VOLTAMMETRIC METHOD FOR DETERMINATION OF MUSCLE RELAXANT DANTROLENE SODIUM USING A BORON-DOPED DIAMOND ELECTRODE

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In this work, the electrochemical behavior of the dantrolene sodium muscle relaxant has been studied and the voltammetric method for its determination using a boron-doped diamond electrode (BDDE) proposed. Cyclic voltammetry and direct current voltammetry has been used for study of the dependences of DAN voltammetric signals on pH and scan rate. Differential pulse voltammetry and direct current voltammetry in combination with BDDE were applied to develop a sensitive method for the determination of the electroactive compound tested and various analytical and statistical parameters were calculated, e.g., the relative standard deviation of repeated measurements or limit of detection and limit of quantification.

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Introduction

Dantrolene (1-{[5-(4-nitrophenyl)-2-furyl]methylideneamino}imidazolidine-2,4-dione, CAS: 7261-97-4) was firstly described in 1967 as one of several hydantoin derivatives proposed as a new class of muscle relaxant [1]. Dantrolene sodium (DAN, Fig. 1) is the primary drug used for treatment and prevention of malignant hyperthermia, neuroleptic malignant syndrome, or muscle spasticity [2].
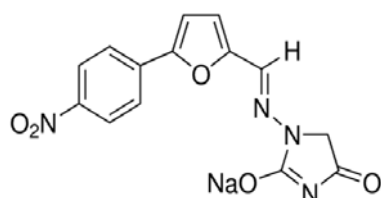

Fig. 1   The chemical structure of dantrolene sodium salt

Various analytical methods for determination of DAN have already been developed due its biological significance; the most widely used being a procedure based on high performance liquid chromatography (HPLC) coupled with various detections, such as fluorescence or chemiluminiscence [3-6]. The respective methods are sensitive and accurate, but the instrumentation employed is rather expensive and, also, the sample pretreatment can be complicated. Electrochemical methods represent good alternative to the above-mentioned analytical approaches; especially, due to the low costs of instrumentation, fast and sensitive analysis or a possibility of miniaturization. DAN is electrochemically active; however, very few articles related to the electrochemistry of DAN have hitherto been published. So far, only mercury electrodes were used to study the voltammetric behavior of this compound [7-9]. Differential pulse polarography (DPP) with the dropping mercury electrode (DME) and differential pulse adsorptive stripping voltammetry (DPAdSV) were the techniques of choice for these purposes. Cox *et al*. [7] applied DPP with the DME for determination of DAN and its metabolites, achieving a limit of detection (LOD) of about 3×10^{-7} mol l^{-1}. Similar method was described by Reddy *et al*. [8] (with LOD 7×10^{-7} mol l^{-1}). Detailed studies focused on polarographic as well as voltammetric behaviour of DAN on mercury electrodes was then described in Ref. [8]. Therein, the authors had utilized various techniques; namely: direct current and differential pulse polarography (DCP and DPP, respectively), direct current adsorptive stripping voltammetry (DCAdSV), differential pulse adsorptive stripping voltammetry (DPAdSV), and square wave adsorptive stripping voltammetry (SWAdSV); all in combination with either DME or hanging mercury drop electrode (HMDE). The lowest LOD was obtained using SWAdSV being ca. 2×10^{-10} mol l^{-1}. All the mentioned papers describe the electrochemical reduction of DAN via the reduction of the nitro group present in

the molecule at a potentialof about –0.25 V and the reduction of the azomethine group at about –0.85 V vs. SKE in an acidic medium. In alkaline solutions, only the reduction signal corresponding to the reduction of –NO$_2$ group could be observed [7-9]. Finally, DPP was also applied to study the physicochemical properties of DAN and, especially, for determination of pK_a value [10].

In electroanalytical chemistry, boron-doped diamond electrodes (BDDEs) were introduced in the early nineties of the twentieth century [11,12]. The pure diamond is distinguished by outstanding mechanical and chemical stability and it is one of the well-known natural insulators. Thus, for its electrochemical use, it needs to be doped with the atoms of other elements, most often with boron. The electrochemical properties of the diamond materials prepared differ depending on the abundance of these atoms in the final structure [13]. Diamond films are formed by chemical vapor deposition (CVD) with heated filaments (HF) or by microwave heating. The mixture of methane and hydrogen is usually used for such a diamond film deposition, when diborane or trimethylboron are being added into the mixture for the proper boron doping. As a substrate for the diamond films, silicon served most commonly although, in some cases, molybdenum or wolfram could also be used. In this way, the prepared boron-doped diamond films exhibit a polycrystalline structure [14,15].

