Talanta 85 (2011) 441–448

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Voltammetric behavior of benzo[*a*]pyrene at boron-doped diamond electrode: A study of its determination by adsorptive transfer stripping voltammetry based on the enhancement effect of anionic surfactant, sodium dodecylsulfate

Yavuz Yardım[a], Abdulkadir Levent[b], Ertuğrul Keskin[a], Zühre Şentürk[a,*]

[a] *Yüzüncü Yıl University, Faculty of Science, Department of Analytical Chemistry, 65080 Van, Turkey*
[b] *Batman University, Faculty of Science and Letters, Department of Analytical Chemistry, 72100 Batman, Turkey*

ARTICLE INFO

Article history:
Received 26 October 2010
Received in revised form 28 March 2011
Accepted 3 April 2011
Available online 8 April 2011

Keywords:
Benzo[*a*]pyrene
Cyclic voltammetry
Adsorptive transfer stripping voltammetry
Boron-doped diamond electrode
Non-aqueous, aqueous and aqueous/surfactant media
Tap water

ABSTRACT

Benzo[*a*]pyrene (BaP), a member of the polycyclic aromatic hydrocarbon (PAH) class, is one of the most potent PAH carcinogens. The electrochemical oxidation of BaP was first studied by cyclic voltammetry at the boron-doped diamond electrode in non-aqueous solvent (dimethylsulphoxide with lithium perchlorate). The compound was irreversibly oxidized in a single step at high positive potential, resulting in the well-resolved formation of a couple with a reduction and re-oxidation wave at much lower potentials. Special attention was given to the use of adsorptive stripping voltammetry together with a medium exchange procedure in aqueous and aqueous/surfactant solutions over the pH range of 2.0–8.0. The technique in aqueous solutions had little value in practice because of too small oxidation peak current. This problem was solved when surfactants were added into the sample solution, by which the oxidation peak currents of BaP were found enhanced dramatically. The employed surfactants were sodium dodecylsulfate (anionic, SDS), cetyltrimethylammonium bromide (cationic, CTAB) and Tween 80 (nonionic). Using square-wave stripping mode, the compound yielded a well-defined voltammetric response in Britton–Robinson buffer, pH 2.0 containing 2.5×10^{-4} M SDS at +1.07 V (vs. Ag/AgCl) (after 120 s accumulation at +0.10 V). The process could be used to determine BaP in the concentration range of 16–200 nM (4.04–50.46 ng mL^{-1}), with a detection limit of 2.86 nM (0.72 ng mL^{-1}). This method was also applied to determine BaP in model water sample prepared by adding its different concentrations into tap water.

1. Introduction

Benzo[*a*]pyrene (BaP) (its structure is shown in Fig. 1), as well as other polycyclic aromatic hydrocarbons (PAHs), is formed from the incomplete combustion of various biogenic or anthropogenic carbonaceous materials [1]. It is an environmentally important chemical carcinogen that exerts its carcinogenic activity through metabolites which react with and modify nucleic acids and proteins. Mammals metabolize BaP primarily by enzymatic oxidation to epoxides, phenols, dihydrodiols and water-soluble conjugates. It forms DNA adducts in vitro and in vivo by one-electron oxidation with reaction of the BaP cation radical at C-6 (80%) and by reaction of bay-region diol epoxides at C-10 (20%) [2–4]. Since it is the best known of the toxic PaHs, BaP has been often used as an indicator of the presence of other members of this class of compounds in environmental samples such as urban air, water, soil, and foodstuffs [5,6].

As a result of the human health risk of BaP even at trace levels, there has been increasing concern for the development of efficient and reliable analytical techniques for its detection and quantification together with other PAHs in a wide range of environmental matrices. BaP is routinely assayed by gas [7–12] or liquid [13–18] chromatography, requiring tedious pre-concentration and extraction steps. The most common procedures are the use of either solid sorbents or liquid–liquid extraction which are time-consuming, solvent-consuming, matrix dependent and involve a number of post-extraction clean up steps. Several biosensors including immunosensors [19–21] and DNA biosensors [22,23] have also been set up for environmental monitoring of BaP.

Of the most commonly used instrumental techniques, electroanalytical approach is one of choices, due to its certain advantages, such as relatively low operational cost, moderate or no sample preparation, no time-consumption and its dynamic range offer. Stripping voltammetry has provoked particular interest because it is currently the most sensitive and widely used electrochemical technique. Its possibility of applications covers many fields ranging from environment, pharmaceutical and clinical to food and industrial samples. Moreover, the investigations of the redox behavior of

---

* Corresponding author. Tel.: +90 432 2251024; fax: +90 432 2251188.
E-mail address: zuhresenturk@hotmail.com (Z. Şentürk).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.04.005

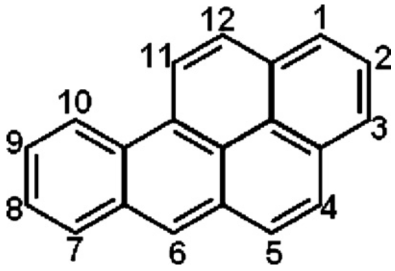

Fig. 1. Chemical structure of BaP.

environmental contaminants have the potential for providing valuable insights into the action mechanisms of these chemicals and the design of preventive strategies [24]. Concerning BaP, however, a limited number of studies on its anodic voltammetric characteristics have been carried out. Most of these reports were quite old and carried out with relatively old-fashioned electroanalytical approaches. The first investigation performed by Jeftic and Adams [25] was concerned with studying the electrochemical oxidation of BaP using cyclic voltammetry at rotated platinum disc electrode in a variety of solvent systems. In other early reports, its redox properties were not well documented, only the oxidation potentials of BaP and related polycyclic carcinogenic hydrocarbons have been studied in organic solvents using platinum and/or glassy carbon electrodes [26–29]. There have also been reports concerning the electrochemical measurement of BaP which involve high-pressure liquid chromatography in combination with electrochemical detection [30,31]. In a very recent work of our research group, first attempt was made describing the electrochemical behavior and voltammetric determination of BaP in aqueous solutions and real samples such as spiked human urine using adsorptive stripping voltammetry (AdSV) at glassy carbon (GC) and pencil graphite (PG) electrodes [32].

In recent years, boron-doped diamond (BDD) electrodes for application in electroanalytical determination have been receiving increasing attention [33–40], mainly due to the number of their advantages over traditionally employed electrodes (e.g., glassy carbon or platinum electrodes), such as high corrosion resistance, extreme hardness, chemical inertness, high thermal conductivity, low sensitivity of dissolved oxygen, very low and stable background currents and a wide working potential window in aqueous solutions (up to 3 V) [41,42]. However, the analytical performance of BDD electrodes observed in different laboratory experiments cannot be entirely compared because their properties are strongly affected by the quantity and kind of doping agent, morphologic factors and defects on the film, presence of impurities (sp^2 carbon), crystallographic orientation, and surface termination (e.g., hydrogen or oxygen terminated) that may be markedly determined by electrochemical pre-treatments [43].

