



## Analytical Methods

# 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



Maryam Najafi <sup>a</sup>, Mohammad A. Khalilzadeh <sup>a,\*</sup>, Hassan Karimi-Maleh <sup>b,\*</sup>

<sup>a</sup> Department of Food Science, Mazandaran Science and Research Branch, Islamic Azad University, Mazandaran, Iran

<sup>b</sup> Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran

## ARTICLE INFO

## Article history:

Received 2 January 2014  
Received in revised form 13 February 2014  
Accepted 18 February 2014  
Available online 28 February 2014

## Keywords:

Bisphenol A  
Sudan I  
Sensor  
Ionic liquid  
Modified electrode  
Food analysis

## ABSTRACT

The electrochemistry of bisphenol A (BPA) was studied by voltammetric methods at a surface of carbon paste electrode modified by a ZnO/CNTs nanocomposite and room-temperature ionic liquid of 1,3-dipropylimidazolium bromide. The ratio of ZnO/CNTs and ionic liquid (IL) on the surface of the electrode has to be controlled carefully because the charging currents. The anodic peaks of BPA and Sudan I in their mixture can be well separated. At pH 7.0 the two peaks are separated ca. 0.47 and 0.70 V, respectively; hence BPA can be determined in the presence of Sudan I and more than 8.7 times current excess of BPA. The peaks current of square wave voltammograms (SWV) of BPA and Sudan I increased linearly with their concentration in the ranges of 0.002–700  $\mu\text{mol L}^{-1}$  BPA and 0.2–800  $\mu\text{mol L}^{-1}$  Sudan I. The detection limits for BPA and Sudan I were 9.0  $\text{nmol L}^{-1}$  and 80  $\text{nmol L}^{-1}$ , respectively. The modified electrode has been successfully applied for the assay of BPA in food samples. This study provides a simple and easy approach to selectively detect BPA in the presence of Sudan I.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Foodborne illnesses are a burden on public health and contribute significantly to the cost of health care. Food safety is a scientific discipline describing handling, preparation, and storage of food in ways that prevent foodborne illness. This includes a number of routines that should be followed to avoid potentially severe health hazards ([http://en.wikipedia.org/wiki/Food\\_safety](http://en.wikipedia.org/wiki/Food_safety); 30 December, 2013). Bisphenol A is a chemical used in the manufacture of epoxy resins for the lacquer lining of metal food cans, as a monomer of polycarbonates, and the monomer of plastic used in the base paste of dental sealants (Zhuang, Zhang, & Cao, 2008). But polycarbonate and epoxy resins, inner surface coating of food and beverage cans, from which BPA can leach into food and environment (Kim, Kim, Kim, Choi, & Lee, 2013). Exposure to BPA has resulted to extensive human health effects since it exhibits estrogenic activity. These include reproduction dysfunctions, endometrial hyperplasia, recurrent miscarriages, abnormal karyotypes and polycystic ovarian syndrome. Therefore, it is quite urgent to search for an efficient approach for the degradation and detection of such a chemical so as to minimize its contamination in food samples. On the other hand, because of its ubiquitous nature and its endocrine disrupting

potential, BPA has been included in environmental water monitoring or determination studies using several methods (Ntsendwana, Mamba, Sampath, & Arotiba, 2012). Between all of the methods that used for determination of BPA, electrochemical methods have attracted more attention in two decades for due to their sensitivity, accuracy; lower cost, high dynamic range and simplicity (Sanghavi & Srivastava, 2011; Gupta, Atar, Yola, Üstündağ, & Uzun, 2014; Sanghavi et al., 2013; Yola, Atar, Qureshi, Üstündağ, & Solak, 2012; Yola, Atar, Üstündağ, & Solak, 2013; Sanghavi & Srivastava, 2010; Gupta, Singh, Al Khayat, & Gupta, 2007; Goyal, Gupta, & Chatterjee, 2009; Gupta, Singh, Ashok, Mehtab, & Gupta, 2006; Gupta, Jain, Maheshwari, Lang, & Ishtaiwi, 2006; Gupta et al., 2011). Therefore, electrochemical methods were used as performance techniques for determination of some pharmaceutical, biological, environmental and food compounds in recent years (Gupta, Chandra, & Lang, 2005; Gupta, Prasad, & Kumar, 2003; Gupta, Jain, & Kumar, 2006; Sanghavi et al., 2013; Sanghavi & Srivastava, 2013; Goyal, Gupta, & Bachheti, 2007; Gupta et al., 2014; Raof, Ojani, & Karimi-Maleh, 2008; Yola & Atar, 2014; Yola, Gupta, Eren, Şen, & Atar, 2014; Yola et al., 2014; Gupta, Singh, & Gupta, 2007; Gupta, Chandra, & Mangla, 2002; Gupta, Jain, & Khurana, 1997; Gupta, Agarwal, & Singhal, 2011; Gupta, Mangla, Khurana, & Kumar, 1999; Gupta, Jain, Kumar, Agarwal, & Maheshwari, 2006).

Sudan I (sudan red), a synthetic azo dye, is considered to be a genotoxic carcinogen and classified as a category 3 carcinogen by the International Agency for Research on Cancer (IARC) (1975)

\* Corresponding authors. Tel.: +98 911 113 0400 (M.A. Khalilzadeh).

E-mail addresses: [khalilzadeh73@gmail.com](mailto:khalilzadeh73@gmail.com) (M.A. Khalilzadeh), [h.karimi.maleh@gmail.com](mailto:h.karimi.maleh@gmail.com) (H. Karimi-Maleh).

(Stiborova, Martinek, Rydlova, Hodek, & Frei, 2002). Unluckily, it was still found in foodstuffs as additive due to its bright colour, low cost, and long maintenance, such as, poultry feed, paprika, ketchup, sausage, pie, etc. So, it is essential to develop a sensitive, selective, simple, fast and accurate method for identification and quantification of Sudan I in foodstuffs (Yin et al., 2011). Sudan I and BPA are two important compound that put in black list as a unsafe compounds in food samples by the International Agency for Research on Cancer (IARC). So, simultaneous determinations of these compounds are very important for customer for prevention of foodborne illnesses.

