

## Voltammetric Determination of Carcinogenic Nitrobiphenyls at a Hanging Mercury Drop Electrode

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**Abstract:** Differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) at a hanging mercury drop electrode (HMDE) was used for the determination of trace amounts of carcinogenic nitrobiphenyls, namely 2-nitrobiphenyl (2-NBP), 3-nitrobiphenyl (3-NBP) and 4-nitrobiphenyl (4-NBP) within the concentration range from  $2 \cdot 10^{-8}$  to  $1 \cdot 10^{-5}$  mol·L<sup>-1</sup> for DPV and from  $2 \cdot 10^{-9}$  to  $1 \cdot 10^{-7}$  mol·L<sup>-1</sup> for AdSV using a Britton-Robinson buffer – methanol (1:1) mixture with resulting pH 12 as a base electrolyte. The practical applicability of newly developed methods was verified using model samples of drinking and river water and liquid-liquid extraction for a preliminary separation and preconcentration.

**Keywords:** Hanging mercury drop electrode, Differential pulse voltammetry, Adsorptive stripping voltammetry, 2-nitrobiphenyl, 3-nitrobiphenyl, 4-nitrobiphenyl

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### Introduction

Nitrated polycyclic aromatic hydrocarbons (NPAH) are well known chemical carcinogens [1,2], which are often found in the industrial and general environment. Therefore, there is an ever-increasing demand for the determination of trace amounts of these substances. So far, mostly chromatographic methods, such as GC-MS or HPLC with fluorimetric detection are used for these purposes [3]. However, these methods are characterized by high investment and running costs. Modern

electroanalytical methods, especially differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) at a hanging mercury drop electrode (HMDE) [4,5] satisfy even the highest demands on sensitivity required for the determination of extremely dangerous chemical carcinogens, their main advantage being much lower investment and running costs. HMDE, which was introduced by Kemula nearly 50 years ago [6], is still among the best sensors for voltammetric determination which combines ideal properties of mercury as an electrode material (broad potential window in cathodic region, homogenous, easily renewable, uniform and atomically smooth surface) with the possibility to increase the sensitivity of the voltammetric determination via electrochemical or adsorptive accumulation of the analyte on its surface. User friendliness of modern computer driven HMDEs makes them very useful sensors for voltammetric trace analysis [7]. In spite of this, systematic investigation of possible applications of modern voltammetric methods for the determination of traces of chemical carcinogens started relatively recently [8]. NPAH are very promising candidates for a successful adsorptive stripping voltammetric determination at HMDE because of their easy electrochemical reducibility [9] and extensive aromatic system enabling their strong adsorption at a HMDE surface. Therefore, in this paper we devoted attention to DPV and AdSV determination of nanomolar concentrations of 2-nitrobiphenyl (2-NBP), 3-nitrobiphenyl (3-NBP) and 4-nitrobiphenyl (4-NBP), which are potential occupational carcinogens [10].

## Experimental

### Reagents

The stock solutions ( $1.10^{-3}$  mol L<sup>-1</sup>) of 2-NBP (C.A.S. Name: [1,1'-biphenyl], 2-nitro, C.A.S. Registry Number: 86-00-0), 3-NBP (C.A.S. Name: [1,1'-biphenyl], 3-nitro, C.A.S. Registry Number: 2113-58-8), and 4-NBP (C.A.S. Name: [1,1'-biphenyl], 4-nitro, C.A.S. Registry Number: 92-93-3) were prepared by dissolving 0.0199 g of the pure substance (Aldrich) in 100 mL of methanol. The purity of the substance was controlled by HPLC [11]. 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 solutions [11] that the solutions in methanol are stable for at least 90 days. Methanol was of analytical grade purity (Lachema, Brno, Czech Republic). Hexane for trace analysis (Merck) was used for liquid-liquid (LLE) extractions. Chemicals for the preparation of the Britton-Robinson buffers were obtained from Sigma. Britton-Robinson buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 mol·L<sup>-1</sup> in phosphoric acid, 0.04 mol L<sup>-1</sup> in acetic acid and 0.04 mol L<sup>-1</sup> in boric acid with the appropriate amount of 0.2 mol L<sup>-1</sup> sodium hydroxide solution. De-ionized water was produced by Milli-Q Plus system, Millipore.

