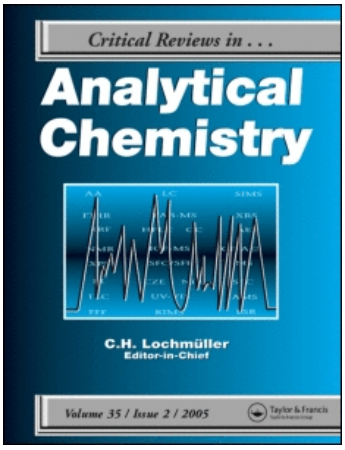

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Boron-Doped Diamond Film Electrodes—New Tool for Voltammetric Determination of Organic Substances

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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), ultranano- (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 **FIA/AD**, end column, buffer as for DPV	2–10[b,e] 2–10[b]	2.05, 1.22 0.41, 0.65	(120)
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[j])–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**[l], 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**[l], 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 [l]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**[l], 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)

(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.
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, 0.2–10	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[o]	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)

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[e,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 ($\Phi = 0.01\ \mu$m)	**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)

(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.
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**[I], 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)	**ChrA** 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**[l], 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[s]	Si(111), Cu implanted MPCVD BDD	**ChrA**, 0.2 M NaOH	1000–5000	not given	(144)
Glucose[s]	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	**SWV**, 1 M NaOH	500–10000	not given	(70)

(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.
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 **FIA/AD**, TL cell (GL Sciences)	10–100 0.05–10000	not given 0.0005	(78)
EDTA	Single crystal KDB-silicon substrate, HFCVD BDD, activation by cycling between +0.5 V to +1.7 V	**Amp**, acetate–ammonia buffer pH 3.9	10–500	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[r]	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)[t]	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[u] 1–8[v]	not given 35[u] 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-nitrosopyrrolidine, 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 oxidation product 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) (Bioanalytical 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.

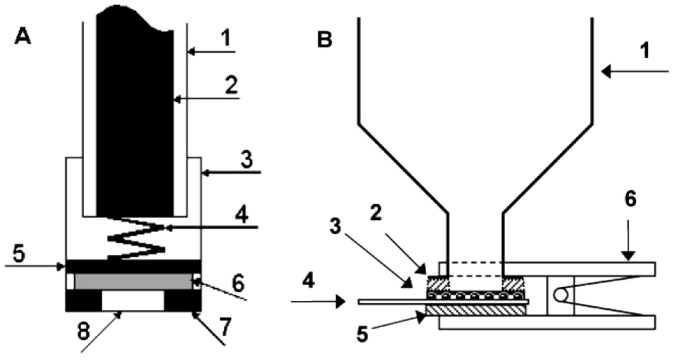

FIG. 1. The detailed scheme of BDDE constructed in our laboratory: A) disc electrode – 1) electrode body made of Teflon®, 2) stainless steel, 3) screw attachment, 4) small metal spring, 5) brassy sheet, 6) Si/BDDE, 7) Viton® gasket, 8) access for solution. B) Glass cell with clamped BDDE – 1) glass cell, 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.

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.

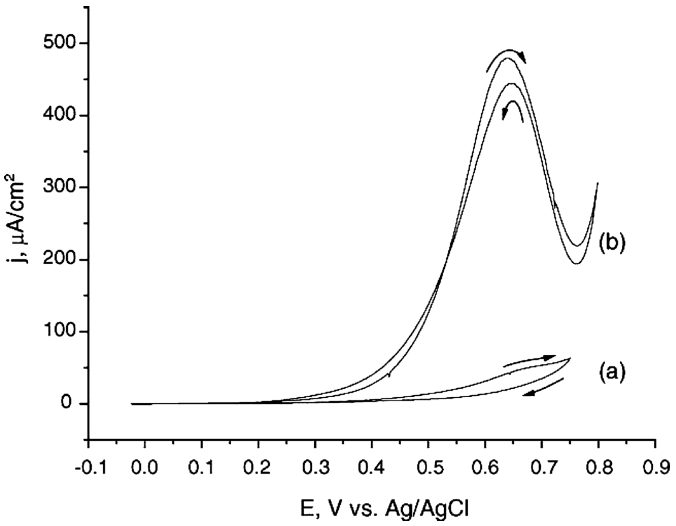

FIG. 2. CVs for 5.0 mmol/L glucose at (a) BDDE after severe anodic polarization, and (b) hydrogen flame annealed BDDE. Supporting electrolyte 1.0 mol/L NaOH, scan rate 20 mV/s. Reprinted with permission from (70) J. Lee and S. M. Park, *Analytica Chimica Acta* 545 (2005):27–32.

