

Hydroxylamine Electrochemical Sensor Based on a Modified Carbon Nanotube Paste Electrode: Application to Determination of Hydroxylamine in Water Samples

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The electrochemical behaviors of hydroxylamine at the benzoylferrocene modified carbon nanotubes paste electrode (BFCNPE) have been studied. The modified electrode shows an excellent electrocatalytic activity for the oxidation of hydroxylamine and accelerates electron transfer rate. The electrocatalytic currents increased linearly with the hydroxylamine concentration in the ranges of 0.9–400.0 μM and the detection limit for hydroxylamine was 0.1 μM . The diffusion coefficient and the kinetic parameters such as the electron transfer coefficient and the heterogeneous rate constant for hydroxylamine were determined using electrochemical approaches. Finally, the method was employed for the determination of hydroxylamine in water samples.

Keywords: Hydroxylamine, Carbon Paste Electrode, Carbon Nanotubes, Square Wave Voltammetry, Electrochemical Sensor

1. INTRODUCTION

Hydroxylamine, a derivative of ammonium is one of the reducing agents widely used in industry and pharmacy. It is identified as a key intermediate in the nitrogen cycles and production of nitrous oxide [1]. Hydroxylamine is a well-known mutagen, which induces highly specific mutations with the nucleic acid cytosine. Modest levels of hydroxylamine can be toxic to the humans, animals

and even plants [2]. It is known to cause both reversible and irreversible physiological changes associated with methernoglobobinemia [3].

Further, in industrial standpoint, it can be used as a raw material for the synthesis of pharmaceutical intermediates and final drug substances. Therefore, from the industrial, environmental and health viewpoints, development of a sensitive analytical method for the determination of hydroxylamine is very important. Many methods have been developed for the determination of hydroxylamine including chromatography [4], spectrophotometry [5], indirect potentiometry [6], and electrochemistry [7-10]. Among the different methods, electrochemical method of determination has several advantages over other methods such as less time consuming and more selective and sensitive [11-12].

Electrochemical sensors constructed by modified electrodes have been proven as an inexpensive and simple analytical method with remarkable detection sensitivity, reproducibility, and ease of miniaturization rather than other instrumental analysis methods [12-18]. They have found a vast range of important applications in the fields of clinical, industrial, environmental, and agricultural analyses [19-26]. The modification of electrodes using redox modifiers is an interesting field in analytical chemistry. Redox modifiers are electroactive compounds that effectively shuttle electrons between the analyte and the electrode. One of the most important effects of any modifier is a reduction of the overpotential required for electrochemical reaction, which enhances the sensitivity and selectivity of the method [27-32].

Carbon nanotubes (CNTs), an unique class of one-dimensional functional structures, are a promising building block for nanoscience and nanotechnology because of their high surface area, good mechanical strength and rich electronic properties [33-37]. The subtle electronic behavior of carbon nanotubes reveals that they have the ability to promote electron-transfer reactions when used as an electrode material in electrochemical reactions [38-40]. In recent years, considerable efforts have been made to fabricate different CNT morphologies and explore their application in various fields including composites, electrochemical devices and sensors [41-48].

Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrode consisting of mixture prepared from carbon powder and a suitable water-immiscible or non-conducting binder [49-59]. CPEs are widely applicable in both electrochemical studies and electroanalysis thank to their advantages such as ease and speed of preparation and of obtaining a new reproducible surface, very low background current (compared to solid graphite or noble metal electrodes), low cost, large potential window, simple surface renewal process. The level of background currents cannot be exactly defined; it strongly depends on the composition of carbon paste as well as upon the type of measurement [60-80]. 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 [80-98].

To our knowledge, no study has reported the electrocatalytic oxidation of hydroxylamine by using benzoylferrocene (BF) modified carbon nanotube paste electrode (BFCNPE). Thus, in the present work, we described initially the preparation and suitability of a BFCNPE as a new electrode in the electrocatalysis and determination of hydroxylamine in an aqueous buffer solution. Then, in order

to demonstrate the catalytic ability of the modified electrode in the electrooxidation of hydroxylamine in real samples, we examined this method for the voltammetric determination of hydroxylamine in water samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, 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 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the BFCNPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Hydroxylamine and all other reagents were of analytical grade from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-11.0. Multiwalled 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 μm were prepared from Nanostructured & Amorphous Materials, Inc. Benzoylferrocene was synthesized in our laboratory as reported previously [33].

2.2. Preparation of the modified electrodes

The BFCNPEs were prepared by hand mixing 0.01 g of BF with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~ 0.7 mL of paraffin oil 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 15 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, BF modified CPE (BFCPE) without CNTs, CNTs paste electrode (CNPE) without BF, and unmodified CPE in the absence of both BF and CNTs were also prepared in the same way.

