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ORIGINAL PAPER

Factors influencing voltammetric reduction of 5-nitroquinoline at boron-doped diamond electrodes

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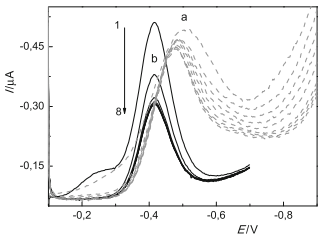
Abstract The voltammetric signal of 5-nitroquinoline with reducible nitro and quinoline moieties largely depends on the pH of the indifferent electrolyte, electrode pretreatment, activation between individual scans, and boron concentration of the BDD film electrode. Anodic pretreatment at +2.4 V for 5 min in 0.5 mol dm^{-3} H_2SO_4 and 20 s stirring between individual scans assured repeatable signals of nitro group in the whole pH range 2.0–12.0; in acetate buffer pH 5.0 limit of detection is 2×10^{-7} mol dm^{-3} for differential pulse voltammetry. The reduction of quinoline skeleton is visible in the pH range of 6.0–11.0. Presence of oxygen in the measured solutions led to slight increase of peak heights and acceptable increase of its relative standard deviation. BDD films with metallic type of conductivity deposited at B/C ratio 2000–8000 ppm exhibit faster electron transfer at lower potential for nitro group reduction than semiconductive films 500 and 1000 ppm.

Graphical abstract



Keywords Voltammetry · Boron-doped diamond electrode · Boron concentration · Reduction · Electrochemistry

Introduction

Boron doped diamond introduced for electroanalysis in 1992 [1] gained a deserved popularity especially for electrooxidation of organic compounds of biological, pharmaceutical, and environmental significance [2–5]. Its mechanical and electrochemical properties are among others significantly influenced by morphology of the BDD films, boron concentration, and electrode pretreatment, when high positive/negative current densities or potentials (Correctly $\geq \pm 2.0$ V) in the region of water decomposition reactions are applied for few seconds to minutes. As results of this anodic/cathodic pretreatment, oxygen-terminated (O-BDD) or hydrogen-terminated (H-BDD) surfaces are produced, very often with different capabilities of prevention of surface passivation, enhancement of the voltammetric signals, and ensuring of repeatable and reproducible response of particular analytes [6–9].

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Boron-doping level plays crucial role in basic electrochemical characteristics, e.g., electrical conductivity of the BDD film and kinetics of electron transfer [1, 7, 10]. The few studies concerned with influence of boron concentration on electroanalytical parameters for organic compounds [11, 12] including our reports on oxidation of benzophenone-3 [13] and 2-aminonaphthalene [14] report that semiconductive films exhibit more sluggish kinetics for surface-sensitive redox marker $[Fe(CN)_6]^{3-/4-}$ as well as decreased sensitivity towards mentioned analytes than metallic films. The predicted threshold for the semiconductive/metallic transition is at $\sim 2 \times 10^{20}$ boron atoms per cm^3 [15] (theoretical value), i.e. $\sim$1000–2000 ppm (experimental values) [14, 16, 17], which is the B/C ratio in the gaseous phase during the chemical vapour deposition of BDD films.

It can be traced in reviews [2–4] and monographs [5, 9] devoted to electroanalysis of organic compounds by means of BDD-based electrodes that lower attention has been paid to their utilization for electrochemical reductions despite the favorable characteristic for such applications: relatively wide potential window in the cathodic region and low sensitivity towards oxygen evolution [18, 19]. Among organic reducible compounds, substances containing nitro group at the aromatic skeleton represent an extensive group, where pharmaceuticals, agrochemicals, and environmental pollutants are present. Most of them are toxic, probably due to a reactive nitro-radical in their metabolic pathway [20, 21].

The few determinations based on nitro group reduction at BDD-based materials were suggested for some nitrophenols [22–26] and aminonitrophenols [27], and nitro-group containing pesticides (methylparathion [28]), drugs (chloramphenicol [29], nitrofurazone [30, 31], selected benzazepines [32]), and derivatives of polycyclic aromatic hydrocarbons (1-nitropyrene [33], 3-nitrofluoranthene [35]).The reduction of nitro group has been investigated among the first electrochemical processes of organic compounds at dropping mercury and other mercury electrodes [20, 35, 36], later on it was extended on solid electrodes including carbon and amalgam based electrodes [20, 37]. In aqueous acidic and neutral media, independently on the electrode material, the first step of the reduction relies on the four-electron reduction of nitro group to the hydroxylamino group [Eq. (1)]. In acidic media, further two-electron reduction to amine may occur (Eq. 2) [35, 36, 40].