Since surface modification is an important area of study in modern electrochemistry, the several application possibilities of the chemically modified electrodes will be of interest. Introduction of surface-active agents (surfactants) in this area of work adds a new and useful dimension to these investigations. The adsorption of surfactants at the interface between electrode and solution as well as the solubilization of electrochemically active compounds into micelle aggregates may significantly change and control the properties of electrode surfaces, heavily influence the electrochemical process of electroactive species [44]. Analytically, surfactants have also been widely used to improve the sensitivity and selectivity of the voltammetric measurements of organic compounds of environmental and clinical interest [45–51]. On the other hand, surfactants, as safer and cheaper components, can be used in the cloud point separation methodology for the extraction and pre-concentration of PAHs and offer several advantages over the use of conventional methods such as liquid–liquid and liquid–solid extractions. Further, they constitute a valid alternative for preservation, desorption from containers of samples collected without additives and pre-concentration of PAHs in environmental water samples [52–56]. These agents are known to play a very important role in increasing the solubility of PAH substances, which are sparingly soluble in water. There are two potential sites of solubilization of PAHs: the hydrophobic core by a partition process and the surface solubilization into the palisade layer of the micelles, due to specific interactions. Although BaP is solubilized in all types of surfactants, the cationic surfactant is the most efficient towards the solubilization in micellar phase, surface solubilization being the major contribution [57].

A survey of literature reveals that no electrochemical data were available concerning the voltammetric behavior of BaP either at BDD electrode or in the presence of surfactants. Keeping the above knowledge in mind, the current paper followed two purposes. The first was to study the cyclic voltammetric characterization of the redox behavior of BaP in non-aqueous solvent at surface of BDD electrode. The second purpose was to give special attention on the coupling of adsorptive transfer stripping voltammetry with the unique properties of the BDD electrode for the development and optimization of a sensitive and rapid method for the determination of BaP in aqueous solutions utilizing the enhancement effect of surfactant. The practical use of the method was demonstrated by measuring the concentration of BaP in samples of spiked tap water.

2. Experimental

2.1. Caution

The work described involves the handling of hazardous agent (BaP) and was therefore conducted in accordance with NIH guidelines for the Laboratory use of Chemical Carcinogens.

2.2. Materials and reagents

Solutions at all stages of the study were prepared by using analytical grade reagents and purified water from a Millipore Milli-Q system. A stock solution of 4×10^{-3} M was prepared by dissolving appropriate amount of BaP (Sigma–Aldrich Chemical Company, Inc.) in dimethylsulphoxide (DMSO). The prepared stock solutions were kept in refrigerator (stable for at least 1 week). When it was necessary, more dilution of working solutions was prepared with the use of same solvent. In non-aqueous studies, cyclic voltammetric (CV) experiments were recorded in DMSO and ionic strength was maintained at 0.1 M with lithium perchlorate ($LiClO_4$) as the supporting electrolyte. Oxygen was removed from the measured solutions by bubbling with nitrogen for 5 min. In the case of stripping analysis, the working aqueous solutions were prepared daily by diluting aliquots of the stock solution with 0.1 M Britton–Robinson buffer solution as supporting electrolyte. The pH of the solutions ranged from 2.0 to 8.0. The surfactants tested were anionic type, sodium dodecylsulfate (SDS), cationic type, cetyltrimethylammonium bromide (CTAB) and non-ionic type, Tween 80. They were prepared by dissolving the necessary quantity of reagent in water. Surfactants and all other chemicals were obtained from Sigma–Aldrich or Merck.

2.3. Apparatus

Electrochemical experiments were performed with an Autolab PGSTAT 128N potentiostat, controlled by GPES 4.9 electrochemical software from Eco-Chemie (The Netherlands). The raw data were also treated in all square-wave voltammetric (SWV) measurements with the aid of Savitzky and Golay filter (level 2) of the GPES software, followed by the moving average baseline correction with a peak width of 0.01 V. The three electrode system used in this study contained a BDD working electrode (Windsor Scientific Ltd.; Ø: 3 mm, diameter), an Ag/AgCl (3 M NaCl) reference electrode (Model RE-1, BAS, USA) and a platinum wire auxiliary electrode. The measurements were carried out in a standard 10-mL one-compartment voltammetric cell, at a laboratory temperature (20 ± 5 °C).

The BDD electrode was polished with 0.01 μm wet alumina powder and copiously rinsed with water. After this mechanical treatment, BDD electrode was electrochemically activated in an independent electrochemical cell containing the selected supporting electrolyte by applying a potential of +1.3 V for 30 s. In order to achieve reproducible results and enhance the electrochemical response, these mechanical/electrochemical cleaning steps were repeated before every voltammetric assay.

For stripping analysis, two cells were used, a pre-concentration cell containing the analyte solution and measurement cell containing a blank background electrolyte. The solutions were stirred using a bar magnet (10 mm × 3 mm) rotating at 900 rpm. The pH values of solutions were measured using a WTW inoLab pH 720 meter with a combined electrode (glass-reference electrodes).

2.4. Adsorptive stripping voltammetric procedure

For stripping studies, the pre-concentration/medium exchange/voltammetry scheme was adopted. The general procedure to obtain voltammograms was as follows: the required aliquot of the BaP working solutions was placed in a pre-concentration cell containing Britton–Robinson supporting buffer at desired pH in the absence or presence of surfactants with a required concentration. The pre-treated BDD electrode was kept in the cell, and the solution was stirred either at open-circuit or under a chosen accumulation potential for a given accumulation period of time. The electrode was then placed in the measurement cell containing only the same buffer solution, previously washed with water and with the blank background electrolyte. Subsequently, a sweep was carried out towards positive potentials using the selected voltammetric technique. For analytical application, the following parameters for SWV were employed: pulse amplitude, 20 mV; frequency, 50 Hz; scan increment, 8 mV; rest period, 10 s; stirring rate, 900 rpm. The calibration curves were measured three times.

2.5. Analysis of spiked tap water samples

Tap water samples were filtered through filter paper (Whatman, No. 42) and stored in dark brown glass bottles at 4 °C until used. According to the procedure, an 8-mL water sample was transferred into a 10-mL glass tube with 1.5 mL of Britton–Robinson buffer, pH 2.0 containing SDS at the final concentration of 2.5×10^{-4} M. The apparent pH was adjusted with hydrochloride acid solution and then the volume was completed to 10 mL with water. This solution was placed in the voltammetric cell and by micropipette a small aliquot volume (20 μL) of concentrated BaP standard solution was added. The pre-treated BDD electrode was immersed in the final solution for 120 s at a fixed potential of +0.10 V using 900 rpm stirring rate (pre-concentration step). The electrode was then washed with water and with the blank Britton–Robinson buffer (pH 2.0), and transferred into the measurement cell containing Britton–Robinson buffer at pH 2.0. Subsequently, the SW voltammogram was recorded from +0.40 to +1.30 V in scan increment of 8 mV at 50 Hz with pulse amplitude of 20 mV. Sets of triplicate measurements were carried out with successive addition of small aliquots of concentrated BaP standard solution. The amount of BaP was determined directly by interpolation using the new calibration graph obtained in tap water sample.