3. RESULT AND DISCUSSION

3.1. Electrochemical properties of BFCNPE

BFCNPE was constructed and its electrochemical properties were studied in a 0.1 M PBS (pH 7.0) using CV (Fig. 1). The experimental results show well-defined and reproducible anodic and

cathodic peaks related to benzoylferrocene / benzoylferricenium redox system, which show a quasireversible behavior in an aqueous medium.

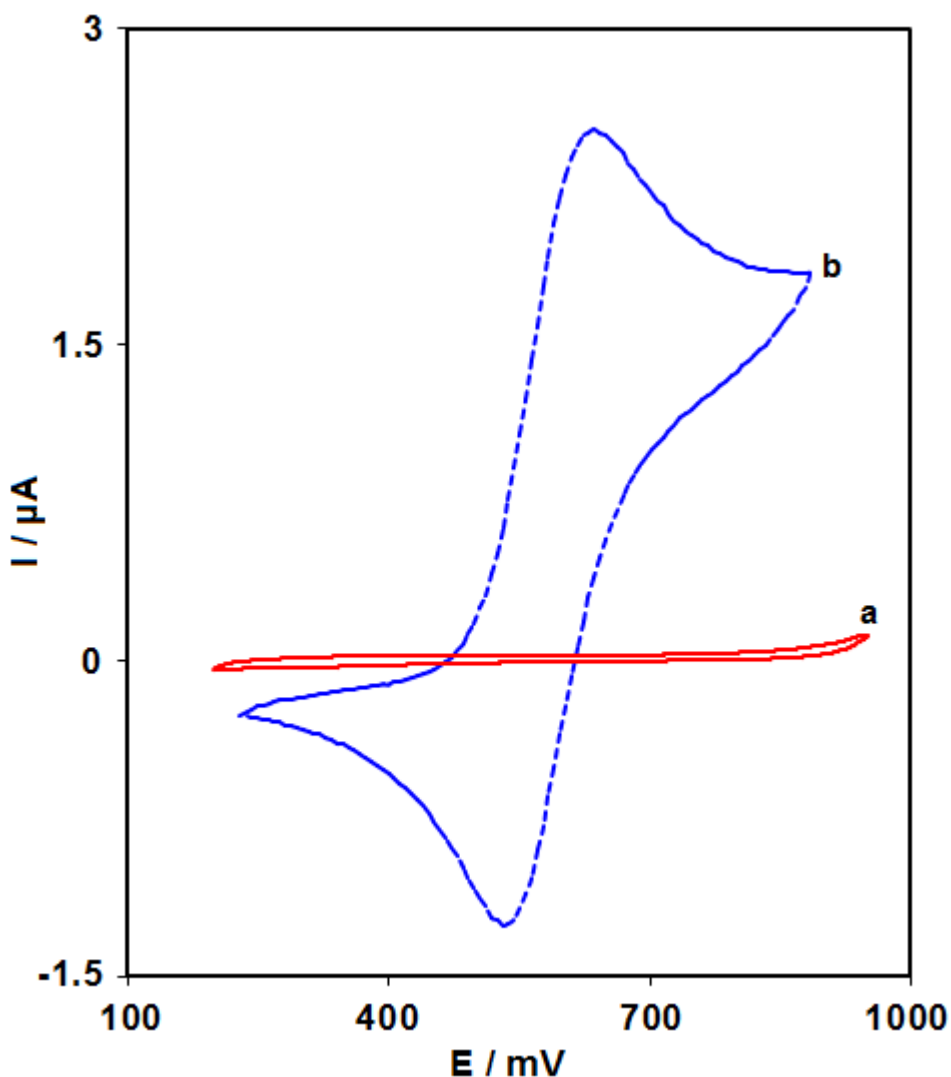


Figure 1. CVs of CPE (a) and BFCNPE (b) in 0.1 M PBS (pH 7.0). In all cases scan rate is 100 mV s⁻¹.

The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH 7.0 from five separately prepared BFCNPEs (Table 1).

Table 1. Cyclic voltammetric data obtained for constructed BFCNPE in 0.1 M PBS (pH 7.0) at 100 mV s⁻¹.

