A simple hydroxylated multi-walled carbon nanotubes modified glassy carbon electrode for rapid amperometric detection of bisphenol A

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ABSTRACT

A novel amperometric sensor for the determination of bisphenol A (BPA) was fabricated using a glassy carbon electrode easily modified with multi-walled carbon nanotubes functionalized with hydroxyl groups. The catalytic activity of the modifier toward the oxidation of BPA was demonstrated by cyclic voltammetry, giving a well-defined peak at 0.55 V in sodium glycine buffer solution (pH 8.0). The flow injection analysis (FIA) system of BPA exhibited a linear response in the 1–24 $\mu g\,L^{-1}$ concentration range, with a detection limit of 0.81 $\mu g\,L^{-1}$. The current reached the steady-state value with a very fast response time (less than 10 s). The proposed method was successfully applied for the determination of BPA in real samples (water contained in plastic and baby bottles) with satisfactory results, in optimum agreement with those obtained by an independent HPLC method. In the light of our results and previous reports, the proposed system combines good analytical performance with simplicity of sensor fabrication, being ideal for routine sensing applications.

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1. Introduction

Bisphenol A (BPA) also referred to as [2,2-bis(4-hydroxyphenyl)] propane is a synthetic compound widely used in the polymer industry, in particular as a monomer for producing polycarbonate plastics (PC) [1] and epoxy resins [2]. Indeed, this material can be commonly found in clear shatterproof plastics used in small kitchen accessories, metal food containers, baby bottles, rigid water bottles, in the lining of beverage cans and in food packages in general [3,4].

BPA has been proved to be an endocrine disruptor chemical and, as such, to be implicated in a wide number of illnesses, ranging from infertility, obesity, breast and prostate cancer to diabetes, thyroid malfunction, and even the attention deficit syndrome [5]. The effect of BPA in the occurrence of these diseases has been observed even at very low exposures [6].

BPA has been detected in freshwater, seawater, landfill, sludges, air and dust particles [7,8]. Moreover, it has been shown that it can migrate from packaging into a wide range of food matrices, from water storage tanks to drinking water [9].

Currently, there are no regulatory restrictions on the amount of BPA in most final plastic products, but the tendency of BPA to migrate in the food from the contact materials and its negative impact especially on children and infants and has been largely acknowledged in the European Union food law. In January 2011, the use of BPA in baby bottles was forbidden in all EU countries [10] and the Canadian and Chinese government are considering similar restrictions [11,12].

In January 2015, the European Food Safety Authority (EFSA) indicated a lower tolerable daily intake (TDI) for BPA based on the results of specific health studies. The TDI has been set from 0.05 to 0.004 mg kg^{-1} body weight/day [13] and Specific Migration Limit (SML) of 0.6 mg kg^{-1} food.

Therefore, the development of new and rapid methods with cheap instrument and real time detection for the determination of BPA has become one attractive approach of research in analytical chemistry because of the practical applications.

Various analytical methods, have been employed such as high performance liquid chromatography coupled to UV [14,15], fluorescence [16] and electrochemical detection [17,18], gas chromatography [19], liquid chromatography-mass spectrometry [20,21] and gas chromatography-mass spectrometry [22]. These methods can offer accurate and precise results, but they often require skilled operators and expensive equipment. A number of other methods, such as chemiluminescence immunoassay [23,24], enzyme-linked immunosorbent assay [25], and electrochemical methods [26], have been developed. Among them, the latter have attracted wide attention because they usually offer fast response, portability, simplicity for operators, low cost, high sensitivity and the possibility to perform on-site measurement [27].

The BPA electrochemical activity is due to the presence of phenolic hydroxyl groups that can be oxidized. It has been studied at different electrode materials, including carbon [28] and metals [29,30]. However, the relatively high potential required for the oxidation of phenolic compounds results in an increase of the background current and hence in a decreased sensitivity.

