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Voltametrické a amperometrické stanovení nitrofenolů pomocí borem dopované diamantové filmové elektrody

Voltammetric and Amperometric Determination of Nitrophenols Using Boron-Doped Diamond Film Electrode

Disertační práce

Vedoucí práce: Prof. RNDr. Jiří Barek, CSc.

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Abstrakt

Tato práce je věnována použití borem dopované diamantové (BDD) elektrody pro voltametrické a amperometrické stanovení vybraných nitrofenolů – 2-nitrofenolu (2NP), 4-nitrofenolu (4NP) a 2,4-dinitrofenolu (2,4DNP). Tyto látky jsou vedeny v seznamu United States Environmental Protection Agency (US EPA) jako významné polutanty, neboť mají negativní vliv na organismy. V zemědělství jsou používány jako hnojiva – stimulátory růstu. BDD elektrody jsou používány pro stanovení širokého spektra jak oxidovatelných, tak redukovatelných látek, a pro svoji dostupnost a vynikající mechanické a elektrochemické vlastnosti se staly populárním elektrodovým materiálem.

Pro stanovení nitrofenolů byla použita diferenční pulsní voltametrie, a to s použitím jak redukce (pro 2NP, 4NP a 2,4DNP), tak i oxidace (pro 4NP a 2,4DNP). Metoda byla úspěšně aplikována pro stanovení těchto látek v pitné a říční vodě v koncentračním rozsahu od 4×10^{-7} do 2×10^{-5} mol.L^{-1}. Po použití prekoncentrace pomocí extrakce tuhou fází ze 100 ml a z 1000 ml vzorků vody bylo dosaženo meze stanovitelnosti pro tyto látky 2×10^{-8} mol.L^{-1} (vzorky pitné vody) a 2×10^{-7} mol.L^{-1} (vzorky říční vody).

Pro stanovení nitrofenolů byla BDD elektroda úspěšně použita také jako amperometrický detektor ve wall-jet uspořádání pro vysokoúčinnou kapalinovou chromatografii (HPLC) za pomocí jak elektrochemické redukce, tak oxidace. Optimální podmínky pro separaci na koloně C_{18} s převrácenými fázemi (125×4 mm, 5 μm) a amperometrickou detekci v katodické oblasti jsou: mobilní fáze 0.05 mol.L^{-1} acetátový pufr pH 4.7/methanol (58/42, v/v) a detekční potenciál –1.2 V, v anodické oblasti mobilní fáze 0.05 mol.L^{-1} fosfátový pufr pH 6.75/methanol (65/35, v/v), detekční potenciál +1.3 V. Obě metody byly úspěšně použity pro analýzu modelových vzorků pitné a říční vody po jejich přímém dávkování do systému HPLC s amperometrickým wall-jet detektorem v koncentračním rozsahu od 2×10^{-6} do 1×10^{-4} mol.L^{-1}. Pro obě metody bylo dosaženo srovnatelných hodnot citlivosti i mezí detekce.

Dosažené výsledky potvrzují, že jak voltametrie, tak HPLC s elektrochemickou detekcí s BDD elektrodou bez úpravy jejího povrchu patří mezi spolehlivé a citlivé analytické metody pro stanovení nitrofenolů, neboť dosažené limity detekce jsou srovnatelné s limity detekce jiných elektrodových materiálů.

Abstract

Presented Ph.D. Thesis is focused on the use of the boron-doped diamond (BDD) electrodes for voltammetric and amperometric determination of selected nitrophenols: 2-nitrophenol (2NP), 4-nitrophenol (4NP), and 2,4-dinitrophenol (2,4DNP). These compounds are listed as "priority pollutants" by United States Environmental Protection Agency (US EPA) due to their negative impact on living organisms and are mainly used in agriculture as plant growth stimulators. BDD electrodes are used for determination of wide range of electrochemically both reducible and oxidisable organic compounds and have become a popular electrode material thanks to its commercial availability and excellent mechanical and electrochemical properties.

A differential pulse voltammetric method was developed for the determination of 2NP, 4NP and 2,4DNP at a BDD film electrode using electrochemical reduction and of 4NP and 2,4DNP using electrochemical oxidation. The method was successfully applied for the direct determination of these compounds in drinking and river water in the concentration range from 4×10^{-7} to 2×10^{-5} mol.L^{-1}. To improve the limit of quantification, a preconcentration by solid phase extraction from 100 mL (drinking and river water) and 1000 mL (drinking water) of water samples was used with limit of determination around 2×10^{-8} and 2×10^{-7} mol.L^{-1}, respectively.

The possibility to employ BDD film electrodes for amperometric detection in wall-jet arrangement in High-performance liquid chromatography (HPLC) was verified by determination of these nitrophenols based on both, electrochemical reduction and oxidation. Optimal conditions for separation at C_{18} reverse phase column (125×4 mm, 5 μm) and amperometric detection are as follows: for cathodic detection mobile phase 0.05 mol.L^{-1} acetate buffer pH 4.7/methanol (58/42, v/v), detection potential –1.2 V; for anodic detection mobile phase 0.05 mol.L^{-1} phosphate buffer pH 6.75/methanol (65/35, v/v), detection potential +1.3 V. The applicability of the developed methods was demonstrated on the analysis of the model drinking and river water samples using their direct injection in the HPLC-ED setup in the concentration range from 2×10^{-6} to 1×10^{-4} mol.L^{-1}. Comparable sensitivities and limits of detection were achieved for both detection modes.

The obtained results confirm that both batch voltammetry and HPLC with electrochemical detection with unmodified BDD electrode represent reliable and sensitive analytical techniques for determination of nitrophenols with limits of detection similar to other electrodes.

Content

List of Symbols and Abbreviations

2NP	2-nitrophenol
2,4DNP	2,4-dinitrophenol
4NP	4-nitrophenol
AA	ascorbic acid
AdSV	adsorptive stripping voltammetry
AgSAE	silver solid amalgam electrode
BDD	boron-doped diamond
BR	Britton-Robinson
CE	capillary electrophoretic
CZE	capillary zone electrophoresis
CV	cyclic voltammetry
CVD	chemical vapour deposition
CVs	cyclic voltammograms
DA	dopamine
DPV	differential pulse voltammetry
ED	electrochemical detection
FIA	flow injection analysis
FIA-ED	flow injection analysis with electrochemical detection
GCE	glassy carbon electrode
GC/FID	gas chromatography with flame ionization detector
GC/MS	gas chromatography with mass spectrometric detection
H-BDD	hydrogen-terminated boron-doped diamond
HF CVD	hot filament chemical vapour deposition
HPLC	high-performance liquid chromatography
HPLC-ED	high-performance liquid chromatography with electrochemical detection
LOD	limit of detection
*LOD*s	limits of detection
LOQ	limit of quantification
*LOQ*s	limits of quantification
MEA	microelectrode arrays
MIP	molecularly imprinted polymer
MP CVD	microwave plasma assisted chemical vapour deposition
NPs	nitrophenols
O-BDD	oxygen-terminated boron-doped diamond
RSD	relative standard deviation
SPE	solid phase extraction
SWV	square wave voltammetry
US EPA	United States Environmental Protection Agency

1. INTRODUCTION

This PhD Thesis has been submitted as a contribution to the ever growing efforts of environmental analysis. It was elaborated under the framework of a long-term research at UNESCO Laboratory of Environmental Electrochemistry in Prague to develop highly sensitive and selective analytical methods and sensors applicable for determination of biologically active organic compounds significant in environmental protection, medicine, pharmacy and/or toxicology. **The presented PhD Thesis is based on the following five scientific publications [1-5], which are attached as Appendix parts I–V. To distinguish the references referring to these publications in entire text of this Thesis, corresponding numbers are in bold and underlined.**

1. **Musilova, J.**; Barek, J.; Peckova, K., The use of boron-doped diamond film electrodes for detection of organic compounds (Použití diamantových filmových elektrod dopovaných borem pro stanovení organických látek). *Chemicke Listy* **2009,** 103, (6), 469-478.

2. Peckova, K.; **Musilova, J.**; Barek, J., Boron-doped diamond film electrodes – New tool for voltammetric determination of organic substances. *Critical Reviews in Analytical Chemistry* **2009,** 39, (3), 148-172.

3. **Musilova, J.**; Barek, J.; Drasar, P.; Peckova, K., Differential pulse voltammetry of selected nitrophenols on boron-doped diamond film electrode. In *Sensing in Electroanalysis*, Vytřas, K.; Kalcher, K.; Švancara, I., Eds.University of Pardubice: Pardubice, 2009; Vol. 4, pp 135-142.

4. **Musilova, J.**; Barek, J.; Peckova, K., Determination of nitrophenols in drinking and river water by differential pulse voltammetry at boron-doped diamond film electrode. *Electroanalysis* **2011,** 23, (5), 1236-1244.

5. **Karaova, J.**; Schwarzova-Peckova, K.; Barek, J., The Use of Boron-Doped Diamond Film Electrode for the Determination of Selected Nitrophenols by HPLC with Amperometric Detection. *Analytical Letters* **2016**, 49, (1), 66-79.

The still-growing world population puts major demands on food production and its availability which leads to the use of higher amounts of agrochemicals. That causes negative impact on the environment and further degradation of food and water quality. Therefore, one of the serious problems of the modern world remains the pollution of the environment by undesirable chemical compounds. Electrochemical techniques may play in this context the role of sensitive and in some cases reasonably selective tool for analysis of environmental matrices.

Electroanalytical methods have become nowadays more attractive, thanks to advantages such as low investment and running costs, short time of analysis, possible miniaturization and mobility, simple handling and sufficient sensitivity and selectivity. The miniaturization plays a very important role in the field of analytical and bioanalytical chemistry. Most of the fabricated microelectrodes are used for end-column amperometric detection in flow injection analysis (FIA), high-performance liquid chromatography (HPLC) capillary zone electrophoresis (CZE), microchips, or for *in vitro* / *in vivo* detection of biogenic compounds. The electrochemical sensors and detectors are unique in comparison with frequently bulky and expensive instrumentation of spectrometric and separation techniques. Development and testing of new suitable electrode materials, possibility of their mechanical and/or chemical modifications, and detection arrangements are one of the major research pathways in modern electroanalysis.

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Presented PhD Thesis is focused on the use of the boron-doped diamond (BDD) electrodes for voltammetric and amperometric determination of selected environmental organic pollutants: 2-nitrophenol (2NP), 4-nitrophenol (4NP), and 2,4-dinitrophenol (2,4DNP). These compounds are listed as "priority pollutants" by United States Environmental Protection Agency (US EPA) [6] and mainly used in agriculture as plant growth stimulators [7]. BDD electrodes are used for determination of wide range of electrochemically both reducible and oxidisable organic compounds (see in chapter 2.2) and have become a popular electrode material thanks to its commercial availability and excellent mechanical and electrochemical properties [2, 8]. Furthermore, BDD electrodes may be advantageously utilized in amperometric detection in liquid-flow systems [9] (see in chapter 2.3).

2. BORON-DOPED DIAMOND ELECTRODES

2.1. Preparation and Characterization of Boron-Doped Diamond Thin Film Electrodes

In recent years, BDD has become a popular electrode material thanks to its commercial availability and excellent mechanical and electrochemical properties [1-2, 8, 10-12]. The properties of BDD films are influenced by the quantity and kind of the doping agent, morphologic factors and defects in the film, crystallographic orientation, presence of impurities (sp^2 carbon), and surface termination (most frequently hydrogen or oxygen).

The preparation of doped diamond films relies on energy-assisted chemical vapour deposition (CVD) methods, when a hydrocarbon gas (typically methane) in hydrogen is energetically activated to decompose the molecules into methyl-radicals and atomic hydrogen and deposited on a suitable substrate. The gas activation is accomplished using hot filament (HF CVD) or microwave plasma assisted CVD (MP CVD). The boron doping agent is most frequently added as small amounts of diborane or trimethyl boron in the gas phase. The material must contain enough boron for the electrode to show metal-like conductivity; electrical measurements demonstrate that this is achieved at $[B] > 10^{20}$ B atoms cm^{-3} (ref.[13]). Typical growth conditions are 0.3–1.0 % CH_4 in H_2, pressures of 10–150 torr, substrate temperatures of 700–1000 °C, and microwave powers of

1000–1300 W, or filament temperatures up to ~ 2800 °C. The film grows by nucleation at rates in the 0.1–2 μm h^{-1} range to thickness at least ~1 μm. The resulting films differ in morphology (microcrystalline films are characterized by crystallite size < 1–5 μm, nanocrystalline films have crystallite size 10–500 nm) and quality.

The as-deposited diamond surface is hydrogen (H-) terminated (as-grown), because the films are grown under a hydrogen plasma or in a hydrogen atmosphere. During the H-termination, a bond between the hydrogen and carbon atoms is formed at the diamond surface. Due to the positive charge of such a layer, positively charged substances are repelled and negatively charged are attracted to the diamond surface and the surface is hydrophobic. H-termination causes a semiconducting BDD electrode to behave metal-like due to the additional surface conductivity hydrogen termination brings [13].

In contrast to the H-termination, by the oxygen (O-) termination a layer of oxygen atoms is formed. The oxygen atoms bond with the carbon atoms in the form of carbonyl,

ether, hydroxyl and carboxylic groups, that are negatively charged and thus attractive for positively and repulsive for negatively charged substances [14]. O-terminated BDD (O-BDD) is hydrophilic and does not possess a measurable surface conductivity [13]. Therefore, the change of the chemical termination from H-terminated to the O-terminated surface affects the electrochemical properties of the diamond electrode.

At the beginnings many studies were presented to be performed at H-terminated BDD (H-BDD) surfaces, but the maintenance of H-termination is complicated due to the easiness of electrochemical oxidation and even oxidation of BDD surface by air oxygen [13]. The re-hydrogenation of an oxidized BDD surface is achievable only by hydrogen-flame annealing or hydrogen-plasma treatment, which requires adequate equipment. Alternative method of rehydrogenation is cathodic pre-treatment at potentials leading to hydrogen evolution on the BDD surface [15]. It can be presumed that many of the early studies performed using supposedly H-terminated surfaces were in fact conducted at oxidized BDD surfaces [13].

The effects of both surface terminations on the shape of the cyclic voltammograms (CVs) of dopamine (DA) and ascorbic acid (AA) at BDD nanoelectrode arrays have been investigated in ref. [14]. To improve the peak separation between DA and AA, differential pulse voltammetry (DPV) was employed. DA detection at O-BDD surfaces provides a signal widely independent of AA. For low-level dopamine measurements, the presence of AA is even beneficial. The much higher current density for DA can be attributed to the well-known enhancement of the electrochemical response for DA in the presence of AA due to the regeneration of DA by reaction with AA. The positive shift of the AA oxidation signal relative to DA oxidation signal on the O-BDD nanoelectrode arrays can additionally promote this effect, as the major part of AA still exists in its reduced form at a potential when DA is already oxidized.

The O-terminated surface can be formed by exposing the surface to oxygen plasma, boiling in strong acid or electrochemical exposure to the high anodic potential in the region of water decomposition. At BDD electrode, water decomposes according to the following equation (Eq. 1):

$$H_2O\ (BDD) \rightarrow HO^{\bullet}(BDD) + H^+ + e^- \qquad \text{(Eq. 1)}$$

The formation of $OH^{\bullet}$ radicals causes oxidation and stabilization of the electrode surface with the prevalence of the carbonyl, hydroxo, and carboxylic groups [16]. The $OH^{\bullet}$ radicals are confined to the BDD surface and as powerful oxidizing agents are capable of oxidation of a wide range of compounds, non-oxidizable at other electrode materials.

Reaction (Eq. 1) is enabled by the high oxygen overvoltage at BDD surface. The water decomposition reaction is extremely important for the applications of BDD electrodes.

BDD materials produced in research laboratories are gradually substituted by available materials from commercially suppliers – Element Six (UK) [17], Windsor Scientific (UK) [18], NeoCoat (formerly Adamant Technologies, Switzerland) [19], Condias (Germany) [20], sp3 Diamond Technologies (USA) [21], and ESA Biosciences (USA) [22]. The analytical techniques routinely used to characterize the morphological, optical, chemical and electronic properties of diamond thin films, include Raman, Auger electron and X-ray photoelectron spectroscopies, scanning electron micrography, scanning tunnelling and force microscopies, powder X-ray diffraction analysis, and secondary ion mass spectrometry [23].

In the publications presented in this Ph.D. Thesis **[3-5]**, the commercial Windsor Scientific BDD electrode was used (see in Figure 1A) for voltammetric methods and also as working electrode in the amperometric wall-jet detector (see in Figure 1B) for HPLC with electrochemical detection (ED) **[5]**.

2.2 Applications and Properties of Boron-Doped Diamond Film Electrodes

There are the following main application fields of BDD electrodes [8]: (i) electrochemical oxidation of organic and inorganic species at BDD anodes for their quantitative conversion or destruction in wastewaters (reviewed in [24-26]), (ii) electrochemical disinfection of drinking and bathing water [27-28], (iii) electrochemical synthesis, in particular inorganic electrosynthesis of strong oxidizing agents and further electroorganic synthesis [29-30], (iv) technical galvanic applications such as lead free chroming [31], and, finally, (v) the use of BDD electrodes in electroanalysis as simple electrochemical sensors employed in voltammetric methods or coupled to liquid flow methods (HPLC, FIA, CZE) for detection of organic and inorganic species, or specialized selective applications of BDD-based bioelectrochemical sensors (introduced in chapter 2.3).

For voltammetric techniques a low and stable background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, extreme electrochemical stability in both alkaline and acidic media, good responsiveness for many redox analytes without pre-treatment, and resistance to electrode fouling are the most

important advantages. The mechanical durability substantiates the popularity of BDD film electrodes in liquid flow methods including FIA and HPLC with electrochemical detection. Because of the wide potential window in both cathodic and anodic region, BDD film electrodes can be used to determine a wide variety of inorganic and organic compounds (such as drugs, pesticides, environmental pollutants, and other biologically active compounds) using electrochemical reduction and/or oxidation. The possibility of miniaturization of BDD electrodes and modification of the BDD surface opened research fields for detection in capillary electrophoretic (CE) techniques including electrophoretic microchips and other liquid flow systems, and further for *in vivo / in vitro* detection of biogenic compounds [9, 32].

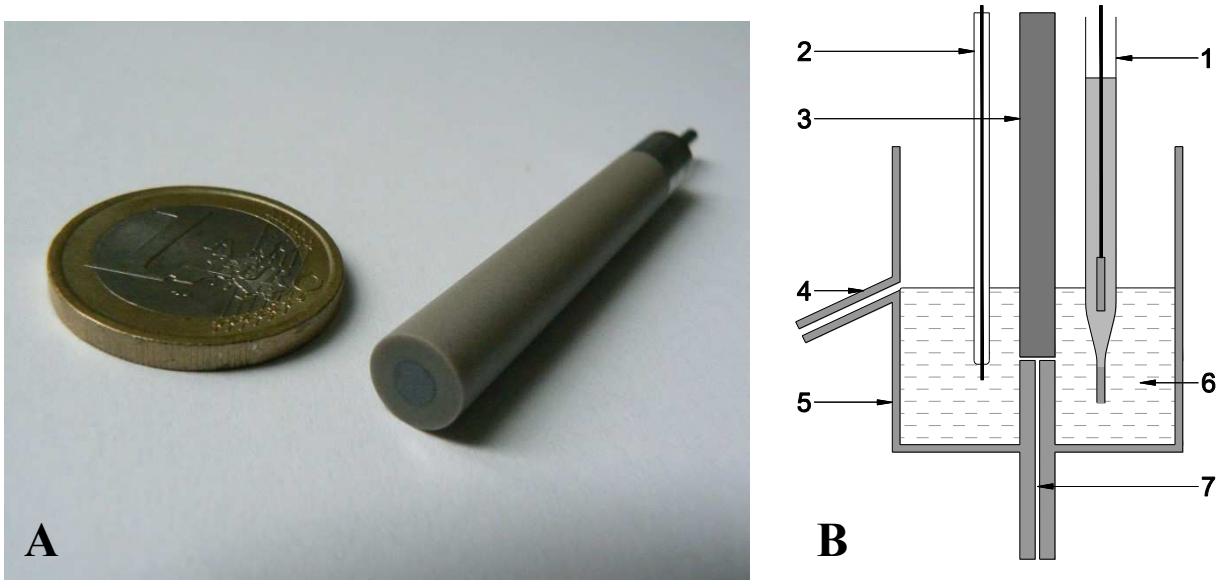

Figure 1 (A) *BDD electrode, Windsor Scientific, UK, BDD electrode in PEEK body, 3 mm diameter, flat bottom part, boron doping level 0.1 %, resistivity 0.075 Ω cm.* ***(B)*** *Scheme of amperometric wall-jet detector.: Ag/AgCl reference electrode (1); platinum wire auxiliary electrode (2), BDD working electrode (3); outlet – overflow (4), overflow whole-glass vessel (5), mobile phase (6), inlet Teflon tubing connected to FIA and/or HPLC output (7), adapted from [5].*

2.3 Boron-Doped Diamond Film Electrodes in Organic Electroanalysis

An overview of organic analytes determined by means of BDD electrodes is available in our recent reviews [1-2, 11, 33]. The review [1] summarizes the use of BDD film electrodes in electroanalysis of organic compounds and obtained analytical figures of

merits since the beginnings in 1997 to 2007. The review [2] provides a critical overview on the development in the field of organic analytes, based on the summary, which characterizes selected studies devoted to particular organic analytes since the beginnings in 1997 to 2008. Furthermore, an outlook in current trends in research using BDD-based sensors including their modification and miniaturization is given. In the overview [11], progress since 2008 to 2013 in the development and applications of bare BDD electrodes in voltammetry of organic compounds is summarized. Attention is paid to important issues reflected in electroanalytical studies, *e.g.* fouling and pre-treatment of BDD surface, influence of boron doping level on performance of BDD-based sensors, and application of adsorptive stripping voltammetry. The review [33] is devoted to detection of aromatic hydrocarbons and their derivatives using either BDD film electrodes or carbon paste electrodes, popular sensors in environmental detection.

BDD electrodes are used for the determination of wide range of electrochemically both reducible and oxidisable organic compounds. As seen in the table 2.1, that brings an overview of selected applications of BDD-based sensors in organic analysis since 2009 to 2017, prevalence of oxidisable analytes is remarkable.

Organic compounds can be oxidised on BDD electrodes directly by electron transfer from BDD surface to a compound, or indirectly by oxidising entities, *e.g.* hydroxyl radicals, generated on electrode surface by reaction given in Eq. 1.

Reducible compounds are in minority, most of the described methods rely on the reduction of the nitro group at the aromatic skeleton. Methods based on reductive determinations benefit from the low sensitivity of BDD surface to dissolved oxygen [4-5, 34], however, they are still not that frequent. Despite the fact that BDD is less sensitive to oxygen reduction than other electrode materials, its presence in HPLC-ED or FIA-ED setups causes increase in the background current and also limits the useful working electrode potential window for amperometric determination of reducible organic analytes [35-37].

Initially, BDD electrodes have been considered as resistant to fouling due to the paraffin-like, hydrogen terminated surface [38]. Nevertheless, it has been proven that this is not a general rule and a lot of studies demonstrated fouling problems. Aromatic amines [39-41] and phenolic compounds [4] can cause BDD passivation, because both compounds produce reactive radicals (phenoxy radicals or amino cation radicals) capable of further dimerization and polymerization on the electrode surface. Formation of polymeric film on the electrode surface causes rapid deactivation of electrode by blocking

electron transfer and slowing down further oxidation. The chemical and electrochemical properties of diamond electrodes were found to be strongly influenced by the surface treatment [16]. Electrochemical pre-treatment can be applied for conditioning of the electrode surface, enhancement of the voltammetric signals, preventing the passivation of electrode surface, and ensuring of repeatable and reproducible response of particular analytes.

The basic way for conditioning of the electrode surface is its electrochemical anodic oxidation (~ < +2.0 V) for few minutes in the region of water decomposition (Eq. 1), leading to O-terminated BDD surface [42-45]. This pre-treatment can be performed as the long-lasting activation or before each scan. An alternative method to obtain O-BDD surface is repeated application of short potential pulses close or in the onset of the decomposition of supporting electrolyte curve [46-48].

The cathodic pre-treatment (~ < –2.0 V), leading to H-terminated BDD surface, has to be applied just before the electrochemical experiments to ensure reliable and reproducible results, especially when the electrode has not been used for a long period of time due to its instability in air [49]. It caused enhanced electrochemical activity – faster electron transfer for $[Fe(CN)_6]^{4-/3-}$, signal increase and improved repeatability. The importance of cathodic pre-treatment was investigated for the detection of selected chlorophenols [50], estriol [51] or butylated hydroxyanisole [52].

A mixed-mode of surface activation includes application of cyclic voltammetry (CV) in acidic media to the onset of decomposition on supporting electrolyte curve [4-5, 53-59] that is recommended by commercial suppliers of BDD electrodes and can also lead to stabilization of their electrochemical response.

Further, the combination of more types of pre-treatment is used (both anodic and cathodic [34, 46, 60-72], long-lasting activation before the electrochemical experiments with another activation before each scan [44, 51], anodic and/or cathodic pre-treatment coupled with CV [67], see examples in table 2.1 in the column BDD electrode, pre-treatment).

Bare BDD surfaces have been considered as relatively inert to the adsorption for organic compounds; however, studies using anodic adsorptive stripping voltammetry (AdSV) for oxidisable compounds have been reported. Major advantages of the AdSV, where the analyte is partly deposited on the working electrode by various mechanism (*e.g.* adsorption, extraction, chemical binding) include low detection limits coupled with good selectivity and reproducibility due to the *in situ* pre-concentration step. An electrode material is needed providing not only good adsorption of the analyte but also a stable and reproducible electrode surface, which is a property of BDD films. Methods based on AdSV

on these films include utilization of the adsorption of the analyte itself [44-45, 73-74] or the adsorption of surfactants interacting with organic analytes on the BDD surface [47, 61, 70-72, 75].

Surfactants are usually linear molecules with a hydrophilic head and a hydrophobic end and are often used as selective masking agents to improve selectivity and sensitivity of electrochemical analysis and they also play a very important role in the electrode reaction, not only by solubilizing the organic compounds but also by providing specific orientation of the molecules on the electrode interface. Adsorption of surfactants on electrodes and solubilisation of electrochemically active compounds in micellar aggregates might significantly change the redox potential, charge transfer coefficients, and diffusion coefficients of electrode processes, thus changing the stability of electrogenerated intermediates and electrochemical products, which becomes an advantage for its use in electrochemistry and modification of electrodes [72].

This leads to improved analytical figures of merit as presented for detection of capsaicin [72] or benzo(*a*)pyrene [47] in the presence of sodium dodecylsulfate, and benzophenone-3 [70-71], 4-chloro-3-methylphenol [75] or resveratrol [61] in the presence of cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide). The main disadvantage of this approach is the necessity of manual polishing of the BDD surface after each scan. On the other hand, the interaction of the surfactant or transfer of the adsorbed species from the matrix to pure supporting electrolytes can substantially increase the selectivity of the method.

Perspective trends in electroanalysis include miniaturization of BDD sensors for their utilization in *in vivo / in vitro* analysis or for detection in CE or micro total analytical systems [76-77]. Numerous attempts were made to design BDD-based microelectrodes, BDD microdisc arrays or other variations, summarized in reviews [9, 12, 78]. The ability of microelectrodes to deliver steady state responses at suitable scan rates, low analyte concentrations and in the absence of any supporting electrolyte is an attractive feature when comparing them to conventional macroelectrodes. These responses are usually obtained when the scan rate is kept low so as to minimize the ohmic drop [79]. The main drawback of microelectrodes, low total current output, can be avoided by construction of microelectrode arrays (MEA). In this way, the total current can be multiplied (for ideal arrays up to 1000 fold) as it corresponds to the total area of the electrode including the isolated portions between the single microelectrodes. The noise corresponds to the sum of their areas [9]. Regardless of the miniaturization trend, benefits of increase of active electrode area and roughness of the surface were demonstrated in detection of dopamine

and nonenzymatic amperometric detection of glucose using 3D-structured BDD nanorod forest electrode [80]. Also the overlap problem of oxidation peaks for determination of dopamine and ascorbic acid in their mixture can be solved by using BDD MEA [42]. Recent progress and achievements concerning diamond nanoelectrochemistry (nanotextures, nanowires, networks, porous film, nanoelectrodes, undoped nanoparticles, and boron-doped particles) are considered in review [81].

Even though diamond surfaces are chemically inert, photochemical, electrochemical and chemical approaches have shown their strength in tethering functional groups to this interface. Many studies exist on modified BDD surfaces and their utilizations in construction of BDD-based sensors [10, 82-84]. Promising strategies include *e.g.*, amination or carboxylation of BDD surface to bond various receptor biomolecules [85-86], or covering of BDD thin films by molecularly imprinted conducting polymers such as polypyrrole [87-88]. Special interest for the development of molecularly imprinted polymer (MIP) is related to their potential to recognize selected molecules. The typical synthesis of the molecularly imprinted polypyrrole involves the formation of polymer in the presence of template molecules. The template molecules that are used for MIP preparation are usually the same as target molecules. Conductive BDD powder and polyester binder were used to fabricate screen-printed electrode on polyimide sheets and exhibited greater durability to fouling by dopamine than carbon screen-printed electrode [89]. Further development in this field can be foreseen thanks to the progress in the deposition technology of the BDD films, their modification and widening insights in the principles of biosensing.

The commercialization of BDD electrodes at the beginning of this century accelerated the development. Specialized electroanalytical studies using batch voltammetric and amperometric methods or liquid flow methods with amperometric detection at BDD electrodes under optimized conditions in pure solvents proved in most cases notable reproducibility, high sensitivity, low detection limits, and linear dynamic range often over three orders of magnitude compared to other, particularly carbonaceous electrode materials.

Table 2.1. Selected applications of BDD-based sensors in organic analysis

Analyte	BDD electrode, pretreatment	Electroanalytical method and conditions; (matrix)	*LDR* [µmol L^{-1}]	*LOD*[A] [µmol L^{-1}]	Ref.
Neurotransmitters, their metabolites and precursors					
Epinephrine	Windsor Scientific	**SWV,** 0.5 M $HClO_4$; (human urine)	0.7–60	0.21	[90]
Dopamine Ascorbic acid	CSEM; 3 $mA.cm^{-2}$ in 0.5 M H_2SO_4 and then in 0.1 M KOH	**SWV,** 0.1 M $HClO_4$,	0.49–5.4 [e] 1.5–54 [e]	0.28 [e] 0.97 [e]	[91]
Dopamine Ascorbic acid	BDD-MEA, Adamant Technologies SA; +1.92 V, 60 min in 0.1 M KOH	**DPV,** phosphate buffer pH 7.4	0.2–1[e] 20–200 [e]	0.44 [e] 7.5 [e]	[42]
Dopamine	BDD-NEAs, Fraunhofer; –2.4 V, 45 s (H-terminated), +2.4 V, 45 s (O-terminated) in 2 M H_2SO_4	**DPV,** phosphate buffer; in presence of 100 µM ascorbid acid	0.1–20	0.1 [H]	[14]
Dopamine Adenosine	Thermo Scientific ESA.; Thermo Scientific ESA 5041 analytical cell, no pre-treatment	**HPLC-AD**, mobile phase: 45 mM $(NH_4)_3PO_4$, 1.1 mM $Na_4P_2O_7$, and 4% acetonitrile, adjusted to pH 3 using phosphoric acid	0.001–5 [e] 0.001–200 [e]	0.000021 [e, B] 0.0012 [e, B]	[92]
Melatonin	Windsor Scientific polished with 0.01 and 0.03 µm grade alumina aq. slurry	**CV**, 1 M KCl, presence of 10 % CMC and 90 % DCP; (pharmaceutical formulations)	8610–17220	258 [C]	[93]
Phenolic compounds					
Bisphenol A Bisphenol F	WindsorScientific; sonicated in ethanol and deionised water 5 and 10 min; CV from –0.5 V to +2 V, 50 mM phosphate	**CE-AD**, 50 mM Na_2HPO_4-NaOH pH 10.5 / acetonitrile (97/3, v/v), (SPE – drinking water samples)	1–400 0.1–10 [SPE] 1–300 0.05–5 [SPE]	0.3 0.06 [SPE, D] 0.3 0.01 [SPE, D]	[58]

4-Ethylphenol	buffer pH 7		1–300 0.05–5 [SPE]	0.3 0.01 [SPE, D]	
Bisphenol A diglycidil ether			1–200 0.05–5 [SPE]	0.5 0.01 [SPE, D]	
Bisphenol A	Adamant Technologies; 250 mA.cm^{-2}, 60 s and –250 mA.cm^{-2}, 180 s in 0.5 M H_2SO_4	**DPV**, 0.5 M H_2SO_4	0.44–5.2	0.21[C]	94
Bisphenol A	MWCNTs / tyrosinase film BDD	**CV**, phosphate buffer pH 7.2; (water samples)	0.00001–0.1	0.00001	85
Butylated hydroxyanisole	CSEM; 0.5 M H_2SO_4, –1 mA.cm^{-2}, 120 s and +1 mA.cm^{-2}, 120 s	**SWV**, 0.01 M KNO_3 pH 1.5 / ethanol (7/3, v/v); (food products)	0.6–10	0.14 [C, e]	95
Butylated hydroxytoluene			0.6–10	0.25[C, e]	
Butylated hydroxyanisole	CSEM; 0.5 M H_2SO_4, –1 mA.cm^{-2}, 120 s and +1 mA.cm^{-2}, 120 s	**FIA-MPA**, 0.01 M KNO_3 pH 1.5 / ethanol (7/3, v/v); (food products)	0.05–3	0.03 [e]	96
Butylated hydroxytoluene			0.7–70	0.4 [e]	
Catechol	As-grown BDD electrode Nanograss array BDD electrode; both sonicated in 2-propanol and deionised water	**CV**, 0.07 M phosphate buffer	5–100	2.8[C] 1.3[C]	97
Caffeine Chlorogenic acid	Windsor Scientific; +2 V, 180 s in 0.5 M H_2SO_4	**SW-AdSV**, BRB pH 10; 60 s preconcentration; (beverages)	3.1–28.3 [e] 14–127 [e]	0.551 [e, C] 1.26 [e, C]	45

Chlorogenic acid	Windsor Scientific; polished with slurries (0.01 μm Al_2O_3 on a smooth polishing pad), then rinsed with deionized water	**SW-AdSV**, BRB pH 3.0, accumulation 120 s at +0.40 V	0.706–11.29	0.138 [C]	[74]
4-chloro-3-methylphenol	Windsor Scientific; +2.40 V, 900 s in stirred 0.10 M H_2SO_4. Absence of cetyltrimethylammonium bromide: +2.40 V, 30 s, N_2 atmosphere.	0.1 M phosphate buffer pH 2.0		[C]	[75]
		DCV	5–100	0.85	
		DPV	2.5–100	0.46	
		SWV	5–100	0.34	
	Presence of cetyltrimethylammonium bromide: polishing pad and alumina with subsequent rinse by deionized water after each scan.	**DPV**, B/C ratio/ppm:			
		500	1–100	0.25	
		1000	1–100	0.29	
		2000	0.5–100	0.11	
		4000	0.5–100	0.12	
		8000	0.9–100	0.20	
p-cresol	Biofunctional ZnO nanorod microarrays / nanocrystalline BDD	**Amperometry;** 0.1 M phosphate buffer pH 7	1–175	0.1 [C]	[98]
4-chlorophenol			1–150	0.2 [C]	
Phenol			1–150	0.25 [C]	
Estradiol	Element Six; oxidised BDD: CV from –1.5 V to +2.5 V, 10 min, in 0.1 M HNO_3;	**SWV**, 0.1 M phosphate buffer pH 12	5–100	0.86; 1.6 [C]	[53]
Estradiol	CB/BDD		5–100	0.0021; 0.022 [C]	
Nonylphenol				0.003	
Bisphenol A				0.07	
Ethynylestradiol				0.009	

Estriol	BDD film electrode, B/C 8000 ppm, –3 V, 3 min in 0.5 M H_2SO_4, then –3 V, 30 s in supporting electrolyte before each run	**SWV**, NaOH pH 12; (pharmaceutical sample, urine)	0.2–20	0.17 [E]	51
Parabens Methylparaben Ethylparaben Propylparaben	BDD, B/C8000 ppm, thin layer arrangement; +3 V, 30 s; then –3 V, 30 s	**HPLC-AD,** mobile phase 0.025 M phosphate buffer pH 7 / acetonitrile (4:6, v/v); (shampoos)	0.0125–0.5 %, w/w	 0.01 %, w/w, D 0.01 %, w/w, D 0.01 %, w/w, D	60
Phenol	BDD/AuNPs/Tyr; stored in 0.1 M phosphate buffer pH 7 at 4 °C	**SWV**, 0.1 M phosphate buffer pH 7	0.10–11.0	0.07	86
Phenol	HFCVD BDD treated with H_2 microwave plasma, 400 W, 20 min	**SWV**, 0.05 M H_2SO_4	40–250	0.85 [C]	99
Phenol	HFCVD BDD; +2.8 V, 10 s and –2.8 V, 10 s	**SWV**, 0.05 M H_2SO_4	30–130	1.06 [C]	46
Resveratrol	Windsor Scientific; –1.5 V, 180 s, +1.5 V, 180 s, 0.5 M H_2SO_4; polished manually with Al_2O_3 slurry (0.01µm), then rinsed with deionized water	**SW-AdSV**, 0.1 M HNO_3 with 100 µM hexadecyltrimethylammonium bromide	0.1–26	0.0276 [C]	61
Nitrophenols and other nitroaromatics					
Aminonitrophenols (xAyNP)	Adamant Technologies; 1M HNO_3, –3 V, 10 s and +3 V, 10 s	**DPV ^{ox},** BRB / methanol (9/1, v/v)		[F]	62
2A3NP		pH 2	1–100	0.5	
2A4NP		pH 12		0.9	
2A5NP		pH 8		0.6	

4A2NP		pH 8		0.5
4A3NP		pH 2		0.4
		DPV ^{red}, BRB / methanol (9/1, v/v)		
2A3NP		pH 2	0.2–100	0.3
2A4NP		pH 6	0.2–40	0.4
2A5NP		pH 8	0.4–100	0.3
4A2NP		pH 2	1–100	0.6
4A3NP		pH 6	0.4–100	0.2
2A3NP		**HPLC-AD ^{ox},** phosphate buffer	0.2–100	0.31
2A4NP		pH 2 / methanol (65/35, v/v)		0.15
2A5NP				0.21
4A2NP				0.16
4A3NP				0.18
Nitrophenols	Windsor Scientific; CV from –2.5 to +2.5 V in 1 M HNO_3			K 4
2NP		**DPV ^{red}**, BR buffer pH 4.0; (water samples)	0.4–80 [a]	0.3/0.02 [SPE, a]
			0.4–200 [b]	0.2/0.02 [SPE, b]
			0.8–20 [c]	0.3/0.2 [SPE, c]
4NP		**DPV ^{red}**, BR buffer pH 6; (water samples)	0.8–200 [a]	0.1/0.03 [SPE, a]
			0.8–20 [b]	0.1/0.04 [SPE, b]
			0.4–20 [c]	0.1/0.2 [SPE, c]
		DPV ^{ox}, BR buffer pH 11; (water samples)	4–80 [a]	0.5 [a]
			4–40 [b]	1 [b]
			4–20 [c]	1 [c]
2,4DNP		**DPV ^{red}**, BR buffer pH 4; (water samples)	0.4–20 [a]	0.1/0.02 [SPE, a]
			0.4–20 [b]	0.1/0.02 [SPE, b]
			0.8–20 [c]	0.6/0.2 [SPE, c]

