Liquid phase determination of bisphenol A in food samples using novel nanostructure ionic liquid modified sensor

Bahareh Nikahd [a], Mohammad A. Khalilzadeh [b,*]

[a] Department of Food Science, Sari Branch, Islamic Azad University, Sari, Iran
[b] Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

ABSTRACT

Bisphenol A (BPA) is a structural component in polycarbonate beverage bottles that can be released in food samples. So, we focus for preparation of a novel voltammetric sensor in BPA determination. Towards this aim, a fast and sensitive voltammetric sensor based on the use of NiO/CNT nanocomposite/ionic liquid carbon paste electrode (NiO/CNT/IL/CPE) is proposed for the determination of BPA. The proposed sensor exhibited a good electro-catalytic activity towards the electro-oxidation of BAP, which can be confirmed by the increased peak current and the decreased peak potential when compared with the unmodified electrode. The linear response range and detection limit were found to be 0.08–500 μM and 0.04 μM, respectively. The suggested sensor was successfully applied for the voltammetric determination of BPA in food samples with satisfactory results.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

BPA has been used in food packaging since the 1960s (http://www.fda.gov/NewsEvents/PublicHealthFocus/ucm064437.htm). BPA can leach into food samples from the protective internal epoxy resin coatings of canned foods and from consumer products such as food storage containers, polycarbonate tableware and water bottles. The degree leaches of BPA into liquid may depend more on the temperature condition of the liquid or bottle. On the other hand, BPA can also be found in breast milk [1]. Bisphenol A can be an increased risk of breast tumors in human body. Therefore, it is very important for suggestion a high sensitive and good selective sensor in BPA determination in food samples.

Some papers are available regarding the determination of BPA in real samples using different analytical methods [2–8]. Between the analysis methods, electrochemical methods and especially modified sensors have attracted more attention in recent years due to their high sensitivity and selectivity, accuracy, high dynamic range, lower cost, and simplicity [9–13].

As we know, unmodified electrodes have a number of limitations, such as high charge transfer resistance, high overpotential, low selectivity and sensitivity and low stability for electrochemical analysis [14–18]. Therefore, attention to the modification of electrode surfaces using suitable mediators such as nanomaterials and ionic liquid is key point in electrochemical determination of food, biological and pharmaceutical compounds in recent years [19–23].

Electrochemical sensors based on ionic liquid or nanomaterial base have received much attention due to their specific properties such as high electrochemical conductivity and wide electrochemical windows in recent years [24–29]. Room temperature ionic liquids can be used to make different modified sensors, which could increase the electron transfer rate of electroactive compounds [30–33].

In this research, we describe the synthesis and application of a novel NiO/CNTs modified carbon ionic liquid paste electrode, which utilizes 1-butyl-3-methylimidazolium hexafluoro phosphate as a binder. The electrochemical behavior of BPA at NiO/CNT/IL/CPE, at carbon paste electrode modified with 1-butyl-3-methylimidazolium hexafluoro phosphate (IL/CPE), at NiO/CNT carbon paste electrode (NiO/CNT/CPE), and at bare carbon paste electrode (CPE) was investigated. The obtained results show the advantages of NiO/CNT/IL/CPE to the other electrodes in terms of better reversibility and higher sensitivity. Results show that the oxidation peak current was proportional to the BPA concentration in the range of 0.08–500 μM with the detection limit of 0.04 μM. The proposed sensor is good selective and high sensitive enough for the determination of BPA in food samples.

2. Experimental

2.1. Chemicals and apparatus

Nickel nitrate and phosphoric acid were purchased from Sigma-Aldrich and were used as received without any further purification. Bisphenol A, good viscous paraffin oil, pure graphite powders and

* Corresponding author.
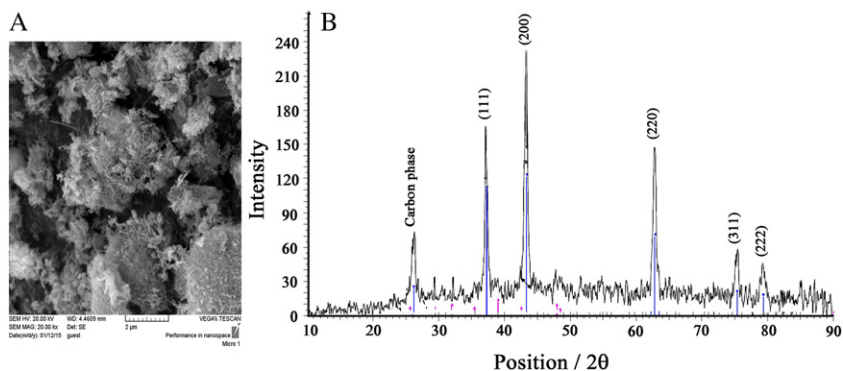E-mail address: khalilzadeh73@gmail.com (M.A. Khalilzadeh).