Different approaches have been proposed to minimize this drawback, including the use of enzymes [31] and other catalysts like

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cobalt phthalocyanine [32] and the modification of the electrode surface [33–37]. Some chemically modified electrodes, for example, decrease the oxidation potential of BPA and weakly increase the selectivity [38]. Most of the proposed sensor fabrications were complicated and time-consuming, even if offering remarkable limits of detection [39,40].

Despite the good results, it is still a challenge developing new electrochemical sensors based on common nanomaterials using a simple treatment. In particular, carbon nanotubes (CNTs) have attracted a large interest in BPA sensing, after being activated by grafting specific chemical functionalities at their surface, since they allowed improving the electrochemical reactivity, promoting the electron-transfer reactions, minimizing surface fouling and modulating their responsiveness under certain conditions [41–44].

In this work, multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrodes (MWCNTs/GCEs) have been used to investigate the electroxidation of BPA. For this purpose, MWCNTs were chemically modified by three simple approaches: by acid activation, either with or without cobalt phthalocyanine functionalization (MWCNTs-COOH/CoPc and MWCNTs-COOH, respectively) and by basic activation (MWCNTs-OH). Based on the literature, MWCNTs treated with acid contain carboxyl groups with a small part of hydroxyl groups while MWCNTs-OH contains more hydroxyl groups [45,46]. The optimal working conditions and pH effect on the overall sensors performance were investigated by cyclic voltammetry. A comparison with unmodified GCE was also considered. Among the modified GCEs, the MWCNTs-OH/GCE showed the best performances and was used for BPA measurement. To date, examples concerning hydroxyl and MWCNTs are very limited [46–48] and moreover, there are no previous reports on its application in BPA analysis.

Sensitivity, stability, linear range, limit of detection and quantification of MWCNTs-OH/GCE were evaluated in flow injection analyses (FIA).

Finally, this method was applied to evaluate, at different storage conditions, the migration of BPA from PC baby bottles and drinking bottles (including non-PC bottles), using water as food simulant. The results were compared with those obtained by an independent chromatographic method.

2. Experimental

2.1. Chemicals and solutions

BPA (>99% purity), multi-walled carbon nanotubes (MWCNTs) (purity 95%, 0.7–1.2 nm diameter, 2–20 μm length), cobalt phthalocyanine (CoPc) (97%), glycine (99%), sodium hydroxide (50%), nitric acid (69%), sulfuric acid (96%), acetic acid (99%), methanol and ethanol (99%), acetonitrile (≥99.9%), sodium di-hydrogen phosphate, di-sodium hydrogen phosphate and glycine (>99%) were purchased from Sigma-Aldrich (Steinham, Germany). All chemicals were of analytical grade and used without any further purification.

The following solutions prepared in ultrapure water were also tested: 0.1 M phosphate buffer, pH 6.5; 0.1 M acetate buffer pH 4.5 and 0.1 M sodium glycine buffer pH 8–10.

The BPA stock solution (100 mg L^{-1}) in ethanol was kept at 4 °C in the darkness. Working solutions were freshly prepared before use by properly diluting the stock solution in the different buffer solutions. All the solutions were prepared with Millipore Milli-Q ultrapure (>18 MΩcm) water. HPLC-grade water (BPA-low water, herein after referred to as "water") was used to simulate migration to aqueous foods as outlined by EU Regulation [10].

pH measurements were carried out using an Orion STAR A2115 digital pH meter (Thermo Scientific, Waltham, MA, USA).

2.2. Electrochemical apparatus

Cyclic voltammetric experiments were performed with a multi-potentiostat CHI 1010 (CH Instruments Inc., USA). The three electrodes cell consisted of a modified or bare glassy carbon disk (GC) working electrode (0.3 mm, BAS, IN, USA), an Ag/AgCl (KCl 3 M) reference electrode and a Pt wire counter electrode.

The apparatus for amperometric flow injection analysis already described elsewhere [49], consisted in a carrier solution reservoir, a peristaltic pump (Ismatec, Switzerland), a portable potentiostat (DS-Drop Sens μSTAT 100) and an injection valve with a 10 μL loop.

All measurements were carried out at room temperature.