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,

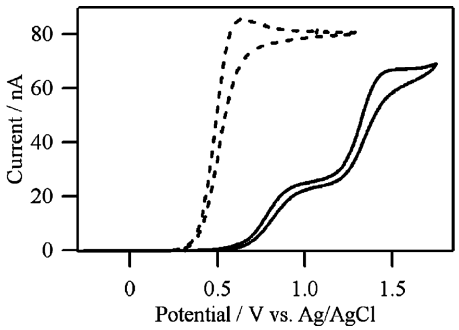

FIG. 3. CVs of a mixture of 0.1 mmol/L DA and 1 mmol/L AA at HBDD (dotted lines) and OBDD (full lines) with a scan rate of 50 mV/s. Reprinted with permission from (15) A. Suzuki, T. A. Ivandini, K. Yoshimi, A. Fujishima, G. Oyama, T. Nakazato, N. Hattori, S. Kitazawa, and Y. Einaga, *Analytical Chemistry*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

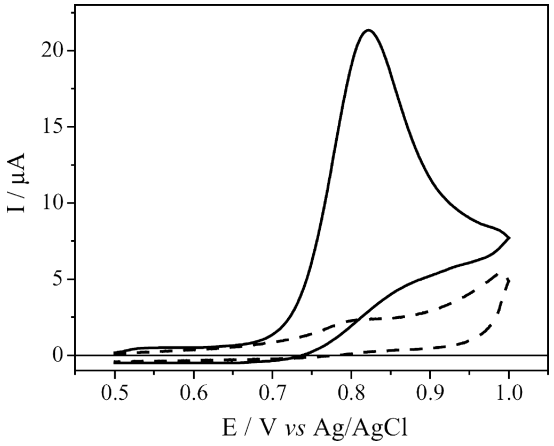

FIG. 4. CVs on BDDE for $5{\cdot}10^{-5}$ mol/L pentachlorophenol in 0.1 mol/L BR buffer, pH 5.5, after anodic pre-treatment at 3.0 V vs. Ag/AgCl (dotted lines) or cathodic pre-treatment at −3.0 V vs. Ag/AgCl (full lines). Scan rate 50 mV/s. Reprinted with permission from (135) H. B. Suffredini, V. A. 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

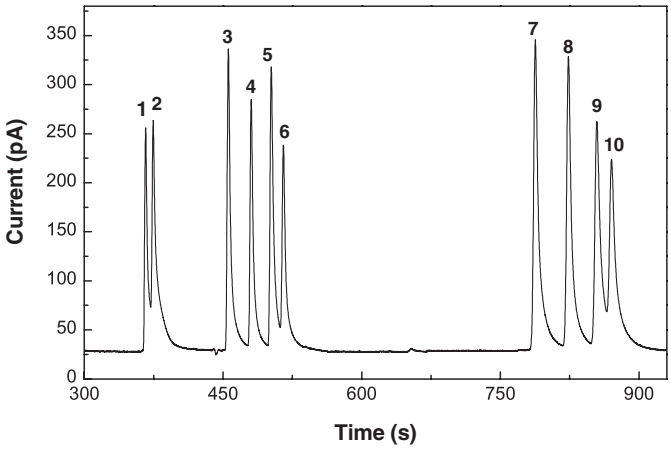

FIG. 5. Electropherogram of a standard solution containing 5 μmol/L MN (1), NMN (2), 10 μmol/L DA (3), E (4), NE (5), MOPEG (6), 30 μmol/L L-DOPA (7), 50 μmol/L DOPEG (8), VMA (9), HVA (10). Silica capillary 70 cm, 27 μm ID, run buffer 0.25 μmol/L boric acid/KOH at pH 8.80, separation voltage 24 kV, 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 sandwidched 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 ($d = 20 \pm 10$ 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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