DETERMINATION OF BISPHENOL A FROM WATER SAMPLES

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Water pollution is a very important problem that the world must face. That is why it is very important to detect small concentrations of organic pollutants in water, e.g., bisphenol A (BPA). An important requirement was the development of a method of analyzing bisphenol A (BPA) in water to prevent as soon as possible its negative impact on man and environment. The purpose of this study was to determine bisphenol A (BPA), 2,2-bis (4-hydroxyphenyl) propane from water samples by using differential pulse voltammetry (DPV) using a microsensor. The matrix used for the microsensor designed was graphene nanopowder. There are many ways to determine bisphenol A, but they require time and have high costs. This is why a fast and inexpensive method for bisphenol A detection in water is needed.

Keywords: bisphenol A, electrochemical microsensor, differential pulse voltammetry, water analysis

1. Introduction

Chemical compounds introduced into the environment by human activity can be harmful to both the human body and the environment. Bisphenol A, 2,2-bis (4-hydroxyphenyl) propane (BPA), is a monomer used in the production of polycarbonate plastics and epoxy resins. Current research had highlighted the fact that human exposure to bisphenol A has increased due to the increasing use of epoxy resin and polycarbonate plastic products, both of which are very practical materials often present in food containers [1,2].

Bisphenol A (BPA) is an endocrine disrupter (EDC) that has been studied due to problems raised by physicians and researchers as well, because it can migrate from containers into the food and water we consume [3,4]. Studies have shown that humans, as well as wild and domestic animals, may suffer from exposure to chemicals that interact with the endocrine system, interfering with the

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production, release, transport and metabolism of natural hormones [5]. BPA has been reported to exhibit estrogenic activity and is released from polycarbonate balloons during autoclaving [6].

Following studies, it has been found that BPA is capable of disrupting the endocrine system of fish, wildlife and humans [7].

Bisphenol A is not naturally found in the environment, it reaches the surface waters, following the manufacturing process, by the discharge of effluent from the production plants [8-11]. Waste water containing bisphenol A may be a source of aquatic media contamination endangering the life of aquaculture by disrupting the endocrine glands [12,13]. The negative effects of BPA on the human body are related to the reduction of fertility, even in very small quantities is very dangerous and can cause hypertension, prostate cancer cell proliferation, heart disease, diabetes and abnormalities in human liver enzymes [14, 15].

The European Union sets a limit of 0.1ng/mL for organic pollutants in water. Therefore, Bisphenol A determination in the aquatic environment is of great importance. In 2000, Fürhacker et al. reported that 90% of BPA was disposed of during sewage treatment in an installation in southern Austria; similar findings have been reported in the United States [16]. However, despite efforts to treat BPA, its detection in the environment continues to be reported [17]. Bisphenol A concentrations in effluent from wastewater treatment plants range from undetected to 370 mg/L, but in most cases studied, effluent levels were less than 5 mg/L. The detection limit in the studies was also between 0.006 ng/L and 10 mg/L. Due to the ubiquitous nature and effects of endocrine disruption potential, BPA has been included in environmental monitoring, which is done through several techniques and methods.

For the BPA analysis in water, the following methods were used to date: high performance liquid chromatography (HPLC) [18,19], mass spectrometry, mass spectrometry with gas chromatography [20], fluorimetry [21,22], chemiluminescence [23], the most commonly used are MS chromatography and techniques. Although chromatographic and spectroscopic methods are extremely sensitive and have a low detection limit, they have high costs [24].

To respond to new challenges, new sensors with improved sensitivity for the determination of pollutants like BPA in water, must be developed. Therefore, an electrochemical microsensor based on the immobilization of the complex between Co and porphyrin IX on the nanographene paste (made from graphene nanopowder and paraffin oil) was designed, characterized, and used for the assay of bisphenol A (BPA), using differential pulse voltammetry (DPV), in water samples.

2. Experimental

2.1 Materials and reagents

Analytical purity reagents were used for all measurements. Bisphenol A, melatonin, and the cobalt complex of porphyrin IX were purchased from Sigma Aldrich (Milwaukee, USA) and paraffin oil from Fluka (Buchs, Switzerland). The graphene nanopowder was obtained from SkySpring Nanomaterials Inc. (SSNANO, USA).

