POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF N,N'-DINITROSOPIPERAZINE*

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Polarographic reduction of the genotoxic N,N'-dinitrosopiperazine was studied and its mechanism was suggested. Optimum conditions were established for the determination of this substance by tast polarography over the concentration region of $1 . 10^{-3}$ to $1 . 10^{-6}$ mol l^{-1} and by differential pulse polarography on the conventional dropping mercury electrode or by fast scan differential pulse voltammetry and linear sweep voltammetry on a hanging mercury drop electrode over the concentration region of $1 . 10^{-3}$ to $1 . 10^{-7}$ mol l^{-1}. Attempts at increasing further the sensitivity via adsorptive accumulation of the analyte on the surface of the hanging mercury drop failed. The methods are applicable to the testing of the chemical efficiency of destruction of the title chemical carcinogen based on its oxidation with potassium permanganate in acid solution.

N,N'-Dinitrosopiperazine, along with a number of other heterocyclic nitrosamines, is among suspect chemical carcinogens[1-5]. Although not industrially produced, these substances frequently occur in trace concentrations in various components of the working and living environment and in tobacco products and foods because they arise readily from nitrosation of the corresponding secondary amines[3,4]. Attention has been therefore paid not only to the analysis of the substances[6] but also to their chemical destruction[7]. For biological or toxicological investigation, N,N'-dinitrosopiperazine in diverse matrices has been determined mainly by gas[6,7], thin layer[8] or high performance liquid[9] chromatography. Gas chromatography, which may use the TEA detector[7], has been recommended as the technique of choice for testing the chemical efficiency of destruction of this substance in laboratory waste, although this technique is rather time consuming and instrumentation and technically demanding. Since N-nitrosocompounds are readily reduced polarographically[10], attention is paid in this paper to the determination of N,N'-dinitrosopiperazine by modern polarographic methods, viz. tast polarography and differential pulse polarography (DPP) on the conventional dropping mercury electrode (DME), fast scan differential pulse voltammetry (FS DPV), and linear sweep voltammetry (LSV) on

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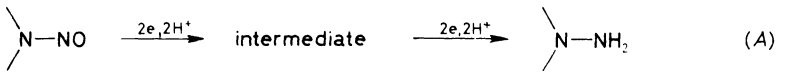
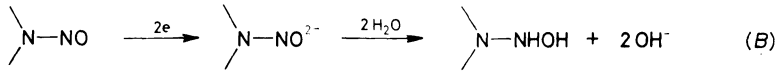
a hanging mercury drop electrode (HMDE), which have proved to suit well to the testing of the chemical efficiency of destruction of some antitumour drugs derived from N-nitrosourea[11] and to the quantitation of a number of heterocyclic N-nitrosamines (N-nitrosopyrrolidine, N-nitrosopiperidine, N-nitrosomorpholine and N--nitrosoproline) in the blood plasma of laboratory rats[2,12,13].

As to the mechanism of polarographic reduction of N-nitrosamines derived from saturated nitrogen heterocycles, it has been observed[14–18] that in acid solutions (pH < 5), irreversible four-electron reduction occurs in a single wave whose half--wave potential is pH-dependent, which is explained in terms of Scheme *A*:



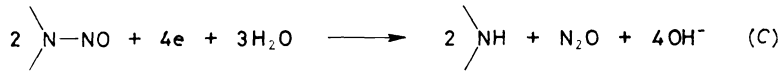
(*A*)

The nature of the intermediate product usually is not specified, only Holleck and Schindler[16] suggest that it is >N—NHOH. This mechanism has been corroborated by isolation of the corresponding hydrazines after preparative electrolysis[18]. The p*K* values of the nitrosamines suggest[17] that at pH 2–14 they are present in solution as the neutral molecules; this is also confirmed by their extractability, e.g., into dichloromethane[19]. Thus it can be assumed that, as in the case of dipropyl-N-nitrosamine[20], also in the case of N-nitroso derivatives of saturated nitrogen heterocycles at pH < 5 the electroactive substance diffuses first to the drop surface, where it adsorbs. Only then it is protonated, and the reduction follows. The height of the wave drops at pH > 6 and vanishes altogether at pH ≈ 8. At the same time, a new wave appears at pH > 6; its half-wave potential is nearly pH-independent and its height is about one-half that of the acid-medium wave. Holleck and Schindler[16] attribute this wave to the two-electron reduction according to Scheme *B*:



(*B*)

However, Zahradník and coworkers[17] failed to identify the hydroxylamine derivative after preparative electrochemical reduction, and thus it is more likely that the reduction follows the pathway *C* suggested by Lund[15], which for N-nitrosomorpholine has been proved by detecting N_2O and morpholine in preparative electrolysis:



(*C*)

An analogous mechanism is assumed for N-nitrosopiperidine[19]. The mechanism of polarographic reduction of N,N'-dinitrosopiperazine has not been investigated,

and therefore this problem is studied in the present work, attention being paid to the possible mutual influencing of the two nitroso groups in the molecule.

EXPERIMENTAL

Chemicals

Stock solution of N,N′-dinitrosopiperazine, $c = 1 . 10^{-2}$ mol l^{-1}, was prepared by diluting the pure chemical (Research Institute of Organic Synthesis, Pardubice-Rybitví) in redistilled water. Working solutions were obtained by dilution. All solutions of the analyte were stored in darkness. The other chemicals used were or reagent grade purity (Lachema, Brno). Water was distilled twice in a quartz still.

Apparatus

Polarographic and voltammetric measurements were performed on a PA 3 polarographic analyzer interfaced to an XY-4105 recorder (both Laboratorní přístroje, Prague). The three-electrode connection was applied, using a saturated calomel reference electrode and a platinum sheet auxiliary electrode. Thus, all potentials are given relative to SCE. Unless stated otherwise, the polarization rate for the conventional dropping mercury electrode (i.e. in the DC, tast, and DPP techniques) was 5 mV s^{-1}, the electronically controlled drop time in the tast and DPP measurements was 1 s, mercury reservoir height 36 cm and modulation amplitude in DPP was −100 mV. The parameters of the DME were as follows: mercury flow rate $m = 1{\cdot}53$ mg s^{-1}, drop time $\tau = 3{\cdot}91$ s (in 0·1M-KCl at the applied voltage of 0 V). An SMDE 1 static mercury drop electrode (Laboratorní přístroje, Prague) connected as a hanging mercury drop electrode served as the working electrode in the cyclic voltammetry, LSV and FS DPV measurements. The capillary diameter was 0·136 mm. The polarization rate was 20 mV s^{-1}, maximum drop size determined by the valve opening for 160 ms and modulation amplitude in FS DPV −100 mV unless stated otherwise.

Coulometric measurements were performed with an OH 404 coulcmetric analyzer (Radelkis, Budapest) in a 200 ml all-glass vessel whose cathode and anode compartments were separated by a frit. A mercury pool anode, a saturated calomel reference electrode and a platinum sheet auxiliary electrode were used. During the measurement, the solution was stirred with a magnetic stirrer; inert atmosphere was provided by constant nitrogen feed.

Spectrophotometric measurements were carried out on a Unicam SP-800 instrument (Cambridge, U.K.) using 1 cm quartz cells.

All measurements proceeded at room temperature.

Procedures

Calibration curves were measured in triplicate and evaluated by linear regression using the least squares method. The limit of determination over the range of $(1-10) . 10^{-x}$ mol l^{-1} was calculated[21] as the tenfold standard deviation of the analyte determination at a concentration of $2 . 10^{-x}$ mol l^{-1}.

The procedure for determining the number of exchanged electrons by constant potential coulometry was as described previously[22], only 90 ml of the Britton-Robinson buffer were pipetted into the coulometric vessel, and 10·00 ml of N,N′-dinitrosopiperazine solution, $c = 1 . . 10^{-3}$ mol l^{-1}, were added after the preelectrolysis.