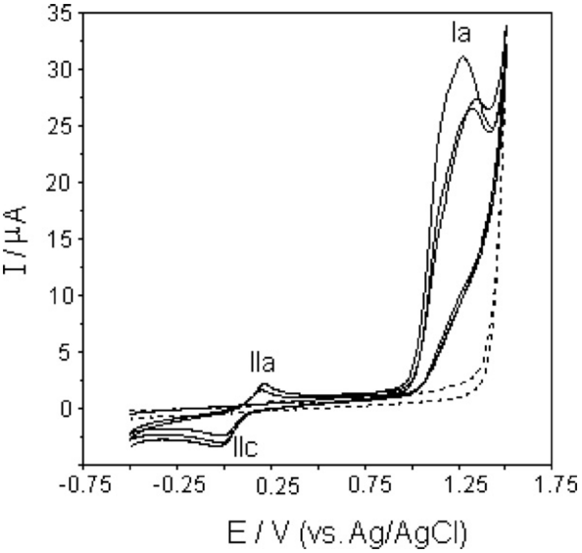

Fig. 2. The repetitive cyclic voltammograms of 4×10^{-4} M BaP solutions in DMSO (with 0.1 M $LiClO_4$). Electrode, BDD; scan rate, 100 mV s^{-1}. Dashed lines represent background current.

3. Results and discussion

3.1. Cyclic voltammetry in non-aqueous solvent

In our previous work [32] using GC and PG electrodes in DMSO which was not used before for voltammetry of BaP, we found that BaP was irreversibly oxidized in a single step at high positive potential, resulting in the well-resolved formation of a couple with a reduction and re-oxidation wave at much lower potentials. A similar study without performing an accumulation step was carried out to investigate the electrochemical process occurring on the BDD electrode over the potential range −0.50 to +1.50 V. Fig. 2 depicts the three-successive cyclic voltammograms of 4×10^{-4} M BaP in DMSO at scan rate of 100 mV s^{-1}. From our experimental results, the background current for BDD electrode was lower than those for GC and PG electrodes, which is ascribed to the low double layer capacitance of the BDD surface [58]. However, the potential limits obtained from background voltammograms for all three electrodes were almost similar in presence of organic solvent. On the other hand, cyclic voltammograms of BaP in DMSO showed that BDD electrode behaves in a way similar to GC and PG electrodes, in terms of the oxidation of BaP in this solvent. At potentials of about +1.2 V, near to the supporting electrolyte cut-off, a sharp and well-defined oxidation peak (Ia) was observed, which corresponds to an irreversible process. This process took place at more positive potential than those previously reported for the oxidation of BaP at GC and PG electrodes [32], indicating that the oxidation process of the compound requires higher overpotential at the diamond surface, compared to other carbon electrodes. Similarly to the observations at GC and PG electrodes, in the first reverse scan a new cathodic peak (IIc) was obtained, which formed a redox couple with peak IIa, observed in the second and subsequent scans. This couple appears only if the potential is switched beyond the process Ia in the first positive-going potential scan. However, in the case of BDD electrode the separation between IIc and IIa was bigger (≈215 mV), which reveals that the reversibility of this process was reduced. The peak Ia lost intensity during the second potential cycle while the magnitude of IIc/IIa increased slightly in consecutive scans.

The effect of the scan rate at BDD electrode was investigated under the above conditions. From the cyclic voltammograms, it was found that the initial oxidation peak current of BaP gradually increased and a positive shift in the peak potential existed with increasing scan rate. The current response (i_p) was linearly proportion to the scan rate (ν) within the range 100–600 mV s^{-1} according to the relationship; i_p (μA) = 0.03 ν (mV s^{-1}) + 16.92 (n = 6, r = 0.996), suggesting a typical adsorption-controlled process.

For an irreversible electrode process, the peak potential (E_p) and scan rate (ν) are defined by the following equation [59]:

$$E_p = E^0 + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right)\log\upsilon$$

where α is charge transfer coefficient, n is electron transfer number, and R, T, and F have their usual meanings. Thus the value of αn can be easily calculated from the slope of E_p versus log v. Herein, the slope is 0.092 and the αn was calculated to be 0.64. Generally, α is assumed to be 0.5 in totally irreversible electrode process. Therefore, the value of n = 1.29 (≈1) was obtained for the main oxidation peak (Ia) which is in agreement with the result in previous report [25]. From the experimental data on BDD electrode and in keeping with the voltammetric behavior on platinum electrode in different non-aqueous solutions [25], a short comment can be made. The initial oxidation step is the removal of one electron to form BaP radical cation intermediate. It has been previously discussed in detail [25] that the initial oxidation is followed by a series of chemical and additional electrochemical steps. Other expected reaction of the BaP radical cation is the formation of BaP-dimer, which is further oxidized, probably to polymeric products.

3.2. Stripping analysis in aqueous and surfactant solutions

In this section, due to the limited solubility of BaP in water, ≤1% (v/v) DMSO–water solutions were used, which will be referred to as aqueous solutions. BaP was initially dissolved in DMSO to avoid the modification of the voltammograms due to the solubilizing effect which can be exerted by adding surfactants.

To verify whether BaP pre-concentrate at the BDD surface, medium exchange experiences (not shown) were initially carried out. The BDD electrode was kept in contact with a quiescent solution of assayed concentration of BaP in the background electrolyte for a fixed pre-concentration period under open-circuit. Then it was rinsed and immersed in a pure buffer solution where a voltammogram was recorded. On the contrary, when the experiment was repeated maintaining the electrode in a stirred solution of BaP, the recorded voltammogram presented higher peak current. This behavior could be indicative of the adsorptive accumulation of BaP on the electrode surface. As was noted in Section 1, the voltammetric behavior of BaP in aqueous medium was also demonstrated on GC and PG electrodes in our previous work [32]. By using BDD electrode, the first measurements in aqueous solutions were performed by CV after pre-concentration for 180 s at an open-circuit condition. Typical cyclic voltammogram in aqueous Britton–Robinson buffer at pH 2.0 containing 4 × 10^{-5} M BaP is shown in Fig. 3 (dashed line). In the present work, for BaP oxidation a voltammogram with nearly peak-shaped feature at around +0.91 V was more clearly observed at BDD electrode than those at GC and PG electrodes predicted by our previous report [32]. Moreover, a poorly developed current at ca. +1.10 V was noticed under experimental conditions reported above, as discussed later in more detail. Redox couple could not be detected, which is consistent with the earlier observations on GC and PG electrodes [32]. It is noteworthy that at high pHs (in more alkaline solutions, not presented), the background current (presumably due to oxygen evolution) began to interfere, and also BaP oxidation peak was not well separated from the background discharge.

