Int. J. Electrochem. Sci., 12 **(2017)** 11656 – 11665, doi: 10.20964/2017.12.39

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Determination of Vanillin in Food Samples Using MgO/SWCNTs-ionic Liquid Modified Electrode

Maryam Abbasghorbani

Gas Division, Research Institute of Petroleum Industry, P.O. Box 14665-137, Tehran, Iran
E-mail: aghorbani2003@yahoo.com

Received: 25 August 2017 / *Accepted:* 8 October 2017 / *Published:* 12 November 2017

The development of a novel electrochemical sensor, based on modification of the carbon paste electrode with MgO/SWCNTs nanocomposite and 1-butyl-3-methylimidazolium hexafluoro phosphate (MgO/SWCNTs/$BMPF_6$/CPE) has been reported. The electro-oxidative behavior of vanillin in food samples at MgO/SWCNTs/$BMPF_6$/CPE using square wave and linear sweep voltammetry was investigated. The oxidation signal of vanillin at MgO/SWCNTs/$BMPF_6$/CPE increased when compared with the unmodified electrode. The catalytic current showed a linear relationship with vanillin concentration in the range 0.02 to 800 μM with a detection limit of 8.0 nM. The MgO/SWCNTs/$BMPF_6$/CPE was applied for vanillin determination in food samples.

Keywords: Vanillin, MgO/SWCNTs, 1-butyl-3-methylimidazolium hexafluoro phosphate, Modified electrode.

1. INTRODUCTION

Food additives are the main category in food branch investigations [1]. There are different types of food additives in food products such as anti-caking agents, emulsifiers, antioxidants, food acids and artificial sweeteners. Although the application of food additives enhances the quality and flavor of food products, some of them have undesirable effects on the human body; hence, their concentration must be strictly regulated in food products [2].

Vanillin is a flavoring additive used in food products worldwide [3]. Vanillin is suggested for food and beverages as an additive, as well as in fragrances and pharmaceutical samples. As a result of the wide application of vanillin, it is very important to determine and regulate its presence in food and pharmaceutical products [4, 5]. Among the analytical methods for the analysis of vanillin, the

application of electrochemical methods is the best, due to its high sensitivity, low interference and fast response [6-16].

Electrochemical sensors modified with conductive materials help to improve the sensitivity of electro-active compounds [17-30]. In addition, many published papers have suggested the coupling of two or more mediators to improve the quality of the electrochemical sensor used for analysis [31-35]. Nanomaterials with a high surface area and good electrical conductivity are appropriate choices for the modification of electrodes in electrochemical systems such as voltammetric sensors or super-capacitance [36-43]. They can reduce the charge transfer resistance of the electrode and increase the sensitivity of the electrode surface for electrochemical investigations [44-49]. On the other hand, ionic liquids are good electrical binder for modification of the electrode surface, so as to improve the sensitivity of electrochemical sensors [50-53]. Due to the points above, some studies have suggested the coupling of nanomaterials and ionic liquids for modification of the electrode surface in trace level analysis of electroactive compounds [54-57].

Therefore, in continuation of the group work for fabrication of electrochemical sensors [58-61], a new voltammetric sensor was fabricated based on modification of the carbon paste electrode with MgO/SWCNTs nanocomposite and 1-butyl-3-methylimidazolium hexafluoro phosphate for analysis of vanillin in food samples.

2. EXPERIMENTAL

2.1. Materials and apparatus

Vanillin, magnesium nitrate, single wall carbon nanotubes, sodium hydroxide and phosphoric acid were purchased from Sigma-Aldrich. Graphite powder, 1-butyl-3-methylimidazolium hexafluoro phosphate and paraffin oil were purchased from Merck Company. A μ-Autolab PGSTAT 12, connected to an electrochemical cell with GPES software was used for electrochemical investigations. Morphological investigation was conducted using a KYKY-EM3200 digital scanning electron microscope.

2.2. Synthesis of MgO/SWCNTs

In this study, 3.0 g of SWCNTs/COOH was dispersed in 100 mL of 1.0 M sodium hydroxide by ultrasonication for 35 min. In continuation, 100 mL of 0.5 M magnesium nitrate was added drop wise to the previous solution, followed by stirring for 20 min. The precipitated composite was washed and dried at 100^0C for 12 h. In the final step, the nanocomposite was calcined at 500^0C for 2 h.