For the polarographic detection of coulometric reduction products, 75 ml of hydrochloric acid, $c = 1{\cdot}33 \cdot 10^{-3}$ mol l^{-1}, were pipetted into the coulometric vessel, and after nitrogen purging, preelectrolysis at a constant potential of −1 150 mV, and adjustment of the parameters of the circuit for automatic residual current compensation, 25 ml of N,N'-dinitrosopiperazine solution, $c = 1 \cdot 10^{-3}$ mol l^{-1}, were added. After terminating the electrolysis, 5·00 ml of the solution in the coulometric vessel were pipetted into a 25 ml volumetric flask and diluted to the mark with a solution containing 20 g of Na_2SO_3 and 9 g of KOH in a litre of water, and the tast polarogram was recorded over the region of −0·9 to −0·2 V. A blank experiment with 5 ml of the supporting electrolyte alone after the coulometric reduction and an experiment with 5 ml of piperazine solution, $c = 2{\cdot}5 \cdot 10^{-4}$ mol l^{-1}, in hydrochloric acid, $c = 1 \cdot 10^{-3}$ mol l^{-1}, were performed in parallel.

For detecting the coulometric reduction product by colour reaction with ninhydrin, the 95 ml of solution after the coulometric reduction which remained after taking the aliquot for polarographic detection were evaporated to dryness in a rotary vacuum evaporator, and to the residue were added 5 ml of 0·1% aqueous solution of ninhydrin. A blank experiment was performed in parallel using 95 ml of piperazine solution, $c = 2{\cdot}5 \cdot 10^{-4}$ mol l^{-1}, in hydrochloric acid, $c = 1 \cdot 10^{-3}$ mol l^{-1}.

When applying FS DPV to the testing of the chemical efficiency of chemical destruction of N,N'-dinitrosopiperazine with potassium permanganate[7], 5 ml of 0·3M-$KMnO_4$ in 3M-H_2SO_4 were added to one ml of aqueous solution of the substance ($c = 1 \cdot 10^{-3}$ mol l^{-1}), and the solution was stirred with a magnetic stirrer for 12 h. Thereafter the unreacted permanganate was reduced with an addition of 5 ml of aqueous solution of oxalic acid, $c = 1$ mol l^{-1}, and the whole was extracted with 10 ml of dichloromethane. The extract was evaporated to dryness in a rotary vacuum evaporator at room temperature, the residue was dissolved in 10 ml of Britton–Robinson buffer at pH 2·4, and its voltammogram was recorded. Additional four solutions to which 5, 10, 20 and 30 μl, respectively, of N,N'-dinitrosopiperazine solution, $c = 1 \cdot 10^{-3}$ mol . l^{-1}, had been added after the destruction and removal of the unreacted permanganate, were treated likewise.

RESULTS AND DISCUSSION

Investigation of the Mechanism of Polarographic Reduction of N,N'-*Dinitrosopiperazine*

The effect of pH on the behaviour of the substance during tast and DP polarography at the DME was first examined. The results are given in Table I. Over the pH 2–13 range, the substance exhibits a single wave or peak, which indicates that, owing to their separation by the alicyclic ring, the two nitroso groups do not affect each other and they are both reduced at the same potential. This is borne out by the coulometrically established number of exchanged electrons (see later) and by the fact that at pH 2,4 the N,N'-dinitrosopiperazine wave is roughly twice as high as the N-nitroso-N-methylaniline wave measured under the same conditions. The observed shift of $E_{1/2}$ (or E_p) to more negative values with increasing pH can be explained by the preceding protonation of the substance. Over the pH 2–5 range, the potentials obey the relations $E_{1/2}(\text{mV}) = -680 - 75{\cdot}4\,\text{pH}$ (correlation coefficient 0·9936)