$$ArNO_2 + 4e^- + 4H^+ \rightarrow ArNHOH + H_2O \quad (1)$$

$$ArNHOH + 2e^- + 2H^+ \rightarrow ArNH_2 + H_2O \quad (2)$$

At mercury-based electrodes and solid electrodes, in the alkaline or non-aqueous media the lack of protons may lead to a split of the original four-electron reduction described in Eq. (1) and two reductive signals corresponding to Eqs. (3) and (4), also leading to hydroxylamine as the final product can be observed [36, 37, 40].

$$ArNO_2 + e^- \leftrightarrow ArNO_2^{\cdot -} \quad (3)$$

$$ArNO_2^{\cdot -} + 3e^- + 4H^+ \rightarrow ArNHOH + H_2O \quad (4)$$

Compared to the reduction of the nitro group, the reduction of the quinoline skeleton proceeds at more negative potentials, close to the onset of supporting electrolyte [38, 39]. Quinoline (Q) itself is polarographically reducible in two steps in alkaline media according to Eq. (5) and (6) yielding dihydroquinoline (QH_2) in the first step [Eq. (5)] and tetrahydroquinoline (QH_4) in the second one [Eq. (6)] [38, 41]:

$$Q + 2e^- + 2H^+ \rightarrow QH_2 \quad (5)$$

$$QH_2 + 2e^- + 2H^+ \rightarrow QH_4 \quad (6)$$

Also electrooxidation of the quinoline skeleton is relatively hardly achievable [42, 43] and thus there are not many studies devoted to utilization of these processes in voltammetry. Modification of electrode surface [42, 43] or presence of surfactant [39] was tested to afford results utilizable in electroanalysis.

The aim of this study is to extend the knowledge on the electro reduction of aromatic nitro group and quinoline skeleton at BDD electrodes. For this purpose, an environmental pollutant, formed as product of incomplete combustion of fossil fuels, 5-nitroquinoline was selected as model compound [38, 45]. It was previously studied in our laboratory at mercury, amalgam-based and carbon film electrodes, as obvious from the overview in Table 1 summarizing voltammetric methods used for determination of 5-nitroquinoline [38, 44, 45]. In this study, special attention has been paid to the influence of BDD electrode pretreatment, boron-doping level, and oxygen presence on voltammetric signal of 5-nitroquinoline to present the variety of specific factors influencing voltammetric analysis at BDD electrodes.

Results and discussion

Mechanism of reduction of 5-nitroquinoline

The mechanism of reduction of 5-nitroquinoline was studied using pH dependence in BR buffer of pH 2.0–12.0 using DC and DP voltammetry and further by cyclic voltammetric experiments. As relatively extended literature exists on the mechanism of reduction of nitro group at aromatic skeleton at liquid mercury and solid electrodes

Table 1 Overview of voltammetric methods for the determination of 5-nitroquinoline

Electrode	LOQ/μmol dm^{-3}	LDR/μmol dm^{-3}	Method	pH, medium	References
m-AgSAE	0.3	0.2–100	DPV	pH 9.0; 0.05 mol dm^{-3} borate buffer	[46]
	0.5	0.4–100	DCV		
Carbon film	0.5	–[a]	DPV	pH 11.0, BR buffer	[44]
DME	0.9	–[a]	DCTP	pH 3.0, BR buffer	[45]
	0.09	–[a]	DPP	pH 3.0, BR buffer	
	0.01	–[a]	DPP	0.2 mol dm^{-3} NaOH	
HMDE	0.02	–[a]	DPV	0.2 mol dm^{-3} NaOH	

DCTP direct current tast polarography, *DCV* direct current voltammetry, *DPV/P* differential pulse voltammetry/polarography, *DME* dropping mercury electrode, *HMDE* hanging mercury drop electrode, *m-AgSAE* mercury meniscus-modified silver solid amalgam electrode, *LDR* linear dynamic range, *LOQ* limit of quantification

[a] Not given

[20, 35–37], analogies and differences could be found in the behavior of the studied compound.

