# POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF SUBMICROMOLAR CONCENTRATIONS OF GENOTOXIC 1,5-DINITRONAPHTHALENE

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*Dedicated to the memory of Profesor Jaroslav Heyrovský on the occasion of 45th Anniversary of Nobel Prize for polarography.*

Polarographic and voltammetric behavior of 1,5-dinitronaphthalene was investigated using tast polarography and differential pulse polarography at a classic dropping mercury electrode and differential pulse voltammetry and adsorptive stripping voltammetry at a hanging mercury drop electrode. Optimum conditions have been found for the determination of tested substance in the concentration range 2–10 μmol $l^{-1}$ in tast polarography, 0.2–1 μmol $l^{-1}$ in differential pulse polarography at a classic dropping mercury electrode or differential pulse voltammetry at a hanging mercury drop electrode, and 0.02–0.1 μmol $l^{-1}$ using adsorptive stripping voltammetry. A possible mechanism of the electrochemical reduction of 1,5-dinitronaphthalene at mercury electrodes is discussed.

**Keywords**: Tast polarography; Differential pulse polarography; Differential pulse voltammetry; Adsorptive stripping voltammetry; Nitro compounds; Electrochemistry.

Nitrated polycyclic aromatic hydrocarbons (NPAHs) have been recognized as important environmental hazards, mainly because of their carcinogenic properties[1–4]. The mutagenic activity and specificity of dinitronaphthalenes is dependent on positions of nitro groups. While the 1,8-isomer is inactive, the 1,5-isomer, also with nitro groups in both rings, shows appreciable base-substitution as well as a frame shift activity. It would seem that the 1,5-configuration is the preferred one for the formation of DNA adducts, which results in base-displacement resulting in the frame shift mutation[5]. The genotoxicity of various dinitronaphthalenes was also confirmed by Rodriguez et al.[6] Iwata et al. concluded in their studies[7] that enzymatic nitroreductase activities towards various nitronaphthalenes in cytosol of rat

liver were closely related to the single-electron reduction potentials measured by the electrochemical assays and hence there was a good relationship between logarithm of nitroreductase activities and electrochemical reduction potentials.

Because of their dangerous biological properties, there is an ever-increasing demand for the determination of trace amounts of various dinitronaphthalenes. So far, mostly chromatographic methods, such as GC-MS or HPLC with fluorimetric detection have been used for these purposes[8]. Modern electroanalytical methods, in particular adsorptive stripping voltammetry (AdSV)[9,10] satisfy high demands on the sensitivity and thus they can be a reasonable alternative to more costly separation methods. Nevertheless, the use of voltammetric methods for the determination of NPAH is not too frequent[11] in spite of the easy polarographic reducibility of the nitro group[12–14] and the fact that polarographic and voltammetric methods are much cheaper as far as investment and running costs are concerned, presenting an independent important alternative. Although polarographic behavior of all ten possible dinitronaphthalenes was studied in the early sixties[15], no report was found in the literature on the use of modern polarographic and voltammetric methods for the determination of trace amounts of these substances in the environmental samples. So far, 1,5-dinitronaphthalene has been determined only by HPLC [16] or combination of HPLC and GC [17].

Therefore, we have selected 1,5-dinitronaphthalene as a typical representative of this group and investigated its polarographic and voltammetric behavior using direct current tast polarography (DCTP) and differential pulse polarography (DPP) at a classic dropping mercury electrode (DME) and differential pulse voltammetry (DPV), adsorptive stripping voltammetry (AdSV) and cyclic voltammetry (CV) at a hanging mercury drop electrode (HMDE).

## EXPERIMENTAL

### Reagents

A stock solution of 1,5-dinitronaphthalene ($c = 1 \times 10^{-3}$ mol $l^{-1}$) was prepared by dissolving 0.02187 g of the pure substance (Fluka, Switzerland) in 100 ml of methanol. The purity of the substance was controlled by HPLC. More diluted solutions were prepared by exact dilution of the stock solution with methanol. All the solutions were stored in the dark. It followed from a spectrophotometric study of the stability of the stock solution that the solution in methanol is stable for at least 180 days. Methanol was of analytical grade purity (Lachema, Brno, Czech Republic). Britton–Robinson buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 M phosphoric acid, 0.04 M acetic acid and 0.04 M boric acid

with an appropriate amount of 0.2 M sodium hydroxide solution. Deionized water was produced with Milli-Qplus system, Millipore.