		DPV ^{ox}, BR buffer pH 10; (water samples)	2–20 [a] 0.8–20[b] 2–20[c]	0.3 [a] 0.5[b] 0.3[c]	
Nitrophenols	Windsor Scientific; CV from –2.5 to +2.5 V in 1 M HNO_3	**HPLC-AD** ^{red}**,** 0.05 M acetate buffer pH 4.7–methanol (58/42, v/v); (water samples)		F	**5**
2NP			2–80 [a], 2–100 [b], 4–100 [c]	1.2 [a], 1.5 [b], 1.8 [c]	
4NP			2–100 [a], 1–100 [b, c]	0.8 [a], 1.3 [b, c]	
2,4DNP			2–60 [a], 1–100 [b, c]	0.7 [a, b, c]	
2NP		**HPLC-AD** ^{ox}**,** 0.05 M phosphate buffer pH 6.75 – methanol (65/35, v/v); (water samples)	6–80 [a], 4–100 [b, c]	1.0 [a], 2.9 [b], 3.5 [c]	
4NP			2–80 [a], 2–100 [b, c]	1.5 [a], 2.5 [b], 2.4 [c]	
2,4DNP			4–100 [a, c], 2–100 [b]	0.6 [a], 1.5 [b], 1.2 [c]	
Trinitrotoluene	MPCVD nanocrystalline BDD	**SWV**, 0.05 M KCl / acetonitrile (95/5, v/v) pH 7; (sea water)	0.048–0.964 0.550–10.479	0.044	100
Amines					
2-Aminobiphenyl	Si(100), MPCVD nanocrystalline BDD	**DPV**, BRB pH 7	0.16–10 [HPLC]	0.2 [HPLC]	101
4-Aminobiphenyl		**HPLC-AD**, mobile phase acetonitrile / 0.01 M phosphate buffer pH 3 (40/60 v/v); (azo dye sunset yellow with SPE)	0.09–10 [HPLC]	0.13 [HPLC]	
1-Aminonaphtalene			0.02–10 [HPLC] 1–100 [DPV]	0.07 [HPLC] 2.96 [DPV]	
2-Aminonaphtalene			0.02–10 [HPLC] 1–66 [DPV]	0.06 [HPLC] 1.48 [DPV]	
2-Aminobiphenyl	Si(100), MPCVD microcrystalline BDD; thin layer (T) and wall jet (W) arrangement	**HPLC-AD**, mobile phase 0.01 M acetate buffer pH 5 / acetonitrile / methanol (40/30/30 v/v/v);	0.4–10 [T] 0.06–100 [W]	0.54 [T, F] 0.070 [W, F]	102
3-Aminobiphenyl			0.2–10 [T] 0.06–100 [W]	0.25 [T, F] 0.075 [W, F]	
4-Aminobiphenyl			0.2–10 [T] 0.06–100 [W]	0.35 [T, F] 0.065 [W, F]	

2-Aminobiphenyl	Si(100), MPCVD microcrystalline BDD; +2.4 V, 60 min in 0.1 MH_2SO_4	**HPLC-AD,** mobile phase 0.01 M acetate buffer pH 5 / acetonitrile / methanol (40/30/30 v/v/v); (drinking and river water with SPE)	0.2–10 0.1–10 [c] 0.025–0.1 [c, SPE] 0.005–0.1 [b, SPE]	0.21 0.21[c] 0.0084 [c, SPE] 0.0034[b, SPE]	[43]
3-Aminobiphenyl			0.2–10 0.1–10 [c] 0.0025–0.1 [c, SPE] 0.0075–0.1 [b, SPE]	0.3 0.28 [c] 0.013 [c, SPE] 0.0044 [b, SPE]	
4-Aminobiphenyl			0.2–10 0.2–10 [c] 0.005–0.1 [c, SPE] 0.0075–0.1 [b, SPE]	0.62 0.55 [c] 0.017 [c, SPE] 0.011 [b, SPE]	
Polycyclic aromatic hydrocarbons					
Benzo[a]pyrene	Windsor Scientific; polished with 0.01 μm alumina, +1.3 V, 30 s in supporting electrolyte	**SW-AdSV,** BRB pH 2.0 containing 2.5×10^{-4} M sodium dodecylsulfate; (tap water)	0.016–0.2	0.00072 [C]	[47]
1-hydroxypyrene	Windsor Scientific Ltd	**HPLC-AD/SPE,** mobil phase methanol / 0.05 M phosphate buffer pH 5 (80:20 v/v); (urine)	0.01–10	0.013	[103]
1-nitropyrene	Windsor Scientific Ltd; oxidative scan +0.15 to +0.5V; +0.23 to + 0.68 V; 50× pulses + 0.8V, 0.3 s and –0.5 V, 0.3 s	**DPV,** methanol / BRB pH 3 (70:30 v/v)	1–100	0.3 [G]	[48]
1-aminopyrene		**DPV,** methanol / BRB pH 5 (70:30 v/v); (urine)	0.1–10	0.06[G]	
1-hydroxypyrene			0.1–10	0.1[G]	
Pharmaceuticals					
Amlodipine	polycrystalline HFCVD BDD electrode	**DPV,** BRB pH 5; (pharmaceuticals, urine)	0.2–6 6–38	0.07 [C]	[104]

Albendazole	Adamant Technologies; +0.5 A.cm^{-1}, 30 s or –0.5 A.cm^{-1}, 180 s in 0.5 M H_2SO_4	**SWV**, 0.05 M H_2SO_4 **DPV,** 0.05 M H_2SO_4	0.200–7.41 0.0797–8.36	0.162 [C] 0.0625 [C]	[105]
Bezafibrate	Adamant Technologies; 0.5 M H_2SO_4, +0.5 A.cm^{-2}, 20 s, then –0.5 A.cm^{-2}, 80 s	**SWV**, BRB pH 2, (pharmaceutical formulations – tablets)	0.1–9.1	0.098 [C]	[106]
Brimonidine	Windsor Scientific; polished with aqueous slurry of Al_2O_3 powder, +1.2 V, 60 s, and –1.5 V, 60 s, in 0.25 M H_2SO_4	**DPV,** 0.1M H_2SO_4 **SWV**,0.1M H_2SO_4 (eye drops)	2–30 0.5–15	0.631 [C] 0.128 [C]	[34]
Captopril	CSEM; +3 V, 30 s and –3 V 30 s in 0.1 M $HClO_4$	**SWV,** BRB pH 9	92.04–460.21	0.759	[63]
Captopril Hydrochlorothiazide	Adamant Technologies; +0.01 A, 1000 s in 0.04 M BRB pH 2, then –0.01 A, 1000 s in 0.1 M H_2SO_4	**BIA-MPA**, 0.01 M acetic acid / acetate buffer pH 4.7; (pharmaceutical formulations)	27–81 [e] 10–30 [e]	0.14 [e, H] 0.27 [e, H]	[107]
Ciprofloxacin	Adamant Technologies	**BIA-AD**, BRB pH 10, dispensing rate 153 µL.s^{-1}	1–100	0.3	[108]
Codeine	Windsor Scientific; CV from –2 to +2 V in 1 M HNO_3, microwave-inducted hydrogen plasma, 5 min	**DPV**, BRB pH 7; (pharmaceuticals, human urine)	0.1–60	0.08 [C]	[54]
Coumarin	BDD film (8000 ppm boron), +3 V, 10 min and –3 V 10 min	**SWV,** 0.1 M BRB pH 8; (aq. infusion of *Mikania glomerata*)	0.00499–0.1	0.01 [C]	[64]
Erythromycin	As-grown double-bias-enhanced HF CVD BDD, CV from –2 to +2Vin the supporting electrolyte	**SWV**, ammonium acetate buffer pH 5, (water samples)	6.8–68.1	1.1 [C]	[59]

Hydrochlorothiazide (HCTZ) Losartan (LOS)	Adamant Technologies; +0.5 A.cm^{-1}, 40 s in 0.5 M H_2SO_4	**SWV,** 0.1 M BRB pH 8 **DPV**, BRB pH 9.5	4–83 [1, HCTZ] 4–74 [2, HCTZ] 4–74 [2, LOS] 1–20 [1, LOS] 3–74 [2, HCTZ] 3–74 [2, LOS]	1 [1, HCTZ, C] 1.8 [2, HCTZ, C] 0.98 [2, LOS, C] 0.92 [1, LOS, C] 1.2 [2, HCTZ, C] 0.95 [2, LOS, C]	109
Glutathion (GSH)	BDD microelectrode; ultrasonication in 2-propanol, 10 min	**ChrA**, 0.1 M phosphate buffer pH 7.4	0–10000	300 [C]	110
Ibuprofen	Adamant Technologies, 0.50 cm^2; +0.01 A, 1000 s in 0.04 M BRB and –0.01 A, 1000 s in 0.1 M H_2SO_4/ ethanol (9/1 v/v)	**DPV**, 0.1 M H_2SO_4/EtOH (9/1 v/v)	20–400	5 [C]	111
Methamphetamine	polycrystalline HF CVD BDD electrode; +2 V, 180 s and –2 V, 180 s in 1 M H_2SO_4	**DPV**, BRB pH 10; (human urine)	0.07–80	0.05 [C]	65
Nimesulide	Adamant Technologies, wall jet arrangement, 7 mm^2; –10.5 mA, 60 s, then +11.7 mA, 30 s in 0.5 M H_2SO_4	**FIA-MPA;** phosphate buffer pH 7 / EtOH (9/1 v/v); **(**pharmaceutical formulations)	0.2–80	0.081 [C]	112
Paracetamol Caffeine Orphenadrine	CSEM; +0.5 A.cm^{-2}, 30 s and –0.5 A.cm^{-2}, 150 s in 0.5 M H_2SO_4	**SWV**, 0.5 M H_2SO_4; (pharmaceutical formulations)	0.54–61 [e] 0.78–35 [e] 0.78–35 [e]	0.23 [e, C] 0.096 [e, C] 0.084 [e, C]	113
Paracetamol Ibuprofen	Adamant Technologies; 0.13 cm^2; +0.01 A, 60 s in 0.5 M H_2SO_4	**DPV**, 0.1 M H_2SO_4/EtOH (9/1 v/v)	20–400	7.1 [C] 3.8 [C]	114

Paracetamol Nimesulide	Adamant Technologies, 0.13 cm^2; –0.01 A, 1000 s in 0.1 M H_2SO_4	**BIA-MPA**, 0.1 MH_2SO_4/EtOH (7/3 v/v)	331–1654 [e] 32–162 [e]	1.94 [e, H] 0.96 [e, H]	115
Paracetamol Tramadol	NeoCoat; 0.5 M H_2SO_4, 0.04 A cm^{-2} or−0.04 A cm^{-2}, 30 s or 180 s	**FIA-MPA**, 0.05 M H_2SO_4,(pharmaceutical samples and synthetic biological fluids)	1–100 [e] 0,08–10 [e]	0.03 [e] 0.04 [e]	116
Penicilin V	Windsor Scientific; no pre-treatment	**DPV**, acetate buffer pH 4; (pharmaceutical formulations, human urine)	0.5–40	0.25 [C]	117
Propylthiouracil	Adamant Technologies; 0.5 M H_2SO_4, 30 s, +0.5 A.cm^{-2}, then 150 s, –0.5 A.cm^{-2}	**DPV**, BRB pH 2	1–29.1	0.9 [C]	118
Xylitol	CSEM; +3 V, 120 s and –3 V, 240 s in 0.5 M H_2SO_4	**SWV,** 0.1 M phosphate buffer pH 7; (mouthwash products)	5–64	1.3 [C]	66
Agrochemicals					
Atrazine	Windsor Scientific; CV from –2 to +2 V in 1 M HNO_3	**SWV**, BRB pH 3; (river water)	0.05–40	0.01 [C]	55
Carbaryl Paraquat	BDDGR (Windsor Scientific Ltd – modified); 15 CV (stable and reproducible background current)	**DPV,** acetate buffer pH 5.6; natural apple juice	1–6 0.2–1.2	0.07 [C, d] 0.17 [C, e] 0.01 [C, d] 0.4 [C, e]	119
Linuron	Adamant Technologies; –0.5 A.cm^{-2}, 80 s in 0.5 M H_2SO_4 BDD/ PtNPs	**DPV**;BRB pH 2 **SWV**;BRB pH 2, (water samples) **DPV**;BRB pH 2 **SWV**;BRB pH 2	0.46–26.6 0.61–26 0.61–6.6 2.1–14.9	0.12[C] 0.18[C] 0.18[C] 0.82[C]	120

Kresoxim-methyl	Adamant Technologies, 1 cm^2; GCHP, + 0.01 A, 1000 s, then –0.01 A, 1000 s, then CV from –0.5 to +1.5 V in 0.1 M H_2SO_4	**SWV**, 0.05 M acetate buffer pH 4; SPE, (grape juices)	0.87–34	0.26[C]	121
Metamitron	Windsor Scientific;+2.0 V, 60 s in 1 M HNO_3, then –2.0 V, 60 s. Then rinsed with deionized water and polished with a piece of damp silk cloth. Finally, 20 CV from –1.0 to +2.0 V in 1 M HNO_3	**DPV**, BRB pH 2 **SWV**, BRB pH 2 (river water)	0.5–110	1.2 [C] 0.98 [C]	67
Methiocarb	Windsor Scientific; no regeneration	**DPV,** 0.1 M H_2SO_4 in MeOH (10 %, v/v)	4.4–244	0.67 [C]	122
Methomyl	BDD electrode (surface area 0.36 cm^2), +3.0 V, 120 s, −3.0 V, 240 s in 0.5 M H_2SO_4	**SWV** **DPV** BRB pH 2; river water, tap water, commercial formulations	66–420 5.0–410.0	19 1.2	68
Picloram	Windsor Scientific; CV from –2 V to +2 V, 10 min, 1 M HNO_3	**DPV**; 1 M H_2SO_4; (tap and natural water, human urine)	0.5–48.1	0.07 [C]	56
Triclopyr	Windsor Scientific; +2 V, 60 s, then –2 V, 60 s, then CV 20 cycles from –1 to +2 V in 1 M HNO_3	**DPV**; BRB pH 2 (tap water, river water, human urine) **SWV**; BRB pH 2	1.0–108.8 2.5–99	0.82 [C] 1.85 [C]	57
Ziram	Windsor Scientific;+2.0 V, 180 s,then −2.0 V, 180 sin 1 M H_2SO_4	**FIA**, BRB pH 4	0.01–1	0,0027 [C]	69

Aminoacids, peptides, proteins					
Guanin	WindsorScientific	**DPV**, BRB pH 6; (fish sperm and human placenta DNA, urine)	0.21–23 [d] 0.3–19 [e]	0.037 [d, C] 0.19 [e, C]	123
Adenin			0.12–25 [d] 0.3–19 [e]	0.019 [d, C] 0.067 [e, C]	
Tryptophan	NeoCoat; NWs/BDD–UV irradiation in air, 2 h, low pressure mercury arc lamp	**DPV**, 0.1 M KCl pH 7.4	5–500	5 [d, BDD, I] 10 [e, BDD, I] 0.5 [d, NWs/BDD, I] 0.5 [e, NWs/BDD, I]	124
Tyrosine				5 [d, BDD, I] 20 [e, BDD, I] 0.2 [d, NWs/BDD, I] 0.2 [e, NWs/BDD, I]	
Food components and additives					
Glucose	BDDNF	**Amperometry;** 0.1 M NaOH, presence of AA and UA	7000–15000	0.2	80
Glucose	Nanocrystalline BDD, sonicated in isopropanol, acetone, ultrapure water 15 min	**LSV**, 0.1 M NaOH, presence of AA and UA	40–11000	not given	125
Glucose	L-BDD NWs, 30 min in 0.5 M H_2SO_4	**LSV,** 0.1 M NaOH pH 12.5	60–8000	60 [I]	126

Vanillin	Windsor Scientific; daily +3 V, 180 s in 0.5 M H_2SO_4; 30 s experimental conditions, +3 V before each voltammetric experiment	**SW-AdSV**, phosphate buffer pH 2.5, 60 s preconcentration	3.3–380	0.16 [C]	[44]
Other compounds					
Benzophenone-3	CSEM; +3.2 V and –2.8 V, 30 s in 0.1M $HClO_4$	**SWV,** 0.1M BRB pH 6 in the presence of cetyltrimethylammonium bromide; (commercial sunscreen)	15–195	0.137 [C]	[70]
Benzophenone-3	MPCVD BDD (BDD_A); Windsor Scientific (BDD_B); +2.4 V, 60 s in 0.5 M H_2SO_4 BDD_A:+3 V, –3 V, +3 V, –3 V, +3 V, each for 10 s in 0.5 M H_2SO_4.BDD_B: polishing pad and alumina with subsequent rinse by deionized water after each scan.	**DPV**, BRB pH 12 B/C ratio/ppm(BDD_A): 2000 4000 8000 Presence of cetyltrimethylammonium bromide (BDD_B):	 1–100 1–100 2.5–100 10–75 0.8–10 0.4–0.8	 1.5 1.9 0.8 0.1	[71]
Butylated hydroxyanisole	Adamant Technologies; 0.05 MH_2SO_4, –3 V, 900 s	**BIA**, 0.1 M $HClO_4$ / ethanol (50/50 v/v)	10–50	0.05	[52]
Capsaicin	Windsor Scientific; –3 V and +3.0 V in 0.5 M H_2SO_4, 180 s; before each experiment polished manually with Al_2O_3 slurry (0.01mm), then rinsed with deionized water	**SW-AdSV,** BRB pH 1.0 with 800 µM sodium dodecylsulfate; (commercial pepper products)	0.16–20	0.034 [C]	[72]
Cholesterol	AgNPs/BDD coupled with PAD	**ChrA**, phosphate buffer pH 7.4; (bovine serum)	10–7000	6.5 [C]	[127]

Hydrazine	Au-NPs BDD Pt-NPs BDD	**DPV**, presence of APIs	10–1000	11.1 [J] 3.3 [J]	[128]
Hydrazine	BDD film on titanium sheet	**DPV**, phosphate buffer pH 7	2–400	1 [C]	[129]
Nicotine	Windsor Scientific	**DPV**, BRB pH 10; (cigarettes, cigar, pharmaceuticals)	0.5–202.5	0.3 [C]	[130]
Ozone	Si (111) – BDD microelectrodes	**CV**, electrolyte-free media	0.49–740	0.185	[131]
Rutin	WindsorScientific; manually polished with Al_2O_3 slurry (0.1 μM), then ultrasonically cleaned, no pre-treatment	**SW-AdSV**, BRB, pH 4.0, accumulation 60 s at +0.2 V	0.0164–0.164	0.00278 [C]	[73]
α-tocopherol Ubiquinone	Si-BDD [132]; UV/ozone treating 60 min	**FIA-AD**, mobile phase: 50 mM $NaClO_4$ in MeOH; 50 mM $NaClO_4$ in MeOH/hexane (76.7/23.3 v/v)	0.5–100 0.5–100	0.041 0.017	[133]
Urea	Element Six; Pt-NPs/BDD, sweeping cell potential between –1 V and +2.5 V in 0.5 M HNO_3, 45 cycles	**DPV**, phosphate buffer pH 8.3, (protein urease)	1000–25000	1790	[134]

[a] – in deionized water; [b] – in drinking (tap) water; [c] – in river water; [d] – individual determination; [e] – simultaneous determination; [A] – *LOD* for *S/N* = 3, if not otherwise specified; [B] – $LOD = 3.3\ S_B/b$, where S_B is standard deviation for the blank solution and *b* the slope of the linear concentration dependence; [C] – $LOD = 3\ S_B/b$, where S_B is standard deviation for the blank solution and *b* the slope of the linear concentration dependence; [D] – *LOD* measured in matrix; [E] – $LOD = 2\ S_B/b$, where S_B is standard deviation for the blank solution and *b* the slope linear concentration dependence; [F] – *LOD* calculated as the concentration of the analyte which gave a signal ten times the standard deviation of the lowest evaluable concentration; [G] – *LOD* calculated using three times the standard deviation corresponding to the lowest point of concentration dependence; [H] no details on calculation given; [I] – *LOD* determined from five blank noise signals (95% confidence level); [J] – $LOD = \mu + 3\ S_B$, where μ and S_B are the mean and standard deviation of the background response; [K] – $LOQ = 10\sigma/m$ where σ is the standard deviation of the

signal measured for the lowest analyte concentration corresponding to calibration plot, *m* is slope of the analytical curve; ^{ox} – oxidation; ^{red} – reduction; ^{SPE} – using SPE; $^{\%, w/w}$ – concentration in mg/mL; AD – amperometric detection; AdSV – adsorptive stripping voltammetry; AgNPs – silver nanoparticles; APIs – active pharmaceutical ingredients; AuNPs – gold nanoparticles; BDDGR – graphene-modified boron-doped diamond electrode; BIA – batch-injection analysis; BRB – Britton-Robinson buffer; CB – carbon black; CCL – Center for Coatings and Laser Applications; CE – capillary electrophoresis; ChrA – chronoamperometry; CMC – carboxymethyl celulose; CSs – carbon spheres; CSEM – Centre Suisse de Electronique et de Microtechnique SA; CV – cyclic voltammetry; DCP – dibasic calcium phosphate; EIS – electrochemical impedance spectroscopy; GCHP – galvanostatic chronopotentiometry; GOx-CoPc/BDDP – glucose-oxidase-immobilized cobalt phthalocyanine/boron-doped diamond powder; HF CVD – hot filament chemical vapor deposition; HPLC – high-performance liquid chromatography; L-BDD NWs – long boron-doped diamond nanowires; L-DOPA – L-3,4-dihydroxyphenylalanine; LSV – linear sweep voltammetry; MEA – microelectrode arrays; MPA – multi pulse amperometric detection; MP CVD – microwave plasma assisted chemical vapor deposition; MWCNTs – multi-walled carbon nanotubes; NEAs – nanoelectrode arrays; NF – nanorod forest; Ni-NPs – nickel nanoparticles; NWs/BDD – boron doped diamond modified by nanowires; PAD –paper-based analytical device; Pt-NPs/BDD – boron doped diamond modified by platinum nanoparticles; SPE – solid phase extraction; SWV – square wave voltammetry; Tyr – tyrosin.

3. PROPERTIES AND ANALYTICAL METHODS FOR DETERMINATION OF NITROPHENOLS

3.1 Sources, Formation, Occurrence, and Biological Effects

Nitrophenols (NPs) belong among both reducible and oxidisable compounds and thus are often used as model compounds in electrochemistry. Together with substituted NPs they are frequently used in industry as reactants or intermediates in production of drugs and dyes and in agriculture, where pesticides based on simple NPs are used as growth stimulators [7, 135].

Toxicologically, NPs are poisons exhibiting appreciable cumulative effects and blocking the oxidative phosphorylation in cells. The NPs may also affect methaemoglobin formation, liver and kidney damage, anaemia, skin and eye irritation, and systemic poisoning [136]. Therefore, they are listed by US EPA on the List of Priority Pollutants [6]. No carcinogenic or genotoxic effects have been reported for this class of compounds.

3.2 Analytical Methods for Determination of Nitrophenols

3.2.1 Methods for Determination of Nitrophenols

The US EPA maintains test methods, which are approved for monitoring the presence and concentration of chemical pollutants. The methods in the Agency index are known as EPA Methods [137] and are the most widely accepted and used. For 2NP, 4NP and 2,4DNP, gas chromatography with mass spectrometric detection (GC/MS) or flame ionization detector (GC/FID) is used [138]. The methods provide guidelines for the analysis of phenols in water and include all the steps necessary to collect, prepare, and analyse samples and data.

For the determination of 2NP, 4NP, and 2,4DNP the following US EPA Method 528 (ref. [139]) or 604 (ref. [140]) is recommended: compounds are extracted by passing a 1 L water sample through a solid phase extraction (SPE) cartridge containing 0.5 g of a modified polystyrene-divinylbenzene copolymer and eluted from the solid phase with a small quantity of dichloromethane. The extract is concentrated and subjected to analysis by GC/MS [139] or GC/FID [140].

Beside US EPA Methods, a number of other studies was published, including GC [141-143], spectrophotometry [144], CE [145-146] or HPLC [147-153]. Among them,

chromatographic methods are used more frequently due to the high separation efficiency [141, 152]. Before analysis, enrichment step is necessary, because the contents of NPs compounds in real samples are generally quite low. Therefore, various pre-treatment techniques have been developed to extract NPs from aqueous samples, such as liquid-liquid microextraction [153], solid-phase extraction [150-152], solid-phase microextraction [142-143], multiple monolithic fibre solid-phase microextraction [147], single-drop microextraction [148], stir bar sorptive extraction [149] and hollow-fibre liquid-phase microextraction [145].

However, easily reducible nitrogroup(s) or oxidisable hydroxyl group in conjunction with aromatic ring offer simple possibility for their detection using voltammetric and amperometric methods in combination with separation techniques that are summarized in the next chapter 3.2.2.

3.2.2 Electrochemical Methods for the Determination of Nitrophenols

Electrochemical methods for determination of selected NPs between 2000–2011 have been reviewed in the Ph.D. Thesis [154]. Further developed selected electrochemical methods applied for determination of NPs between 2012 and 2017 are presented in Table 3.1. It summarizes the type of the working electrode, electroanalytical method used and achieved limit of detection. It can be seen from the table that the methods rely on both electrochemical oxidation and reduction, including the studies developed for 2NP, 4NP, and 2,4DVP by the author of this Thesis **4-5**.

Reduction of nitroaromatic compounds is based on the reduction of a nitro group [155]. Reduction of a nitro group proceeds in the acidic media in two steps (Eq. 2 and Eq. 3):

$$Ar–NO_2 + 4e^- + 5H^+ \rightarrow Ar–N^+H_2OH + H_2O \quad \text{(Eq. 2)}$$

$$Ar–N^+H_2OH + 2e^- + H^+ \rightarrow Ar–NH_2 + H_2O \quad \text{(Eq. 3)}$$

In the neutral media, only one step is observed (Eq. 4):

$$Ar–NO_2 + 4e^- + 4H^+ \rightarrow Ar–NHOH + H_2O \quad \text{(Eq. 4)}$$

In the alkaline media, usually two voltammetric waves are observed, corresponding to a two-step mechanism (Eq. 5 and 6):

$$Ar–NO_2 + e^- \rightarrow Ar–NO_2^{\bullet -} \quad \text{(Eq. 5)}$$

$$Ar–NO_2^{\bullet -} + 3e^- + 4H^+ \rightarrow Ar–NHOH + H_2O \quad \text{(Eq. 6)}$$

Oxidation of NPs is based on the dissociation of aromatic hydroxo group that leads to the formation of phenolate (Eq. 7) (dominant form in alkaline solution), then oxidation

to the phenoxy radical (Eq. 8) or phenoxy cation (Eq. 9), acting as intermediates of the reaction [156].

$$Ar–OH– e^- \rightarrow Ar–O^- + H^+ \quad \text{(Eq. 7)}$$

$$Ar–O^- – e^- \rightarrow Ar–O^\bullet \quad \text{(Eq. 8)}$$

$$Ar–O^\bullet – e^- \rightarrow Ar–O^+ \quad \text{(Eq. 9)}$$

The aforementioned electrochemically formed compounds (phenoxy radical and phenoxy cation) are very reactive and form polymers or undergo other chemical transformations [157]. This may be the cause of the passivation of the electrode surface during electrochemical oxidation.

Electrochemical detection of NPs at bare electrodes seriously suffers from interference issues, low sensitivity or high overpotential during electrochemical oxidation. Therefore, modified electrodes are widely used to avoid these issues aiming to the preparation of highly efficient electrochemical sensors for the determination of NPs [158]. As seen from Table 3.1 commonly used glassy carbon is the most popular electrode material for modification by various compounds to increase its selectivity and sensitivity.

This Ph.D. Thesis is focused on the electrochemical detection of NPs at BDD film electrodes.

Voltammetric determination of 2NP, 4NP, and 2,4DNP, investigated in this Thesis, at BDD film electrodes has been described utilizing their oxidation [159-162], reduction [79, 163], or comparing both these detection modes [3-4, 164-165]. Beside these compounds, other NPs and their derivatives were investigated.

Most of the phenolic compounds and/or their reaction intermediates and products are easily adsorbed on the surface of electrodes, because their oxidation reactions result in formation of a polymeric layer as highlighted above. The adsorption behaviour has a great influence on the refreshment of electrode surface and electrochemical determination, for it might badly foul the electrode, greatly shorten the lifetime of the electrode, and even destroy the feasibility of the application of the electrode. However, even BDD electrode is not entirely resistant to passivation; different ways to activate the electrode surface have been reported. For the determination of phenolic compounds, anodic oxidation [162], short potential pulses close or in the onset of supporting electrolyte decomposition curve [62], cyclic voltammetry in acidic media to the onset of supporting electrolyte decomposition curve [4] or ultrasound traetment [163, 165] are possibilities of conditioning of the electrode surface.

Anodic activation was reported for simultaneous determination of phenol, hydroquinone and 4NP [162], by simple treatment in sulfuric acid solution at a highly positive potential of +2.8 V for 10 s.

The determination of aminonitrophenols as dyeing agents using BDD electrode in DPV and HPLC-ED was proposed [62]. For the activation of the electrode, applying potential of –3 V for 10 s and of +3 V for 10 s in 1M HNO_3 was used. For DPV determination, Britton-Robinson (BR) buffer pH 4:MeOH (9:1, v/v) was used, detection limits were 0.2–0.9 $\mu mol.L^{-1}$ in both cathodic and anodic potential region. For HPLC-ED, phosphate buffer pH 2 containing 35 % (v/v) of methanol was selected as optimum mobile phase. Detection limits were 0.2–0.9 $\mu mol.L^{-1}$ for DPV and 0.15–0.31 $\mu mol.L^{-1}$for the HPLC-ED determination.

Large cathodic part of potential window of BDD electrodes was used for a couple of determinations of pesticides based on the reduction of nitro group in methylparathion [163], or parathion [166]. The direct determination of methylparathion in potato and corn extracts and its degradation product 4NP in lemon and orange juices by square wave voltammetry (SWV) using BDDE was reported [163] with the limits of detection for methylparathion 4.86 $\mu g.L^{-1}$ (0.0185 $\mu mol.L^{-1}$) in water and 10.1 $\mu g.L^{-1}$ (0.0384 $\mu mol.L^{-1}$) in corn extract and for 4NP 5.53 $\mu g.L^{-1}$ (0.0210 $\mu mol.L^{-1}$) in orange juice and 8.32 $\mu g.L^{-1}$ (0.0316 $\mu mol.L^{-1}$) in lemon juice. The SWV was combined with the ultrasound treatment to minimise the inactivation of the BDD surface and to improve the sensitivity of the responses.

Both electrochemical reduction and oxidation were used for the detection of 4NP in spiked pure and natural waters using SWV [164]. As the supporting electrolyte, BR buffer pH 6.0 was used. For the reduction process, the detection limits varied between 0.03 and 0.133 $\mu mol.L^{-1}$ and for the oxidation from 0.02 to 0.115 $\mu mol.L^{-1}$. Then, the determination of 4NP was studied by SWV on a BDD electrode when associated to ultrasound waves [165]. Significant improvements in the analytical sensibility were observed due to electrode surface cleaning and the enhancement in the transport of species to the electrode surface provided by ultrasound. Thus, for the oxidation and reduction process, the limit of detection was 0.028 and 0.018 $\mu mol.L^{-1}$, respectively.

For direct detection of 4NP in the absence of any supporting electrolyte BDD-MEA have been used over the concentration range 1.8–9.2 $\mu mol.L^{-1}$ with no pre-treatment [79]. The detection of 4NP in aqueous media is of great importance as its presence is related to several organophosphorus pesticides (*e.g.*, methylparathion, ethylparathion, fenitrothion,

etc.) and these decompose in water and soils with 4NP being produced as an intermediate or final product.

Determination of NPs using simultaneously both electrochemical reduction and oxidation improves the selectivity and reliability of the analysis. As can be seen in the table 3.1, determination of NPs at bare BDD electrode achieves similar results as at modified GCE or graphite electrodes (GE).

Table 3.1. Selected electroanalytical methods for the determination of 2NP, 4NP, and 2,4DNP.

Analyte	Electrode	Technique	*LOD*, μmol.L^{-1}	Ref.
2NP	polyfurfural film/GCE	DPV ^{red}	0.3	167
	CD-RGO/GCE	DPV ^{red}	50 ^{sim}	168
	OMCs/GCE	DPV ^{red}	0.08	169
	poly(p-ABSA)/GE	SDV ^{ox}	0.28	170
	PPI-AuNP/GE	SWV ^{red}	0.033	171
	Mg/Fe-LDH/GCE	Amperometry ^{red}	4	172
	*n*Au-Si4Pic^{+}Cl^{-}/GCE	DPV ^{red}	0.046	173
	BDD	DPV ^{red}	0.3 ^{a}, 0.2 ^{b}, 0.1 ^{c}	**4**
4NP	SWNTs-Ag/GCE	DPV ^{ox}	1	174
	DB β-CD-MWCNT	DPV ^{ox}	0.048	175
	polyfurfural film/GCE	DPV ^{red}	0.041	167
	CD-RGO/GCE	DPV ^{red}	100 ^{sim}	168
	OMCs/GCE	DPV ^{red}	0.1	169
	SWCNT/GCE	DPV ^{ox}	0.0077	176
	GO/GCE	LSV ^{red}	0.02	177
	CeO_2-ZnONPs	Amperometry ^{red}	1.163	178
	NMP-exfoliated GNS	DPV ^{ox}	0.01	179
	GR/MIPs composite	DPV ^{red}	0.005	180
	ZnO NPs MWCNT CTS	DPV ^{ox}	0.001	181
	S-CHIT/ABPE	Derivative voltammetry ^{red}	0.03	182
	Mg(Ni)FeO/CPE	DPV ^{ox}	0.2	183
	Ag-NPs modified electrode	DPV ^{ox}	0.015	184
	*n*Au-Si4Pic^{+}Cl^{-}/GCE	DPV ^{red}	0.055	173
	ePADs	DPV ^{ox}	1.1	185

	Imprinted CS/PTMS/AuNP/GCE	DPV ^{ox}	0.005	186
	ZnO NPs	Amperometry ^{red}	0.832	187
	α-Fe_2O_3 NPs	Amperometry ^{red}	3.52	187
	Graphene-Au composite/GPE	Amperometry ^{red}	0.47	188
	MIP Au-NPs gold electrode	DPV ^{ox}	0.1	189
	PNPI-PANI-PVSA/ITO	DPV ^{ox}	1	190
	poly(p-ABSA)/GE	SDV ^{ox}	0.3	170
	GCE/GNS-FePc	CV ^{red}	10	158
	β-CD-Au-CGS-nanohybrid /GCE	DPV ^{ox}	0.0038	191
	ZnO/F/GCE	SWV ^{red}	0.008	192
	LiTCNE/PLL/GCE	DPV ^{ox}	0.01	193
		SWV ^{ox}	0.02	
	GNFs/GCE	DPV ^{red}	0.7	194
	β-CD/PBNCs/RGO/GCE	LSV ^{red}	0.0023	195
	PDPA/MWCNT-*β*-CD/GCE	AdSV ^{red}	0.02	196
	PDDA-G/GCE	LSV ^{red}	0.02	197
	PCZ/N-GE/GCE	CV ^{red}	0.062	198
	DTD/AgNP/CPE	DPV ^{red}	0.25	199
	Cu-GPE	Amperometry ^{red}	1.91	200
	N-rGO/GCE	LSV ^{ox}	0.007	201
	PMB/GCE	DPV ^{ox}	0.093	202
	BDD	SWV ^{red}	0.0185	163
	BDD	DPV ^{ox}	1.44	159
	BDD	SWV ^{ox}	0.02	160
	BDD	CV ^{ox}	11	162
	BDD	SWV ^{red}	0.032	164
		SWV ^{ox}	0.020	
	BDD	SWV ^{red}	0.018	165
		SWV ^{ox}	0.028	
	BDD	DPV ^{red}	0.1 $^{a, b, c}$	**4**
		DPV ^{ox}	0.5 ^{a}, 0.1 $^{b, c}$	
2,4DNP	MWCNT/GCE	CV ^{red}	0.144	203
	HAP/GCE	DPV ^{ox}	0.75	204
	BDD	DPV ^{red}	0.1 $^{a, b}$,0.6 ^{c}	**4**

BDD	DPV [ox]	0.3 [a, c], 0.5 [b]	4

[a] – in deionized water; [b] – in drinking (tap) water; [c] – in river water; AdSV – adsorptive stripping voltammetry; AuNP-SPC – AuNP-electrodeposited screen printed carbon electrodes; *β*-CD-Au-CGS-nanohybrid – *β*-cyclodextrin functionalized Au-graphene nanohybrids; *β*-CD/PBNCs –*β*-cyclodextrin Prussian blue nanocubes, CS/PTMS – chitosan phenyltrimethoxysilane; CP – carbon paste; Cu-GPE – Cu-modified graphite pencil electrode; CTS – chitosan; CV – cyclic voltammetry; DB *β*-CD – disulphides bridged beta-cyclodextrin dimer; DPV – differential pulse voltammetry; ePADs – electrochemical paper-based devices; GE – graphite electrode; GNFs – graphite nanoflakes; GNS-FePc – graphene nanosheets decorated iron phthalocyanine; GR/MIPs – molecularly imprinted polymers modified graphene sheet; HAP – hydroxylapatite, HCA – hydrodynamic chronoamperometry; LSV – linear sweep voltammetry; Mg/Fe-LDH – Mg/Fe layered double hydroxides; MIP – macroporous imprinted polymer;*n*Au-Si4Pic^{+}Cl^{-} – gold nanoparticles modified *n*-propyl-4-picolinium silsesquioxane chloride polymer; MWCNT – multi-walled carbon nanotube; NMP-exfoliated GNS – N-methyl-2-pyrrolidone exfoliated graphene nanosheets; NPs – nanoparticles; N-rGO – nitrogen-doped reduced graphene oxide; PCZ/N-GE/GCE – polycarbazole (PCZ)/nitrogen-doped graphene; poly(p-ABSA)/GE – poly(p-aminobenzene sulfonic acid)-modified graphite electrode; PDDA-G – poly(diallyldimethylammonium chloride) functionalized graphene; PDPA – poly(diphenylamine); PMB – polymethylene blue; PNPI-PANI-PVSA/ITO – para-nitrophenol imprinted electrode with polyvinyl sulphonic acid doped polyaniline onto indium tin oxide glass substrate; PPI-AuNP – poly(propyleneimine) dendrimer-gold nanocomposite modified exfoliated; RGO – reduced graphene oxide; S-CHIT/ABPE – acetylene black paste electrode coated with salicylaldehyde-modified chitosan; SDV – semi-derivative voltammetry; [sim] – simultaneous determination of 2NP, 3NP, and 4NP; SWCNT – single-walled carbon nanotube, SWNTs-Ag – single-walled carbon nanotubes/silver nanowires hybrids; SWV – square wave voltammetry; ZnO/F/GCE – ZnO film-coated GCE.