The stock solution of 10^{-2} mol L^{-1} bisphenol A was prepared in dimethylsulfoxide (DMSO). Standard work solutions 10^{-3}-10^{-15} mol/L were prepared from the stock solution by the successive dilution method, in phosphate buffer, pH 7.00. BPA solutions were kept in the refrigerator at 2-8°C.

2.2 Apparatus

All DPV measurements were performed with a potentiostat/galvanostat AUTOLAB/PGSTAT 302 (Metrohm, Utrecht, The Netherlands) which was connected to a computer with GPES software, used to control experiments and data acquisition. The electrochemical cell was composed of three electrodes: a reference electrode (Ag/AgCl, 0.1 mol L^{-1} KCI), a platinum counter electrode and a working electrode (the new designed microsensor).

2.3 The design of the stochastic microsensors

Graphene nanopowder was mixed with paraffin oil in a ratio of 1:10 (mg:μL) to form a homogeneous paste. The paste was modified with a solution of 10^{-3} mol L^{-1} of the cobalt complex of protorphyrine IX in a ratio of 10:3 (mg:μL).

The modified paste was inserted into a plastic tube having the internal diameter of 50 microns. A silver wire was inserted into the paste and connected to the outer circuit. Prior to each measurement, the microsensor was washed with deionized water. When not in use, the microsensor was kept at room temperature in a dry and dark place.

2.4 Procedure

All differential pulse voltammetry (DPV) measurements were performed at 25°C. Standard solution with concentrations of bisphenol A between 10^{-3} and 10^{-15} mol L^{-1} were measured. The working parameters were: potential range was between -1.2 and 1.0 mV, scanning speed was 50 mVs^{-1} and amplitude modulation was 100 mV. The proposed electrochemical microsensor together with the reference and auxiliary electrodes were immersed in a glass container containing the standard solutions while the height of the peak (Ip) was recorded.

Peak height was measured and graphically plotted against the concentrations of bisphenol A solutions. The unknown concentrations of bisphenol A in the samples were determined from the equations of calibration.

3. Results and discussion

3.1. Response characteristics of the proposed electrochemical microsensor

Differential pulse voltammetry (DPV) technique was used to determine the response characteristics of the proposed electrochemical microsensor. The response characteristics of the electrochemical sensors were: the linear concentration range was from $1.35x10^{-9}$ to $1.35x10^{-6}$ mol/L, with a limit of determination of $1.35x10^{-9}$ mol/L, and a detection limit of $9.06x10^{-10}$mol/L, for a half wave potential of 600mV. The sensitivity of the electrochemical sensor was 1.40mA/mol L^{-1}. The equation of calibration was:

$$Ip=2x10^{-9}+ 0.0045xConc._{BPA}$$

with a correlation coefficient, r of 0.9976.

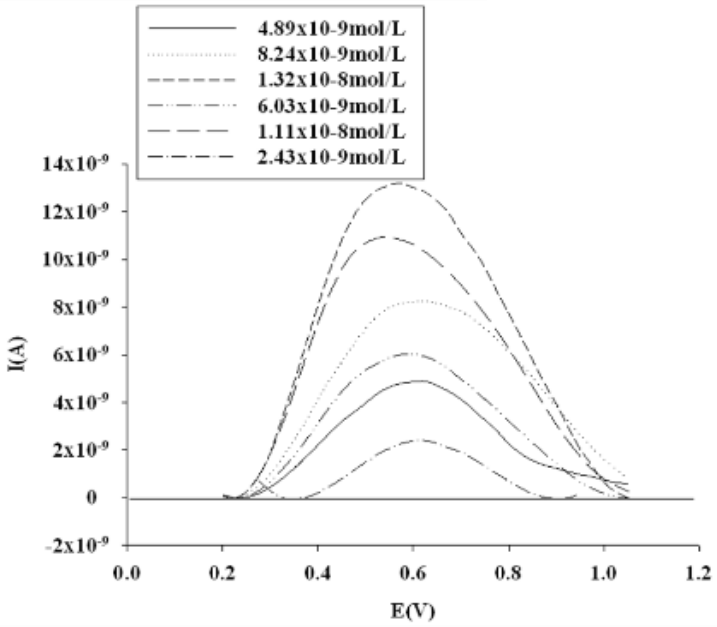

Fig. 1 Typical differential pulse voltamograms obtained for the bisphenol A (BPA) linear concentration range using the microsensor based on graphene.