For BPA analyses in samples, solid phase extraction (SPE) cartridges (Strata-X × 33 μm polymeric reverse phase sorbent, 200 mg/6 mL) from Phenomenex (Torrance, CA, USA) were used.

2.3. Preparation of chemically-modified MWCNTs

It is known that MWCNTs have a hydrophobic surface, which is prone to aggregation and precipitation in water in the absence of a surfactant. Up to now, many efforts have been made to prepare water-soluble MWCNTs and numerous procedures for their chemical functionalization have been proposed. The procedures chosen in this work were the following.

First procedure: MWCNTs were treated by an acid solution previously described [12,50]. Briefly, 100 mg of MWCNTs were dispersed in 100 mL of sulfuric acid/nitric acid 3/1 v/v and then sonicated for 2 h. According to previous results, by this treatment, acidic groups are produced on the nanotubes surface. MWCNTs obtained with this step are herein referred to as MWCNTs-COOH.

Second procedure: MWCNTs-COOH obtained with the first method were further treated with cobalt phthalocyanine (CoPc) by mixing a slurry of CoPc (4 mg) in 1 mL of ultra-pure water with a 1 mg mL^{-1} slurry of MWCNTs-COOH, followed by ultrasonication for 30 min. MWCNTs obtained with this procedure are herein referred to as MWCNTs-COOH/CoPc [50].

Third procedure: 100 mg of MWCNTs were added to 100 mL of potassium hydroxide (25% by weight) and ultrasonicated for 2 h. Then, the solution was filtered and the filtrate washed with redistilled water until neutralization. According to literature results [45,46] this treatment introduces hydroxyl groups onto the MWCNTs surface. MWCNTs obtained with this procedure are herein referred to as MWCNTs-OH.

After each treatment, MWCNTs were separated from the solution by filtration and washed with redistilled water up to neutral pH, then dried overnight in an oven at 70 °C.

2.4. Preparation of the MWCNTs modified GCEs

Glassy carbon electrodes were mirror polished with 0.5 and 0.05 μm alumina slurries. The residual polishing material was removed by ultrasonication in a water bath. The modification was achieved by dropping 10 μL of the chosen functionalized MWCNTs suspension onto the surface of the GCE. It is noteworthy that in a series of preliminary assays, lower amounts of MWCNTs (2 and 8 μL of MWCNTs suspension) led to lower sensitivities toward BPA, whereas a higher amount (20 μL of MWCNTs suspension) did not show any improvement. After solvent evaporation, for overnight, at

room temperature, the electrode was rinsed with deionized water and stored in a refrigerator at 4 °C.

2.5. Water samples preparation and BPA extraction

Baby bottles of 250 mL of two different brands (PC and non-PC, the latter with the "BPA-free" claim), and drinking bottles of 500 mL of two different brands (PC and non-PC) were purchased from supply retailers and used to evaluate the oral intake of BPA. Water was used to simulate migration into aqueous foods.

The migration testing using baby bottles was carried out at 40 °C for two storage times: 24 and 240 h (10 days). The bottles (brand new) were filled with water (250 mL) and heated to 40 °C in a water bath. Additionally, in other experiment, baby bottles were filled with boiling water at 100 °C, then incubated at 60 °C for 24 h. The 40 °C condition was selected to simulate use at body temperature, the 10-days scenario was included to estimate migration from repetitive use, and finally the 60 °C condition was selected as a "worst-case" scenario.

The migration testing using drinking bottles was instead carried out for a storage time of 24 h at two storage temperatures: 4 and 40 °C. The bottles were filled with water (500 mL) and placed in a refrigerator at 4 °C or in a water bath at 40 °C, for 24 h.

At the end of each migration period, all the bottles were allowed to reach room temperature for 2 h before the samples were pre-concentrated using solid-phase extraction (SPE). In all cases, 100 mL aliquots of the water samples were loaded onto a preconditioned (methanol, water) SPE cartridge at approximately at a flow of 1 mL min^{-1} under vacuum and BPA was eluted with 4 mL of methanol according Phenomenex protocol. The extract was concentrated to dryness under a gentle nitrogen stream and reconstituted with 1 mL of ultrapure water (100-fold concentration). Samples were analyzed after appropriate dilution.