There are well-developed methods to synthesize nanomaterials such as carbon nanotubes, nanorod, nanocube, nanoshell, metal nanocomposite, which have found real applications in pharmaceutical, food industrial, environmental and biological process (Elyasi, Khalilzadeh, & Karimi-Maleh, 2013; Olivé-Monllau, Martínez-Cisneros, Bartrolí, Baeza, & Céspedes, 2011; Olivé-Monllau, Pereira, Bartrolí, Baeza, & Céspedes, 2010; Olivé-Monllau, Esplandiú, Bartrolí, Baeza, & Céspedes, 2010; Sanghavi, Kalambate, Karna, & Srivastava, 2014). One of the most important functions of nanocomposite is electrocatalysis, especially with noble metal nanoparticles, which have high catalytic activity for many chemical reactions and high surface area for increasing current density (Karimi-Maleh, Biparva, & Hatami, 2013; Moradi et al., 2013; Tavana et al., 2012; Sanati, Karimi-Maleh, Badiei, Biparva, & Ensafi, 2013; Roodbari Shahmiri, Bahari, Karimi-Maleh, Hosseinzadeh, & Mirnia, 2013). Because nanomaterials also have good biocompatibility, they are used for the fabrication of biosensors in biological and food compound analysis (Beitollah et al., 2012; El-Ansary & Faddah, 2010; Ensafi, Karimi-Maleh, Mallakpour, & Hatami, 2011; Ensafi, Karimi-Maleh, Mallakpour, & Rezaei, 2011; Gupta, Jain, Radhapyari, Jadon, & Agarwal, 2011; Wang et al., 2013).

Its base electrochemical sensors have received much attention due to their specific characteristics such as good chemical and thermal stability, negligible vapour pressure, high ionic conductivity and wide electrochemical windows in the recent years (Afsharmanesh, Karimi-Maleh, Pahlavan, & Vahedi, 2013; Bijad, Karimi-Maleh, & Khalilzadeh, 2013; Ensafi, Bahrami, Rezaei, & Karimi-Maleh, 2013a; Ensafi, Izadi, & Karimi-Maleh, 2013b). ILS can be used to make different modified electrodes, which could increase the transfer rate of different compounds (Sadeghi, Karimi-Maleh, Bahari, & Taghavi, 2013; Salmanpour et al., 2012; Vahedi et al., 2013).

According to the above points, in this study we describe synthesis and application of novel ZnO/CNTs nanocomposite as a novel nanosensor and 1,3-dipropylimidazolium bromide as suitable binder in carbon paste matrix for voltammetric determination of BPA. We have also evaluated the analytical performance of the modified electrode for quantification of BPA in the presence of Sudan I in food samples.

## 2. Experimental

### 2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout.

Bisphenol A (from Merck) stock solution,  $1 \times 10^{-3}$  mol L<sup>-1</sup>, was prepared by dissolving 0.023 g of the reagent in a 100-mL volumetric flask.

Sudan I (from Fluka) stock solution,  $1 \times 10^{-3}$  mol L<sup>-1</sup>, was prepared by dissolving 0.028 g of the reagent in a 100-mL volumetric flask (ethanol–water (1:1) solution). Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate

plus sodium hydroxide, 0.1 mol L<sup>-1</sup>) solutions (PBS) with different pH values were used.

High viscosity paraffin ( $d = 0.88$  kg L<sup>-1</sup>) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes.

### 2.2. Apparatus

Cyclic voltammetry, chronoamperometry, and square wave voltammetry were performed in an analytical system,  $\mu$ -Autolab with PGSTAT (Eco Chemie, the Netherlands). The system was run on a PC using NOVA software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl<sub>sat</sub> electrode as a reference electrode was used. The working electrode was either an unmodified carbon paste electrode (CPE), ZnO/CNTs/IL/CPE, IL/CPE or a ZnO/CNTs/CPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-K $\alpha$  radiation ( $k = 1.54$  Å). Samples for transmission electron microscopy (TEM) analysis were prepared by evaporating a hexane solution of dispersed particles on amorphous carbon coated copper grids.

### 2.3. Synthesis of ZnO/CNTs

The commercial functional multi-walled carbon nanotubes (COOH group) with tube diameters of about 5–10 nm were used. The preparation of ZnO/CNTs catalysts includes two steps. In the first step, certain amounts of purified CNTs (3 g) were dispersed into distilled water solution of NaOH (0.5 M; 50 ml) by ultrasonication for 30 min. The second step is the supporting of zinc oxide on functional carbon nanotubes by a direct deposition process. 3.2 g ZnO (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 100 cm<sup>3</sup> distilled water. In the constant magnetic stirring, the solution of ZnO (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added drop wise to the solution of CNTs at 50 °C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 30 ml/h. After completion of the precipitation procedure, the mixture was stirred at room temperature for 12 h, washed and filtered continually in distilled water (pH 7.0), and dried at 120 °C. The solid samples were then calcined at 300 °C for 2 h.

### 2.4. Preparation of the sensor

ZnO/CNTs/CPE was prepared by hand-mixing of 0.85 g of graphite powder and 0.15 g ZnO/CNTs plus paraffin at a ratio of 70/30 (w/w) and mixed well for 50 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper ZnO/CNTs/IL/CPE was prepared by mixing of 0.2 g of 1,3-dipropylimidazolium bromide, 0.8 g of the liquid paraffin, 0.15 g of ZnO/CNTs, and 0.85 g of graphite powder. Then the mixture was mixed well for 40 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare ZnO/CNTs/IL/CPE.

### 2.5. Preparation of real samples

Fifteen cans of each group of foods (corn, tomato paste, stew, water bottle and tuna fish), totally 45 samples all bearing the same batch number and near their expiration date, were purchased from retail outlets in Sari. The distribution of types of samples tested in this survey was similar across Iran. Purchasing of the samples was carried out in October 2013. Samples were stored and sealed at room temperature. After opening the cans, the total contents of

each can were homogenized and an aliquot was taken for analysis. The remaining contents of each can were then frozen and stored in a freezer at 4 °C. Water samples analysis without any pretreatment for real sample analysis.

### 3. Results and discussion

#### 3.1. Characterization of nanocomposite

Fig. 1 shows X-ray patterns of the ZnO coated MWNTs. The diffraction angles at  $2\theta = 31.8, 34.5, 36.5, 47.6, 56.6, 63.1, 66.4, 68.0, 69.3, 72.8$  and  $77.3$  (Fig. 1B), can be assigned to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of ZnO nanoparticle. The peak at  $26.9$  can be nicely indexed to the (002) plane of MWNTs as marked with star in Fig. 1A. The broad peaks in the XRD patterns indicate that the ZnO nanoparticles are small. The mean particle size of ZnO nanoparticles calculated by the Scherrer equation is about  $30$  nm. Zn (101) is used to calculate the size of ZnO nanoparticles. To ascertain morphology of sample obtained here, ZnO/MWNTs composite was further characterized by TEM. Clearly, nanocomposites present a rough surface in comparison with pristine MWNTs. As shown in Fig. 1B, outside surface of MWNTs is uniformly dotted with ZnO nanoparticles with the size of less than  $30$  nm, which is consistent with the result calculated by Scherrer equation. EDX spectrum (not shown) indicates the presence of Zn, O, and C, which confirms that nanoparticles absorbed on MWNTs are ZnO nanoparticles.

