the electrochemical behavior of hydrazine was studied in 0.1 M PBS in different pH values ( $2.0 < \text{pH} < 9.0$ ) at the surface of 2,7-BFEGPE by CV. It was found that the electrocatalytic oxidation of hydrazine at the surface of 2,7-BFEGPE was more favored under neutral conditions than in acidic or basic medium. This appears as a gradual growth in the anodic peak current and a simultaneous decrease in the

cathodic peak current in the CVs of 2,7-BFEGPE. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of hydrazine oxidation at the surface of 2,7-BFEGPE.

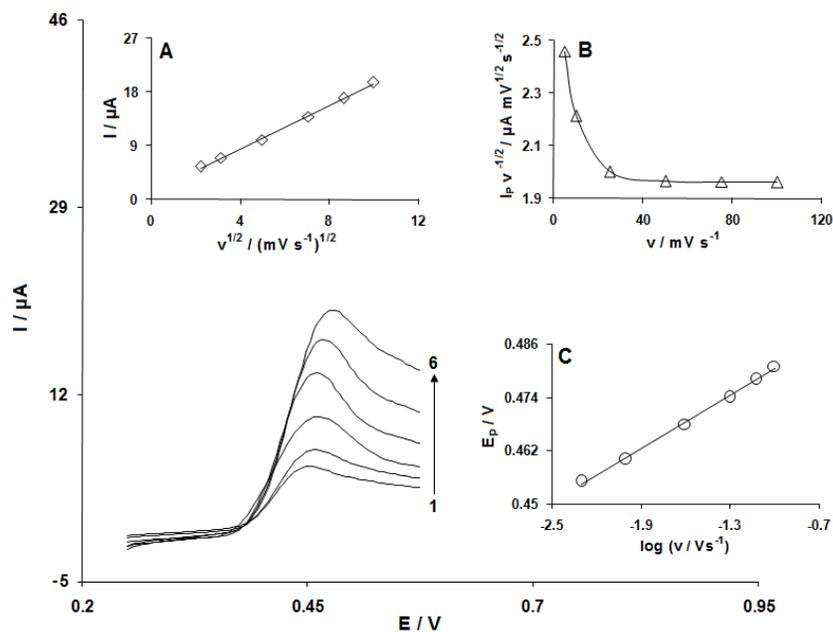
### 3.3. Electrocatalytic oxidation of hydrazine at a 2,7-BFEGPE

Fig. 2 depicts the CV responses for the electrochemical oxidation of 150.0  $\mu\text{M}$  hydrazine at unmodified CPE (curve b), graphene oxide nano- sheets paste electrode (GPE curve d), 2,7-BFECPE (curve e) and 2,7-BFEGPE (curve f). As it is seen, while the anodic peak potential for hydrazine oxidation at the GPE, and unmodified CPE are 820 and 870 mV, respectively, the corresponding potential at 2,7-BFECPE and 2,7-BFEGPE is  $\sim 460$  mV. These results indicate that the peak potential for hydrazine oxidation at the 2,7-BFECPE and 2,7-BFEGPE electrodes shift by  $\sim 360$  and 410 mV toward negative values compared to GPE and unmodified CPE, respectively. However, 2,7-BFEGPE shows much higher anodic peak current for the oxidation of hydrazine compared to 2,7-BFECPE, indicating that the combination of G and the mediator (2,7-BFE) has significantly improved the performance of the electrode toward hydrazine oxidation. In fact, 2,7-BFECPE in the absence of hydrazine exhibited a well-behaved redox reaction (Fig. 2, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 150.0  $\mu\text{M}$  hydrazine (curve f), which can be related to the strong electrocatalytic effect of the 5AEBCNPE towards this compound [50].



**Fig. 2.** CVs of (a) unmodified CPE in 0.1 M PBS (pH 7.0), (b) unmodified CPE in 150.0  $\mu\text{M}$  hydrazine, (c) 2,7-BFEGPE in 0.1 M PBS, (d) GPE in 150.0  $\mu\text{M}$  hydrazine, (e) 2,7-BFECPE in 150.0  $\mu\text{M}$  hydrazine, and (f) 2,7-BFEGPE in 150.0  $\mu\text{M}$  hydrazine. In all cases the scan rate was 10  $\text{mV s}^{-1}$ .