### Apparatus

Measurements were carried out using a computer-driven EcoTriboPolarograph with PolarPro software, version 2.0 (both PolaroSensors, Prague, Czech Republic) in combination with a classic DME or a hanging mercury drop electrode (HMDE) UMμE (PolaroSensors, Prague), a platinum-wire auxiliary electrode and saturated silver chloride reference electrode, to which all potential values are referred. The parameters of the classic DME used in tast and DP polarography were as follows. At a mercury reservoir height of $h$ = 49 cm, the flow rate was $m$ = 0.593 mg $s^{-1}$ and the drop time was $\tau$ = 6.5 s (at an applied voltage of 0 V in 0.1 M KCl). If not stated otherwise, the work with the DME was carried out at a polarization rate 4 mV $s^{-1}$, controlled drop time 1 s, mercury reservoir height 49 cm and modulation amplitude in differential pulse polarography –50 mV. For DPV and AdSV at UMμE HMDE, the drop size obtained by opening the valve for 100 ms (the average weight of one drop was 1.17 mg, which corresponds to the surface 0.94 $mm^2$), a polarization rate of 20 mV $s^{-1}$, and the modulation amplitude –50 mV were used. pH measurements were carried out by Jenway 4330 conductivity & pH meter (Jenway, U.K.).

### Procedures

The general procedure for obtaining polarograms or voltammograms was as follows. A required amount of the stock solution of the test substance in methanol was placed in a 10-ml volumetric flask, an appropriate volume of methanol was added and the system was diluted to the volume with a Britton–Robinson buffer of required pH or 0.01 M NaOH. (A different order of mixing the solutions resulted in a precipitation of the test substance). Oxygen was removed from the measured solutions by bubbling with nitrogen for 10 min. A prebubbler containing a water–methanol mixture in the same ratio as in the polarographed solution was placed before the polarographic vessel. The calibration curves were measured in triplicate and evaluated by the least-squares linear regression method. The limit of determination was calculated as the tenfold standard deviation from 7 analyte determinations at the concentration corresponding to the lowest point on the appropriate calibration straight line[18].

## RESULTS AND DISCUSSION

### *Tast Polarography, Differential Pulse Polarography, and Differential Pulse Voltammetry*

First, the influence of pH on the polarographic and voltammetric behavior of 1,5-dinitronaphthalene was investigated using tast, DPP and DPV techniques. With a $1 \times 10^{-4}$ M solution of 1,5-dinitronaphthalene in a mixture of methanol with Britton–Robinson buffer (1:1), the observed currents decreased considerably with time due to precipitation of the measured substance. Therefore, the influence of pH was investigated using $4 \times 10^{-5}$ M so-

lution of 1,5-dinitronaphthalene. It can be seen from Figs 1–3 that the best developed waves or peaks were obtained at pH 12.

We presume (Fig. 4) that at low pH values, 1,5-dinitronaphthalene is reduced with the exchange of 12 electrons to the corresponding 1,5-diaminonaphthalene in three consecutive four-electron steps, corresponding to the reduction of the first nitro group to hydroxyamino group followed by anal-

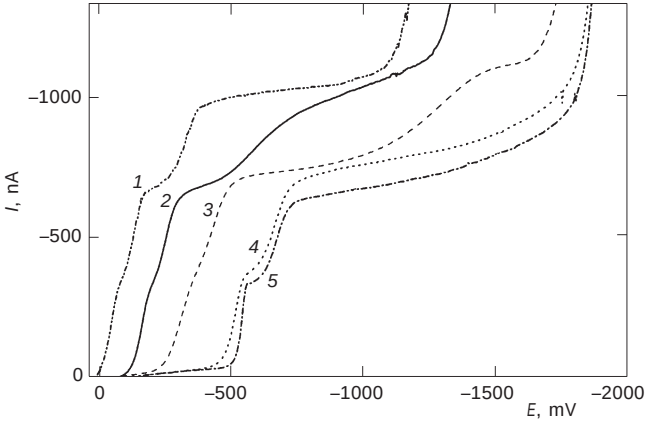


FIG. 1
Selected DC tast polarograms on DME of 1,5-dinitronaphthalene ($c$ = 4 × $10^{-5}$ mol $l^{-1}$) in a Britton–Robinson buffer and methanol (1:1) mixture at pH: 2.7 (*1*), 4.6 (*2*), 6.9 (*3*), 10.5 (*4*) and 12.3 (*5*)