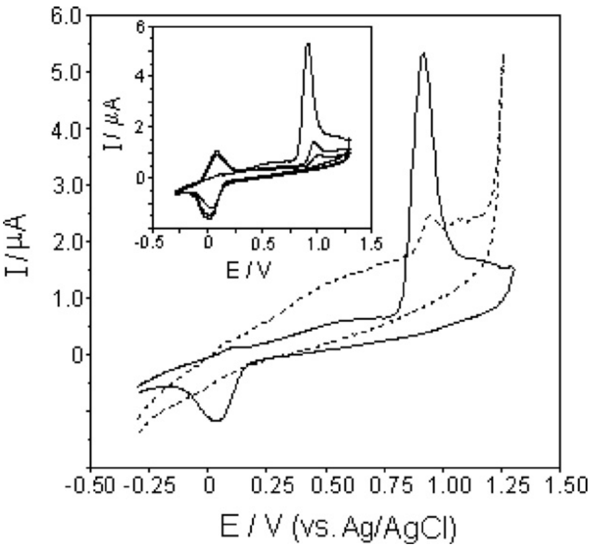

Fig. 3. The stripping voltammograms of 4 × 10^{-5} M BaP solutions in Britton–Robinson buffer pH 2.0 in absence (dashed line) and presence (solid line) of SDS. Inset represents the repetitive cyclic voltammograms of BaP in presence of SDS. Electrode, BDD; surfactant concentration, 4 × 10^{-4} M; pre-concentration period, 180 s at open circuit condition. CV parameters: scan rate, 100 mV s^{-1}.

In order to test the effect of anionic surfactants on the ease of the oxidation of BaP, SDS was added to the electrolyte solution having a final concentration of 4 × 10^{-4} M. Voltammograms obtained at pH 2.0 using Britton–Robinson buffer after 180 s of accumulation at an open-circuit condition showed that SDS played a significant role on the electrode process (Fig. 3, solid line) when compared with SDS-free solution (Fig. 3, dashed line). It is important to stress out that, in the potential range considered, there was no SDS oxidation process observed. When the solution contains SDS, an important signal enhancement with the better-defined peak shape (measured peak potential at around +0.91 V) was observed. Another important observation is the background current level, which was lower in the presence of SDS than in its absence. Because of the critical micelle concentration (CMC) of SDS is about 8.2 × 10^{-3} M [60], the formation of micelles at such a low concentration is not possible. However, in the case of relatively higher concentrations below the CMC of surfactants, the bilayers or hemimicelles (surface micelles) are formed on the electrode surface [44]. We suppose that when the analyte approaches the vicinity of the electrode surface, an attraction by chemical affinity (lipoaffinity) created between the nonpolar moiety of the adsorbed surfactant and highly lipophilic substance, such as BaP, via its surface solubilization into the surfactant film, allows the pre-concentration of analyte, as will be seen later from the data obtained in the presence of different surfactants with varying charges. Such an attraction could explain the increase in the BaP peak height in SDS-containing solution [61]. According to the medium exchange technique (transfer voltammetry) applied in this study for stripping studies, CV was performed in buffer solution without SDS and BaP. An important enhancement action caused by surfactant is also evidence of SDS film formation on the electrode surface. In surfactant solution, the intensity of ill-defined current (see above for CV studies) became less evident compared to the main oxidation peak. With the addition of anionic surfactant, multisweep cyclic voltammetry revealed the presence of redox pair again in the potential range 0 V to +0.1 V (Fig. 3, inset), with a very small peak potential separation (45 mV). These processes are better defined than those recorded in DMSO,

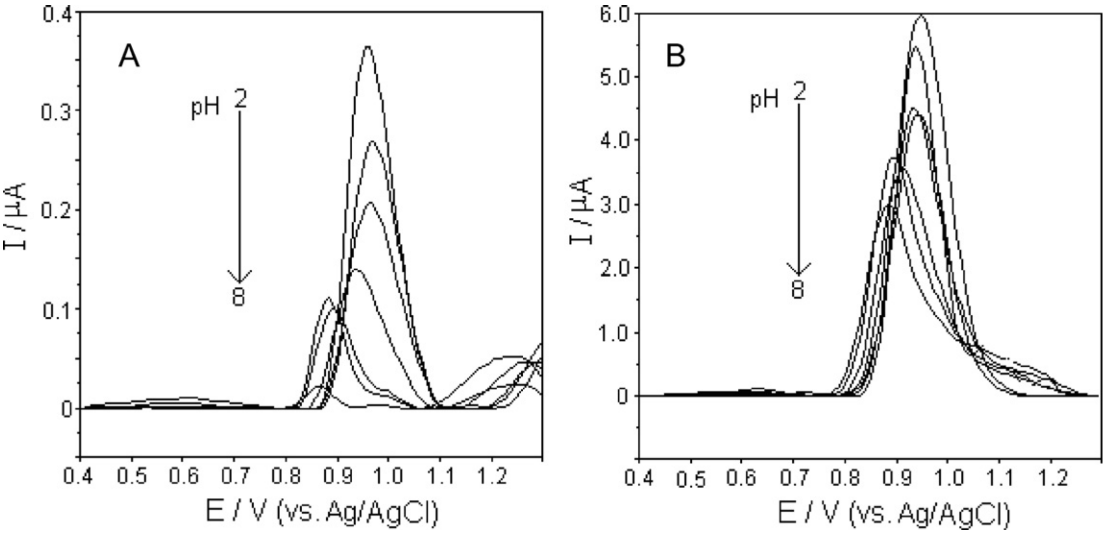

Fig. 4. The stripping voltammograms of 8×10^{-6} M BaP in Britton–Robinson buffer between pH 2.0 and 8.0 in absence (A) and presence (B) of SDS. Electrode, BDD; surfactant concentration, 4×10^{-4} M; pre-concentration period, 180 s at open circuit condition. SWV parameters: frequency, 50 Hz; scan increment, 8 mV; pulse amplitude, 20 mV.

indicating that surfactant is strongly involved in the follow-up reaction in the electrochemical cell. Transfer voltammetric experiments between pre-concentration and measurement provide even more evidence for the strongly adsorption of the electrochemical reaction products responsible for the process (IIc/IIa) on the electrode surface in presence of surfactant. From the three-successive cyclic voltammograms (Fig. 3, inset), it was also observed that at the second cycle the initial oxidation peak almost disappeared in this media. It is expected that the first cycle is due to the oxidation of the BaP adsorbed molecules, and the second and following ones due to diffusion of the compound. It seems that the BDD allows for a strong mono or multilayer adsorption of surfactant allowing for a pre-concentration of hydrophobic species at the electrode/solution interface. The electrooxidation of BaP clearly gives a compound more readily oxidized than the parent species, this new quasi reversible redox couple (IIc/IIa) is likely a dihydrodiol derivative of BaP. It is inferred the formation of a dimer which is likely an additional (parallel) pathway.

It is also important to underline that in the case of GC electrode SDS did not play any role in the oxidation of BaP in any of the media. This seems apparently related to the nature of the electrode and it should thus be pointed out the different nature of the BDD surface comparing to the GC one (e.g., in terms of hydrophobicity of the electrode surface).