2.3. Fabrication of MgO/SWCNTs/$BMPF_6$/CPE

MgO/SWCNTs/$BMPF_6$/CPE was prepared by mixing 0.05 g of MgO/SWCNTs, and 0.95 g of graphite powder in the presence of suitable amount of binders (paraffin oil and $BMPF_6$). The obtained paste was introduced into one glass tube and copper wire was used for electrical conductivity.

2.4. Preparation of vanillin real sample

To study the ability of MgO/SWCNTs/$BMPF_6$/CPE in real sample analysis, we selected biscuit, coffee milk and chocolate for this goal. The real samples were prepared according to the study of Khalilzadeh and Arab [4].

3. RESULTS AND DISCUSSION

3.1. Morphological investigation of MgO/SWCNTs

The morphology of MgO/SWCNTs was investigated by scanning electron microscopy. Figure 1 presents the spherical MgO nanoparticle decorated at a surface of single wall carbon nanotubes.

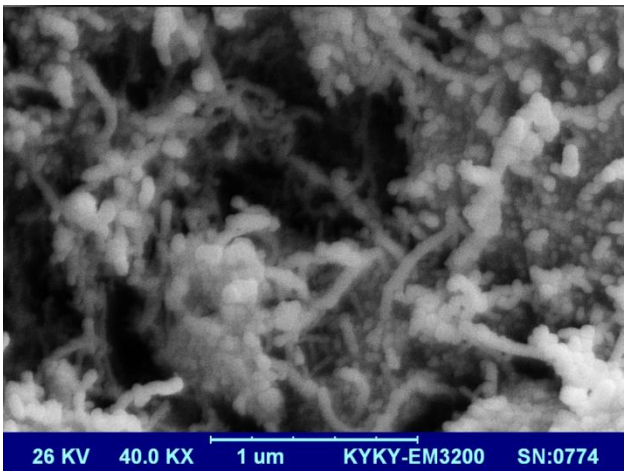


Figure 1. SEM image of MgO/SWCNTs.

3.2. Electrochemical investigation

The electrochemical behavior of vanillin depends on pH, due to the presence of a phenolic group in the presence of the vanillin structure [4]. Figure 2 shows the square wave voltammograms of 750.0 μM vanillin on MgO/SWCNTs/$BMPF_6$/CPE for pH range (4.0 - 8.0).

The maximum oxidation peak current has high values at pH=7.0 (Figure 2). Figure 3 shows that with increase in pH, the oxidation peaks potential shifts and becomes negative with equation E_{pa} = -0.0507 pH + 0.9174 (r^2 = 0.9930). This value of slope confirms one-electron and one-proton process for vanillin electro-oxidation (scheme 1) [5]. The electrochemical behavior of vanillin was investigated at the surface of different electrodes in 0.1 M PBS (pH 7.0) (Fig. 4). The electrochemical behavior of vanillin at the MgO/SWCNTs/$BMPF_6$/CPE (Fig.4, curve a), $BMPF_6$/CPE (Fig. 4, curve b), MgO/SWCNTs/CPE (Fig. 4, curve c) and CPE (curve d) exhibited anodic peak potential at 0.556, 0.576, 0.606, and 0.625 V, respectively.