Easily reducible nitrogroup(s) or oxidisable hydroxyl group in conjunction with aromatic ring offer simple possibility for the detection of NPs using amperometric detection in combination with separation techniques.

Chromatographic methods, particularly HPLC, are common in the combination of the high selectivity of a separation method and a high sensitivity and relative selectivity of

amperometric detection. A wide concentration range, a small volume of a cell, a rapid response to a change in the concentration of an electroactive substance, and a low background signal are the advantages [205]. The simple construction of the electrochemical cell (thin-layer or wall-jet system) allows to employ a variety of electrodes in several arrangements using silver solid amalgam (AgSAE) [37], glassy carbon (GCE) [206], solid amalgam composite [207], or BDD [5] electrodes.

The application of CZE has become increasingly widespread because of the minimal sample and solvent volume requirement, short analysis time and high separation efficiency. However, the miniaturized dimensions of the instrumentation increase the demands on the detection settings. In this context, electrochemical detection offers the advantage that it is not compromised by the miniaturization, in contrast with the path-length dependent methods, *e.g.* the spectrometric ones [208]. For the successful application, it is necessary to cope with the difficulty in performing electrochemistry in the presence of the high voltage associated with CZE separations. This can be overcome by inserting a porous decoupler between the separation and detection section of the capillary, which allows to ground the high voltage system ahead of the electrochemical detector, while the analytes are carried to the detector by the electroosmotic flow [209]. Micromachined CE chip with a glassy carbon detector enables a rapid (120 s/sample) simultaneous determination of five priority nitrophenolic pollutants (2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 2-methyl-4,6-dinitrophenol) [210].

Closer characteristics and achieved detection limits of selected amperometric determinations are listed in Table 3.2.

Table 3.2. Selected electroanalytical methods using amperometry for the determination of 2NP, 4NP, and 2,4DNP.

Analyte	Electrode	Technique	*LOD*, μmol.L^{-1}	Ref.
2NP	GCE	HPLC ^{ox}	0.009	206
	GCE	CE chip ^{red}	60	210
	AgSAE	HPLC ^{red}	10 ^{a}, 25 ^{b}	37
	BDD	HPLC ^{red}	1.2	[5]
	BDD	HPLC ^{ox}	1.0	[5]
4NP	GCE	HPLC ^{ox}	0.011	206
	GCE	CE chip ^{red}	60	210

	AgSAE	HPLC [red]	10 [a], 25 [b]	37
	BDD	HPLC [red]	0.8	**5**
	BDD	HPLC [ox]	1.5	**5**
2,4DNP	GCE	HPLC [ox]	0.023	206
	GCE	CE chip [red]	60	210
	AgSAE	HPLC [red]	5 [a], 10 [b]	37
	BDD	HPLC [red]	0.7	**5**
	BDD	HPLC [ox]	0.6	**5**

[red] – reduction, [ox] – oxidation, [a] thin-layer arrangement, [b] wall-jet arrangement

Liquid and gas chromatography coupled with mass spectrometry are sensitive techniques for the detection of selected NPs, but the investment and running costs are incomparable with electrochemical detectors and thus their research and development is so promising and attractive.

4. RESULTS AND DISCUSSION

4.1 Boron-Doped Diamond Film Electrodes in Organic Electroanalysis

As theoretical basis summarizing and critically evaluating *status-quo* in the field of applications of BDD thin film electrodes in organic electroanalysis, two reviews were published by the author of this Thesis in Chemické Listy [1] and Critical Reviews in Analytical Chemistry [2]. These reviews (89 and 194 references, respectively) summarize the recent progress in the development and applications of BDD film electrodes in electroanalysis of organic compounds since the beginnings in 1997 to 2007 and 2008. They are based on the survey listed in a comprehensive table devoted to batch voltammetric and liquid flow amperometric methods using BDD electrodes. The varieties in their construction, surface pre-treatment and electroanalytical methods used are discussed. Further, these reviews also focus on the possibilities and limitations of surface modifications. As a follow-up of these published reviews selected applications of BDD-based sensors in organic analysis in recent few years is summarized in the Table 2.1.

4.2 Differential Pulse Voltammetry of 2-Nitrophenol, 4-Nitrophenol and 2,4-Dinitrophenol at Boron-Doped Diamond Film Electrode

A DPV method was developed for the determination of selected nitrophenols − 2NP, 4NP, and 2,4DNP − at BDD film electrode in BR buffer using electrochemical reduction (2NP) and using both electrochemical reduction and oxidation (4NP and 2,4DNP). All the obtained results were published as a chapter in the monography Sensing in Electroanalysis [3].

The influence of pH on both cathodic and anodic DPV curves of tested NPs (1.10^{-4} mol.L^{-1}) was investigated in BR buffer, pH 2.0–12.0. For electrochemical reduction, based on the reduction of nitro group, well-developed peaks were obtained in acidic media, the highest and the most easily evaluated peaks have been found at pH 4.0 for 2NP and 2,4DNP and pH 6.0 for 4NP. The optimum conditions were used for the construction of calibration dependences. Prior the first electrochemical measurement and also for renewing electrode's surface after observed passivation, BDD film electrode was activated by cycling the potential in vigorously stirred aqueous 1M HNO_3 solution between −2.5 V and +2.5 V vs. SCE until a stable signal was detected (5–10 cycles with 0.1 V.s^{-1}

scan rate). The stable performance of the electrode was regularly verified by measuring cyclic voltammograms of 1×10^{-4} mol.L^{-1} potassium hexacyanoferrate, which exhibited well defined peaks. Repeatability of the determination was confirmed by series of 20 consecutive measurements, carried out for the highest concentration of the linear dynamic range. The limits of quantification (*LOQ*s) were calculated as the concentration of the analyte, which gave the signal equal to ten times the standard deviation estimated from the lowest measurable concentration, and for all analytes, *LOQ*s were 0.4 μmol.L^{-1}. All obtained results are summarized in the Table 4.1.

On the other hand, for electrochemical oxidation, based on the oxidation of phenolic group, peaks were better developed in alkaline media and optimum conditions have been found at pH 11.0 for 4NP and pH 10.0 for 2,4DNP. During electrochemical oxidation of 2NP, passivation of electrode's surface became evident and the calibration dependences were not linear. Pre-treatment of the electrode prior the measurement in HNO_3 or activation before each scan using highly positive or negative potentials (±2.0 V) applied in the supporting electrolyte were not sufficient for this compound. Further, the position of the peak near the end of the potential window caused the difficult evaluation. Therefore, for 2NP, voltammetric determination using electrochemical oxidation at BDD film electrode is not a suitable method. *LOQ*s were 2 μmol.L^{-1} for 4NP and 0.8 μmol.L^{-1} for 2,4DP.

Determination of NPs using simultaneously both electrochemical reduction and oxidation improves the reliability of the analysis.

4.3 Determination of Nitrophenols in Drinking and River Water by Differential Pulse Voltammetry at Boron-Doped Diamond Film Electrode

The DPV method for the determination of selected NPs developed in previously mentioned paper [3] was successfully applied for the direct determination of these compounds in drinking and river water. To improve the limit of quantification, preconcentration by SPE from 100 mL and 1000 mL of water samples was used. All the obtained results were published in the journal Electroanalysis [4].

The direct determination of NPs in model samples of drinking and river water was applied in the concentration range from 0.4 to 20 μmol.L^{-1} using both electrochemical reduction and oxidation (4NP and 2,4DNP) and only electrochemical reduction (2NP). The

sensitivity of this direct determination is comparable with the previous DP voltammetric experiments carried out with redistilled water [3], as is seen in the Table 4.1. Also the *LOQ*s lie within the same concentration range. For electrochemical reduction, *LOQ*s of 2NP, 4NP, and 2,4DNP were 0.3, 0.1, and 0.1 μmol.L^{-1} in deionised water, 0.2, 0.1, and 0.1 μmol.L^{-1} in drinking water, and 0.1, 0.1, and 0.6 μmol.L^{-1} in river water. For electrochemical oxidation, *LOQ*s of 4NP and 2,4DNP were 0.5 and 0.3 μmol.L^{-1} in deionised water, 1 and 0.5 μmol.L^{-1} in drinking water, and 1 and 0.3 μmol.L^{-1} in river water.

To improve the *LOQ*s, preconcentration by SPE from 100 mL and 1000 mL water samples to the final volume of 10 mL was used. As the determination based on electrochemical reduction was more sensitive than oxidation, conditions were optimised for the reductive mode and this mode was used after preconcentration by SPE. Lichrolut EN cartridges containing polymeric sorbent (based on ethylvinylbenzene-divinylbenzene copolymer) with large specific surface and the adsorption capacity for polar organic substances were used. Recovery of NPs using SPE was calculated from the ratio of the peak height of the substance after SPE and peak height of the standard solution at concentration corresponding to expected concentration after extraction. Passing 1000 mL river water through the SPE column was not successful because of the decrease of the sample flow rate (the flow rate for sucking 100 mL sample was 100 mL per hour), and therefore unacceptable prolongation of analysis time, so the *LOQ*s of river water samples are ten times higher than *LOQ*s of the deionized and drinking water samples due to lower preconcentration factor. The *LOQ*s of 2NP, 4NP, and 2,4DNP in deionized water samples were 0.02, 0.03, and 0.02 μmol.L^{-1}with recovery 99, 81 and 81 %, 0.02, 0.04, and 0.02 μmol.L^{-1} in drinking water samples with recovery 99, 75 and 80 %, and 0.2 μmol.L^{-1} (for all NPs) with recovery 99, 80 and 82 % in river water samples.

4.4 The Use of Boron-Doped Diamond Film Electrode for the Determination of Selected Nitrophenols by HPLC with Amperometric Detection

The mechanical durability substantiates the popularity of BDD film electrodes in liquid flow methods including FIA-ED and HPLC-ED. The possibility to use BDD film electrodes for amperometric determination of trace amounts of NPs after their HPLC separation was investigated and results presented in the journal Analytical Letters [5].

Firstly, the separation and detection conditions for HPLC-ED determination in reductive detection mode were optimized. As the voltammetric behaviour of NPs using BDD film electrode (using both electrochemical reduction and oxidation) was already investigated in our previous study [4] and the highest current response of NPs was obtained at pH 4.0 – 6.0, acetate buffer was chosen as aqueous part of mobile phase. Optimization of conditions for HPLC separation of 2NP, 4NP, and 2,4DNP included optimization of flow rate of mobile phase, pH of acetate buffer and content of organic modifier (methanol) in the mobile phase. Further, detection potential E_{det} was set at –1.2 V, where the hydrodynamic voltammograms of studied NPs reached out a plateau. The optimum separation was achieved in 0.05 mol.L^{-1} acetate buffer pH 4.7 – methanol (58:42,*v/v*) mobile phase at the flow rate of 1 mL.min^{-1}. The capacity factors of 2,4DNP, 4NP, and 2NP in this system were 0.88, 4.29, and 7.79, respectively and total separation time was 12 min.

The reduction of NPs is problematic due to possible interference of 2,4DNP and/or 4NP peak with the signal of oxygen. While the oxygen dissolved in the mobile phase causes higher and less stable background current, oxygen in aerated injected samples gives wide and relatively high peak characterized by capacity factor 1.71 – 2.12 depending on the pH of the aqueous part of mobile phase. Prevention of oxygen presence included 10 min sonication and bubbling of the mobile phase by nitrogen before filling it to linear high-pressure pump, keeping of the wall-jet overflow vessel under nitrogen atmosphere, and deaeration of injected samples using 5 min bubbling by nitrogen prior to injection. Nevertheless, it was not possible to remove all oxygen, as obvious from frequent presence of oxygen peak, because the residual oxygen is present in the injected samples, where it penetrates during the manipulation prior to the manual injection into the HPLC system. Attempts to use automatic injection failed due to low reproducibility of signal of oxygen, which was in average substantially higher than using manual injection. It is caused by the autosampler, where the injection procedure requires washing steps and the injected zone of analyte is separated by microliter volumes of air. Thus, it is impossible to ensure complete or at least reproducible oxygen removal. Thus, manual injection is preferable in our HPLC setup and the indistinctive peak of the oxygen does not interfere with the peaks of NPs which are baseline separated, well-developed and sharp, as confirmed in previous studies [35, 37, 211].

For electrochemical oxidation, the highest response current of NPs was obtained at pH 10.0 – 11.0 in batch voltammetric studies [4]. However, basic media are not compatible

with silica-based columns and the optimization of pH of phosphate buffer revealed that the highest current response of NPs was obtained at pH 6.75. At higher pH values baseline drift was observed and at lower pH values undesirable prolongation of separation was observed. Relatively problematic was the detection of the firstly eluting 2,4DNP exhibiting lower peak currents than 2NP and 4NP. It was greatly influenced by the content of methanol in the mobile phase. Finally, 0.05 mol.L^{-1} phosphate buffer pH 6.75 – methanol (65:35, *v/v*) as mobile phase and detection potential +1.3 V, where the measured signals reached out a plateau at hydrodynamic voltammograms, were used as an optimum. The capacity factors of 2,4DNP, 4NP, and 2NP in this system were 0.89, 2.42, and 5.37, respectively, and the total separation time was 10 min. In contrast with the DPV measurement, the passivation of electrode's surface during the detection of 2NP was not observed. The main reasons are most likely different pH of the support electrolyte and also smaller amount of the analyte in the contact with electrode's surface, and most importantly the removal of the intermediate and product of the chemical oxidation by the flowing mobile phase.

The optimized chromatographic conditions for both cathodic and anodic detection modes were successfully applied for the direct determination of 2NP, 4NP and 2,4DNP in model samples of drinking and river water in the concentration range from 2 to 100 μmol.L^{-1}. After filtration through glass fibre filter, the samples were directly injected into the HPLC column protected by a precolumn.

For the amperometric detection based on reduction, the sensitivity of the direct determination in both drinking and river water is mostly comparable with the previous experiments carried out with deionized water. Amperometric detection based on oxidation exhibits comparable sensitivity for deionized and drinking water, but lower for the river water. Thus, reductive detection mode is preferable for this matrix as it is less affected by its complex composition. Furthermore, sensitivity using reductive determination is markedly higher for 2,4DNP than for the other NPs because of the presence of two nitro groups in its structure. Relatively low limits of detection (*LOD*s) in the micromolar concentration range were achieved for all analytes, as is seen in the Table 4.1. The *LOD*s were calculated as the concentration of the analyte, which gave a signal three times higher than the background noise (*S/N* = 3). In reductive detection mode, the *LOD*s of 2NP, 4NP, and 2,4DNP were 1.2, 0.8, and 0.7 μmol.L^{-1} in deionized water samples, 1.5, 1.3, and 0.7 μmol.L^{-1} in drinking water samples, and 1.8, 1.3, and 0.7 μmol.L^{-1} in river water samples. In oxidative detection mode, the *LOD*s of 2NP, 4NP, and 2,4DNP were 1.0, 1.5,

and 0.6 μmol.L^{-1} in deionized water samples, 2.9, 2.5, and 1.5 μmol.L^{-1} in drinking water samples, and 3.5, 2.4, and 1.2 μmol.L^{-1} in river water samples.

Other electroanalytical methods based on connection of liquid flow techniques with amperometric detection offer similar detection limits as seen in the Table 3.2 in the Chapter III. The robustness of the method is documented by relatively low RSD, even for micromolar concentrations. At the micromolar concentration close to *LOD*s the relative standard deviation (RSD) of peak height is mostly 6.0−10.0 %. For high concentration of NPs ($c = 1\times10^{-4}$ mol.L^{-1} of each analyte) it is mostly < 3.0 % for oxidative and < 6.0 % for the reductive detection mode. In the latter case, the higher values of RSD could be caused by peak height fluctuations as the result of traces of oxygen influencing background current.

Thus, it can be concluded that BDD film electrode employed as amperometric sensors in wall-jet detector exhibited good electroanalytical performance with stable background current and sensitive, reproducible and stable responses for all tested NPs using both reductive and oxidative detection mode. Nevertheless, reductive determination is recommendable as it more efficiently eliminates possible negative matrix effects as recognized for river water samples. The method fulfils requirements on fast, reliable, sensitive, and relatively inexpensive determination of NPs.

Table 4.1

Analyte	**Method**	**Matrix**	***LDR*** **[μmol.L^{-1}]**	***LOD*** **[μmol.L^{-1}]**	**Ref.**
2NP	**DPV** ^{red}, BR buffer pH 4	Redistilled water	0.2−40	0.4 [A]	3
	DPV ^{red}, BR buffer pH 4	Water Deionized Drinking River	 0.4−80 0.4−200 0.8−20	Direct / after SPE [A] 0.3/0.02 0.2/0.02 0.3/0.2	4
	HPLC/AD ^{red}, wall-jet arrangement, 0.05 M acetate buffer pH 4.7 / MeOH (58/42)	Water Deionized Drinking River	 2−80 2−100 4−100	[B] 1.2 1.5 1.8	5
	HPLC/AD ^{ox}**,** wall-jet arrangement, 0.05 M phosphate buffer pH 6.75 / MeOH (65/35)	Water Deionized Drinking River	 6−80 4−100 4−100	[B] 1.0 2.9 3.5	5
4NP	**DPV** ^{red}, BR buffer pH 6	Redistilled water	0.4−100	0.4 [A]	3

	DPV ^{red}, BR buffer pH 6	Water Deionized Drinking River	 0.8−200 0.8−20 0.4−20	Direct / after SPE [A] 0.1/0.03 0.1/0.04 0.1/0.2	4
	DPV ^{ox}, BR buffer pH 11	Redistilled water	2−40	2 [A]	3
	DPV ^{ox}, BR buffer pH 11	Water Deionized Drinking River	 4−80 4−40 4−20	[A] 0.5 1 1	4
	HPLC/AD ^{red}, wall-jet arrangement, 0.05 M acetate buffer pH 4.7 / MeOH (58/42)	Water Deionized Drinking River	 2−100 1−100 1−100	[B] 0.8 1.3 1.3	5
	HPLC/AD ^{ox}**,** wall-jet arrangement, 0.05 M phosphate buffer pH 6.75 / MeOH (65/35)	Water Deionized Drinking River	 2−80 2−100 2−100	[B] 1.5 2.5 2.4	5
2,4DNP	**DPV** ^{red}, BR buffer pH 4	Redistilled water	0.2−100	0.4 [A]	3
	DPV ^{red}, BR buffer pH 4	Water Deionized Drinking River	 0.4−20 0.4−20 0.8−20	Direct/after SPE [A] 0.1/0.02 0.1/0.02 0.6/0.2	4
	DPV ^{ox}, BR buffer pH 10	Redistilled water	0.8−100	0.8 [A]	3
	DPV ^{ox}, BR buffer pH 10	Water Deionized Drinking River	 2−20 0.8−20 2−20	[A] 0.3 0.5 0.3	4
	HPLC/AD ^{red}, wall-jet arrangement, 0.05 M acetate buffer pH 4.7 / MeOH (58/42)	Water Deionized Drinking River	 2−60 1−100 1−100	[B] 0.7 0.7 0.7	5
	HPLC/AD ^{ox}**,** wall-jet arrangement, 0.05 M phosphate buffer pH 6.75 / MeOH (65/35)	Water Deionized Drinking River	 4−100 2−100 4−100	[B] 0.6 1.5 1.2	5

[A] $LOQ = 10\sigma/m$ where σ is the standard deviation of the signal measured for the lowest analyte concentration corresponding to calibration plot, m is slope of the analytical curve; [B] LOD for $S/N = 3$.

5. CONCLUSION

The presented Ph.D. Thesis describes development of new electrochemical methods for the determination of nitrophenols (2NP, 4NP, and 2,4DNP) that are listed as the priority pollutants by US EPA, due to their negative impact on living organisms. Therefore, large scale monitoring of these environmental pollutants has become more and more important. This requires development of independent, sensitive and selective detection techniques and appropriate instrumentation. The methods presented in this Thesis are based on the technique of DPV and HPLC with amperometric detection employing BDD as the working electrode.

A DPV method was developed for the determination of trace concentrations of 2NP, 4NP, and 2,4DNP at BDD electrode using electrochemical reduction (2NP) and using both electrochemical reduction and oxidation (4NP, 2,4DNP). The method was successfully applied for the direct determination of these compounds in drinking and river water. To improve the limit of quantification and to increase selectivity, a preliminary separation and preconcentration by SPE was used.

The possibility to employ BDD film electrodes for amperometric detection in wall-jet arrangement in HPLC was verified by determination of 2NP, 4NP, and 2,4DNP based on both, electrochemical reduction and oxidation. Different separation conditions with respect to the detection mode were employed, nevertheless, in both cases baseline separation of NPs was achieved in max. 12 minutes. Relatively low limits of detection in the micromolar concentration range were achieved for all analytes. The applicability of the developed methods was demonstrated on the analysis of the model drinking and river water samples using their direct injection in the HPLC-ED setup. Comparable sensitivities and limits of detection were achieved for both detection modes.

Thus, it can be concluded that BDD film electrode employed as voltammetric and/or amperometric sensor in wall-jet detector exhibits good electroanalytical performance with stable background current and sensitive, reproducible and stable responses for all tested NPs using both reductive and oxidative detection mode without problems with passivation of electrode surface, frequent problem of the electrochemical detection of phenolic compounds. These methods fulfil requirements on fast, reliable, sensitive, and relatively inexpensive determination of NPs. The obtained results confirm that both batch voltammetry and HPLC-ED with unmodified BDD electrode represent

reliable and sensitive analytical techniques for determination of NPs with limits of detection similar to other electrodes.

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7. Appendix I

The Use of Boron-Doped Diamond Film Electrodes for Detection of Organic Compounds

(Použití diamantových filmových elektrod dopovaných borem pro stanovení organických látek)

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POUŽITÍ DIAMANTOVÝCH FILMOVÝCH ELEKTROD DOPOVANÝCH BOREM PRO STANOVENÍ ORGANICKÝCH LÁTEK

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Obsah

1. Úvod

V posledních dvou desetiletích je věnována pozornost novému elektrodovému materiálu, diamantovému filmu dopovanému borem (BDD). Mezi jeho výhodné vlastnosti patří mechanická i chemická stabilita, nízký zbytkový proud a biokompatibilita[1–4]. Další důležitou vlastností BDD filmu je široké potenciálové okno, závislé na kvalitě filmu a dosahující nejčastěji hodnot kolem 3,5 V. Borem dopované diamantové filmové elektrody (BDDFE) proto umožňují provádět elektrochemické reakce při potenciálech, kterých není možné dosáhnout jiným způsobem[3,5]. Při elektrochemickém stanovení organických látek na pevných elektrodách dochází velmi často k ireverzibilní adsorpci reakčních produktů či některých složek vzorku na povrchu elektrody, což má za následek její pasivaci. Na adsorpci polárních látek jsou citlivé téměř všechny sp^2 uhlíkové elektrody (tj. elektrody v nichž převažují uhlíkové atomy s sp^2 hybridizací, např. grafitové). Je to způsobeno hlavně přítomností polárních skupin na jejich povrchu[6]. BDD je díky svému sp^3 charakteru (tj. skutečnosti, že uhlíkové atomy jsou zde v sp^3 hybridizaci) vůči adsorpci polárních látek na jeho povrchu značně rezistentní, což je dáno v podstatě parafinickým charakterem jeho povrchu v případě převládající terminace povrchových vazeb vodíkem. Díky malé náchylnosti k pasivaci jsou BDD filmy v mnoha případech ideálním elektrodovým materiálem, který je možné použít k vysoce citlivému stanovení velkého množství organických i anorganických látek bez předchozí úpravy povrchu elektrody[1]. Příprava vodivých diamantových filmů i jejich analytické aplikace byly v minulých letech popsány v přehledných referátech[1,7–10] a v knize[11].

2. Použití diamantových filmových elektrod dopovaných borem

Použití vodivých diamantových filmů jako elektrodových materiálů v elektrochemii bylo rozsáhle popsáno Fujishimou[11]. Pro použití BDDFE v elektrochemii organických látek existují dva hlavní směry: elektrochemická oxidace organických látek obsažených v odpadních vodách na BDD anodě založená na jejich úplné konverzi nebo destrukci a užití BDDFE jako elektrochemických senzorů ve voltametrii nebo při ampérometrické detekci v průtokových metodách (HPLC, průtoková injekční analýza, kapilární elektroforéza).

Cílem čištění odpadních vod je úplná oxidace organických polutantů na CO_2 nebo jejich konverze na biologicky odbouratelné sloučeniny. K tomuto účelu je výhodné použití BDDFE, neboť při oxidaci vody, která je umožněna vysokým přepětím tvorby kyslíku na povrchu BDDFE, vzniká velké množství hydroxylových radikálů. Tyto silné oxidanty zajišťují přímou oxidaci organických látek na povrchu BDD anody, čímž je zabráněno pasivaci povrchu. Toto téma bylo popsáno v přehledných referátech[7,12,13].

3. Příprava diamantových filmových elektrod dopovaných borem

BDD filmy se obvykle připravují metodou chemické depozice par. K depozici diamantového filmu je nejčastěji používána směs methanu a vodíku, dopování borem je dosaženo přidáváním diboranu do směsi plynů. Koncentrace atomů boru v diamantovém filmu je obvykle 10^{20} cm^{-3}, což odpovídá 1 atomu boru na 1000 atomů uhlíku[9,14]. Přípravou BDD filmu se podrobně zabývá článek Cvačky a spol.[5] Ačkoliv byly studovány i jiné typy dopantů (vodík, dusík, fosfor, síra)[1,8], většina prací v elektroanalýze využívá jako dopant bor. Téměř všechny publikované elektroanalytické aplikace byly provedeny na BDD filmech nanesených na křemíku (BDD/Si), třebaže jejich průmyslová výroba je problematická kvůli křehkosti a relativně nízké vodivosti křemíkového substrátu. V dnešní době je snaha

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nalézt nový substrát pro BDD film, byl testován niob, tantal, wolfram, molybden nebo podstatně levnější titan[15–19]. Tyto substráty jsou vhodné pro i pro velkoplošné elektrody používané pro úplnou elektrochemickou oxidaci organických polutantů při jejich odstraňování z odpadních vod, v elektroanalytické chemii se zatím příliš neuplatnily. Pro výrobu mikroelektrod lze jako substrát použít platinový drátek[3]. Jako substrát pro BDD film byl testován také grafit, uhlík a uhlíková vlákna[8]; jejich analytické aplikace jsou však zatím omezené.

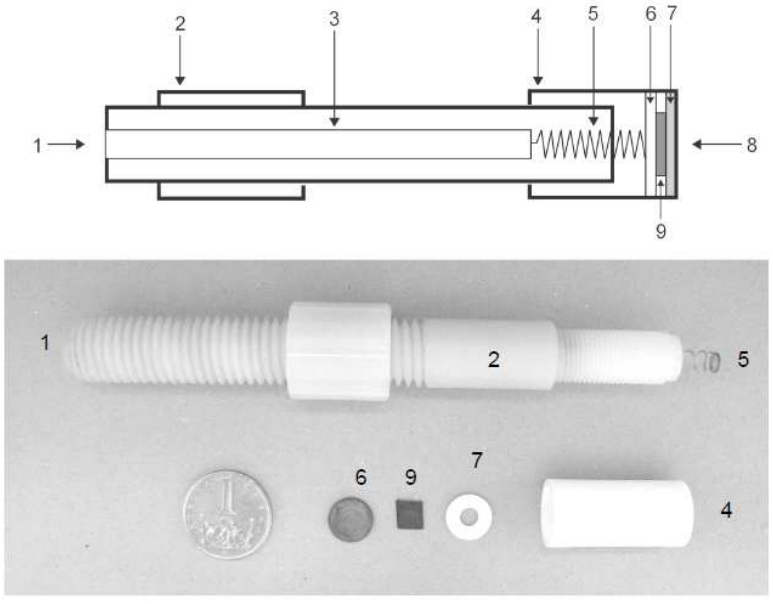
4. Konstrukce diamantových filmových elektrod dopovaných borem

Při vsádkovém uspořádání je BDDFE pro voltametrická měření vložena do těla elektrody z teflonu nebo polyetheretherketonu (PEEK) (obr. 1) nebo tvoří dno pracovní nádobky[20,89]. Pro elektrochemickou detekci v průtokovém uspořádání lze použít tenkovrstvou detekční celu, která byla poprvé popsána v práci[21]. Lze však použít i většinu komerčně dostupných tenkovrstvý cel. Pro práci s kapilárními technikami (HPLC, kapilární elektroforéza) je vhodná cela pro detekci za kolonou s pracovní BDD mikroelektrodou[3,22].

V dnešní době již existuje několik dodavatelů komerčních elektrod[20,23,24]: Windsor Scientific (Velká Británie)[25], Adamant Technologies (Švýcarsko)[26], Element Six (Velká Británie)[27], Condias (Německo)[28], Sumitomo (Japonsko)[29] a sp3 Technologies (USA)[30].

4.1. Mikroelektrody

Významným trendem v konstrukci ampérometrických detekčních systémů je jejich miniaturizace, řada prací se tedy zabývá přípravou BDD mikroelektrod. Cvačka a spol. studoval použití BDD mikroelektrod jako elektrochemického detektoru pro kapilární elektroforézu (CE)[3]. Mikroelektrody byly připraveny nanesením tenkého BDD filmu na platinové drátky o průměru 75, 25 či 10 μm vyleptané do tvaru kužele. Kvalita mikroelektrod závisí na úplném pokrytí platiny BDD filmem a na tvaru elektrody, jehož reprodukovatelnost je třeba zajistit. Toho se dosáhlo oddělením kuželové části elektrody zatavením její zbylé části do polypropylenu nebo jejím pokrytím lakem na nehty nebo polyimidem. Výhodnější je použít zatavení do polypropylenu, neboť lak na nehty a polyimid mají omezenou chemickou stabilitu, omezující jejich použití ve vzorcích životního prostředí, a omezenou elektrochemickou stabilitu, zužující použitelný rozsah potenciálů. Další typy BDD mikroelektrod byly použity jako ampérometrický detektor při CE na mikročipu pro analýzu purinů a jejich derivátů[31], 2,4-dinitrotoluenu a 1,3-dinitrobenzenu[32] nebo 4-aminofenolu a 2-aminonaftalenu[33].



Obr. 1. **Schéma BDDFE v diskovém uspořádání**; kontakt pro připojení k potenciostatu (1), teflonové tělo elektrody (2), elektrický kontakt (3), šroubovací nástavec (4), pružina (5), kovová destička z obou stran pokrytá grafitem (6), těsnění (7), kontakt s roztokem (8), BDDFE na křemíkové podložce (9)

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4.2. Elektrody s modifikovaným povrchem

Poslední dobou roste využití modifikovaných diamantových povrchů. Techniky modifikace jsou chemické, elektrochemické nebo fotochemické[11]. Chemická modifikace BDD povrchu může zajistit zvýšenou citlivost a selektivitu při detekci různých látek[1]. Nejčastěji se používá povrchová oxidace, navázání organických funkčních skupin nebo biomolekul a elektrochemická depozice kovů nebo jejich oxidů. Modifikace povrchu anodickou oxidací vede k výraznému zvýšení selektivity k některým analytům, např. k dopaminu nebo kyselině močové, které je pak možné stanovit i v přítomnosti nadbytku kyseliny askorbové[34–37]. Vzhledem k biokompatibilitě diamantu je výhodné jeho využití pro senzory *in vivo*. Diamantové elektrody s deponovaným kovem lze použít v případě katalýzy vícestupňových elektrochemických reakcí (oxidace alkoholů a uhlovodíků), které mohou být na nemodifikované BDDFE poměrně pomalé. Elektrody s deponovaným niklem nebo mědí vykazují výbornou elektrochemickou stabilitu a dobrou adhezi částeček kovu k povrchu elektrody[1]. Použití enzymaticky modifikovaných BDD filmů je perspektivní i pro přípravu senzorů se specifickou citlivostí[1]. BDDFE modifikovaná tyrosinasou byla použita jako elektrochemický detektor při stanovení estrogenních derivátů fenolu průtokovou injekční analýzou (FIA)[38]. Mikrosenzor z mikrovláknových BDD elektrod modifikovaných oxidovaným polypyrrolem byl použit jako ampérometrický detektor pro stanovení dopaminu v přítomnosti kyseliny askorbové[37]. Pro stanovení glukosy byl zkonstruován BDDFE biosenzor s imobilizovanou glukosooxidasou[39].

5. Analytické aplikace

Analytické aplikace BDDFE byly v posledních pěti letech popsány v referátech[1,8–10,20,23]. V oblasti organické analýzy nalezla BDDFE uplatnění při stanovení pesticidů, léčiv, environmentálních polutantů (fenoly a jejich chlorované deriváty, polycyklické aromatické uhlovodíky (PAH) a jejich deriváty) a dalších biologicky aktivních dusíkatých a sirných látek. Většina prací porovnává stanovení s použitím BDDFE s elektrodou ze skelného uhlíku či doplňuje elektroanalytické metody aplikací BDDFE v ampérometrických detektorech pro FIA, HPLC nebo CE. Přehled aplikací BDDFE při stanovení organických látek je uveden v tabulce I. V následujícím textu jsou uvedeny příklady stanovení, ve kterých je třeba vyřešit řadu problémů, např. odstraňovaní polymerního filmu na povrchu elektrody nebo detekci analytů v přítomnosti rušících látek.

Dopamin je jeden z nejdůležitějších neurotransmiterů a proto je zřejmá snaha nalézt vhodný voltametrický senzor k jeho stanovení v nitrobuněčných tekutinách centrálního nervového systému[36]. Jedním z největších problémů detekce dopaminu, jehož koncentrace se zde pohybuje v rozmezí 10^{-9}–10^{-5} mol L^{-1}, je přítomnost velkého množství (10^{-4} mol L^{-1}) kyseliny askorbové, která se na standardních elektrodách oxiduje při téměř stejném potenciálu jako dopamin. Stanovení dopaminu na BDDFE modifikované částečkami zlata (Au/BDDFE) bylo provedeno v práci[36]. Částečky zlata o velikosti 20–400 nm byly deponovány na povrch BDDFE cyklickou voltametrií při potenciálu od −0,7 do 0 V proti SCE v 0,05 mM-$KAuCl_4$ a 1 M-KCl. Na Au/BDDFE se dopamin oxiduje při potenciálu 0,11 V a kyselina askorbová při 0,26 V. Dopamin lze tedy stanovit selektivně v přítomnosti kyseliny askorbové s mezí detekce $1 \cdot 10^{-7}$ mol L^{-1}, dochází však k pasivaci elektrodového povrchu. Au/BDDFE potažená samoskladnou vrstvou kyseliny merkaptooctové (sulfanyloctové), (SAM/Au/BDDFE) poskytuje vyšší odezvu a k její pasivaci nedochází. Kalibrační závislost pro stanovení dopaminu na SAM/Au/BDDFE je lineární v koncentračním rozsahu $1 \cdot 10^{-8}$–$1 \cdot 10^{-5}$ mol L^{-1} s detekčním limitem $1 \cdot 10^{-9}$ mol L^{-1}.

Fenoly a chlorované fenoly (CP) se do životního prostředí dostávají při výrobě antioxidantů, barviv a léků, při chlorování pitné vody nebo při bělení papíru[20]. Jejich elektroanalýza je komplikovaná, protože se na povrchu elektrody tvoří polymerní film. Bylo publikováno několik studií, které se zabývaly stanovením a odbouráváním chlorovaných fenolů s různými přístupy k problematice pasivace elektrodového povrchu a odstraňováním vzniklého filmu laserem, ultrazvukem nebo vložením vysokého kladného potenciálu během měření. K detekci CP byla použita průtoková cela[40] a dále laserová ablační voltametrie s Nd:YAG laserem, při níž je adsorpce oxidačních produktů zanedbatelná. Stanovení CP pomocí HPLC a FIA s elektrochemickou detekcí na anodicky oxidované BDDFE prováděl Terashima a spol[41]. Naadsorbovaný polymerní film byl odstraňován přímo v měřeném roztoku vložením potenciálu 2,64 V proti SCE po dobu 4 min. Při takto vysokém potenciálu vznikají hydroxylové radikály, které způsobí oxidaci pasivační vrstvy. Stanovení 4-chlorfenolu, jednoho z nejvýznamnějších polutantů, bylo provedeno voltametrií s lineárně rostoucím potenciálem (LSV) s použitím ultrazvuku[42]. Působením ultrazvuku se zvýší transport elektroaktivních látek k povrchu elektrody a zároveň se naruší polymerní film a tím omezí pasivace elektrody. Výhoda této metody spočívá v její použitelnosti pro analýzu vzorků životního prostředí.