Further work was dedicated towards studying the influence of changing the pH upon the AdSV performance in the absence and the presence of 4×10^{-4} M SDS at BDD electrode. Due to the poorly resolved signal obtained by CV with an increase in pH, the effect of solution acidity was studied using SW mode. This parameter was established in the pH range 2.0–8.0 of Britton–Robinson buffer by carrying out adsorptive measurements on 8×10^{-6} M BaP solution, with an open-circuit mode at 180 s. As seen in Fig. 4, decreasing the solution acidity resulted in a decrease of the peak heights in both aqueous and aqueous/SDS media. For a solution with pH between 2.0 and 5.0, BaP oxidation peak potential did not depend practically on pH. On increasing pH > 5.0, peak potential was slightly displaced to less positive values till pH 6.0 then became again almost pH independent. In some pH ranges one and/or two additional peaks (one of them as post-peak) occurred at more positive potentials than the main oxidation peak. Post-peak was only observed at about pH $\geq$4.0 (in the medium pH range) and it disappeared by operating at low pH. The reasons for these additional peaks remain ambiguous. Considering the previously reported results in aqueous and non-aqueous solutions using platinum and carbon electrodes [25,32], these behaviors could be attributed to the oxidation products of interfacial species formed during the oxidation of BaP. The tailing and overlapping of the peaks experienced became disadvantageous for measurement of peak currents and potentials. As was explained above for CV studies, in the case of SDS-free solution when more alkaline Britton–Robinson buffer (at pH > 8.0) was used, BaP was barely detectable and nearly no stripping voltammetric signal was observed.

Taking into account all of the results thus far, it is clear that the best voltammetric signal in terms of sensitivity (peak height) and resolution from extraneous peaks (peak shape) was secured at pH 2.0. On the other hand, BDD electrode in the presence of SDS as modifying solution showed current intensities that were almost 18 times higher than those obtained in free solution.

Next, to select the most appropriate one for analytical purposes, the effect of other types of surfactants including cationic, CTAB and non-ionic, Tween 80 was also explored on the electrochemical response of BaP at selected pH. Fig. 5 shows comparison of SW voltammograms in the presence of different types of surfactants having a concentration of 4.0×10^{-4} M. In all of the investigated surfactants, the significant increase with different degrees in the peak currents was observed as compared with the value obtained in their absence. These results provide further evidence that the hydrophobicity of BaP induce strong interaction with all kinds of surfactants that possess long-chain hydrophobic group. Regarding the peak potentials, the surfactant type showed no obvious differences, except a slight shifting towards less positive values by using anionic surfactant. However, it is interesting to note that, for cationic and non-ionic cases, additional peaks appeared again (see above) within the potential window studied in such a strongly acidic solution. Although CMC of CTAB has been reported as 8.7×10^{-4} M [62], bearing in mind that several factors such as the type of buffer used (supporting electrolyte) and nature of the analyte studied should affect greatly the estimate of CMC from voltammetric results, the formation of micelles can probably start at a concentration just below its CMC. On the other hand, at 4×10^{-4} M level which is above the CMC (2.4×10^{-5} M) for Tween 80, surfactant forms aggregates [63]. Thus, the above observations in both cases might be attributed to the capabilities of these surfactant micelles in stabilizing radicals and intermediate reaction products. A more pronounced increase in the height of these peaks in Tween 80-containing solution can be explained on the basis of interaction of such an intermediate with

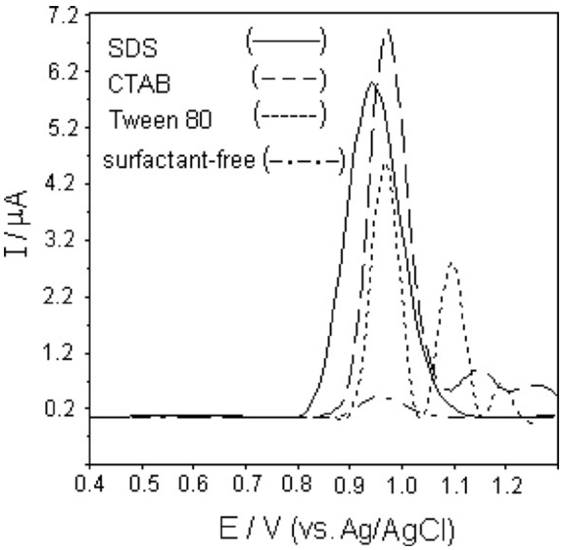

Fig. 5. The stripping voltammograms of 8×10^{-6} M BaP in Britton–Robinson buffer pH 2.0 in absence and presence of surfactants. Electrode, BDD; surfactant concentration, 4×10^{-4} M; pre-concentration period, 180 s at open circuit condition. SWV parameters as indicated in Fig. 4.

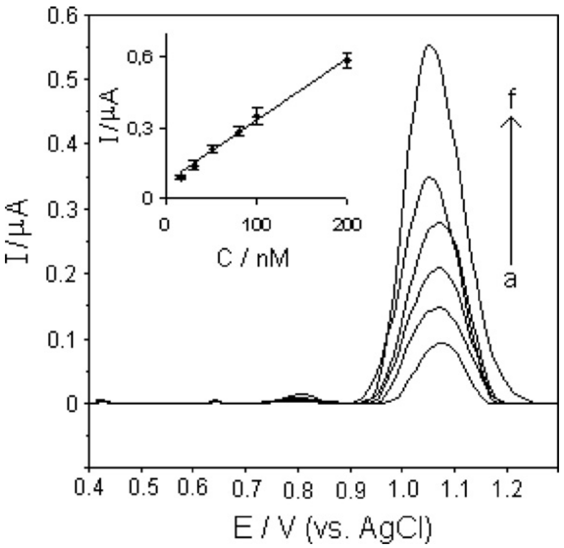

Fig. 6. The stripping voltammograms for BaP levels of (a) 16, (b) 30, (c) 50, (d) 80, (e) 100 and (f) 200 nM in Britton–Robinson buffer, pH 2.0 containing 2.5×10^{-4} M SDS. Inset depicts a corresponding calibration plot for the quantitation of BaP. Electrode, BDD; pre-concentration period, 120 s at a fixed potential of +0.1 V. SWV parameters as indicated in Fig. 4.

hydrophobic regions of the micelle below the level of the Stern layer causing its stabilization [64]. The strongly hydrated shell of ionic surfactants reduces the penetration into the Stern layer of the micelle and thus the stabilization capacity when compared to non-ionic ones [57]. Taking into account the superiority of the stripping voltammetric approach in terms of resolution, SDS, therefore, was chosen as the most suitable one for further studies.

The influence of SDS concentration on BaP stripping peak was studied (not shown) in Britton–Robinson buffer (pH 2.0) using a 180-s open-circuit accumulation. As the concentration of SDS increased gradually up to 10^{-4} M, the peak current also increased gradually. When the SDS concentration was further improved to 2.5×10^{-4} M, the significant increase in the signal was observed. However, above this concentration the peak current began to decrease gradually. The results showed that SDS concentration had little effect on the peak potential. To sum up, the chosen electrolyte for subsequent studies were Britton–Robinson buffer at pH 2.0 in the presence of 2.5×10^{-4} M SDS solution.