E_{pa} (V) ^a	E_{pc} (V)	$E_{1/2}$ (V)	E_p (V)Δ	I_{pa} (μA)	I_{pc} (μA)
0.645±1.3	0.540±1.4	0.592±1.3	0.105±1.4	5.2±1.7	-2.4±1.6

^aVersus Ag/AgCl/KCl (3.0 M) as reference electrode

^bAll the '±' values are RSD% (n=5)

3.2 Electrocatalytic oxidation of hydroxylamine at a BFCNPE

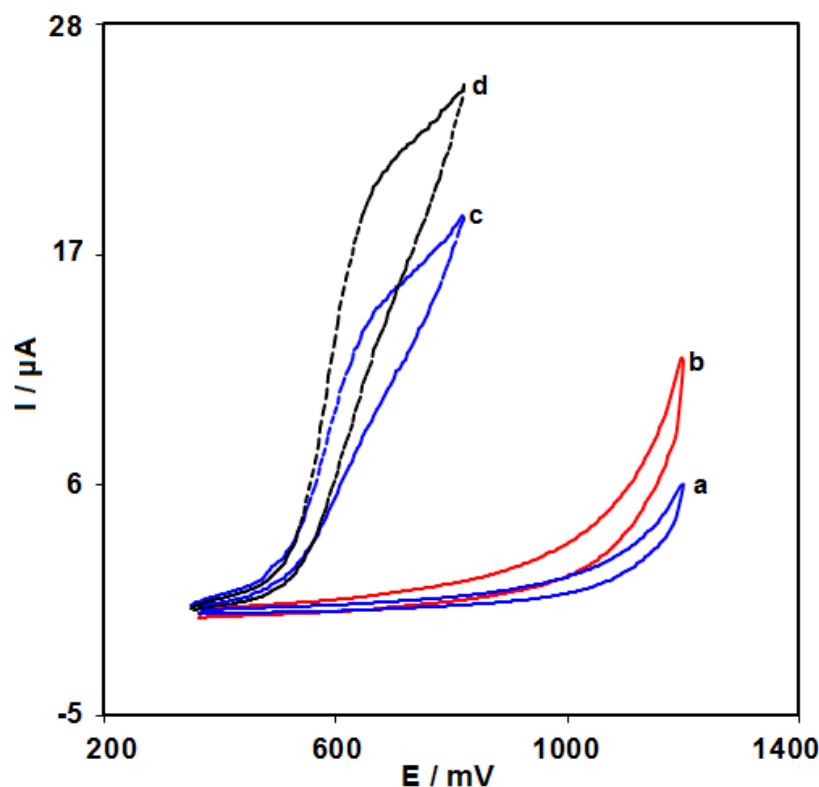


Figure 2. CVs of BFCNPE (d) and BFCPE (c) in 0.1 M PBS (pH 7.0) containing 75.0 μM hydroxylamine. (a) and (b) are CVs of CPE and CNPE in 0.1 M PBS (pH 7.0) containing 75.0 μM hydroxylamine. In all cases scan rate is 10 mV s^{-1} .

Fig. 2 depicts the CV responses for the electrochemical oxidation of 75.0 μM hydroxylamine at unmodified CPE (curve a), CNPE (curve b), BFCPE (curve c) and BFCNPE (curve d). As can be seen from curves c and d the anodic peak potential for the oxidation of hydroxylamine at BFCPE (curve C) and BFCNPE (curve d) is about 645 mV, while at the CNT modified CPE (curve b) and bare CPE (curve A) no current is observed in the presence of hydroxylamine.

However, BFCNPE shows much higher anodic peak current for the oxidation of hydroxylamine compared to BFCPE, indicating that the combination of CNTs and the mediator (BF) has significantly improved the performance of the electrode toward hydroxylamine oxidation. The BFCNPE, in 0.1 M PBS (pH 7.0) and without hydroxylamine in solution, exhibited a well-behaved redox reaction (Fig. 1 curve b) and with addition of 75.0 μM hydroxylamine, increased the anodic peak current (Fig. 2 curve d), indicating a strong electrocatalytic effect [99].

The effect of scan rate on the electrocatalytic oxidation of hydroxylamine at the BFCNPE was investigated by linear sweep voltammetry (LSV) (Fig. 3A). As can be seen in Fig. 3A, 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 10-100 mV s^{-1} , suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 3B).

A plot of the scan rate-normalized current ($I_p/v^{1/2}$) vs. scan rate (Fig. 4B) exhibits the characteristic shape typical of an EC' process [99].