#### 3.2. Electrochemical investigation

The active surface area of the modified electrode was estimated according to the slope of the  $I_p$  versus  $v^{1/2}$  plot for a known concentration of  $K_4Fe(CN)_6$ , based on the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_0 \quad (2)$$

where  $I_p$  refers to the anodic peak current,  $n$  the electron transfer number,  $A$  the surface area of the electrode,  $D_R$  the diffusion coefficient,  $C_0$  the concentration of  $K_4Fe(CN)_6$  and  $v$  is the scan rate. The microscopic areas were calculated from the slope of the  $I_p$ - $v^{1/2}$  relation (taking concentration of  $K_4Fe(CN)_6$  as  $1.0$  mmol  $L^{-1}$ , concentration of KCl electrolyte as  $0.10$  mol  $L^{-1}$ ,  $n = 1$ ,  $D_R = 7.6 \times 10^{-6}$  cm  $s^{-1}$ ). The results obtained were  $0.23, 0.18, 0.14$  and  $0.09$  cm<sup>2</sup>

for ZnO/CNTs/IL/CPE, IL/CPE, ZnO/CNTs/CPE and CPE, respectively. The results further show that the presence of ZnO/CNTs and IL together contributed to an increase in the active surface area of the electrode.

According to previous reports, the oxidation peak current of BPA is closely related to the pH value of electrolyte solution (Ntsewawana et al., 2012). Therefore, the effect of pH was investigated using cyclic voltammetry technique. In order to ascertain this, the voltammetric response of BPA at a surface of ZnO/CNTs/IL/CPE was obtained in solutions with varying pH. It was found that the oxidation peak current increased gradually from pH 5.0 to 7.0, and then the current conversely decreased when the pH value increased from 7.0 to 8.0. So pH 7.0 was chosen as the optimal experimental condition. The relationship between the oxidation peak potential and pH was also constructed. A linear shift of  $E_{pa}$  towards negative potential with an increasing pH can be obtained and obeyed the regression equation of  $E_{pa}$  (V) =  $-0.052pH + 0.890$  ( $R^2 = 0.998$ ), which indicates that protons are directly involved in the oxidation of BPA. A slope of  $52$  mV/pH suggests that the number of electron transfer is equal to the proton number involved in the electrode reaction (Ntsewawana et al., 2012). Because the two electrons involved in the oxidation of BPA (phenolic oxidation peak in this case) at Pt/CNTs/IL/CPE, the transfer proton number was 2.

Fig. 2 (inset) shows the current density derived from the cyclic voltammograms of  $300 \mu\text{mol L}^{-1}$  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 ZnO/CNTs and ILs together causes the increase of the electrode. The direct electrochemistry of BPA on the modified electrode was investigated by cyclic voltammetry. Fig. 2 shows cyclic voltammograms of  $300 \mu\text{mol L}^{-1}$  BPA at pH 7.0 at the surface of different electrodes with a scan rate of  $100$  mV  $s^{-1}$ . ZnO/CNTs/IL/CPE exhibited significant oxidation peak current around  $455$  mV with the peak current of  $21.6 \mu\text{A}$  (Fig. 2, curve a), and no reduction signal was observed in the reversed scan. In contrast, low redox activity peak was observed at ZnO/CNTs/CPE (Fig. 2, curve c) and at unmodified CPE (Fig. 2 curve d) over the same condition. The BPA oxidation peak potential at ZnO/CNTs/CPE and at CPE observed around  $495$  and  $485$  mV vs. the reference electrode with the oxidation peak current of  $11.3$  and  $8.0 \mu\text{A}$ , respectively. In addition, at the surface of bare IL/CPE, the oxidation peak appeared at  $465$  mV with the peak current was  $2.5 \mu\text{A}$  (Fig. 2, curve b), which indicated the presence of ILs in CPE could enhance the peak currents and decrease the oxidation potential (decreasing the

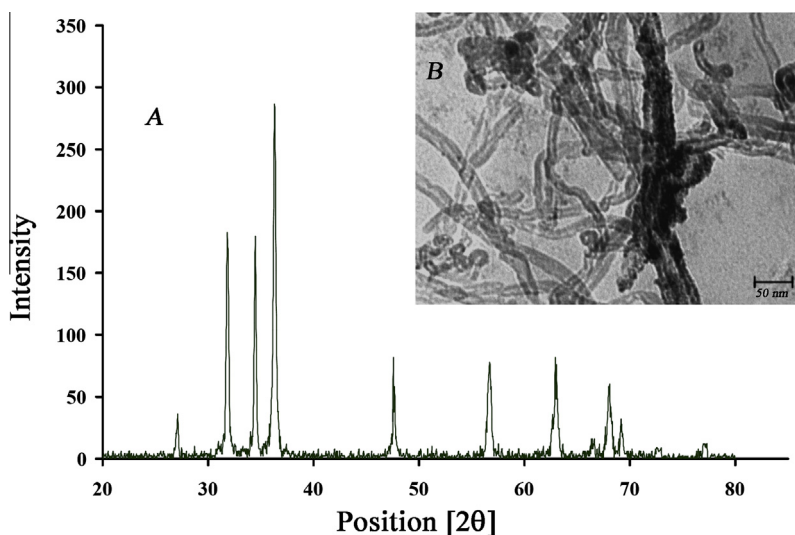
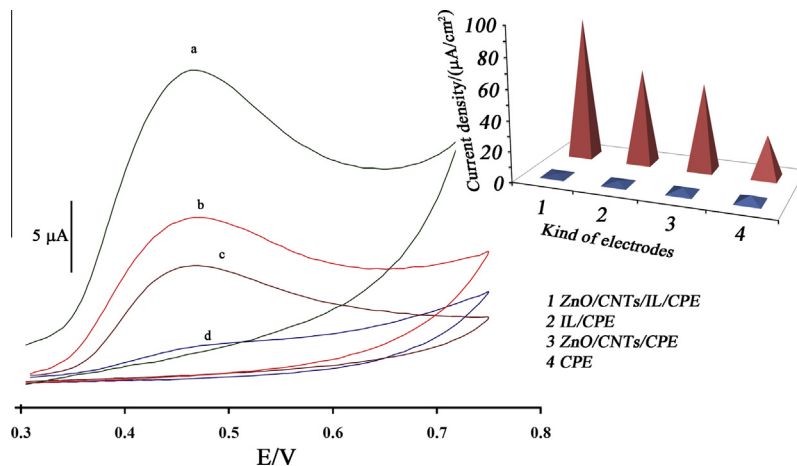


Fig. 1. (A) XRD patterns of as-synthesized ZnO/CNTs nanocomposite. (B) TEM image of ZnO/CNTs nanocomposite.