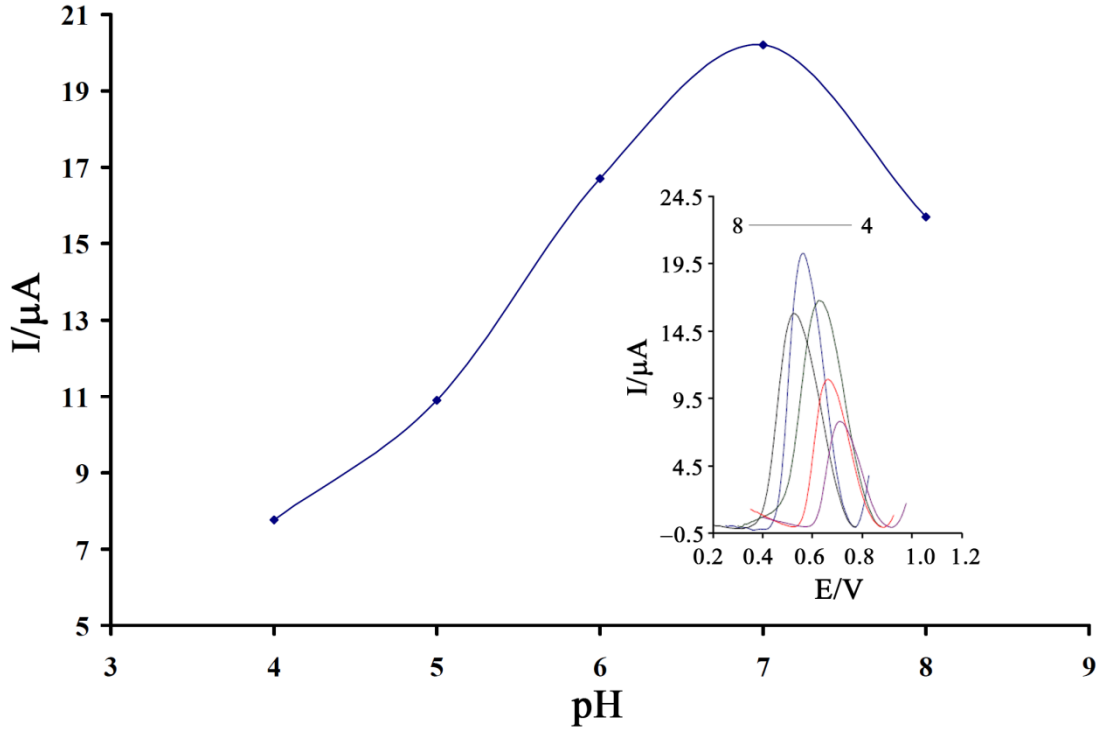


Figure 2. Current-pH curve for the electro-oxidation of vanillin. Square wave voltammograms of 750 µM vanillin at the surface of MgO/SWCNTs/$BMPF_6$/CPE

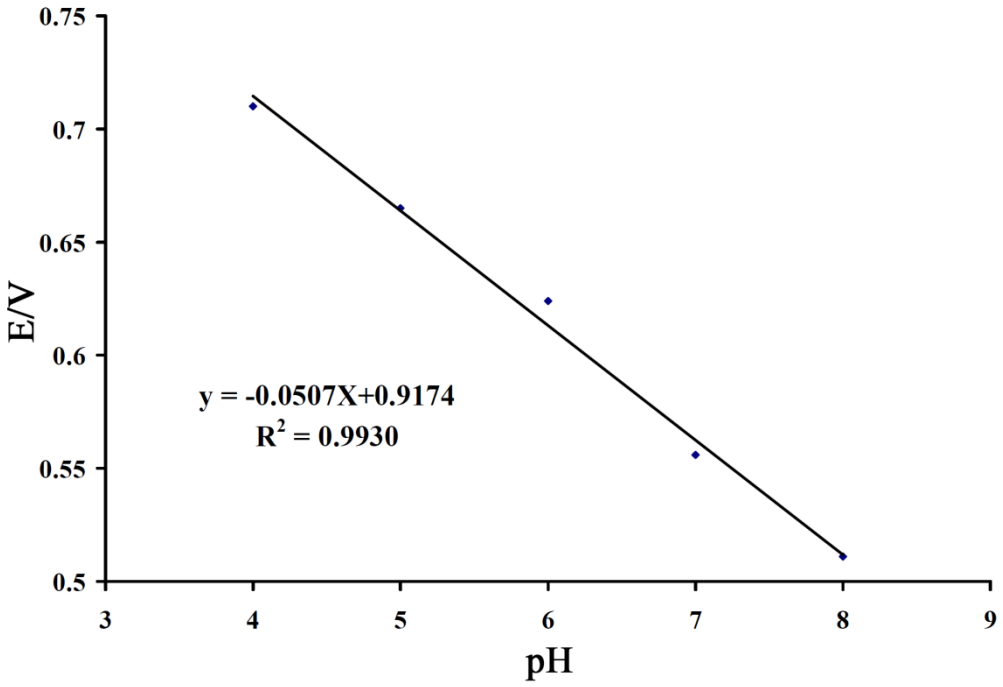
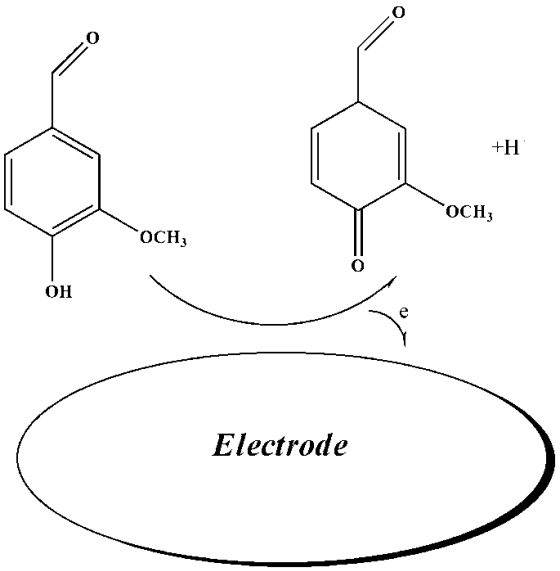