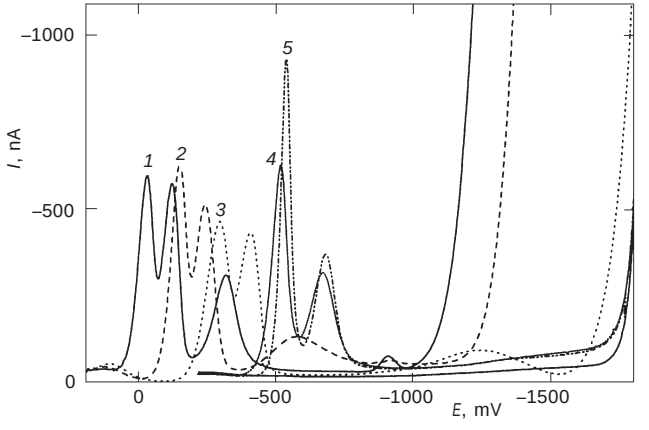


FIG. 2
Selected DP polarograms on DME of 1,5-dinitronaphthalene ($c$ = 4 × $10^{-5}$ mol $l^{-1}$) in a Britton–Robinson buffer and methanol (1:1) mixture at pH: 2.7 (*1*), 4.6 (*2*), 6.9 (*3*), 10.5 (*4*) and 12.3 (*5*)

ogous reduction of the second group and finally by the four-electron reduction of both hydroxyamino groups formed in previous steps. The third wave shifts towards more negative potentials with increasing pH, it becomes distorted and eventually completely disappears, which suggests that 1,5-bis(hydroxyamino)naphthalene is the final product of eight-electron reduction in alkaline medium. This behavior is reflected in DPP and DPV curves as well, resulting in three or two peaks depending on pH.

Concentration dependences were measured in a mixture of methanol with 0.01, 0.1, and 0.2 M NaOH (1:1). It was found that the height of DPP or DPV peaks slightly increases with decreasing concentration of sodium hydroxide in the base electrolyte. Moreover, peaks of impurities decreased with decreasing sodium hydroxide concentration as well. Therefore, we have chosen an 0.01 M NaOH–methanol (1:1) mixture as optimum base electrolyte.

The parameters of calibration curves are summarized in Table I.

Figures 5–7 show tast and DP polarograms, and DP voltammograms of 1,5-dinitronaphthalene in 0.01 M NaOH–methanol (1:1) medium for lowest accessible concentration ranges.

*Adsorptive Stripping Voltammetry*

It has been found that the presence of methanol decreases the adsorption of the test substance on the surface of HMDE. To improve the sensitivity of

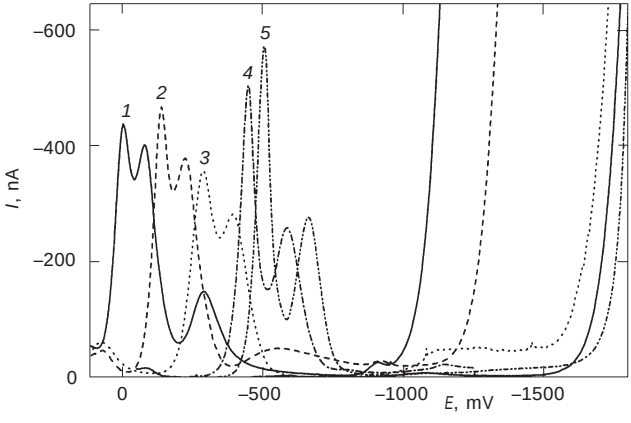


FIG. 3

Selected DP voltammograms on HMDE of 1,5-dinitronaphthalene ($c = 4 \times 10^{-5}$ mol $l^{-1}$) in a Britton–Robinson buffer and methanol (1:1) mixture at pH: 2.7 (*1*), 4.6 (*2*), 6.9 (*3*), 10.5 (*4*) and 12.3 (*5*)