The SPE procedure was initially evaluated using water as a blank to verify the absence of BPA in the final eluate. For the recovery test, 0.1, 0.5 and 1 µg L^{-1} of BPA were added to water before the extraction.

2.6. Chromatographic method

The HPLC system consisted of a model 2080 plus PU pump and a UV–Vis 2070 plus detector (Jasco, Japan). A Kinetex, C$_{18}$ Phenomenex (250 × 4.6 mm, diameter 3 µm) column was used. The injection volume and the detection wavelength were 5 µL and 228 nm, respectively. For the separation, a mobile phase consisting of water and acetonitrile (65:35 v/v) in isocratic at a flow rate of 0.8 mL min^{-1} was used. Retention time of BPA was 6 min. Integration of peak areas was performed with Borwin v. 1.2 software (Jmbs Developments, France).

3. Results and Discussion

3.1. Electrochemical behavior of BPA at the MWCNTs modified GCEs

As known, MWCNTs can largely increase sensitivity and reduce the overpotential in the electrochemical detection of many species, BPA included [12,51]. Moreover, it was also reported that MWCNTs modification by proper functional groups can modulate the electrostatic interactions with target molecules [43].

Preliminary cyclic voltammetric experiments were performed to study the BPA redox behavior at the three different MWCNTs modi-

fied GCEs. The corresponding voltammograms were compared with that recorded at the unmodified GCE.

Fig. 1 shows the cyclic voltammograms of 200 µg L^{-1} BPA, recorded in 0.1 M sodium glycine buffer (pH 8) at the scan rate 100 mV s^{-1}. The oxidation system was characterized by an anodic peak in the positive-going step and by the absence of any cathodic peak on the reverse scan, indicating that the oxidation of BPA is irreversible in accordance with other reports [30,32,52,53].

As it can be seen in Fig. 1, the best sensitivity was shown by the MWCNTs-OH/GCE, whose peak current (I_p) was about 15 times higher than that recorded at the unmodified GCE. The peak potential (E_p) shifted from 0.64 V at the GCE to 0.55 V (Ag/AgCl), demonstrating the efficient catalytic ability of the activated MWCNTs-OH/GCE toward BPA oxidation and the promotion of the electron transfer.

A similar behavior, with a lower sensitivity, even if still higher than at the GCE, was observed at the MWCNTs-COOH/GCE and MWCNTs-COOH/CoPc/GCE. For these two modified GCEs, the oxidation current of BPA resulted slightly higher than that at GCE (accompanied by a decrease in E_p). Therefore, these slight improvements at MWCNTs-COOH/CoPc/GCE, still indicate a synergetic activity produced by the use of MWCNTs functionalized with CoPc.

Considering that the mechanism governing the redox reaction of BPA is mediated by H$^+$ ions [12,53] the pH of the supporting electrolyte should have a great influence. Based on this information, experiments were carried out to evaluate the performances of all electrodes in different 0.1 M buffer solutions (sodium acetate, sodium phosphate, sodium glycine) in the 4.5−10 pH range.

The variations of I_p and E_p on changing the pH are shown in Table 1.