Fig. 1. (A) SEM image of NiO/CNT nanocomposite. (B) XRD patterns of as-synthesized NiO/CNT nanocomposite.

sodium hydroxide were purchased from Merck Company. Double distilled water was used for preparation of all of the buffer solutions. For pH optimization, phosphate buffer solutions (0.1 mol L^{-1}) (PBS) were used with different pH values.

For nanocomposite analysis, X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Ka radiation. All of the voltammetric investigations were performed in an electroanalytical system, μ-Autolab PGSTAT 12, potentiostat/galvanostat connected to a three-electrode cell, Metrohm Model 663 VA stand linked with a computer (Pentium IV) and with Autolab software. The system was run on a PC using GPES for voltammetric and FRA 4.9 software for impedance spectroscopy study. NiO/CNTs synthesized according to previous report [34]. Bisphenol A stock solution, 1×10^{-2} M, was prepared by dissolving 0.112 g of the reagent in a 50-mL volumetric flask.

2.2. Preparation of real samples

Some cans of each group of foods (water bottle, tomato paste, stew, corn, and tuna fish), totally 30 samples all bearing the same batch number and near their expiration date, were purchased from retail outlets in Qaemshahr. The distribution of types of cans tested in this study was similar across Iran. Purchasing of the samples was carried out in February 2013. Used samples were stored at 20 °C (laboratory condition). After the preparation and opening of the cans, the total contents of each can were homogenized and an aliquot was taken for electrochemical analysis. The remaining contents of each can were then frozen and stored in a freezer at 4 °C. Tap and drinking water samples analysis without any pretreatment for more analysis.

2.3. Preparation of the sensor

NiO/CNT nanocomposite modified ionic liquid carbon paste electrode was prepared by mixing 0.26 g of ionic liquids, 0.74 g of the liquid paraffin, 0.1 g of NiO/CNT nanocomposite, and 0.90 g of pure graphite powder. Then the mixture was mixed well for 2 h until a uniformly wetted paste was obtained. Suitable amount of the preparation paste was filled firmly into one glass tube as described above to prepare NiO/CNT/IL/CPE.

3. Results and discussion

3.1. Characterization of NiO/CNTs

Fig. 1A shows a typical SEM image of NiO/CNT composite. The dark spots correspond to NiO nanoparticles, which were only deposited on the surface of multiwalled carbon nanotubes. Metal oxide nanoparticle with near spherical shapeswas synthesized onto multiwalled carbon nanotubes. NiO/CNTs were analyzed by XRD analyses. The XRD pattern of NiO/CNT nanopowders, in the 2θ range of 10–80°, is shown in Fig. 1B. It obviously proves the presence of NiO nanoparticle, with a diffraction peak at about 26° from multiwalled carbon nanotubes. An average diameter of as-synthesized NiO nanopowder was calculated from the
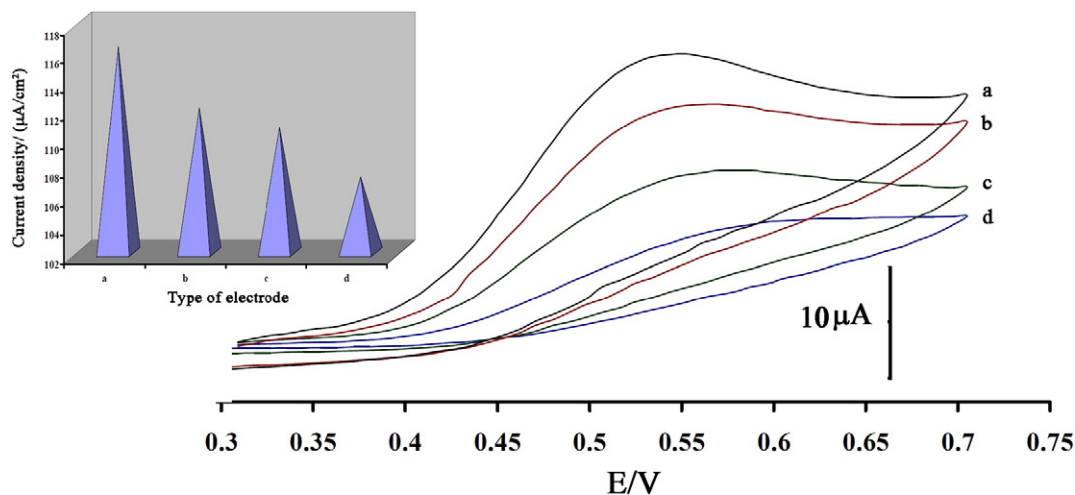