DP and DC voltammetry–influence of pH

Figure 1a, b represents pH-dependence of DC and DP voltammograms of 5-nitroquinoline. Relatively well-shaped main reduction signal can be traced in the whole pH range tested (2.0–12.0), with the slope of the peak potential E_p vs. pH dependence of −83.52 mV between pH 2.0–5.0. It corresponds to the nitro group reduction to hydroxylamine according to Eq. (1). This signal is accompanied by indistinctive signals at more negative potential at pH values 6.0–12.0, as obvious from peak potential E_p vs. pH dependence at Fig. 2a. These are of different origins:

1. For the most alkaline media 11.0 and 12.0 the splitting of the nitro-group reduction into two steps according to Eqs. (3) and (4) is foreseen, the reduction peaks of both processes lay within a narrow potential region of 250 mV. Thus, the first, pH-independent step corresponds to a fast one electron reduction of the nitro group to a nitro radical [Eq. (3)] and the second step

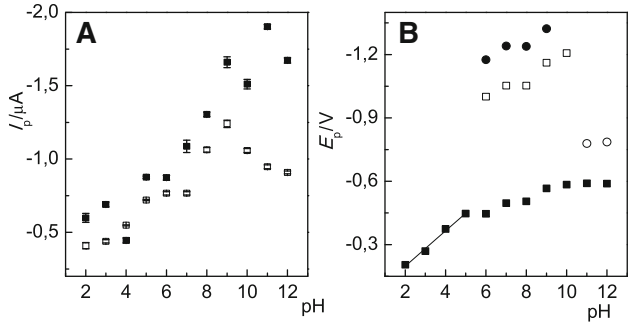

Fig. 2 Dependence of the **a** peak currents (I_p) of the first cathodic peak in the presence (*closed square*) and absence (*open square*) of oxygen and dependence of the **b** peak potentials (E_p) on pH. Measured for 5-nitroquinoline ($c = 1\times10^{-4}$ mol dm^{-3}) using DP voltammetry. The *error bars* are constructed as standard deviations ($n = 5$)

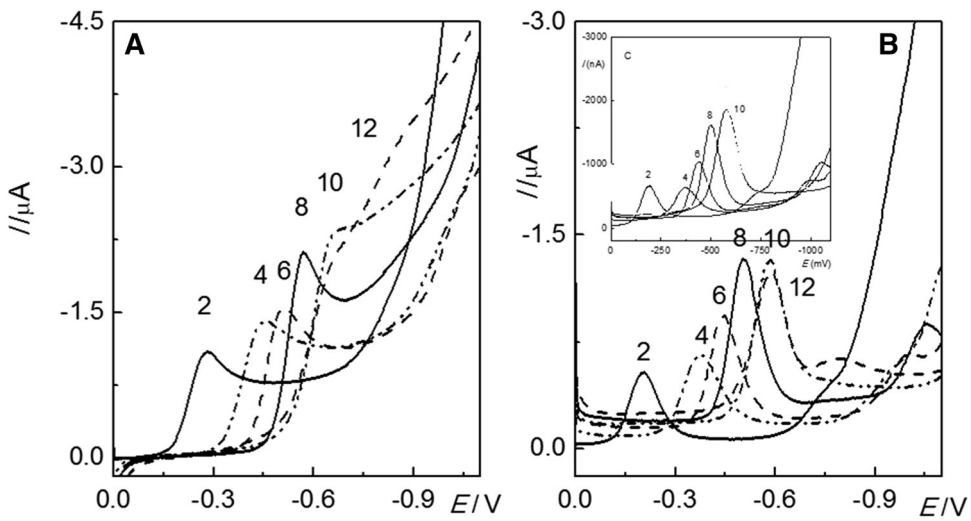

Fig. 1 Selected **a** DC, **b** DP voltammograms of 5-nitroquinoline ($c = 1 \times 10^{-4}$ mol dm^{-3}) at BDD electrode ($B/C = 4000$ ppm) in BR buffer pH 2.0–12.0; the pH values are noted by the curves. The *inset* (**c**) in (**b**) shows DP voltammograms in the presence of oxygen. Scan rate for DPV is 20 mV s^{-1} and for DCV is 50 mV s^{-1}

corresponds to the three electron reduction of the nitro radical to the hydroxylamine [Eq. (4)]. This type of splitting of the main reduction peak was described for example for reduction of 5-nitroquinoline and 6-nitroquinoline [38] and nitronaphtalenes [37] at amalgam electrodes. Generally it occurs when the transfer of the second electron in the overall four-electron reduction [Eq. (1)] is inhibited, as e.g., in non-aqueous media or surfactant containing media at mercury electrodes [20, 36] or at solid electrodes in alkaline media [37], including BDD electrode [30, 31], where the rate of electron transfer is diminished by the solid character of the electrode surface and simultaneously the lack of protons influences the reaction pathway. Clearly the surface of BDD electrodes has the same inhibiting effect on nitro group reduction of 5-nitroquinoline in alkaline media as other solid electrode materials. Nevertheless, this reduction splitting of aromatic nitro group cannot be assessed as general rule at BDD electrodes, because in previous reports on reduction of 3-nitrofluoranthene [34], formation of $ArNO_2^{\bullet -}$ was not reported and its stabilization is obviously connected to boron-doping level and other factors influencing electrochemical properties of BDD surface, and further content of organic cosolvent, and structure of the aromatic compound itself [30, 31].