Senzory pro stanovení glukosy pracují na principu její elektrochemické oxidace. Existují dva hlavní typy senzorů: enzymatické, používající enzym glukosooxidasu (GOx)[39,43], a neenzymatické. Největší uplatnění nacházejí biosenzory pro stanovení glukosy v krvi, kde se její koncentrace pohybuje mezi $3 \cdot 10^{-3}$–$8 \cdot 10^{-3}$ mol L^{-1}. V práci[43] byl popsán biosenzor pro stanovení glukosy zlatou elektrodou modifikovanou nedopovaným nanokrystalickým diamantovým filmem (N-NCD) s kovalentně imobilizovanou GOx na jeho povrchu. Na povrch zlaté elektrody byla deponována vrstva poly(allylamin-hydrochloridu) (PAA) s koncovými skupinami $-NH_2$ a sloužící jako podklad N-NCD filmu se skupinami –COOH, které interagují s aminoskupinami z vrstvy PAA. Vodivost N-NCD je $1{,}3 \cdot 10^{-8}\ \Omega^{-1}\ cm^{-1}$. Na N-NCD film byla imobilizována vrstva GOx. Elektroda byla před měřením anodicky oxidována při 0,7 V proti SCE po dobu 5 min, aby se zvýšil

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Tabulka I
Analytické aplikace BDDFE pro stanovení organických látek

Analyt	Metoda	Mez detekce [mol L^{-1}]	Lit.
1,3-Dinitrobenzen	CE-ED, mikročip	$4 \cdot 10^{-7}$	32
1-Aminonaftalen	HPLC-ED	$1 \cdot 10^{-7}$	5
2,4-Dinitrotoluen	CE-ED, mikročip	$7 \cdot 10^{-7}$	32
2-Aminobifenyl	HPLC-ED	$1 \cdot 10^{-7}$	5
2-Aminonaftalen	CE-ED, mikročip	$1 \cdot 10^{-6}$	33
2-Chlorfenol	FIA-ED	$5 \cdot 10^{-8}$	45
	HPLC-ED	$1 \cdot 10^{-7}$	45
	LAV	$1 \cdot 10^{-5}$	40
3-Aminofluoranthen	DPV	$2 \cdot 10^{-7}$	46
3-Chlorfenol	FIA-ED, HPLC-ED	$1 \cdot 10^{-7}$	45
3-Nitrofluoranthen	DPV	$3 \cdot 10^{-8}$	46
4-Aminofenol	CE-ED, mikročip	$2 \cdot 10^{-6}$	33
4-Chlorfenol	FIA-ED	$5 \cdot 10^{-7}$	45
	HPLC-ED	$1 \cdot 10^{-7}$	45
	LAV	$1 \cdot 10^{-8}$	40
	LSV – ultrazvuk	$1 \cdot 10^{-6}$	42
4-Chlor-3-methylfenol	CHA	$1 \cdot 10^{-8}$	40
4-Methylpyrokatechol	FIA-ED	$2 \cdot 10^{-9}$	47
4-Nitrofenol	LSV, BDD-MEA	$2 \cdot 10^{-6}$	48
	SWV – oxidace	$6 \cdot 10^{-8}$	49
	SWV – redukce	$9 \cdot 10^{-8}$	49
Paracetamol (acetaminophen)	CV	$1 \cdot 10^{-5}$	50
	FIA-ED	$1 \cdot 10^{-8}$	
Adenosin	FIA-ED	$2 \cdot 10^{-9}$	51
Captopril	CV	$3 \cdot 10^{-5}$	52
	FIA-ED	$1 \cdot 10^{-10}$	
Clenbuterol	CV, pyrrol-DNA/BDDFE	$9 \cdot 10^{-7}$	53
Cystein	HPLC-ED	$1 \cdot 10^{-9}$	54
	CHA	$6 \cdot 10^{-6}$	55
	CV	$9 \cdot 10^{-7}$	56
	FIA-ED	$2 \cdot 10^{-8}$	56
Cystin	HPLC-ED	$1 \cdot 10^{-9}$	54
Cytochrom c	CV	$3 \cdot 10^{-5}$ [a]	57
Dichlorfenoly (2,6-DCP; 2,3-DCP; 2,5-DCP; 2,4-DCP; 3,4-DCP; 3,5-DCP)	FIA-ED	$2 \cdot 10^{-8}$	41
	HPLC-ED	$2 \cdot 10^{-10}$	
Dopamin, dopamin vedle kyseliny askorbové	CHA	$5 \cdot 10^{-8}$	34,
	FIA-ED	$3 \cdot 10^{-9}$	58
	SWV, Au/BDDE	$1 \cdot 10^{-7}$	47
	SWV, SAM/Au/BDDFE	$1 \cdot 10^{-9}$	36
	CE-ED	$4 \cdot 10^{-8}$	36
	CE-ED	$8 \cdot 10^{-8}$	59
	Amp·-ED, BDDMFibE-OPP_y	$1 \cdot 10^{-8}$	3
			37
D-penicillamin	CV	$3 \cdot 10^{-5}$	60
	FIA-ED	$1 \cdot 10^{-8}$	

Tabulka I
Pokračování

Analyt	Metoda	Mez detekce [mol L^{-1}]	Lit.
Estrogenní deriváty fenolu (bisfenol A; 17β-estradiol)	FIA-ED, tyr/BDDE	$1 \cdot 10^{-6}$	38
Ethylamin, ethylendiamin	FIA-ED	$1 \cdot 10^{-5}$	21
Fenol	FIA-ED	$3 \cdot 10^{-7}$	45
	HPLC-ED	$1 \cdot 10^{-7}$	45
	LAV	$1 \cdot 10^{-5}$	40
Glukosa	CHA, GOx/BDDE	$2 \cdot 10^{-5}$	39
	SWV	$5 \cdot 10^{-4}$ [a]	44
	LSV, GOx/Au-N-NCD	$5 \cdot 10^{-6}$	43
Glutathion	HPLC-ED – redukce	$1 \cdot 10^{-6}$	54
	HPLC-ED – oxidace	$2 \cdot 10^{-6}$	54
	CHA	$6 \cdot 10^{-6}$	55
	LC-ED	$1 \cdot 10^{-9}$	61
Glutathiondisulfid	LC-ED	$2 \cdot 10^{-9}$	61
Histamin	FIA-ED	$5 \cdot 10^{-7}$	62
Homocystein	HPLC-ED	$1 \cdot 10^{-9}$	54
	FIA-ED	$1 \cdot 10^{-6}$	54
	CHA	$4 \cdot 10^{-6}$	55
Homocystin	HPLC-ED	$2 \cdot 10^{-9}$	54
Hydrazin	LSV, Pd/BDDFE	$7 \cdot 10^{-6}$	63
	LSV, Pd/BDDEA	$2 \cdot 10^{-6}$	
Chlorpromazin	FIA-ED	$4 \cdot 10^{-9}$	47
Pyrokatechol	CE-ED	$1 \cdot 10^{-7}$	3
Katecholaminy	CE-ED, mikroelektrody		59
NE		$5 \cdot 10^{-8}$	
NM		$4 \cdot 10^{-8}$	
DOPEG		$3 \cdot 10^{-7}$	
VMA		$2 \cdot 10^{-7}$	
Kyselina askorbová	FIA-ED	$1 \cdot 10^{-8}$	47
Kyselina močová vedle kyseliny askorbové	CHA	$2 \cdot 10^{-8}$	35
Kyselina šťavelová	FIA-ED	$5 \cdot 10^{-10}$	64
Leucin-encefalinamid a jeho metabolity	LC-ED		65
tyrosin		$3 \cdot 10^{-9}$	
tyrosyl-alanin		$2 \cdot 10^{-9}$	
tyrosyl-alanyl-glycin		$3 \cdot 10^{-9}$	
leucin-encefalinamid		$1 \cdot 10^{-8}$	
leucin-encefalin		$2 \cdot 10^{-8}$	
Linkomycin	FIA-ED	$2 \cdot 10^{-8}$	66
Malachitová zeleň, leukomalachitová zeleň	FIA-ED	$5 \cdot 10^{-8}$	67
Methionin	HPLC-ED	$1 \cdot 10^{-9}$	54
NADH vedle kyseliny askorbové	CHA	$1 \cdot 10^{-8}$	58, 68
Naproxen	DPV	$3 \cdot 10^{-8}$	69
Nikotin	SWV	$3 \cdot 10^{-6}$	70

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Tabulka I
Pokračování

Analyt	Metoda	Mez detekce [mol L^{-1}]	Lit.
N-Methylkarbamátové pesticidy	LC-ED		71
Carbofuran		$5 \cdot 10^{-9}$	
Carbaryl		$3 \cdot 10^{-9}$	
Bendiocarb		$1 \cdot 10^{-8}$	
Nukleové báze			
Cytosin	HPLC-ED	$2 \cdot 10^{-7}$	72
5-Methylcytosin	HPLC-ED	$8 \cdot 10^{-8}$	72
Guanin	HPLC-ED	$4 \cdot 10^{-8}$	72
	SWV	$7 \cdot 10^{-8}$	73
Thymin	HPLC-ED	$1 \cdot 10^{-7}$	72
Adenin	HPLC-ED	$2 \cdot 10^{-8}$	72
	SWV	$3 \cdot 10^{-8}$	73
Polycyklické aromatické uhlovodíky	HPLC-ED		74
naftalen		$3 \cdot 10^{-8}$	
acenaftylen		$3 \cdot 10^{-8}$	
acenaften		$2 \cdot 10^{-8}$	
fluoren		$2 \cdot 10^{-8}$	
fenanthren		$2 \cdot 10^{-8}$	
anthracen		$4 \cdot 10^{-8}$	
fluoranthen		$1 \cdot 10^{-8}$	
pyren		$1 \cdot 10^{-8}$	
benzo[*a*]anthracen		$2 \cdot 10^{-8}$	
chrysen		$2 \cdot 10^{-8}$	
benzo[*b*]fluoranthen		$2 \cdot 10^{-8}$	
benzo[*k*]fluoranthen		$2 \cdot 10^{-8}$	
benzo[*a*]pyren		$1 \cdot 10^{-8}$	
dibenzo[*a*,*h*]anthracen		$3 \cdot 10^{-8}$	
benzo[*g*,*h*,*i*]perylen		$4 \cdot 10^{-8}$	
indeno[1,2,3-*cd*]pyren		$2 \cdot 10^{-8}$	
Pentachlorfenol	FIA-ED	$6 \cdot 10^{-7}$	45
	HPLC-ED	$1 \cdot 10^{-7}$	45
	SWV	$2 \cdot 10^{-8}$	75
Polyaminy (putrescin, kadaverin, spermin, spermidin)	FIA-ED	$1 \cdot 10^{-6}$	76, 77
Puriny (guanin, hypoxanthin, guanosin, xanthin, kyselina močová)	CE-ED, mikročip	$2 \cdot 10^{-6}$	31
Serotonin	FIA-ED	$1 \cdot 10^{-8}$	62, 78
Sulfonamidy	FIA-ED	$1 \cdot 10^{-7}$	79
	HPLC-ED		80
Sulfadiazin		$4 \cdot 10^{-8}$	
Sulfamonomethoxin		$4 \cdot 10^{-8}$	
Sulfamethazin		$4 \cdot 10^{-8}$	
Sulfadimethoxin		$1 \cdot 10^{-7}$	

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Tabulka I
Pokračování

Analyt	Metoda	Mez detekce [mol L^{-1}]	Lit.
Tetracyklinová antibiotika	FIA-ED	$1 \cdot 10^{-8}$	81
	FIA-ED, Ni/BDDFE	$1 \cdot 10^{-8}$	82
tetracyklin	HPLC-ED, Ni/BDDFE	$2 \cdot 10^{-8}$	83
	HPLC-PAD	$1 \cdot 10^{-7}$	84
chlortetracyklin	HPLC-ED, Ni/BDDFE	$1 \cdot 10^{-7}$	83
	HPLC-PAD	$2 \cdot 10^{-7}$	84
oxytetracyklin	HPLC-ED, Ni/BDDFE	$2 \cdot 10^{-8}$	83
	HPLC-PAD	$1 \cdot 10^{-7}$	84
doxycyklin	HPLC-ED, Ni/BDDFE	$1 \cdot 10^{-7}$	83
	HPLC-PAD	$2 \cdot 10^{-7}$	84
Trichlorfenoly (2,3,6-TCP; 2,3,4-TCP; 2,4,6-TCP; 2,4,5-TCP; 2,3,5-TCP)	FIA-ED	$2 \cdot 10^{-8}$	41
	HPLC-ED	$2 \cdot 10^{-9}$	
Tiopronin	CV	$5 \cdot 10^{-5}$	52
	FIA-ED	$1 \cdot 10^{-8}$	
Tricyklická antidepresiva	FIA-ED	$1 \cdot 10^{-8}$	85
	HPLC-ED		
imipramin		$3 \cdot 10^{-9}$	
desipramin		$3 \cdot 10^{-9}$	
clomipramin		$5 \cdot 10^{-10}$	
amitriptylin		$2 \cdot 10^{-7}$	
nortriptylin		$1 \cdot 10^{-6}$	
doxepin		$9 \cdot 10^{-8}$	
Tryptofan	DPV	$1 \cdot 10^{-5}$	86
Tyrosin	DPV	$1 \cdot 10^{-6}$	86
Vitamin B_6 vedle B_1 a B_2	SWV, Ru/BDDFE	$6 \cdot 10^{-8}$	87
Xanthin, theofylin, theobromin, kofein	DPV	$1 \cdot 10^{-6}$ [a]	88

[a] Dolní hranice kalibrační závislosti, mez detekce neuvedena; seznam použitých zkratek je uveden na konci práce

přenos elektronů ve vrstvě N-NCD a redukce rozpuštěného kyslíku. Stanovení glukosy bylo provedeno LSV při negativním potenciálu (–0,3 V proti SCE) na základě sledování změny proudové odezvy redukce kyslíku v přítomnosti kyseliny askorbové, močové a paracetamolu s lineárním dynamickým rozsahem $1 \cdot 10^{-5}$–$1{,}5 \cdot 10^{-2}$ mol L^{-1} a detekčním limitem $5 \cdot 10^{-6}$ mol L^{-1}. Přímé stanovení glukosy na BDDFE bez jakékoliv modifikace bylo provedeno v práci[44] „square wave" voltametrií v přítomnosti kyseliny močové a askorbové. BDDFE poskytovala lineární odezvu v celém rozsahu fyziologické koncentrace glukosy v krvi. Aktivace elektrody po dlouhodobém používání byla prováděna cyklickou voltametrií v 1 M-NaOH mezi 0 a –0,8 V proti SCE. Před jednotlivými měřeními postačuje opláchnutí elektrody deionizovanou vodou. Stanovení glukosy bylo provedeno také ve vzorcích krve a porovnáno s komerčními detektory. Možnosti využití BDDFE ke stanovení různých organických polutantů v pitné vodě jsou popsány v monografii[23].

6. Závěr

BDDFE lze již nyní použít ve velkém množství analytických aplikací a zcela jistě před sebou mají další perspektivní vývoj. Přestože v katodické oblasti nemohou zcela nahradit senzory na bázi rtuti, disponují řadou vynikajících vlastností, které umožňují jejich použití při měření za extrémních podmínek (vysoký tlak nebo teplota, koncentrované kyseliny nebo hydroxidy, mechanické namáhání, přítomnost laseru nebo ultrazvuku), a jejich použití jako biosenzorů při měření v živých tkáních, neboť díky biokompatibilitě nevyvolávají nežádoucí odezvu organismu. V anodické oblasti nabízejí celou řadu výhod ve srovnání s dosud nejčastěji používaným skelným uhlíkem, zejména značnou odolnost vůči pasivaci a podstatně nižší šum.Lze očekávat, že v budoucnu poroste množství praktických aplikací BDDFE jako biosenzorů, senzorů pro online monitorování nebo detektorů k průtokovým analyzátorům, ale také jako velkoplošných elektrod pro elektrochemickou degradaci polutantů v čistírnách odpadních vod.

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Seznam zkratek

Amp.	ampérometrie
Au/BDDFE	BDDFE modifikovaná částečkami zlata
BDD	diamant dopovaný borem
BDDFE	diamantové filmové elektrody dopované borem
BDD-MEA	soubor BDD mikroelektrod
BDDMFibE-OPP$_y$	BDD mikrovláknové elektrody modifikované oxidovaným polypyrrolem
BDD/Si	BDD film nanesený na křemíku
CE	kapilární elektroforéza
CHA	chronoampérometrie
CV	cyklická voltametrie
DCP	dichlorfenol
DOPEG	DL-(3,4-dihydroxyfenyl) ethylenglykol
DPV	diferenční pulzní voltametrie
ED	elektrochemická detekce
FIA	průtoková injekční analýza
GOx	glukosooxidasa
GOx/Au-N-NCD	zlatá elektroda modifikovaná nanokrystalickým nedopovaným diamantem s imobilizovanou glukosooxidasou
GOx/BDDFE	BDDFE modifikovaná glukosooxidasou
LAV	laserová ablační voltametrie
LOD	mez detekce
NADH	redukovaná forma nikotinamidadenindinukleotidu
NE	norepinefrin (noradrenalin)
Ni/BDDFE	BDDFE modifikovaná Ni
NM	DL-normetanefrin-hydrochlorid
PAA	poly(allylamin)-hydrochlorid
PAD	pulzní ampérometrická detekce
PAH	polycyklické aromatické uhlovodíky
PEEK	polyetheretherketon
Pd/BDDEA	soubor BDDFE modifikovaných Pd
Pd/BDDFE	BDDFE modifikovaná Pd
pyrrol-DNA/BDDFE	BDDFE modifikovaná membránou DNA s navázaným pyrrolem
Ru/BDDFE	BDDFE modifikovaná tris(2,2'-bipyridin)rutheniem
SAM/Au/BDDFE	BDDFE modifikovaná částečkami zlata potažená samoskladnou vrstvou kyseliny merkaptooctové
SWV	„square wave" voltametrie
TCP	trichlorfenol
tyr/BDDFE	BDDFE modifikovaná tyrosinem
VMA	vanilmandlová kyselina

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J. Musilová, J. Barek, and K. Pecková *(Charles University in Prague, Faculty of Science, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry):* **The Use of Boron-Doped Diamond Film Electrodes for Detection of Organic Compounds**

The use of the title electrodes in electroanalysis of organic compounds is reviewed. The electrodes have gained popularity in a variety of electrochemical applications such as electrochemical sensors employed in voltammetric or liquid flow methods (HPLC, flow injection analysis, capillary electrophoresis). Due to their excellent properties, they are useful also in measurements under extreme conditions or in bioelectrochemical applications. The review summarizes the results obtained in the last decade.

8. Appendix II

Boron-Doped Diamond Film Electrodes – New Tool for Voltammetric Determination of Organic Substances

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Boron-Doped Diamond Film Electrodes—New Tool for Voltammetric Determination of Organic Substances

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This review with 194 references summarizes the recent progress in the development and applications of boron-doped diamond film electrodes in electroanalysis of organic compounds. It is based on the survey of 106 papers listed in a comprehensive table devoted to batch voltammetric and liquid flow amperometric methods using boron-doped diamond electrodes. The varieties in their construction, surface pre-treatment and electroanalytical methods used are discussed. Special attention is paid to miniaturized boron-doped diamond electrodes for in vitro/in vivo sensing, or electrochemical detection coupled to conventional or chip-based electrophoretic detection systems. Further, possibilities and limitations of surface modification are discussed.

Keywords Boron-doped diamond electrode, voltammetry, amperometry, review

INTRODUCTION

The era of diamond electrodes started in the eighties by isolated studies of Japanese researchers who suggested the ion-implanted diamond electrodes (1) and Russians suggesting semi-conducting diamond electrodes for photoelectrochemistry (2). Since then, a tremendous progress could be traced in applications ranging from electrosynthesis, electroanalysis, use in Li-ion batteries, fuel cells, to diamond-based biosensors. During these years it was well established that conductive diamond thin films are in many ways ideal as electrode materials.

The highest popularity have gained polycrystalline, boron-doped diamond (BDD) thin films introduced in 1992 by Fujishima (3). The first studies conducted with BDD electrodes (BDDE) a year later outlined their suitability for electrosynthesis (4), electroanalysis (5), and electrochemical waste treatment (6). The number of papers devoted to these topics has exceeded 400. Simultaneously, the continuous fundamental research on diamond materials recognized them as potential wide band gap semi-conductors with good electronic, mechanical and chemical properties. Intensive research, especially in the last five years, was focused on the use of diamond-based electronic devices in biosensing, optoelectronics, acoustic, quantum computing and other advanced technologies. Nevertheless, the applications of BDDE for electrochemical sensing of both inorganic and organic analytes hold unceasing interest acknowledged by an increasing number of publications each year.

This review is based on the survey of applications of BDD-based sensors in electroanalysis of organic compounds since the first proposal in 1993 (5). The fast progress in electroanalytical methods used, construction of sensors, surface treatment and surface modification since that time can be highlighted by the following boundary stones documenting the crucial role of research groups of Profs. Swain (Michigan State University, East Lansing, MI, USA) and Fujishima (formerly University of Tokyo, Tokyo, Japan): The applications of BDD-based detectors for liquid flow methods started in 1997 for flow injection analysis with amperometric detection (FIA-AD) of ethylenediamine and ethylamine using BDDE housed in a home-made thin layer cell (7). In 1999, the same detection cell was coupled with ion chromatography of nitrites and azides (8). In 1998, the first BDD microelectrodes (BDDμE) exhibited steady state cyclic voltammograms (CVs) (9) and 5 years later were used in capillary zone electrophoresis (CZE) (10, 11), chip-based devices (12), or under *in vitro/in vivo* conditions (13–15). In 2000, arrays of BDDμE were proposed (16) and the continuous trend on miniaturization is illustrated by a recent report on construction of a random array of BDD nano-disc electrodes (17). To extend selectivity of BDDE, intensive research on surface oxidation (18) and other modifications was done. The easy electrochemical oxidation and the surprising inertness of such

Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th Anniversary of the Nobel Prize for polarography.

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O-terminated BDD (OBDD) surface towards adsorption was shown in 2000 (19) in the example of serotonin (5-HT) electrooxidation. Together with earlier reports on electrochemical properties of O-terminated surfaces (20), this drew attention to their use especially for electroanalysis of charged organic species. Further biofunctionalization of bare and oxidized diamond surfaces was enabled by introduction of carboxylic (21) and amino groups (22). Since 1998, such functionalized surfaces have been modified by DNA (23, 24), enzymes (25) and proteins (26), which opened the way for applications of diamond-based sensors in biotechnologies.

This stunning development inspires a number of scientists and technologists in both fundamental and applied research, which can be documented by a number of reviews devoted to the particular aspects of diamond-related research. Reviews on general electrochemical properties (27) and surface modifications (28, 29), electrosynthesis and anodic waste treatment (30–33), and electroanalytical applications (34–39) appeared in the last 5 years together with compact reviews (40, 41) and books devoted to diamond electrochemistry, physics and applications (42, 43). This review concentrates on the use of BDDE for determination of organic compounds. Furthermore, an outlook in current trends in research using BDD-based sensors including their modification and miniaturization is given.

BORON-DOPED DIAMOND AS ELECTRODE MATERIAL

The common BDD films used in electroanalysis usually grow on Si supports from dilute mixtures of a hydrocarbon gas (typically methane) in hydrogen using one of several energy-assisted chemical vapor deposition (CVD) methods, the most popular being hot-filament (HFCVD) and microwave plasma assisted CVD (MPCVD). These methods mainly differ in the manner in which the gas activation is accomplished. Typical growth conditions are C/H ratios of 0.5–2%, pressures of 10–150 torr, substrate temperatures of 700–1000°C, and microwave powers of 1000–1300 W, or filament temperatures up to ~2800°C. The film grows by nucleation at rates in the 0.1–3 μm/h range to thickness at least ~1 μm. Controlled doping levels ranging from 10^{17} to 10^{21} cm^{-3} are usually achieved resulting in film resistivities <0.1 Ω cm (44, 45). MPCVD and HFCVD are the most popular for BDD preparation although they proceed under non-equilibrium conditions, which limit the crystalline quality, control of growth rate and level of eventual dopant. The newest trends involve development and characterization of nano- (crystallite size <100 nm), ultrananо- (5–15 nm) and single-crystalline diamond surfaces and search for other dopants and substrates for diamond deposition (43). Such specialized films were so far rarely used in electroanalysis; nevertheless, these studies may help to understand the CVD diamond growth under non-equilibrium conditions and thus increase their quality.

BDD materials produced in research laboratories are gradually substituted by commercially available materials (Table 1). The analytical techniques routinely used to characterize the morphological, optical, chemical and electronic properties of diamond thin films include Raman, Auger electron and X-ray photoelectron spectroscopies, scanning electron micrography, scanning tunneling and force microscopies, powder X-ray diffraction analysis, and secondary ion mass spectrometry (44).

BDD thin films possess several excellent electrochemical properties: low and stable background current over a wide potential range, corrosion resistance, high thermal conductivity and high current densities. They offer superb micro structural stability at extreme cathodic and anodic potentials and resistance to fouling because of weak adsorption of polar species on the H- and O-terminated surface, which results in good responsiveness for many redox analytes without pre-treatment (42, 44, 46, 47).

Besides other electrochemical applications of BDDE described in monograph (42), great attention is paid to their use in electroanalysis as simple electrochemical sensors employed in voltammetric methods or coupled to liquid flow methods (HPLC, FIA, CZE) for detection of organic and inorganic species, or specialized selective applications of BDD-based bioelectrochemical sensors.

BORON-DOPED DIAMOND ELECTRODES IN ORGANIC ANALYSIS

The analytical applications of BDDE were subject to several reviews in the last 5 years (34–39, 42, 48, 49). In general, attention is paid to both inorganic and organic species. The intensive research regarding organic analytes is documented by Table 2, which characterizes selected (and we hope all important) studies devoted to particular organic analytes since the beginnings in 1997 to 2008. It involves the studies, where at least some of the analytical characteristics [i.e., linear dynamic range (*LDR*), slope and intercept for linear calibration dependences, limit of detection or quantitation (*LOD* or *LOQ*), and repeatability/reproducibility of the electrode signal] appeared.

Surveying Table 2, prevalence of oxidisable analytes is remarkable. The only determinations based on reduction were suggested for some nitrophenols and nitro-group containing pesticides and drugs (50, 51), and for cytochrome c (52). This indicates that despite the fact that BDDE are mentioned to be a suitable alternative to mercury-based electrodes for stripping analysis of inorganic species (53), their possibilities in analysis of reducible organics remain relatively unexploited.

The popularity of BDDE for oxidisable substances is given by the wide potential window in anodic region. This enabled direct determination of aliphatic amines (54), polyaromatic hydrocarbons (55) and sulfur-containing analytes [e.g., aminothiols (56), disulfides (57–59)], which are rarely detectable at conventional bare electrodes. The other advantage is the fouling resistance or easy removal of adsorbed reaction by-products and products by rinsing BDDE with appropriate solvent or treatment at high anodic or cathodic potential. Methods for problematic surface passivators [chlorophenols (CP), nitrophenols (NP) and amino group containing aromatics] were reported with signal

TABLE 1
Commercial suppliers of BDD materials

Supplier	Characterization of provided BDD materials and electrodes and related equipment	Ref.
Element Six (UK)[a]	As deposited BDD, individual pieces 10 × 10 mm, 0.6 mm thickness, boron level $>10^{20}$ cm^{-3}, resistivity 0.038–0.105 Ω cm	(170)
Windsor Scientific (UK)	For a) and b) boron doping level 0.1%, resistivity 0.075 Ω cm a) BDDE in PEEK body, 3 mm diameter, flat bottom part b) Individual pieces 10 × 10, 5 × 5 or 3 × 3 mm, 0.5 mm thickness, both sides polished c) Single crystal BDD, resistivity < 5 Ω cm, 0.25 mm thickness, boron level > 10^{20} cm^{-3}	(174)
Adamant Technologies (Switzerland)[b]	a) p-Si/BDD circular discs [resistivity 0.09 Ω cm, diameter 8 mm, 1.3 μm thickness, boron level > 1200 ppm, reversible infixed in RDE head (circular surface 12.4 mm^2, diameter 3.7 mm)] b) Customized Adamant® BDD electrodes on monocrystalline or polycrystalline Si, one or both sides coated, 0.1–5 μm thicknesses, boron level ~ 0–8000 ppm c) BDD–MEA mounted in SenSys sensor, configuration X–Y/Z = 5–150/473 and 15–300/127, where X is microelectrode diameter (μm),Y is distance between microelectrodes (μm) and Z is number of microelectrode in the array	(67)
Condias (Germany)[c]	HFCVD BDD, discs, plates, mesh, pins and combinations thereof, areas up to 100 × 50 cm^2, standard substrate material Nb, Si and graphite, BDD thickness >15μm	(68)
sp3 Diamond Technologies (USA)	Undoped or conductive HFCVD Si/BDD films (resistivity 0.05–10 Ω cm), wafer diameters (*d*) 50, 75, 100, 150, 200 and 300 mm, 0.2–10.0 μm thickness (thicker films available), grain size down to 10 nm	(193)
ESA Biosciences (USA)	Thin layer cell for FIA and HPLC with a BDD disc electrode	(194)

[a]formerly De Beers Industrial Diamond; [b]spin-off company of Swiss Center of Electronic and Microtechnology (CSEM); [c]spin-off company of the Fraunhofer Institute for Thin Films and Surface Technology

repeatability typically better than 5%. Their electrooxidation proceeds via initial one-electron oxidation step leading to formation of phenoxy radicals (60, 61) or radical cation at the nitrogen atom (62–64), respectively. These radicals subsequently undergo radical-radical coupling to form dimeric, oligomeric and polymeric species possibly passivating the electrode surface. BDDE represents usually no exception on fouling problems when using batch voltammetric methods. Nevertheless, in contrast to other solid surfaces where the activation approaches rely either on in situ repetitive electrochemical treatment in the presence of various deactivating compounds (65, 66), or on mechanical removal by polishing with diamond or alumina powder, simple regeneration of BDDE as described above is sufficient.

It should be mentioned that voltammetric or amperometric methods for determination of organic analytes characterized by exact analytical figures of merit are outnumbered by general voltammetric investigations concerning basic electrochemical properties of selected substances, i.e., investigation of the reaction mechanism and its kinetics in dependence on the experimental conditions and BDD surface pre-treatment, passivation of the electrode surface and its remediation, etc. Typically, these studies precede further applications of BDDE either for anodic decomposition of organic compounds or amperometric applications.

Boron-Doped Diamond Electrodes and Their Construction and Arrangements for Electroanalytical Measurements

MPCVD or HFCVD BDD films were used in the studies presented in Table 2, in which deposition technique and electrode pre-treatment or further modification are also listed. The support material is given in the case it was specified in the particular study, otherwise unspecified silica was used. This support was used exclusively for common-sized BDDE with areas typically ranging between 0.05–0.2 cm^2. Larger areas up to 0.7 cm^2 were reported for BDDE provided from the Swiss Center of Electronic and Microtechnology (CSEM, Neuchâtel, Switzerland) (67).

Several sources of BDDE can be traced in Table 2. The beginnings of electroanalysis are confined to research groups equipped with MPCVD reactors: polycrystalline BDD films deposited on both n- and p-type Si by Fujishima and Einaga groups and microcrystalline (crystallite size 1–3 μm) and nanocrystalline (crystallite size 50–100 nm in aggregates of ~15 nm diameter) BDD films deposited on p-type Si in Swains' group appear exclusively till 2001. The HFCVD BDD films from Fraunhofer Institute for Surface Engineering and Thin Films (Braunschweig, Germany) available since 2001 through the spin-off company Condias (68) (Itzehoe, Germany) and the HFCVD films from CSEM available

TABLE 2
Selected applications of BDD-based sensors in organic analysis

Analyte	BDD electrode, pre-treatment[a]	Electroanalytical method, arrangement, conditions	*LDR* [μmol/L]	*LOD*[A] [μmol/L], (matrix[B])	Ref.
Neurotransmitters, their metabolites and precursors					
Histamine	Si(100), MPCVD BDD	**LSV**, 0.1 M PB pH 7.0	Not given	1[b]	(19, 89)
5-HT 5-HIAA		**FIA/AD**, TL cell (BAS), 0.1 M PB pH 7.0	0.5–100 0.01–50 0.1–100	0.5, $S/N = 13.8$ 0.01, $S/N = 18.1$ 0.1, $S/N = 32.9$	(19)
DA, 4-methylCA, AA	p-Si(100), MPCVD BDD	**FIA/AD**, home-made TL cell (7), 0.1 M PB pH 7.2	0.1–3000[b]	0.0025, 0.0020, 0.0120	(8)
DA[c]	Si(100) MPCVD BDD, AT at +2.6 V for 75 min in 0.1 M KOH	**LSV**, 0.1 M $HClO_4$ **ChrA**	1–70 0.1–1	not given 0.05	(89–91)
DA[c]	Oxygenated[d] MPCVD TW/BDDμE	**ChrA**, ultrapure water	0.05–100	0.05	(15)
DA, E, NE	MPCVD BDD microline electrode	**CZE/AD**, end column, 30 mM MES pH 5.7	0.1–100[b]	0.020, 0.019, 0.023	(163)
5-HT melanine	MPCVD Pt/BDDμE	**DPV**, Krebs buffer pH 7.4	2–10[b,e]	2.05, 1.22	(120)
	MPCVD Pt/BDDμE	**FIA/AD**, end column, buffer as for DPV	2–10[b]	0.41, 0.65	
DA CA[c]	MPCVD Pt/BDDμE	**CZE/AD**, end column, 10 mM PB pH 6.0	0.08–100 0.1–100	0.078 0.120	(10)
DA, NE NMN DOPEG VMA	MPCVD Pt/BDDμE	**CZE/AD**, end column, 250 mM BB pH 8.8	0.050–100 0.050–100 0.250–50 0.100–50	0.044, 0.052 0.040 0.250 0.150	(14)
DA DOPAC, 5-HT[c]	n-Si(100), MPCVD BDD modified by PDMA	**ChrA**, 0.2 M PB pH 7 **SWV**, 0.2 M PB pH 7	0.2–2.6 (SWV) not given	0.06 (ChrA) not given	(141) (133)
DA[c]	Si(100), ABDD modified by negatively charged gold nanoparticle/polyelectrolyte-coated polystyrene colloids	**LSV**, 0.07 M PB pH 7.2	5–100	0.8[C]	(169)
DA[f]	MPCVD TW/BDDμE modified by OPPy	**ChrA**, 0.1 M PB pH 7	0.0005–100	0.0001	(161)
Phenolic compounds					
Ph 2-CP 3-CP 4-CP PCP	p-Si(100), MPCVD microcrystalline and nanocrystalline BDD[g]	**FIA/AD**, home-made TL cell (7), 0.05 M PB, pH 3.5 **HPLC/AD**, two-step gradient elution, 0.05 M PB, pH 3.5/acetonitrile 65:35 (v/v) for 10 min, after change to 20:80 (v/v)	FIA[h]; HPLC[h] 0.30–100; 0.1–80 0.05–200; 0.1–60 0.10–100; 0.1–60 0.50–100; 0.3[i] (0.1[i])–60 0.60–1200; 0.1–80	FIA[h]; HPLC[h] 0.30; 0.1 0.05; 0.1 0.10; 0.1 0.50; 0.1 0.60; 0.1	(134)
2,4-DCP	MPCVD BDD, AT at +2.64 V for 4 min in BR buffer, pH 2	**FIA/AD**, TL cell (GL Sciences), 60% methanol/0.5% phosphoric acid	0.02–100	0.02	(129)

(Continued on next page)

TABLE 2
Selected applications of BDD-based sensors in organic analysis (*Continued*)

Analyte	BDD electrode, pre-treatment[a]	Electroanalytical method, arrangement, conditions	*LDR* [μmol L]	*LOD*[A] [μmol L], (matrix[B])	Ref.
2,6-; 2,3-DCP 2,5-; 2,4-DCP 3,4-; 3,5-DCP 2,3,6-; 2,3,4-TCP 2,4,6-; 2,4,5-TCP 2,3,5-TCP	MPCVD BDD, AT at +2.64 V for 4 min in BR buffer, pH 2	**HPLC/AD**, TL cell (GL Sciences), 60% methanol/0.5% phosphoric acid. Column switching technique for pre-concentration (50×)	not given	0.00023, 0.00050 0.00047, 0.00040 0.00044, 0.00221 0.00030, 0.00037 0.00050, 0.00052 0.00047	(129)
Ph, 2-CP 4-CP, 2,4-DCP 4-C-3-MP	Commercial polished BDD film (170), bare or activated for 30 s with 532 nm Nd:YAG laser at 1.6 W cm^{-2}	**ChrA** in hydrodynamic flow, channel flow cell, 0.1 M HNO_3,	0.01–10 0.01–50, 0.01–20 0.01–20	0.01[b,D]	(171)
4-CP 4-CP in the presence of 2,4-DCP+2,4,6-TCP	HFCVD BDD, AT at +3.0 V followed by CT at –3.0 V, 30 min of each	**SWV**, 0.1 M BR buffer pH 6 **SWV** combined with mathematical deconvolution procedure	7–40 not given	0.16[C] 0.31 (river water)	(103, 104)
PCP	HFCVD BDD, AT + CT as in (104), polarized at –3.0 V for 30 s between scans	**SWV**, BR buffer pH 5.5	1–60	0.020, 0.056 [C] (river water)	(111, 112)
4-CP	Commercial polished BDD (170), 60 s of insonated electrodeactivation or AT at +5.0 V followed by CT at –5.0 V, 10 s of each in 0.1 M HNO_3	**Sono-CV**, 0.1 M HNO_3	1–300	1[E]	(117)
Ph, 2,4-DCP 2,4,6-TCP, PCP 2-CP, 3-CP, 4-CP	MPCVD Pt/BDDμE	**CZE/AD**, end column, 0.01 M/0.02 M mixed BB/PB, pH 8.4	0.5–100 0.5–100 0.1–100	0.5 0.5 0.1	(158)
2-CP, 3-CP 2,4-DCP	MPCVD Pt/BDDμE	**CZE**/indirect **AD**, 0.8 mM ferrocene carboxylic acid in 0.01 M PB, pH 8.1	30–600 50–600	30, $S/N = 6$ 50, $S/N = 6$	(158)
2-CP,3-CP,4-CP 2,4-DCP 2,4,6-TCP PCP	MPCVD Pt/BDDμE	**CZE/AD** after off-line SPE, end column, 0.01 M/0.02 M mixed BB/PB, pH 8.4, pre-concentration factor 250:1	0.00016–0.78 0.00025–0.80 0.0010–0.76 0.00019–0.76	0.00016 0.00025 0.00100 0.00019 (river water)	(162)
Ph, 2-CP, 2,4-DCP, 2,3-DCP 2,4,6-TCP	MPCVD BDD microline electrode, Si(100) support removed by chemical etching	**CZE/AD**, end column, 10 mM/10 mM mixed BB/PB, pH 7.8	not given	not given	(163)