Fig. 2. Cyclic voltammograms of (a) NiO/CNT/IL/CPE, (b) IL/CPE, (c) NiO/CNT/CPE and (d) CPE in the presence of 300 μM BPA at pH 7.0, respectively. Inset: the current density derived from cyclic voltammogram responses of 300 μM BPA at pH 7.0 at the surface of different electrodes.
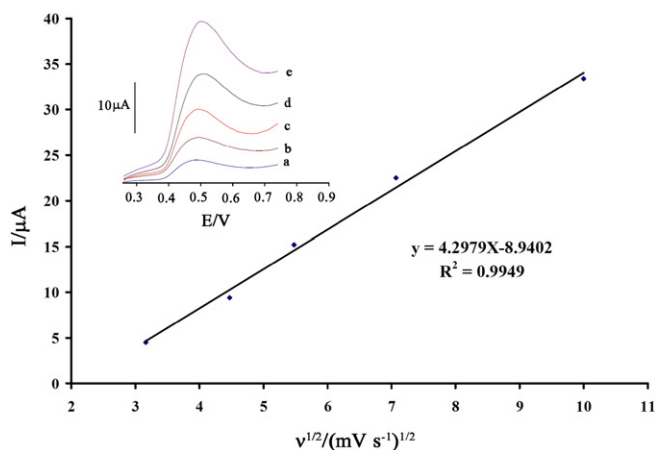
Fig. 3. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of BPA at NiO/CNT/IL/CPE. Inset shows cyclic voltammograms of BPA at NiO/CNT/IL/CPE at different scan rates (from inner to outer (a–e)) of 10, 20, 30, 50 and 100 mV s^{-1} in 0.1 M phosphate buffer, pH 7.0.

broadness peak of $2\theta = 43.5°$ by using Scherrer equation $D = K\lambda/(\beta \cos\theta)$, and it is about 23.0 nm.

3.2. Electrochemical investigation

The active surface area of the using sensors was estimated according to the Randles–Sevcik equation for a known concentration of $K_4Fe(CN)_6$. The results obtained were 0.22, 0.19, 0.14 and 0.11 cm^2 for NiO/NP/IL/CPE, IL/CPE, NiO/CNT/CPE and CPE, respectively. The obtained results show that the presence of nanocomposite and 1-butyl-3-methylimidazolium hexafluoro phosphate together contributed to an increase in the active surface area of the used sensor.