In electroanalytical applications, an extraordinarily wide potential window (about more than 3 V) is consensually the greatest advantage of BDDEs. Furthermore, these electrodes exhibit a low background signal with favourable signal-to-noise ratio. In general, the working surface of these electrodes exhibits a "paraffinic" character and, therefore, fairly low adsorption capabilities in electroanalytical measurements, minimizing the problems with passivation of the surface. Last but not least, thanks to good mechanical stability, BDDEs are also suitable for measurements in flowing streams [16,17].

Most often, the BDDEs are used in analysis of organic compounds. Regarding this, various methods have already been described for the determination of hydrocarbons and their derivatives [18], phenols [19-21], nitrophenols [22,23], or amines [24,25]. Different carcinogenic substances [26,27], pharmaceuticals [28-31], pesticides [32-37], and other bioactive compounds (e.g. [38]) were also analyzed. Besides organic analysis, BDDEs could be applied to the determination of metal cations as well [39,40]. Thus, it is evident that BDDEs are widely applicable in practical electroanalysis and hence, they belong among the most promising electrodes also for the future.

Possibility of voltammetric analysis of DAN *via* its electrochemical oxidation on the BDDE is for the first time described in this paper, focused on the definition of the proper operational conditions and the development of the respective method that has successfully been tested for the determination of DAN in model solutions.

Experimental

Materials

All chemicals used for preparation of the standard solutions, supporting electrolytes, and other stock solutions were of p.a. grade; all the corresponding solutions being prepared in distilled water. The standard solution of DAN (98 %, Sigma-Aldrich) with the concentration of 0.001 mol l^{-1} was prepared by dissolution of the appropriate amount in methanol (Penta-Švec, the Czech Republic) and then stored in the dark in a refrigerator. Britton–Robinson buffer solutions (BRBSs) of pH from 2 to 12 were prepared by mixing of the alkaline component (0.2 mol l^{-1} NaOH) and of the acidic component (0.04 mol l^{-1} H_3PO_4, H_3BO_3, and CH_3COOH; all from Lachema Brno, the Czech Republic). The electrolytes based on various concentrations of H_2SO_4 were prepared from 96% H_2SO_4 (Penta-Švec, the Czech Republic).

Instrumentation

All voltammetric measurements were performed by computer controlled Eco-Tribo polarograph (Polaro-Sensors, the Czech Republic) equipped by the POLAR.PRO software (version 5.1) and by the Multielchem 3.1 software (J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i.). All measurements were performed with a three-electrode set up, where a commercially purchased BDDE with the B/C (boron-to-carbon) ratio of 1000 ppm (declared by producer Windsor Scientific, United Kingdom) and with surface area of 7.07 mm^2 served as the working electrode. Saturated silver/silver chloride electrode (Ag/AgCl/sat.) was used as the reference and a platinum wire as the auxiliary electrode (both Monokrystaly, Turnov, the Czech Republic). The measurements were performed at laboratory temperature (23 ± 2 °C), when oxygen did not need to be removed from the measured solutions. The values of pH were measured using a Accumet pH-meter (model AB150; Fisher Scientific, USA) and solutions of DAN were prepared applying an ultrasonic bath (Bandelin Sonorex; Schalltec, Germany).

Voltammetric Measurements

At the beginning of each working day, the BDDE was activated in a solution of 1 mol l^{-1} H_2SO_4 by insertion of anodic potential of +2000 mV and cathodic potential −1000 mV; both for 60 s. The anodic pretreatment was performed in order to oxidize possible pollutants, whereas the cathodic pretreatment enabled to improve the peak definition and to increase the current signal. Finally, twenty

cyclic voltammetric scans from -1000 mV to $+2000$ mV in 1 mol l^{-1} H_2SO_4 were recorded; these conditions being in accordance with those described in Ref. [41].

