

## THE VOLTAMMETRIC DETERMINATION OF 4-NITROBIPHENYL\*

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Optimum conditions were found for the determination of 4-nitrobiphenyl by fast scan differential pulse voltammetry at a hanging mercury drop electrode in the concentration range  $1 \cdot 10^{-5}$  to  $2 \cdot 10^{-7} \text{ mol l}^{-1}$ . A further increase in sensitivity was attained by adsorptive accumulation of this substance on the surface of the working electrode, permitting determination in the concentration range  $(2-10) \cdot 10^{-8} \text{ mol l}^{-1}$  with one minute accumulation of the substance in unstirred solution or  $(2-10) \cdot 10^{-9} \text{ mol l}^{-1}$  with three-minute accumulation in stirred solution. Linear scan voltammetry can be used to determine 4-nitrobiphenyl in the concentration range  $(2-10) \cdot 10^{-9} \text{ mol l}^{-1}$  with five-minute accumulation in stirred solution, with the advantage of a smoother baseline and smaller interference from substances that yield only tensametric peaks.

4-Nitrobiphenyl is suspected of chemical carcinogenicity as it can be enzymatically reduced to the proven chemical carcinogen 4-aminobiphenyl<sup>1,2</sup>. As extremely small amounts of these substances can unfavourably affect biological processes, it is essential that methods for their determination be as sensitive as possible. These methods are also required to control the effectiveness of chemical destruction of these detrimental substances<sup>3</sup>. Because of the easy reducibility of the nitro group, 4-nitrobiphenyl has been determined by classical polarography<sup>4</sup> in the concentration range  $1 \cdot 10^{-3} - 1 \cdot 10^{-5} \text{ mol l}^{-1}$  and differential pulse polarography<sup>5</sup> in the concentration range  $1 \cdot 10^{-4} - 1 \cdot 10^{-7} \text{ mol l}^{-1}$ , which was also used to control the efficiency of the chemical destruction of this substance<sup>6</sup>. As even lower concentrations of this substance must be determined, we have studied the usefulness of fast scan differential pulse voltammetry (FSDPV) and linear scan voltammetry (LSV) at a hanging mercury drop electrode (HMDE) and the increase in the sensitivity of these methods provided by adsorptive accumulation of the test substance on the surface of the working electrode<sup>7</sup>. This technique has been employed in the determination of the nitration products of biphenyl and trichlorobiphenyl<sup>8</sup> with a detection limit of less than  $1 \cdot 10^{-7} \text{ mol l}^{-1}$ , but has not yet been used for 4-nitrobiphenyl.

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## EXPERIMENTAL

### Reagents

The stock solution of 4-nitrobiphenyl in methanol ( $c = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ ) was prepared by dissolving a precisely weighed amount of the substance (Merck, Darmstadt) in p.a. methanol that was freshly purified by the method of Lund and Bjerrum<sup>9</sup>. More dilute solutions were prepared by precise dilution of the stock solution and were stored in the dark. Britton–Robinson buffer solutions were prepared in the usual manner<sup>10</sup>. The actual pH value of the Britton–Robinson buffer–methanol mixture (1 : 1) was measured by a glass electrode calibrated using acetate, borate and phosphate buffers in 50% (v/v) methanol<sup>11,12</sup>. The pH was measured in 10% (v/v) methanol medium using a glass electrode calibrated using aqueous buffer solutions. The remaining chemicals were of p.a. purity (Lachema, Brno). Water was doubly distilled in a quartz apparatus.

### Apparatus

A PA 4 polarographic analyzer was used in combination with an XY 4106 recorder and static mercury drop electrode SMDE 1 (all from Laboratorní přístroje, Prague) connected as a hanging mercury drop electrode. A three-electrode arrangement was employed with a saturated silver chloride reference and platinum wire auxiliary electrode. The capillary employed had a diameter of 0.136 mm and the maximum drop size was used, attained by opening the valve for 160 ms. Where not stated otherwise, FSDPV and LSV were carried out at a polarization rate of  $20 \text{ mV} \cdot \text{s}^{-1}$  and FSDPV at a modulation amplitude of  $-100 \text{ mV}$ . Prior to entering the voltammetric cell, nitrogen was passed through a mixture of water and methanol in the same ratio as in the voltammetric solution. All the measurements were carried out at laboratory temperature.