Fig. 2 inset shows the current density derived from the cyclic voltammograms of 300 μM BPA (pH 7.0) at the surface of different electrodes with a scan rate of 100 mV s^{-1}. The results show that the presence of NiO/NPs and 1-butyl-3-methylimidazolium hexafluoro phosphate together causes the increase of the electrode. The direct electrochemistry of BPA on the modified and unmodified electrodes was investigated by cyclic voltammetry. Fig. 2 shows cyclic voltammograms of 300 μM BPA at pH 7.0 at the surface of different electrodes with a scan rate of 100 mV s^{-1}. NiO/CNT/IL/CPE exhibited significant oxidation peak current around 545 mV with the peak current of 25.6 μA (Fig. 2, curve a). In contrast, low redox activity peak was observed at NiO/CNT/CPE (Fig. 2, curve c) and at unmodified CPE (Fig. 2, curve d) over the same condition. The BPA oxidation peak potential at NiO/CNT/CPE
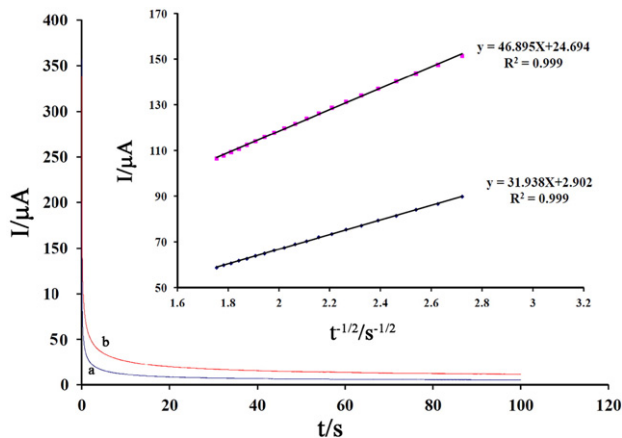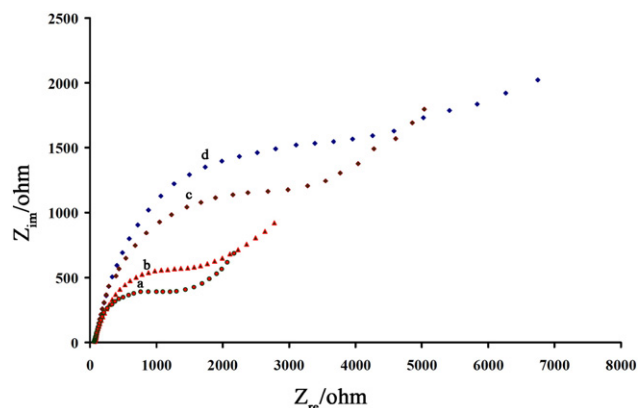

Fig. 5. Nyquist plots of NiO/CNT/IL/CPE (a), IL/CPE (b), NiO/CNT/CPE (c), and CPE (d) in the presence of 500 μM CPZ. Conditions: pH, 7.0; E_{dc}, + 0.45 V vs. Ag/AgCl; E_{ac}, 5 mV; frequency range, 0.1–100,000 Hz.

and at CPE was observed around 575 and 590 mV vs. the reference electrode with the oxidation peak current of 15.5 and 11.8 μA, respectively. In addition, at the surface of IL/CPE, the oxidation peak appeared at 550 mV with the peak current was 21.3 μA (Fig. 2, curve b), which indicated that the presence of 1-butyl-3-methylimidazolium hexafluoro phosphate in CPE could enhance the peak currents and decrease the oxidation potential. A substantial negative shift of the currents starting from oxidation potential for BPA and a dramatic increase of current of BPA indicated the catalytic ability of NiO/CNT/IL/CPE to BPA oxidation. The results indicated that the presence of nanocomposite on NiO/CNT/IL/CPE surface had great improvement with the electrochemical response, which was partly due to excellent characteristics of NiO/CNTs such as good electrical conductivity, high chemical stability, and high surface area. The suitable electronic properties of NiO/CNTs together with the 1-butyl-3-methylimidazolium hexafluoro phosphate gave the ability to promote charge transfer reactions and good anti-fouling properties, especially when mixed with a higher conductive compound such as 1-butyl-3-methylimidazolium hexafluoro phosphate when used as an electrode.

The effect of scan rate (ν) on the oxidation current of BPA was also examined (Fig. 3 inset). The results showed that the peak current increased linearly with increasing the square root of scan rate that ranged from 10 to 100 mV s^{-1} according to regression equation of: (Fig. 3)

$$I_p = 4.2979\,\nu^{1/2} - 8.9402\ (r^2 = 0.9949, I \text{ in } \mu A, \nu \text{ in mV s}^{-1}). \tag{1}$$

Fig. 4. (A) Chronoamperograms obtained at NiO/CNT/IL/CPE in the presence of (a) 300; and (b) 400 μM BPA in the buffer solution (pH 7.0). (B) Cottrell's plot for the data from the chronoamperograms.
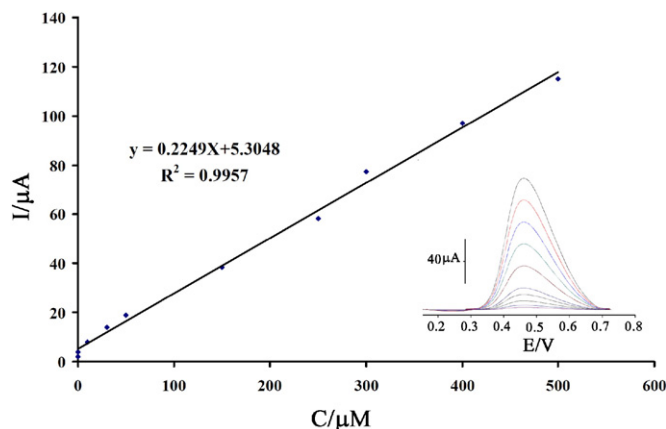

Fig. 6. The plots of the oxidation peak current as a function of BPA concentration. Inset shows the SWVs of NiO/CNT/IL/CPE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of BPA. From inner to outer correspond to 0.08, 0.1, 10.0, 30.0, 50.0, 150.0, 250.0, 300.0, 400.0 and 500.0 of BPA.