**Fig. 2.** Cyclic voltammograms of (a) ZnO/CNTs/IL/CPE, (b) IL/CPE, (c) ZnO/CNTs/CPE and (d) CPE in presence of  $300 \mu\text{mol L}^{-1}$  BPA at a pH 7.0, respectively. Inset: the current density derived from cyclic voltammograms responses of  $300 \mu\text{mol L}^{-1}$  BPA at pH 7.0 at the surface of different electrodes with a scan rate of  $100 \text{ mV s}^{-1}$ .

overpotential). A substantial negative shift of the currents starting from oxidation potential for BPA and dramatic increase of current of BPA indicated the catalytic ability of ZnO/CNTs/IL/CPE to BPA oxidation. The results indicated that the presence of ZnO/CNTs on ZnO/CNTs/IL/CPE surface had great improvement with the electrochemical response, which was partly due to excellent characteristics of ZnO/CNTs such as good electrical conductivity, high chemical stability, and high surface area. The suitable electronic properties of ZnO/CNTs together with the ionic liquid gave the ability to promote charge transfer reactions, good anti-fouling properties, especially when mixed with a higher conductive compound such as ILs when used as an electrode.

The effect of scan rate ( $\nu$ ) on the oxidation current of BPA was also examined (Fig. 3 inset). The results showed that the peaks current increased linearly with increasing the square root of scan rate that ranged from  $50$  to  $200 \text{ mV s}^{-1}$  according to regression equation of (Fig. 3):

$$I_p = 2.687 \nu^{1/2} - 11.627 (r^2 = 0.994, I \text{ in } \mu\text{A}, \nu \text{ in } \text{mV s}^{-1}) \quad (1)$$

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. At higher scan rate, the dependence of the peak potential ( $E_{pa}$ ) and  $\ln(\nu)$  showed a linear relationship with a regression equation of:

$$E_{pa} = 0.046 \ln(\nu) + 0.297 (r^2 = 0.994, E_p \text{ in V}, \nu \text{ in } \text{V s}^{-1}) \quad (2)$$

According to the following equation (Nicholson and Shain, 1964):

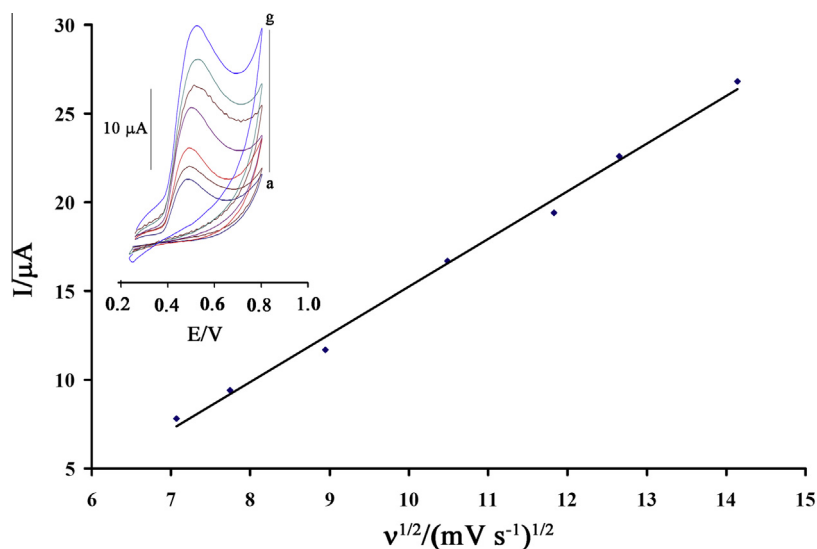
$$E_{pa} = E^{0'} + m[0.78 + \ln(D^{1/2} k_s^{-1}) - 0.5 \ln m] + (m/2) \ln(\nu) \quad (3)$$

with:

$$m = RT / [(1 - \alpha) n_z F] \quad (4)$$

where  $E_{pa}$  is oxidation peak potential,  $E^{0'}$  is the formal potential,  $\nu$  is the sweep rate,  $k_s$  is electron transfer rate constant. A plot of  $E_{pa} = f(\ln(\nu/\text{V s}^{-1}))$  yields a straight line with slopes equal to  $2(RT / [(1 - \alpha) n_z F])$  where  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 298 \text{ K}$  and  $F = 96485 \text{ C mol}^{-1}$ . The value of  $n(1 - \alpha)$  is calculated 0.267 from Eq. (4), which indicates that the activation free energy curve is not symmetrical in such an irreversible oxidation process.

Chronoamperometry results obtained for the various concentrations of BPA solution using ZnO/CNTs/IL/CPE are shown in Fig. S1 (Supporting information data). The plot of current ( $I$ ) versus  $t^{-1/2}$  for BPA solution at various concentrations using ZnO/CNTs/IL/



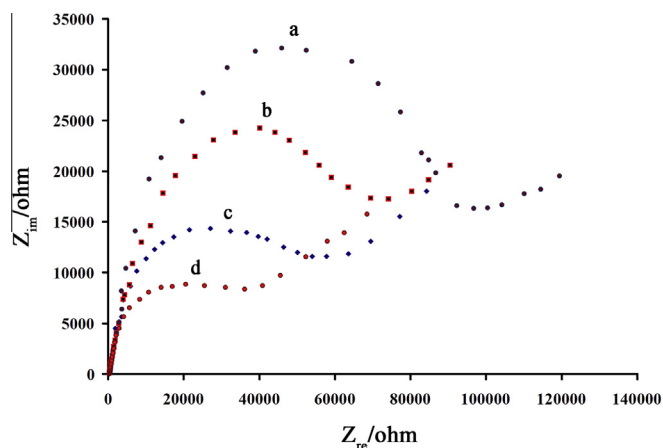
**Fig. 3.** Plot of  $I_{pa}$  vs.  $\nu^{1/2}$  for the oxidation of BPA at ZnO/CNTs/IL/CPE. Inset shows cyclic voltammograms of BPA at ZnO/CNTs/IL/CPE at different scan rates of (a) 50, (b) 60, (c) 80, (d) 110, (e) 140, (f) 160 and (g)  $200 \text{ mV s}^{-1}$  in 0.1 M phosphate buffer, pH 7.0.

CPE (Fig. 4b) gives straight lines with different slopes (Fig. S1 Supporting information data). From the slopes we calculated a diffusion coefficient of  $8.46 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (assuming  $n = 2$  and the electrode surface area ( $A$ ) of  $0.23 \text{ cm}^2$ ) for BPA using the Cottrell equation.