2. In BR buffer pH 5.0–10.0 two pH-dependent signals at far negative potentials of ca −1000 to −1250 mV were observed. To confirm whether these signals can be assigned to the reduction of the quinoline skeleton, the reduction of quinoline has been investigated under the same conditions. An example of DP voltammogram of quinoline in BR buffer pH 9.0 is given in Fig. 3. It shows one reduction peak at the potential of −1183 mV while the curve of 5-nitroquinoline shows two steps reduction at the potentials of −1117 and −1255 mV, presumably corresponding to processes described in Eqs. (2) and (5): The reduction of the quinoline skeleton [Eq. (5)] is preceded by reduction of the hydroxylamino derivative to 5-aminoquinoline [Eq. (2)]. The latter reaction is enabled by stabilization of the product of dehydration of the hydroxylamine intermediate through resonance structures involving heterocyclic nitrogen. This pathway was found for several heterocyclic nitro derivatives [36, 40], nevertheless is not common for nitro derivatives of polycyclic aromatic hydrocarbons, which undergo reduction to the amino derivative only in acidic media [36]. The peak corresponding to reduction of the quinoline skeleton is characterized by dE_p/dpH value of 52.2 mV in pH range 6.0–10.0, which is close to the theoretical value of 59 mV for an electrochemical reaction with equal number of protons and electrons, in accordance with Eq. (5). At these pH values the quinoline skeleton is not protonized (pK_A of 5-nitroquinoline is 2.73) [46]. The reduction of quinoline skeleton does not appear in the range of pH 2.0–5.0 of BR buffer at BDD electrode probably due to shorter potential window in acidic media for BDD electrode.

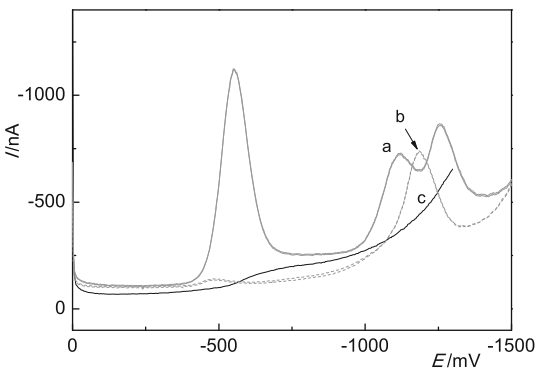

Fig. 3 DP voltammograms (scan rate 20 mV s^{-1}) of 5-nitroquinoline (**a**) and quinoline (**b**) (for both $c = 1 \times 10^{-4}$ mol dm^{-3}) in BR buffer medium pH 9.0 (**c**)

These two reduction peaks at the end of potential window appeared also in voltammograms of 5-nitroquinoline at meniscus modified silver solid amalgam electrode in pH range 7.0–12.0 [38].

Furthermore, the influence of oxygen presence on the peak height and repeatability of 5-nitroquinoline reduction was investigated in solutions open to air in all pH range tested. Obviously oxygen reduction is inhibited at BDD electrode and the potential of the first cathodic reduction peak is in the range from ca −450 mV to −750 mV, i.e. in the region of reduction of 5-nitroquinoline. As expected, the DP voltammograms (Fig. 1b) of oxygen-free solution exhibit of about 10–30 % lower current response in the presence of 5-nitroquinoline than these when oxygen is present (DP voltammograms at Fig. 1c, evaluation of peak heights at Fig. 2a). This effect is mostly pronounced in alkaline media, but importantly, the peak height repeatability is not affected and remains acceptable for all investigated media, mostly in the range from 0.7 to 3.3 % for DPV with oxygen, and from 0.8 to 4.5 % for DPV without oxygen. For DCV higher values with maximum of 7.1 % with oxygen and 6.5 % without oxygen were achieved (relative standard deviation evaluated from five measurements). These results are promising for determination of electrochemically reducible organic compounds by means of BDD-based sensors in the presence of oxygen. This could be very advantageous from the analytical point of view because oxygen removal from solutions might be problematic and its traces cause problems e.g. when using electrochemical detection at mercury-based electrochemical sensors in liquid flow techniques [38, 47, 48].