### Procedure

The voltammetric solutions were prepared by measuring the required amount of the methanol solution of 4-nitrobiphenyl with the appropriate concentration, addition of the required amount of methanol and dilution with Britton–Robinson buffer with a suitable pH to the mark. The calibration curves were measured in triplicate and evaluated by the method of linear regressions. The determination limit in the concentration range  $(2-10) \cdot 10^{-x} \text{ mol l}^{-1}$  was calculated<sup>13</sup> as ten times the standard deviation of 10 determinations of the analyte at a concentration of  $2 \cdot 10^{-x} \text{ mol l}^{-1}$ .

## RESULTS AND DISCUSSION

The effect of the pH on the voltammetric behaviour of the test substance was studied in 50% (v/v) methanol medium (see Table I). The test substance yields a single peak in the studied pH range, with a height that is practically pH-independent and position that shifts to more negative potentials with increasing pH, where it holds that  $E_p(\text{mV}) = 111.4 - 59.3 \text{ pH}$  (correlation coefficient 0.9992). An additional peak was observed in acidic medium (pH 2–3) at about  $-850 \text{ mV}$ , which is quite broad and about ten times smaller and could be connected with the catalytic evolution of hydrogen in the presence of the products of the electrochemical reduction of 4-nitro-

biphenyl at the hanging mercury drop. The height of the FSDPV peak is practically pH-independent, while the heights of the DC (ref.<sup>4</sup>) and TAST (ref.<sup>5</sup>) polarographic waves and DPP peak<sup>5</sup> are about 50% higher in acidic medium than in alkaline medium. This difference is apparently connected with adsorption of the test substance or its reduction products on the surface of the hanging mercury drop electrode. The analytically most useful peaks were obtained in medium with pH 4.8, where the peaks are symmetrical, in contrast to lower pH values, where the peaks are considerably drawn out to more negative potentials. This asymmetrical peak shape, which complicates their evaluation, is apparently connected with splitting of the wave of 4-nitrobiphenyl in acidic medium, observed in TAST polarography<sup>5</sup>. At pH 4.8 the peak height vs 4-nitrobiphenyl concentration dependence is linear in the range  $1 \cdot 10^{-5} - 2 \cdot 10^{-7} \text{ mol l}^{-1}$  (see Table II). The peak height was measured from the line connecting the minima on both sides. Deviations from linearity occur in the concentration range  $(2-10) \cdot 10^{-5} \text{ mol l}^{-1}$ , apparently as a result of electrode passivation, as the electrode surface is not renewed during recording of the voltammetric curve. It is preferable to employ a classical dropping mercury electrode with a constantly renewed surface in this concentration range.

A further increase in the sensitivity can be attained through adsorptive accumulation of 4-nitrobiphenyl on the HMDE surface. It has been found that the height of the FSDPV peak depends on the time elapsed between formation of the drop and recording of the voltammogram, where this increase can be favoured by stirring of the solution (see Fig. 1). It was further found that this increase is greater at lower methanol concentrations, connected with the decreasing solubility of the substance at lower methanol concentrations and also with smaller competitive adsorption of methanol on the HMDE surface. Consequently, a medium containing only 10% (v/v) methanol was employed for the adsorptive accumulation; one-minute accumula-

TABLE I

The effect of the pH on the potential ( $E_p$ ) and height ( $I_p$ ) of the peak of 4-nitrobiphenyl ( $c = 1 \cdot 10^{-4} \text{ mol l}^{-1}$ ) in FS DPV at the HMDE in Britton-Robinson buffer-methanol medium (1 : 1)

pH	$E_p$ mV	$I_p$ $\mu\text{A}$	pH	$E_p$ mV	$I_p$ $\mu\text{A}$
2.80	-55	2.08	7.94	-365	2.36
3.91	-130	2.23	8.69	-405	2.33
4.80	-170	2.33	9.29	-430	2.31
5.80	-220	2.31	10.24	-500	2.31
6.90	-300	2.26	11.29	-560	2.58

tion in unstirred solution is sufficient in the concentration range  $(2-10) \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1}$  and three-minute accumulation must be employed with stirring in the range  $(2-10) \cdot 10^{-9} \text{ mol l}^{-1}$ . In this concentration range it is preferable to employ ten-