Figure 3. Potential-pH curve for electro-oxidation of 750 µM vanillin at the surface of MgO/SWCNTs/$BMPF_6$/CPE.



Scheme 1. Electro-oxidation mechanism for vanillin.

It can be seen that with movement from CPE to MgO/SWCNTs/$BMPF_6$/CPE, the over-potential for electro-oxidation of vanillin became reduced. Additionally, the MgO/SWCNTs/$BMPF_6$/CPE (Fig.5, curve a) enhanced the sensitivity for vanillin by 4.62 folds compared to the CPE (Fig. 4, curve d).

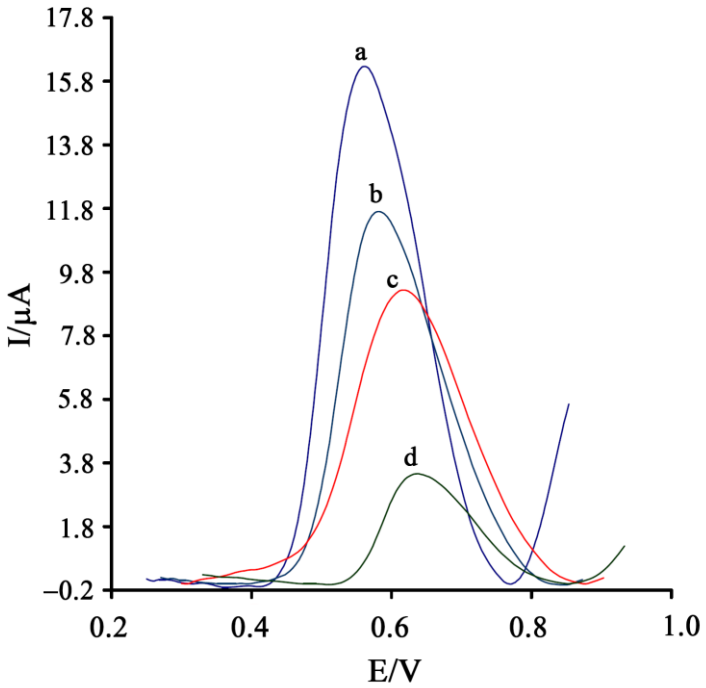


Figure 4. Square wave voltammograms of 550.0 μM vanillin at the surface of a) MgO/SWCNTs/$BMPF_6$/CPE; b) $BMPF_6$/CPE; c) MgO/SWCNTs/CPE and d) CPE.

The Tafel plot and its relative linear sweep voltammogram has been presented in Fig. 5. Using the slope of figure 5 and Tafel equation ((1-α) n_α F/2.3RT), the value of α= 0.32 was determined, which confirms an irreversible electro-oxidation process [5]. The effect of the concentration of vanillin on MgO/SWCNTs/$BMPF_6$/CPE was investigated and is shown in Figure 6.