Cyclic voltammetry (CV) and direct current voltammetry (DCV), respectively, were used at first to examine the voltammetric behaviour of DAN on the BDDE in dependence on pH of the supporting electrolyte and upon the scan rate (v). First tentative CV measurements were carried out in the potential range from -800 mV to $+2000$ mV with a scan rate of 50 mV s^{-1}. Voltammetric behaviour of DAN in dependence on pH of the supporting electrolyte was investigated using CV under the same parameters. The effect of the scan rate was studied by recording in the potential range from -500 mV to $+1700$ mV, with scan rates from 25 to 500 mV s^{-1}. Then, DCV and/or DPV, respectively, were chosen for the DAN determination. A pulse width of 20 ms, pulse height of 50 mV and a scan rate of 40 mV s^{-1} were the set of instrumental conditions selected for the determination of DAN. The DPV peaks were evaluated from the straight line connecting the minima before and after the peak (a tangent to the curve connecting the beginning and the end of a given peak). When using DCV, the method of baseline correction was applied before the peak height (I_p) evaluation.

The limits of detection (LOD) and limit of quantification (LOQ) were calculated as three-fold (in the case of LOD) and ten-fold (in the case of LOQ) standard deviation of the blank (i.e. the supporting electrolyte) divided by the slope of the calibration curve. The parameters of calibration curves (e.g., the slope, intercept) were calculated using software MS Excel 2010 (Microsoft, USA).

Results and Discussion

As mentioned above, the electrochemical oxidation of DAN has not been yet studied, whereas the reduction mechanism (on mercury electrodes) was described in detail [7-9], when the authors proposed a slightly acidic medium. Therefore, the first cyclic voltammogram of DAN (5×10^{-5} mol l^{-1}) on the BDDE was measured in BRBS with pH 4. The curves obtained are shown in Fig. 2. As can be seen, DAN provides one significant anodic signal at a potential ($E_{p,a}$) about $+1360$ mV and the corresponding, much lesser cathodic wave was recorded at a potential ($E_{p,c}$) of $+1260$ mV vs. ref. Accordingly, the electrode reaction of DAN on BDDE can be classified as quasi-reversible.

Effect of Supporting Electrolyte on Voltammetric Behavior of DAN

In general, the supporting electrolyte plays an important role for the respective electrochemical reaction. The pH effect of supporting electrolyte on the electrochemical oxidation of DAN (5×10^{-5} mol l^{-1}) was investigated in BRBS with pH

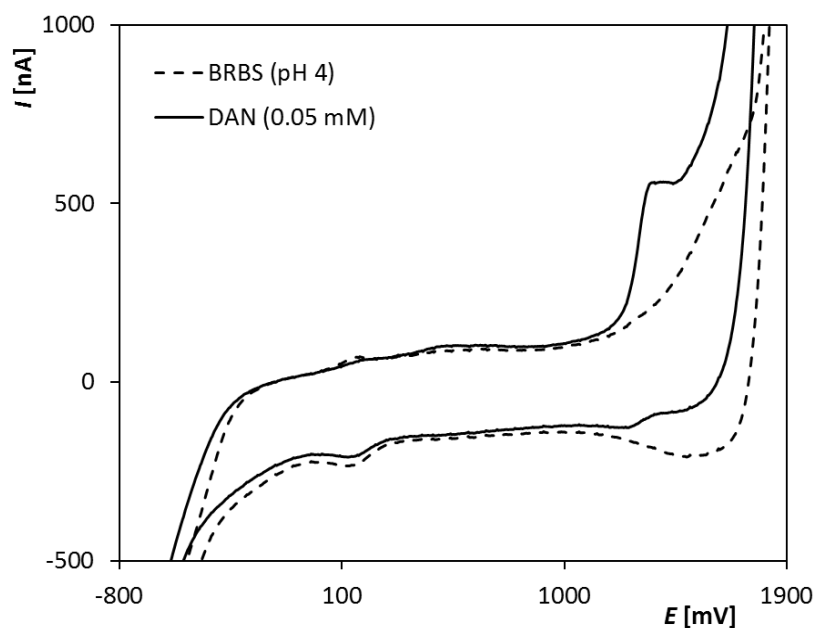Fig. 2   The cyclic voltammograms of 5×10^{-5} mol l^{-1} DAN on BDDE in BRBS with pH 4. Method: CV, parameters: $E_{in} = -800$ mV, $E_{fin} = +1900$ mV, and $v = 50$ mV s^{-1}