The effect of scan rate on the electrocatalytic oxidation of hydrazine at the 2,7-BFEGPE was investigated by LSV (Fig. 3). As can be observed in Fig. 3, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height ( $I_p$ ) vs. the square root of scan rate ( $v^{1/2}$ ) was found to be linear in the range of 5-100  $\text{mV s}^{-1}$  (Fig. 3A), suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled [50].



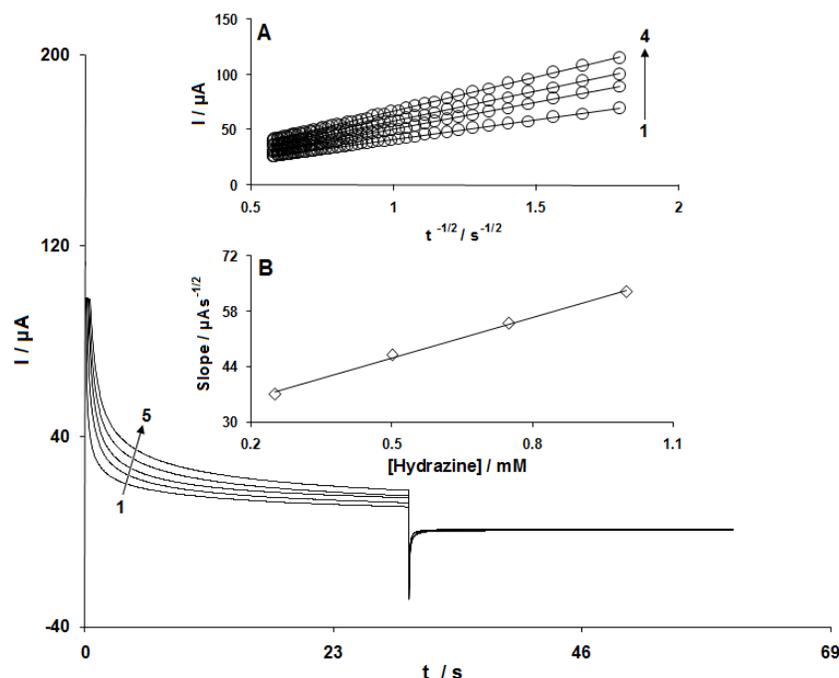
**Fig. 3.** LSVs of 2,7-BFEGPE in 0.1 M PBS (pH 7.0) containing 50.0  $\mu\text{M}$  hydrazine at various scan rates; Numbers 1-6 correspond to 5, 10, 25, 50, 75 and 100  $\text{mV s}^{-1}$ , respectively. Insets: Variation of (A) anodic peak current vs.  $v^{1/2}$ ; (B) normalized current ( $I_p/v^{1/2}$ ) vs.  $v$ , and (C) anodic peak potential vs.  $\log v$

A plot of the scan rate-normalized current ( $I_p/v^{1/2}$ ) vs. scan rate (Fig. 3B) exhibits the characteristic typical shape of an EC' process [50].

The Tafel slope ( $b$ ) can be obtained from the slope of  $E_p$  vs.  $\log v$  using Eq. (1) [50].

$$E_p = b/2 \log v + \text{constant} \quad (1)$$

The Tafel slope was found to be 0.02 V (Fig. 4.C), which indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient ( $\alpha$ ) is about 0.47.



**Fig. 4.** Chronoamperograms obtained at 2,7-BFEGPE in 0.1 M PBS (pH 7.0) for different concentration of hydrazine. The numbers 1–5 correspond to 0.0, 0.25, 0.5, 0.75 and 1.0 mM of hydrazine. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 2–5. (B) Plot of the slope of the straight lines against hydrazine concentration

### 3.4. Chronoamperometric measurements

Chronoamperometric measurements of hydrazine at 2,7-BFEGPE were carried out by setting the working electrode potential at at 0.55 V (at the first potential step) and at 0.2 V (at second potential step) vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of hydrazine in PBS (pH 7.0) (Fig. 4). For an electroactive material (hydrazine in this case) with a diffusion coefficient of  $D$ , the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [50]:

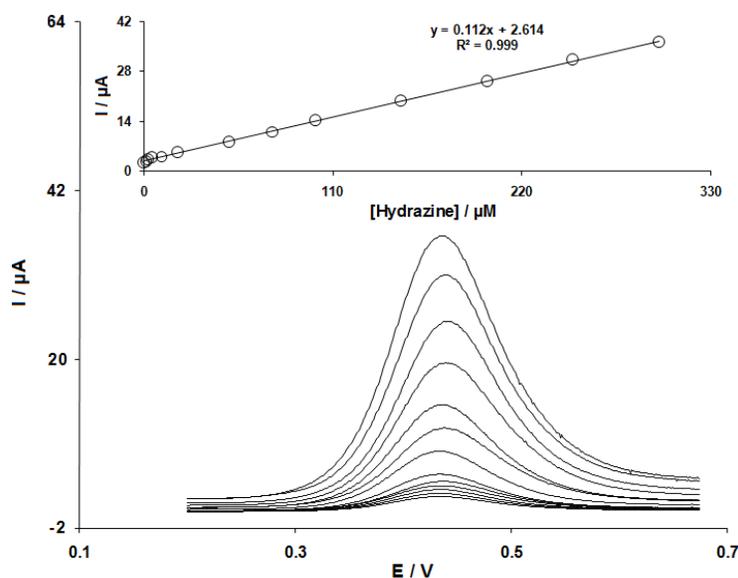
$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (2)$$

Where  $D$  and  $C_b$  are the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) and the bulk concentration ( $\text{mol cm}^{-3}$ ), respectively.

Experimental plots of  $I$  vs.  $t^{-1/2}$  were employed, with the best fits for different concentrations of hydrazine (Fig. 4A). The slopes of the resulting straight lines were then plotted vs. hydrazine concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the  $D$  was found to be  $1.2 \times 10^{-5} \text{ cm}^2/\text{s}$ .

### 3.5. Calibration plot and limit of detection

The peak current of hydrazine oxidation at the surface of the modified electrode can be used for determination of hydrazine in solution. Therefore, SWV experiments were done for different concentrations of hydrazine (Fig. 5). The oxidation peak currents of hydrazine at the surface of 2,7-BFEGPE were proportional to the concentration of the hydrazine within the ranges  $2.2 \times 10^{-7}$  to  $3.0 \times 10^{-4}$  M with a detection limit ( $3\sigma$ ) of  $9.8 \times 10^{-8}$  M.



**Fig. 5.** SWVs of 2,7-BFEGPE in 0.1 M PBS (pH 7.0) containing different concentrations of hydrazine; From inner to outer correspond to 0.22, 1.0, 2.5, 5.0, 10.0, 20.0, 50.0, 75.0, 100.0, 150.0, 200.0, 250.0 and 300.0  $\mu\text{M}$  of hydrazine. Inset B show the plots of the peak current as a function of hydrazine concentration in the range of 0.22-300.0  $\mu\text{M}$

### 3.6. Interference study

The influences of various substances as potential interfering compounds with the determination of hydrazine were studied under the optimum conditions. The potential interfering substances were chosen from the group of substances commonly found with hydrazine in water samples. The tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximately  $\pm 5\%$  relative error in the determination. The result of interfering studied shows that  $\text{Ni}^{2+}$ ,  $\text{CN}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Br}^-$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{+2}$ ,  $\text{Co}^{3+}$ ,  $\text{Cr}^{2+}$ , and  $\text{SCN}^-$ , glucose, sucrose, urea, lactose and fructose did not affect the selectivity. These results demonstrate that the modified electrode has a good selectivity for hydrazine.

### 3.7. Real sample analysis

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of hydrazine in water samples. Known amount of hydrazine were added to the water samples and their concentrations were estimated with the proposed method. The results for determination of the hydrazine in real samples are given in Table 1. Satisfactory recoveries of the experimental results were found for hydrazine. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

**Table 1.** The application of 2,7-BFEGPE for determination of hydrazine in water samples

Sample	Spiked ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	R.S.D. (%)
Well water	0	ND <sup>a</sup>	-	-
	2.5	2.4	96.0	3.4
	7.5	7.6	101.3	3.1
	12.5	12.8	102.4	1.9
	17.5	17.4	99.4	2.5
River water	0	ND <sup>a</sup>	-	-
	5.0	5.1	102.0	2.9
	10.0	9.9	99.0	2.1
	15.0	15.2	101.3	3.3
	20.0	19.5	97.5	2.7