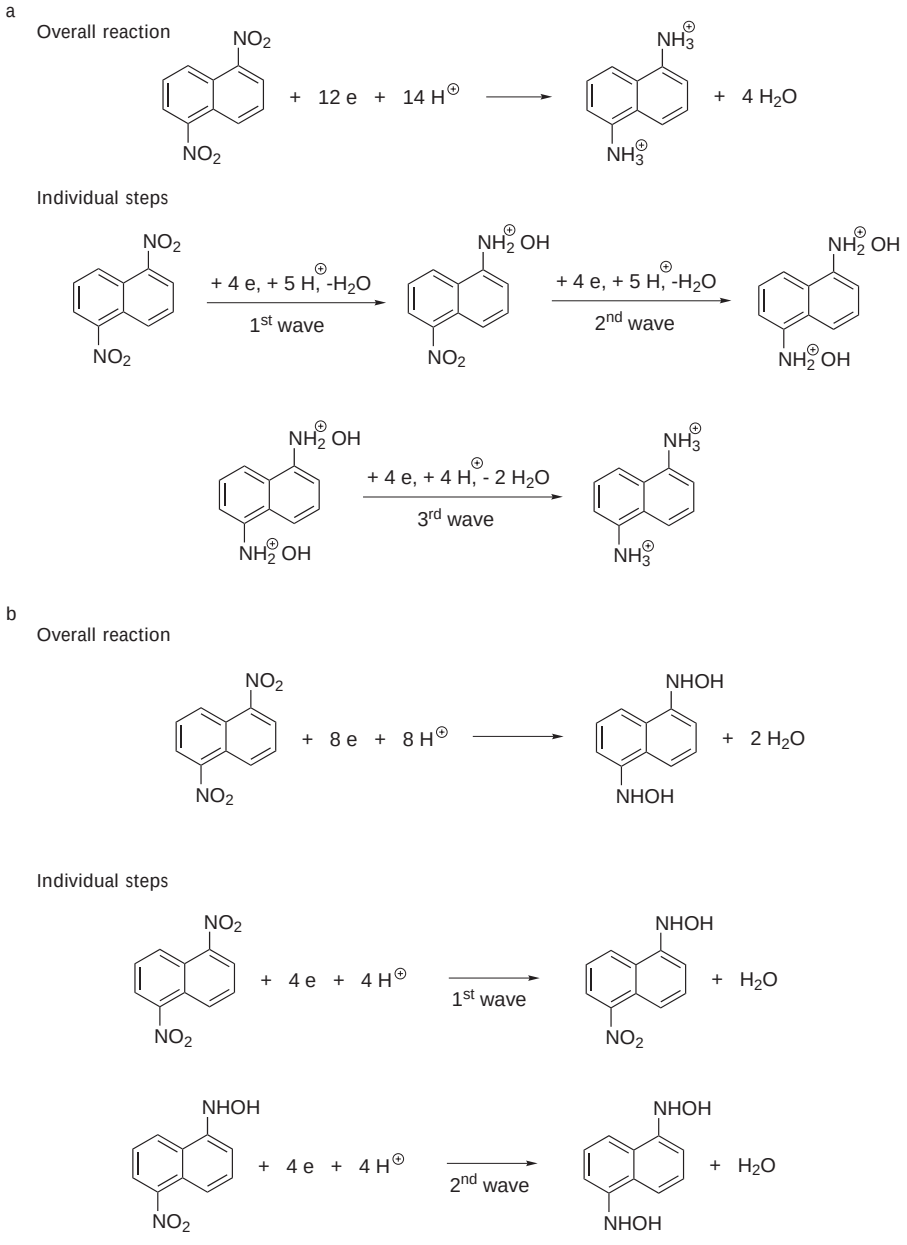


FIG. 4
Polarographic reduction of 1,5-dinitronaphthalene in acid (a) and alkaline (b) medium

TABLE I

Parameters of the calibration lines for the determination of 1,5-dinitronaphthalene by various polarographic and voltammetric techniques in 0.01 M NaOH–methanol (1:1) medium

| Technique | *c* μM | Wave or peak | Slope mA M$^{-1}$ | Intercept nA | Correl. coef. | LOD[a] μM |
|---|---|---|---|---|---|---|
| Tast/DME | 2–10 | 1st | 7.33 | –2.28 | 0.9889 | 2 |
| | | 2nd | 6.77 | 0.77 | 0.9567 | 2 |
| | | 1st+2nd | 15.10 | 6.59 | 0.9886 | 2 |
| DPP/DME | 2–10 | 1st | 23.31 | –12.71 | 0.9988 | |
| | | 2nd | 9.49 | –6.21 | 0.9960 | |
| | 0.2–1.0 | 1st | 21.46 | 0.26 | 0.9933 | 0.1 |
| | | 2nd | 8.99 | –0.82 | 0.9741 | |
| DPV/HMDE | 2–10 | 1st | 15.98 | –4.12 | 0.9735 | |
| | | 2nd | 6.40 | –8.48 | 0.9886 | |
| | 0.2–1.0 | 1st | 15.42 | 0.00 | 0.9985 | 0.1 |
| | | 2nd | 5.20 | –0.20 | 0.9703 | |
| AdSV/HMDE[b] | 0.02–0.1 | 1st | 138.00 | 0.36 | 0.9967 | 0.02 |
| | | 2nd | 111.95 | –0.18 | 0.9972 | |

[a] Limit of determination. [b] $t_{acc}$ = 30 s, $E_{acc}$ = –0.25 V.