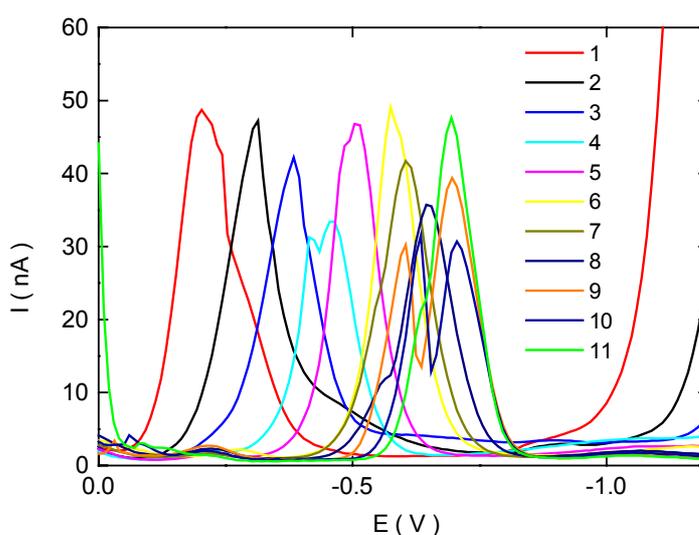
### Apparatus

Measurements were carried out using a computer driven AUTOLAB analyzer controlled by PGSTAT 10 with GPES ver. 4.3 software (all Eco-Chemie, The Netherlands) running under operation system Windows 3.11. A pneumatically controlled HMDE of the MME type 6.1246.020 and VA STAND 663 (both Metrohm, Switzerland) with glassy carbon rod auxiliary electrode and Ag/AgCl

reference electrode (to which all the potential values are referred) were used. Where not stated otherwise, the medium drop size 2 at VA STAND 663, a polarization rate of  $10 \text{ mV s}^{-1}$ , and the modulation amplitude of  $-50 \text{ mV}$  were used. Oxygen was removed by passing nitrogen through measured solution for 5 minutes, and a pre-bubbler containing mixture of water and methanol in the same ratio as in measured solution was placed before polarographic vessel. pH was measured using Conductivity&pH meter Jenway 4330 (Jenway, England).

### Procedures

The general procedure to obtain 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 volume with a Britton - Robinson buffer of the required pH. (A different order of mixing the solutions resulted in a precipitation of the test substance). The solution was transferred into a polarographic vessel, oxygen was removed from the measured solutions by bubbling with nitrogen for five minutes and the voltammogram was recorded. The procedure for voltammetric determination of 3-NBP in drinking or river water after liquid-liquid extraction was as follows: 100 mL of model sample of drinking water containing  $(2-10) \cdot 10^{-9} \text{ mol L}^{-1}$  of added 3-NBP was extracted with 5 mL of hexane, the organic phase was evaporated under decreased pressure to dryness using rotary vacuum evaporator, the residue was dissolved in 1 mL of methanol using sonication, 1 mL of Britton-Robinson buffer, pH 12 was added and DP voltammogram was recorded. Calibration curves were measured in triplicate and their statistical parameters (e.g. slope, intercept, limit of decision, limit of detection, limit of determination) were calculated according to Oppenheimer [12], Schwartz [13], and Ebel [14] using statistic software Adstat ver. 2.0 (Trilobyte, Czech Republic).