Catechin	BDD modified by ruthenium tris (2, 2′) bipyridyl	**CV**, 0.1 M $NaNO_3$ pH 12 **ChrA**, 0.1 M $NaNO_3$ pH 12	10–800 0.3268–159.1	not given 0.121	(172)
Flavonoids	HFCVD BDD, AT + CT as in (104)	**FIA/AD**, TL cell, BR buffer pH 5.0	10–250	7.7	(173)
Methylparaben, Ethylparaben, Propyl-paraben	Commercial polished BDD (174), oxidation by repeated cycling between large potential limits in neutral media	**CV**, EtOH/0.1 M Na_2SO_4 pH 7 (1:4; v/v) **ChrA**, conditions as for CV, quiescent solution	2–104, 20–180, 20–140 10–80, 2–112, 10–80	1.5, 1.97, 3.6 0.7, 1.03, 0.97[F]	(175)
Nitrophenols and other nitroaromatics					
Ph hydroquinone 4-NP	MPCVD BDD[g]	**CV**, 0.5 M H_2SO_4 **DPV**, 0.5 M H_2SO_4	CV[e], DPV[e] 50–2000, 50–1400 50–10000, 50–3000 50–10000, 50–7000	[D,e] 8.2, 1.82 12, 1.67 11, 1.44	(121, 122)
4-NP	HFCVD BDD, pre-treatment as in (104)	**SWV**, 0.1 M BR pufr pH 6	5–50[k] 5–40[l]	0.068[k], 0.101[l] 0.382[k], 0.441[l] (river water)[C]	(105–107)
4-NP	Commercial BDD (67), AT at +3.0 (5 s) followed by CT at –3.0 V (30 s) in 0.5 M H_2SO_4	**Sono-SWV**, 0.1 M BR buffer pH 6	2.99–48.7	0.093[k] 0.062[l,C]	(118)
4-NP	BDD-MEA	**LSV**[j], PB pH 6.8	1–12	not given	(86)
4-NP, 2,4-DNP, 2-NP	Commercial BDD (174), oxidation by repeated cycling between –2.5 V and +2.5 V in 1 M HNO_3	**DPV**[k], BR buffer pH 11.0, pH 10.0 **DPV**[l], BR buffer pH 6.0, pH 4.0 **HPLC/AD**[j], wall jet, 0.05 M AB pH 4.7/methanol (60/40; v/v)	[k]2–40, 0.8–10, - [l]0.4–100, 0.2–10, 0.2–100 [i]0.4–100, 2–100, 6–100	[k]2, 0.8,- [l]0.3, 0.4, 0.4 [l]4, 2, 6	(85)
2-methyl-4,6-dinitrophenol	MPCVD microcrystalline BDD	**DPV**, BR buffer pH 8.0[k], BR buffer pH 5.0[l]	0.2–10[k] 0.3–10[l]	7[k,G] 0.3[l,G]	(176)
Dichloran	MPCVD microcrystalline BDD, oxidation as in (85)	**DPV**[l], BR buffer pH 6.0 methanol (9:1) **LSV**[l], BR buffer pH 6.0/methanol (9:1)	0.5–100[l] 1–100[l]	0.5[l,F] 1.9[l,F]	(177)
2-NP	Commercial BDD (174)	**ChrA**, 50 mM PB pH pH 7.0,	not given	0.32	(178)
1,3-DNB 2,4-DNT	BDD film band electrode	**CE microchip/AD**[j], 15 mM BB pH 9.2 (containing 15 mM SDS)	1.19–8.33 1.10–7.70	0.42 0.60	(12)
Aliphatic amines; aromatic amines; dyes and dye-related compounds					
Polyamines[m]	p-Si(100), MPCVD BDD	**FIA/AD**, home-made TL cell (7), 0.1 M $NaClO_4$+ 0.01 M CB, pH 10	1–1000[b]	1.0	(54)
N-nitrosoamines[n]	Commercial HFCVD BDD (67), CT at –3.0 V followed by AT at +3.0 V, 30 s each, in 0.1 M $HClO_4$	**SWV**, 0.1 M BR buffer pH 2	2–13.6	0.2 [C]	(80)

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TABLE 2
Selected applications of BDD-based sensors in organic analysis (*Continued*)

Analyte	BDD electrode, pre-treatment[a]	Electroanalytical method, arrangement, conditions	*LDR* [μmol L]	*LOD*[A] [μmol L], (matrix[B])	Ref.
Aniline	Si(111), MPCVD BDD	**LS-AdSV** (cathodic), BR buffer pH 1.8	1–30	not given	(116)
3-amino-fluoranthene	Si(100), MPCVD nanocrystalline BDD	**DPV**, BR buffer pH 4.0/MeOH (1:1)	0.2–10	0.2[G]	(179)
		HPLC/AD, home made TL cell (7), MeOH/PB pH 4 (9:1, v/v)	0.02–100	0.05	(35, 180)
4-aminophenol	BDD film band electrode	**CE microchip/AD**, end column, 30 mM AB pH 4.5	2–50	2.0	(159)
2-AN			2–50	1.3	
1-AN	Si(100), MPCVD microcrystalline BDD	**HPLC/AD**, TL cell (BAS), MeOH/0.01 M PB,pH 6 (3:7, v/v)	0.1–100	0.13	(181)
2-AB			0.1–100	0.12	
2-AB, 3-AB, 4-AB	Si(100), MPCVD nanocrystalline BDD	**DPV**, BR buffer pH 7.0 (2-AB), pH 8.0 (3-AB), pH 9.0 (4-AB)	0.1–10, 0.2–8, 0.1–10	0.12, 0.13, 0.25	(182)
2-AB, 3-AB, 4-AB	Si(100), MPCVD microcrystalline BDD, AT at +2.4 V in 0.1 M H_2SO_4 for 60 min	**HPLC/AD**, TL cell (7), 0.01 M AB pH 5.0/acetonitrile/methanol (40/30/30)	0.4–10, 0.2–10	0.20, 0.32 0.51	(183)
		HPLC/AD after off-line SPE, pre-concentration factor 100:1	0.025–0.1, 0.0025–0.1, 0.005–0.1	0.0084, 0.0130, 0.0170 (river water)	
4-aminophenol	BDD film band electrode	**CE microchip/AD**, end column, 30 mM AB pH 4.5	2–5	2.0	(159)
2-AN			2–50	1.3	
Malachite green, leukomalachite green	MPCVD BDD	**FIA/AD**, 0.1 M PB pH 2.0, TL cell: commercial (BAS); Home-made	1–100, 8–80 1–100, 4–40	0.05, 0.05	(184)
Aromatic hydrocarbons					
16 polycyclic aromatic hydrocarbons[D]	Commercial BDD (174), AT in phosphoric acid/acetonitrile at +2.5 V for 10 min	**HPLC/AD**, home-made wall jet cell, gradient elution 0.04 mol/L phosphoric acid/acetonitrile from 50:50 to 10:90 (v/v) in 10 min, after kept at 10:90	2–3 orders of magnitude, range cca 0.050–50	0.0113[C] (naphthalene) - 0.0368 (benzo-(*g,h,i*)perylene)	(55)
Benzene	HFCVD BDD, AT + CT as in (104)	**CV**, 0.5 M H_2SO_4	360–1050	not given	(87)
Agrochemicals					
Carbaryl	HFCVD BDD, AT + CT as in (104)	**SWV**, 0.1 M Na_2SO_4, pH 6.0	2.5–30	0.14[C], 0.16 (river water)	(110)

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Carbofuran, carbaryl, bendiocarb, dichloron, methyl-2-benz-imidazole-carbamate	Si(100), MPCVD BDD, AT at +3.0 V for 30 min in case of electrode fouling	**FIA/AD+HPLC/AD**, thin layer cell (BAS), **HPLC/AD**, 0.1 M PB pH 2.25/acetonitrile (80%, 20%) **FIA/AD**, 0.1 M PB pH 2.25. **Indirect determination** after alkali hydrolysis to phenols: **HPLC/AD**, 0.01 M $NaClO_4$ in acetic acid/acetonitrile/water/(0.5%, 40%, 59.5%)	FIA direct determination 0.1–100[b], for other methods not given	HPLC: 0.06, 0.1, 0.1, 0.025, – HPLC indirect: 0.005, 0.003 0.010, –, – $S/N = 2$	(130)
Parathion	HFCVD BDD, AT + CT as in (104)	**SWV**, BR buffer pH 7.0	1–8	0.030[H], 0.132 (river water)	(109)
Pharmaceuticals					
Acetaminophen	Si(100), MPCVD BDD	**CV**, 0.1 M PB pH 8 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 8	100–8000 0.5–50	10 0.01, $S/N = 4$	(76)
Acetaminophen, AA	Commercial BDD (174), oxidation by repeated cycling between +1.8 V and −1 V vs. SCE in Na_2SO_4	**CV**, BR buffer pH 1.96 **ChrA**, BR buffer pH 1.96,	10–100[b] 10–70	not given 0.86, 1.42[c,C]	(98)
Captopril	n-Si(111), MPCVD BDD	**CV**, 0.1 M PB pH 9 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 8	50–3000 0.5–100	25 0.01	(72)
Chloramphenicol	Commercial BDD (67)	**CV**[I], 0.1 M PB pH 6 in 1% ethanol **FIA/AD**[I], TL cell (BAS), MP as for CV	100–10000 0.1–50	not given 0.03	(50)
Chlorpromazine	p-Si(100), MPCVD BDD	**FIA/AD**, home-made TL cell (7), 0.1 M KCl + 0.01 M $HClO_4$	0.3–3000	0.004	(8)
D-penicillamine	Si(100), MPCVD BDD	**CV**, 0.1 M PB pH 7 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 7	500–10000 0.5–50	25 0.01, $S/N = 4$	(73)
Fluvastatin sodium; pefloxacin	Commercial BDD (174), before each experiment manually polished with aqueous slurry of alumina powder ($\Phi = 0.01$ μm)	**DPV**, BR buffer pH 10 (fluvastatin sodium); 0.5 M H_2SO_4 (pefloxacin) **SWV**, as for DPV	1–600; 2–200 2–100; 2–200 (serum) as for DPV	0.457; 1.37[F] 0.710; 1.55 (serum) 0.481; 0.512 0.108; 1.93 (serum)	(101); (102)
Imipramine, desipramine, clomipramine, amitryptyline, nortryptyline, doxepin	Si(100), MPCVD BDD	**FIA/AD**, wall jet arrangement, 0.1 M PB pH 6.9 **HPLC/AD**, acetonitrile/0.1 M PB pH 6.9 ± 0.1, 375:625 (v/v) for all except for clomipramine (50:50).	0.01–100[b] 0.05–100[b]	FIA: 0.01[b], nortryptyline 0.1 HPLC:0.003, 0.003, 0.0005, 0.163, 1.080, 0.062	(71)
Lidocaine	Commercial HFCVD BDD (67), AT at +3.2 V followed by CT at −2.8 V, 30 s of each, in 0.1 M $HClO_4$	**SWV**, BR buffer pH 2	20–120	0.015[C]	(79)

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TABLE 2
Selected applications of BDD-based sensors in organic analysis (*Continued*)

Analyte	BDD electrode, pre-treatment[a]	Electroanalytical method, arrangement, conditions	*LDR* [μmol L]	LOD^A [μmol L], (matrix^B)	Ref.
Lincomycin	Si(100), MPCVD BDD	**CV**, 0.1 M PB pH 7 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 7	20–630 0.5–125	40 0.02	(75)
Naproxen, AMN	p-Si(111), MPCVD BDD	**DPV**, 0.1 M $LiClO_4$ in CH_3CN	0.5–50[b]	0.097, 0.096	(185)
Nitrofurazone	Si, HFCVD BDD	**DPV**[d], direct in BR buffer pH 4, indirect in the presence of O_2 in BR buffer pH 8.	0.99–11, 0.99–17	0.34, 0.41	(51)
Procaine	Si(100), MPCVD BDD	**CV**, 0.07 M PB pH 7.0	5–200	0.5 [C]	(100)
Promethazine hydrochloride	HFCVD BDD	**SW-AdSV (anodic)**, BR buffer pH 4.0	0.596–4.76[p] 0.596–4.76[q]	0.0886[p, C] 0.154[q]	(81)
SDZ, SMZ, SMM, SDM	Si(100) MPCVD BDD	**HPLC/AD**, TL cell (GL Science), acetonitrile/0.1 M PB pH 3.0 (20:80, v/v)	0.20–400, 0.18–360 0.18–360, 0.32–970	0.15, 0.14 0.13, 0.10[C]	(77)
Sulfadiazine sulfamerazine sulfamethazine	Si(100), MPCVD BDD	**FIA/AD** TL cell (BAS),0.1 M PB pH 7.1 **HPLC/AD**, 0.1 M PB pH 7.1/MeOH (8.5:1.5)	0.05–50[b] not given	0.05[D,b] 0.1[E,b]	(186)
Tetracycline chlortetracycline oxytetracycline doxycycline	n-Si(111) MPCVD BDD, oxidation by cycling between 0 and +2.2 V vs. Ag/AgC in 0.1 M KOH for 30 min	**FIA/AD**, TL cell (BAS), 0.1 M PB pH 2	0.1–50 0.5–50 0.5–50 0.5–50	0.01[b]	(187)
Tetracycline	n-Si(100), Ni-implanted MPCVD BDD	**CV**, 0.1 M PB pH 2 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 2	100–3000 1–100	not given 0.01	(99)
Tiopronin	n-Si(111), MPCVD BDD	**CV**, 0.1 M PB pH 8 **FIA/AD**, TL cell (BAS), 0.1 M PB pH 8	50–10000 0.5–50	50 0.01	(74)
Aminoacids, peptides, proteins					
Trypthophan tyrosine	Si(100), MPCVD BDD, AT at +2.8 V for 10 s in 1 M H_2SO_4	**DPV**, Na_2PO_4/NaOH buffer pH 11.2	20–1000[e]	10 1	(124)
L-cysteine	Si(100), MPCVD BDD	**CV**, 0.5 M $KHCO_3$. Scan rate 50 mV/s, 20 mV/s **FIA/AD**, TL cell (BAS), 0.1 M PB pH 7	1–10, 10–200[r] 0.1–100	0.9 0.021	(94)

GSH GSSG	Si(100), MPCVD BDD, AT at i = +8 mA cm^{-2} in pH 2 BR buffer (20 min)	**LC/AD**, TL cell (GL Sciences), 0.1% trifluoroacetic acid/acetonitrile (98:2)	0.025–250 0.025–250	0.0014 0.0019	(58, 59)
Homocysteine homocysteine, GSH, methionine Cystine, cysteine homocystine, GSSG	Si(100) MPCVD BDD, AT at +2.4 V (vs. Ag/AgCl) for 30 min in 0.1 M KOH	**FIA/AD**, TL cell (GL Sciences), 2% acetonitrile/0.05 M PB pH 2.7 **HPLC/AD**, TL cell (GL Sciences), 0.2 mM 1-octanesulfonic acid in 3% acetonitrile/0.05 M PB pH 2.7	0.005–100 0.05–100 0.1–100	0.001 0.05 0.1	(57)
Homocysteine, GSH, cephalexin	n-Si(111), MPCVD BDD	**CV**, 0.1 M CB pH 9.2	510–1005, not given, 10–25	not given[b]	(95)
Cysteine homocysteine GSH	Commercial polished BDD (170)	**Chr.A** detection of TNBA—product of catalytic reaction of the detected thiol with 50 μM in 0.1 M PB pH 7.5	not given	5.7[c] 4.4 5.8	(56)
LEA, T, TA, TAG, LE	Si(100), MPCVD BDD	**LC/AD**, wall jet cell (GL Sciences), 35 mM PB—acetonitrile (gradient elution)	0.06–30[b]	0.011, 0.003 0.0022, 0.0027 0.020	(188)
BSA-native form BSA-denaturated	Si(100), MPCVD BDD	**FIA/AD**, TL cell (GL Sciences), 0.1 M PB pH 7.4	50–400 μg/mL 50–400 μg mL	190 μg/mL 0.190 μg/mL	(189)
BSA IAP	Si(100), MPCVD BDD	**FIA/AD**, TL cell (GL Sciences), 0.1 M PB pH 7.4	5–3000 μg/mL 200–800 μg/mL	5 μg/mL 100 μg/mL	(139)
Mouse IgG	Si(111), MPCVD BDD modified by poly-*o*-aminobenzoic acid, soaked in H_2SO_4/H_2O_2 (30 % *v/v*) (3:1) (30 min)	**AD** of AA generated from 2-phospho-L-ascorbic acid, alkaline phosphatase conjugated antimouse IgG label	1–1000 ng/mL	0.3 ng/mL	(149)
Myoglobin, Hemoglobin	Commercial polished BDD (174), activation as in (88)	**CV**, 0.2 M AB pH 4	1–200 1–100	not given	(92)
Cytochrome c	MPCVD nanocrystalline BDD	**CV**[d], 1 mM Tris HCl buffer pH 7 containing 20 mM NaCl	25–200	not given	(52)
Food components and additives					
Aspartame, sodium cyclamate	Commercial BDD (67), CT at i = −1 A cm^{-2} in 0.5 M H_2SO_4 for 60 s	**SWV**, 0.5 M H_2SO_4	9.9–52, 50–410 5–40[e], 50–400[e]	0.23, 4.8 0.35[e], 4.5[e]	(136) (137) (123)
2-MESA	n-Si(111), MPCVD BDD	**FIA/AD**, 0.1 M carbonate buffer pH 9.2	not given	50	(95)
Glucose[e] Glucose[f]	Si(111), Cu implanted MPCVD BDD Commercial BDD (67), oxidized in H_2SO_4/H_2O_2, after annealed with H_2 flame for 10 min and cycled in 1 M NaOH between 0 and +0.8 V	**Chr.A**, 0.2 M NaOH **SWV**, 1 M NaOH	1000–5000 500–10000	not given not given	(144) (70)

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TABLE 2
Selected applications of BDD-based sensors in organic analysis (*Continued*)

Analyte	BDD electrode, pre-treatment[a]	Electroanalytical method, arrangement, conditions	*LDR* [μmol L]	*LOD*[A] [μmol L], (matrix[B])	Ref.
Carboxylic acids and substituted carboxylic acid					
Oxalic acid	MPCVD BDD MPCVD BDD modified by ATAB	**FIA/AD**, TL cell (GL Sciences), 0.1 M PB pH 7.0	5–100 0.8–100	0.125 0.32	(142)
Oxalic acid	Si(100) MPCVD BDD	**CV**, 0.1 M PB pH 2.1	10–100	not given	(78)
EDTA	Single crystal KDB-silicon substrate, HFCVD BDD, activation by cycling between +0.5 V to +1.7 V	**FIA/AD**, TL cell (GL Sciences) **Amp**, acetate–ammonia buffer pH 3.9	0.05–10000 10–500	0.0005 1	(190)
Thiourea	Si(100), MPCVD BDD	**LSV**, 0.04 M BR buffer + 0.1 M $LiClO_4$ pH 1.8	4–1000 1000–4000[y]	not given	(93)
TNBA	Commercial polished BDD (170)	**CV**, 0.1 M PB pH 7.5	250–2000	not given	(96)
Uric acid	Single crystal homoepitaxial BDD	**LSV**, 0.1 M $HClO_4$	0.1–1	not given	(191)
Uric acid	MPCVD BDD, AT as in (91)	**ChrA**, 0.1 M $HClO_4$	0.05–1	0.015	(119)
Other compounds					
Escherichia coli (detection of 2-NP)[z]	Commercial BDD (174), cleaning when passivated by 40 cycles from +1.0 V to −1.7 V range	**Amp**, 50 mM PB pH 7, containing 1 mM ONPG + 0.05 mg mL SDS	6–20 20–400	400 cells mL^{-1}[D]	(178)
NADH	Si(100) MPCVD BDD	**ChrA**, 0.1 M PB pH 7.1	0.01–0.5	0.01, $S/N = 7$	(192)
Nicotine	HFCVD BDD, AT + CT as in (104)	**SWV**, BR buffer pH 8	20–500	3[C]	(108)
Sodium diethyldithio-carbamate	Commercial polished BDD (174) activation by cycling between −1.0 V and +1.5 Vin 0.1 M Na_2SO_4 pH 7	**CV**, 0.1 M Na_2SO_4 pH 7 **ChrA**, 0.1 M Na_2SO_4 pH 7	20–90 10–100[a] 1–8[v]	not given 35[a] 0.3[v]	(88)
Xanthin, Caffeine theophylline theobromine	Si(100), MPCVD BDD	**LSV**, 0.04 M BR buffer containing 0.1 M $NaClO_4$, pH 1.8	1–100, 1–400 1–400 1–400	not given	(97)
ss-DNA ds-DNA	Si(100), MPCVD BDD	**SWV**, 1 M acetate buffer solution pH 5	0.1–8 μg/L	3.7[w], 10[x] μg/L 5.2[w], 10[x] μg/L	(132)

[a]if no details are given, as-deposited polycrystalline H-terminated electrodes and undefined silica support used; [b]for all given analytes; [c]in the presence of AA; [d]no details on oxidation are given; [e]simultaneous voltammetric determination; [f]in the presence of AA and DOPAC; [g]no intentional AT, nevertheless BDD presumably oxygen-terminated due to experiments at high anodic potentials; [h]for both microcrystalline and nanocrystalline BDD; [i]microcrystalline BDD; [j]nanocrystalline BDD; [k]oxidative determination; [l]reductive determination; [m]ethylendiamine, putrescine, cadaverine, spermine, spermidine; [n]mixture containing N-nitrosopyrolidine, N-nitrosopiperidine, N-nitrosodiethylamine; [o]naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracenechrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenz(*a,h*)anthracene, benzo(*g,h,i*)perylene, indeno(1,2,3-*cd*)pyrene; [p]oxidation peak of premathazine; [q]oxidation peak of premathazine; [r]biphasic linearity; [s]in the presence of uric acid and AA; [t]detection of 2-NP released from *o*-nitrophenyl-β-D-galactopyranose as catalyzed by β -galactosidase, a tetramer of *Escherichia coli*; [u]quiescent solution; [v]stirred solution; [w]adenosine peak; [x]guanosine peak.

[A]*LOD* for $S/N = 3$, if not otherwise specified; [B]if no matrix given, listed *LODs* are for model experiments in solutions prepared with deionized water; [C]$LOD = 3s_b/m$, $LOQ = 10s_b/m$, where s_b is the standard deviation of the mean of the current of the blank in AD or current at the peak potential for repeated voltammograms of the blank solution and m is slope of the analytical curve; [D]no details on calculation given; [E]experimental *LOD*—the first appearance of a limiting-current wave; [F] $LOD = 3\sigma/m$, $LOQ = 10\sigma/m$ where σ is the standard deviation of the signal measured for the lowest analyte concentration corresponding to calibration plot and m is slope of the analytical curve; [G]*LOQ* calculated using statistic software ADSTAT version 2.0 (Trilobyte, Czech Republic). This software uses confidence bands ($\alpha = 0.05$) for calculation of the *LOQ*. It corresponds to the lowest signal for which relative standard deviation RSD is equal 0.1; [H] $LOQ = y_b + 10s_b$, where intercept value y_b and standard deviation of the slope s_b are calculated from the analytical curve.

through Adamant Technologies (67) (Le-Chaux-de-Fonds, Switzerland) enabled the participation of other research groups. Nowadays, there are at least six commercial suppliers of BDD materials and equipment (Table 1), but many research groups still use BDD from their own sources. HFCVD and MPCVD (69) reactors are also commercially available.

For voltammetric measurements, there exist several strategies to accomplish the conductive connection of freestanding circular or quadratic Si/BDD discs from the supplier. Their popular placement as the bottom of electrochemical cell requires foolproof sealing and has the disadvantage in the need of manipulation with the whole cell during measurements. In this case, the electrode area is given by the opening in the gasket and the ohmic contact made by placing the backside of the Si substrate on a conductive metal (brass, copper) plate (50, 70–78). A similar principle is used in the pen-type holders, where the reusable Si/BDD disc is pressed against the gasket in the bottom part of the holder. These robust electrodes are easier to manipulate; nevertheless, they may also be inclined to leak, especially in mixed aqueous-organic and non-aqueous media. As the BDD disc is dipped into the bottom part of the holder exposed to the solution, problems with bubbles sticking in the cavern may complicate the handling. Examples of both described arrangements designed in our laboratory are shown in Figure 1. Rotating pen-type holder and compact non-renewable electrode with flat bottom BDD containing parts are also available (Table 1). The other approach relies on simple electrodes prepared by gluing the Si/BDD disc onto a conductive plate (usually using an Ag paste) and insulating of all other parts by a suitable insulator. Araldite epoxy resin (79, 80), Teflon® (81), silicon wax and rubber (51, 82, 83) or adhesive ribbon (51, 83) were used for this purpose.

The amperometry coupled to FIA or HPLC is most frequently realized in home-made or commercial thin layer cells (84) (Bio-

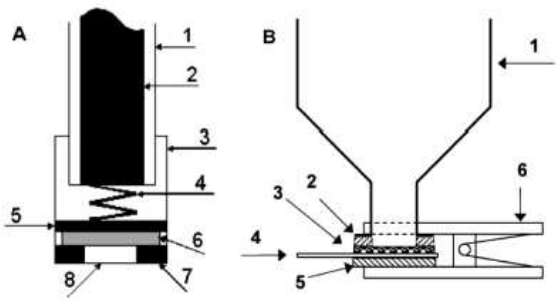

FIG. 1. The detailed scheme of BDDE constructed in our laboratory: A) disc electrode – 1) electrode body made of Teflon®, 2) stainless steel, 3) screw attachment, 4) small metal spring, 5) brassy sheet, 6) Si/BDDE, 7) Viton® gasket, 8) access for solution. B) Glass cell with clamped BDDE – 1) glass cell, 2) Viton® gasket, 3) Si/BDDE, 4) Cu current collecting plate, 5) insulating pad, 6) clamp. Reprinted with permission from (38) J. Barek, J. Fischer, T. Navratil, K. Peckova, B. Yosypchuk, and J. Zima, *Electroanalysis* 19 (2007):2003–2014.

analytical System, West Lafayette, IN, USA; GL Sciences Terrance, CA, USA). The wall-jet arrangement with pen-type electrodes has been also tested (55, 85). The specialized arrangements for CZE and electrophoretic chips are described further.

Voltammetric and Amperometric Methods

Voltammetric methods are used to investigate electrochemical processes at the electrode surface and as an analytical tool for quantitation of analytes. In the former case, CV is most frequently used. Therefore, brief results on linearity of concentration dependences in a limited range without investigation of the lowest and high concentrations using CV or linear scan voltammetry appear in many studies (19, 50, 52, 72–76, 78, 86–99) devoted to other topics, e.g., electrochemical combustion, comparison of performance of BDD and other carbon electrodes (100) or determinations using amperometric methods. In these cases, very often the *LOD* is not given or it is relatively high, in the 10^{-5} to 10^{-6} mol/L range.

The specialized electroanalytical studies most frequently use differential pulse and square wave voltammetry possessing the advantage of good discrimination against background current. The results using these methods are often comparable as shown on the example of the drugs sodium fluvastatin (101) and pefloxacin (102). Extended optimization studies in this field were published particularly by Avaca and coworkers (79, 80, 103–112). LOD in the 10^{-8} mol/L concentration range were usually achieved in these cases.

The enhancement of analytical sensitivity by using an adsorptive step to pre-concentrate the analyte into, or onto, the working electrode, which is very popular at mercury and carbon electrodes (113), is in principle difficult to achieve due to the well known adsorption resistivity of the BDD surface because of lack of adsorption sites. Slower kinetics in comparison to GC was demonstrated, e.g., on the example of dopamine (DA) oxidation, which is catalyzed by hydrogen bonding of surface carbonyl to adsorbed DA molecules; these bondings are rarely present on the H-terminated surface of BDD (HBDD) (114). In contrary, adsorption on HBDD prepared by annealing of OBDD in hydrogen flame was proved for glucose (70), readily adsorbed on almost all electrode materials. Its CVs obtained at both surfaces are depicted in Figure 2. It can be seen that at the OBDD the anodic peak of glucose is diminishing while at HBDD an interesting feature may be seen—the recorded CVs possess an anodic peak appearing also during the reverse, cathodic scan. This indicates that glucose is strongly adsorbed on the electrode surface, and is continuously oxidized during the reverse scan. Such shapes of the CVs are similar to those of polyamines (54) and organic acids (115) at OBDD electrodes. In these cases it was suggested that the reaction mechanism involves an anodic oxygen transfer between adsorbed OH radicals coming from anodic discharge of the water molecule and adsorbed analyte. Nevertheless, no adsorptive anodic determination for these compounds has been published.

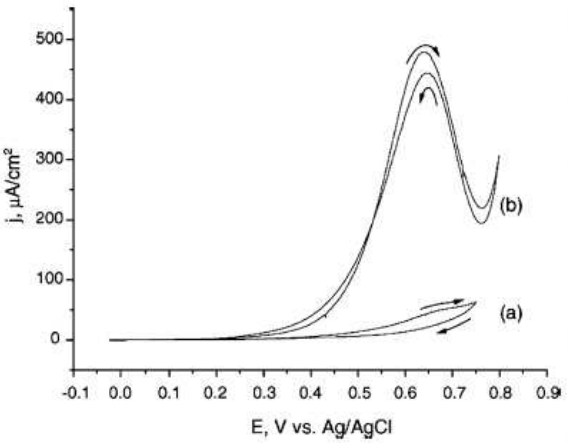

FIG. 2. CVs for 5.0 mmol/L glucose at (a) BDDE after severe anodic polarization, and (b) hydrogen flame annealed BDDE. Supporting electrolyte 1.0 mol/L NaOH, scan rate 20 mV/s. Reprinted with permission from (70) J. Lee and S. M. Park, *Analytica Chimica Acta* 545 (2005):27–32.

The few examples of adsorptive stripping voltammetry (AdSV) for organic analytes using bare BDD surfaces rely, in fact, on determination of oxidation products of the analyte of interest. In the case of aniline these are dimeric species (p-aminodiphenylamine and benzidine) formed by its anodic oxidation during the accumulation period (116). Promethazine (PM) oxidizes forming an adsorbed product with lower oxidation potential than PM and enabling indirect detection of PM when accumulation potential more positive than both peaks is applied (81). These studies document that quantitative analysis using AdSV at bare BDD surfaces provides interesting results in infrequent specialized cases contrary to common applications of stripping methods for inorganic analytes (53).

The other general strategy to increase the sensitivity—employment of the ultrasound—has also the advantage of overcoming potential electrode fouling problems. Both issues were appreciated in the sono-voltammetric determination of commonly surface passivating 4-chlorophenol (4-CP) (117) and 4-nitrophenol (4-NP) (118). Nevertheless, the possibility of BDD reactivation in situ using high anodic potential in the region of water decomposition favors classical voltammetric measurements in simple detection cells and wide-spread use of sono methods is not probable despite the fact that BDD usually shows no signs of mechanical damage under sonication. More frequently, chronoamperometric determinations in stirred solutions under potentiostatic conditions may be expected as suggested in several studies of Fujishima (90, 91, 119).

When considering batch voltammetric methods, their selectivity is a big issue in complex matrices. In comparison to classical electrode materials with a relatively narrow potential window, the wider potential window of BDD is not that big advantage, as the structurally relative group of organic compounds, which are often found together in an environmental or biological matrix, usually possess near oxidation/reduction potentials. Nevertheless, several reports appeared analyzing two to three component mixtures (98, 120–124). Insufficient selectivity can also be solved by preliminary off-line separation of analytes using common extraction techniques, which complicates the analysis. Therefore, AD of mixtures of organic analytes in flowing liquids is preferred to batch voltammetric analysis because of lower problems with passivation (reaction products and intermediates creating the passivation films are removed from the electrode) and because of possible separation of complex mixtures using HPLC or CZE.

BDDE offer several advantages compared to other solid electrodes used in flowing systems. Usually no mechanical or electrochemical pre-treatment of BDDE is needed. The creation of passivation films is less probable due to decreased adsorptivity of reaction by-products and products at their relatively hydrophobic surface. The low electrostatic capacity of the BDD surface minimizes the time to stabilize the background current prior and the current drift during AD. Thus, the background current stabilizes within seconds to a few minutes after detector turn-on in contrast to solid, especially other carbon-based electrodes, where it frequently takes about one hour to reach a constant current value. These advantages mirror those in many of the FIA-AD and HPLC-AD studies summarized in Table 2. The CZE-AD coupling is less common, as this requires the technically exacting miniaturization of BDDE and adaptation of the appropriate electrophoretic system.

Pre-Treatment of Boron-Doped Diamond Surface

The surface termination contributes greatly to the physical and chemical properties of BDD and thus is of big importance for electroanalysis. Usually, the as-grown BDD electrodes produced commercially or in research laboratories are initially H-terminated as they are deposited in a hydrogen plasma CVD chamber. The HBDD surface was first believed to be responsible for the adsorptive inertness as shown by Swain et al. on the example of polar 2,6-anthraquinonedisulfonate (2,6-AQDS) (125) on intentionally hydrogenated glassy carbon and BDD surfaces. Surprisingly, the results of Fujishima et al. in 2000 (19) on oxidation of 5-HT, presumably leading to easily absorbable quinoic products, indicated that the OBDD surface behaves differently from a polished GC electrode with oxygen surface groups and is also inert with respect to adsorption. Since that time, the intensive research on oxidative functionalization of BDD surfaces resulted in interesting results for electrochemists and several comparative studies appeared on HBDD and OBDD (20, 126).

BDD surface oxygenation may be achieved by several methods, including vapor phase oxidation in O_2, oxygen plasma treatment, boiling in strong acid, oxidizing agent or radical oxidation, long-term exposure to air and electrochemical oxidation [reviews (28) and (127) and references therein]. The last method

is very convenient for electroanalysis, as no specific instrumentation is needed, the oxidation is simply accomplished either by anodic treatment of the BDD surface at high positive potentials or repetitive cycling in positive potential range as suggested in Table 2. Under these conditions, the powerful oxidants OH radicals are produced from water at the BDD surface, which precedes the oxygen evolution having high anodic overpotential at BDD. The re-hydrogenation of an OBDD surface is achievable only by hydrogen-flame annealing or hydrogen-plasma treatment.

The structure of the OBDD surface depends on the oxygenation technique and on the type of Si-support. Based on the diamond structure, it is expected that the sp^3 C–H bonds on the (111) facets are terminated with hydroxyl groups, while the CH_2 bonds on the (100) facets are transformed to carbonyl and ether functional groups. By surface oxygenation, the unique BDD properties are not affected, the OBDD surfaces are hydrophilic, have lower conductivity and relatively negative surface charge, while the HBDD are hydrophobic and have high conductivity (128). The advantages of the OBDD electrodes include a somewhat wider potential window (80, 90), higher surface stability to fouling (15, 129, 130) and the possibility of on-line reactivation by applying a highly anodic potential, which enables the oxidative destruction of the adsorbed species (59).

The preference of HBDD or OBDD surface for electroanalysis of some analytes was announced, while for the others negligible differences were reported. Compounds with positive charge may be more easily oxidized at OBDD than at HBDD due to the electrostatic attraction between these compounds and negatively charged OBDD. A typical example is the shift of response of oxidized aminothiols (58, 59, 131). The positively charged reduced form of glutathione (GSH) (59) or homocysteine (57) itself also exhibited an increased response at OBDD in comparison to HBDD; nevertheless, a positive peak shift was observed and a change in oxidation mechanism involving the oxygen transfer suggested. In this case, the OH radicals produced during the initial stage of O_2 evolution presumably serve as a source of oxygen as suggested for polyamines (54). Also, the redox species with negative charge are sensitive to the surface oxygenation, exhibiting slower electron transfer (20). Anodic peaks for such species were more clearly observed at a HBDD than at an OBDD electrode due to the existence of the electrostatic repulsion between the analyte and the negative charge on the electrode surface as reported for 2,6-AQDS (125), oxalic acid (78), uric acid (119), and nucleic acids (132). Dopamine (DA) (89–91) or 5-HT (133) have almost the same oxidation potential as ascorbic acid (AA) in acidic media at HBDD, but the peaks were separated due to a positive shift of AA peak at an OBDD as documented at Figure 3 for DA. At BDDμE the separation was even clearer than at common BDD macroelectrodes (15).

Decreased adsorbability of oxidation products on OBDD in comparison with HBDD may favor the former surface, as reported for di- and trichlorophenols (129), with negligible fouling of OBDD in contrary to fast passivation of HBDD. Surprisingly,

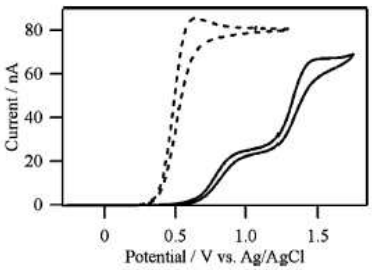

FIG. 3. CVs of a mixture of 0.1 mmol/L DA and 1 mmol/L AA at HBDD (dotted lines) and OBDD (full lines) with a scan rate of 50 mV/s. Reprinted with permission from (15) A. Suzuki, T. A. Ivandini, K. Yoshimi, A. Fujishima, G. Oyama, T. Nakazato, N. Hattori, S. Kitazawa, and Y. Einaga, *Analytical Chemistry* 79 (2007):8608–8615.

no significant electrode fouling of HBDD, even without any reactivation, was reported for phenol and monochlorophenols in aqueous media (134). Nevertheless, the authors admitted that, in this case, the H-termination is questionable due to experiments performed at relatively high anodic potentials. This problem arises also in other studies reported for HBDD surfaces (121, 122). The merits of cathodic pre-treatment prior to detection of chlorophenols (CPs) suggested by the group of Avaca (103, 104, 135) are discussed later. The use of OBDD electrodes is also advantageous for all analytes passivating the electrode surface by oxidation products, because in these cases its regeneration by anodic oxidation is compatible with O-termination.

The cathodic pre-treatment of BDD surfaces was also reported in some electroanalytical studies (79, 87, 103–107, 109–111, 123, 136, 137), because it may improve the voltammetric response as reported by Avaca and coworkers (135). A pronounced increase of peak current of pentachlorophenol after cathodic pre-treatment in comparison to OBDD is shown on Figure 4. It should be performed just before measurement because the loss of superficial hydrogen due to the oxidation by air oxygen was reported (138). Cathodic reduction may be also used for the regeneration of passivated electrode surface as shown for bovine serum albumin (139). It is believed that hydrogen generation by reduction treatment plays an important role in the process. A negligible effect of the surface termination on the peak potential was noted for several purines and pyrimidines (140), DA (126), and procaine (100).

It is obvious that the anodic or cathodic pre-treatment of the BDD surface, performed easily *in situ*, can change the response of the analyte of interest. This is a on one side, undoubtedly a substantial advantage; on the other, it represents a potential risk of unwanted surface change. Therefore, the compliance of pre-treatment and cleaning of BDDE with defined standard operation procedures must be strictly enforced when considering their applications in practice. Electroanalytical methods developed for OBDD presumably will be preferred due to the

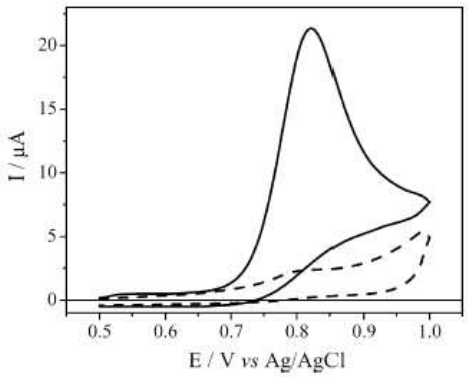

FIG. 4. CVs on BDDE for $5 \cdot 10^{-5}$ mol/L pentachlorophenol in 0.1 mol/L BR buffer, pH 5.5, after anodic pre-treatment at 3.0 V vs. Ag/AgCl (dotted lines) or cathodic pre-treatment at −3.0 V vs. Ag/AgCl (full lines). Scan rate 50 mV/s. Reprinted with permission from (135) H. B. Suffredini, V. A. Pedrosa, L. Codognoto, S. A. S. Machado, R. C. Rocha-Filho, and L. A. Avaca, *Electrochimica Acta* 49 (2004):4021–4026.

long-term stability of such surfaces and the possibility of its regeneration using high anodic potentials.

SOME TRENDS IN ELECTROCHEMICAL STUDIES WITH BORON-DOPED DIAMOND ELECTRODES

Boron-Doped Diamond Surface Modifications

Both HBDD and OBDD usually outperform classical carbon and metal electrode materials thanks to chemical inertness and fouling resistivity. Therefore, the efforts on its modifications must be driven by a concrete purpose, i.e., impart of catalytic activity or increase of selectivity toward the analyte of interest, which includes also the surface biofuctionalization for biosensing.