varied from 2 to 12, when applying CV. The pH 1 was accomplished with a solution of 0.05 mol l^{-1} H$_2$SO$_4$. Figure 3 illustrates the anodic parts of cyclic voltammograms obtained in the whole pH range tested. DAN provides one anodic wave which can be seen for all curves. In alkaline media, the shapes of these signals getting worse and consequently, they cannot be properly evaluated. This is caused by narrowing of the potential window of BDDE with the increasing pH of the supporting electrolytes. The dependences of peak heights (I_p) and of the peak potentials (E_p) on pH values are given in the inset of Fig. 3. It is evident that, in acidic medium, I_p is almost unchanged. At neutral and slightly alkaline pH, the peak currents significantly increase with a maximum at pH 8, and then rapidly decrease. Simultaneously, there is a gradual shift of the peak position toward the more negative potentials. This dependence is nearly linear and can be described by the following equation with the respective correlation coefficient

$$E_p[\text{mV}] = (-18.8 \pm 1.1)\text{pH} + 1407.2 \pm 7.8, \quad R = 0.984 \tag{1}$$

In view of the above-mentioned results, the BRBS with pH 8 was chosen as the most suitable supporting electrolyte for all subsequent measurements with DAN using BDDE.
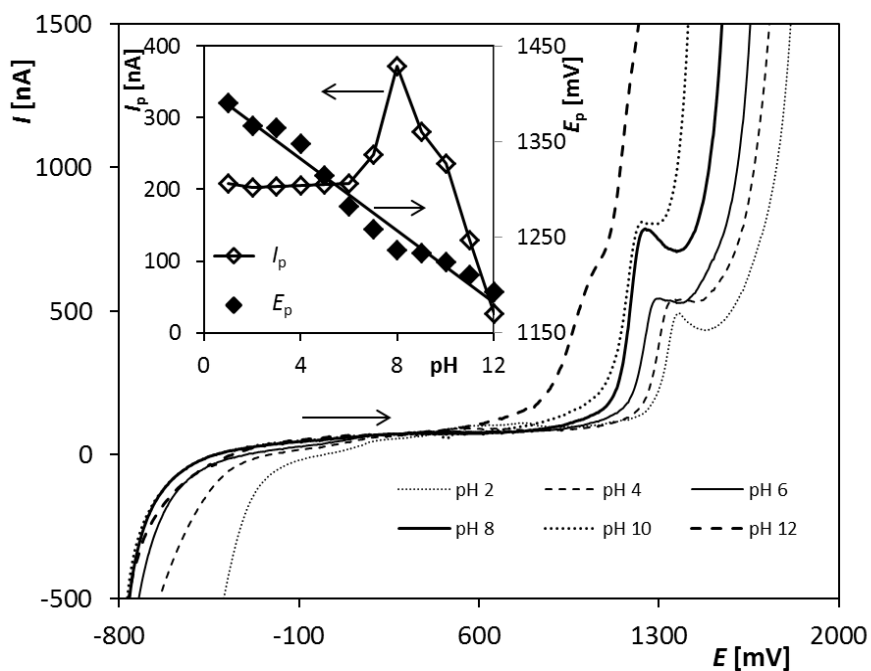
Fig. 3 The anodic parts of cyclic voltammograms of 5×10^{-5} mol l^{-1} DAN in supporting electrolytes with pH 1-12 obtained at the BDDE. Method: CV, electrolyte: 0.05 mol l^{-1} H_2SO_4 (pH 1), BRBS (pH 2-12), parameters: $E_{in} = -800$ mV, $E_{fin} = +1900$ mV, $v = 50$ mV s^{-1}. Inset: Dependences of I_p and of E_p on pH of the supporting electrolytes

Effect of Scan Rate on the Voltammetric Behavior of DAN

Useful information on electrochemical mechanism (rate-limiting step) may be derived from the dependence of the peak current on the scan rate. The effect of the scan rate on the voltammetric behaviour of 5×10^{-5} mol l^{-1} DAN was examined by CV in the range of scan rates (v) from 25 to 500 mV s^{-1} and the voltammetric curves obtained are shown in Fig. 4.