and $E_p(mV) = -618 - 82{\cdot}5\,pH$ (correlation coefficient 0·9911), the wave or peak height decreasing slightly with increasing pH. The slope of the dependence of $E_{1/2}$ on pH is somewhat higher than as found by Holleck and Schindler[16] for N-nitrosopiperidine, which will be related with the presence of two nitroso groups in the substance studied by us. A comparison of the logarithmic analysis slope and the slope of the dependence of $E_{1/2}$ on pH indicates that the process involved is no simple irreversible process. It can be assumed that, as with other N-nitroso compounds[10], molecules of the substance diffuse first to the electrode surface, are adsorbed, and only in the adsorbed form the protonation occurs, followed by electron transfer. This concept is borne out by the fact observed by us, viz. that from a solution at pH 2·40, N,N'-dinitrosopiperazine is easily extracted into dichloromethane (extraction recovery is 86%), which gives evidence of the presence of unprotonated molecules of the substance in this solution. According to Zahradník and coworkers[17], the occurrence of the absorption maximum at 341 nm (ε = 180 l . . mol^{-1} cm^{-1}) in 0·001M to 1M-HCl also indicates the presence of the unprotonated nitroso group. At pH about 7, the pH-dependent wave or peak vanishes and a new wave or peak appears; its position is nearly pH-independent. The wave or peak height decreases gradually with increasing pH to reach a value which is roughly one-half of the height of the former wave at pH 2–4.

TABLE I

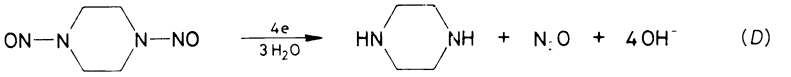
Effect of pH on tast and DP polarographic curves of N,N'-dinitrosopiperazine ($c = 5 . 10^{-5}$ mol . . l^{-1})

pH	$E_{1/2}$ mV	I_{lim} μA	Slope[a] mV	E_p mV	I_p μA
2·10	−845	1·00	85·5	−800	1·42
2·42	−865	1·03	84·4	−820	1·48
3·20	−915	1·03	83·0	−875	1·38
3·75	−950	1·00	103·1	−910	1·17
4·84	−1 055	0·88	114·8	−1 030	0·74
5·83	−1 215	0·69	131·7	−1 205	0·46
6·87	−1 350	0·82	90·1	−1 330	0·98
7·90	−1 375	0·80	73·7	−1 340	1·06
8·72	−1 385	0·70	72·5	−1 350	0·99
9·88	−1 420	0·62	95·0	−1 390	0·71
10·93	−1 430	0·55	99·0	−1 405	0·57
11·62	−1 425	0·55	107·0	−1 405	0·56
12·93	−1 390	0·57	98·0	−1 365	0·54

[a] Logarithmic analysis slope.

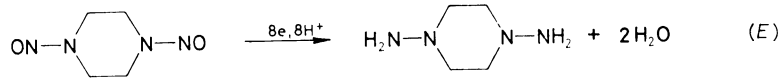
As found by tast polarography, the $I_{lim}/(m^{2/3}\tau^{1/6})$ value at a given pH (pH 2·42, 6·87 or 10·93) is constant at mercury flow rates m varied over the region of 1–3·5 mg . s^{-1} and electronically controlled drop time varied over the region of 1–4 s; this indicates the diffusion nature of the recorded limiting current. This is also confirmed by the linear shape of the dependence of the DC polarography wave height on the square root of mercury reservoir height. The plots passed through the origin at pH 2·42, 5·83, 7·90 as well as 10·93. Hence, in contrast to the case of di-n-propyl-N-nitrosamine[20], no kinetic control of the observed limiting current exists in our case at any pH.

Potentiostatic coulometry on a mercury pool cathode revealed that 8 electrons are exchanged at pH 2·4 and applied potential −1 150 mV, whereas 4 electrons are exchanged at pH 10·1 and applied potential −1 650 mV. From spectrophotometric and tast polarographic examination of the coulometric reduction at pH 10·1 and applied potential −1 650 mV it follows that under these conditions, reduction of the chromophor gives rise to a product which is polarographically inactive over the entire accessible potential region. The plot of the absorbance or tast wave height in dependence on the charge passed is linear and intersects the horizontal axis at the theoretically expected value. The four-electron reduction thus can be assumed to follow the path shown in Scheme *D*,



(*D*)

In contrast to this, at pH 2·4 and applied potential −1 150 mV the dependences of the absorbance at 239 nm and of the tast wave height on the passed charge are not linear, which suggests that some interaction of the nitroso group with the products or intermediates of its coulometric reduction is involved. The final product of this reduction, however, is N,N′-diaminopiperazine (see Scheme *E*), which was detected via occurrence of yellow colour in the reaction with ninhydrin and also polarographically, an anodic wave appearing in the presence of hydrogen sulfite[23]. The observed anodic wave at a potential near −0·4 V (Fig. 1) is an evidence of the presence of the $>N—NH_2$ group in the coulometric reduction product. Reference solution obtained by mixing 5 ml of piperazine solution, $c = 2{\cdot}5 \cdot 10^{-4}$ mol l^{-1}, and 20 ml of supporting electrolyte gave the same tast polarographic curve as the supporting electrolyte alone.