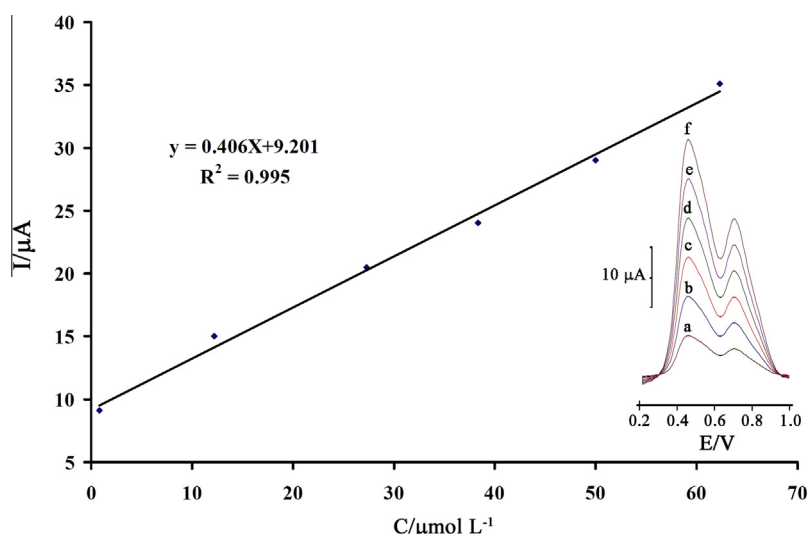
Electrochemical impedance spectroscopy was used to study the behaviour of  $300 \mu\text{mol L}^{-1}$  BPA (at optimum condition) at the surface of ZnO/CNTs/IL/CPE, IL/CPE, ZnO/CNTs/CPE, and CPE (Fig. 4). The curve corresponding to CPE is a big semicircle plus a straight line (Fig. 4 curve a); the electron transfer resistance ( $R_{ct}$ ) can be estimated to be  $95.3 \text{ K}\Omega$ . For ZnO/CNTs/CPE, IL/CPE, and ZnO/CNTs/IL/CPE,  $R_{ct}$  decreases dramatically (Fig. 4, curves b–d), indicating that ZnO/CNTs and ILs can act as an effective electron conduction pathway between the electrode and electrolyte. Therefore, ZnO/CNTs/IL/CPE composite film has good electronic conductivity.

### 3.3. Analytical features

Square wave voltammetry (SWV) was used to determine BPA and Sudan I concentrations. The SW voltammograms clearly show that the plot of peak current versus BPA concentration is linear for



**Fig. 4.** Nyquist plots of CPE (a), ZnO/CNTs/CPE (b), IL/CPE (c), and ZnO/CNTs/IL/CPE (d) in the presence of  $300 \mu\text{mol L}^{-1}$  BPA. Conditions: pH, 7.0;  $E_{dc}$ , +0.4 V vs. Ag/AgCl;  $E_{ac}$ , 5 mV; frequency range, 0.1–100000 Hz.



**Fig. 5.** The plots of the electrocatalytic peak current as a function of BPA concentration. Inset; SWVs of ZnO/CNTs/IL/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of BPA–Sudan I in  $\mu\text{mol L}^{-1}$ . (a–f)  $0.8 + 5.0$ ;  $12.2 + 24.0$ ;  $27.3 + 43.0$ ;  $38.4 + 60.0$ ;  $50 + 80$  and  $62.3 + 100.0$ , respectively.

$0.002\text{--}700 \mu\text{mol L}^{-1}$  of BPA, the regression equation being  $I_p(\mu\text{A}) = (0.405 \pm 0.002)C_{\text{BPA}} + (12.176 \pm 0.423)$  ( $r^2 = 0.997$ ,  $n = 16$ ) while the regression equation for Sudan I in the range of  $0.2\text{--}800 \mu\text{mol L}^{-1}$  is  $I_p(\mu\text{A}) = (0.229 \pm 0.003)C_{\text{Sudan I}} - (3.034 \pm 0.051)$  ( $r^2 = 0.991$ ,  $n = 15$ ), where  $C$  is  $\mu\text{mol L}^{-1}$  concentration of BPA or Sudan I and  $I_p$  is the peak current. The detection limit were determined at  $9.0 \text{ nmol L}^{-1}$  BPA and  $80.0 \text{ nmol L}^{-1}$  Sudan I according to the definition of  $Y_{\text{LOD}} = Y_B + 3\sigma$ .

The main object of this study was to detect BPA and Sudan I simultaneously using ZnO/CNTs/IL/CPE. This was performed by simultaneously changing the concentrations of BPA and Sudan I, and recording the SWVs. The SW voltammograms showed two well-defined anodic peaks with a 240 mV separation of the peaks (Fig. 5 inset). Current sensitivities towards BPA in the absence and in the presence of Sudan I were found to be  $0.405 \pm 0.002 \mu\text{A}/\mu\text{M}$  (in the absence of Sudan I) and  $0.406 \pm 0.004 \mu\text{A}/\mu\text{M}$  (in its presence of Sudan I) (Fig. 5). It is interesting to note that the sensitivities of the modified electrode towards BPA in the absence and presence of Sudan I were virtually the same, which indicates that the oxidation processes of BPA and Sudan I at the modified electrode are independent and that simultaneous or independent measurements of the two compounds are, therefore, possible without any interference.

### 3.4. Interference studies

The influence of various substances as potentially interfering compounds with the determination of BPA was studied under the optimum conditions with  $5.0 \mu\text{mol L}^{-1}$  BPA at pH 7.0. The potential 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 of less than  $\pm 5\%$  for the determination of BPA. After the experiments, we found that neither 1000-fold of glucose, sucrose, lactose, fructose, methanol and ethanol nor 800-fold of  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{ClO}_4^-$ , nor 700-fold citric acid, methionine, alanine, phenylalanine, valine, tryptophan, glycine, valine, histidine and glutamic acid affected the selectivity. Nor did saturation of starch solution and 500-fold of urea, ascorbic acid (after addition 1 mM ascorbic oxidase) and thiourea were interfered with the determination of BPA.