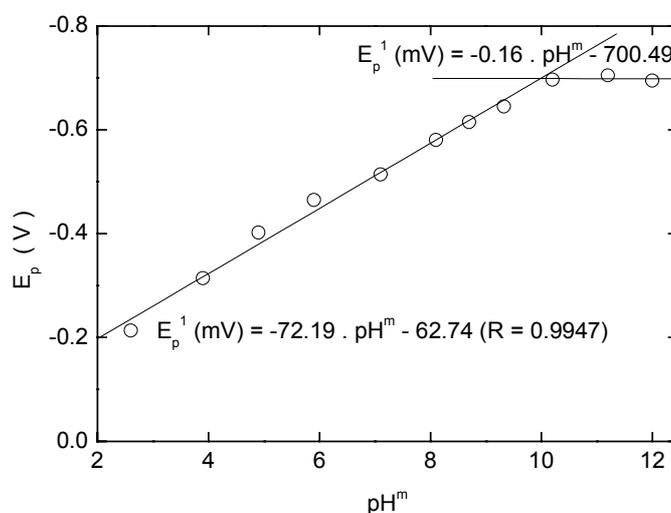


**Figure 1.** DP voltammograms of  $1 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  2-NBP at HMDE in the mixed Britton-Robinson buffer – methanol (1:1) medium at resulting  $\text{pH}^m$  2.6 (1), 3.9 (2), 4.9 (3), 5.9 (4), 7.1 (5), 8.1 (6), 8.7 (7), 9.3 (8), 10.2 (9), 11.2 (10), 12.0 (11).

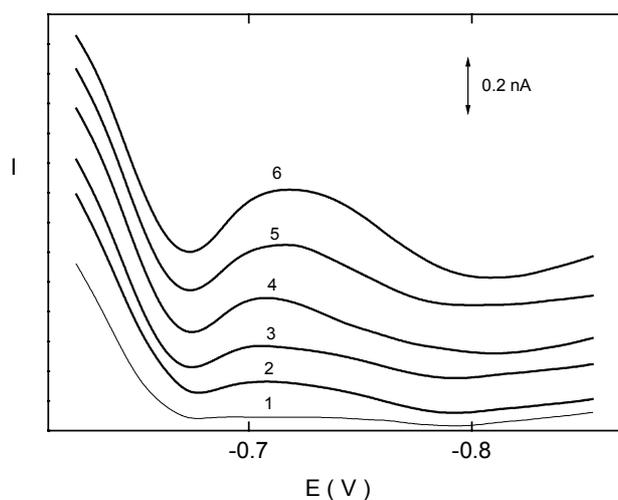
## Results and Discussion

### Differential Pulse Voltammetry of 2-Nitrobiphenyl at HMDE

The effect of pH on differential pulse voltammograms of 2-NBP was investigated in the mixture of Britton-Robinson buffer and methanol (1:1) (see Fig. 1). It was found that the substance gives one, well developed peak shifting towards more negative potentials with increasing resulting pH of the mixture (further denoted as  $\text{pH}^m$ ) (see Fig. 2). At  $\text{pH}^m$  5.9, 10.2 and 11.2 the peak was splitted (see Table 1). The highest, best-developed and most easily evaluated peak was obtained at pH 12 (see Fig. 1). The height of the peak was measured from the straight line connecting the minima before and after the peak.



**Figure 2.** The dependence of the first peak potential  $E_p^1$  of 2-NBP ( $c = 1 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) at HMDE on the resulting  $\text{pH}^m$  of the Britton-Robinson buffer – methanol (1:1) mixture.



**Figure 3.** DP voltammograms of 2-NBP at HMDE in the lowest attainable concentration range. Britton-Robinson buffer – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0. Concentration of 2-NBP ( $\text{mol} \cdot \text{L}^{-1}$ ): 0 (1),  $2 \cdot 10^{-8}$  (2),  $4 \cdot 10^{-8}$  (3),  $6 \cdot 10^{-8}$  (4),  $8 \cdot 10^{-8}$  (5),  $10 \cdot 10^{-8}$  (6).