(*E*)

Cyclic voltammetry of N,N′-dinitrosopiperazine on a hanging mercury drop electrode (Fig. 2) revealed that the process is irreversible irrespective of the pH. Over the 2–50 mV s^{-1} range the dependence of the cathodic peak height on the square

root of polarization rate is linear, which confirms that the process is irreversible, diffusion-controlled one. A hint of another peak appears in alkaline solutions (Fig. 2*b*), which is apparently associated with the multistep mechanism of the reduction.

Analytical Application of the Polarographic Reduction of N,N′-*Dinitrosopiperazine*

First, the stability of the stock solutions of N,N′-dinitrosopiperazine in redistilled water was examined by measuring their absorbance at 239 nm, where the substance exhibits a maximum ($\varepsilon = 1{\cdot}462 \cdot 10^4$ l mol^{-1} cm^{-1}). For the solution of a concentration of $1 \cdot 10^{-4}$ mol l^{-1}, the absorbance decrease was 0·1%, 0·2%, 0·9%, 1·8% and 2·7% in 20, 30, 40, 50 and 60 days, respectively. Hence, stored in darkness, the solution is sufficiently stable for at least one month. Solutions with $c = 1 \cdot 10^{-5}$ mol l^{-1} were prepared weekly and more dilute solutions, daily.

Stability of solutions of the analyte in polarographic medium, i.e. in the Britton–Robinson buffer at pH 2·4, was examined by FS DPV on HMDE. Table II demonstrates that for dilute solutions, the polarographic trace should be recorded as soon as possible.

Tast and differential pulse polarography on conventional dropping mercury electrode. The highest and best developed waves or peaks were obtained in acid

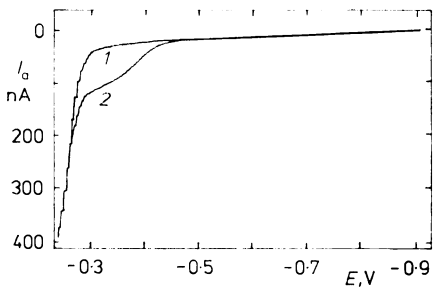


FIG. 1

Tast polarographic detection of N,N′-diaminopiperazine in the coulometric reduction of N,N′-dinitrosopiperazine at a constant potential of −1 150 mV in a solution at pH 2·9. *1* Supporting electrolyte (20 g of Na_2SO_3 + 9 g of KOH in a litre); 2 5 ml of solution after coulometric reduction of N,N′-dinitrosopiperazine + 20 ml of supporting electrolyte. Recording from −0·9 V towards −0·3 V

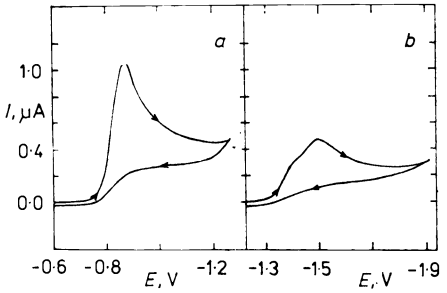


FIG. 2

Cyclic voltammogram of N,N′-dinitrosopiperazine ($c = 5 \cdot 10^{-5}$ mol l^{-1}). Polarization rate 50 mV s^{-1}, pH 2·41 (*a*) and pH 10·93 (*b*)

solutions (Figs 3 and 4). The dependences of the wave or peak heights on the analyte concentration in the Britton–Robinson buffer at pH 2·4 are linear over the regions of $1 . 10^{-3}$ to $1 . 10^{-6}$ and $1 . 10^{-3}$ to $1 . 10^{-7}$ mol l^{-1} for tast polarography and DPP, respectively. The calculated calibration curve parameters and limits of determination are given in Table III.