Table 1
Interference study for the determination of 15.0 μM BPA under the optimized conditions.

Species	Tolerance limits ($W_{Substance}/W_{BPA}$)
Glucose, fructose, methionine, leucine, alanine, lactose, sucrose, alanine, serine, aspartic acid, threonine, glycine, valine, glycine, phenylalanine	1000
F^-, Ba^{2+}, Ca^{2+}, Li^+, Br^-, SCN^-, Na^+, Mg^{2+}, K^+, ClO_4^-, SO_4^{2-}, ascorbic acid[a]	700
Starch	Saturation

[a] After the addition of 1 mmol L^{-1} ascorbate oxidase.

The result shows that the electrode process is controlled under the diffusion step. On the other hand, the peak potential shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is irreversible.

The value of α was calculated for the oxidation of BPA at pH 7.0 for the NiO/CNT/IL/CPE using the following equation [35].

$$\alpha_{n\alpha} = 0.048/(E_P - E_{P/2}) \qquad (2)$$

where $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The value for $\alpha_{n\alpha}$ was found to be 0.53 at the surface of NiO/CNT/IL/CPE.

Single step chronoamperometric measurements of BPA at NiO/CNT/IL/CPE were carried out by setting the working electrode potential at 650 mV for the 300 and 400 μM of BPA in buffered aqueous solutions (pH 7.0) (Fig. 4A). For BPA 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. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of BPA (Fig. 4B). The slopes of the resulting straight lines were then plotted vs. BPA concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be 2.3×10^{-5} cm^2/s.

Fig. 5 shows Nyquist diagrams of the imaginary impedance (Z_{im}) vs. the real impedance (Z_{re}) of the EIS obtained at CPE (curve d); NiO/CNT/CPE (curve c); IL/CPE (curve b) and NiO/CNT/IL/CPE (curve a) in the presence of 500 μM BPA at pH 7.0, respectively. It can be seen that all of the electrodes exhibit an almost straight line that is characteristic of a diffusion limiting step of the electrochemical process. Nyquist diagrams follow the theoretical shapes and include a squeezed semi-circle portion, observed at higher frequencies, which corresponds to the electron transfer limited process. The respective semicircle diameters at the high frequency correspond to the electron transfer resistance at the electrode surface. The curve corresponding to CPE is a big semicircle plus a straight line (Fig. 5d). For NiO/CNT/CPE, IL/CPE, and NiO/CNT/IL/CPE, R_{ct} decreases dramatically (Fig. 5a–c), indicating that NiO/CNTs and 1-butyl-3-methylimidazolium hexafluoro phosphate can act as an effective electron conduction pathway between the electrode and electrolyte. Therefore, NiO/CNT/IL/CPE composite electrode has good electronic conductivity for electro-oxidation of BPA.

3.3 Calibration plot and limit of detection

Square wave voltammetry (SWV) was used to determine BPA concentrations (Fig. 6 inset). The SW voltammograms clearly show that the plot of peak current vs. BPA concentration is linear for 0.08–500 μM of BPA, the regression equation being $I_p(\mu A) = (0.2294 \pm 0.0181)C_{BPA} + (5.3048 \pm 0.5123)$ ($r^2 = 0.9957$, n = 10), where C is the μM concentration of BPA and I_p is the peak current (Fig. 6). The detection limit was 0.04 μM BPA according to the definition of $Y_{LOD} = Y_B + 3\sigma$.

3.4. Stability and reproducibility

The repeatability and stability of NiO/CNT/IL/CPE were investigated by square wave voltammetry measurements of 15.0 μM BPA. The relative standard deviation (RSD%) for eleven successive assays was 1.5%. When using seven different electrodes, the RSD% for seven measurements was 2.7%. When the electrode was stored in the laboratory, the modified electrode retains 95.5% of its initial response after two weeks and 92% after 40 days. These results indicate that NiO/CNT/IL/CPE has good stability and reproducibility, and could be used for BPA.