As can be seen, the evaluability of the DAN current signal is more difficult with the increase of scan rate (v) due to the vicinity of the end of the useful anodic potential window attainable at BDDE. Despite this, the dependence of I_p on v was evaluated and is depicted in the inset of Fig. 4. The non-linear character of this dependence excludes the adsorption to be the controlling process of the DAN oxidation reaction. It is evident that the process is much more complicated. Nevertheless, the $\log(I_p)$ - $\log(v)$ analysis was successfully applied to elucidate the controlling processes of the oxidation, too. The linear dependence between $\log(I_p)$ and $\log(v)$ was confirmed *(R = 0.988)* and described by Eq. (2).

$$\log I_p [\text{nA}] = (0.424 \pm 0.016) \log v [\text{mV s}^{-1}] + 1.727 \pm 0.037,$$
$$R = 0.988$$

(2)

The slope of the straight line, $k = (0.424 \pm 0.016)$, is approaching to 0.5, which corresponds to the diffusion controlled process. On the other hand, the value 0.5 is out of its confidence interval ($p \leq 0.05$). Therefore, it can be assumed that the process investigated is more complicated being partially influenced also by kinetics.
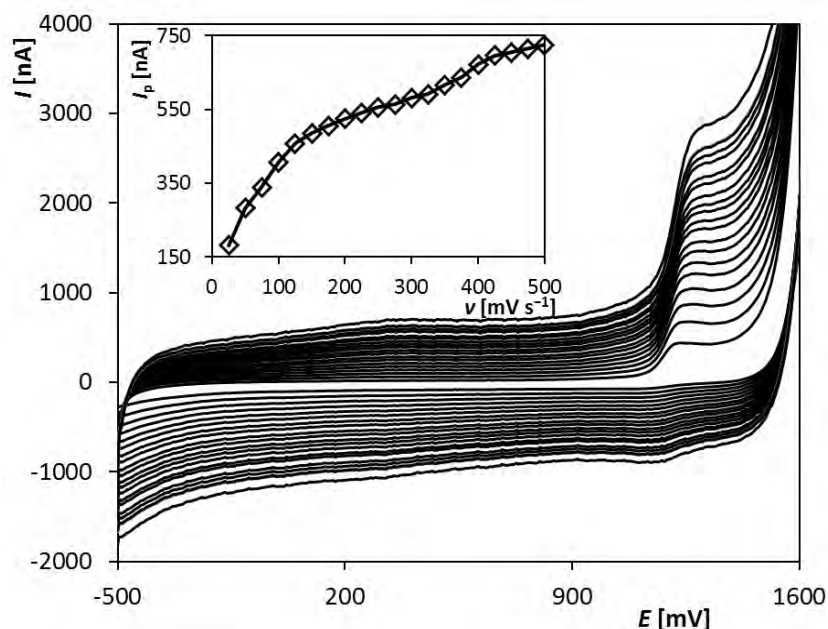

Fig. 4   DC voltammograms of 5×10^{-5} mol l^{-1} DAN in BRBS with pH 8 recorded at the BDDE. Method: CV, parameters: $E_{in} = -800$ mV, $E_{fin} = +1800$ mV, $v = 25$-500 mV s^{-1}. Inset: Dependence of I_p on v

Analysis of Model Solutions

DPV is considered to be an effective electrochemical technique that has already been applied for analysis of numerous electrochemically and biologically active compounds. Therefore, this technique was chosen also for the determination of DAN using BDDE. The optimization of the DPV working parameters influencing the current response of the analyte is an important step in the development of any electroanalytical methodology. The effect of the scan rate on the height and shape of the DAN oxidation signal was tested with the solution of BRBS (pH 8) and the analyte content of 2×10^{-5} mol l^{-1}. The other experimental and instrumental parameters are specified in the legend of Fig. 5A, depicting the I_p vs. v dependence obtained, when the value of scan rate has been changed from 10 to 100 mV s^{-1}. As seen, the current signal measured significantly increased with faster v up to the value of 50 mV s^{-1}, then, its height had grown more slowly and the current was almost constant from 80 mV s^{-1} and higher. Therefore, the scan rate 40 mV s^{-1} was chosen as a compromise between the peak height and its shape. The pulse height