<sup>a</sup> ND: Not detected

### 4. CONCLUSION

The 2,7-BFEGPE was prepared and used for the investigation of the electrochemical behavior of hydrazine. Two pairs of well-defined redox peaks were obtained at the 2,7-BFEGPE. The 2,7-BFEGPE showed excellent electrocatalytic activity for the hydrazine. The SWV currents of hydrazine at 2,7-BFEGPE increased linearly with the hydrazine concentration in the range from  $2.2 \times 10^{-7}$  to  $3.0 \times 10^{-4}$  M with a detection limit of  $9.8 \times 10^{-8}$  M. Finally, this method was used for the determination of hydrazine in some water samples.

### REFERENCES

- [1] S. Garrod, M. E. Bollard, A. W. Nicholls, S. C. Connor, J. Connelly, J. K. Nicholson, and E. Holmes, *Chem. Res. Toxicol.* 18 (2005) 115.

- [2] E. H. Vernot, J. D. MacEwen, R. H. Bruner, C. C. Haus and E. R. Kinkead, *Fund. Appl. Toxicol.* 5 (1985) 1050.
- [3] J. W. Mo, B. Ogorevc, X. Zhang, and B. Pihlar, *Electroanalysis* 12 (2000) 48.
- [4] S. Amlathe, and V. K. Gupta, *Analyst* 113 (1988) 1481.
- [5] [online] available: <http://www.asi.org/adb/04/03/09/hydrazine-info.html>.
- [6] S. Koçak, and B. Aslışen, *Sens. Actuators B* 196 (2014) 610.
- [7] R. Ojani, S. Safshekan, and J. B. Raoof, *J. Solid State Electrochem.* 18 (2014) 779 .
- [8] H. Beitollahi, S. Tajik, H. Karimi Maleh, and R. Hosseinzadeh, *Appl. Organometal. Chem.* 27 (2013) 444 .
- [9] H. Mashhadizadeh, *Anal. Bioanal. Electrochem.* 1 (2009) 224.
- [10] M. Hosseini, M. M. Momeni, and M. Faraji, *J. Mol. Catal. A* 335 (2011) 199.
- [11] Y. Y. Tang, C. L. Kao, and P. Y. Chen, *Anal. Chim. Acta* 711 (2012) 32.
- [12] S. Ershad, and M. Bejani, *Anal. Bioanal. Electrochem.* 4 (2012) 518.
- [13] M. A. Aziz, and A. N. Kawde, *Talanta* 115 (2013) 214.
- [14] S. Ershad, K. Dideban, and F. Faraji, *Anal. Bioanal. Electrochem.* 5 (2013) 178 .
- [15] S. Zhang, P. He, W. Lei, and G. Zhang, *J. Electroanal. Chem.* 724 (2014) 29.
- [16] R. Zhang, S. Liu, L. Wang, and G. Yang, *Measurement* 46 (2013) 1089 .
- [17] H. Soltani, H. Beitollahi, A. H. Hatefi-Mehrjardi, S. Tajik, and M. Torkzadeh-Mahani, *Anal. Bioanal. Electrochem.* 6 (2014) 67.
- [18] H. Beitollahi, and I. Sheikhshoaie, *Electrochim. Acta* 56 (2011) 10259.
- [19] T. Thomas, R. J. Mascarenhas, P. Martis, Z. Mekhalif, and B. E. K. Swamy, *Mater. Sci. Eng. C* 33 (2013) 3294 .
- [20] V. F. Ferreira, C. R. A. Do Prado, C. M. Rodrigues, L. Otubo, A. A. Batista, J. W. da Cruz Jr., J. Ellena, L. R. Dinelli, and A. L. Bogado, *Polyhedron* 78 ( 2014) 46.
- [21] L. Fotouhi, S. Arabiyan, and O. Moradlou, *Anal. Bioanal. Electrochem.* 5 (2013) 283 .
- [22] H. Beitollahi, S. Tajik, H. Parvan, H. Soltani, A. Akbari, and M. H. Asadi, *Anal. Bioanal. Electrochem.* 6 (2014) 54.
- [23] P. K. Brahman, R. A. Dar, and K. S. Pitre, *Sens. Actuators B* 177 (2013) 807 .
- [24] S. Pundir, N. Chauhan, J. Narang, and C. S. Pundir, *Anal. Biochem.* 427 (2012) 26 .
- [25] H. Beitollahi, and I. Sheikhshoaie, *J. Electroanal. Chem.* 661 (2011) 336.
- [26] F. F. Hudari, L. César de Almeida, B. Ferreira da Silva, and M. V. Boldrin Zanoni, *Microchem. J.* 116 (2014) 261.
- [27] X. Zhou, A. M. Cao, L. J. Wan, and Y. G. Guo, *Nano Res.* 5 (2012) 845 .
- [28] S. Tajik, M. A. Tahera, and H. Beitollahi, *Sens. Actuators B* 197 (2014) 228.
- [29] Z. Xing, Q. Chu, X. Ren, J. Tian, A. M. Asiri, K. A. Alamry, A. O. Al-Youbi, and X. Sun, *Electrochem. Commun.* 32 (2013) 9.
- [30] S. Tajik, M. A. Taher, and H. Beitollahi, *Electroanalysis* 26 (2014) 796.
- [31] M. B. Gholivand, M. Khodadadian, *Electroanalysis* 25 (2013) 1263.