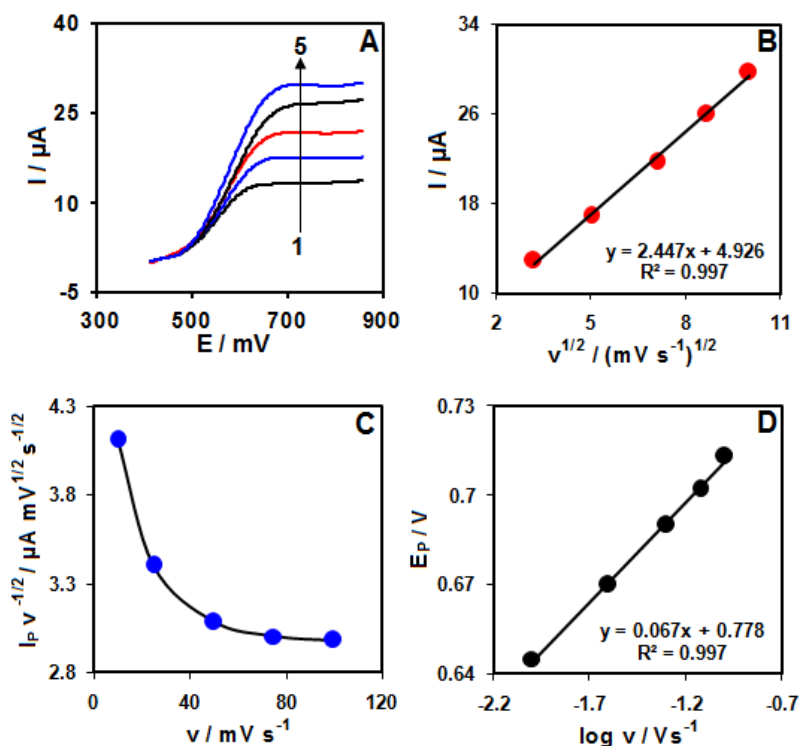


Figure 3. (A) LSVs of BFCNPE in 0.1 M PBS (pH 7.0) containing 50.0 μM hydroxylamine at various scan rates; numbers 1-5 correspond to 10, 25, 50, 75 and 100 mV s^{-1} , respectively. (B) Variation of anodic peak current vs. square root of scan rate; (C) normalized current ($I_p/v^{1/2}$) vs. v ; (D) anodic peak potential (E_p) vs. logarithm of scan rate.

The Tafel slope (b) can be obtained from the slope of E_p vs. $\log v$ using Eq. (2) [100]:

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

The Tafel slope was found to be 0.134 V (Fig. 3D), which indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient (α) is about 0.56.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of hydroxylamine at BFCNPE were carried out by setting the working electrode potential at 0.75 V vs. Ag/AgCl/KCl (3.0 M) for the various concentration of hydroxylamine in PBS (pH 7.0) (Not shown). For an electroactive material (hydroxylamine 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 [99].

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

Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of hydroxylamine. The slopes of the resulting straight lines were then plotted vs. hydroxylamine

concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be $6.8 \times 10^{-6} \text{ cm}^2/\text{s}$.

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k, for the reaction between hydroxylamine and the BFCNPE according to the method of Galus [101]:

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

where I_C is the catalytic current of hydroxylamine at the BFCNPE, I_L is the limited current in the absence of hydroxylamine and $\gamma = kC_b t$ is the argument of the error function (C_b is the bulk concentration of hydroxylamine). In cases where γ exceeds the value of 2, the error function is almost equal to 1 and therefore, the above equation can be reduced to:

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

where t is the time elapsed. The above equation can be used to calculate the rate constant, k, of the catalytic process from the slope of I_C/I_L vs. $t^{1/2}$ at a given hydroxylamine concentration. From the values of the slopes, the average value of k was found to be $6.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