was the next parameter tested. It was varied from +10 to +100 mV and the voltammograms obtained accompanied by the respective dependence of I_p on the pulse height are shown in Fig. 6; detailed parameters being summarized in figure legend. It is evident that the peak increases with the increasing pulse height, but the evaluability of the signal is worse due to the vicinity of the potential limit. Finally, the value of the pulse height +50 mV was applied in all the following DPV measurements. The last of the parameters studied was the pulse width that was changed from 10 to 100 ms and the corresponding I_p-to-pulse width dependence can be seen in Fig. 5B. Based on these results, the value of 20 ms was selected as optimal for following analysis.
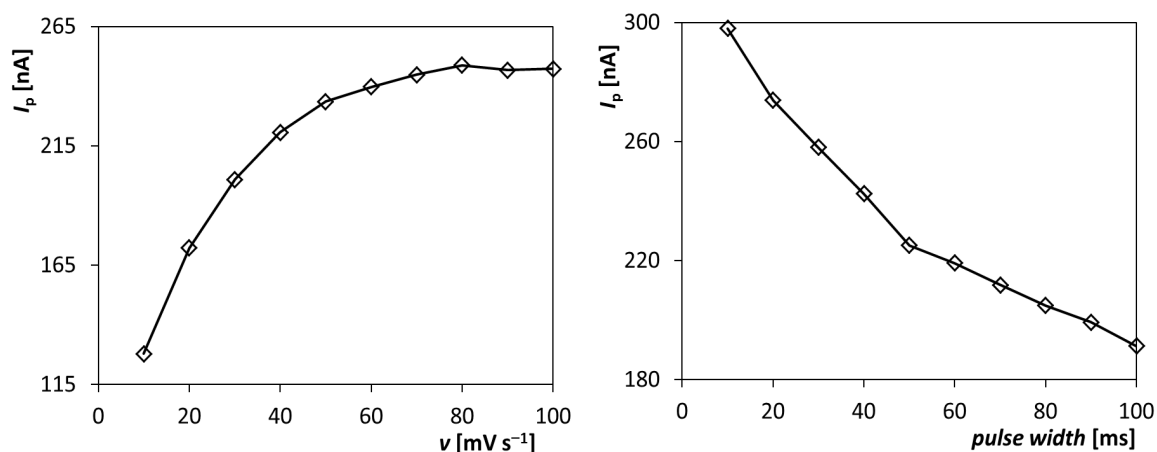

Fig. 5 Dependences of the peak height on the scan rate (A) and on the pulse width (B) obtained at BDDE. Method: DPV, electrolyte: BRBS (pH 8), parameters: E_{in} = +200 mV, E_{fin} = +1500 mV, v = 10-100 mV s^{-1} (A), 40 mV s^{-1} (B), pulse height = +50 mV, pulse width = 50 ms (A) and 10-100 ms (B), c_{DAN} = 2×10^{-5} mol l^{-1}
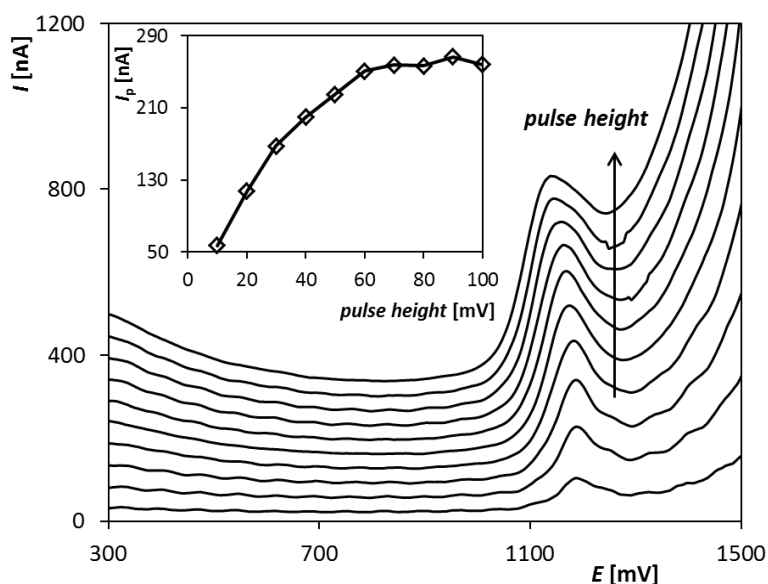