Fast scan differential pulse voltammetry and linear sweep voltammetry on a hanging mercury drop electrode. The potentials and peak heights in dependence on pH are given in Table IV, demonstrating that the dependences are of the same nature as those in tast polarography and DPP.

The highest and best-evaluable peaks were obtained in solution at pH 2·4. The dependences of the peak height on the analyte concentration were therefore measured at this pH, and linear plots were obtained across the concentration region of $1 . 10^{-5}$

TABLE II
Stability of polarographed solutions of N,N'-dinitrosopiperazine

c mol l^{-1}	Relative concentration[a] (%) in time (min)						
	0	10	20	30	40	50	60
$5 . 10^{-5}$	100	100	100	100	100	100	100
$5 . 10^{-6}$	100	100	100	100	100	97	97
$5 . 10^{-7}$	100	100	98	93	86	76	67

[a] With respect to the concentration of fresh solution.

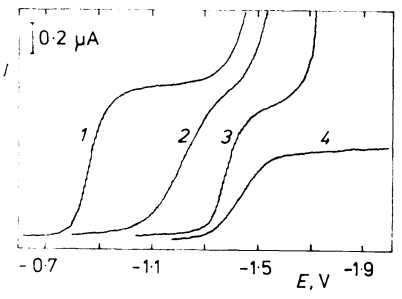


FIG. 3
Tast polarograms of N,N'-dinitrosopiperazine ($c = 5 . 10^{-5}$ mol l^{-1}). pH: *1* 2·42, *2* 5·83, *3* 7·90, *4* 10·93

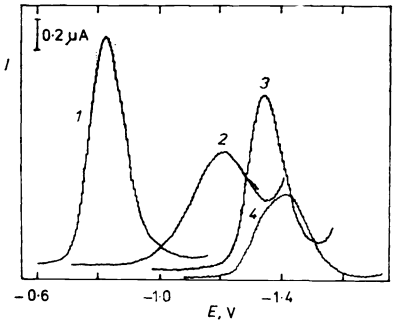


FIG. 4
DP polarograms of N,N'-dinitrosopiperazine ($c = 5 . 10^{-5}$ mol l^{-1}). pH: *1* 2·42, *2* 5·83, *3* 7·90, *4* 10·93

TABLE III

Calibration curve parameters and limits of determination of N,N′-dinitrosopiperazine

Method	c mol l^{-1}	Slope mA l mol^{-1}	Intercept nA	r^a	$L_Q{}^b$ mol l^{-1}
TAST	$(1-10) . 10^{-4}$	21·7	−40	0·9999	—
	$(1-10) . 10^{-5}$	21·3	9	0·9997	—
	$(1-10) . 10^{-6}$	20·5	−1	0·9994	$0·6 . 10^{-6}$
DPP	$(1-10) . 10^{-4}$	29·2	55	0·9995	—
	$(1-10) . 10^{-5}$	30·2	−4	0·9992	—
	$(1-10) . 10^{-6}$	30·9	−5	0·9990	—
	$(1-10) . 10^{-7}$	34·4	−2	0·9988	$0·8 . 10^{-7}$
FS DPV	$(1-10) . 10^{-6}$	18·9	−14	0·9992	—
	$(1-10) . 10^{-7}$	18·0	−1	0·9990	$0·7 . 10^{-7}$
LSV	$(1-10) . 10^{-6}$	10·9	−7	0·9994	—
	$(1-10) . 10^{-7}$	11·0	−1	0·9938	$1·6 . 10^{-7}$

[a] Correlation coefficient; [b] limit of determination.