3.5. Interference study

The influence of various substances as potentially interfering compounds with the determination of BPA was studied under the optimum conditions of 10.0 μM BPA at pH 7.0. The potentially interfering substances were chosen from the group of substances commonly found with BPA in food samples. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than ± 5% for the determination of BPA. The results are shown in Table 1. Those results confirm the suitable selectivity of the proposed method for the determination of these compounds.

3.6. Real sample analysis

In order to evaluate the analytical applicability of the NiO/CNT/IL/CPE, also it was applied to the determination of BPA food samples. Standard addition method was used for measuring BPA concentration in the samples. The proposed sensor was compared with a HPLC method, too [36]. The results are given in Table 2, which confirm that the NiO/CNT/IL/CPE retained its efficiency for the determination of BPA in real samples.

4. Conclusions

A high sensitive voltammetric sensor based on NiO/CNTs and 1-butyl-3-methylimidazolium hexafluoro phosphate (ionic liquid) was developed as a novel sensor for the fast and selective determination of BPA in food samples. Compared to unmodified carbon paste electrode, a decrease of overpotential of oxidation of BPA with 2.3-fold increment in the oxidation current was observed when using NiO/CNT/IL/CPE as a high sensitive tool. Results show that the oxidation peak current was proportional to the BPA concentration in the range of 0.08–500 μM with the detection limit of 0.04 μM. In the final step, the novel sensor was successfully used for the determination of BPA in food samples.

Acknowledgments

Table 2
Determination of BPA in food samples under optimum condition (sample placed in 60 °C for 30 min).

Sample	Added	Founded (μmol L^{-1})	HPLC method (μmol L^{-1})	F_{ex}	F_{tab}	t_{ex}	t_{tab}
Corn	–	3.03 ± 0.17	2.95 ± 0.27	7.5	19.0	1.7	3.8
Tomato paste	–	2.3 ± 0.45	2.5 ± 0.49	8.7	19.0	1.9	3.8
Water bottle	–	1.01 ± 0.09	0.93 ± 0.13	5.3	19.0	1.4	3.8
Tuna fish	–	5.81 ± 0.74	6.04 ± 0.85	9.5	19.0	2.4	3.8
Stew	–	4.84 ± 0.55	4.35 ± 0.58	9.0	19.0	1.8	3.8
Tap water	–	<LOD	<LOD	–	–	–	–
	10.00	10.45 ± 0.85	9.85 ± 0.87	10.0	19.0	2.9	3.8
Drinking water	–	<LOD	<LOD	–	–	–	–
	20.00	19.56 ± 0.95	20.96 ± 1.01	12.0	19.0	3.3	3.8

F_{ex} calculated F value; reported F value from F-test table with 95% confidence level and 2/2 degrees of freedom; t_{ex} calculated t; t_{tab}(95%); reported t value from Student's t-test table with 95% confidence level.

References

[1] Y. Sun, M. Irie, N. Kishikawa, M. Wada, N. Kuroda, K. Nakashima, Determination of bisphenol A in human breast milk by HPLC with column-switching and fluorescence detection, Biomed. Chromatogr. 18 (2004) 501–507.

[2] M. Del Olmo, A. Gonzalez-Casado, N. Navas, J. Vilchez, Determination of bisphenol A (BPA) in water by gas chromatography–mass spectrometry, Anal. Chim. Acta 346 (1997) 87–92.

[3] G. Gatidou, N.S. Thomaidis, A.S. Stasinakis, T.D. Lekkas, Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography–mass spectrometry, J. Chromatogr. A 1138 (2007) 32–41.

[4] M. Najafi, M.A. Khalilzadeh, H. Karimi-Maleh, A new strategy for determination of bisphenol A in the presence of Sudan I using a ZnO/CNTs/ionic liquid paste electrode in food samples, Food Chem. 158 (2014) 125–131.

[5] M. Rezaee, Y. Yamini, S. Shariati, A. Esrafili, M. Shamsipur, Dispersive liquid–liquid microextraction combined with high-performance liquid chromatography-UV detection as a very simple, rapid and sensitive method for the determination of bisphenol A in water samples, J. Chromatogr. A 1216 (2009) 1511–1514.