Fig. 6 DP voltammograms of 2×10^{-5} mol l^{-1} DAN recorded after applying the different pulse height to the BDDE. Method: DPV, electrolyte: BRBS (pH 8), parameters: E_{in} = +200 mV, E_{fin} = +1500 mV, v = 40 mV s^{-1}, pulse height = +10-+100 mV, pulse width = 50 ms. Inset: Dependence of I_p on the pulse height

The parameters proposed for the proper determination were used in eleven repeated measurements of the same DAN concentration (5×10^{-6} mol l^{-1}), from which the relative standard deviation, $RSD_{(11)}$, was calculated to be 5.8 %. The value obtained did not suggest a very good repeatability of DAN measurements, when applying DPV with optimized experimental conditions. Moreover, the linear dynamic range (LDR) of the proposed method for the DAN determination that had been obtained from various measured concentration dependences was relatively narrow (from 2×10^{-6} to 4×10^{-5} mol l^{-1}). Therefore, some concentration dependences were also measured with the aid of DC voltammetry.

It was found that the results obtained for the DAN determination at the BDDE in combination with DCV were better, giving a $RSD_{(11)}$ of about 1.3 % for the concentration of 5×10^{-6} mol l^{-1} DAN. An example of DC voltammograms in the concentration range from 2.50×10^{-6} to 2.25×10^{-5} mol l^{-1} DAN is depicted in Fig. 7. It can be noticed that the evaluation of the dependence could be performed after the baseline correction. This approach proved to be suitable for evaluation of I_p values when using DCV, enabling to analyse lower concentrations compared to DPV. The concentration range of LDR_{DCV} for this method was from 5×10^{-7} to 3×10^{-5} mol l^{-1}. As evident from the inset of Fig. 7, the value of I_p increases linearly with increasing concentration of DAN in polarographic vessel and this dependence can be described by Eq. (3)

$$I_p[\text{nA}] = (11.33 \pm 0.06)c\,[\mu\text{mol l}^{-1}] + 2.03 \pm 0.82,$$
$$R = 1.0000 \tag{3}$$

$$I_p[\text{nA}] = (15.69 \pm 0.21)c\,[\mu\text{mol l}^{-1}] + 0.10 \pm 0.50,$$
$$R = 0.9999 \tag{4}$$

The statistical parameters of the method proposed, such as a limit of detection (LOD) and limit of quantification (LOQ) were calculated from the concentration dependence measured at the lowest evaluable signals corresponding to DAN concentrations from 5×10^{-7} to 8×10^{-7} mol l^{-1} (Eq. (4)). The LOD for this case was ca. 1.0×10^{-7} mol l^{-1} and LOQ being 3.4×10^{-7} mol l^{-1}. These results indicate a very sensitive electrochemical method for DAN determination.

After that, the sufficient accuracy and repeatability of the determination of DAN with DPV, as well as with DCV at the BDDE was confirmed by analysis of various model solutions containing two different concentration levels of DAN. The standard addition method was applied and every determination was five times repeated.

The examples of model analyses are shown in Fig. 8 including a graphical evaluation (in insets). The results for both applied methods are summarised in Table I. It was proved that all methods are very accurate and the values of $RSD_{(5)}$

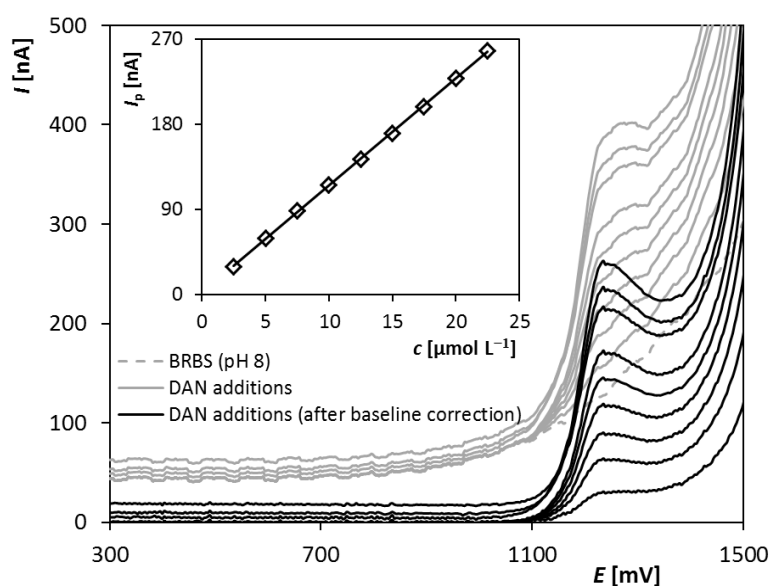calculated fairly low (< 5 %), which can be considered as a very good repeatability of determinations.