Further work was dedicated towards studying the effect of pre-concentration/stripping conditions, such as accumulation potential and time (data not presented). The dependence of the stripping peak current on the accumulation potential was evaluated either at open-circuit condition or over the potential range 0 to +0.5 V in stirred 8×10^{-6} M BaP solution with an accumulation time of 180 s. The value for the stripping current obtained at +0.4 V was nearly equal to the value obtained at open-circuit voltage. The maximum peak current was achieved between +0.1 V and +0.2 V. Hence, an accumulation potential of +0.1 V was used throughout the present study. After fixing the accumulation potential at this value, the accumulation time was varied between 30 and 480 s. As expected, the peak current increased with the accumulation time. Specifically, it increased at a fast rate up to about 120 s then rather slowly between 120 s and 480 s. Thus, 120 s was deemed to be the optimum accumulation time for pre-concentration prior to stripping.

The dependence of stripping responses on SWV parameters was finally analyzed in order to optimize the experimental set-up for BaP determination. The ranges studied were 25–125 Hz for frequency, 2–16 mV for scan increment and 5–60 mV for pulse amplitude (not shown). The scan rate in SWV is the result of the product of the frequency and scan increment. Therefore, the peak heights increased with the increase in the frequency and scan increment. At higher values than 50 Hz and 8 mV, a broadening and a distortion in the voltammograms were observed. The analytical signal is also dependent on the pulse amplitude even if this parameter seems to be less important than the frequency. Peak heights increased linearly up to 20 mV. However, with higher pulse amplitudes a broadening of the peak occurred. For all subsequent work the selected conditions were: frequency, 50 Hz; scan increment, 8 mV; and pulse amplitude, 20 mV.

The electrochemical mechanism of BaP underlying such an electron transfer is expected to be complicated in aqueous and aqueous/surfactant solutions and is beyond the scope of the present work. It only shows how the compound is oxidized in all above media at BDD electrode. Although the sufficient data are not available to determine the exact oxidation mechanism, we may assume that the parent BaP, its radical cation which may further react with constituents of the aqueous/surfactant solutions and in additional electrochemical oxidation steps, and BaP-dimer which is further oxidized, could be responsible of such a voltammetric behavior depending on surfactant. According to the results exposed hitherto, the use of BDD electrode in SDS-containing buffer solution at pH 2.0 could allow the development of an adsorptive voltammetric method for the determination of BaP.

3.3. *Analytical application*

Once the most ideal and suitable chemical conditions and instrumental parameters for the adsorptive determination were established, a calibration plot for the analyzed BaP was recorded to estimate the analytical characteristics of the developed method.

The analytical curve shown in the inset of Fig. 6 for BaP, using the peak currents at about +1.07 V of the experiments shown in Fig. 6 depicts a linear response in the range of 16–200 nM (4.04–50.46 ng mL^{-1}). Least-square treatment of the calibration graph yielded the following regression equation: i_p (µA) = 0.0027 C (nM) + 0.0679, r = 0.997, where i_p is the adsorptive stripping peak current, C BaP concentration and r the correlation coefficient.

The sensitivity of the proposed method was checked in terms of the limits of detection (LOD) and quantitation (LOQ) values. LOD and LOQ were calculated according to the calculated formulas $3\,s/m$ and $10\,s/m$, respectively, where s is the standard deviation of the response (blank) (six runs), and *m* the slope of the calibration plot. LOD and LOQ were found to be 2.86 nM (0.72 ng mL^{-1}) and 9.53 nM (2.41 ng mL^{-1}), respectively. Such remarkable enhancement for the sensitivity, clearly demonstrates the superiority of this electroanalytical approach over our recently reported adsorptive stripping voltammetric method at PG electrode [32] which only succeeded to achieve 27 nM (6.82 ng mL^{-1}) concentration levels.

The precision of the method, expressed as repeatability was calculated by means of eight independent measurements of 100 nM BaP. The relative standard deviation (RSD %) value was found to be 8.9%.

Since BaP solutions undergo photooxidation in air and light [65], they were freshly prepared and kept in dark-colored, tightly closed containers. However, the stability of stock solutions of BaP stored in the dark and in refrigerator was evaluated by monitoring the changes in the voltammograms over a period of 1 week. No obvious changes in the anodic peak current were found, demonstrating that BaP solutions were stable for this period. Taking into account that the stability of aqueous solutions containing PAHs is a major problem due to their tendency to be absorbed on surfaces of polyethylene containers [10], all solutions were stored in glass vials. Further, surfactant medium used for voltammetric studies is able to minimize losses due to the sorption of PAHs on the sample container walls during sampling, storage and voltammetric procedure [53]. In daily laboratory practice, no significant decrease was evident among the calibration samples throughout the study period.

The effects of some usual ions (cations and anions) to be found in tap water and two other PAH compounds upon the determination of 200 nM BaP in Britton–Robinson buffer, pH 2.0 containing 2.5×10^{-4} M SDS were evaluated on the BDD electrode. For testing anions (Cl^- and $NO_3{}^-$) corresponding sodium salts were used. Cations were used as nitrates (Fe^{2+}, Ca^{2+}, and Mg^{2+}) or chloride (Na^+). Four- (chrysene) and five-ring (benzo[*k*]fluoranthene) aromatic compounds were tested as model for effect of PAHs with different rings. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than ±5% for the determination of BaP. The results showed that 100-fold Fe^{2+} and 1000-fold Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and $NO_3{}^-$ did not interfere with the analysis of BaP. The observations revealed that benzo[*k*]fluoranthene and chrysene are electrochemically inactive in the potential region where the BaP molecule is detected. Moreover, under the conditions assayed, these PAHs caused no interference up to a ratio of 1:10 compared to BaP. On the other hand, the performance of the stripping step in clean electrolyte by using medium exchange technique could be very convenient from the point of eliminating possible electroactive interferences such as other environmental pollutants (not or slightly adsorbed). In addition, the presence of surfactants could improve the selectivity of these pre-concentrations because surfactant adsorbed surfaces may show intense barrier effects such as induced adsorption, kinetic and electrostatic barrier for species of the same charge.

The applicability of the proposed methodology for the determination of this pollutant in aqueous environmental samples was tested in tap water samples. Since these samples did not contain BaP at levels higher than the attained detection limits, model water samples were prepared by adding different concentrations of BaP into tap water. In order to check if the linearity persists, a new calibration plot was carried out in the samples. In this case, the voltammetric response measured in spiked tap water was linearly related to the concentration of BaP within the range of 40–160 nM (10.09–40.37 ng mL^{-1}) followed the regression equation: i_p (μA) = 0.0023 C (nM) − 0.0295 (correlation coefficient, 0.997). The achieved LOD was 10.20 nM (2.57 ng mL^{-1}). The slope of the standard curve and the spiked sample calibration was almost identical, however, a decrease in the signal was observed in this matrix comparing to that obtained in pure solutions.