Interestingly, the MWCNTs-COOH/GCE shows the maximum I_p value at pH 6.5. As already reported [12], at higher pH values, the residual carboxylic groups on the surface of carbon nanotubes are deprotonated to anions, thus resulting in mutual repulsions with the BPA phenolic oxide anions. The result is a decrease of peak current with the increase of pH. Differently, the MWCNT-OH/GCE reached the maximum current at pH 8.0, lower than the pKa of BPA (pKa = 9.73 [54]) which suggested that the non-dissociated BPA could be adsorbed on the electrode surface better than the dissociated
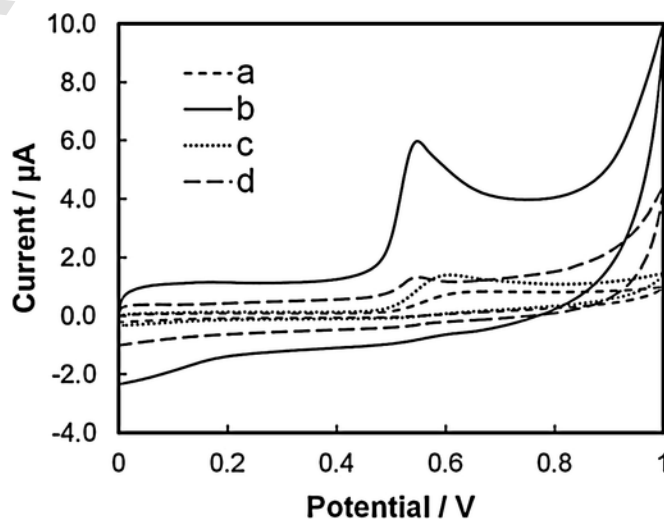

Fig. 1. Cyclic voltammograms of 200 µg L^{-1} BPA at different electrodes: GCE (a), MWCNTs-OH/GCE (b), MWCNTs-COOH/GCE (c) and MWCNTs-COOH/CoPc/GCE (d) in 0.1 M sodium glycine buffer (pH 8); sweep from 0.0 to 1.0 V (Ag/AgCl); scan rate: 100 mV s^{-1}.

Table 1

Effect of pH value on the peak oxidation potential (E_p, V) and peak current (I_p, μA) of BPA (200 μg L^{-1}) at GCE, MWCNTs-COOH/GCE, MWCNTs-COOH/CoPc/GCE and MWCNTs-OH/GCE in different buffer electrolytes as reported in the text; scan rate: 100 mV s^{-1}.

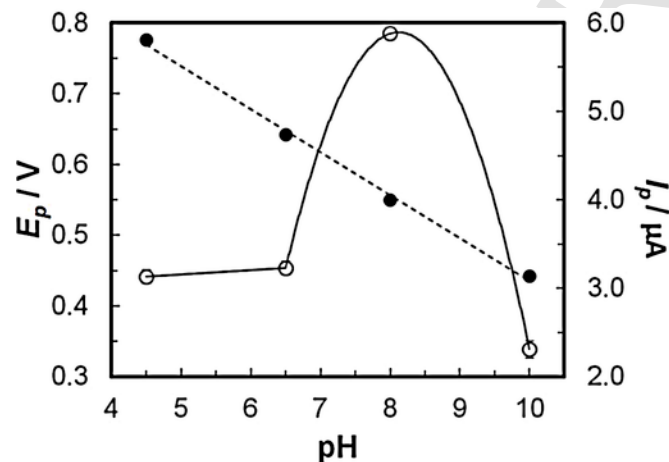| Electrodes	Electrolytes							
	Acetate pH 4.5		Phosphate pH 6.5		Glycine pH 8		Glycine pH 10	
	E_p	I_p	E_p	I_p	E_p	I_p	E_p	I_p
GCE	0.80	0.35	0.69	0.45	0.64	0.39	0.54	0.31
MWCNT-COOH/GCE	0.76	0.84	0.68	1.30	0.61	1.10	0.51	0.43
MWCNT-COOH/ CoPc/GCE	0.73	0.99	0.64	1.53	0.56	1.35	0.48	0.65
MWCNT-OH/GCE	0.76	3.13	0.64	3.23	0.55	5.88	0.44	2.34

one [55]. The current increase can be explained considering that hydroxyl groups of the MWCNTs do not change so much the charge of the surface, but they affect the absorption features of the electrode. These groups can interact with phenolic BPA, favoring the electron transfer rate and consequently the electrocatalytic property to the electrode.

For what concern the peak potential (E_p) of all the electrodes (Table 1), it can be observed, that it shifted to lower values by increasing the pH. As already underlined [52], this could be explained by the fact that at lower pH, there is an excess of H$^+$ from the supporting electrolyte, which tends to compete with those of BPA. As a consequence, BPA oxidation requires a driving force, shifting the peak potential at higher values.