3.4. Calibration plot and limit of detection

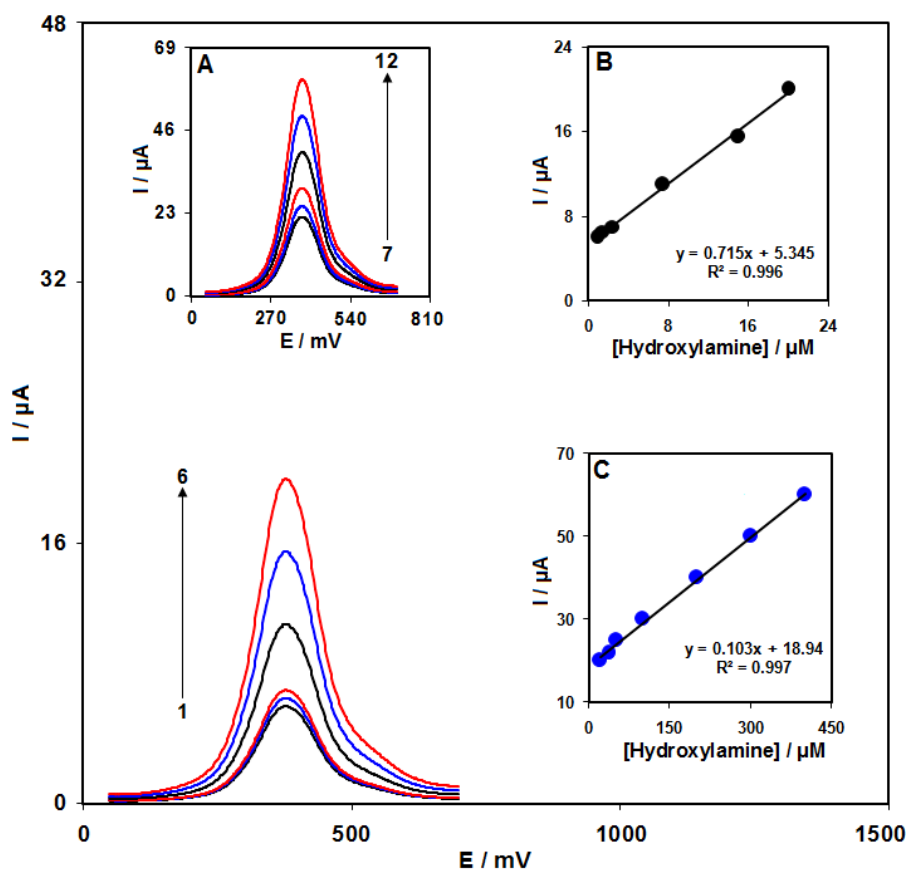


Figure 4. SWVs of BFCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of hydroxylamine in μM . Numbers 1-12 correspond to 0.9, 1.5, 2.5, 7.5, 15.0, 20.0, 35.0, 50.0, 100.0, 200.0, 300.0 and 400.0 μM hydroxylamine. Insets: (B) plots of I_p vs. hydroxylamine concentration in the first linear segment and (C) as (B) in the second linear segment.)

SWV method was used to determine the concentration of hydroxylamine (Fig.4). The plot of peak current vs. hydroxylamine concentration consisted of two linear segments with slopes of 0.7038 and $0.103 \mu\text{A } \mu\text{M}^{-1}$ in the concentration ranges of 0.9 to 20.0 μM and 20.0 to 400.0 μM , respectively (Figs.4B and 4C). The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation. The detection limit (3σ) of hydroxylamine was found to be 0.1 μM .

3.5. Determination of hydroxylamine in real samples

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of hydroxylamine in water samples. The samples tested were found to be free from hydroxylamine and thus, synthetic samples were prepared by adding known amounts of hydroxylamine to water samples. Satisfactory recovery of the experimental results were found for hydroxylamine. The results are given in Table 2.

Table 2. The application of BFCNPE for determination of hydroxylamine in water samples (n=5)

Sample	Added (μM)	Expected (μM)	Found (μM)	Recovery (%)	RSD (%)
Tap Water					
	5.0	5.0	5.1	102.0	3.3
	10.0	10.0	9.9	99.0	1.9
	15.0	15.0	14.6	97.3	2.1
	20.0	20.0	19.7	98.5	2.9
Drinking Water					
	7.0	7.0	6.8	97.1	1.4
	12.0	12.0	12.3	102.5	3.2
	17.0	17.0	17.2	101.2	2.8
	22.0	22.0	21.6	98.2	2.2
River Water					
	9.0	9.0	9.2	102.2	2.1
	14.0	14.0	14.1	100.7	1.7
	19.0	19.0	18.6	97.9	3.5
	24.0	24.0	23.7	98.7	2.6

4. CONCLUSION

In this paper, we have constructed a novel modified carbon paste electrode for the detection of hydroxylamine. The results of this study indicated that the electrode exhibited linear response over a wide concentration range ($9.0 \times 10^{-7} \text{ M}$ – $4.0 \times 10^{-4} \text{ M}$) with a detection limit of 0.1 μM . Finally, this method was used for the determination of hydroxylamine in water samples.