The calibration curves are linear within the concentration range from  $2 \cdot 10^{-8}$  to  $1 \cdot 10^{-5}$  mol·L<sup>-1</sup> and their parameters are given in Table 2. DP voltammograms corresponding to the lowest attainable concentration range are depicted in Fig. 3.

**Table 1.** The dependence of the peak potential ( $E_p$ ) and peak current ( $I_p$ ) of 2-NBP measured by DPV at HMDE on resulting pH<sup>m</sup> of the Britton-Robinson buffer – methanol (1:1) mixture.

pH <sup>a</sup>	pH <sup>b</sup>	$E_p^1$ (mV)	$I_p^1$ (nA)	$E_p^2$ (mV)	$I_p^2$ (nA)
2.0	2.6	-213	46.7	--	--
3.0	4.0	-314	45.9	--	--
4.0	4.9	-402	39.6	--	--
5.0	5.9	-465	31.5	-415	28.5
6.0	7.1	-514	45.2	--	--
7.0	8.1	-580	47.9	--	--
8.0	8.7	-615	40.8	--	--
9.0	9.3	-645	35.1	--	--
10.0	10.2	-696	38.5	-605	-18.5
11.0	11.2	-705	29.4	-634	-29.4
12.0	12.0	-695	46.5	--	--

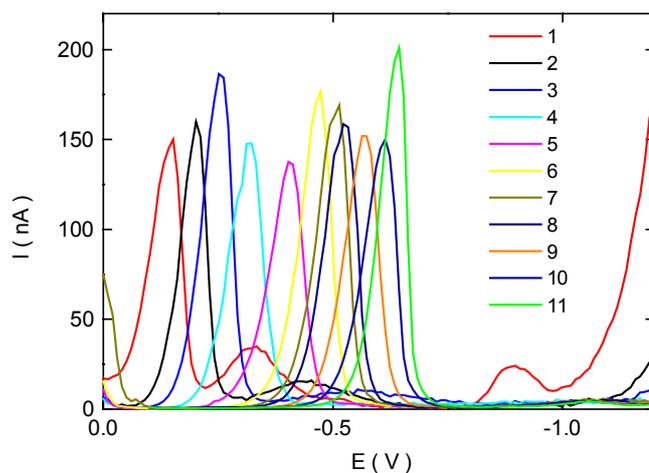
<sup>a</sup> pH of Britton-Robinson buffer; <sup>b</sup> resulting pH<sup>m</sup> of the Britton-Robinson buffer – methanol (1:1) mixture; <sup>1</sup> first peak; <sup>2</sup> second peak

**Table 2.** Parameters of calibration curves for the determination of 2-NBP by DPV at HMDE in Britton-Robinson buffer – methanol (1:1) mixture of resulting pH<sup>m</sup> 12.

c (mol·L <sup>-1</sup> )	Slope (mA mol <sup>-1</sup> L)	Intercept (nA)	Correlation coefficient	$L_Q$ (mol·L <sup>-1</sup> )
(2-10) · 10 <sup>-6</sup>	5.3	0.5	0.9998	----
(2-10) · 10 <sup>-7</sup>	5.3	-0.1	0.9998	----
(2-10) · 10 <sup>-8</sup>	4.8	0.0	0.9957	$3.1 \cdot 10^{-8}$

### Differential Pulse Voltammetry of 3-Nitrophenyl at HMDE

The effect of pH on DP voltammograms of 3-NBP is shown in Fig. 4. This substance gives one or two (at pH<sup>m</sup> 2.6, 4.0, and 4.9) well-developed peaks, which are shifted towards more negative potential with increasing pH (see Table 3). The highest, best-developed and most easily evaluated peak was again obtained at pH<sup>m</sup> 12 (see Fig. 4) where linear calibration curves were obtained (see Table 4). In the lowest attainable concentration range, a coinciding peak around -0.6 V was observed (see Fig. 5) which caused high intercept of the calibration curve (see Fig. 6, straight line 1). However, if the height of this peak was subtracted from the peaks of the test substances, the calibration straight line passed nearly through the origin (see Fig. 6, straight line 2).