The methods for modification of diamond surfaces were reviewed recently (28, 29) and may be classified in following categories: i) chemical modification, ii) photochemical modification, iii) electrochemical modification, iv) ion implantation techniques and v) combined methods. Many of the modification methods were developed for various purposes omitting electroanalysis. This regards, e.g., the fluorinated diamond formed through radio-frequency-based plasma fluorination (28). It displays, so far, the widest range of potentials for an electrode material in aqueous solution, being limited only by the formation of free hydrogen [E^0 (H^+/H_2) = −2.3 V] and hydroxyl radicals [E^0 (OH^-,H^+/H_2O) = +2.74 V]. A relatively simple approach to BDD modification represents electrochemical polymerization, firstly reported by Roy et al. (141). In their study, the surface of the HBDD electrode was modified by N,N-dimethylaniline forming cationic polymer film. This electrode was used as a sensor for selective detection of DA and its metabolite 3,4-dihydroxyphenyl acetic acid (DOPAC) (141) or 5-HT in the presence of AA (133). Nevertheless, it should be remembered here that the same selectivity was achieved at OBDD electrodes.

The photochemical methods rely on the cycloaddition reaction of alkenes with HBDD surface under UV irradiation. By this method, long alkyl chains, fluorocarbon chains and amino and carboxylic groups, among others, have been introduced onto diamond surfaces via stable covalent C–C bonds. Kondo et al. (142) used this approach to fabricate positively charged BDD surfaces modified by allyltriethylammonium bromide (ATAB). The stability and sensitivity of electrode response to negatively charged oxalate was improved at this surface compared to the unmodified HBDD.

Interesting results were also achieved at metal-modified BDDE in detection of carbohydrates and aminoacids (99, 143, 144). They can be prepared by using chemical precipitation, electrochemical deposition or, most frequently, metal implantation. The last type with implanted Cu was used for highly sensitive and stable glucose detection (144). Ni implanted BDDE succeeded in FIA/AD of tetracycline, an aminoacidic antibiotic (99).

Of big importance in the surface modification is the introduction of amino and carboxylic groups, as they enable attaching of large biomolecules (DNA, peptides, proteins, enzymes) and, thus, encourage the development in biosensing. The influential studies in this field were performed by Takahashi et al. (145), who introduced a photochemical chlorination/amination/carboxylation process for the HBDD in 2000 and Yang et al. (23), who modified ultrananocrystalline diamond using alkenes followed by electrochemical reduction of diazonium salts and presented long-term stability of DNA bonded to a prepared surface.

Several approaches exist to prepare amino-terminated BDD (ABDD) surfaces. Already in 1998, Troupe et al. (25) reacted a vapor phase-oxidized BDD surface with 3-aminopropyltriethoxysilane (APTES) and consequently prepared a glucose-sensitive amperometric sensor by attachment of glucose oxidase. Similar silanization of hydroxyl groups on anodically oxidized diamond was also used by Notsu et al. who prepared a BDD-APTES-tyrosinase amperometric sensor for detection of phenol estrogenic derivatives (146). Zhou and Zhie et al. (147, 148) combined chemical and electrochemical modifications of BDD film with 4-nitrobenzenediazonium tetrafluoroborate to produce aminophenyl-modified BDD, followed by immobilizing tyrosinase covalently at the BDD surface via carbodiimide coupling. They used this sensor for detection of phenol, p-kresol and 4-CP and reported 90% of its original activity after intermittent use for 5 weeks. The hydrophillic ABDD surface modified with negatively charged gold nanoparticle/polyelectrolyte-coated polystyrene colloids was also preferred in DA determination in comparison to modified HBDD surface, presumably due to preferable immobilization of the nanocomposite colloids (149).

Also, the carboxylation of the BDD surface offers possibilities of functionalizing by biomolecules. This principle was used in the development of a protein immunosensor, when the BDD surface was covered by electropolymerization of o-aminobenzoic acid (o-ABA) and the carboxyl groups were then used to covalently attach protein probes (150).

This short excursion documents the wide variety of modification approaches. Undoubtedly, research in this field is very attractive in the academic sphere. Nevertheless, the success or failure in praxis will depend on the quality of coverage of the surface, durability, ease of preparation and, consequently, on performing parameters (sensitivity, selectivity, reproducibility) for particular analytes. New approaches may be expected facilitating the construction of BDD-based sensors, e.g., recently, direct amination using plasma treatment of HBDD in NH_3 atmosphere was introduced (28, 151).

Miniaturized Boron-Doped Diamond-Based Sensors

Miniaturization of electrodes offers following advantages: (i) Miniaturized electrodes incorporated in detection systems can be produced by means of advanced microfabrication technologies; (ii) Miniaturized electrodes are compatible with *in vitro/in vivo* measurements; (iii) Integration of the electrical circuit and devices controlling the separation and detection systems enables construction of complete micro-total analysis systems (μ-TAS); (iv) Concentration detection limits are normally not affected; (v) There is a low cost for development and production, and low-power requirements for operation; (vi) Detected analytes are direct begetters of electric signals handled by electrochemical detectors; conversion to other forms of signals is not necessary.

So far, there have been only a few reports describing fabrication of BDDμE (9–12, 152–155) and BDD microelectrodes arrays (BDD-MEA) (16, 86, 155–157), and only Swain et al. (10, 14, 158) and Fujishima and Wang et al. have published well described electroanalytical applications using CZE-AD or chip-based detectors with BDDμE (11, 12, 159). The other research is focused on *in vitro/in vivo* detection of biogenic compounds (13–15, 160).

The fabrication of BDDμE from BDD films classically deposited at macro-sized Si supports is problematic, because of its sturdy character resulting in difficulties by mechanical handling. Moreover, the thin BDD film can easily be inadvertently removed or damaged during the manipulation. Therefore, other materials such as platinum or tungsten wires (TW) are being used as support for BDD deposition. Their desired shape is usually manufactured prior to BDD deposition. Cooper et al. (9) prepared BDDμE using MPCVD for the growth of electrically conducting single microcrystalline diamonds as well as diamond films on etched TW (diameter $d = 25$ μm), which were subsequently sealed in glass and the electrode exposed by polishing or etching in HF. TW were used also by Sarada et al. for construction of microdisc (152) or microfiber (161) BDDμE. Xie et al. (153) deposited BDD films onto a 25 μm diameter TW pre-sealed in a quartz glass tube, resulting in non-planar, needle-like microdisc electrodes of diameter 30 μm with unusual grain structure due to different diamond growth rates on the quartz and the TW. This BDDμE was used for detection of 10 nmol/L of adenosine by FIA and for its *in vitro* detection in neonatal rodent medullar slice preparation.

The more detailed studies from the electroanalytical point of view were published by Swain et al. (10, 14, 158, 162) and Fujishima and Wang et al. (11, 12, 159). Both worked out methods for CZE/AD determination of CPs; the latter researchers focused later on electrophoretic microchip/AD and tested these systems also on other organic analytes (neurotransmitters, aromatic amines). End column detection was used in all these cases. Swain used fiber BDDμE prepared by MPCVD of microcrystalline BDD on electrochemically sharpened platinum wires ($d = 76$ μm, Pt/BDDμE) (10). The BDD-coated wires were then attached to copper wires and sealed in a polypropylene pipette tip. Resulting electrodes had conically-shaped microcylindrical geometry and an area of $\sim 10^{-4}$ cm^2. These were placed in a detection cell fabricated from a glass vial. The separation efficiency for the system is influenced by the dimensions of the electrode and the precision of the Pt/BDDμE fixation opposite the column end as proved during preliminary tests with DA and catechol (10) and detection of ten neurotransmitters and their metabolites or precursors (14). As seen from Figure 5, baseline resolution was achieved for nearly all of the solutes.

Another approach on fabrication of BDDμE was used by Fujishima and Wang. They prepared a freestanding BDD thin

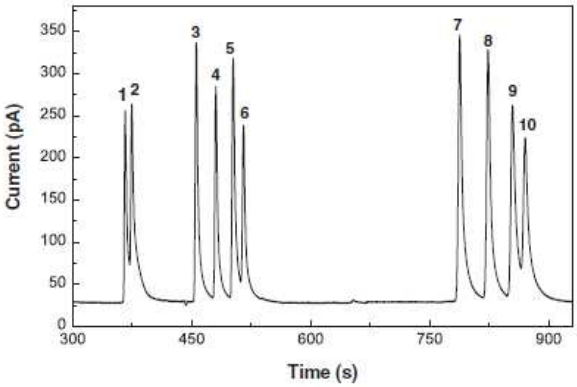

FIG. 5. Electropherogram of a standard solution containing 5 μmol/L MN (1), NMN (2), 10 μmol/L DA (3), E (4), NE (5), MOPEG (6), 30 μmol/L L-DOPA (7), 50 μmol/L DOPEG (8), VMA (9), HVA (10). Silica capillary 70 cm, 27 μm ID, run buffer 0.25 μmol/L boric acid/KOH at pH 8.80, separation voltage 24 kV, electrokinetic injection at 15 kV for 4 s. Detection at Pt/BDDμE, detection potential +0.95 V vs. Ag/AgCl. Reprinted with permission from (14) J. Park, V. Quaiserova-Mocko, K. Peckova, J. J. Galligan, G. D. Fink, and G. M. Swain, *Diamond and Related Materials* 15 (2006):761–772.

film by MPCVD on Si wafers, removed the substrate by chemical etching with a mixed solution of HNO_3 and HF (1:1) and sandwiched this film between two glass slides with UV adhesive forming a BDD microline electrode (163) or glued the film onto ceramic plates and used as film band electrode in electrophoretic microchips (12, 159). The BDD microline electrode (exposed area 50 × 300 to 500 μm) was tested in end-column CZE/AD on determination of a catecholamine mixture and exhibited low, stable noise levels (1–1.5 pA) (11). The BDD film band μelectrode (dimension 0.3 × 6 mm^2) (12, 42) used in microchips provided higher sensitivity, lower noise, better resistance to fouling, sharper peaks and enhanced resolution than a screen-printed carbon electrode for CPs, organophosphate nerve agents (methylparathion, paraoxon), nitroaromatic explosives and dye-related amino-substituted aromatics (159). These electrophoretic studies will hopefully be continued and lead to field-deployable devices inspirative for the environmental, forensic, pharmaceutical, and clinical laboratories.

Furthermore, several types of BDD-MEA were constructed (16, 86, 155–157) with microdisc electrodes with d = 5–30 μm separated by 100–250 μm. One type is commercially available (67). Their function as assemblies of single microelectrodes was typically confirmed by sigmoidal CVs of $[Fe(CN)_6]^{4-}$. Firstly, in 2000 Madore et al. (16) have reported on BDD-MEA fabricated using CVD and photolithographic techniques producing microdisc electrodes with d = 5 μm separated by 100 μm. BDD-MEA on structured silicon substrates was described by Fujishima et al. (155). Beside $[Fe(CN)_6]^{4-}$, the microelectrodic behavior was tested with biologically important species such as AA and DOPAC; nevertheless, no analytical results were reported. Rychen et al. (156) fabricated a BDD array by forming a BDD film onto which a silicon nitride layer (5 μm thick) was patterned, resulting in a recessed BDD-MEA. Swain et al. (157) have reported on diamond *ultra* microelectrode arrays, based on forming a pattern via photolithography onto a silicon wafer with CVD diamond grown into the mold. Compton (164) fabricated an all diamond BDD-MEA using a combination of CVD growth and laser ablation shaping techniques to prepare and coat a patterned BDD substrate with an intrinsic diamond insulating layer. This approach is advantageous since the resulting electrode has no seals, recesses or elevations as the BDD discs are co-planar to the dielectric surroundings. The enhanced sensitivity (sevenfold) of this BDD-MEA over the conventional macro electrode has been demonstrated for 4-NP (86). The first construction of a random array of BDD nano-disc electrodes consisting of 650 ± 25 million BDD disc electrodes (d = 20 ± 10 nm) per cm^2 was proposed recently (17).

The *in vitro*/*in vivo* applications of BDDμE are substantiated by BDD biocompatibility (42, 165) and the outstanding resistivity to fouling in physiological environment. The *in vitro* applications have been recently reviewed by Park et al. (160). On the other hand, the dimensions required for *in vivo* applications ($d \leq 10$ μm, length of 25–500 μm) generally required for minimal tissue damage (166) are not easily achievable. Therefore, very few reports on the *in vitro* application of BDDμE (with d = 10–80 μm) in biological tissues have been published (13, 14, 120, 153) and pioneering *in vivo* applications appeared in 2007 (15) using TW/BDDμE (d = 5 μm, length 250 μm) for DA detection in mouse brain.

From this short overview, the tendency on further miniaturization of BDD devices is obvious and can be documented by other studies (154, 157, 167–169). Coupling the advantages of the microelectrodes and their arrays with the usefulness of BDD has potential use in electroanalysis (e.g., in CZE, electrophoretic and other microchips, *in vivo*/*in vitro* sensing, sensors in flow systems to detect target species at fast scan rates). Applications in praxis can be foreseen in case more reasonable ways to construct them will be suggested.

CONCLUSIONS

BDD thin films as an electrode and electrochemical sensor material has gained a lot of attention since its introduction in early 1990s. Many analytical methods for the determination of organic and inorganic species in biological, environmental and pharmaceutical matrices have been published. The commercialization of BDD electrodes at the beginning of this century accelerated the development. In this review, the range of possible analytes was restricted to organic compounds. Basic voltammetric studies were performed for a number of them, including phenolic compounds (neurotransmitters, chlorophenols, nitrophenols), monocyclic and polycyclic aromatic hydrocarbons and their derivatives, thiols and disulfides, selected pesticides, pharmaceuticals, etc. demonstrating the possibility of their oxidation/reduction at BDD thin films. Specialized elecroanalytical studies using batch voltammetric and amperometric methods or liquid flow methods with amperometric detection at BDD electrodes under optimized conditions in pure solvents proved, in most cases, notable reproducibility, high sensitivity, low detection limits and linear dynamic range often over three orders of magnitude compared to other, particularly carbon, electrode materials. Thus, the actual challenges in organic electroanalysis may be seen in: i) Development of new voltammetric and amperometric methods using BDD electrodes and their validation so that they can be routinely used in environmental, biochemical, clinical, pharmaceutical and other laboratories; ii) Search on reasonable ways for construction of BDD microelectrodes and extension of their applications for *in vivo*/*in vitro* sensing and μ-TAS; iii) Impartation of selectivity or catalytic activity by modification of the BDD surface, especially for biosensing; iv) Characterization of new diamond-based materials for electroanalytical purposes.

Thus, it can be concluded that BDD electrodes have proven useful in overcoming the limitations of conventional carbon and other solid electrodes; continuous research activity, especially regarding the above-given points, is expected in near future.

ABBREVIATIONS

AA	Ascorbic acid
AB	Acetate buffer
2-AB	2-aminobiphenyl
3-AB	3-aminobiphenyl
4-AB	4-aminobiphenyl
ABDD	Amino-terminated BDD
AD	Amperometric detection
AdSV	Adsorptive stripping voltammetry
AMN	2-acetyl-6-methoxynaphthalene
1-AN	1-aminonaphthalene
2-AN	2-aminonaphthalene
APTES	3-aminopropyltriethoxysilane
2,6-AQDS	2,6-anthraquinonedisulfonate
AT	Anodic treatment
ATAB	Allyltriethyl ammonium bromide
BAS	Bioanalytical System Inc.
BB	Borate buffer
BDD	Boron-doped diamond
BDDE	BDD electrodes
BDD-MEA	BDD microelectrodes arrays
BDDμE	BDD microelectrodes
BR buffer	Britton-Robinson buffer
BSA	Bovine serum albumin
CA	Catechol
CB	Carbonate buffer
ChrA	Chronoamperometry
4-C-3-MP	4-chloro-3-methylphenol
CP	Chlorophenols
2-CP	2-chlorophenol
3-CP	3-chlorophenol
4-CP	4-chlorophenol
CSEM	Swiss Center of Electronic and Microtechnology
CT	Cathodic treatment
CVD	Chemical vapor deposition
CVs	Cyclic voltammograms
CZE	Capillary zone electrophoresis
DA	Dopamine
2,3-DCP	2,3-dichlorophenol
2,4-DCP	2,4-dichlorophenol
2,5-DCP	2,5-dichlorophenol
2,6-DCP	2,6-dichlorophenol
3,4-DCP	3,4-dichlorophenol
3,5-DCP	3,5-dichlorophenol
Dichloran	2,6-dichloro-4-nitroaniline
1,3-DNB	1,3-dinitrobenzene
2,4-DNP	2,4-dinitrophenol
2,4-DNT	2,4-dinitrotoluene
DOPA	3,4-dihydroxy-l-phenylamine
DOPAC	3,4-dihydroxyphenylacetic acid
DOPEG	3,4-dihydroxyphenylethyleneglycol
E	Epinephrine
EDTA	Ethylenediaminetetraacetic acid
FIA	Flow injection analysis
GC	Glassy carbon
GSH	Glutathione
GSSG	Glutathione disulfide
HBDD	H-terminated surface of BDD
HFCVD	Hot-filament CVD
5-HIAA	5-hydroxyindoleacetic acid
5-HT	Serotonin
HVA	4-hydroxy-3-methoxyphenylacetic acid
IAP	Immunosuppressive acidic protein
IgG	Immunoglobulin G
LDR	Linear dynamic range
LE	Leucine-enkephalin
LEA	Leucine-enkephaline amide
LOD	Limit of detection
LOQ	Limit of quantitation
LS-AdSV	Linear scan adsorptive stripping voltammetry
LSV	Linear sweep voltammetry
4-methylCA	4-methylcatechol
MES	Morpholinoethanesulfonic acid
2-MESA	2-mercaptoethanesulfonic acid
MN	Metanephrine
MOPEG	3-methoxy-4-hydroxyphenylethyleneglycol
MP	Mobile phase
MPCVD	Microwave plasma assisted CVD
NADH	Reduced form of nicotinamide adenine dinucleotide
NE	Norepinephrine
NMN	Normetanephrine
NP	Nitrophenols
2-NP	2-nitrophenol
4-NP	4-nitrophenol
o-ABA	o-aminobenzoic acid
OBDD	O-terminated BDD
PB	Phosphate buffer
PCP	Pentachlorophenol
PEEK	Polyetheretherketon
Ph	Phenol
PM	Promethazine
RDE	Rotating disk electrode
SDM	Sulfadimethoxine
SDZ	Sulfadiazine
SMM	Sulfamonomethoxine
SMZ	Sulfamethazine
SPE	Solid phase extraction
SWV	Square wave voltammetry
T	Tyrosine
TA	Tyrosyl-alanine
TAG	Tyrosyl-alanine-glycine
2,4,5-TCP	2,4,5-trichlorophenol
2,4,6-TCP	2,4,6-trichlorophenol
2,3,4-TCP	2,3,4-trichlorophenol
2,3,5-TCP	2,3,5-trichlorophenol
2,3,6-TCP	2,3,6-trichlorophenol

TL	Thin layer
TNBA	5-thio-2-nitrobenzoic acid
TW	Tungsten wires
VMA	Vanillylmandelic acid
μ-TAS	Micro-total analysis systems

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9. Appendix III

Differential Pulse Voltammetry of Selected Nitrophenols on Boron-Doped Diamond Film Electrode

Jana Musilová, Jiří Barek, Pavel Drašar, and Karolina Pecková

Sensing in Electroanalysis
Vytřas, K.; Kalcher, K.; Švancara, I., Eds. University of Pardubice: Pardubice

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Percentage of participation of Ing. J. Karaová (Musilová) ~ **75 %**

background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, extreme electrochemical stability in both alkaline and acidic media, high current densities, good responsiveness for many redox analytes without pretreatment, and resistance to electrode fouling [5]. BDDFE can be used to determine a wide variety of inorganic and organic compounds using electrochemical reduction and oxidation. [6]

Nitrophenols coming from pesticide degradation, car exhausts, and industrial wastes [7] are listed as priority pollutants by the US Environmental Protection Agency (US EPA) as they are considered to be potentially carcinogenic and mutagenic. [8] Pesticides based on simple nitrophenols are used as growth stimulators in agriculture. [9] US EPA has restricted the concentration of 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) in natural water to be less than 10 μg/L. [10] Moreover, nitrophenols are a suitable model of nitrated explosives.

Experimental

Reagents

Stock solution of 2-NP, 4-NP (1.10^{-3} mol.L^{-1}, 98%, Sigma-Aldrich, Germany) and 2,4-DNP (1.10^{-3} mol.L^{-1}, 97%, Reakhim, Russia) were prepared by dissolving an accurately weighed amount of the pure substance in 100 ml of redistilled water using sonication. Solutions of lower concentrations were prepared by dilution of stock solution with redistilled water. Sodium hydroxide, glacial acetic acid, boric acid, phosphoric acid and potassium hexacyanoferrate (all p.a. purity) were obtained from Lachema Brno (Czech Republic). All solutions were kept in glass vessels in dark at laboratory temperature.

Apparatus

Voltammetric measurements were carried out using Eco-Tribo Polarograph with software PolarPro version 5.1 (both Polaro-Sensors, Czech Republic) in a three-electrode system – platinum wire electrode (Monokrystaly, Czech Republic) as auxiliary electrode, Ag/AgCl reference electrode (type RAE 113, 3 mol.L^{-1} KCl, Monokrystaly, Czech Republic) and boron-doped diamond film electrode (3 mm diameter, Windsor Scientific, UK) as

working electrode. In differential pulse voltammetry (DPV), the polarization rate 20 $mV.s^{-1}$, the pulse amplitude ±50 mV and the width of pulse 80 ms were used.

Procedures

The general procedure to obtain DP voltammograms was as follows: the required amount of the stock solution of the tested substance was placed in 10 mL volumetric flask and diluted to the mark with a Britton-Robinson (BR) buffer of appropriate pH. Oxygen was removed from the measured solutions by bubbling with nitrogen for five minutes. Between individual measurements, the measured solution was always bubbled with nitrogen for 15 s.

Between measurements of different solutions, the electrode was activated by cycling the potential in vigorously stirred aqueous 1M HNO_3 between -2.5 and +2.5 V vs. SCE until a stable signal was obtained (5-10 cycles with 0.1 $V.s^{-1}$ scan rate). The good performance of the electrode was regularly verified by measuring cyclic voltammograms of 1.10^{-4} $mol.L^{-1}$ potassium hexacyanoferrate.

Results and Discussion

The influence of pH on both cathodic and anodic DPV curves of tested nitrophenols (1.10^{-4} $mol.L^{-1}$) was investigated in BR buffer, pH 2-12. All curves were measured 5 times. First measurement always gave higher peaks and thus was not evaluated. For electrochemical reduction, well-developed peaks were obtained in acidic media, when the highest and most easily evaluated peaks have been found at pH 4 for 2-NP and 2,4-DNP, as well as at pH 6 for 4-NP (Fig.1).

On the other hand, for electrochemical oxidation, peaks were better developed in alkaline media and optimum conditions have been found at pH 11 for 4-NP and pH 10 for 2,4-DNP (Fig.2). During electrochemical oxidation of 2-NP, passivation of electrode's surface became evident and the calibration dependences were not linear. Also, the position of the peak near the end of the potential window caused the difficult evaluation. Therefore, for 2-NP, voltammetric determination based on principles of electrochemical oxidation at BDDFE does not seem to be a suitable method.

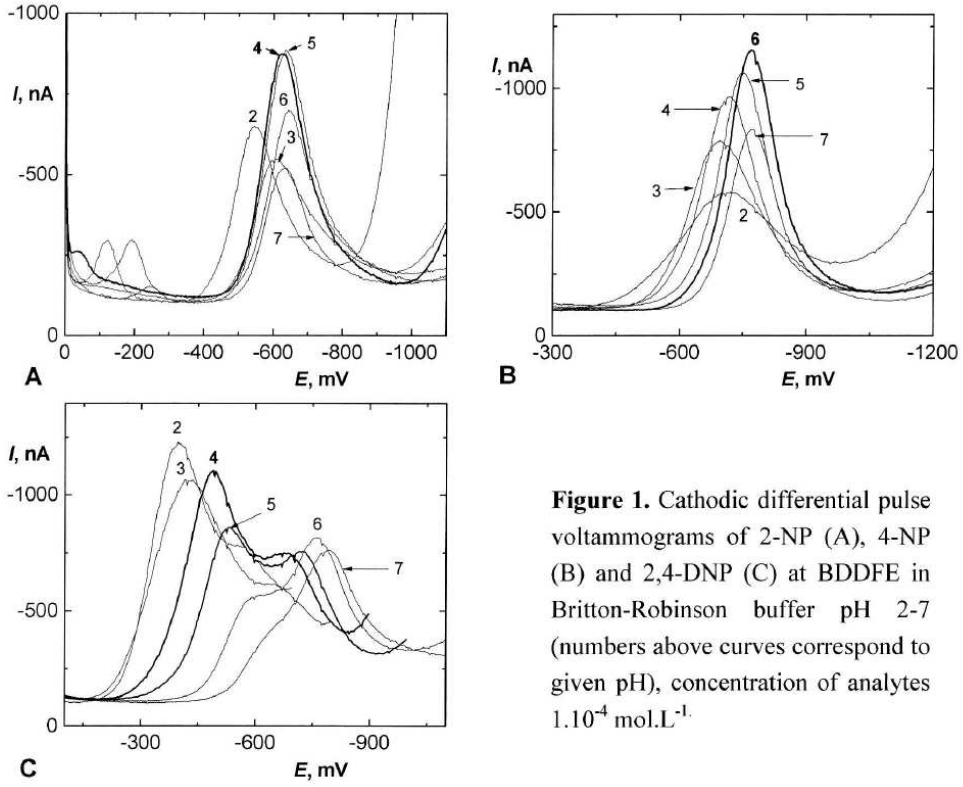

Figure 1. Cathodic differential pulse voltammograms of 2-NP (A), 4-NP (B) and 2,4-DNP (C) at BDDFE in Britton-Robinson buffer pH 2-7 (numbers above curves correspond to given pH), concentration of analytes 1.10^{-4} mol.L^{-1}.

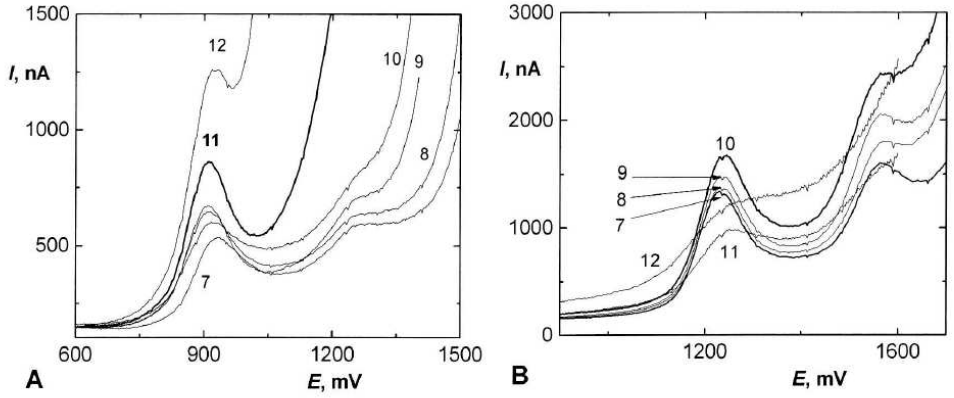

Figure 2. Anodic differential pulse voltammograms of 4-NP (A) and 2,4-DNP (B) at BDDFE in Britton-Robinson buffer pH 7-12 (numbers above curves correspond to given pH), concentration of analytes 1.10^{-4} mol.L^{-1}.

The optimum conditions were used for the construction of calibration dependences. The parameters of calibration curves are summarized in Table I. Cathodic DP-voltammograms and calibration plots of 2-NP, 4-NP and 2,4-DNP of the concentration range (2-10).10^{-6} mol.L^{-1} are depicted in Fig. 3-5. Anodic DP voltammograms and calibration plots of 4-NP and 2,4-DNP of the concentration range (2-10).10^{-6} mol.L^{-1} are depicted in Fig. 6-7.

Repeatability of the determination was confirmed by series of 20 consecutive measurements, carried out for the highest concentration of the linear dynamic range. The limits of quantification were calculated as the concentration of the analyte, which gave rise to the signal being ten-fold higher compared to that for the lowest measurable concentration expressed via the standard deviation estimated.

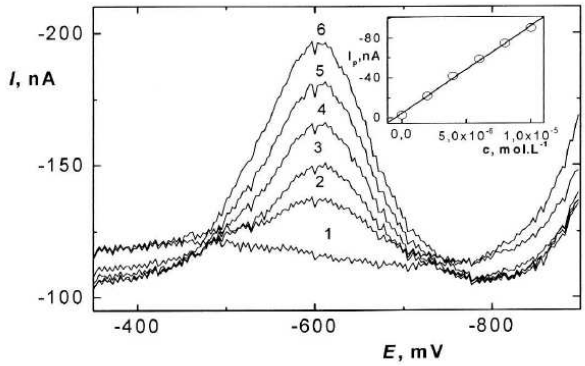

Figure 3. Cathodic DP voltammograms and calibration dependence for 2-NP at the BDDFE in BR buffer (pH 4); c(2-NP): 0 (1), 2.10^{-6} (2), 4.10^{-6} (3), 6.10^{-6} (4), 8.10^{-6} (5), 10.10^{-6} (6) mol.L^{-1}.

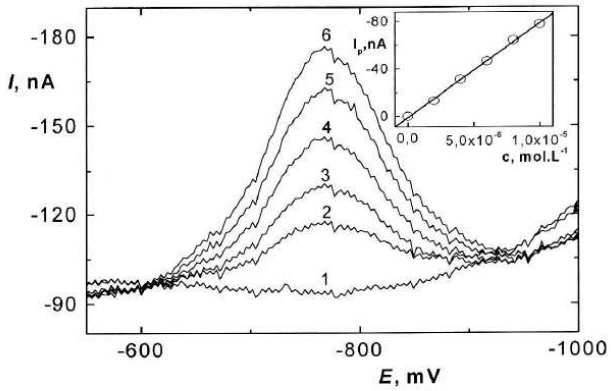

Figure 4. Cathodic DP voltammograms and calibration dependence for 4-NP at the BDDFE in BR buffer (pH 6); c(4-NP): 0 (1), 2.10^{-6} (2), 4.10^{-6} (3), 6.10^{-6} (4), 8.10^{-6} (5), 10.10^{-6} (6) mol.L^{-1}.

Table I. Parameters of the calibration straight lines for determination of nitrophenols by DPV at BDDFE in B-R buffer

Analyte	pH	LDR [mol.L^{-1}]	Repeatability (n=20)* RSD [%]	Slope [nA.mol.L^{-1}]	Intercept [nA]	R	L_Q [mol.L^{-1}]
2-NP	4_{red}	2.10^{-7} - 4.10^{-5}	2.2	-9.10^{6}	-5.6	0.9918	4.10^{-7}
4-NP	6_{red}	4.10^{-7} - 1.10^{-4}	1.0	-9.10^{6}	1.7	0.9999	4.10^{-7}
	11_{ox}	2.10^{-6} - 4.10^{-5}	7.9	7.10^{6}	- 4.2	0.9955	2.10^{-6}
2,4-DNP	4_{red}	2.10^{-7} - 1.10^{-5}	1.8	-1.10^{7}	-0.1	0.9999	4.10^{-7}
	10_{ox}	8.10^{-7} - 1.10^{-5}	3.8	2.10^{7}	3.1	0.9980	8.10^{-7}

Legend: *Replicate measurements were carried out for the highest concentration of the linear range.

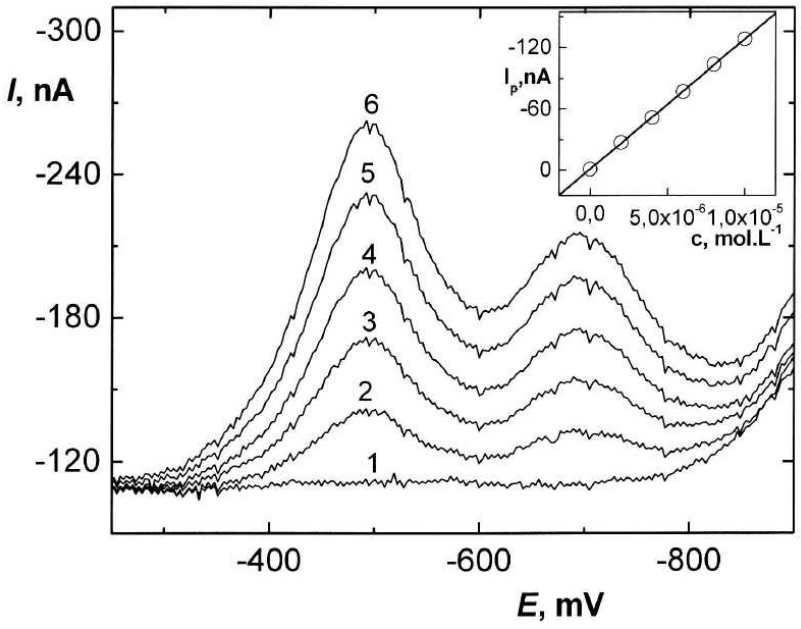

Figure 5. Cathodic DP voltammograms and calibration dependence for 2,4-DNP at BDDFE in BR buffer (pH 4); c(2,4-DNP): 0 (1), 2.10^{-6} (2), 4.10^{-6} (3), 6.10^{-6} (4), 8.10^{-6} (5), 10.10^{-6} (6) mol.L^{-1}.

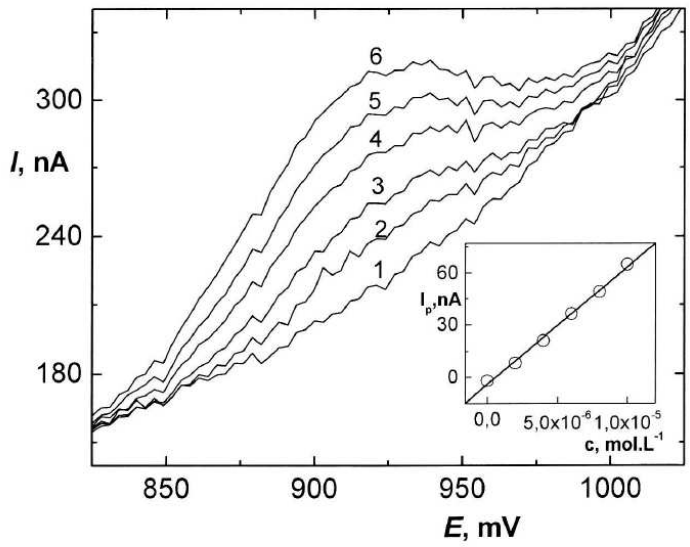

Figure 6. Anodic DP voltammograms and calibration dependence for 4-NP at BDDFE in BR buffer (pH 11); c(4-NP): 0 (1), 2.10^{-6} (2), 4.10^{-6} (3), 6.10^{-6} (4), 8.10^{-6} (5), 10.10^{-6} (6) mol.L^{-1}.

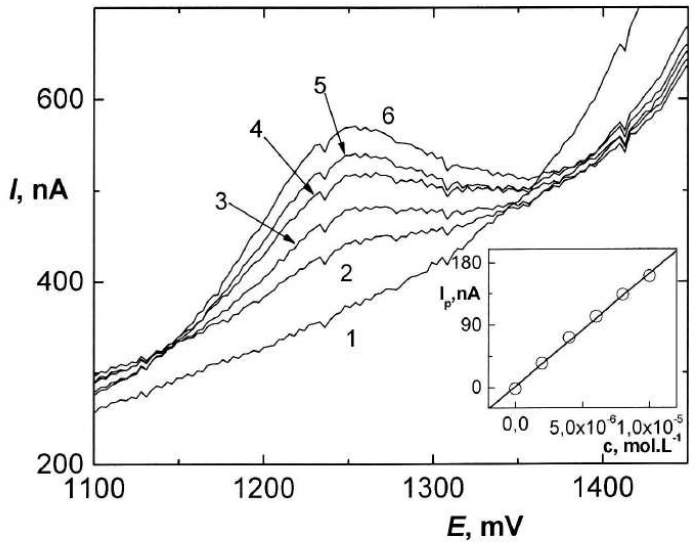

Figure 7. Anodical DP voltammograms and calibration dependence for 2,4-DNP at BDDFE in BR buffer (pH 10); c(2,4-DNP): 0 (1), 2.10^{-6} (2), 4.10^{-6} (3), 6.10^{-6} (4), 8.10^{-6} (5), 10.10^{-6} (6) mol.L^{-1}.

Conclusions

A differential pulse voltammetry method was developed for the determination of 2-NP, 4-NP and 2,4-DNP at BDDFE using electrochemical reduction and 4-NP and 2,4-DNP using electrochemical oxidation. It can be expected that this approach can be used for the detection of trace amounts of nitrated explosives.

Acknowledgements

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10. Appendix IV

Determination of Nitrophenols in Drinking and River Water by Differential Pulse Voltammetry at Boron-Doped Diamond Film Electrode

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Electroanalysis

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Full Paper **ELECTROANALYSIS**

Determination of Nitrophenols in Drinking and River Water by Differential Pulse Voltammetry at Boron-Doped Diamond Film Electrode

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Abstract
A differential pulse voltammetric method was developed for the determination of 2-nitrophenol, 4-nitrophenol and 2,4-dinitrophenol at a boron-doped diamond film electrode using electrochemical reduction and of 4-nitrophenol and 2,4-dinitrophenol using electrochemical oxidation. The method was successfully applied for the direct determination of these compounds in drinking and river water in the concentration range from 4×10^{-7} to 2×10^{-5} mol L^{-1}. To improve the limit of quantification, a preconcentration by solid phase extraction from 100 mL and 1000 mL of water samples was used with limit of determination around 2×10^{-8} and 2×10^{-7} mol L^{-1}, respectively.

Keywords: Boron-doped diamond film electrode, Differential pulse voltammetry, Nitrophenols, Drinking water, River water, Solid phase extraction

DOI: 10.1002/elan.201100016

1 Introduction

Boron doped diamond (BDD) is a versatile electrode material, which has gained popularity in a variety of electrochemical applications [1–8]. BDD film electrodes (BDDFE) possess excellent electrochemical properties, such as extreme hardness, low and stable background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, extreme electrochemical stability in both alkaline and acidic media, high current densities, good responsiveness for many redox analytes without pretreatment, and resistance to electrode fouling [9]. Because of the wide potential window both in cathodic and in anodic region, BDDFE can be used to determine a wide variety of inorganic and organic compounds using electrochemical reduction and/or oxidation. In our laboratory, BDDFE was successfully used for voltammetric [10,11] and amperometric [12,13] determination of both oxidizable and reducible compounds, namely aminobiphenyls [10,13], 3-nitrofluoranthene and 3-aminofluoranthene [11] and phenols [12].