**Table 1**  
Determination of BPA and Sudan I in food samples.

Sample	Added BPA ( $\mu\text{mol L}^{-1}$ )	Added Sudan I ( $\mu\text{mol L}^{-1}$ )	Founded BPA ( $\mu\text{mol L}^{-1}$ )	Founded Sudan I ( $\mu\text{mol L}^{-1}$ )	HPLC method ( $\mu\text{mol L}^{-1}$ )	HPLC method ( $\mu\text{mol L}^{-1}$ )	$F_{\text{ex}}$	$F_{\text{tab}}$	$t_{\text{ex}}$	$t_{\text{tab}}$
Tomato paste	–	–	$1.1 \pm 0.21$	–	$1.4 \pm 0.37$	–	6.5	19.0	1.5	3.8
Corn Stew	–	–	$2.1 \pm 0.32$	–	$1.4 \pm 0.37$	–	6.9	19.0	1.7	3.8
Tuna fish	–	–	$4.2 \pm 0.18$	–	$1.4 \pm 0.37$	–	7.3	19.0	2.1	3.8
Water bottle	–	–	$6.3 \pm 0.45$	–	$1.4 \pm 0.37$	–	8.5	19.0	2.2	3.8
Chilli sauce	–	–	<Limit of detection	<Limit of detection	–	–	–	–	–	–
	–	0.5	–	$0.47 \pm 0.05$	–	$0.52 \pm 0.07$	6.5	19.0	1.8	3.8

$F_{\text{ex}}$  calculated  $F$  value; reported  $F$  value from  $F$ -test table with 95% confidence level and 2/2 degrees of freedom  $t_{\text{ex}}$  calculated  $t$ ;  $t_{\text{tab}}$  (95%); reported  $t$  value from Student  $t$ -test table with 95% confidence level.

±Shows the standard deviation ( $n = 3$ ).

### 3.5. Stability and reproducibility of the modified electrode

The stability and reproducibility of any sensor are two important parameters for application of a suggestion sensor. Our experiments showed that after ZnO/CNTs/IL/CPE was stored for 4 weeks at 4 °C, only a small decrease of peak current sensitivity with a relative standard deviation (RSD) of 1.5% (for  $5.0 \mu\text{mol L}^{-1}$  BPA) was observed. This showed good stability of the modified electrode. Furthermore, the reproducibility of the determination was performed with ten successive scans in the solution containing  $5.0 \mu\text{mol L}^{-1}$  BPA. The RSD values were found to be 2.0% for the analyte, indicating good reproducibility of the modified electrode. The electrode can be immersed in an aqueous media for 2.5 h with stable response. After that, the background current began to increase, which may be due to the partly leakage of ionic liquid from the electrode and the roughness of the electrode surface was increases gradually.

### 3.6. Real sample analysis

In order to evaluate the analytical applicability of the proposed nanosensor, also it was applied to the determination of BPA and Sudan I in food samples. Standard addition method was used for measuring BPA and Sudan I concentration in the samples. The proposed method was compared with a HPLC method too (Sungur, Köroglu, & Özkan, 2014 (for BPA); Ertaş, Özer, & Alasalvar, 2007 (for Sudan I)). The results are given in Table 1, confirm that the modified electrode retained its efficiency for the determination of BPA in real samples.

## 4. Conclusion

In this work, the 1,3-dipropylimidazolium bromide modified ZnO/CNTs carbon paste electrode was used to investigate the electrochemical behaviours of BPA. The ZnO/CNT/IL/CPE showed great improvement to the electrode process of BPA compare to the traditional carbon paste electrode. The modified electrode successfully resolves the overlapped voltammetric peaks of BPA and Sudan I by  $\approx 240$  mV, so that the modified electrode displays high selectivity in the SWV measurement of BPA and Sudan I in their mixture solutions. The electrode was successfully used for the determination of BPA and Sudan I in food samples.

## Acknowledgements

The authors wish to thank Graduate University of Advanced Technology, Kerman and Science and Research Branch, Islamic Azad University, Mazandaran, Iran, for their support.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2014.02.082>.

## References

- Afsharmanesh, E., Karimi-Maleh, H., Pahlavan, A., & Vahedi, J. (2013). Electrochemical behavior of morphine at ZnO/CNT nanocomposite room temperature ionic liquid modified carbon paste electrode and its determination in real samples. *Journal of Molecular Liquids*, 181, 8–13.
- Beitollah, H., Goodarziyan, M., Khalilzadeh, M. A., Karimi-Maleh, H., Hassanzadeh, M., & Tajbakhsh, M. (2012). Electrochemical behaviors and determination of carbido-pa on carbon nanotubes ionic liquid paste electrode. *Journal of Molecular Liquids*, 173, 137–143.
- Bijad, M., Karimi-Maleh, H., & Khalilzadeh, M. A. (2013). Application of ZnO/CNTs nanocomposite ionic liquid paste electrode as a sensitive voltammetric sensor for determination of ascorbic acid in food samples. *Food Analytical Methods*, 6, 1639–1647.
- Elyasi, M., Khalilzadeh, M. A., & Karimi-Maleh, H. (2013). High sensitive voltammetric sensor based on Pt/CNTs nanocomposite modified ionic liquid carbon paste electrode for determination of Sudan I in food samples. *Food Chemistry*, 141, 4311–4317.
- El-Ansary, A., & Faddah, L. M. (2010). Nanoparticles as biochemical sensors. *Nanotechnology, Science and Applications*, 3, 65–76.
- Ensafi, A. A., Karimi-Maleh, H., Mallakpour, S., & Hatami, M. (2011a). Simultaneous determination of N-acetylcysteine and acetaminophen by voltammetric method using N-(3,4-dihydroxyphenethyl)-3,5-dinitrobenzamide modified multiwall carbon nanotubes paste electrode. *Sensors and Actuators B*, 155, 464–472.
- Ensafi, A. A., Karimi-Maleh, H., Mallakpour, S., & Rezaei, B. (2011b). Highly sensitive voltammetric sensor based on catechol-derivative-multiwall carbon nanotubes for the catalytic determination of captopril in patient human urine samples. *Colloids and Surfaces B*, 87, 480–488.
- Ensafi, A. A., Bahrami, H., Rezaei, B., & Karimi-Maleh, H. (2013a). Application of ionic liquid–TiO<sub>2</sub> nanoparticle modified carbon paste electrode for the voltammetric determination of benserazide in biological samples. *Materials Science and Engineering C*, 33, 831–835.
- Ensafi, A. A., Izadi, M., & Karimi-Maleh, H. (2013b). Sensitive voltammetric determination of diclofenac using room-temperature ionic liquid-modified carbon nanotubes paste electrode. *Ionics*, 19, 137–144.
- Ertaş, E., Özer, H., & Alasalvar, C. (2007). A rapid HPLC method for determination of Sudan dyes and Para Red in red chilli pepper. *Food Chemistry*, 105(2007), 756–760.
- Goyal, R. N., Gupta, V. K., & Bachheti, N. (2007). Fullerene-C<sub>60</sub>-modified electrode as a sensitive voltammetric sensor for detection of nandrolone—An anabolic steroid used in doping. *Analytica Chimica Acta*, 597(2007), 82–89.
- Goyal, R. N., Gupta, V. K., & Chatterjee, S. (2009). A sensitive voltammetric sensor for determination of synthetic corticosteroid triamcinolone, abused for doping. *Biosensors and Bioelectronics*, 24(2009), 3562–3568.
- Gupta, V. K., Atar, N., Yola, M. L., Üstündağ, Z., & Uzun, L. (2014). A novel magnetic Fe@Au core-shell nanoparticles anchored grapheme oxide recyclable nanocatalyst for the reduction of nitrophenol compounds. *Water Research*, 48, 210–217.
- Gupta, V. K., Jain, S., & Khurana, U. (1997). A PVC-based pentathia-15-crown-5 membrane potentiometric sensor for mercury (II). *Electroanalysis*, 9, 478–480.
- Gupta, V. K., Singh, Ashok K., Mehtab, S., & Gupta, B. (2006). A cobalt(II)-selective PVC membrane based on a Schiff base complex of N,N'-bis(salicylidene)-3,4-diaminotoluene. *Analytica Chimica Acta*, 566(2006), 5–10.