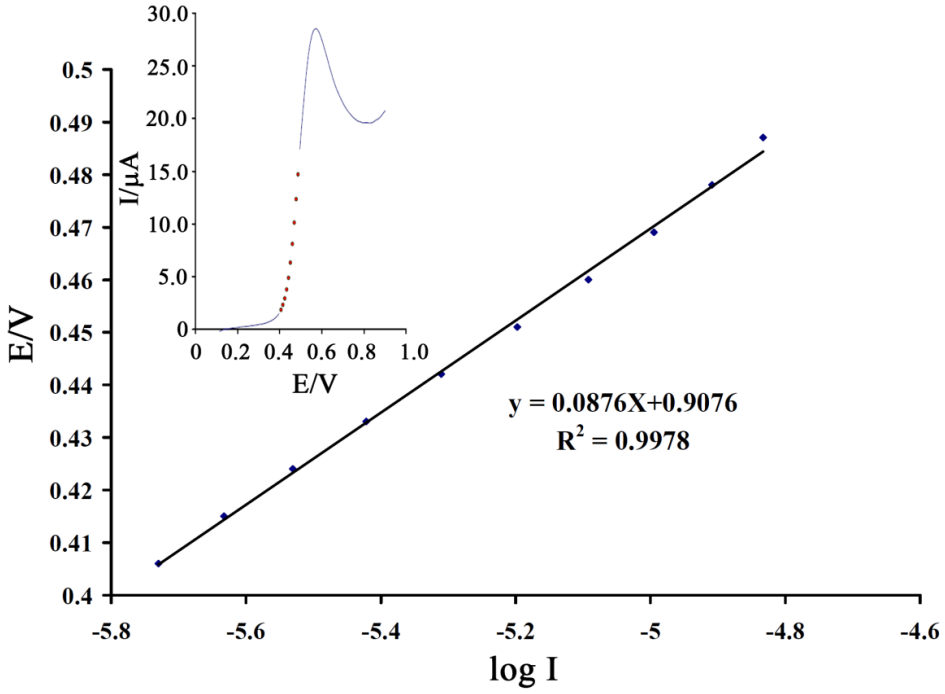


Figure 5. Tafel plot for electro-oxidation of 500 μM vanillin at the surface of MgO/SWCNTs/$BMPF_6$/CPE.

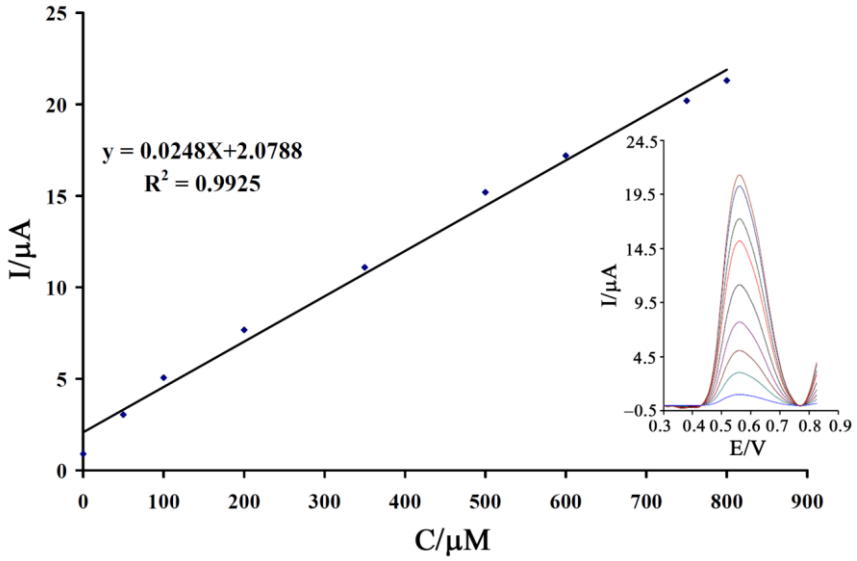


Figure 6. The plots of the oxidation peak current as a function of vanillin concentration. Inset shows the SWVs of MgO/SWCNTs/$BMPF_6$/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of vanillin. From inner to outer, corresponding to 0.02, 50.0, 100.0, 200.0, 350.0, 500.0, 600.0, 750.0 and 800.0 μM of vanillin.

Where, the oxidation peak current of vanillin increased with increasing concentration (0.02 – 800 μM). Also, we detected a limit of detection (8.0 nM) for analysis of vanillin at the surface of MgO/SWCNTs/BMPF6/CPE. This value of the limit of detection and linear dynamic range is comparable with previous published papers (see Table 1).

Table 1. Comparison with early electro-chemical reported methods for vanillin analysis.

Electrode	pH	Linear dynamic range (μM)	Limit of detection (μM)	Ref.
boron-doped diamond	2.5	3.3–9.8	0.16	[62]
glassy carbon	0.1 M H_2SO_4	0.1–40	0.02	[63]
carbon paste	7.0	0.1–700	0.07	[4]
carbon paste	6.0	0.03–1200	0.009	[5]
carbon paste	7.0	0.02-800.0	0.008	This work

3.3. Interference study

The selectivity of MgO/SWCNTs/$BMPF_6$/CPE has been investigated as one of the most important advantages of sensors [64-67]. To test the selectivity of MgO/SWCNTs/$BMPF_6$/CPE upon the determination of 10.0 μM vanillin using square wave voltammetry, we added some interferents to the solution and 5% error was selected as acceptable results. The selectivity of the investigation data are presented in Table 2.