TABLE II  
Parameters of the calibration curves and determination limits for 4-nitrobiphenyl

Method	Concentration $\text{mol l}^{-1}$	Slope $\text{mA mol}^{-1} \text{ l}$	Intercept nA	Correl. coef.	Determination limit $\text{mol l}^{-1}$
FS DPV <sup>a</sup>	$(2-10) \cdot 10^{-6}$	53.7	0.9	0.9993	—
FS DPV <sup>a</sup>	$(2-10) \cdot 10^{-7}$	49.9	0.5	0.9988	$0.9 \cdot 10^{-7}$
FS DPV <sup>b</sup>	$(2-10) \cdot 10^{-8}$	109.5	0.2	0.9985	$1.4 \cdot 10^{-8}$
FS DPV <sup>c</sup>	$(2-10) \cdot 10^{-9}$	1 190	0.3	0.9983	$2.5 \cdot 10^{-9}$
LSV <sup>d</sup>	$(2-10) \cdot 10^{-9}$	880	0.3	0.9985	$2.1 \cdot 10^{-9}$

<sup>a</sup> Britton-Robinson buffer-methanol medium (1 : 1) at pH 4.8; <sup>b</sup> adsorptive accumulation for 1 min in unstirred solution in Britton-Robinson buffer-methanol medium (9 : 1) at pH 4.2; <sup>c</sup> adsorptive accumulation for 3 min in stirred solution in ten-fold diluted Britton-Robinson buffer-methanol medium (9 : 1) at pH 4.3; <sup>d</sup> adsorptive accumulation for 5 min in stirred solution in hundred-fold diluted Britton-Robinson buffer-methanol medium (9 : 1) at pH 4.5.

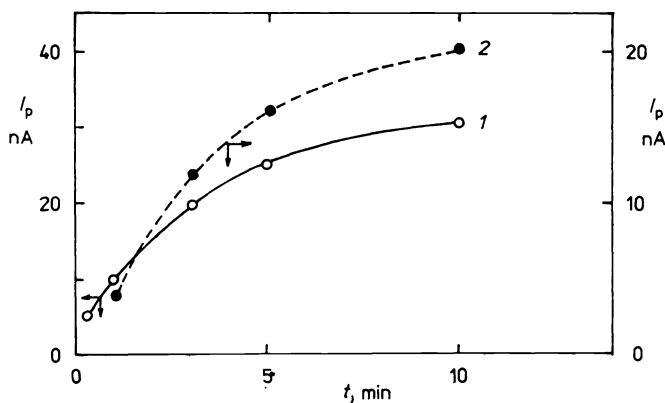


FIG. 1

The effect of time on the height of the peak of 4-nitrobiphenyl (*I*) in FSDPV. 1 adsorptive accumulation without stirring in Britton-Robinson buffer-methanol mixture (9 : 1) at pH 4.2,  $c(I) = 1 \cdot 10^{-7} \text{ mol l}^{-1}$ ; 2 adsorptive accumulation in stirred solution in ten-fold diluted Britton-Robinson buffer-methanol (9 : 1) mixture at pH 4.3,  $c(I) = 1 \cdot 10^{-8} \text{ mol l}^{-1}$

-fold diluted Britton–Robinson buffer, which yields a smoother baseline as a result of smaller peaks for trace impurities contained in the chemicals employed. The parameters of these calibration curves and the calculated determination limit are given in Table II.

The stability of the stock solutions of 4-nitrobiphenyl in methanol (see Table III) and of the voltammetric solutions, i.e. in a Britton–Robinson buffer–methanol (1 : 1)

TABLE III

The stability of stock solutions of 4-nitrobiphenyl (*I*) in methanol

<i>t</i> , days	<i>c(I)</i> , mol l <sup>-1a</sup>				
	1 . 10 <sup>-3</sup>	1 . 10 <sup>-4</sup>	1 . 10 <sup>-5</sup>	1 . 10 <sup>-6</sup>	1 . 10 <sup>-7</sup>
0	100	100	100	100	100
1	100	100	100	99	97
2	100	100	99	97	92
3	100	100	98	95	85
7	100	100	95	90	80
30	100	98	90	—	—
60	99	96	84	—	—

<sup>a</sup> Relative concentration of 4-nitrobiphenyl in % compared to the concentration of a freshly prepared solution.