Table 1
Recoveries of BaP in spiked tap water samples by adsorptive stripping square-wave voltammetry on BDD electrode.

BaP added (nM)	Level determined[a] (nM)	Recovery (%) ± RSD (%)
40	41.96	105 ± 4
80	75.87	95 ± 7
120	125.43	105 ± 8

[a] Values are the average of three independent analysis of each spiked sample.

The matrix of the sample did not reduce the reproducibility of the signal as demonstrated by recording three voltammograms for each of the water samples spiked with three concentration levels. Table 1 shows the added quantities, as well as the values found with their RSD values and the obtained recovery percentages. A good agreement between the spiked and found quantities was observed, with an average recovery of 101.4%.

4. Conclusions

In the present study, the BaP molecule was chosen for its importance from an environmental point of view, being one of the most potent carcinogens among the PAHs, and the apparent parallelism between its electrochemical and biological reactions to warrant extensive study of the electrochemistry of this compound. In conclusion, we were able to examine the voltammetric behavior of BaP in non-aqueous, aqueous and aqueous/surfactant media on the BDD electrode. On the one hand, the easy voltammetric oxidation of BaP encourages its use for a simple, cheap, rapid and very sensitive voltammetric determination which will be competitive with existing methodology for the determination of not only BaP, but also several structurally related PAHs in environmentally important matrices for future studies. On the other hand, bearing in mind that aqueous micellar environment can serve as simple and primitive model systems for biological membranes, the findings obtained in this study may be useful, at least in part, and shed considerable light on the fundamentals of the complex enzymatic mechanism and perhaps in vivo reactions of PAHs.

Taking advantage of the significant surfactant effect on the electrochemical response of BaP, anodically pretreated BDD electrode combined with more highly sensitive and accurate adsorptive stripping voltammetry could allowed to an attractive trace analysis of this compound in the SDS-containing aqueous solutions. For the proposed approach which is rapid, requiring less than 5 min to run a sample, the detection limits reached the levels as low as 0.72 and 2.57 ng mL^{-1} for bulk solutions and tap water samples, respectively.

Many environmental agencies have adopted very low levels for BaP-contaminated aquatic samples. LOD values obtained in our work are lower than the maximum amount of BaP (61 ng mL^{-1}) allowed in wastewater [66]. On the other hand, the maximum contaminant level (MCL) for drinking water has been set at 0.2 ng mL^{-1} for BaP by USEPA [67]. Obviously, such low detection limits (in the ppb order) still are not sufficient for most practical applications; however, they give hope for future improvement. Due to the fact that Nafion with hydrophobic backbones and hydrophilic–$SO_3{}^-$ group can attract cationic substances, surfactants with a positive charge (cationic type) can adsorb on the Nafion-modified electrode via ion-exchange interaction. Considering this knowledge and keeping in mind the adsorption of BaP induced by cationic surfactant such as CTAB, more work is now being carried out in our laboratory to investigate the Nafion coating on the BDD electrode in presence of cationic surfactants in order to improve the sensitivity together with the selectivity of presented voltammetric method.

For practical purposes it is very important that some problems concerned with the requirement of extraction into of potentially hazardous organic solvents for enhancing the removal of BaP or structurally related PAH compounds from environmental and biological samples can be avoided by their displacement by surfactants [57]. Therefore, the use of surfactants (the eliminating or at least minimizing the organic solvent) in this study makes proposed method more environment friendly than the most common reference methods, as well as an attractive alternative for the analysis in different matrix such as soil, sediments or sewage sludge containing the higher concentration of BaP.

Finally, it should be mentioned once again that this article is a part of our continuing studies on the electroanalytical characteristics of PAH compounds in aqueous and non-aqueous systems using different carbon-based electrodes [32,68]. As far as we know, this paper is also the first report describing the usefulness of BDD electrode in the presence of surfactants for electroanalysis of organic compounds.