Table 2. Interference of some foreign substances for 10.0 μM of vanillin.

Interferents	Folds
Glucose, methanol, tryptophan	700
Li^+, K^+, NO_3^-, Br^-, Cl^-	600
Vitamin B_9	300

3.4. Stability and reproducibility

Throughout one month, the stability of MgO/SWCNTs/$BMPF_6$/CPE towards the electro-oxidation of vanillin was investigated. Recorded signals showed no significant shift in potential and no significant change in current for the electro-oxidation of vanillin when MgO/SWCNTs/$BMPF_6$/CPE was kept at room temperature. The reproducibility of MgO/SWCNTs/$BMPF_6$/CPE was evaluated by measuring nine solutions of 30.0 μM of vanillin in pH=7.0, leading to a relative standard deviation of

4.32%. The above results indicated that MgO/SWCNTs/$BMPF_6$/CPE has high stability and good reproducibility.

3.5. Analysis of vanillin in food samples

The MgO/SWCNTs/$BMPF_6$/CPE was applied for analysis of vanillin in food samples by the standard addition method. The results are shown in Table 3 and recovery data confirms the possibility of using MgO/SWCNTs/$BMPF_6$/CPE for analysis of vanillin in food samples.

Table 3. Determination of vanillin in real samples (n = 4).

Sample	Added (μM)	Founded (μM)	Recovery %
Chocolate	---	1.93±0.55	---
	5.00	6.87±0.67	99.13
Biscuit	---	2.57±0.68	---
	10.00	12.98±0.88	103.26
Coffee milk	---	4.13±0.65	---
	10.0	14.01±0.67	99.15

4. CONCLUSION

In this research, a carbon paste electrode modified with MgO/SWCNTs nanocomposite and $BMPF_6$ was developed for the investigation of vanillin. The MgO/SWCNTs/$BMPF_6$/CPE has great capability to determine vanillin relative to the unmodified carbon paste electrode. We detected a limit of detection of 8.0 nM for analysis of vanillin at a surface of MgO/SWCNTs/$BMPF_6$/CPE. The MgO/SWCNTs/$BMPF_6$/CPE was used for analysis of vanillin in food samples.

References

1. T. Helgason and M.R. Jonasson, *Lancet,* 318 (1981) 716.
2. B.J. Shiau, D.A. Sabatini and J.H. Harwell, *Groudwater,* 32 (1994) 561.
3. C.S. Frings and R.T. Dunn, *Am. J. Clin. Pathol.*, 53 (1970) 89.
4. M.A. Khalilzadeh and Z. Arab, *Curr. Anal. Chem.*, 13 (2017) 81.
5. S. Cheraghi, M.A. Taher and H. Karimi-Maleh, *J. Food Compost. Anal.,* 62 (2017) 254.
6. H. Karimi-Maleh, F. Amini, A. Akbari and M. Shojaei, *J. Colloid Interface Sci.,* 495 (2017) 61.
7. M. Shabani-Nooshabadi, M. Roostaee and H. Karimi‑Maleh, *J. Iran. Chem. Soc.,* 14 (2017) 955
8. S. Cheraghi, M.A. Taher and H. Karimi-Maleh, *Appl. Surf. Sci.*, 420 (2017) 882.
9. F. Safari, M. Keyvanfard, H. Karimi-Maleh and K. Alizad, *Iran. J. Pharm. Res.*, 16 (2017) 1019.
10. V. K. Gupta, A. K. Jain and G. Maheshwari, *Talanta,* 72 (2007) 1469.
11. T. Alizadeh, M.R. Ganjali, M. Akhoundian and P. Norouzi, *Microchim. Acta,* 183 (2016) 1123.
12. M.R. Ganjali, B. Larijani and E. Pourbasheer, *Int. J. Electrochem. Sci.,* 11 (2016) 2119.