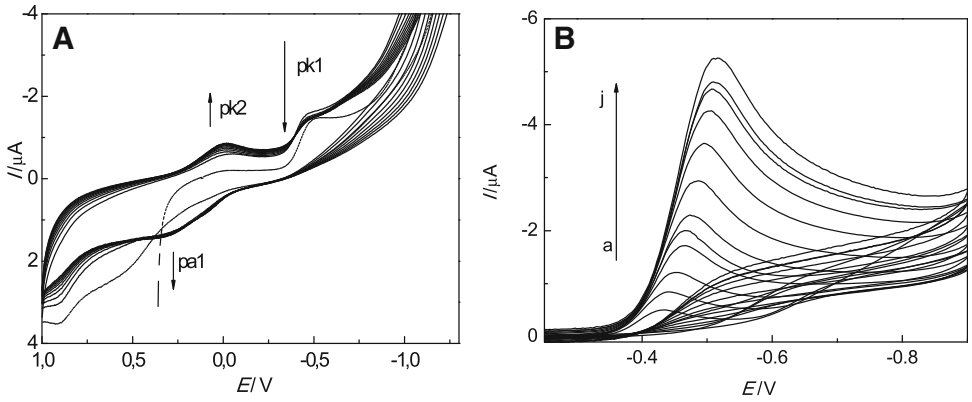

Fig. 4 Cyclic voltammograms of 5-nitroquinoline ($c = 1 \times 10^{-4}$ mol dm^{-3}) in 0.1 mol dm^{-3} acetate buffer pH 5.0: **a** ten consecutive cycles from +1.0 V to −1.3 V with the first cathodic scan starting at +0.36 V (*dashed line*), scan rate 100 mV s^{-1}, and **b** the first cycle for scan rates (mV s^{-1}): 5 (*a*), 10 (*b*), 20 (*c*), 40 (*d*), 80 (*e*), 160 (*f*), 320 (*g*), 640 (*h*), 1280 (*ch*), 2560 (*i*), 5120 (*j*)

Further measurements were performed in 0.1 mol dm^{-3} acetate buffer pH 5.0; in this media only the main reduction signal corresponding to Eq. (1) is present.

Cyclic voltammetry

Cyclic voltammograms in 0.1 mol dm^{-3} acetate buffer pH 5.0 exhibited features typical for electrochemical reduction of aromatic nitro group (Fig. 4a). It is the main irreversible cathodic peak p_{k1}, corresponding to nitro group reduction to hydroxylamine [Eq. (1)], followed by the pair of peaks p_{a1} and p_{k2} in the reversed anodic/second cathodic scan at the potentials of ca +300 and 0 mV, corresponding to quasireversible oxidation/reduction of the pair hydroxylamino/nitroso derivative [Eq. (7); p_{a1} and p_{k2} in Fig. 4a]. This suggestion is confirmed by the fact that the cathodic peak p_{k2} is absent in the first cathodic scan, similarly, the anodic peak p_{a1} is absent when starting the scan at 0 V in positive direction. The behavior is in agreement with literature [40].

$$\mathrm{ArNHOH} \leftrightarrow \mathrm{ArNO} + 2\mathrm{e}^- + 2\mathrm{H}^+ \quad (7)$$

Further cycling leads to decrease of p_{k1} and increase of p_{a1} and p_{k2} as result of surface passivation (p_{k1}) and formation of reaction products (p_{a1} and p_{k2}). The main reaction–reduction of nitro group to hydroxylamine [Eq. (1)] is controlled by diffusion as proved by linear course of the peak current I_p vs. scan rate $v^{1/2}$ dependence in the range from 10 to 80 mV s^{-1} characterized by the regression line: $I_p/\mathrm{nA} = -257.3v^{1/2}/(\mathrm{mV\ s^{-1}}) + 2.8$ ($R = 0.996$); corresponding voltammograms are depicted at Fig. 4b.