References

1. T. Hofman, H. Lees, *Biochem. J.*, 54 (1953) 579.
2. R.P. Smith, W.R. Layne, *J. Pharmacol. Exp. Ther.*, 165 (1969) 30.
3. K. Higasa, J.I. Manabe, T. Yubisui, H. Sumimoto, P. Pung-amritt, V.S. Tanphaichitr, Y. Fukumaki, *Br. J. Haematol.*, 103 (1998) 922.
4. A.M. Prokai, R.K. Ravichandran, *J. Chromatogr. A*, 667 (1994) 298.
5. A. Afkhami, T. Madrakian, A. Maleki, *Anal. Sci.*, 22 (2006) 329.
6. R. Christova, M. Ivanova, M. Novkirishka, *Anal. Chim. Acta*, 85 (1976) 301.
7. H. Zhang, J. Zheng, *Talanta*, 93 (2012) 67.
8. J. Li, H. Xie, *Ionics*, 19 (2013) 105.
9. C. Zhang, G. Wang, M. Liu, Y. Feng, Z. Zhang, B. Fang, *Electrochim. Acta*, 55 (2010) 2835.
10. J. Li, H. Xie, *J. Appl. Electrochem.*, 42 (2012) 271.
11. J. Li, H. Xie, Y. Li, *J. Solid State Electrochem.*, 16 (2012) 795.
12. P. Kannan, S. Abraham John, *Anal. Chim. Acta*, 663 (2010) 158.
13. H. Beitollahi, J.B. Raoof, R. Hosseinzadeh, *Anal. Sci.*, 27 (2011) 991.
14. S. Tajik, M.A. Taher, H. Beitollahi, *J. Electroanal. Chem.*, 704 (2013) 137.
15. A. Carolina Torres, Madalina M. Barsan, Christopher M.A. Brett, *Food Chem.*, 149 (2014) 215.
16. M. Mazloun-Ardakani, H. Rajabi, B. B. F. Mirjalili, H. Beitollahi, A. Akbari, *J. Solid State Electrochem.*, 14 (2010) 2285.
17. R. Zhang, S. Liu, L. Wang, G. Yang, *Measurement*, 46 (2013) 1089.
18. M. Roushani, M. Sarabaegi, *J. Electroanal. Chem.*, 717 (2014) 147.
19. M. Mazloun-Ardakani, A. Talebi, H. Beitollahi, H. Naeimi, N. Taghavinia, *Anal. Lett.*, 43 (2010) 1.
20. L. Fernández, I. Ledezma, C. Borrás, L. A. Martínez, H. Carrero, *Sens. Actuators B*, 182 (2013) 625.
21. F. C.M. de Oliveira, S. H.P. Serrano, *Electrochim. Acta*, 125 (2014) 566.
22. S. Mohammadi, H. Beitollahi, A. Mohadesi, *Sens. Lett.* 11 (2013) 388-394.
23. M. Asadollahi-Baboli, A. Mani-Varnosfaderani, *Measurement*, 47 (2014) 145.
24. R. Zhang, S. Liu, L. Wang, G. Yang, *Measurement*, 46 (2013) 1089.
25. H. Beitollahi, I. Sheikhshoaie, *Electrochim. Acta*, 56 (2011) 10259.
26. K.J. Huang, L. Wang, J. Li, T. Gan, Y.M. Liu, *Measurement*, 46 (2013) 378.
27. M. Baghayeri, M. Namadchian, H. Karimi-Maleh, H. Beitollahi, *J. Electroanal. Chem.*, 697 (2013) 53.
28. A. A. Rabi-Stanković, Z. Mojović, A. Milutinović-Nikolić, N. Jović-Jovičić, P. Banković, M. Žunić, D. Jovanović, *Appl. Clay Sci.*, 77 (2013) 61.
29. H. Beitollahi, J.B. Raoof, H. Karimi-Maleh, R. Hosseinzadeh, *J. Solid State Electrochem.*, 16 (2012) 1701.
30. H. Beitollahi, J.B. Raoof, R. Hosseinzadeh, *Talanta*, 85 (2011) 2128.
31. N. Jia, B. Huang, L. Chen, L. Tan, S. Yao, *Sens. Actuators B*, 195 (2014) 165.
32. H. Beitollahi, I. Sheikhshoaie, *J. Electroanal. Chem.*, 661 (2011) 336
33. F. Mirrahimi, M. A. Taher, H. Beitollahi, R. Hosseinzadehd, *Appl. Organometal. Chem.*, 26 (2012) 194.
34. S. Sheng, L. Zhang, G. Chen, *Food Chem.*, 145 (2014) 555.
35. H. Beitollahi, A. Mohadesi, S. Khalilizadeh Mahani, A. Akbari, *Anal. Methods*, 4 (2012) 1029.
36. D. Deýlová, V. Vyskočil, J. Barek, *J. Electroanal. Chem.*, 717 (2014) 237.
37. A. Mokhtari, H. Karimi-Maleh, A. A. Ensafi, H. Beitollahi, *Sens. Actuators B*, 169 (2012) 96.
38. L. L. C. Garcia, L. C. S. Figueiredo-Filho, G. G. Oliveira, O. Fatibello-Filho, C. E. Banks, *Sens. Actuators B*, 181 (2013) 306.