[6] B. Ntsendwana, B. Mamba, S. Sampath, O. Arotiba, Electrochemical detection of bisphenol A using graphene-modified glassy carbon electrode, Int. J. Electrochem. Sci. 7 (2012) 3501–3512.

[7] H.-W. Kuo, W.-H. Ding, Trace determination of bisphenol A and phytoestrogens in infant formula powders by gas chromatography–mass spectrometry, J. Chromatogr. A 1027 (2004) 67–74.

[8] J. Li, D. Kuang, Y. Feng, F. Zhang, M. Liu, Voltammetric determination of bisphenol A in food package by a glassy carbon electrode modified with carboxylated multiwalled carbon nanotubes, Microchim. Acta 172 (2011) 379–386.

[9] B.J. Sanghavi, A.K. Srivastava, Simultaneous voltammetric determination of acetaminophen, aspirin and caffeine using an in situ surfactant-modified multiwalled carbon nanotube paste electrode, Electrochim. Acta 55 (2010) 8638–8648.

[10] B.J. Sanghavi, A.K. Srivastava, Adsorptive stripping differential pulse voltammetric determination of venlafaxine and desvenlafaxine employing Nafion–carbon nanotube composite glassy carbon electrode, Electrochim. Acta 56 (2011) 4188–4196.

[11] M.L. Yola, N. Atar, A novel voltammetric sensor based on gold nanoparticles involved in p-aminothiophenol functionalized multi-walled carbon nanotubes: application to the simultaneous determination of quercetin and rutin, Electrochim. Acta 119 (2014) 24–31.

[12] M.L. Yola, N. Atar, M.S. Qureshi, Z. Üstündağ, A.O. Solak, Electrochemically grafted etodolac film on glassy carbon for Pb (II) determination, Sensors Actuators B Chem. 171 (2012) 1207–1215.

[13] M.L. Yola, N. Atar, Z. Üstündağ, A.O. Solak, A novel voltammetric sensor based on p-aminothiophenol functionalized graphene oxide/gold nanoparticles for determining quercetin in the presence of ascorbic acid, J. Electroanal. Chem. 698 (2013) 9–16.

[14] R.N. Goyal, V.K. Gupta, S. Chatterjee, Simultaneous determination of adenosine and inosine using single-wall carbon nanotubes modified pyrolytic graphite electrode, Talanta 76 (2008) 662–668.

[15] R.N. Goyal, V.K. Gupta, S. Chatterjee, Voltammetric biosensors for the determination of paracetamol at carbon nanotube modified pyrolytic graphite electrode, Sensors Actuators B Chem. 149 (2010) 252–258.

[16] M.L. Yola, N. Atar, A. Erdem, Oxytocin imprinted polymer based surface plasmon resonance sensor and its application to milk sample, Sensors Actuators B Chem. 221 (2015) 842–884.

[17] M. Bijad, H. Karimi-Maleh, M.A. Khalilzadeh, Application of ZnO/CNTs nanocomposite ionic liquid paste electrode as a sensitive voltammetric sensor for determination of ascorbic acid in food samples, Food Anal. Methods 6 (2013) 1639–1647.

[18] P.K. Brahman, R.A. Dar, K.S. Pitre, DNA-functionalized electrochemical biosensor for detection of vitamin B1 using electrochemically treated multiwalled carbon nanotube paste electrode by voltammetric methods, Sensors Actuators B Chem. 177 (2013) 807–812.

[19] P.K. Brahman, R.A. Dar, S. Tiwari, K.S. Pitre, Electrochemical behavior of gatifloxacin at multi-walled carbon nanotube paste electrode and its interaction with DNA, Rev. Anal. Chem. 31 (2012) 83–92.

[20] M. Elyasi, M.A. Khalilzadeh, H. Karimi-Maleh, High sensitive voltammetric sensor based on Pt/CNTs nanocomposite modified ionic liquid carbon paste electrode for determination of Sudan I in food samples, Food Chem. 141 (2013) 4311–4317.

[21] T. Jamali, H. Karimi-Maleh, M.A. Khalilzadeh, A novel nanosensor based on Pt:Co nanoalloy ionic liquid carbon paste electrode for voltammetric determination of vitamin B 9 in food samples, LWT- Food Sci. Technol. 57 (2014) 679–685.