Nitrophenols coming from pesticide degradation, car exhausts, and industrial wastes [14] are listed as priority pollutants by the US Environmental Protection Agency (US EPA). Pesticides based on simple nitrophenols are used as growth stimulators in agriculture [15]. US EPA has restricted the concentration of 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) in natural water to be less than 10 μg L^{-1}, that is 5×10^{-8} mol L^{-1} for 2,4-DNP and 7×10^{-8} mol L^{-1} for 2-NP and 4-NP [16]. Voltammetric determination of nitrophenols has been already described at hanging mercury drop electrode [17], silver solid amalgam electrode [18] and silver amalgam paste electrode [19]. Determination of nitrophenols using simultaneously both electrochemical reduction and oxidation improves the reliability of the analysis. Therefore, the possibility to use BDDFE for voltammetric determination of trace amounts of selected nitrophenols was investigated in this paper.

2 Experimental

2.1 Reagents

Stock solution of 2-NP, 4-NP (1×10^{-3} mol L^{-1}, 98%, Sigma-Aldrich, Germany) and 2,4-DNP (1×10^{-3} mol L^{-1}, 97%, Reachim, Russia) were prepared by dissolving an accurately weighed amount of the pure substance in 100 ml of deionized water using sonication. Solutions of lower concentrations were prepared by exact dilution of stock solution with deionized water. Sodium hydroxide, glacial acetic acid, boric acid, phosphoric acid and potassium hexacyanoferrate (all p.a. purity) were obtained from Lachema Brno (Czech Republic). All solutions were kept in glass vessels in dark at laboratory temperature. The drinking water was taken from public water line in the chemistry building of Faculty of Science, Charles University in Prague. The river water was taken in the

river Vltava in the centre of the city of Prague and it was analyzed within 3 days after sampling. Before the solid phase extraction, the river water was filtered using S4 sintered glass.

2.2 Apparatus

Voltammetric measurements were carried out using Eco-Tribo Polarograph with software PolarPro version 5.1 (both Polaro-Sensors, Prague, Czech Republic) in a three-electrode system – platinum wire electrode (Monokrystaly, Czech Republic) as auxiliary electrode, Ag/AgCl reference electrode (type RAE 113, 3 mol L^{-1} KCl, Monokrystaly, Czech Republic) and boron-doped diamond film electrode (3 mm diameter, Windsor Scientific, UK) as working electrode. In differential pulse voltammetry (DPV), the polarization rate 20 mV s^{-1}, the pulse amplitude ±50 mV and the pulse width of 100 ms were used. The solution pH was measured with digital Conductivity & pH meter 4330 (Jenway Ltd., Essex, Great Britain) using combined glass electrode (Jenway, type 924 005).

2.3 Procedures

Calibration measurements were carried out by measuring 5 mL of model sample of water spiked with an appropriate amount of analyte from the stock solution into a 10 mL volumetric flask, which was filled up to the mark with a Britton–Robinson buffer (BR buffer) of appropriate pH. Oxygen was removed from measured solutions by bubbling with nitrogen for five minutes. Between individual measurements, the measured solution was always bubbled with nitrogen for 15 s. All measurements were carried out at laboratory temperature.

The calibration curves were measured in triplicate and evaluated by the least squares linear regression method. Repeatability of the determination was confirmed on series of 20 consecutive measurements, replicate measurements were carried out for the highest and lowest concentration of the linear dynamic range. The limits of quantification were calculated as the concentration of the analyte, which gave the signal equal to ten times the standard deviation estimated from the lowest measurable concentration [20].

For solid phase extraction, polymeric SPE Lichrolut EN cartridges purchased from (Merck, Darmstadt, Germany) were used. These cartridges contain 200 mg of sorbent based on ethylvinylbenzene-divinylbenzene copolymer with a large specific area. Cartridge was conditioned by 3 mL methanol and 3 mL water and than the model water sample spiked with different amounts of analyte was sucked through the cartridge at the flow rate 1000 mL per hour. After washing the cartridge with 1 mL of deionized water and drying by air for 10 minutes, analyte was eluted by 6 mL of methanol and filled by Britton–Robinson buffer of appropriate pH up to 10 mL.

Prior the first electrochemical measurement and also for renewing electrode's surface after observed passivation, BDDFE was activated by cycling the potential in vigorously stirred aqueous 1 M HNO_3 between −2.5 and +2.5 V vs. SCE until a stable signal was detected (5–10 cycles with 0.1 V s^{-1} scan rate). The good performance of the electrode was regularly verified by measuring cyclic voltammograms of 1×10^{-4} mol L^{-1} potassium hexacyanoferrate.

3 Results and Discussion

3.1 The Influence of pH on Voltammetric Behavior of Nitrophenols

The influence of pH on both cathodic and anodic DPV curves of tested nitrophenols (1×10^{-4} mol L^{-1}) was investigated in BR buffer, pH 2–12. The presence of both electrochemically oxidizable phenolic group and electrochemically reducible nitro group offers the possibility to use both anodic and cathodic voltammetry which can increase the reliability of the determination. For electrochemical reduction, well-developed peaks were obtained in acidic media; the highest and most easily evaluated peaks have

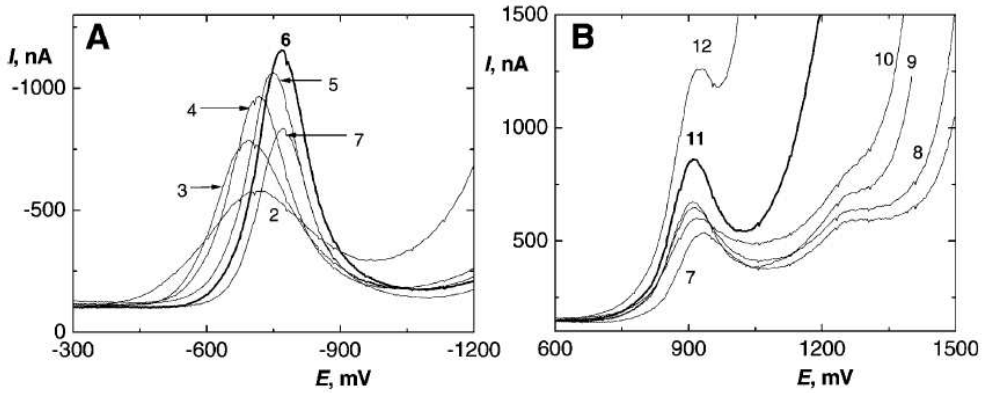

Fig. 1. Cathodic (A) and anodic (B) differential pulse voltammograms of 4-NP ($c=1\times10^{-4}$ mol L^{-1}) at BDDFE in Britton–Robinson buffer pH 2–7 (A) and pH 7–12 (B), numbers above curves correspond to given pH.

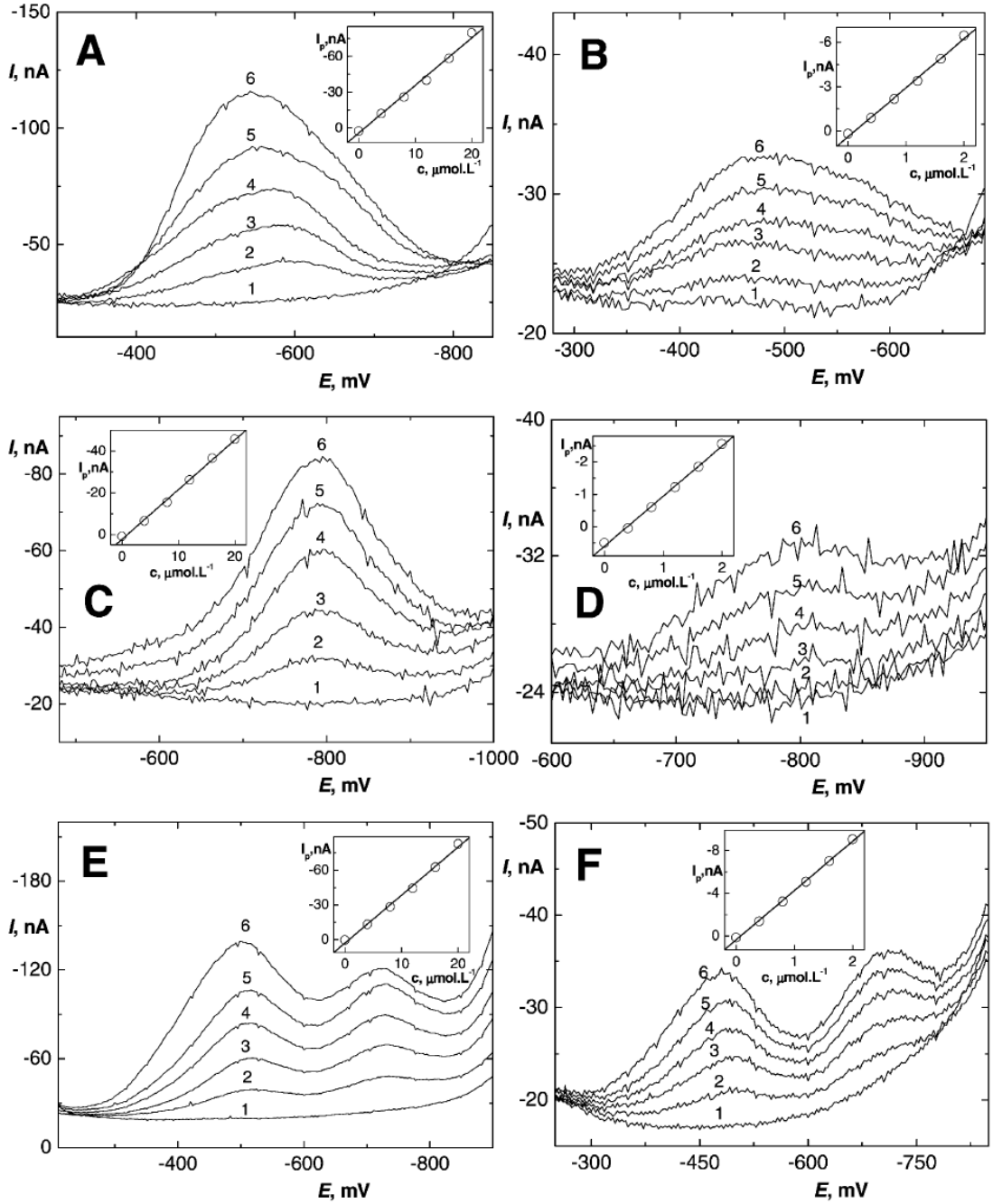

Fig. 2. Cathodic DP voltammograms and calibration dependences for 2-NP (A, B), 4-NP (C, D) and 2,4-DNP (E, F) at BDDFE in drinking water. Base electrolyte BR buffer pH 4 (for 2-NP and 2,4-DNP) and pH 6 (for 4-NP). *c*(2-NP, 4-NP and 2,4-DNP) in drinking water (A, C, E): 0 (1), 4 (2), 8 (3), 12 (4), 16 (5), 20 (6) µmol L^{-1}; *c*(2-NP, 4-NP and 2,4-DNP) in drinking water (B, D, F): 0 (1), 0.4 (2), 0.8 (3), 1.2 (4), 1.6 (5), 2 (6) µmol L^{-1}.

been found at pH 4 for 2-NP and 2,4-DNP and pH 6 for 4-NP (Figure 1A). On the other hand, for electrochemical oxidation, peaks were better developed in alkaline media and optimum conditions have been found at pH 11 for 4 NP (Figure 1B) and pH 10 for 2,4-DNP. During electrochemical oxidation of 2-NP, passivation of electrode's surface became evident (peak currents decreased with repeating determination on the same electrode surface

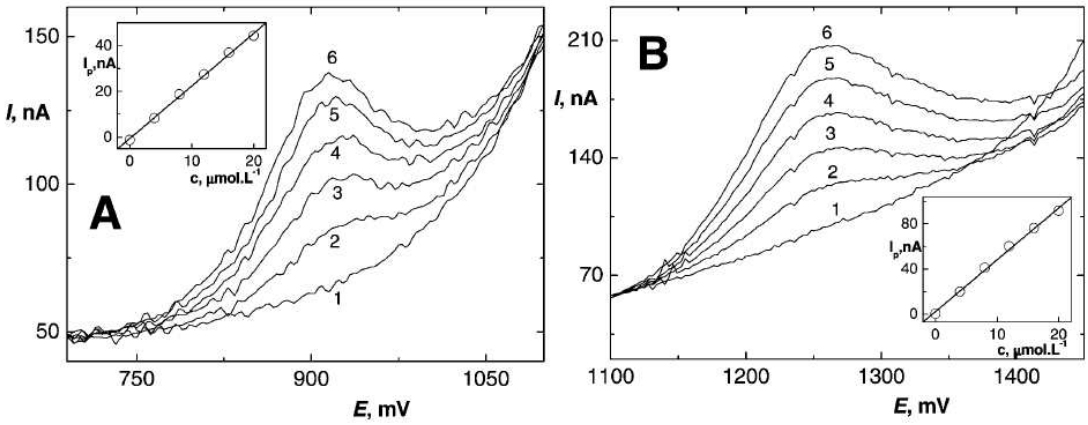

Fig. 3. Anodic DP voltammograms and calibration dependences for 4-NP (A) and 2,4-DNP (B) at BDDFE in drinking water. Base electrolyte BR buffer pH 11 (for 4-NP) and pH 10 (for 2,4-DNP). *c*(4-NP and 2,4-DNP) in drinking water: 0 (1), 4 (2), 8 (3), 12 (4), 16 (5), 20 (6) µmol L^{-1}.

Table 1. Parameters of the calibration straight lines for the determination of tested nitrophenols by DPV at BDDFE in deionized, drinking and river water.

Analyte	Matrix	Mode	*LDR* (mol L^{-1})	*RSD* (%)[e]	*RSD* (%)[f]	Slope (nA mol L^{-1})	Intercept (nA)	Correlation coefficient	L_Q (mol L^{-1})
2-NP [a]	Deionized water	red.	4×10^{-7}–8×10^{-5}	2.8	2.2	-4.71×10^{6}	5.57	0.9918	3×10^{-7}
	Drinking water	red.	4×10^{-7}–2×10^{-4}	3.3	6.5	-3.72×10^{6}	−0.25	0.9991	2×10^{-7}
	River water	red.	8×10^{-7}–2×10^{-5}	7.7	8.2	-9.45×10^{6}	−4.82	0.9983	1×10^{-7}
4-NP [b,c]	Deionized water	red.	8×10^{-7}–2×10^{-4}	3.8	1.0	-4.67×10^{6}	−1.65	0.9999	1×10^{-7}
	Drinking water	red.	8×10^{-7}–2×10^{-5}	5.5	7.8	-2.38×10^{6}	−2.17	0.9999	1×10^{-7}
	River water	red.	4×10^{-7}–2×10^{-5}	5.3	8.9	-2.87×10^{6}	−1.29	0.9940	1×10^{-7}
	Deionized water	ox.	4×10^{-6}–8×10^{-5}	2.0	9.1	3.76×10^{6}	−7.48	0.9955	5×10^{-7}
	Drinking water,	ox.	4×10^{-6}–4×10^{-5}	2.8	9.5	2.43×10^{6}	−1.75	0.9983	1×10^{-6}
	River water	ox.	4×10^{-6}–2×10^{-5}	4.6	8.0	1.07×10^{6}	0.29	0.9962	1×10^{-6}
2,4-DNP [a,d]	Deionized water	red.	4×10^{-7}–2×10^{-5}	1.5	1.7	-6.41×10^{6}	0.12	0.9999	1×10^{-7}
	Drinking water	red.	4×10^{-7}–2×10^{-5}	3.0	7.6	-3.99×10^{6}	0.71	0.9942	1×10^{-7}
	River water	red.	8×10^{-7}–2×10^{-5}	4.5	5.4	-6.12×10^{6}	3.72	0.9988	6×10^{-7}
	Deionized water	ox.	2×10^{-6}–2×10^{-5}	2.1	3.4	8.05×10^{6}	3.12	0.9980	3×10^{-7}
	Drinking water	ox.	8×10^{-7}–2×10^{-5}	4.3	2.5	4.59×10^{6}	2.32	0.9980	5×10^{-7}
	River water	ox.	2×10^{-6}–2×10^{-5}	1.4	5.6	4.88×10^{6}	6.02	0.9971	3×10^{-7}

[a] Base electrolyte BR buffer pH 4 (for reduction). [b] Base electrolyte BR buffer pH 6 (for reduction). [c] Base electrolyte BR buffer pH 11 (for oxidation). [d] Base electrolyte BR buffer pH 10 (for oxidation). [e] Replicate measurements ($n=10$) were carried out for the lowest concentration of the linear dynamic range. [f] Replicate measurements ($n=20$) were carried out for the highest concentration of the linear dynamic range.

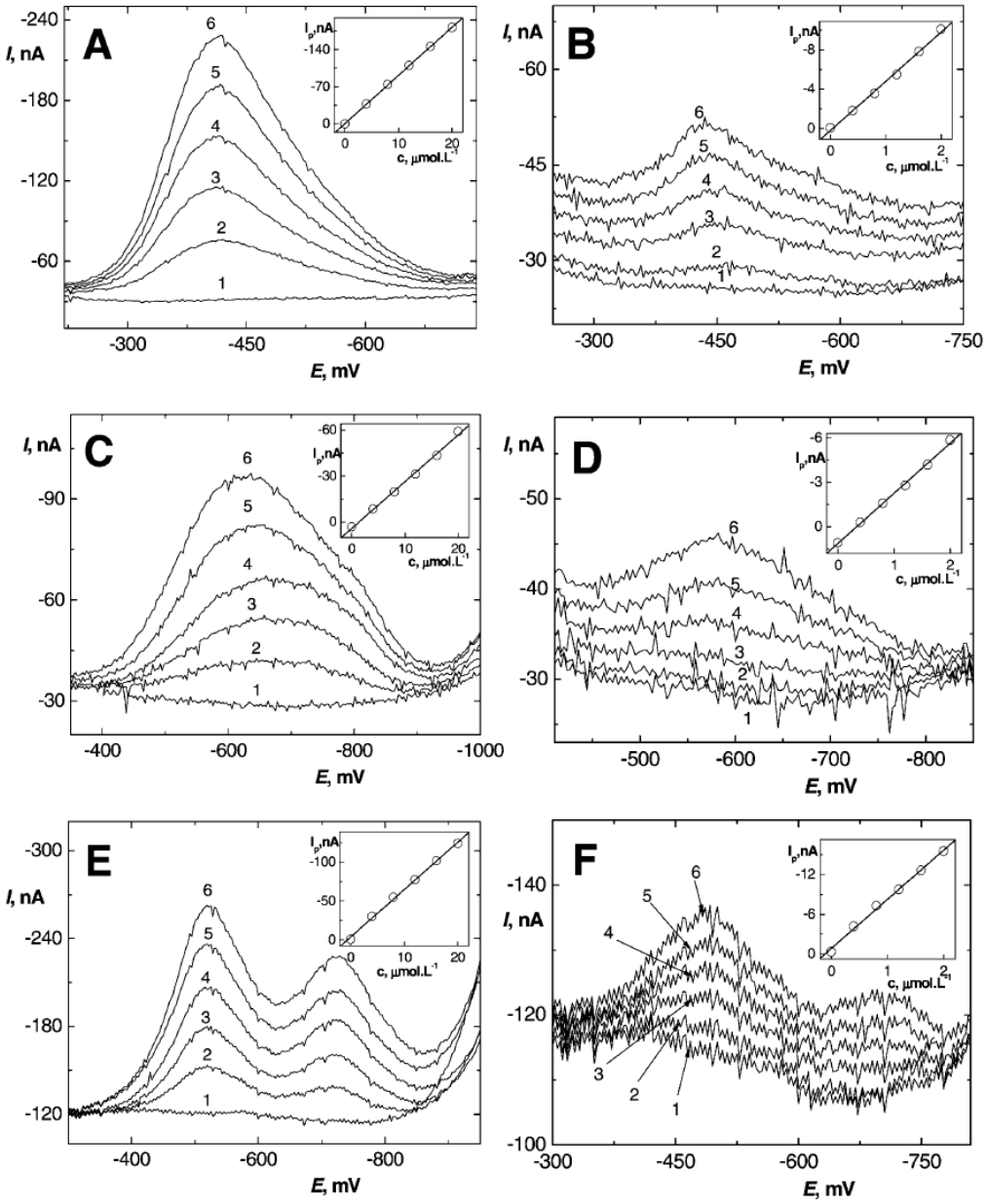

Fig. 4. Cathodic DP voltammograms and calibration dependences for 2-NP (A, B), 4-NP (C, D) and 2,4-DNP (E, F) at BDDFE in river water. Base electrolyte BR buffer pH 4 (for 2-NP and 2,4-DNP) and pH 6 (for 4-NP). *c*(2-NP, 4-NP and 2,4-DNP) in river water (A, C, E): 0 (1), 4 (2), 8 (3), 12 (4), 16 (5), 20 (6) µmol L^{-1}; *c*(2-NP, 4-NP and 2,4-DNP) in river water (B, D, F): 0 (1), 0.4 (2), 0.8 (3), 1.2 (4), 1.6 (5), 2 (6) µmol L^{-1}.

without any pretreatment their peak potential being shifted towards more positive values) and the calibration dependences were not linear. Also, the position of the peak near the end of the potential window caused the difficult evaluation. Therefore, for 2-NP, voltammetric determination using electrochemical oxidation at BDDFE is not a suitable method.

3.2 Direct Determination of Nitrophenols in Drinking and River Water

The above found optimum conditions were successfully applied for the direct determination of these compounds in drinking and river water. The parameters of calibration curves are summarized in Table 1. The sensitivity of this direct determination is comparable with the previous pre-

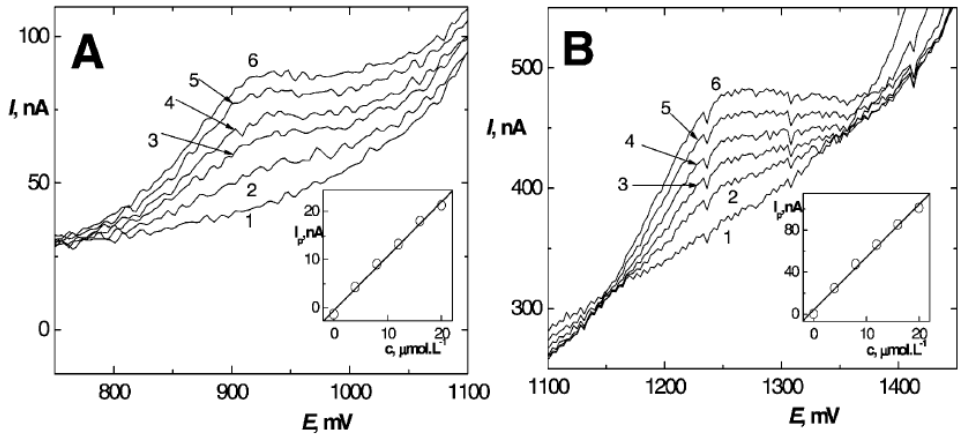

Fig. 5. Anodic DP voltammograms and calibration dependences for 4-NP (A) and 2,4-DNP (B) at BDDFE in river water. Base electrolyte BR buffer pH 11 (for 4-NP) and pH 10 (for 2,4-DNP). *c*(4-NP and 2,4-DNP) in river water: 0 (1), 4 (2), 8 (3), 12 (4), 16 (5), 20 (6) μmol L^{-1}.

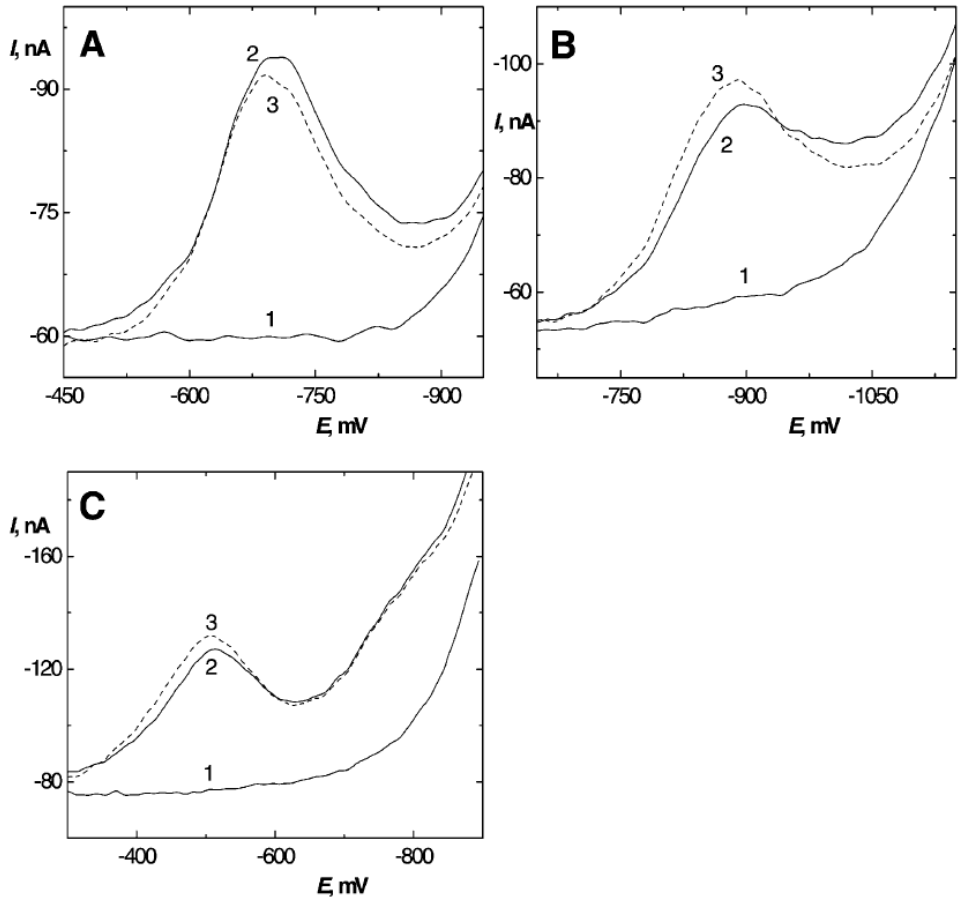

Fig. 6. Cathodic DP voltammograms of 2-NP (A), 4-NP (B) and 2,4-DNP (C) at BDDFE after solid phase extraction from 100 mL of drinking water ($c = 1 \times 10^{-6}$ mol L^{-1}). Base electrolyte BR buffer pH 4 (for 2-NP and 2,4-DNP) and pH 6 (for 4-NP). Blank sample (1), extraction of 2-NP, 4-NP or 2,4-DNP from the water sample (2), direct addition of 2-NP, 4-NP or 2,4-DNP to the blank sample (3).

liminary DP voltammetric experiments carried out with deionized water [21]. Also the limits of quantification lie within the same concentration range. The linear dynamic ranges are wider for the determination in deionized and drinking water than in river water and the slope is somewhat different. Cathodic and anodic DP voltammograms and calibration plots of the determination of 2-NP, 4-NP and 2,4-DNP in drinking water are depicted in Figure 2 and 3 and in river water in Figure 4 and 5.

3.3 Determination of Nitrophenols in Drinking and River Water after Preconcentration by Solid Phase Extraction

To improve the limit of quantification, preconcentration by solid phase extraction (SPE) from 100 mL and 1000 mL water samples was used. Electrochemical reduction was more sensitive than oxidation, so preconcentration by SPE was combined with cathodic DPV at BDDFE. Lichrolut EN cartridges containing polymeric sorbent with large specific surface and the adsorption capacity for polar organic substances were used. Recovery of SPE of nitrophenols was calculated from the ratio of the peak height of the substance after SPE and peak height of the standard solution at concentration corresponding to expected concentration after extraction (see Figure 6 for the sake of illustration). 100 mL and 1000 mL of deionized and drinking water samples and 100 mL of river water samples were used. Passing 1000 mL of river water through the SPE column was not successful because of the decrease of the sample flow rate (the flow rate for sucking 100 mL sample was 100 mL per hour), and therefore unacceptable prolongation of analysis time.

Parameters of calibration dependences for SPE-DPV determination of 2,NP, 4-NP and 2,4-DNP in water samples are summarized in Table 2. Cathodic DP voltammograms and calibration plots of the determination of 2-NP, 4-NP and 2,4-DNP after SPE from model water samples in the concentration range $(2–10)\times10^{-7}$ mol L^{-1} are depicted in Figure 7.

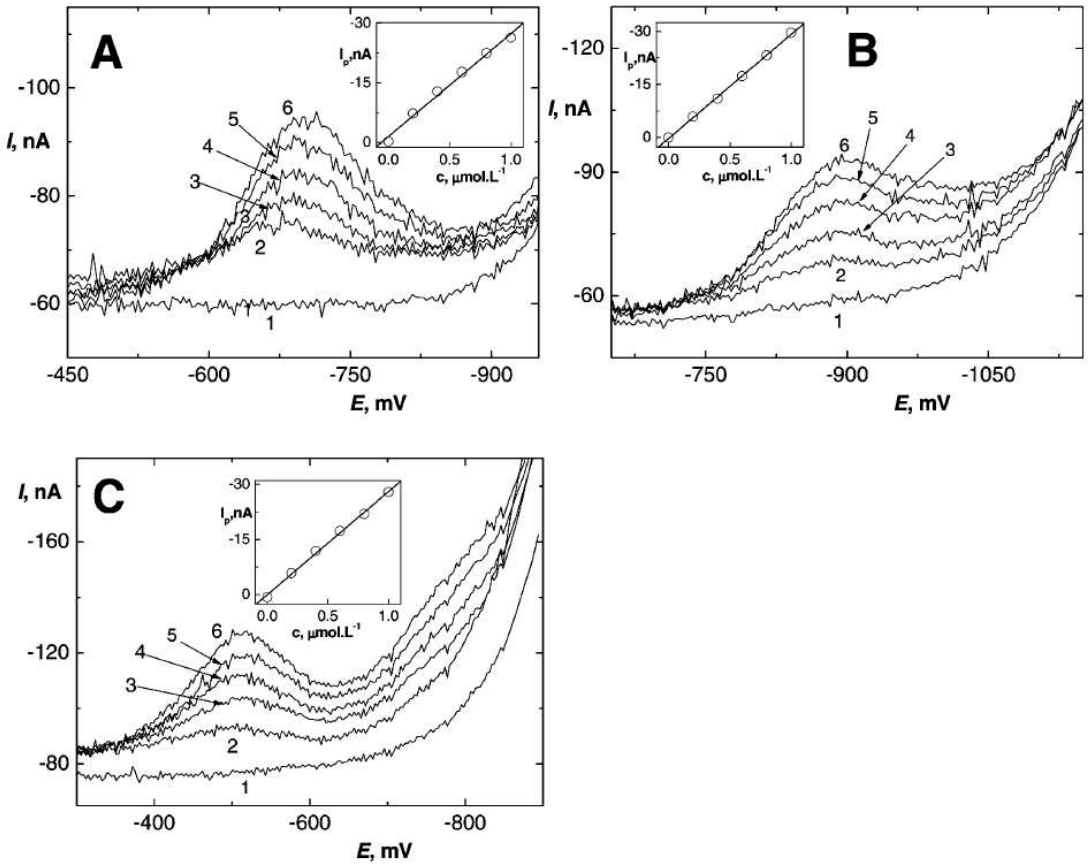

Fig. 7. Cathodic DP voltammograms of 2-NP (A), 4-NP (B) and 2,4-DNP (C) at BDDFE after solid phase extraction from 100 mL of drinking water. Base electrolyte BR buffer pH 4 (for 2-NP and 2,4-DNP), BR buffer pH 6 (for 4-NP). *c*(2-NP, 4-NP, 2,4-DNP in drinking water): 0 (1), 2×10^{-7} (2), 4×10^{-7} (3), 6×10^{-7} (4), 8×10^{-7} (5), 10×10^{-7} (6) mol L^{-1}.

Table 2. Parameters of the calibration straight lines for cathodic DP voltammetric determination of tested nitrophenols in deionized, drinking and river water samples after solid phase extraction.

Model sample	Sample volume (mL)	Analyte concentration (mol L^{-1})	Slope (mA mol^{-1} L)	Intercept (nA)	Correlation coefficient	Recovery[a]	*LOQ* (mol L^{-1})
2-NP							
Deionized water	100	$(2–10)\times10^{-7}$	-3.44×10^{7}	−0.03	0.9970	100	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-3.77×10^{8}	−1.52	0.9942	99	2×10^{-8}
Drinking water	100	$(2–10)\times10^{-7}$	-2.59×10^{8}	−1.53	0.9906	99	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-5.26×10^{8}	−0.03	0.9952	99	2×10^{-8}
River water	100	$(2–10)\times10^{-7}$	-1.38×10^{7}	−0.58	0.9945	99	2×10^{-7}
4-NP							
Deionized water	100	$(2–10)\times10^{-7}$	-2.32×10^{7}	0.05	0.9920	87	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-1.04×10^{8}	0.24	0.9915	81	3×10^{-8}
Drinking water	100	$(2–10)\times10^{-7}$	-2.96×10^{7}	0.32	0.9991	77	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-2.32×10^{7}	1.03	0.9926	75	4×10^{-8}
River water	100	$(2–10)\times10^{-7}$	-2.08×10^{7}	0.47	0.9996	80	2×10^{-7}
2,4-DNP							
Deionized water	100	$(2–10)\times10^{-7}$	-2.32×10^{7}	0.05	0.9920	84	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-3.45×10^{7}	0.93	0.9934	81	2×10^{-8}
Drinking water	100	$(2–10)\times10^{-7}$	-2.08×10^{7}	0.47	0.9996	80	2×10^{-7}
	1000	$(2–10)\times10^{-8}$	-2.28×10^{7}	0.87	0.9945	80	2×10^{-8}
River water	100	$(2–10)\times10^{-7}$	-2.81×10^{7}	0.08	0.9974	82	2×10^{-7}

[a] For the highest concentration of the concentration range

The obtained results confirm that BDDFE is a suitable sensor for determination of both electrochemically oxidizable and reducible organic compounds in drinking and river water. However, it should be pointed out that many similar substances can have similar peak potentials at this electrode thus leading to false positive results. In that case a combination of electrochemical detection at BDDFE with a preliminary separation using HPLC, which is under investigation in our laboratory, can increase the selectivity of these determinations.

4 Conclusions

A differential pulse voltammetric method was developed for the determination of trace concentrations of 2-NP, 4-NP and 2,4-DNP at BDDFE using electrochemical reduction and of 4-NP and 2,4-DNP using electrochemical oxidation. The method was successfully applied for the direct determination of these compounds in drinking and river water in the concentration range of 4×10^{-7} to 2×10^{-5} mol L^{-1} with limit of determination around 2×10^{-7} mol L^{-1} for reduction and 8×10^{-7} mol L^{-1} for oxidation. To improve the limit of quantification and to increase selectivity, a preliminary separation and preconcentration by SPE from 100 mL and 1000 mL of drinking water samples was used with limit of determination around 3×10^{-8} and from 100 mL of river water with limit of determination 2×10^{-7} mol L^{-1}, respectively. Because electrochemical reduction was more sensitive than oxidation, preconcentration by SPE was combined only with cathodic DPV.

Acknowledgements

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11. Appendix V

Oxidative and Reductive Detection Modes for Determination of Nitrophenols by High-Performance Liquid Chromatography with Amperometric Detection at a Boron Doped Diamond Electrode

Jana Karaová, Jiří Barek, and Karolina Schwarzová-Pecková

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Oxidative and Reductive Detection Modes for Determination of Nitrophenols by High-performance Liquid Chromatography with Amperometric Detection at a Boron Doped Diamond Electrode

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ABSTRACT

High performance liquid chromatography with electrochemical detection using a wall-jet arrangement with a working boron-doped diamond film electrode was used for the determination of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol using reduction and oxidation modes. The optimal conditions for separation at a C18 reverse phase column (125 × 4 millimeters, 5 micrometers) and amperometric detection of these nitrophenols were determined. Acetate buffer (0.05 mole per liter pH 4.7/methanol 58/42, *v/v*) was chosen as the mobile phase for cathodic detection at the potential of −1.2 volts. The linear dynamic range was 2×10^{-6} to 1×10^{-4} mole per liter and the limits of detection were from 0.7 to 1.2 micromole per liter. For anodic detection, the mobile phase was 0.05 mole per liter phosphate buffer pH 6.75/methanol (65/35, *v/v*) at a detection potential of +1.3 volts. The linear dynamic range was from 2×10^{-6} to 1×10^{-4} mole per liter with limits of detection from 0.6 to 1.5 micromoles per liter. The method was successfully employed for direct determination of nitrophenols in drinking and river water with limits of detection between 0.7 and 1.8 micromoles per liter.

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Amperometric detection; boron-doped diamond electrode; high-performance liquid chromatography; HPLC; nitrophenols; wall-jet detector

Introduction

Boron-doped diamond (BDD) is a popular electrode material because of its commercial availability and excellent mechanical and electrochemical properties (Fujishima et al. 2005; Luong, Male, and Glennon 2009; Peckova, Musilova, and Barek 2009). For voltammetric techniques, a low and stable background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, extreme electrochemical stability in both alkaline and acidic media, good responsiveness for many analytes without pretreatment, and resistance to electrode fouling are the most important properties. The mechanical durability substantiates the popularity of BDD film electrodes in liquid flow methods including flow injection analysis (FIA) and high performance liquid

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chromatography (HPLC) with electrochemical detection (ED). Because of the wide potential window in the cathodic and anodic regions, BDD film electrodes can be used to determine a wide variety of inorganic and organic compounds (such as drugs, pesticides, environmental pollutants, and other biologically active compounds) using electrochemical reduction and/or oxidation. In our laboratory, BDD film electrodes were successfully used for voltammetric (Barek et al. 2007; Cizek et al. 2007; Yosypchuk, Peckova, and Barek 2010; Dejmkova, Barek, and Zima 2011; Dejmkova et al. 2012; Yosypchuk, Barek, and Vyskocil 2012b; Zavazalova et al. 2013) and amperometric (Peckova et al. 2006; Dejmkova et al. 2009; Peckova, Jandova, et al. 2009; Maixnerova et al. 2010; Dejmkova, Barek, and Zima 2011; Dejmkova et al. 2012; Maixnerova, Barek, and Peckova 2012; Yosypchuk, Barek, and Vyskocil 2012a; Zavazalova et al. 2013) determination of both oxidizable and reducible compounds, including phenolics (Dejmkova et al. 2009) and aminonitrophenols (Dejmkova, Barek, and Zima 2011).

An overview of organic analytes determined by means of BDD electrodes is available in our recent reviews (Musilova, Barek, and Peckova 2009; Peckova, Musilova, and Barek 2009; Peckova and Barek 2011; Zavazalova, Barek, and Peckova 2014; Peckova, Zima, and Barek In press). Reducible compounds are in minority; as most methods rely on the reduction of the nitro group at the aromatic skeleton. Although the BDD is less sensitive to oxygen reduction than other electrode materials, its presence in HPLC-ED or FIA-ED causes an increase in the background current and also limits the useful working electrode potential window for amperometric determination of reducible organic analytes (Danhel et al. 2009; Peckova, Vrzalova, et al. 2009; Yosypchuk, Karasek, et al. 2012).