13. S. Cheraghi, M.A. Taher, H. Karimi-Maleh and R. Moradi, *J. Electrochem. Soc.,* 164 (2017) B60.
14. Z. Keyvani, M. Shabani-Nooshabadi and H. Karimi-Maleh, *J. Colloid Interface Sci.,* 507 (2017) 11.
15. S. Cheraghi, M.A. Taher, H. Karimi-Maleh and E. Faghih-Mirzaei, *New J. Chem.,* 41 (2017) 4985.
16. T. Eren, N. Atar, M.L. Yola and H. Karimi-Maleh, *Food Chem.,* 185 (2015) 430.
17. M.R. Ganjali, P. Norouzi, M. Ghorbani and A. Sepehri, *Talanta,* 66 (2005) 1225.
18. P. Norouzi, G.R. Nabi Bidhendi, M.R. Ganjali, A. Sepehri and M. Ghorbani, *Microchim. Acta,* 152 (2005) 123.
19. P. Norouzi, M.R. Ganjali, A. Sepehri and M. Ghorbani, *Sens. Actuators B Chem.,*110 (2005) 239.
20. H. Karimi-Maleh, M.R. Ganjali, P. Norouzi and A. Bananezhad, *Mater. Sci. Eng. C,* 73 (2017) 472.
21. M. Sheikhshoaie, H. Karimi-Maleh, I. Sheikhshoaie and M. Ranjbar, *J. Mol. Liq.,* 229 (2017) 489.
22. V.K. Gupta, M.L. Yola, N. Atar, A.O. Solak, L. Uzun and Z. Üstündağ, *Electrochim. Acta,* 105 (2013) 149.
23. M.L. Yola, V.K. Gupta, T. Eren, A.E. Şen and N. Atar, *Electrochim. Acta,* 120 (2014) 204.
24. H. Karimi-Maleh, M. Shojaei, F. Amini and A. Akbari, *Electroanalysis,* 29 (2017) 1854.
25. H. Karimi-Maleh, F. Tahernejad-Javazmi, M. Daryanavard, H. Hadadzadeh, A.A. Ensafi and M. Abbasghorbani, *Electroanalysis,* 26 (2014) 962.
26. M.R. Ganjali, P. Norouzi, F. Faridbod, M. Ghorbani and M. Adib, *Anal. Chim. Acta,* 569 (2006) 35.
27. V. Arabali, M. Ebrahimi, M. Abbasghorbani, V.K. Gupta, M. Farsi, M.R. Ganjali and F. Karimi, *J. Mol. Liq.,* 213 (2016) 312.
28. Y. Zhao, Y. Gao, D. Zhan, H. Liu, Q. Zhao, Y. Kou, Y. Shao, M. Li, Q. Zhuang and Z. Zhu, *Talanta,* 66 (2005) 51.
29. A. Safavi, N. Maleki, O. Moradlou and F. Tajabadi, *Anal. Biochem.,* 359 (2006) 224.
30. C. Jayakumar, C.M. Magdalane, K. Kanimozhi, K. Kaviyarasu and B. Jeyaraj, *J. Nanostruct.,* 7 (2017) 155.
31. B.J. Sanghavi and A.K. Srivastava, *Electrochim. Acta,* 56 (2011) 4188.
32. V.K. Gupta, H. Karimi-Maleh and R. Sadegh, *Int. J. Electrochem. Sci.,* 10 (2015) 303
33. A.A. Ensafi, H. Karimi-Maleh and S. Mallakpour, *Electroanalysis,* 23 (2011) 1478.
34. A.A. Ensafi and H. Karimi-Maleh, *Electroanalysis,* 22 (2010) 2558
35. A.A. Ensafi, S. Dadkhah-Tehrani and H. Karimi-Maleh, *Anal. Sci.,* 27 (2011) 409.
36. M. Aghazadeh, M. Ghannadi Maragheh, M.R. Ganjali and P. Norouzi, *RSC Adv.,* 6 (2016) 10442.
37. H.R. Naderi, P. Norouzi and M.R. Ganjali, *Appl. Surf. Sci.,* 366 (2016) 552.
38. H.R. Naderi, M.R. Ganjali, A. Shiralizadeh Dezfuli and P. Norouzi, *RSC Adv.,* 6 (2016) 51211.
39. H.R. Naderi, M.R. Ganjali and P. Norouzi, *Int. J. Electrochem. Sci.,* 11 (2016) 4267.
40. M. Mazloum-Ardakani, F. Farbod and L. Hosseinzadeh, *J. Nanostruct.,* 6 (2016) 293
41. N.F. Atta, A. Galal, A.A. Wassel and A.H. Ibrahim, *Int. J. Electrochem. Sci.,* 7 (2012) 10501.
42. N.F. Atta, A. Galal and S.M. Azab, *Int. J. Electrochem. Sci.,* 6 (2011) 5082.
43. A.A. Ensafi, H. Karimi-Maleh and S. Mallakpour, *Electroanalysis* 24 (2012) 666.
44. Z. Keivani, M. Shabani-Nooshabadi and H. Karimi-Maleh, *J. Colloid Interface Sci.,*507 (2017) 11.
45. Y. Tang and W. Cheng, *Langmuir,* 29 (2013) 3125.
46. H. Karimi-Maleh, M. Hatami, R. Moradi, M.A. Khalilzadeh, S. Amiri and H. Sadeghifar, *Microchim. Acta,* 183 (2016) 2957.
47. A.A. Ensafi, H. Karimi-Maleh and S. Mallakpour, *Colloids Surf., B,* 104 (2013) 186
48. J.B. Raoof, R. Ojani, H. Karimi-Maleh, M.R. Hajmohamadi and P. Biparva, *Anal. Methods,* 3 (2011) 2637.
49. M.A. Khalilzadeh, H. Karimi-Maleh, A. Amiri and F. Gholami, *Chin. Chem. Lett.,* 21 (2010) 1467.
50. W. Sun, Y. Li, Y. Duan and K. Jiao, *Biosens. Bioelectron.,* 24 (2008) 988.
51. C. Shan, H. Yang, D. Han, Q. Zhang, A. Ivaska and L. Niu, *Biosens. Bioelectron.,* 25 (2010) 1504.