In the case of the electrode modified by MWCNT-OH/GCE, the linear relationship between E_p and pH was $E_p = -0.059$ pH $+ 1.0433$ ($r = 0.9985$). The slope of 0.059 V pH^{-1}, as showed in Fig. 2, is practically the same of the theoretical one, indicating that the numbers of protons and electrons involved in the oxidation mechanism is the same [56].

For this electrode, effect of scan rate (v) on the oxidation peak current (I_p) of BPA, was also investigated. Fig. 3 shows the cyclic voltammograms of 500 μg L^{-1} BPA at different scan rates. As shown in the insert of Fig. 3, a linear relationship between I_p and v (in the 20–200 mV s^{-1} range, $r^2 = 0.999$, $n = 12$) was obtained, demonstrating that the electrode reaction was a typical adsorption-controlled
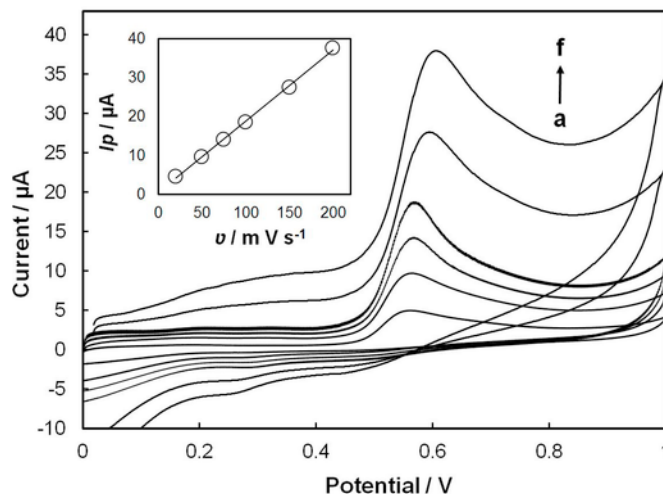
Fig. 3. Cyclic voltammograms of 500 μg L^{-1} BPA in sodium glycine (pH 8) at different scan rates (v). Curve a–f is obtained at 20, 50, 75, 100, 150 and 200 mV s^{-1}, respectively. Insert: relationship between the peak current (I_p) and the scan rate (v).

process, which is favorable for quantitative applications. Even though the peak current was enhanced with the increase of scan rate above 150 mV s^{-1}, the background current increased too. Therefore, for the purpose of this work, a scan rate of 100 mV s^{-1} was considered suitable.

3.2. Flow injection quantitative analysis of BPA standard solutions

Considering that the best sensitivity was achieved by the MWCNTs-OH/GC electrode in sodium glycine buffer solution at pH 8.0, this electrode/supporting electrolyte combination was chosen for the quantification of BPA. Since amperometry has a much higher sensitivity than cyclic voltammetry, it was used for quantitative determination. Based on the data obtained from the cyclic voltammetric experiments, a potential value of + 0.50 V (vs Ag/AgCl) was chosen for the flow injection amperometric (FIA) experiments.

The best results were obtained by using a sample loop of 10 μL at a flow rate of 0.5 mL min^{-1} which proved to be the best compromise between sensitivity, stability and duration of analysis.

As shown in Fig. 4, the current response (peak height) relevant to BPA oxidation increases linearly with the analyte concentration in the 1–24 μg L^{-1} concentration range ($R^2 = 0.9998$, $n = 30$) according to the equation:
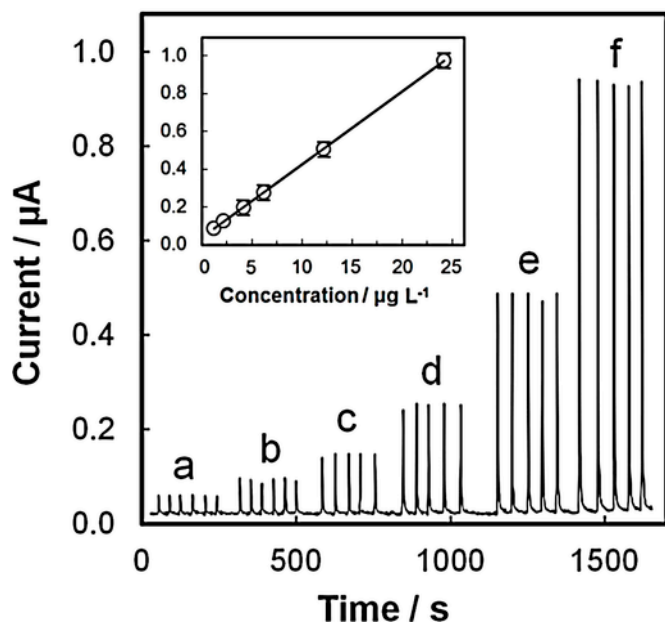
$$I(\mu A) = (0.0386 \pm 0.00024)C + (0.0013 \pm 0.0019)$$