Pretreatment of BDD electrode and calibration dependences of 5-nitroquinoline

Optimal combination of electrode pretreatment and activation between individual scans was tested in 0.1 mol dm^{-3} acetate buffer pH 5.0 with BDD electrode

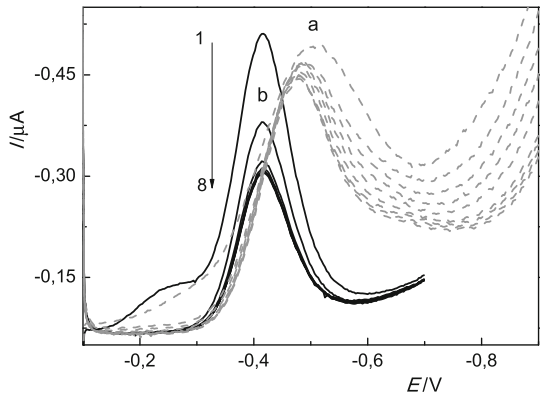

Fig. 5 Eight differential pulse voltammograms of 5-nitroquinoline ($c = 1 \times 10^{-4}$ mol dm^{-3}) in 0.1 mol dm^{-3} pH 5.0 acetate buffer using different pretreatment of the electrode in 0.5 mol dm^{-3} sulfuric acid with positive or negative potential: **a** anodic pretreatment (5 min, +2.4 V), **b** cathodic pretreatment (10 min, −2.4 V). The scan rate was 20 mV s^{-1}

(B/C 4000 ppm). Anodic pretreatment at the potential of +2.4 V for 5 min and cathodic pretreatment at the potential of −2.4 V for 10 min in 0.5 mol dm^{-3} sulfuric acid and three types of activation between individual scans directly in the measured solution were tested: anodic activation, cathodic activation, and stirring without application of potential. It was necessary because without any activation the signal height of 5-nitroquinoline is decreasing as obvious from Fig. 5: For eight consecutive scans, anodic pretreatment exhibits faster stabilization of electrode response and ca 100 mV more negative peak potential than the cathodic pretreatment with a fast decline in peak height for the first three scans. This decline is caused by instability of the H-terminated surface resulting from cathodic pretreatment; that surface is known to be relatively unstable not only in solutions, but also in air [49].

Thus, the activation between individual scans was also necessary. For all activation modes relative stability of electrode response was achieved, but as the application of cathodic or anodic potential had no explicitly positive

Table 2 Parameters of the calibration straight lines and limits of detection and quantification for the reductive determination of 5-nitroquinoline using DC and DP voltammetry with anodic ($E = +2.4$ V, $t = 5$ min) or cathodic ($E = -2.4$ V, $t = 10$ min) pretreated BDD electrode (B/C 4000 ppm)

BDD pretreatment	LDR/μmol dm^{-3}	R	Slope/nA dm^3 μmol^{-1}	Intercept/nA	RSD (%)[a]	LOQ/μmol dm^{-3}	LOD/μmol dm^{-3}
DPV							
Anodic	0.5–100	0.988	−6.02 ± 0.06	−4.1 ± 0.2	6.5	0.66	0.20
Cathodic	0.5–75	0.996	−4.59 ± 0.05	−10.4 ± 0.7	12	1.68	0.50
DCV							
Anodic	10–100	0.997	−9.73 ± 0.12	24.1 ± 6.4	10	8.9	2.7
Cathodic	7.5–75	0.998	−7.61 ± 0.14	−31.1 ± 1.1	13	15.7	4.7

Supporting electrolyte was 0.1 mol dm^{-3} acetate buffer pH 5.0, 20 s stirring between individual scans applied

LOQ limit of quantification, *LOD* limit of detection, *R* correlation coefficient

[a] Relative standard deviation (RSD) of ten times repeated measurement at the lowest concentration of LDR (linear dynamic range)

Table 3 Peak potentials E_p, peak heights I_p and their relative standard deviations (RSD) evaluated from DC and DP voltammograms of 5-nitroquinoline ($c = 1 \times 10^{-4}$ mol dm^{-3}) in 0.1 mol dm^{-3} acetate buffer pH 5.0. Measured by BDD electrodes with B/C ratio in the range of 500–8000 ppm

B/C ratio/ppm	DPV			DCV		
	E_p/mV	I_p/nA	RSD/%	E_p/mV	I_p/nA	RSD/%
500	−561	−579 ± 15	2.7	−797	−2502 ± 84	3.4
1000	−498	−255 ± 13	5.2	−536	−691 ± 53	7.2
2000	−388	−2065 ± 38	1.8	−443	−3616 ± 57	1.6
4000	−438	−1630 ± 40	2.5	−510	−3720 ± 52	1.4
8000	−442	−1589 ± 18	1.2	−519	−3581 ± 83	2.3

effect and RSD values of peak height were comparable with these when using stirring between individual scans, only stirring for 20 s was used to assure repeatable signals. For DC and DP voltammetry the RSD values of peak height were 6.5 and 0.5 % for cathodic pretreatment and 2.1 and 4.6 % for anodic pretreatment ($c = 1 \times 10^{-4}$ mol dm^{-3}, $n = 10$), respectively. For shorter times instability of electrode response was observed for all activation modes.