**Figure 4.** DP voltammograms of  $1.10^{-5}$  mol·L<sup>-1</sup> 3-NBP at HMDE in the mixed Britton-Robinson buffer – methanol (1:1) mixture at resulting pH<sup>m</sup> 2.6 (1), 3.9 (2), 4.9 (3), 5.9 (4), 7.1 (5), 8.1 (6), 8.7 (7), 9.3 (8), 10.2 (9), 11.2 (10), 12.0 (11).

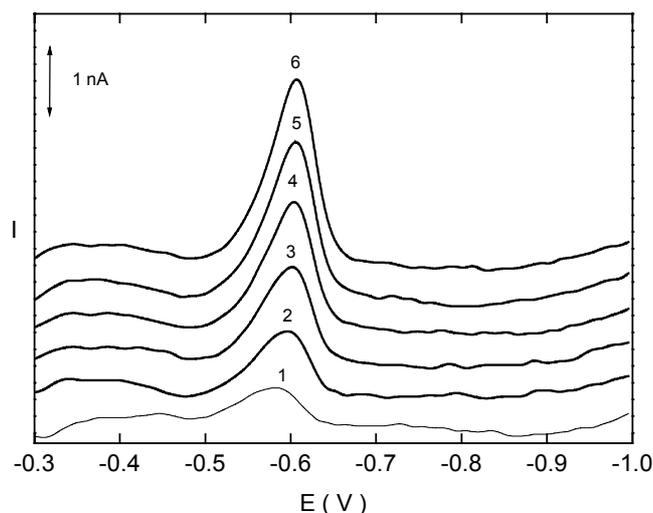
**Table 3.** The dependence of the peak potential ( $E_p$ ) and peak current ( $I_p$ ) of 3-NBP measured by DPV at HMDE on resulting pH<sup>m</sup> of the Britton-Robinson buffer – methanol (1:1) mixture.

pH <sup>a</sup>	pH <sup>b</sup>	$E_p^1$ (mV)	$I_p^1$ (nA)	$E_p^2$ (mV)	$I_p^2$ (nA)
2.0	2.6	-92	133	-323	26.5
3.0	4.0	-151	156	-433	12.1
4.0	4.9	-202	183	-554	6.2
5.0	5.9	-272	146	--	--
6.0	7.1	-380	137	--	--
7.0	8.1	-423	176	--	--
8.0	8.7	-464	168	--	--
9.0	9.3	-473	158	--	--
10.0	10.2	-563	151	--	--
11.0	11.2	-614	149	--	--
12.0	12.0	-644	200	--	--

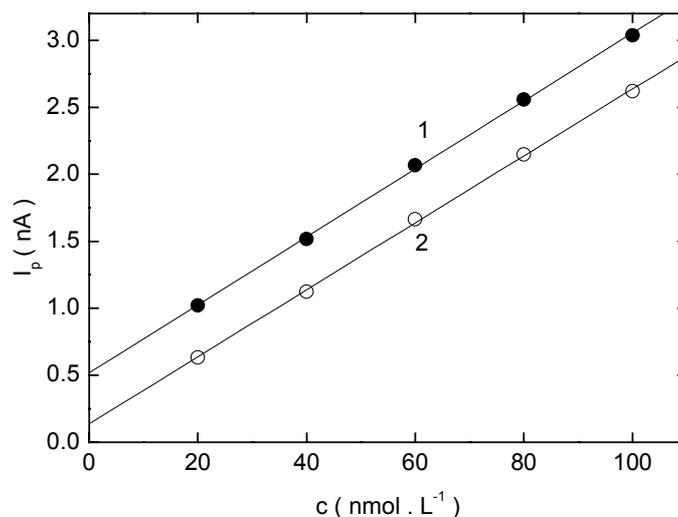
<sup>a</sup> pH of Britton-Robinson buffer; <sup>b</sup> resulting pH<sup>m</sup> of the Britton-Robinson buffer – methanol (1:1) mixture; <sup>1</sup>first peak; <sup>2</sup>second peak