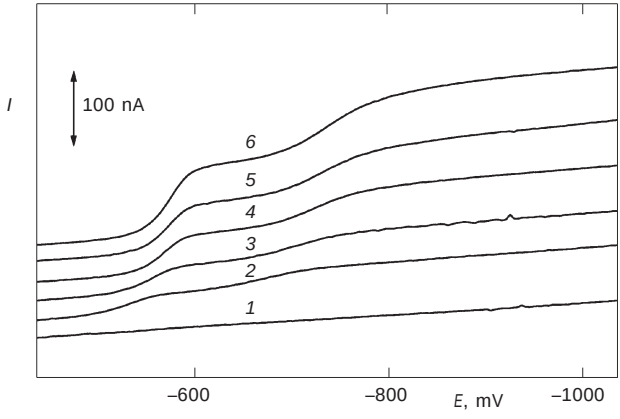


FIG. 5

DC tast polarograms of 1,5-dinitronaphthalene in 0.01 M NaOH–methanol (1:1) medium (pH 11.6). Analyte concentration: 0 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*) and 10 (*6*) × 10$^{-6}$ mol l$^{-1}$

the AdSV determination of 1,5-dinitronaphthalene, we have tried to work in the absence of methanol, which was used for solubility reasons for polarographic and voltammetric determinations. Therefore, 1 l of a $1 \times 10^{-6}$ M stock solution of 1,5-dinitronaphthalene free of methanol was prepared in deionized water by long time stirring of the precisely weighed amount of the substance for two week period.

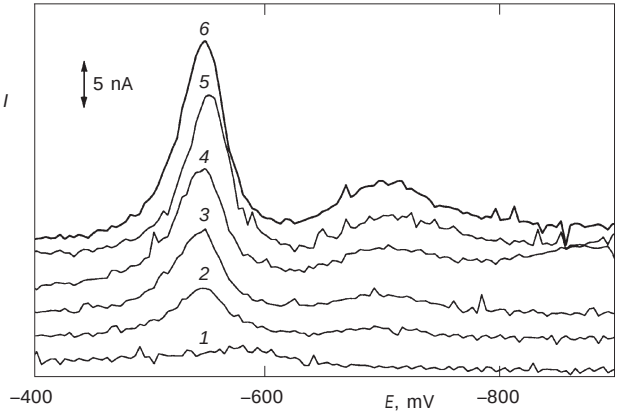


FIG. 6
DP polarograms of 1,5-dinitronaphthalene in 0.01 M NaOH–methanol (1:1) medium (pH 12.2). Analyte concentration: 0 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*) and 10 (*6*) × $10^{-7}$ mol $l^{-1}$

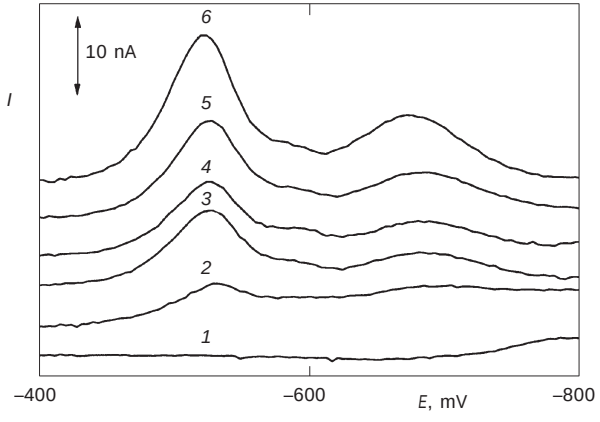


FIG. 7
DP voltammograms of 1,5-dinitronaphthalene in 0.01 M NaOH–methanol (1:1) medium (pH 12.2). Analyte concentration: 0 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*) and 10 (*6*) × $10^{-7}$ mol $l^{-1}$

Optimization of the accumulation time was carried out with a concentration of $2 \times 10^{-8}$ mol $l^{-1}$ using $t_{acc}$ from 0 to 300 s. The highest peak was obtained with $t_{acc}$ = 30 s, the following decrease being probably associated with the passivation of the electrode surface. The influence of accumulation potential was investigated at $E_{acc}$ from –0.15 to –0.40 V. The highest and best developed peaks were obtained at $E_{acc}$ = –0.25 V, so that this value was chosen for measuring calibration dependences in the range of (2–10) × $10^{-8}$ mol $l^{-1}$. Figure 8 shows adsorptive stripping voltammograms of 1,5-dinitronaphthalene in this concentration range. The parameters of the thus obtained calibration line are given in Table I.

*Cyclic Voltammetry*

Cyclic voltammograms of 1,5-dinitronaphthalene ($c = 1 \times 10^{-5}$ mol $l^{-1}$) at HMDE were measured in a mixed medium methanol–0.01 M NaOH (1:1) and in the Britton–Robinson buffer pH 2 and methanol (1:1) medium of pH 2.3 at scan rates from 1000 to 5 mV $s^{-1}$. The cyclic voltammograms of 1,5-dinitronaphthalene at acid pH (Fig. 9) and alkaline pH (Fig. 10) are shown. The scan was reversed just before the onset of the background electrolyte decomposition current, immediately after second peak and immediately after first peak.