TABLE IV

Stability of the solutions of 4-nitrobiphenyl (*I*) used in the voltammetric studies

<i>t</i> , min	<i>c(I)</i> , mol l <sup>-1a</sup>		
	1 . 10 <sup>-6</sup>	1 . 10 <sup>-7</sup>	1 . 10 <sup>-8</sup>
0	100	100	100
15	100	99	97
30	100	97	93
60	99	95	89
120	98	90	84
240	97	80	68
360	95	70	64

<sup>a</sup> Concentration of 4-nitrobiphenyl in % compared to the concentration of a freshly prepared solution.

medium at pH 4.8 (see Table IV) was also studied. The stability of 4-nitrobiphenyl solutions with concentrations of  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-5}$  mol l $^{-1}$  was studied by spectrophotometric measurement of the absorbance at 306 nm. The stability of solutions with concentrations of  $1 \cdot 10^{-5}$  to  $1 \cdot 10^{-7}$  mol l $^{-1}$  was examined by using the appropriate voltammetric technique, where 1.00 ml of the test stock solution in methanol was mixed with the appropriate amount of methanol, the solution was diluted to 10 ml with Britton–Robinson buffer (sometimes ten-fold diluted) and then voltammetric analysis was carried out under the conditions recommended in Table II. It can be seen from Table III that, while it is sufficient to prepare solutions with a concentration of  $1 \cdot 10^{-3}$  to  $1 \cdot 10^{-4}$  mol l $^{-1}$  once a month, solutions of lower concentration should be prepared fresh daily. It can be seen from Table IV that voltammetry of more dilute solutions (of the order of  $10^{-7}$  and  $10^{-8}$  mol l $^{-1}$ ) should be carried out at the shortest possible, constant time after preparation.

In conclusion, the usefulness of LSV at the HMDE for the determination of low concentrations of 4-nitrobiphenyl was tested. This technique has the advantage that it does not yield tensammetric peaks for substances that can be present in trace amounts in the methanol employed, yielding a smoother baseline, especially when hundred-fold diluted Britton–Robinson buffer is employed. Five-minute accumulation in stirred solution seems optimum in the concentration range  $(2-10) \cdot 10^{-9}$  mol . l $^{-1}$ . The parameters of the calibration curves obtained under these conditions and the calculated determination limit values are given in Table II. The FSDP and LS

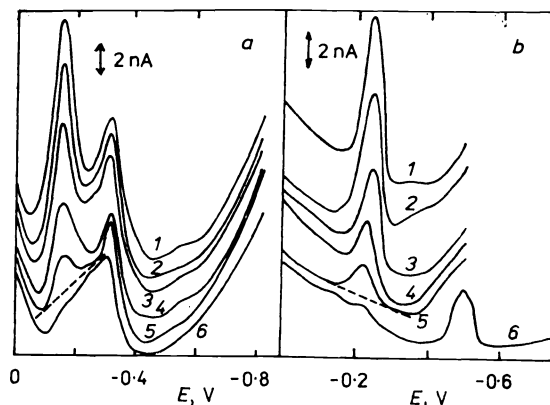


FIG. 2

FS DP (a) and LS (b) voltammograms of 4-nitrobiphenyl (*I*) with three-minute (a) and five-minute (b) adsorptive accumulation in stirred solution.  $c(I)$  (nmol l $^{-1}$ ): 1 10; 2 8; 3 6; 4 4; 5 2; 6 base electrolyte. The dashed line corresponds to the baseline from which the peak height was measured. The composition of the base electrolyte is given in Table II

voltammograms in the lowest useful concentration range are given in Fig. 2. The peak at about  $-0.5$  V corresponds to impurities in the base electrolyte and does not affect the actual determination.

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