TABLE IV

Effect of pH on FS DPV and LSV peak potentials (E_p) and heights (I_p) for N,N′-dinitrosopiperazine ($c = 5 . 10^{-5}$ mol l^{-1})

pH	FS DPV		LSV	
	E_p mV	I_p μA	E_p mV	I_p μA
2·10	−780	0·88	−855	0·52
2·42	−795	0·92	−870	0·57
3·20	−850	0·89	−920	0·55
3·75	−885	0·78	−955	0·48
4·84	−995	0·53	−1 075	0·33
5·80	−1 165	0·33	−1 235	0·21
6·87	−1 295	0·52	−1 370	0·28
7·90	−1 305	0·67	−1 375	0·40
8·72	−1 315	0·62	−1 385	0·40
9·88	−1 360	0·47	−1 435	0·30
10·93[a]	−1 380	0·36	−1 465	0·24
11·62[a]	−1 380	0·30	−1 465	0·24
12·93[a]	−1 340	0·34	−1 430	0·22

[a] A hint of another peak appears at a potential around −1 300 mV.

to $1 . 10^{-7}$ mol l^{-1}. Their parameters, along with the limits of determination, are given in Table III.

Attempts at increasing the sensitivity of determination by means of adsorptive accumulation of analyte on the HMDE surface failed; the FS DPV or LSV peak height was independent of the time elapsed between the formation of the mercury drop and the trace recording. In terms of the assumed reduction mechanism, involving protonation of the substance only adsorbed on the electrode surface, this fact can be explained by a rapid establishment of the adsorption equilibrium. The amount of the adsorbed substance, and hence the analytical signal, reaches its maximum already in the time between the formation of the drop and the attaining of the potential of the peak in the immediate voltammetric curve recording. Thus, extension of the time from the drop formation to the start of the record does not result in any peak increase irrespective of the pH or methanol content of the solvent. No peak increase caused by adsorptive accumulation could be achieved even in completely nonaqueous medium such as dimethylformamide with tetramethylammonium iodide as the supporting electrolyte.

Testing the Chemical Efficiency of Destruction of N,N'-Dinitrosopiperazine with Potassium Permanganate

Practical value of the new analytical methods is documented by the applicability of FS DPV on a HMDE to the testing of the efficiency of destruction of N,N'-dinitrosopiperazine with potassium permanganate according to Castegnaro and coworkers[7]. Direct FS DPV determination of the unreacted N,N'-dinitrosopiperazine in the solution after the destruction is impracticable due to the interference of the destruction products and unfavourable shape of the FS DPV curve of the strongly acid solution containing also Mn(II) ions in a high concentration. The analyte was therefore first separated by extraction into dichloromethane; blank experiments verified that the calibration dependences thus obtained are linear across the region

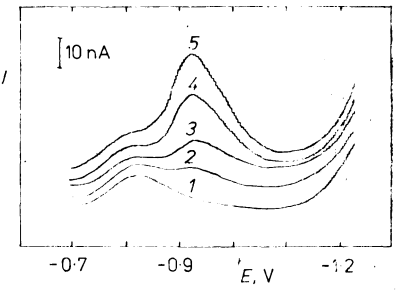


FIG. 5

Application of FS DPV to the testing of efficiency of chemical destruction of N,N'-dinitrosopiperazine with permanganate. *1* Voltammogram corresponding to the solution after destruction; *2*—*5* voltammograms corresponding to the solution to which 0·5% (*2*), 1% (*3*), 2% (*4*) and 3% (*5*) of the initial amount of analyte were added after the destruction

of $(5-50) \cdot 10^{-7}$ mol l^{-1} and their slopes are only slightly lower than those of the dependences obtained by pipetting the same quantities of analyte directly into the supporting electrolyte (the decrease is apparently associated with the effect of trace impurities in the dichloromethane on the reversibility of reduction of N,N'-dinitrosopiperazine). Figure 5 shows voltammograms of a solution obtained by dissolving the evaporation residue of the dichloromethane extract after the destruction and of solutions to which, after the destruction and removal of unreacted permanganate, the analyte was added in a quantity corresponding to 0·5 – 3% of the initially present amount. The traces demonstrate that FS DPV is capable of detecting as little as 0·5% of the initial amount of the substance to be destructed (Fig. 5, curve 2), and hence, giving evidence that at least 99·5% of the substance has been so destructed. FS DPV on an HMDE is less time consuming and less tedious than gas chromatography recommended by Castegnaro and coworkers[7], the sensitivity and selectivity of the electrochemical method being sufficient for the application in question.

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