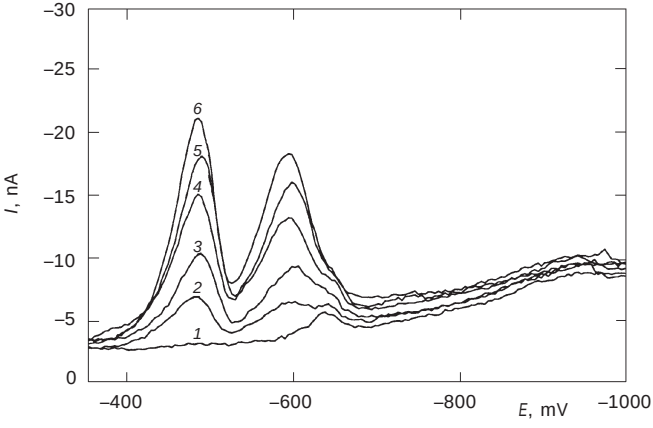


FIG. 8
Adsorptive stripping voltammograms of 1,5-dinitronaphthalene in 0.01 M NaOH (pH 12.4), $t_{acc}$ = 30 s, $E_{acc}$= –0.25 V. Analyte concentration: 0 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*) and 10 (*6*) × $10^{-8}$ mol $l^{-1}$

It can be seen that at low pH neither of the peaks corresponds to a reversible process while at high pH there are signs of quasi-reversible character of some processes. The observed linear dependence of peak currents on the square root of the scan rate confirms the diffusion control of the observed processes.

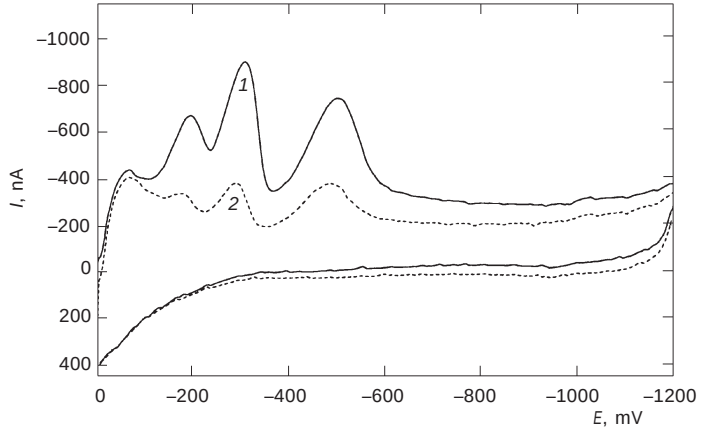


FIG. 9

Cyclic voltammograms of 1,5-dinitronaphthalene ($c$ = 1 × $10^{-5}$ mol $l^{-1}$) in methanol and Britton–Robinson buffer pH 2 (1:1) mixture, pH of the mixture 2.3, scan rate 1000 mV $s^{-1}$. First (*1*) and second (*2*) scan in the potential window from 0 to –1.2 V

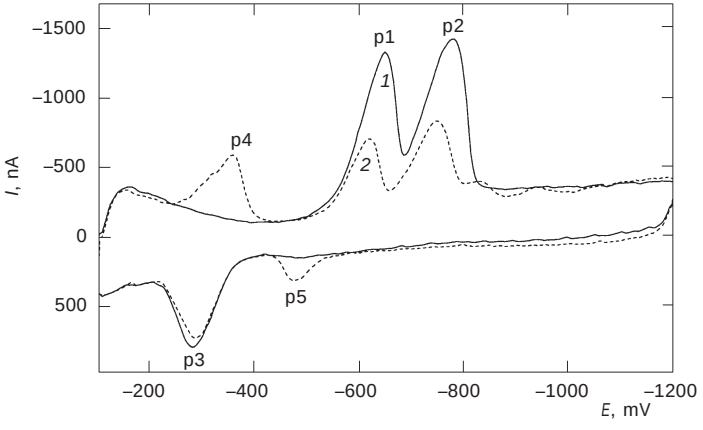


FIG. 10

Cyclic voltammograms of 1,5-dinitronaphthalene ($c$ = 1 × $10^{-5}$ mol $l^{-1}$) in 0.01 M NaOH–methanol (1:1) mixture, pH of the mixture 12.2, scan rate 1000 mV $s^{-1}$. First (*1*) and second (*2*) scan in the potential window from –0.1 to –1.2 V