39. H. Karimi-Maleh, M. A. Khalilzadeh, Z. Ranjbarha, H. Beitollahi, A. A. Ensafi, D. Zareyee, *Anal. Methods*, 4 (2012) 2088.
40. I. Cesarino, V. Cesarino, M. R.V. Lanza, *Sens. Actuators B*, 188 (2013) 1293.
41. B. Dogan-Topal, B. Bozal-Palabiyik, B., Uslu S. A. Ozkan, *Sens. Actuators B*, 177 (2013) 841.
42. A. Khoobi, S. M. Ghoreishi, S. Masoum, M. Behpour, *Bioelectrochemistry*, 94 (2013) 100-107.
43. X. Zhu, X. Niu, H. Zhao, M. Lan, *Sens. Actuators B*, 195 (2014) 274.
44. A. C. M. S. Dias, S. L. R. Gomes-Filho, M. M. S. Silva, R. F. Dutra, *Biosens. Bioelectron.*, 44 (2013) 216.
45. J. Kang, J. Wen, S. H. Jayaram, X. Wang, S.K. Chen, *J. Power Sourc.*, 234 (2013) 208.
46. H. Beitollahi, A. Mohadesi, S. Khalilzadeh Mahani, H. Karimi-Maleh, A. Akbari, *Turk. J. Chem.*, 36 (2012) 526.
47. R. García-González, A. F.L. Villa, A. Costa-García, M. T. Fernández-Abedul, *Sens. Actuators B*, 181 (2013) 353.
48. A. Babaei, A. R. Taheri, M. Aminikhah, *Electrochim. Acta*, 90 (2013) 317
49. M. Mazloun-Ardakani, Z. Taleat, H. Beitollahi, H. Naeimi, *Anal. Methods*, 2 (2010) 149.
50. A. Salmanipour, M. A. Taher, H. Beitollahi, *Anal. Methods*, 4 (2012) 2982.
51. A. Afkhami, T., Madrakian H. Ghaedi, H. Khanmohammadi, *Electrochim. Acta*, 66 (2012) 255.
52. M. Mazloun-Ardakani, H. Rajabi, H. Beitollahi, *Chin. Chem. Lett.*, 23 (2012) 213.
53. S. Tajika, M. A. Taher, H. Beitollahi, *Sens. Actuators B*, 188 (2013) 923.
54. T. Thomas, R. J. Mascarenhas, B.E. Kumara Swamy, P. Martis, Z. Mekhalif, B.S. Sherigara, *Colloids Surf. B*, 110 (2013) 458.
55. M. Mazloun-Ardakani, H. Beitollahi, B. Ganjipour, H. Naeimi, M. Nejati, *Bioelectrochemistry*, 75 (2009) 1.
56. A. Mohadesi, H. Beitollahi, M.A. Karimi, *Chin. Chem. Lett.*, 22 (2011) 1469.
57. J. C. Abbar, S. J. Malode, S. T. Nandibewoor, *Bioelectrochemistry*, 83 (2012) 1.
58. H. Beitollahi, J.B. Raoof, R. Hosseinzadeh, *Electroanalysis*, 23 (2011) 1934
59. J.B. Raoof, R. Ojani, H. Beitollahi, *Electroanalysis*, 19 (2007) 1822
60. J. Huo, E. Shangguan, Q. Li, *Electrochim. Acta*, 89 (2013) 600.
61. H. Beitollahi, J.B. Raoof, R. Hosseinzadeh, *Anal. Sci.*, 27 (2011) 991.
62. M.R. Akhgar, H. Beitollahi, M. Salari, H. Karimi-Maleh, H. Zamani, *Anal. Methods*, 4 (2012) 259.
63. J. Parellada, A. Narváez, E. Domínguez, I. Katakis, *Biosens. Bioelectron.*, 12 (1997) 267.
64. M. Mazloun-Ardakani, H. Beitollahi, M. A. Sheikh-Mohseni, H. Naeimi, *J. Iran. Chem. Soc.*, 9 (2012) 27.
65. H. Beitollahi, A. Mohadesi, S. Mohammadi, A. Akbari, *Electrochim. Acta*, 68 (2012) 220.
66. P. Raghu, T. Madhusudana Reddy, K. Reddaiah, L. R. Jaidev, G. Narasimha, *Enzyme Microb. Tech.*, 52 (2013) 377.
67. M. Mazloun-Ardakani, B. Ganjipour, H. Beitollahi, M.K. Amini, F. Mirkhalaf, H. Naeimi, M. Nejati-Barzoki, *Electrochim. Acta*, 56 (2011) 9113.
68. H. Beitollahi, J.B. Raoof, R. Hosseinzadeh, *Anal. Sci.*, 27 (2011) 991.
69. S. Tajik, M.A. Taher, H. Beitollahi, *Electroanalysis*, DOI: 10.1002/elan.201300589.
70. M. Mazloun Ardakani, Z. Taleat, H. Beitollahi, M. Salavati-Niasari, B.B.F. Mirjalili, N. Taghavinia, *J. Electroanal. Chem.*, 624 (2008) 73.
71. H. Beitollahi, H. Khabazzadeh, H. Karimi-Maleh, A. Akbari, *Chin. Chem. Lett.*, 23 (2012) 719.
72. J. H. Luo, X. X. Jiao, N. B. Li, H. Q. Luo, *J. Electroanal. Chem.*, 689 (2013) 130.
73. M. Mazloun-Ardakani, Z. Taleat, H. Beitollahi, H. Naeimi, *Chin. Chem. Lett.*, 22 (2011) 705.
74. M. Mazloun Ardakani, M. A. Sheikh Mohseni, H. Beitollahi, H. Naeimi, *Turk. J. Chem.*, 35 (2011) 573.
75. M. Amiri, Z. Pakdel, A. Bezaatpour, S. Shahrokhian, *Bioelectrochemistry*, 81 (2011) 81.