**Table 4.** Parameters of calibration curves for the determination of 3-NBP by DPV at HMDE in Britton-Robinson buffer – methanol (1:1) mixture of resulting pH<sup>m</sup> 12.

c (mol L <sup>-1</sup> )	Slope (mA mol <sup>-1</sup> L)	Intercept (nA)	Correlation coefficient	$L_Q$ (mol L <sup>-1</sup> )
(2-10) · 10 <sup>-6</sup>	20.8	6.9	0.9975	----
(2-10) · 10 <sup>-7</sup>	24.8	0.1	0.9984	----
(2-10) · 10 <sup>-8</sup>	24.9	0.1	0.9997	$2.7 \cdot 10^{-8}$



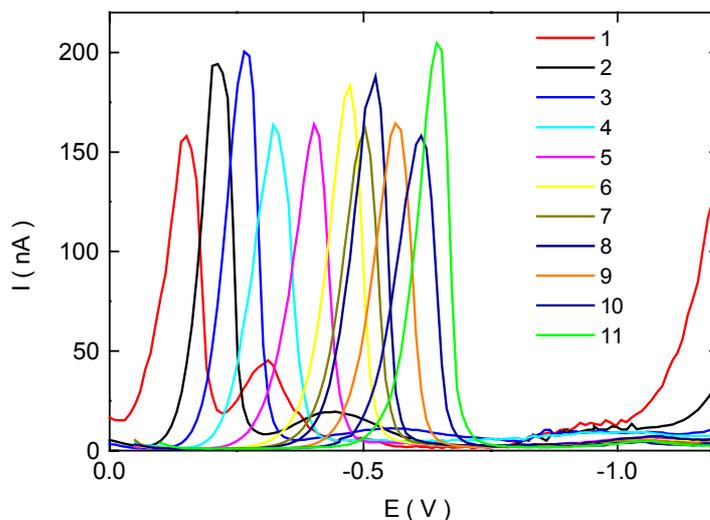
**Figure 5.** DP voltammograms of 3-NBP at HMDE in the lowest attainable concentration range. Britton-Robinson buffer – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0. Concentration of 3-NBP ( $\text{mol}\cdot\text{L}^{-1}$ ): 0 (1),  $2\cdot 10^{-8}$  (2),  $4\cdot 10^{-8}$  (3),  $6\cdot 10^{-8}$  (4),  $8\cdot 10^{-8}$  (5),  $10\cdot 10^{-8}$  (6).



**Figure 6.** The dependence of the peak current ( $I_p$ ) on the concentration of 3-NBP ( $c = (2 - 10)\cdot 10^{-8}$   $\text{mol}\cdot\text{L}^{-1}$ ) measured by DPV at HMDE in the Britton-Robinson buffer – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0. Curve 1 is calibration curve with an interfering peak in the base electrolyte. Curve 2 is corrected calibration line.

#### *Differential Pulse Voltammetry of 4-Nitrobiphenyl at HMDE*

As in previous cases, this substance gives one or two (at  $\text{pH}^m$  2.6, 4.0 and 4.9) well-developed peaks (see Fig. 7) shifting to more negative potential with increasing pH (see Table 5). The parameters of calibration straight lines obtained at optimal  $\text{pH}^m$  12.0 are summarized in Table 6. DP voltammograms corresponding to the lowest measured concentration range are depicted in Fig. 8.



**Figure 7.** DP voltammograms of  $1 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  4-NBP at HMDE in the mixed Britton-Robinson buffer – methanol (1:1) mixture at resulting  $\text{pH}^{\text{m}}$  2.6 (1), 3.9 (2), 4.9 (3), 5.9 (4), 7.1 (5), 8.1 (6), 8.7 (7), 9.3 (8), 10.2 (9), 11.2 (10), 12.0 (11).