*Mechanism of Polarographic Reduction of 1,5-Dinitronaphthalene*

Boyd and Reidlinger[15], who studied the polarographic reduction of 1,5-dinitronaphthalene ($1 \times 10^{-5}$ mol $l^{-1}$) in 80% ethanol at pH 2.1, 6.4, 9.4, and 11.0 found at pH 2.1 one eight-electron wave followed by a four-electron wave, while three consecutive four-electron waves were found at pH 6.4 and two four-electron waves at pH 9.4 and 11.0. Our findings in 50% methanol are different. We can clearly identify three consecutive four-electron waves at pH < 8.7 and only two subsequent four-electron waves at pH > 8.7. On the basis of analogy with polarographic reduction of various dinitrobenzenes[9], we assume that in the acid region 1,5-dinitronaphthalene is reduced in three irreversible four-electron steps according to scheme in Fig. 4. This assumption is confirmed by the cyclic voltammogram at scan rate 1000 mV $s^{-1}$ (see Fig. 9). The separation of the 1st and 2nd wave or peak can be explained by the fact that first $NO_2$ group is reduced in the presence of second $NO_2$ group with the pronounced –M effect which decreases the electron density in the region of the first $NO_2$ group thus making its reduction easier. The second $NO_2$ group is reduced in the presence of NHOH (in alkaline media) or $-NH_2^+OH$ group (in acidic media). The NHOH group with the +M effect increases the electron density in the region of the second $NO_2$ group thus making its polarographic reduction more difficult. This assumption is in agreement with the observed fact that the separation of the 1st and 2nd wave is better in alkaline than in acid region. Protonated $NH_2^+OH$ group withdraws electrons from the second group thus making its reduction easier, i.e. shifts its half-wave potential closer to the first wave. The observed linear dependence of peak currents on the square root of the scan rate confirms the diffusion control of the observed processes. In alkaline region, the 3rd wave disappears which is in agreement with the well-known fact that unprotonated aromatic hydroxyamino compounds are not polarographically reducible. (Protonation of the hydroxyamino groups decreases the electron density resulting in easier acceptance of an electron from the electrode.) In alkaline region only two four-electron steps corresponding to the reduction of $NO_2$ group to NHOH group are observed. On a cyclic voltammogram measured at 1000 mV $s^{-1}$ in alkaline medium (see Fig. 10), first peak (p1) and second peak (p2) in the first cathodic scan correspond to the reduction of first and second nitro group. First anodic peak (p3), the height of which is nearly equal to the height of four-electron cathodic peaks (p1 and p2) can be assigned to a four-electron oxidation of 1,5-bis(hydroxyamino)naphthalene to 1,5-dinitrosonaphthalene (Fig. 11). The cathodic peak (p4) was observed in second cathodic scan around

–350 mV, which is in agreement with the well-known reversibility of NO/NHOH system.

Constant potential coulometry on mercury pool electrode was used to confirm the number of electrons exchanged in the electrode reaction. Electrolysis of 1,5-dinitronaphthalene was carried out in a coulometric cell described earlier[20]. Voltammetric curves at a mercury pool electrode were measured at pH 2.9 and 12.2 in stirred solution (Fig. 12). The constant potential –0.8 V at pH 2.9 and –1.4 V vs saturated calomel electrode (SCEl) at pH 12.2 was chosen for the electrolysis. Electrolysis of 1,5-dinitronaphthalene ($c$ = 1.67 × $10^{-4}$ mol $l^{-1}$) at pH 2.9 and 12.2 gives 11.81 and 8.06 electrons per molecule, respectively. The electrolytic current dependences on the electrolysis time at constant potential are depicted in

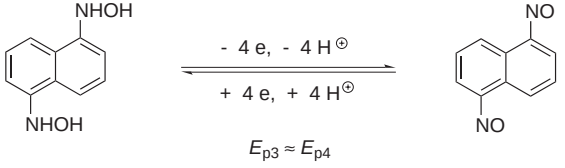


FIG. 11
Reversible oxidation of 1,5-bis(hydroxyamino)naphthalene

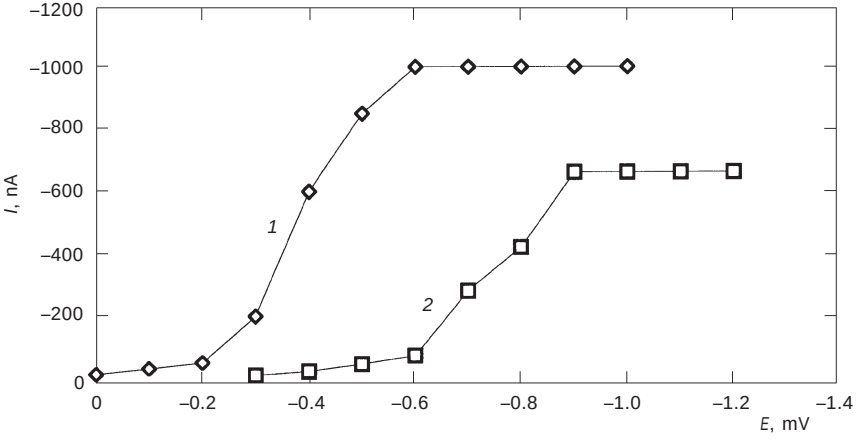


FIG. 12
Voltammetric curves of 1,5-dinitronaphthalene ($c$ = 1.57 × $10^{-5}$ mol $l^{-1}$) in Britton–Robinson buffer and methanol (1:1) medium at pH 2.9 (*1*) and 12.2 (*2*) at mercury pool electrode in stirred solution

Figs 13 and 14, respectively. These findings are in agreement with our assumption that nitro groups of 1,5-dinitronaphthalene are reduced with 12 electrons to diamine at low pH and with 8 electrons to bis(hydroxylamine) at high pH.