Parameters of the calibration straight lines for both types of pretreatment are given in Table 2. Better limits of detection in the 10^{-7} and 10^{-6} mol dm^{-3} concentration range for DPV and DCV was obtained using anodic pretreatment, which is given by lower values of peak height repeatability for the lowest measurable concentration and higher value of the slope, i.e., parameters used for calculation of detection limit. Anodic pretreatment compared to cathodic one should be also preferred with respect to the extent of the linear dynamic range.

Boron-doping level of BDD

Boron-doping level significantly affects the height of the peak and its potential, as summarized in Table 3 and shown in Fig. 6, where are depicted DC and DP voltammograms of 1×10^{-4} mol dm^{-3} solution of 5-nitroquinoline in 0.1 mol dm^{-3} acetate buffer pH 5.0. Obviously, the peak height for electrodes with metallic type of conductivity (2000, 4000, and 8000 ppm) is comparable and significantly higher than for semiconductive BDD electrodes (500 ppm and 1000 ppm). Simultaneously, their peak potential is shifted to more positive values confirming the easier reduction of nitro group using 2000–8000 ppm electrodes. Further, favorable repeatability of peak height with RSD values ≤2.5 % for this set of electrodes was achieved. Among them, the 2000 ppm electrode exhibits additional favorable characteristics: low background current and negative shift in onset of supporting electrolyte caused by hydrogen evolution, which enables visualization of the reduction of the quinoline skeleton at the potential of about −910 mV; at the 4000 and 8000 ppm electrodes this signal is only insinuated.

Obviously, the electrodes with metallic type of conductivity perform similarly as in oxidation of benzophenone-3 [13], where the 2000 ppm electrode exhibited the highest slope of the linear calibration dependence. This electrode with the boron-doping level just above the semiconductive/metallic conductivity threshold seems favorable in terms of electroanalytical performance.

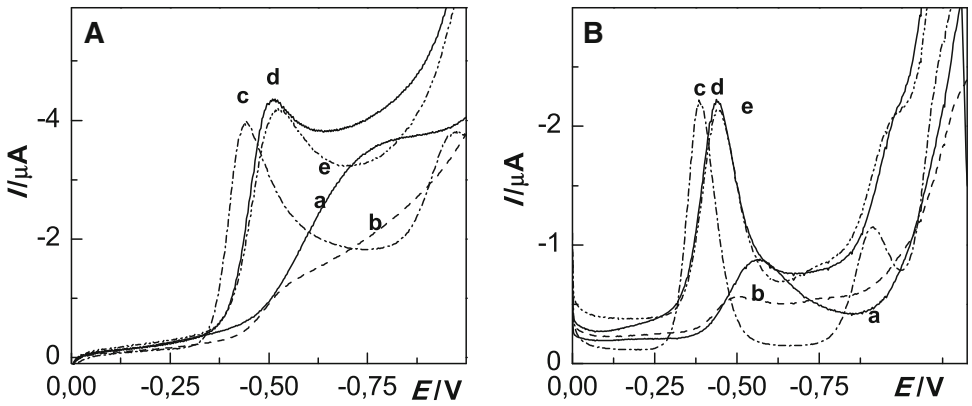

Fig. 6 **A** DC and **B** DP voltammograms of 5-nitroquinoline ($c = 1 \times 10^{-4}$ mol dm^{-3}) in 0.1 mol dm^{-3} acetate buffer pH 5.0 measured with BDD electrodes with different boron concentration (B/C ratio): (*a*) 500 ppm, (*b*) 1000 ppm, (*c*) 2000 ppm, (*d*) 4000 ppm, (*e*) 8000 ppm. Scan rate for DPV is 20 mV s^{-1} and for DCV is 50 mV s^{-1}