76. M. Mazloun-Ardakani, H. Beitollahi, M.K. Amini, F. Mirkhalaf, B.B.F. Mirjalili, A. Akbari, *Analyst*, 136 (2011) 1965.
77. M. Mazloun-Ardakani, H. Beitollahi, M.K. Amini, F. Mirkhalaf, M. Abdollahi-Alibeika, *Anal. Methods*, 3 (2011) 673.
78. A. Afkhani, F. Soltani-Felehgari, Ta. Madrakian, H. Ghaedi, *Biosens. Bioelectron.*, 51 (2014) 379.
79. J. B. Raoof, R. Ojani, H. Beitollahi, R. Hossienzadeh, *Electroanalysis*, 18 (2006) 1193
80. H. Beitollahi, M. Mazloun Ardakani, H. Naeimi, B. Ganjipour, *J. Solid State Electrochem.*, 13 (2009) 353.
81. S. Sadeghi, A. Motaharian, *Mater. Sci. Eng. C*, 33 (2013) 4884.
82. A. Taherkhani, H. Karimi-Maleh, A.A. Ensafi, H. Beitollahi, A. Hosseini, M.A. Khalilzadeh, H. Bagheri, *Chin. Chem. Lett.*, 23 (2012) 237.
83. M. Mazloun-Ardakani, Z. Taleat, H. Beitollahi, H. Naeimi, *J. Iran. Chem. Soc.*, 7 (2010) 251.
84. P. Norouzi, M. Hosseini, M. R. Ganjali, M. Rezapour, M. Adibi, *Int. J. Electrochem. Sci.*, 6 (2011) 2012.
85. M. Mazloun-Ardakani, H. Beitollahi, M. K. Amini, F. Mirkhalaf, M. Abdollahi-Alibeik, *Sens. Actuators B*, 151 (2010) 243.
86. H. Beitollahi, H. Karimi-Maleh, H. Khabazzadeh, *Anal. Chem.*, 80 (2008) 9848.
87. H. Karimi-Maleh, M. Moazampour, H. Ahmar, H. Beitollahi, A. A. Ensafi, *Measurement*, 51 (2014) 156.
88. M. Mazloun-Ardakani, M. A. Sheikh-Mohseni, H. Beitollahi, A. Benvidi, H. Naeimi, *Chin. Chem. Lett.* 21 (2010) 1471.
89. M. Mazloun-Ardakani, H. Beitollahi, M. K. Amini, B.B.F. Mirjalili, F. Mirkhalaf, *J. Electroanal. Chem.*, 651 (2011) 243.
90. H. Beitollahi, M. A. Taher, M. Ahmadipour, R. Hosseinzadeh, *Measurement*, 47 (2014) 770.
91. M. Mazloun-Ardakani, H. Beitollahi, Z. Taleat, M. Salavati-Niasari, *J. Serb. Chem. Soc.*, 76 (2011) 575.
92. M. Mazloun-Ardakani, H. Beitollahi, Z. Taleat, H. Naeimi, *Anal. Methods*, 2 (2010) 1764.
93. A. Mohadesi, H. Beitollahi, *Anal. Methods*, 3 (2011) 2562.
94. M. C. Teixeira, E. de F.L. Tavares, A. A. Saczk, L. L. Okumura, M. das Graças Cardoso, Z. M. Magriotis, M. F. de Oliveira, *Food Chem.*, 154 (2014) 38.
95. Z. Taleat, M. Mazloun Ardakani, H. Naeimi, H. Beitollahi, M. Nejati, H. R. Zare, *Anal. Sci.*, 24 (2008) 1039
96. H. Beitollahi, M. A. Taher, M.Ahmadipour, R. Hosseinzadeh, *Measurement*, 47 (2014) 770
97. M. B. Gholivand, M. Shamsipur, S. Dehdashtian, H. R. Rajabi, *Mater. Sci. Engin.: C*, 36 (2014) 102
98. H. Beitollahi, M. A. Taher, A. Hosseini, *Measurement*, 2014, 10.1016/j.measurement.2014.02.008
99. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn edn, Wiley, New York, 2001.
100. J.A. Harrison, Z.A. Khan, *J. Electroanal. Chem.*, 28 (1970) 131-138.
101. Z. Galus, *Fundamentals of Electrochemical Analysis*, Ellis Horwood, New York, 1976.