Fig. 7 DC voltammograms of DAN measured in dependence on concentration using BDDE. Method: DCV, electrolyte: BRBS (pH 8), parameters: E_{in} = +200 mV, E_{fin} = +1500 mV, v = 50 mV s^{-1}, c_{DAN} = 2.5×10^{-6}-2.25×10^{-5} mol l^{-1}, grey lines – original curves, black lines – curves after baseline correction. Inset: Dependence of I_p on c_{DAN}
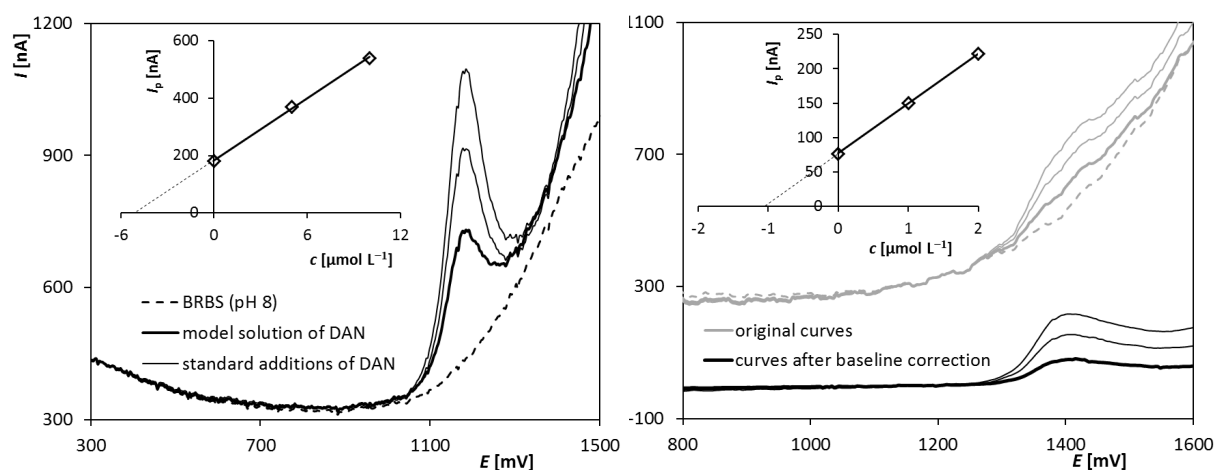

Fig. 8 DP voltammograms of DAN determination in model solution with DAN concentration 5×10^{-6} mol l^{-1} (A) and DC voltammograms of DAN determination in model solution with DAN concentration 1×10^{-6} mol l^{-1} (B) obtained on BDDE in BRBS (pH 8) under the optimized experimental conditions. Insets: Graphical evaluations of standard addition method

Table I   Results of repeated determinations of DAN in model solutions

Method	Added mol l^{-1}	Found mol l^{-1}	Recovery %	RSD ($n = 5$) %
DPV	1×10^{-5}	1.020 ± 0.031	96.0-106.0	4.7
	5×10^{-6}	4.981 ± 0.055	97.6-101.1	1.7
DCV	5×10^{-6}	4.970 ± 0.033	98.0-100.6	1.0
	1×10^{-6}	1.022 ± 0.033	97.0-108.0	4.8

Conclusion

The voltammetric behaviour of DAN at the BDDE has been investigated and a novel analytical method developed for its determination in model solutions. The electrode reaction carried out at BDDE was identified as a diffusion-controlled process without the influence of adsorption. Therefore, the sensitivity of this determination cannot be improved by applying the respective adsorptive (accumulation) techniques. On the other hand, the LOD for DAN obtained at BDDE was quite low (1×10^{-7} mol l^{-1}). Such a result can be considered as satisfactory for this kind of the working electrode. The applicability of DCV and DPV in combination with BDDE has been confirmed by analysing the model solutions of DAN. It can be concluded that the voltammetric methods proposed offer a very attractive and environmentally acceptable approach to the determination of DAN.

Acknowledgement

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