52. S. Cheraghi, M.A. Taher and H. Karimi-Maleh, *Electroanalysis,* 28 (2016) 366.
53. S. Cheraghi, M.A. Taher and H. Karimi-Maleh, *Electroanalysis,* 28 (2016) 2590.
54. B. Nikahd and M.A. Khalilzadeh, *J. Mol. Liq.,* 215 (2016) 253.
55. A. Fallah Shojaei, K. Tabatabaeian, S. Shakeri and F. Karimi, *Sens. Actuators B Chem.*,230 (2016) 607.
56. M. Goodarzian, M.A. Khalilzade, F. Karimi, V.K. Gupta, M. Keyvanfard, H. Bagheri and M. Fouladgar, *J. Mol. Liq.,* 197 (2014) 114
57. M. Elyasi, M.A. Khalilzadeh and H. Karimi-Maleh, *Food Chem.,* 141 (2013) 4311.
58. R. Bavandpour, H. Karimi-Maleh, M. Asif, V.K. Gupta, N. Atar and M. Abbasghorbani, *J. Mol. Liq.,* 213 (2016) 369.
59. F. Khaleghi, A. Elyasi Irai, V.K. Gupta, S. Agarwal, M. Bijad and M. Abbasghorbani, *J. Mol. Liq.,* 223 (2016) 431.
60. A. Pahlavan, N. Rezanejad, H. Karimi-Maleh, M.R. Jamali, M. Abbasghorbani, H. Beitollahi and N. Atar, *Int. J. Electrochem. Sci.,* 10 (2015) 3644.
61. A. Baghizadeh, H. Karimi-Maleh, Z. Khoshnama, A. Hassankhani and M. Abbasghorbani, *Food Anal. Methods,* 8 (2015) 549.
62. Y. Yardım, M. Gülcan and Z. Şentürk, *Food Chem.* 141 (2013) 1821.
63. L. Jiang, Y. Ding, F. Jiang, L. Li and F. Mo, *Anal. Chim. Acta* 833 (2014) 22.
64. H. Karimi-Maleh, F. Tahernejad-Javazmi, A.A. Ensafi, R. Moradi, S. Mallakpour and H. Beitollahi, *Biosens. Bioelectron.,* 60 (2014) 1.
65. B.J. Sanghavi and A.K. Srivastava, *Anal. Chim. Acta,* 706 (2011) 246.
66. B.J. Sanghavi, P.K. Kalambate, S.P. Karna and A.K. Srivastava, *Talanta,* 120 (2014) 1.
67. H. Karimi-Maleh, P. Biparva and M. Hatami, *Biosens. Bioelectron.,* 48 (2013) 270.