- Gupta, V. K., Ganjali, M. R., Norouzi, P., Khani, H., Nayak, A., & Agarwal, S. (2011a). Electrochemical analysis of some toxic metals and drugs by ion selective electrodes. *Critical Reviews in Analytical Chemistry*, 41(2011), 282–313.
- Gupta, V. K., Agarwal, S., & Singhal, B. (2011b). A review on the recent advances on potentiometric membrane sensors for pharmaceutical analysis. *Combinatorial Chemistry & High Throughput Screening*, 14(2011), 284–302.
- Gupta, V. K., Prasad, R., & Kumar, A. (2003). Preparation of ethambutol-copper(II) complex and fabrication of PVC based membrane potentiometric sensor for copper. *Talanta*, 60, 149–160.
- Gupta, V. K., Chandra, S., & Mangla, R. (2002). Dicyclohexano-18-crown-6 as active material in PVC matrix membrane for the fabrication of cadmium selective potentiometric sensor. *Electrochimica Acta*, 47(2002), 1579–1586.
- Gupta, V. K., Chandra, S., & Lang, H. (2005). A highly selective mercury electrode based on a diamine donor ligand. *Talanta*, 66, 575–580.
- Gupta, V. K., Jain, A. K., Maheshwari, G., Lang, H., & Ishtaiwi, Z. (2006a). Copper(II)-selective potentiometric sensors based on porphyrins in PVC matrix. *Sensors and Actuators B*, 117, 99–106.
- Gupta, V. K., Jain, A. K., & Kumar, P. (2006b). PVC-based membranes of N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as Pb(II)-selective sensor. *Sensors and Actuators B*, 120(2006), 259–265.
- Gupta, V. K., Yola, M. L., & Atar, N. (2014). A novel molecular imprinted nanosensor based quartz crystal microbalance for determination of kaempferol. *Sensors and Actuators B*, 194(2014), 79–85.
- Gupta, V. K., Singh, A. K., Al Khayat, M., & Gupta, B. (2007a). Neutral carriers based polymeric membrane electrodes for selective determination of mercury(II). *Analytica Chimica Acta*, 590(2007), 81–90.
- Gupta, V. K., Singh, A. K., & Gupta, B. (2007b). Schiff bases as cadmium(II) selective ionophores in polymeric membrane electrodes. *Analytica Chimica Acta*, 583(2007), 340–348.
- Gupta, V. K., Mangla, R., Khurana, U., & Kumar, P. (1999). Determination of uranyl ions using poly(vinyl chloride) based 4-tert-butylcalix[6] arene membrane sensor. *Electroanalysis*, 11, 573–576.
- Gupta, V. K., Jain, A. K., Kumar, P., Agarwal, S., & Maheshwari, G. (2006). Chromium(III)-selective sensor based on tri-o-thymotide in PVC matrix. *Sensors and Actuators B*, 113(2006), 182–186.
- Gupta, V.K., Jain, R., Radhapyari, K., Jadon, N., Agarwal, S. (2011). Voltammetric techniques for the assay of pharmaceuticals—A review. *Analytical Biochemistry* 408 (2011) 179–196. <[http://en.wikipedia.org/wiki/Food\\_safety](http://en.wikipedia.org/wiki/Food_safety)>; 30 December, 2013.
- Karimi-Maleh, H., Biparva, P., & Hatami, M. (2013). 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. *Biosensor and Bioelectronics*, 48, 270–275.
- Kim, B. K., Kim, J. Y., Kim, D. H., Choi, H. N., & Lee, W. Y. (2013). Electrochemical determination of bisphenol A at carbon nanotube-doped titania-nafion composite modified electrode. *Bulletin of the Korean Chemical Society*, 34, 1065–1069.
- Moradi, R., Sebt, S. A., Karimi-Maleh, H., Sadeghi, R., Karimi, F., Bahari, A., et al. (2013). Synthesis and application of FePt/CNTs nanocomposite as a sensor and novel amide ligand as a mediator for simultaneous determination of glutathione, nicotinamide adenine dinucleotide and tryptophan. *Physical Chemistry Chemical Physics*, 15, 5888–5897.
- Nicholson, R. S., & Shain, I. (1964). Theory of stationary electrode polarography. *Analytical Chemistry*, 36(4), 706–723.
- Ntsendwana, B., Mamba, B. B., Sampath, S., & Arotiba, O. A. (2012). Electrochemical detection of bisphenol A using graphene-modified glassy carbon electrode. *International Journal of Electrochemical Science*, 7, 3501–3512.
- Olivé-Monllau, R., Pereira, A., Bartroli, J., Baeza, M., & Céspedes, F. (2010). Highly sensitive CNT composite amperometric sensors integrated in an automated flow system for the determination of free chlorine in waters. *Talanta*, 81, 1593–1598.
- Olivé-Monllau, R., Martínez-Cisneros, C. S., Bartroli, J., Baeza, M., & Céspedes, F. (2011). Integration of a sensitive carbon nanotube composite electrode in a ceramic microanalyzer for the amperometric determination of free chlorine. *Sensors and Actuators B*, 151, 416–422.
- Olivé-Monllau, R., Esplandiú, M. J., Bartroli, J., Baeza, M., & Céspedes, F. (2010). Strategies for the optimization of carbon nanotube/polymer ratio in composite materials: Applications as voltammetric sensors. *Sensors and Actuators B*, 146, 353–360.
- Raoof, J. B., Ojani, R., & Karimi-Maleh, H. (2008). Carbon paste electrode incorporating 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone for electrocatalytic and voltammetric determination of tryptophan. *Electroanalysis*, 20, 1259–1262.
- Roodbari Shahmiri, M., Bahari, A., Karimi-Maleh, H., Hosseinzadeh, R., & Mirnia, N. (2013). Ethynylferrocene-NiO/MWCNT nanocomposite modified carbon paste electrode as a novel voltammetric sensor for simultaneous determination of glutathione and acetaminophen. *Sensors and Actuators B*, 177, 70–77.