The 0.81 μg L^{-1} limit of detection was estimated according to the approach LOD = 3.3 ($s_{y/x}/b$), where $s_{y/x}$ is the residual standard deviation and b is the slope of the regression equation. This approach allows to control both false positive and false negative errors ($\alpha = \beta = 0.05$) [57].

The limit of quantification (LOQ = 2.54 μg L^{-1}) was estimated using the approach 10 ($s_{y/x}/b$).

The sensor responded rapidly to the dynamic changes of BPA concentration, allowing about 40 determinations per hour. This indicates a rapid reaction mechanism which includes transport of the substrate to the reactive surface and conversion to a final product away from the electrode.

In order to evaluate the precision (repeatability) of the electrochemical method, subsequent injections ($n = 18$) of BPA standard solutions at the same concentration of 10 μg L^{-1} were analyzed. The resulting relative standard deviation (RSD = 1.81%) demonstrated an excellent repeatability of the electrode preparation procedure.

Fig. 2. Dependence of pH on the peak current Ip (○) and peak potential Ep (●) for 200 μg L^{-1} BPA at MWCNTs-OH/GCE in 0.1 M supporting electrolyte under different pHs: 4.5 (sodium acetate), 6.5 (sodium phosphate), 8 and 10 (sodium glycine); scan rate: 100 mV s^{-1}.

Fig. 4. Flow injection amperometric responses for increasing concentrations of BPA: concentrations of 1 (a), 2 (b), 4 (c), 8 (d), 12 (e), 24 (f) μg L^{-1} at MWCNTs-OH/GCE; supporting electrolyte: 0.1 M sodium glycine buffer, pH 8; potential 0.5 V (Ag/AgCl); flow rate 0.5 mL min^{-1}; injection volume 10 μL. Insert: Calibration curve for the detection of BPA is obtained at the concentrations showed.

In addition, the electrode showed long-term stability. As a matter of fact, testing the repeatability of the same electrode after two weeks, entailed a decrease of less than 5% in the recorded mean current.

Furthermore, to evaluate the selectivity of the proposed method, the influence of common interfering species such as ascorbic acid, catechol, phenol, *p*-nitrophenol and hydroquinone was considered. These species were added at concentration levels similar and superior (10-fold) to those in which they are commonly present in real samples. The tolerance limit was estimated to be less than 10% of the relative standard deviation; therefore, these compounds do not significantly influence the BPA analytical signal.

3.3. Analysis of real samples and recovery test

In order to confirm the performance of the sensing system in practical applications, the concentrations of BPA that could potentially migrate from the material used to manufacture PC and non-PC bottles were evaluated after different storage conditions.

BPA was extracted from the samples and then analyzed in FIA using the MWCNTs-OH/GCE sensor, and by a HPLC/UV independent method.

The results are summarized in Table 2. The Table shows a comparison of the levels of BPA leached from baby bottles stored for 24 h (at 40 and 60 °C) and for 240 h (10 days) at 40 °C and those from drinking bottles stored for 24 h (at 4 and 40 °C), using water as a food simulant.