Nitrophenols are both reducible and oxidizable and thus are often used as model compounds in electrochemistry. Together with substituted nitrophenols, they are frequently used as reactants or intermediates in production of drugs and dyes. Furthermore, they are of great importance in agriculture, where pesticides based on simple nitrophenols are used as growth stimulators (Bynum et al. 2007). They are listed by the U.S. Environmental Protection Agency (EPA) on the List of Priority Pollutants (US EPA 2014) and are frequently determined by various separation techniques (Ruana, Urbe, and Borrull 1993; Cledera-Castro, Santos-Montes, and Izquierdo-Hornillos 2006; Fischer, Barek, and Wang 2006; Hofmann, Hartmann, and Hermann 2008; Danhel et al. 2009; Yang, Chen, and Jiang 2013). These compounds have also been determined by electrochemical detection using silver solid amalgam (AgSAE) (Danhel et al. 2009), glassy carbon (GCE) (Ruana, Urbe, and Borrull 1993; Fischer, Barek, and Wang 2006), and solid amalgam composite (Yosypchuk et al. 2007) electrodes. The characteristics and achieved detection limits of selected amperometric determinations are listed in Table 1.

Voltammetric determination of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol at BDD film electrodes has been already described utilizing their oxidation (Pedrosa, Codognoto, and Avaca 2003; Pedrosa et al. 2005; Lei et al. 2007; Zhao et al. 2007), reduction (Lawrence et al. 2006), or comparing both detection modes (Pedrosa et al. 2004; Garbellini, Salazar-Banda, and Avaca 2007; Musilova, Barek, and Peckova 2011). Determination of nitrophenols using simultaneous electrochemical reduction and oxidation improves the selectivity and reliability of the analysis. Therefore, BDD film electrodes using both detection modes for amperometric determination of trace amounts of nitrophenols after their HPLC separation is reported here. For this purpose, a wall-jet arrangement was used because of favorable analytical figures of merit compared with the thin-layer arrangement (Maixnerova,

Table 1. Selected methods combining liquid flow techniques and amperometric detection for the determination of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol.

Analyte	Technique/electrode [Limit of detection, micromole per liter]	Reference
2-nitrophenol	HPLC/GCE^{ox} [0.009]	Ruana, Urbe, and Borrull (1993)
	CE chip/GCE^{red} [60]	Fischer, Barek, and Wang (2006)
	HPLC/AgSAE^{red} [10]^{a,} $^{(25)b}$	Danhel et al. (2009)
	HPLC/BDD [1.2]^{red,} [1.0]^{ox}	this work
4-nitrophenol	HPLC/GCE^{ox} [0.011]	Ruana, Urbe, and Borrull (1993)
	CE chip/GCE^{red} [60]	Fischer, Barek, and Wang (2006)
	HPLC/AgSAE^{red} [10]^{a,} $^{(25)b}$	Danhel et al. (2009)
	HPLC/BDD [0.8]^{red,} [1.5]^{ox}	this work
2,4-dinitrophenol	HPLC/GCE^{ox} [0.023]	Ruana, Urbe, and Borrull (1993)
	CE chip/GCE^{red} [60]	Fischer, Barek, and Wang (2006)
	HPLC/AgSAE^{red} [5]^{a,} $^{(10)b}$	Danhel et al. (2009)
	HPLC/BDD [0.7]^{red,} [0.6]^{ox}	this work

^{red}Reductive detection mode; ^{ox}Oxidative detection mode.
^{a}Thin-layer arrangement.
^{b}Wall-jet arrangement.

Barek, and Peckova 2012). The applicability of the developed HPLC-ED methods was verified for the direct determination of micromolar concentrations of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol in drinking and river water.

Experimental

Reagents

Stock solutions of 2-nitrophenol and 4-nitrophenol (1×10^{-3} mole per liter, 98%, Sigma-Aldrich, Germany) and 2,4-dinitrophenol (1×10^{-3} mole per liter, 97%, Reachim, Russia) were prepared by dissolving each substance in 100 milliliters of deionized water using sonication. Solutions of lower concentrations were prepared by dilution of the stock with deionized water (Millipore Q-plus System, Millipore, USA).

The mobile phase for HPLC of nitrophenols (oxidative detection mode) contained methanol (HPLC grade, Merck, Prague, Czech Republic) and 0.05 mole per liter phosphate buffer (pH 6.75), prepared from sodium hydrogen phosphate whose pH was adjusted with concentrated phosphoric acid. For the reductive detection mode, the mobile phase contained methanol and 0.05 mole per liter acetate buffer (pH 4.7), prepared from acetic acid whose pH was adjusted with concentrated sodium hydroxide. All solutions were prepared using deionized water. Sodium hydrogen phosphate, phosphoric acid, sodium hydroxide, and acetic acid (all p.a. purity) were obtained from Lachema Brno (Czech Republic). All solutions were kept in glass vessels in the dark at laboratory temperature.

Drinking water was taken immediately before sampling in the Chemistry Building of Faculty of Science, Charles University in Prague. The river water was taken in the river Vltava in the center of the city of Prague and it was analyzed within three days after sampling. Before the measurement, the river water was filtered using S4 Simax (Kavalierglass, Prague, Czech Republic) sintered glass with pores diameter 10 to 16 micrometers.

Oxygen was removed from mobile phase by ten minutes sonication and forty-five minutes bubbling with nitrogen 4.0 purity (Linde, Prague, Czech Republic) before filling to

linear high-pressure pump and from measured solutions by five minutes bubbling before measurements. All experiments and measurements were done at ambient temperature.

Apparatus

The HPLC system consisted of a high-pressure pump HPP 5001 (Laboratorni Pristroje Praha, Czech Republic), a six-way valve D (Ecom, Prague, Czech Republic) fitted with a 20-microliter injection loop, an ultraviolet-visible spectrophotometric detector Sapphire 800 (Ecom, Czech Republic), an amperometric detector ADLC 2 (Laboratorni pristroje Praha, Czech Republic) (with the detectors connected in series), a LiChroCART 125 × 4 millimeters, Purospher RP-18 (5 micrometers) column, and a pre-column RP-18 (Merck, Germany). The system was controlled via Clarity 2.3 software (DataApex, Czech Republic) working under Windows 98 (Microsoft).

The three-electrode wall-jet system (Figure 1) was used for electrochemical detection with a platinum wire electrode (Monokrystaly Turnov, Czech Republic) as the auxiliary electrode, a Ag/AgCl reference electrode (type RAE 113, 3 moles per liter KCl, Monokrystaly Turnov, Czech Republic), and a BDD film electrode (3 millimeters diameter, Windsor Scientific, UK) as the working electrode. The working BDD film electrode was adjusted against the capillary outlet (18 micrometers diameter) at a controlled distance of 1 millimeter.

The BDD film electrode was activated once a day prior to measurement by cycling the potential in vigorously stirred aqueous 1 mole per liter HNO_3 between −2.5 and +2.5 volts vs. Ag/AgCl until a stable signal was detected (five to ten cycles at the scan rate 0.1 volt per second). The performance of the electrode was regularly verified by measuring cyclic voltammograms of 1×10^{-4} mole per liter potassium hexacyanoferrate in 1 mole per liter KCl. Voltammetric measurements were carried out using Eco-Tribo Polarograph with software PolarPro version 5.1 (both Polaro-Sensors, Prague, Czech Republic).

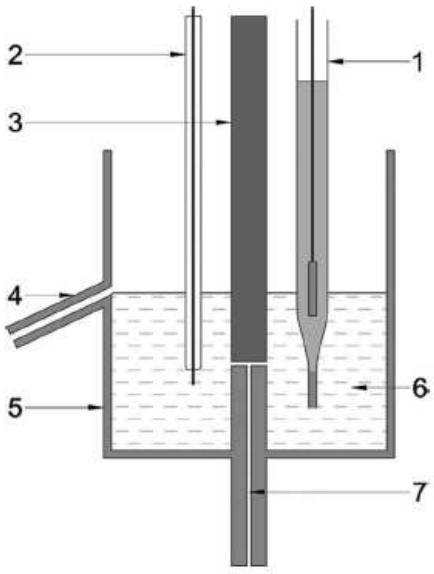

Figure 1. Schematic of the amperometric wall-jet detector.: (1) Ag/AgCl reference electrode; (2) platinum wire electrode; (3) boron-doped diamond film working electrode; (4) outlet–overflow; (5) overflow whole-glass vessel; (6) mobile phase; and (7) inlet Teflon tubing.

Procedures

The calibration curves were measured in triplicate and evaluated by peak height using linear regression. The repeatability of the determination was confirmed by ten consecutive measurements; replicate measurements were carried out for the lowest concentration of the linear dynamic range and for 1×10^{-4} mole per liter of the analytes. The limits of detection were calculated as the concentration of the analyte that gave a signal three times higher than the background noise.

For the direct determination of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol in drinking and river water, standard samples were prepared in deionized water.

Results and discussion

Reductive detection mode: optimization of separation and detection conditions

The separation and detection conditions for HPLC-ED determination using electrochemical reduction and oxidation were optimized. As the voltammetric behavior of nitrophenols using the BDD film electrode was investigated in our previous study (Musilova, Barek, and Peckova 2011) for reductive determination, the highest current response of nitrophenols was obtained from pH 4.0 to 6.0, acetate buffer was chosen as the aqueous part of mobile phase. Optimization of conditions for the separation of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol included optimization of flow rate of the mobile phase (Figure 2), the pH of acetate buffer (Figure 3), and the concentration of methanol in the mobile phase (Figure 4). The detection potential was −1.2 volts where the hydrodynamic voltammograms of the nitrophenols formed a plateau.

The reduction was problematic due to possible interference of 2,4-dinitrophenol and/or 4-nitrophenol with oxygen. While oxygen dissolved in the mobile phases caused higher and less

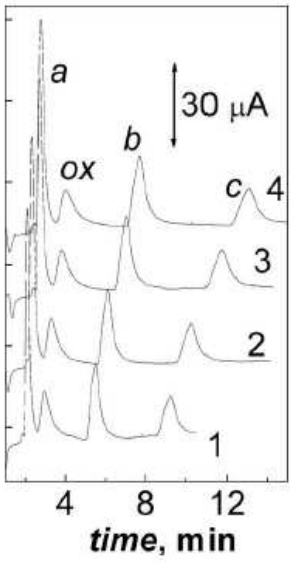

Figure 2. Chromatograms of nitrophenols: (a) 2,4-dinitrophenol; (b) 4-nitrophenol; (c) 2-nitrophenol; and (ox) interfering oxygen as a function of flow rate (milliliter per minute): (1) 1, (2) 0.9, (3) 0.8, and (4) 0.7 in 0.05 mole per liter acetate buffer pH 4.75 – methanol (60:40; *v/v*) mobile phase; detection potential −1.2 volts, injected volume 20 microliters.

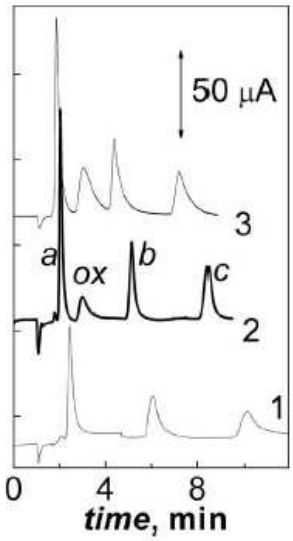

Figure 3. Chromatograms of nitrophenols: (a) 2,4-dinitrophenol; (b) 4-nitrophenol; (c) 2-nitrophenol; and (ox) interfering oxygen as a function of pH in 0.05 mole per liter acetate buffer: (1) 4.50, (2) 4.70, and (3) 4.75. Flow rate: 1 milliliter per minute, acetate buffer – methanol (60:40; *v/v*); detection potential −1.2 volts, injected volume 20 microliters.

stable background current, oxygen in aerated injected samples provided wide and relatively high peak characterized by capacity factors of 1.71 to 2.12 depending on the pH of the aqueous part mobile phase. Procedures for the elimination of oxygen included ten minutes sonication and bubbling of the mobile phase by nitrogen before filling it to the linear high-pressure pump, maintaining the wall-jet overflow vessel under nitrogen atmosphere, and deaeration of samples for five minutes by nitrogen prior to injection. Nevertheless, it was not possible to remove all oxygen, as shown in Figures 2, 3, and 4 because of residual oxygen in the samples where it penetrates during the manipulation prior to the manual injection into the HPLC system. Attempts

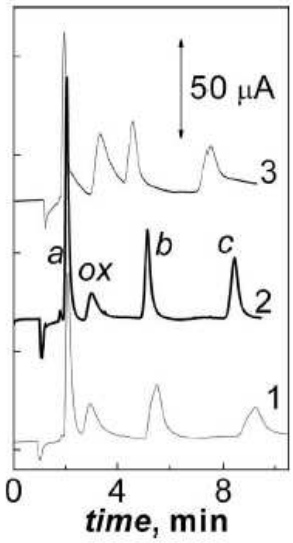

Figure 4. Chromatograms of nitrophenols: (a) 2,4-dinitrophenol; (b) 4-nitrophenol; (c) 2-nitrophenol; and (ox) interfering oxygen as a function of the ratio of 0.05 mole per minute acetate buffer pH 4.7 – methanol (*v/v*): (1) 60:40, (2) 58:42, and (3) 55:45. Flow rate: 1 milliliter per minute; detection potential −1.2 volts, injected volume 20 microliters.

to use automatic injection failed due to low reproducibility of the oxygen signal, which was substantially higher than using manual injection and thus resulted in unacceptable interference with 2,4-dinitrophenol. The problems were caused by the autosampler, where the injection procedure requires washing steps and the injected zone of analyte was separated by microliter volumes of air. Thus, it was impossible to ensure complete or at least reproducible oxygen removal. Manual injection was preferable as confirmed in our previous studies on HPLC-ED determinations for reducible nitro-group containing aromatic compounds (Danhel et al. 2009; Jiranek et al. 2009; Yosypchuk, Karasek, et al. 2012). The optimum separation can be recognized in Figure 4, chromatogram 2 and was achieved in 0.05 mole per liter acetate buffer pH 4.7 – methanol (58:42, *v/v*) mobile phase at a flow rate of 1 milliliter per minute. The capacity factors of 2,4-dinitrophenol, 4-nitrophenol, and 2-nitrophenol in this system were 0.88, 4.29, and 7.79, respectively, and the total separation time was ten minutes.

Oxidative detection mode: optimization of separation and detection conditions

For electrochemical oxidation, the highest response current of nitrophenols was obtained at pH 10.0 – 11.0 in batch voltammetric studies (Musilova, Barek, and Peckova 2011). However, basic media are not compatible with silica-based columns and the optimization of pH of phosphate buffer revealed that the highest current response of nitrophenols was obtained at pH 6.75 (Figure 5). At higher pH values, baseline drift was observed and at lower pH undesirable prolongation of separation was observed. The detection of the firstly eluting 2,4-dinitrophenol exhibited lower peak currents than 2-nitrophenol and 4-nitrophenol. It was greatly influenced by the concentration of methanol in the mobile phase, as shown in Figure 6. Phosphate buffer (0.05 mole per liter at pH 6.75 – methanol, 65:35, *v/v*) as the mobile phase was deemed optimum at a potential of +1.3 volts, where the signals were at a plateau, (Figure 5, curve 2, bold line style). The capacity factors

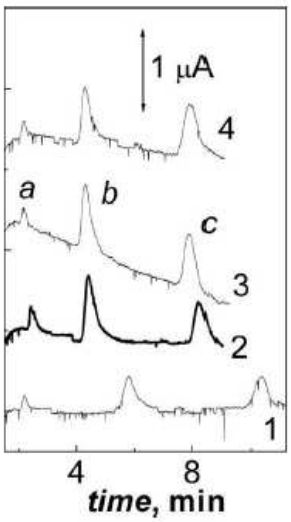

Figure 5. Chromatograms of nitrophenols: (a) 2,4-dinitrophenol; (b) 4-nitrophenol; and (c) 2-nitrophenol as a function of pH of 0.05 mole per liter phosphate buffer: (1) 6.50, (2) 6.75, (3) 7.0, and (4) 7.25. Phosphate buffer – methanol (60:40; *v/v*); detection potential +1.3 volts, injected sample volume 20 microliters, flow rate: 1 milliliter per minute.

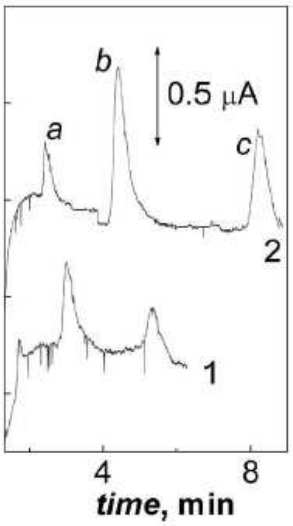

Figure 6. Chromatograms of nitrophenols: (a) 2,4-dinitrophenol; (b) 4-nitrophenol; and (c) 2-nitrophenol as a function of the ratio of 0.05 mole per liter phosphate buffer at pH 6.75. Methanol (*v/v*): (1) 60:40 and (2) 65:35; detection potential +1.3 volts, injected volume 20 microliters, flow rate: 1 milliliter per minute.

of 2,4-dinitrophenol, 4-nitrophenol, and 2-nitrophenol were 0.89, 2.42, and 5.37, respectively, and the total separation time was ten minutes.

Determination of nitrophenols in standard water samples

The optimized chromatographic conditions for cathodic and anodic modes were successfully applied for the direct determination of 2-nitrophenol, 4-nitrophenol, and

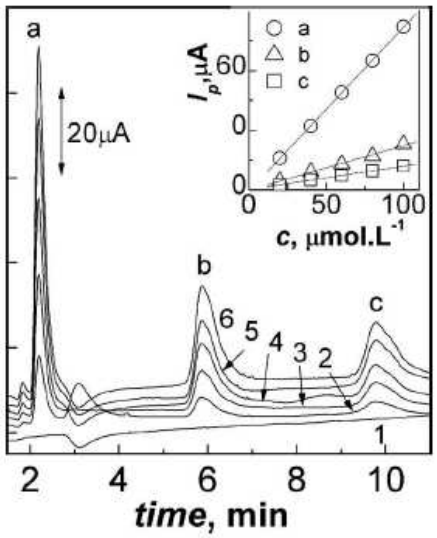

Figure 7. Chromatograms of 2,4-dinitrophenol (a); 4-nitrophenol (b); and 2-nitrophenol (c) using reductive detection at the BDD film electrode. Concentration in drinking water (micromole per liter): (1) 0, (2) 20, (3) 40, (4) 60, (5) 80, and (6) 100. Mobile phase 0.05 mole per liter acetate buffer pH 4.7 – methanol (58:42; *v/v*), detection potential −1.2 volts, flow rate 1 milliliter per minute, injected volume 20 microliters. Inset: calibration plots.

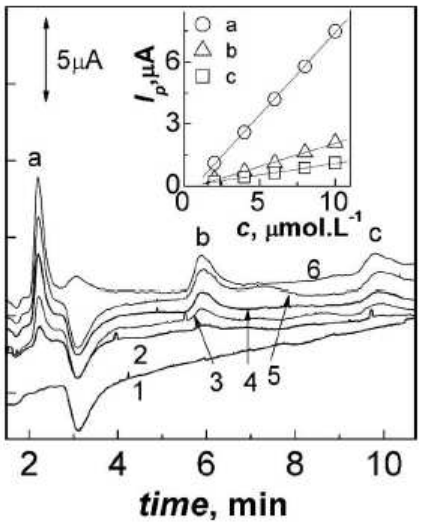

Figure 8. Chromatograms of (a) 2,4-dinitrophenol; (b) 4-nitrophenol; and (c) 2-nitrophenol using reductive detection at the BDD film electrode. Concentration in drinking water (micromole per liter): (1) 0, (2) 2, (3) 4, (4) 6, (5) 8, and (6) 10. Mobile phase 0.05 mole per liter acetate buffer pH 4.7 – methanol (58:42; *v/v*), detection potential −1.2 volts, flow rate 1 milliliter per minute, injected volume 20 microliters. Inset: calibration plots.

2,4-dinitrophenol in model samples of drinking and river water. After filtration through a glass fiber filter, the sample was introduced into the HPLC column protected by a precolumn. Figures 7 and 8 are examples of chromatograms of the nitrophenols for drinking water using the reductive mode. Figures 9 and 10 are examples on chromatograms of the nitrophenols for river water samples using the oxidative mode. Tables 2 and 3 show

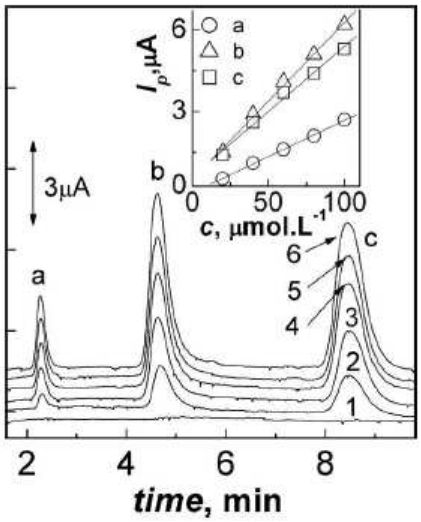

Figure 9. Chromatograms of (a) 2,4-dinitrophenol; (b) 4-nitrophenol; and (c) 2-nitrophenol using oxidative detection at the BDD film electrode. Concentration in river water (micromole per liter) (1) 0, (2) 20, (3) 40, (4) 60, (5) 80, and (6) 100. Mobile phase 0.05 mole per liter phosphate buffer pH 6.75 – methanol (65:35; *v/v*), detection potential +1.3 volts, flow rate 1 milliliter per minute, injected volume 20 microliters. Inset: calibration plots.

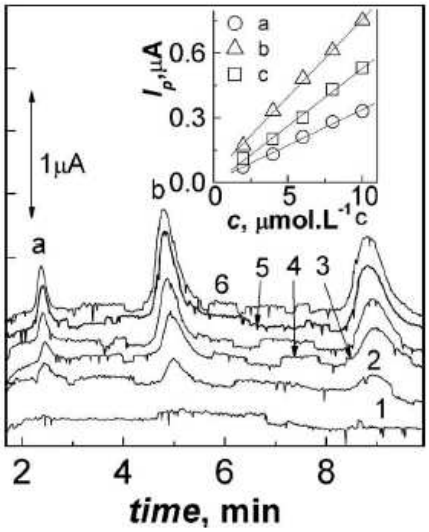

Figure 10. Chromatograms of (a) 2,4-dinitrophenol; (b) 4-nitrophenol; and (c) 2-nitrophenol using oxidative detection at the BDD film electrode. Concentration in river water (micromole per liter) (1) 0, (2) 2, (3) 4, (4) 6, (5) 8, and (6) 10. Mobile phase 0.05 mole per liter phosphate buffer pH 6.75 – methanol (65:35; *v/v*), detection potential +1.3 volts, flow rate 1 milliliter per minute, injected volume 20 microliters. Inset: calibration plots.

that the sensitivity of the direct determination in both drinking and river water is largely comparable with the experiments carried out with deionized water. Amperometric detection based on oxidation exhibits comparable sensitivity for deionized and drinking water, but lower for river water. Thus, the reductive mode is preferable for this matrix as it is less affected by the sample composition. Furthermore, the sensitivity using reductive determination was markedly higher for 2,4-dinitrophenol than for the other nitrophenols because of the presence of two nitro groups.

The limits of detection in the micromolar concentration range are comparable for both detection schemes. The repeatabilities of the detector response, summarized in Tables 2 and 3, were satisfactory: At micromolar concentrations close to the limits of detection,

Table 2. Analytical figures of merit for HPLC-ED determination of nitrophenols at the BDD film electrode using reductive detection mode evaluated by peaks height.

Analyte	Matrix (water)	Linear dynamic range [micromole per liter]	Relative standard deviation [%][a]	Relative standard deviation [%][b]	Slope [microampere liter per micromole]	Intercept [microampere]	R	Limit of detection [micromole per liter]
2-nitrophenol	Deionized	2–80	8.6	5.6	0.290	−0.30	0.9984	1.2
	Drinking	2–100	9.5	4.9	0.119	−0.01	0.9990	1.5
	River	4–100	8.6	1.9	0.133	−0.16	0.9989	1.8
4-nitrophenol	Deionized	2–100	5.6	6.0	0.447	−0.46	0.9991	0.8
	Drinking	1–100	9.6	6.0	0.225	−0.13	0.9990	1.3
	River	1–100	9.5	2.1	0.222	0.00	0.9989	1.3
2,4-dinitrophenol	Deionized	2–60	7.0	9.5	1.094	−1.01	0.9987	0.7
	Drinking	1–100	8.8	4.0	0.823	−0.64	0.9999	0.7
	River	1–100	9.2	3.0	0.854	−0.47	0.9990	0.7

Note: Mobile phase 0.05 mole per liter acetate buffer pH 4.7 – methanol (58:42; *v/v*), detection potential −1.2 volts, flow rate 1 milliliter per minute, injected volume 20 microliters.
[a]Replicate measurements ($n = 10$) for the lowest concentration on the linear dynamic range.
[b]Replicate measurements ($n = 10$) for 1×10^{-4} mole per liter of each analyte.

Table 3. Analytical figures of merit for the HPLC-ED determination of nitrophenols at the BDD film electrode using oxidative detection mode evaluated from by peak height.

Analyte	Matrix (water)	Linear dynamic range [micromole per liter]	Relative standard deviation [%][a]	Relative standard deviation [%][b]	Slope [microampere liter per micromole]	Intercept [microampere]	R	Limit of detection [micromole per liter]
2-nitrophenol	Deionized	6–80	8.6	2.6	0.0857	−0.16	0.9916	1.0
	Drinking	4–100	6.6	3.0	0.0827	−0.19	0.9982	2.9
	River	4–100	7.5	5.0	0.0547	0.10	0.9892	3.5
4-nitrophenol	Deionized	2–80	2.8	2.8	0.0889	0.03	0.9983	1.5
	Drinking	2–100	4.4	3.0	0.0818	0.04	0.9952	2.5
	River	2–100	8.0	5.0	0.0624	0.15	0.9964	2.4
2,4-dinitrophenol	Deionized	4–100	9.1	1.6	0.0426	−0.06	0.9992	0.6
	Drinking	2–100	8.9	1.0	0.0385	0.00	0.9990	1.5
	River	4–100	6.1	2.2	0.0260	0.04	0.9994	1.2

Note: Mobile phase 0.05 mole per liter phosphate buffer pH 6.75 – methanol (65:35; *v/v*), detection potential +1.3 volts, flow rate 1 milliliter per minute, injected volume 20 microliters.
[a]Replicate measurements ($n = 10$) for the lowest concentration on the linear dynamic range.
[b]Replicate measurements ($n = 10$) for 1×10^{-4} mole per liter of each analyte.

the relative standard deviation values (RSD) of peak height were between 6.0 and 10.0 %. For high concentrations of nitrophenols (1×10^{-4} mole per liter of each analyte), the relative standard deviations were largely less than 3.0 % for the oxidative and less than 6.0 % for the reductive mode. In the latter case, the higher values may be caused by peak height fluctuations from oxygen influencing the background.

Conclusions

The use of BDD film electrodes for electrochemical detection in HPLC using a wall-jet arrangement was verified for the determination of 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol by reduction and oxidation. Different separation conditions were employed; nevertheless in both cases baseline separation of nitrophenols was achieved in less than ten minutes. Relatively low limits of detection in the micromolar concentration range were achieved for the analytes. Other electroanalytical methods based on connection of liquid flow techniques with amperometric detection offer similar detection limits. The robustness of the method was documented by the relatively low relative standard deviations at micromolar concentrations. Problems were observed in the reductive detection mode due to the presence of oxygen in the system. Manual injection was preferable and oxygen did not interfere with the nitrophenols whose peaks are baseline separated, well-developed, and sharp. The applicability of the developed methods was demonstrated by the analysis of drinking and river water samples by their direct injection with the HPLC-ED. Comparable sensitivities and limits of detection were achieved for both modes. Nevertheless, reductive determination is recommendable as it more efficiently eliminates matrix effects in river water. Thus, it can be concluded that BDD film electrode employed as an amperometric sensor in wall-jet detector exhibited good performance with stable background current and sensitive, reproducible, and stable responses for the nitrophenols using reductive and oxidative detection. The method allows the rapid, reliable, sensitive, and relatively inexpensive determination of nitrophenols. Our further research is focused on interference studies as well as the determination of nitrophenols in more complex matrices (wastewater, residues of nitrophenols in soils). For this purpose, preliminary

preconcentration of studied analytes using solid phase or liquid-liquid extraction is recommendable to increase the sensitivity and selectivity of the methods.

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12. Appendix VI

Confirmation of Participation

1. **Musilova, J.**; Barek, J.; Peckova, K., The use of boron-doped diamond film electrodes for detection of organic compounds (Použití diamantových filmových elektrod dopovaných borem pro stanovení organických látek). *Chemicke Listy* **2009,** 103, (6), 469-478.

   Impact Factor (2017): **0.26**
   Percentage of participation of Ing. J. Karaová (Musilová) ~ **75 %**.

2. Peckova, K.; **Musilova, J.**; Barek, J., Boron-doped diamond film electrodes – New tool for voltammetric determination of organic substances. *Critical Reviews in Analytical Chemistry* **2009,** 39, (3), 148-172.

   Impact Factor (2017): **3.231**
   Percentage of participation of Ing. J. Karaová (Musilová) ~ **10 %**.

3. **Musilova, J.**; Barek, J.; Drasar, P.; Peckova, K., Differential pulse voltammetry of selected nitrophenols on boron-doped diamond film electrode. In *Sensing in Electroanalysis*, Vytřas, K.; Kalcher, K.; Švancara, I., Eds.University of Pardubice: Pardubice, 2009; Vol. 4, pp 135-142.

   Percentage of participation of Ing. J. Karaová (Musilová) ~ **75 %**.

4. **Musilova, J.**; Barek, J.; Peckova, K., Determination of nitrophenols in drinking and river water by differential pulse voltammetry at boron-doped diamond film electrode. *Electroanalysis* **2011,** 23, (5), 1236-1244.

   Impact Factor (2017): **2.851**
   Percentage of participation of Ing. J. Karaová (Musilová) ~ **75 %**.

5. **Karaova, J.**; Schwarzova-Peckova, K.; Barek, J., The Use of Boron-Doped Diamond Film Electrode for the Determination of Selected Nitrophenols by HPLC with Amperometric Detection. *Analytical Letters* **2016**, 49, (1), 66-79.

   Impact Factor (2017): **1.206**
   Percentage of participation of Ing. J. Karaová (Musilová) ~ **75 %**.

I declare that the percentage of participation of Ing. Jana Karaová at the above given papers corresponds to above given numbers.

Prague, 4. 10. 2018 Prof. RNDr. Jiří Barek, CSc.

13. Appendix VII

List of publications, oral and poster presentations

Journal articles

1. **Musilova, J.**; Barek, J.; Peckova, K., The use of boron-doped diamond film electrodes for detection of organic compounds (Použití diamantových filmových elektrod dopovaných borem pro stanovení organických látek). *Chemicke Listy* **2009,** 103, (6), 469-478.

2. Peckova, K.; **Musilova, J.**; Barek, J., Boron-doped diamond film electrodes – New tool for voltammetric determination of organic substances. *Critical Reviews in Analytical Chemistry* **2009,** 39, (3), 148-172.

3. **Musilova, J.**; Barek, J.; Drasar, P.; Peckova, K., Differential pulse voltammetry of selected nitrophenols on boron-doped diamond film electrode. In *Sensing in Electroanalysis*, Vytřas, K.; Kalcher, K.; Švancara, I., Eds.University of Pardubice: Pardubice, 2009; Vol. 4, pp 135-142.

4. **Musilova, J.**; Barek, J.; Peckova, K., Determination of nitrophenols in drinking and river water by differential pulse voltammetry at boron-doped diamond film electrode. *Electroanalysis* **2011,** 23, (5), 1236-1244.

5. Vyskocil, V.; Danhel, A.; Fischer, J.; Novotny, V.; Deylova, D.; **Musilova-Karaova, J.**; Maixnerova, L.; Peckova, K.; Barek, J., The Beauty and Usefulness of Novel Electrode Materials. *Chem. Listy* **2010**, *104*, 1181-1195.

6. **Karaova, J.**; Schwarzova-Peckova, K.; Barek, J., The Use of Boron-Doped Diamond Film Electrode for the Determination of Selected Nitrophenols by HPLC with Amperometric Detection. *Analytical Letters* **2016**, 49, (1), 66-79.

Chapters in book

1. Barek J., Daňhel A., Fischer J., Jiránek I., **Musilová J.**, Pecková K., Zima J.: Voltammetric Determination of Ecotoxic Compounds Using Non-traditional Electrode Materials. Sensing in Electroanalysis (Vytřas K., Kalcher K., eds.), Vol. 2. University of Pardubice (ISBN 978-80-7194-954-1), Pardubice 2007, p. 121-129.

2. Pecková K., **Musilová J.**, Barek J., Zima J.: Voltammetric and Amperometric Determination of Organic Pollutants in Drinking Watter Using Boron Doped Diamond Film Electrodes, v knize: Progress on Drinking Water Research (Lefebvre H. M., Roux M. M., ed.), kap. 3. Nova Science Publishers, New York 2008 (ISBN 978-1-60456-748-9).

3. **Musilová J.**, Barek J., Drašar P., Pecková K.: Differential Pulse Voltammetry of Selected Nitrophenols on Boron-Doped Diamond Film Electrode. Sensing in Electroanalysis (Vytřas K., Kalcher K., eds.), Vol. 4. University of Pardubice (ISBN 978-80-7395-212-9), Pardubice 2009, p. 135-142.

Oral presentations

1. **Musilová J.**, Barek J., Pecková K.: Use of Boron-Doped Diamond Electrode in Voltammetry of Biologically Active Organic Compounds, Modern Analytical Chemistry – 3rd International Student Conference (Červený V., ed.). Book of Proceedings. Czech Chemical Society (ISBN 80-86238-96-2), Prague 2007, p. 126-131.

2. **Musilová J.**, Barek J., Pecková K, Fischer J.: Voltametrické stanovení 2-nitrofenolu pomocí borem dopované diamantové elektrody, Moderní elektrochemické metody, Sborník přednášek z XXVII. mezinárodního odborného semináře (Barek J., Navrátil T., eds.). Česká společnost chemická (ISBN 978-80-86238-05-0), Praha 2007, str.101-104.

3. Barek J., Pecková K., Daňhel A., **Musilová J.**, Zima J.: Ampérometrická detekce submikromolárních koncentrací genotoxických a ekotoxických látek pomocí netradičních pracovních elektrod, 59. Zjazd chemikov – Vysoké Tatry, ChemZi, 1/3, 55 (2007), ISSN 1336-7242.

4. **Musilová J.**, Barek J., Drašar P., Pecková K.: Voltammetric Determination of 2-nitrophenol at Boron-Doped Diamond Film Electrode. Modern Analytical Chemistry. Proceeding from 4th International Student Conference (Opekar F. and Svobodová E., eds.). Sevcik Consultancy (ISBN 978-80-903103-2-2), Praha 2008, str. 147-152.

5. **Musilová J.**, Barek J., Drašar P., Pecková K.: Voltametrické stanovení 4-nitrofenolu pomocí bórem dopované diamantové elektrody. Moderní elektrochemické metody. Sborník přednášek z XXVIII. mezinárodního odborného semináře (Barek J., Navrátil T., eds.). Česká společnost chemická (ISBN 978-80-86238-39-5), Praha 2008, str. 69-72.

6. **Musilová J.**, Barek J., Drašar P., Pecková K.: Differential Pulse Voltammetry of 2-Nitrophenol, 4-Nitrophenol and 2,4-Dinitrophenol in Drinking and River Water Using Boron-Doped Diamond Film Electrode, Moderní elektrochemické metody, Sborník přednášek z XXIX. mezinárodní odborné konference (Barek J., Navrátil T., eds.). Česká společnost chemická (ISBN 978-80-254-3997-5), Ústí nad Labem 2009, str. 72-73.

7. **Musilova J.**, Barek J., Peckova K. Determination of Nitrophenols by Flow Injection Analysis with Amperometric Detection on Boron Doped Diamond Film Electrode, Modern electrochemical methods XXX (Navratil J., Barek J., eds), Lenka Srsenova-Best Servis (ISBN 978-80-254-6710-7). Ústí nad Labem 2010, p. 116-118.

Poster presentations

1. **Musilová J.**, Barek J., Pecková K., Vyskočil V., Fischer J.: Porovnání elektrochemických vlastností komerčně dodávaných borem dopovaných diamantových elektrod. 59. Zjazd chemikov – Tatranské Matliare, ChemZi, 1/3, 165 (2007), ISSN 1336-7242.

2. Vyskočil V., Deýlová D., **Musilová J.**, Pecková K., Barek J.: Polarografické a voltametrické stanovení submikromolárních množství genotoxického 5-nitrobenzimidazolu. 59. Zjazd chemikov – Tatranské Matliare, ChemZi, 1/3, 160 (2007), ISSN 1336-7242.

3. Fischer J., **Musilová J.**, Jiránek I., Daňhel A., Barek J.: Use of Modern Electrode Materials in Environmental Analysis. Electroanalytical Seminar Dresden-Prague. Book of abstracts. IFW Dresden, Germany, Freital 2007, p. 11-11.

4. **Musilová J.**, Barek J., Drašar P., Pecková K.: Voltammetric Determination of 2,4-Dinitrophenol at Boron-Doped Diamond Film Electrode. 12th International Conference on Electroanalysis, ESEAC 2008 – Prague, Czech Republic, Abstract Book (Chem. Listy, 102), str. 118 (2008). ISSN 0009-2770.

5. **Musilová J.**, Barek J., Drašar P., Pecková K.: Stanovení nitrofenolů pomocí HPLC s elektrochemickou detekcí na borem dopované diamantové filmové elektrodě. 60. jubilejní sjezd Asociací českých a slovenských chemických společností, Olomouc, Česká republika, Sborník (Chem. Listy, 102), str. 709 (2008). ISSN 0009-2770.

6. **Musilová J.**, Barek J., Pecková K.: Voltametrické stanovení nitrofenolů po jejich prekoncentraci extrakcí tuhou fází pomocí bórem dopované diamantové filmové elektrody. 61. Zjazd chemických společnosti – Tatranské Matliare, ChemZi, 5/9, str. 144 (2009), ISSN 1336-7242.

7. **Musilova J.**, Barek J., Peckova K. Voltametrické a amperometrické stanovení nitrofenolů pomocí borem dopované diamantové filmové elektrody. 62. sjezd chemických společností, Pardubice, Česká republika, Sborník (Chem. Listy, 104), str. 458 (2010). ISSN 0009-2770.