- Sadeghi, R., Karimi-Maleh, H., Bahari, A., & Taghavi, M. (2013). A novel biosensor based on ZnO nanoparticle/1,3-dipropylimidazolium bromide ionic liquid-modified carbon paste electrode for square-wave voltammetric determination of epinephrine. *Physics and Chemistry of Liquids*, 51, 704–714.
- Salmanpour, S., Tavana, T., Pahlavan, A., Khalilzadeh, M. A., Ensafi, A. A., Karimi-Maleh, H., et al. (2012). Voltammetric determination of norepinephrine in the presence of acetaminophen using a novel ionic liquid/multiwall carbon nanotubes paste electrode. *Materials Science and Engineering C*, 32, 1912–1918.
- Sanati, A. L., Karimi-Maleh, H., Badiei, A., Biparva, P., & Ensafi, A. A. (2013). A voltammetric sensor based on NiO/CNTs ionic liquid carbon paste electrode for determination of morphine in the presence of diclofenac. *Material Science and Engineering C*, 35, 379–385.
- Sanghavi, B. J., Kalamate, P. K., Karna, S. P., & Srivastava, A. K. (2014). Voltammetric determination of sumatriptan based on a graphene/gold nanoparticles/Nafion composite modified glassy carbon electrode. *Talanta*, 120, 1–9.
- Sanghavi, B. J., & Srivastava, A. K. (2011). Adsorptive stripping differential pulse voltammetric determination of venlafaxine and desvenlafaxine employing Nafion-carbon nanotube composite glassy carbon electrode. *Electrochimica Acta*, 56, 4188–4196.
- Sanghavi, B. J., Sitaula, S., Griep, M. H., Karna, S. P., Ali, M. F., & Swami, N. S. (2013). Real-time electrochemical monitoring of adenosine triphosphate in the picomolar to micromolar range using graphene-modified electrodes. *Analytical Chemistry*, 85, 8158–8165.
- Sanghavi, B. J., & Srivastava, A. K. (2010). Simultaneous voltammetric determination of acetaminophen, aspirin and caffeine using an in situ surfactant-modified multiwalled carbon nanotube paste electrode. *Electrochimica Acta*, 55, 8638–8648.
- Sanghavi, B. J., Mobin, S. M., Mathur, P., Lahiri, G. K., & Srivastava, A. K. (2013). Biomimetic sensor for certain catecholamines employing copper(II) complex and silver nanoparticle modified glassy carbon paste electrode. *Biosensors and Bioelectronics*, 39, 124–132.
- Sanghavi, B. J., & Srivastava, A. K. (2013). Adsorptive stripping voltammetric determination of imipramine, trimipramine and desipramine employing titanium dioxide nanoparticles and an Amberlite XAD-2 modified glassy carbon paste electrode. *Analyst*, 138, 1395–1404.
- Stiborova, M., Martinek, V., Rydlova, H., Hodek, P., & Frei, E. (2002). Sudan I is a potential carcinogen for humans: Evidence for its metabolic activation and detoxication by human recombinant cytochrome P450 1A1 and liver microsomes. *Cancer Research*, 62(374), 5678–5684.
- Sungur, S., Köroglu, M., & Özkan, A. (2014). Determination of bisphenol A migrating from canned food and beverages in markets. *Food Chemistry*, 142, 87–91.
- Tavana, T., Khalilzadeh, M. A., Karimi-Maleh, H., Ensafi, A. A., Beitollahi, H., & Zareyee, D. (2012). Sensitive voltammetric determination of epinephrine in the presence of acetaminophen at a novel ionic liquid modified carbon nanotubes paste electrode. *Journal of Molecular Liquids*, 168, 69–74.
- Vahedi, J., Karimi-Maleh, H., Baghayeri, M., Sanati, A. L., Khalilzadeh, M. A., & Bahrami, M. (2013). A fast and sensitive nanosensor based on MgO nanoparticle room-temperature ionic liquid carbon paste electrode for determination of methylglucuronide in pharmaceutical and patient human urine samples. *Ionics*, 19, 1907–1914.
- Wang, J., Wang, Z., Liu, J., Li, H., Li, Q. X., Li, J., et al. (2013). Nanocolloidal gold-based immuno-dip strip assay for rapid detection of Sudan red I in food samples. *Food Chemistry*, 136, 1478–1483.
- Yin, H., Zhou, Y., Meng, X., Tang, T., Ai, S., & Zhu, L. (2011). Electrochemical behaviour of Sudan I at Fe<sub>3</sub>O<sub>4</sub> nanoparticles modified glassy carbon electrode and its determination in food samples. *Food Chemistry*, 127, 1348–1353.
- Yola, L. M., Atar, N., Üstündağ, Z., & Solak, A. O. (2013). A novel voltammetric sensor based on p-amino thiophenol functionalized graphene oxide/gold nanoparticles for determining quercetin in the presence of ascorbic acid. *Journal Electroanalytical Chemistry*, 698, 9–16.
- Yola, M. L., Atar, N., Qureshi, M. S., Üstündağ, Z., & Solak, A. O. (2012). Electrochemically grafted todolac film on glassy carbon for Pb(II) determination. *Sensors and Actuators B*, 171–172, 1207–1215.
- Yola, M. L., Gupta, V. K., Eren, T., Şen, A. E., & Atar, N. (2014). A novel electroanalytical nanosensor based on graphene oxide/silver nanoparticles for simultaneous determination of quercetin and morin. *Electrochimica Acta*, 120(2014), 204–211.
- Yola, M. L., & Atar, N. (2014). 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. *Electrochimica Acta*, 119(2014), 24–31.
- Yola, M. L., Eren, T., & Atar, N. (2014). Molecular imprinted nanosensor based on surface plasmon resonance: Application to the sensitive determination of amoxicillin. *Sensors and Actuators B*, 195(2014), 28–35.
- Zhuang, Y. F., Zhang, J. T., & Cao, G. P. (2008). Simple and sensitive electrochemiluminescence method for determination of bisphenol A based on its inhibitory effect on the electrochemiluminescence of luminal. *Journal of the Chinese Chemical Society*, 55, 994–1000.