BPA, as expected, was not detectable in a blank sample consisting of ultrapure water (result not reported in Table 2). All the non-PC bottles did not release BPA under the above experimental conditions. Unlike, almost all the PC bottles selected in this study, released the analyte to the water samples, under all the storage conditions tested, in amounts that were detectable both by the electrochemical sensor and the HPLC method.

Table 2

BPA content determined by the proposed (FIA) and reference HPLC method in water samples contained in baby and drinking bottles at different conditions.

Sample	Migration testing method	Measured (μg L^{-1})	
		FIA ($n = 3$)	HPLC ($n = 5$)
Baby bottle PC	24 h, 40 °C	0.14 ± 0.02	0.15 ± 0.03
Baby bottle PC	24 h, 60 °C	1.50 ± 0.02	1.48 ± 0.04
Baby bottle PC	240 h, 40 °C	0.40 ± 0.02	0.38 ± 0.02
Baby bottle non-PC	All conditions	nd	nd
Drinking bottle PC	24 h, 4 °C	nd	nd
Drinking bottle PC	24 h, 40 °C	2.01 ± 0.02	1.99 ± 0.03
Drinking bottle non-PC	All conditions	nd	nd

With regard to PC baby bottles, the results showed that the BPA migration increased with both the testing temperature and storage time, with a concentration of 0.14 μg L^{-1} (40 °C) and 1.5 μg L^{-1} (60 °C) after 24 h, and 0.40 μg L^{-1} for the 10-days scenario.

The results obtained with PC drinking bottles confirm that a higher temperature favors the BPA release, with BPA concentrations lower than the LOD at 4 °C and 2.01 μg L^{-1} at 40 °C.

These results are in agreement with other studies [58–60]. In fact, it has been well documented that BPA migration from polymers to different contact fluids, being mainly a diffusion or hydrolysis phenomenon, increases with larger contact times and higher temperatures.

To evaluate the efficacy of the method, recovery evaluation was also carried out by spiking known concentrations of BPA to a known volume of water. The addition of 0.10–1 μg L^{-1} of BPA resulted in a recovery of 98–102%. The results match the expected values at the tested concentration levels, indicating that this method has good accuracy [61].

As reported in Table 2, the results obtained by the proposed method were compared with those obtained by an independent HPLC-UV method. In this case, the functional relationship (area of the peak vs concentration was: A (μV) = (103938 ± 1795) C + (−2642 ± 412) (linear range 0.05–2.5 μg mL^{-1}, $R^2 = 0.999$, p 95%, $n = 15$), with a LOD of 0.04 μg mL^{-1} calculated as 3.3 ($s_{y/x}/b$).

As it can be seen in Table 2, the results obtained with both the methods are in good agreement. A *t*-paired test showed no statistical differences at the 95% confidence level of significance. These results demonstrate the applicability of the proposed method for the determination of BPA in the samples considered in this study.

4. Conclusions

This paper reports a simple FIA system based on a GCE modified with MWCNTs functionalized with hydroxyl groups to investigate the electrochemical response of BPA. The modifier improves the sensor performances for a rapid and reliable determination of BPA. Quantification of BPA in real matrices was performed after simple extraction with SPE cartridges. This pretreatment is necessary because of the low concentration at which BPA can be found in beverages or foods that have been in contact with plastic containers. The combined use of the proposed sensor with SPE cartridges seems useful for practical applications. The recoveries obtained, as well as the comparison with a HPLC-UV method demonstrate the reliability of the method for the assessment of BPA in real drinking water samples. This analytical system could also be applied to other liquid food matrices with minimum adjustments. Moreover, the simplicity of the procedure used to fabricate this sensor and the possibility to operate it with portable potentiostats makes it ideal for routine analysis, espe-

cially as the use and availability of carbon nanotubes will become more common. Indeed, compared to classical methods, this new approach could represent an alternative and innovative tool for faster and cheaper evaluation of BPA migration. Noticeably, to our knowledge, this is one of the first investigation on BPA migration from plastic bottles to water samples.
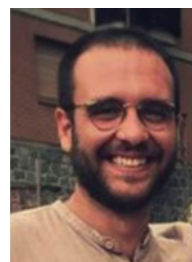
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