References

[1] A.M. Mastral, M.S. Callén, Environ. Sci. Technol. 34 (2000) 3051–3057.
[2] International Agency for Research in Cancer (IARC), Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Available on line at http://www.iarc.fr.
[3] P.D. Devanesan, N.V.S. RamaKrishna, R. Todorovic, E.G. Rogan, E.L. Cavalieri, H. Jeong, R. Jankowiak, G.J. Small, Chem. Res. Toxicol. 5 (1992) 302–309.
[4] E.G. Rogan, P.D. Devanesan, N.V.S. RamaKrishna, S. Higginbotham, N.S. Padmavathi, N.S. Chapman, E.L. Cavalieri, H. Jeong, R. Jankowiak, G.J. Small, Chem. Res. Toxicol. 6 (1993) 356–363.
[5] A. Bjorseth, Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, New York, 1983.
[6] J.P. Butler, G.B. Post, P.J. Lioy, J.M. Waldman, A. Greenberg, J. Air Waste Manage. Assoc. 43 (1993) 970–977.
[7] N.R. Khalili, P.A. Scheff, T.M. Holsen, Atmos. Environ. 29 (1995) 533–542.
[8] M.J. Bogusz, S.A. El Hajj, Z. Ehaideb, H. Hassan, M. Al-Tufail, J. Chromatogr. A 1026 (2004) 1–7.
[9] O. Duke, I.O. Albert, J. Appl. Sci. 7 (2007) 1873–1879.
[10] L. Campo, R. Mercadante, F. Rossella, S. Fustinoni, Anal. Chim. Acta 631 (2009) 196–205.
[11] Y. Wang, J. Zhang, Y. Ding, J. Zhou, L. Ni, C. Sun, J. Sep. Sci. 32 (2009) 3951–3957.
[12] S. Özcan, A. Tor, M.E. Aydın, Anal. Chim. Acta 665 (2010) 193–199.
[13] F. Aygün, A. Demirci, M. Özcimder, J. Agric. Food Chem. 44 (1996) 1488–1490.
[14] S. Vasquez Troche, M.S. Garcia Falcon, S. Gonzalez Amigo, M.A. Lage Yusty, J. Simal Lozano, Talanta 51 (2000) 1069–1076.
[15] D.M. Brum, R.J. Cassella, A.D.P. Netto, Talanta 74 (2008) 1392–1399.
[16] L. Rey-Salgueiro, E. Martínez-Carballo, M.S. García-Falcón, C. González-Barreiro, J. Simal-Gándara, Food Chem. 115 (2009) 814–819.
[17] M. Akyüz, H. Çabuk, J. Hazard. Mater. 170 (2009) 13–21.
[18] M.C. Bruzzoniti, M. Fungi, C. Sarzanini, Anal. Methods 2 (2010) 739–745.
[19] K.A. Fahnrich, M. Pravda, G.G. Guilbault, Biosens. Bioelectron. 18 (2002) 73–82.
[20] S. Boujday, C. Gu, M. Girardot, M. Salmain, C.-M. Pradier, Talanta 78 (2009) 165–170.
[21] S. Boujday, S. Nasri, M. Salmain, C.-M. Pradier, Biosens. Bioelectron. 26 (2011) 1750–1754.
[22] R. Doong, H. Shih, S. Lee, Sens. Actuators B: Chem. 111–112 (2005) 323–330.
[23] M. Del Carlo, M. Di Marcello, M. Perugini, V. Ponzielli, M. Sergi, M. Mascini, D. Compagnone, Microchim. Acta 163 (2008) 163–169.
[24] J. Barek, J. Cvacka, A. Muck, V. Quaiserova, J. Zima, Fresenius J. Anal. Chem. 369 (2001) 556–562.
[25] L. Jeftic, R.N. Adams, J. Am. Chem. Soc. 92 (1970) 1332–1337.
[26] J.F. Coetzee, G.H. Kazi, J.C. Spurgeon, Anal. Chem. 48 (1976) 2170–2174.
[27] V. Podany, E. Rezabkova, L. Bahna, Neoplasma 25 (1978) 57–65.
[28] V. Podany, M. Benesova, L. Bahna, Neoplasma 26 (1979) 685–689.
[29] P. Cremonesi, E. Rogan, E. Cavalieri, Chem. Res. Toxicol. 5 (1992) 346–355.
[30] H.-P. Nirmaier, E. Fischer, G. Henze, Electroanalysis 3 (1998) 187–190.
[31] S.M. van Leeuwen, H. Hayen, U. Karst, Anal. Bioanal. Chem. 378 (2004) 917–925.
[32] E. Keskin, Y. Yardım, Z. Şentürk, Electroanalysis 22 (2010) 1191–1199.
[33] K. Peckova, J. Musilova, J. Barek, J. Zima, in: M.H. Lefebvre, M.M. Roux (Eds.), Progress on Drinking Water Research, Voltammetric and Amperometric Determination of Organic Pollutants in Drinking Water using Boron-doped Diamond Electrodes, Nova Science Publishers, New York, 2008, p. 103.
[34] C.D. Souza, O.C. Braga, I.C. Vieira, A. Spinelli, Sens. Actuators B 135 (2008) 66–73.
[35] M. Gumustas, S.A. Ozkan, Anal. Bioanal. Chem. 397 (2009) 189–203.
[36] H. Dejmkova, M. Scampicchio, J. Zima, J. Barek, S. Mannino, Electroanalysis 21 (2009) 1014–1018.
[37] K. Peckova, J. Musilova, J. Barek, Crit. Rev. Anal. Chem. 39 (2009) 148–172.
[38] K.D. Santos, O.C. Braga, I.C. Vieira, A. Spinelli, Talanta 80 (2010) 1999–2006.
[39] E.R. Sartori, R.A. Medeiros, R.C. Rocha-Filho, O. Fatibello-Filho, Talanta 81 (2010) 1418–1424.
[40] B. Bozal, B. Uslu, Comb. Chem. High Throughput Screen. 13 (2010) 599–609.
[41] Y.V. Peleskov, Russ. J. Electrochem. 38 (2002) 1275–1291.
[42] N.S. Lawrence, M. Pagels, A. Meredith, T.G.J. Jones, C.E. Hall, C.S.J. Pickles, H.P. Godfried, C.E. Banks, R.G. Compton, L. Jiang, Talanta 69 (2006) 829–834.
[43] H.B. Suffredini, V.A. Pedrosa, L. Codognoto, S.A.S. Machado, R.C. Rocha-Filho, L.A. Avaca, Electrochim. Acta 49 (2004) 4021–4026.
[44] R. Vittal, H. Gomathi, K.-J. Kim, Adv. Colloid Interface Sci. 119 (2006) 55–68.
[45] Y. Hongchao, L. Chunya, Russ. J. Electrochem. 43 (2007) 1377–1381.
[46] C. Li, Bioelectrochem 70 (2007) 263–268.
[47] M.C. Blanco-Lopez, M.J. Lobo-Castanon, A.J. Miranda-Ordieres, P. Tunon-Blanco, Electroanalysis 19 (2007) 207–213.
[48] R. Jain, A. Dwivedi, R. Mishra, Langmuir 25 (2009) 10364–10369.
[49] A. Levent, Y. Yardım, Z. Şentürk, Electrochim. Acta 55 (2009) 190–195.
[50] T.A. de Araújo, A. Marcos, J. Barbosa, L. Henrique, V. Valdir, S. Ferreira, J.-C. Dur, R. Rama, Colloids Surf. B: Biointerf. 79 (2010) 409–414.
[51] R. Jain, R.K. Yadav, J.A. Rather, Colloids Surf. A: Physicochem. Eng. Aspects 366 (2010) 63–67.
[52] R. Ferrer, J.L. Beltran, J. Guiteras, Anal. Chim. Acta 330 (1996) 199–206.
[53] D. Sicilia, S. Rubio, D. Perez-Bendito, N. Maniasso, E.A.G. Zagatto, Anal. Chim. Acta 392 (1999) 29–38.
[54] J.-C. Dur, R. Rama, C. Mougin, V. Chaplin, Polycyclic Aromat. Compd. 20 (2000) 143–154.
[55] Z. Zheng, J.P. Obbard, J. Environ. Qual. 31 (2002) 1842–1847.
[56] I.Y. Goryacheva, S.N. Shtykov, A.S. Loginov, I.V. Panteleeva, Anal. Bioanal. Chem. 382 (2005) 1413–1418.
[57] J.-C. Dur, R. Rama, H. Parola, V. Chaplain, Colloids Surf. A: Physicochem. Eng. Aspects 162 (1999) 249–257.
[58] M. Wei, Y. Zhou, J. Zhi, D. Fu, Y. Einaga, A. Fujishima, X. Wang, Z. Gua, Electroanalysis 20 (2008) 137–143.
[59] E. Laviron, J. Electroanal. Chem. 101 (1979) 19–28.
[60] H. Nakamura, A. Sano, K. Matsuura, Anal. Sci. 14 (1998) 379–382.
[61] J.F. Rusling, Colloids Surf. 81 (1997) 123–124.
[62] F. Mutelet, M. Rogalski, M.H. Guerrnouche, Chromatographia 57 (2003) 605–610.
[63] P.A. Willumsen, U. Karlson, P.H. Pritchard, Appl. Microbiol. Biotechnol. 50 (1998) 475–483.
[64] J.F. Rusling, Acc. Chem. Res. 24 (1991) 75–81.
[65] H. Yu, J. Environ. Sci. Health C20 (2002) 149–183.
[66] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs), Agency for Toxic Substances and Disease Registry Information Center, Atlanta, GA, 1995.
[67] Environmental Protection Agency (EPA) of the United States of America, Explanation of Significant Differences, Libby Ground Water Superfund Site, Washington, DC, USA, 1997.
[68] Y. Yardım, E. Keskin, A. Levent, M. Özsöz, Z. Şentürk, Talanta 80 (2010) 1347–1355.