Conclusion

The voltammetric reduction of 5-nitroquinoline was elucidated at boron doped diamond (BDD) electrode in aqueous media of pH 2.0–12.0. The signal of the nitro group largely depends on the pH of the indifferent electrolyte, electrode pretreatment, activation between individual scans, and boron concentration of the BDD film electrode. In alkaline media, the four-electron reduction of the nitro to the hydroxylamino group occurs in two separated steps with the first one being a one electron reduction of the nitro group to the nitro-radical anion—a mechanism pathway previously recognized for 5-nitroquinoline at amalgam [38] electrodes or other nitro group containing aromatics at BDD electrodes [30]. Presence of oxygen in the measured solutions led to slight increase of peak heights and acceptable increase of its relative standard deviation. The detection limit for DPV achieved using optimized protocol, i.e. anodic pretreatment at +2.4 V for 5 min in 0.5 mol dm^{-3} H_2SO_4 and 20 s stirring between individual scans assured limit of detection in the 10^{-7} mol dm^{-3} concentration range, which is comparable with detection limits obtained at other solid electrode materials (compare in Table 1) including amalgam [38] and carbon film [44] electrodes. The nitro group reduction results in well-developed, observable signals at BDD films with metallic type of conductivity deposited at B/C ratio 2000–8000 ppm, but not using semiconductive films 500 and 1000 ppm. On the other hand, the reduction of the quinoline skeleton close to the onset of supporting electrolyte is well observable only at the 2000 ppm electrode. This might be connected with the increasing content of sp^2 impurities, existence of boron clusters [17, 50] and other factors influencing electron transfer and processes limiting the potential window when increasing boron-doping level.

To conclude, BDD electrodes seem to be good analytical alternative to determinations based on reduction of aromatic nitro group. For this purpose, highly doped BDD films are recommendable. The experimental data might be used for the development HPLC-ED method enabling separation and detection of nitro group containing aromatic compounds.

Experimental

Stock solution of 5-nitroquinoline (99 %, Sigma-Aldrich, Czech Republic) was prepared by dissolving exact quantity in deionized water for final concentration of 1×10^{-3} mol dm^{-3}. The experiments were carried out in Britton-Robinson (BR) buffer or 0.1 mol dm^{-3} acetate buffer (pH 5.0) at laboratory temperature. BR buffers were prepared by mixing a solution of phosphoric, acetic and boric acid (concentration of each 0.04 mol dm^{-3}, all p.a., Lach-Ner, Czech Republic) with an appropriate amount of 0.2 mol dm^{-3} sodium hydroxide solution. All solutions were prepared in deionized water (Millipore, Billerica, MA, USA). Other used chemicals were: acetic acid (Lach-Ner, Neratovice, Czech Republic), quinoline (Merck, Czech Republic). All measurements were performed using computer controlled Eco-Tribo Polarograph with PolarPro software (version 5.1, Eco-Trend Plus, Prague, Czech Republic) in a three electrode arrangement involving platinum wire auxiliary electrode and silver–silver chloride reference electrode (AglAgCl, 3 mol dm^{-3} KCl) (both Elektrochemické detektory, Turnov, Czech Republic). As working electrodes served boron doped diamond electrodes with boron-doping level 500, 1000, 2000, 4000, and 8000 ppm (B/C ratio during microwave-plasma assisted chemical vapor procedure described in [13]).Obtained BDD films at Si wafers were placed in Teflon electrode body constructed in our laboratory [32] with geometric surface area of 5.72 mm^2 (disk diameter 2.7 mm). If not otherwise stated, the 4000 ppm films and 0.1 mol dm^{-3} acetate buffer pH 5.0 as supporting electrolyte was used.

Differential pulse voltammetry was performed using the scan rate of 20 mV s^{-1} with pulse amplitude −50 mV for 80 ms. Scan rate 50 mV s^{-1} was used for DC voltammetry

and 100 mV s^{-1} for cyclic voltammetry, if not otherwise stated.

The BDD electrode was pretreated in 0.5 mol dm^{-3} sulfuric acid for 5 min with potential + 2.4 V before the measurement every day. During DP and DC voltammetry was BDD electrode activated for 20 s between each scan.

The influence of boron content was tested at 500–8000 ppm electrodes after anodic pretreatment or 5 min in 0.5 mol dm^{-3} sulfuric acid at the potential of +2.4 V, 20 s stirring between individual voltammetric scans was applied. All measurements were carried out at laboratory temperature. The pH measurements were carried out by digital pH Meter 3510 (Jenway, UK) with combined glass electrode.

The solutions for measurements were prepared in 10 cm^3 volumetric flasks by measuring of proper volume of the 5-nitroquinoline stock solution and filling by BR buffer of the required pH or 0.1 mol dm^{-3} acetate buffer pH 5.0 up to the mark. For DPV, the peak heights (I_p) were measured from the straight line connecting minima on both sides of the peak. In DCV they were measured from the line prolonging the voltammetric curve before the onset of the voltammetric signal of 5-nitroquinoline.

All calibration curves were measured in triplicate. The calibration dependences were processed using linear regression method. For voltammetric measurements, limits of detection (LOD) were calculated as the concentration of the analyte, which gave the signal equal to three times the standard deviation of peak heights estimated from ten consecutive measurements of the lowest measurable concentration.

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