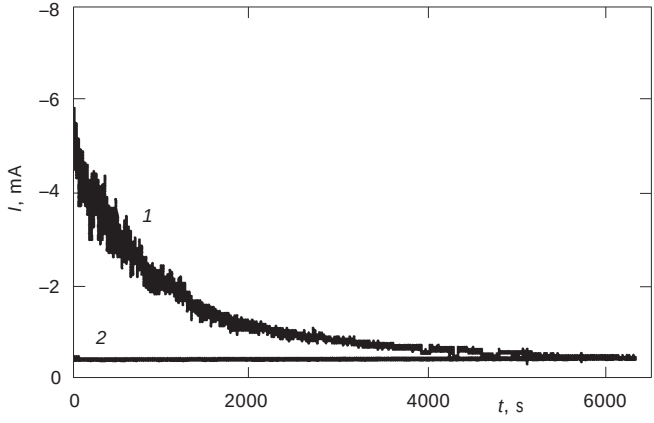


FIG. 13
Electrolysis of 1,5-dinitronaphthalene ($c = 1.67 \times 10^{-4}$ mol $l^{-1}$) in Britton–Robinson buffer and methanol (1:1) medium at pH 2.9 (*1*) and of supporting electrolyte (*2*) at constant potential –0.8 V vs SCE

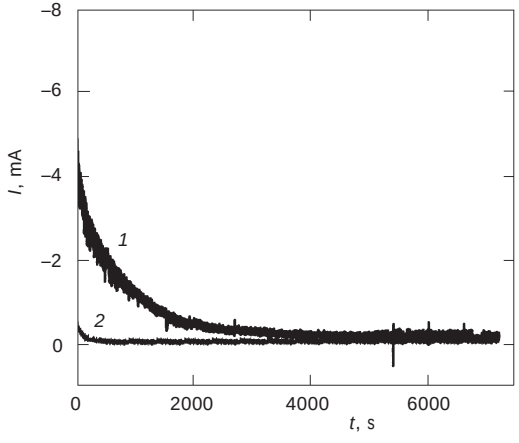


FIG. 14
Electrolysis of 1,5-dinitronaphthalene ($c = 1.67 \times 10^{-4}$ mol $l^{-1}$) in Britton–Robinson buffer and methanol (1:1) medium at pH 12.2 (*1*) and of supporting electrolyte (*2*) at constant potential –1.4 V vs SCE

Tast polarography at DME with different mercury reservoir heights (Fig. 15) confirmed that the limiting current is diffusion-controlled.

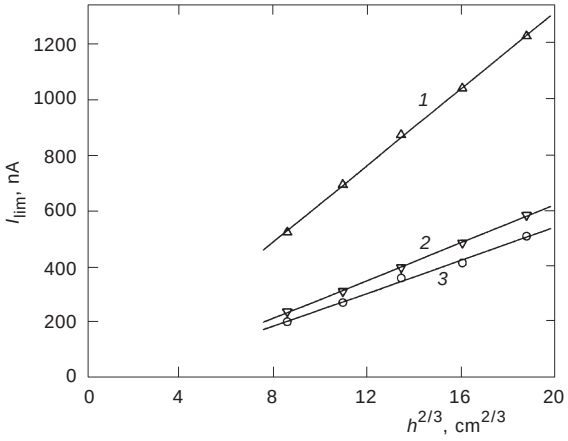


FIG. 15

The dependence of the limiting current ($I_{lim}$) of 1,5-dinitronaphthalene ($c = 1 \times 10^{-5}$ mol $l^{-1}$) on the mercury reservoir height ($h^{2/3}$) measured by tast polarography at DME in Britton–Robinson buffer and methanol (1:1) medium at pH 12. Total (*1*), first- (*2*) and second-wave limiting current (*3*)

## *Conclusions*

It has been proved that modern polarographic and voltammetric techniques are suitable for the determination of submicromolar concentrations of genotoxic 1,5-dinitronaphthalene. The sensitivity and the selectivity of this determination can be further increased by their combination with a preliminary separation and preconcentration using liquid-liquid or solid phase extraction[11].

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