[22] Z. Wang, Z. Wang, H. Zhang, X. Duan, J. Xu, Y. Wen, Electrochemical sensing application of poly (acrylic acid modified EDOT-co-EDOT): PSS and its inorganic nanocomposite with high soaking stability, adhesion ability and flexibility, RSC Adv. 5 (2015) 12237–12247.

[23] Y. Yao, L. Zhang, X. Duan, J. Xu, W. Zhou, Y. Wen, Differential pulse striping voltammetric determination of molluscicide niclosamide using three different carbon nanomaterials modified electrodes, Electrochim. Acta 127 (2014) 86–94.

[24] T. Eren, N. Atar, M.L. Yola, H. Karimi-Maleh, A sensitive molecularly imprinted polymer based quartz crystal microbalance nanosensor for selective determination of lovastatin in red yeast rice, Food Chem. 185 (2015) 430–436.

[25] V.K. Gupta, T. Eren, N. Atar, M.L. Yola, C. Parlak, H. Karimi-Maleh, CoFe$_2$O$_4$@TiO$_2$ decorated reduced graphene oxide nanocomposite for photocatalytic degradation of chlorpyrifos, J. Mol. Liq. 208 (2015) 122–129.

[26] N. Atar, T. Eren, M.L. Yola, A molecular imprinted SPR biosensor for sensitive determination of citrinin in red yeast rice, Food Chem. 184 (2015) 7–11.

[27] N. Atar, T. Eren, M.L. Yola, H. Karimi-Maleh, B. Demird¨ogena, Magnetic iron oxide and iron oxide@gold nanoparticle anchored nitrogen and sulfurfunctionalized reduced graphene oxide electrocatalyst for methanol oxidation, RSC Adv. 5 (2015) 26402–26409.

[28] H. Karimi-Maleh, F. Tahernejad-Javazmi, N. Atar, M.L. Yola, V.K. Gupta, A.A. Ensafi, A novel DNA biosensor based on a pencil graphite electrode modified with polypyrrole/functionalized multiwalled carbon nanotubes for determination of 6-mercaptopurine anticancer drug, Ind. Eng. Chem. Res. 54 (2015) 3634–3639.

[29] A. Baghizadeh, H. Karimi-Maleh, Z. Khoshnama, A. Hassankhani, M. Abbasghorbani, Voltammetric sensor for simultaneous determination of vitamin C and vitamin B6 in food samples using ZrO2 nanoparticle/ionic liquids carbon paste electrode, Food Anal. Methods 8 (2015) 549–557.

[30] H. Karimi-Maleh, S. Rostami, V.K. Gupta, M. Fouladgar, Evaluation of ZnO nanoparticle ionic liquid composite as a voltammetric sensing of isoprenaline in the presence of aspirin for liquid phase determination, J. Mol. Liq. 201 (2015) 102–107.

[31] M. Fouladgar, H. Karimi-Maleh, V.K. Gupta, Highly sensitive voltammetric sensor based on NiO nanoparticle room temperature ionic liquid modified carbon paste electrode for levodopa analysis, J. Mol. Liq. 208 (2015) 78–83.

[32] V.K. Gupta, S. Khosravi, H. Karimi-Maleh, M. Alizadeh, S. Sharafi, A voltammetric sensor for determination of methyldopa in the presence of hydrochlorothiazide using Fe:Co nanoalloy modified carbon paste electrode, Int. J. Electrochem. Sci. 10 (2015) 3269–3281.

[33] M.A. Khalilzadeh, H. Karimi-Maleh, V.K. Gupta, A nanostructure based electrochemical sensor for square wave voltammetric determination of L-cysteine in the presence of high concentration of folic acid, Electroanalysis 27 (2015) 1766–1773.

[34] H. Karimi-Maleh, P. Biparva, M. Hatami, A novel modified carbon paste electrode based on NiO/CNTs nanocomposite and (9, 10-dihydro-9, 10-ethanoanthracene-11, 12-dicarboximido)-4-ethylbenzene-1, 2-diol as a mediator for simultaneous determination of cysteamine, nicotinamide adenine dinucleotide and folic acid, Biosens. Bioelectron. 48 (2013) 270–275.

[35] A.J. Bard, L.R. Faulkner, Fundamentals and Applications. Electrochemical Methods, 2nd ed, Wiley, New York, 2001.

[36] Ş. Sungur, M. Köroğlu, A. Özkan, Determination of bisphenol a migrating from canned food and beverages in markets, Food Chem. 142 (2014) 87–91.