The electrochemical microsensor was tested for one month, every day, when its sensitivity varied with less than 1.50%, proving its stability in time.

3.2 Interferences

The possible interference investigated for the determination of bisphenol A, using the proposed electrochemical microsensors were: melatonin, copper, cadmium and lead.

Mixed solution method was used to assess if there were any interferences. The ratio between the concentrations of BPA and of the possible interference was 1:10 (mol: mol) in the mixed solution.

Table 1

Amperometric selectivity coefficients obtained for the proposed electrochemical sensor

Interference	K^{amp}_{sel}
Melatonine	1.4×10^{-4}
Cadmium	1.7×10^{-3}
Copper	1.5×10^{-4}
Lead	8.0×10^{-4}

The results presented in Table 1 shown no interference of melatonin, copper, cadmium and lead in the assay of BPA using the proposed electrochemical microsensor.

3.3. Analytical applications

Five water samples tested in accredited laboratories for BPA were analysed using the proposed electrochemical microsensor using DPV. No pretreatment of the water sample was performed before the assay using the DPV.

The results obtained using the proposed DPV method as well as the standard method performed in the accredited laboratories were shown in Table 2.

A very good correlation of the results shown in Table 2 was observed.

An example of a voltamogram obtained from the measurements using the DPV mode for determining bisphenol A in the water samples was shown in Fig. 2.

Table 2

Determination of bisphenol A in water samples

Sample no.	**Bisphenol A (ng/L)**	
	DPV	***Standard method***
1	0.21±0.08	0.23
2	23.01±0.09	22.83
3	1.12±0.08	1.14
4	15.80±0.10	15.98
5	2.19±0.07	2.28

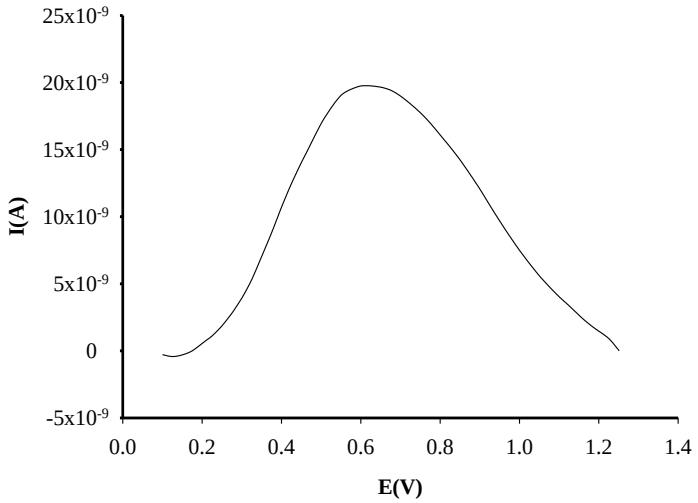

Fig. 2. Voltammogram obtained for the assay of BPA in water sample, using the electrochemical microsensor

The relative standard deviations values were less than 0.10% shown a very good precision for the performed measurements.

Accordingly, the proposed DPV method based on the utilization of the electrochemical microsensor based on graphene is reliable for the assay of BPA in water samples.

4. Conclusions

A novel electrochemical microsensor based on graphene modified with a cobalt complex of protoporphyrin IX was proposed for the assay of bisphenol A in water samples. High sensitivity, and selectivity, as well as low limit of determination was obtained when differential pulse voltammetry was used for the assay of bisphenol A.

Very good correlations between results obtained using the proposed method and the standard were obtained, when bisphenol A was analysed from water samples, proving the high reliability of the proposed method.

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