- [32] H. Silva, J. G. Pacheco, J. M. C. S. Magalhães, S. Viswanathan, and C. Delerue-Matos, *Biosens. Bioelectron.* 52 (2014) 56.
- [33] Y. Ke, Y. Zeng, X. Pu, X. Wu, L. Li, Z. Zhu, and Y. Yu, *RSC Adv.* 2 (2012) 5676.
- [34] Q. Shi, G. Diao, and S. Mu, *Electrochim. Acta* 133 (2014) 335.
- [35] V. S. Reddy Channu, D. Ravichandran, B. Rambabu, and R. Holze, *Appl. Surf. Sci.* 305 (2014) 596.
- [36] V. Jouikov, and J. Simonet, *Electrochem. Commun.* 42 (2014) 34.
- [37] C. Serpi, L. Kovatsi, and S. Girousi, *Anal. Chim. Acta* 812 (2014) 26.
- [38] R. N. Adams, *Anal. Chem.* 30 (1958) 1576.
- [39] H. Beitollahi, J. B. Raoof, H. Karimi-Maleh, and R. Hosseinzadeh, *Anal. Bioanal. Electrochem.* 4 (2012) 32.
- [40] K. K. Aswini, A. M. Vinu Mohan, and V. M. Biju, *Mater. Sci. Engin. C* 37 (2014) 321.
- [41] S. Dönmez, F. Arslan, N. Sar, N. K. Yetim, and H. Arslan, *Biosens. Bioelectron.* 54 (2014) 146.
- [42] M. C. Teixeira, E. de F. L. Tavares, A. A. Saczk, L. L. Okumura, M. das Graça Cardoso, Z. M. Magriotis, and M. F. de Oliveira, *Food Chem.* 154 (2014) 38.
- [43] S. Tajik, M. A. Taher, and H. Beitollahi, *J. Electroanal. Chem.* 704 (2013) 137.
- [44] T. Thomas, R. J. Mascarenhas, O. J. D' Souza, S. Detriche, Z. Mekhalif, and P. Martis, *Talanta* 125 (2014) 352.
- [45] N. F. Atta, S. M. Ali, E. H. El-Ads, and A. Galal, *Electrochim. Acta* 128 (2014) 16.
- [46] H. Beitollahi, H. Karimi-Maleh, and H. Khabazzadeh, *Anal. Chem.* 80 (2008) 9848.
- [47] H. Beitollahi, J. B. Raoof, and R. Hosseinzadeh, *Talanta* 85 (2011) 2128.
- [48] J. Raoof, R. Ojani, and H. Beitollahi, *Int. J. Electrochem. Sci.* 2 (2007) 534.
- [49] W. S. Hummers, and R. E. Offeman, *J. Am. Chem. Soc.* 80 (1958) 1339
- [50] A. J. Bard, and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd edition, Wiley, New York (2001).