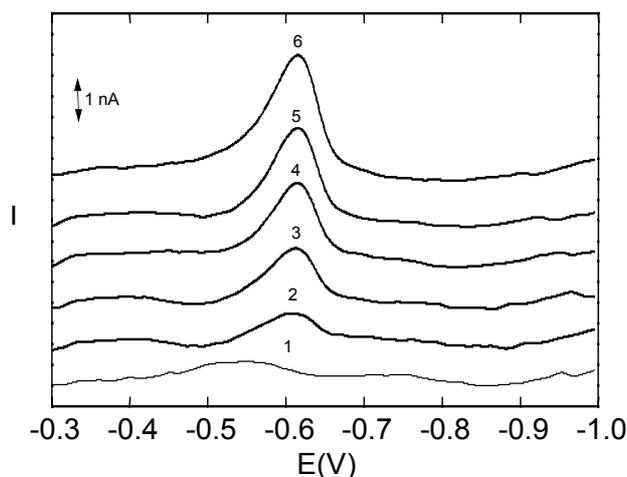
**Table 5.** The dependence of the peak potential ( $E_{\text{p}}$ ) and peak current ( $I_{\text{p}}$ ) of 4-NBP measured by DPV at HMDE on resulting  $\text{pH}^{\text{m}}$  of the Britton-Robinson buffer – methanol (1:1) mixture.

$\text{pH}^{\text{a}}$	$\text{pH}^{\text{b}}$	$E_{\text{p}}^1(\text{mV})$	$I_{\text{p}}^1(\text{nA})$	$E_{\text{p}}^2(\text{mV})$	$I_{\text{p}}^2(\text{nA})$
2.0	2.6	-151	139	-312	32.3
3.0	4.0	-223	195	-444	13.3
4.0	4.9	-273	200	-555	6.1
5.0	5.9	-322	160	--	--
6.0	7.1	-403	162	--	--
7.0	8.1	-473	182	--	--
8.0	8.7	-503	160	--	--
9.0	9.3	-523	186	--	--
10.0	10.2	-563	163	--	--
11.0	11.2	-614	157	--	--
12.0	12.0	-644	203	--	--

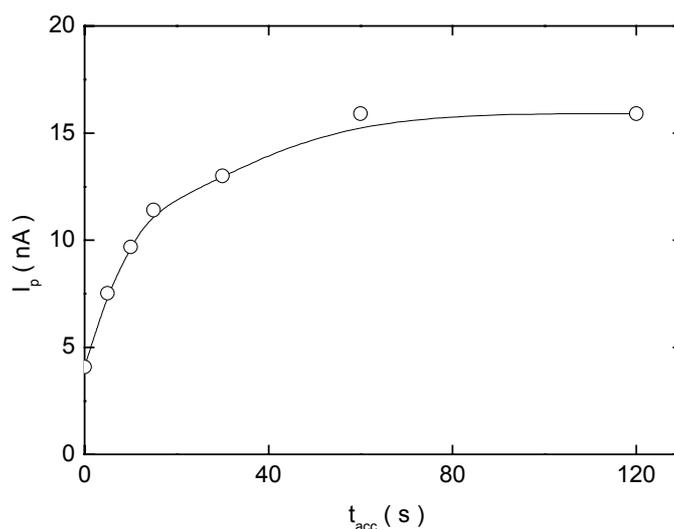
<sup>a</sup> pH of Britton-Robinson buffer ; <sup>b</sup> resulting  $\text{pH}^{\text{m}}$  of the Britton-Robinson buffer – methanol (1:1) mixture;  
<sup>1</sup> first peak; <sup>2</sup> second peak

**Table 6.** Parameters of calibration curves for the determination of 4-NBP by DPV at HMDE in Britton-Robinson buffer – methanol (1:1) mixture of resulting  $\text{pH}^{\text{m}}$  12.

$c \text{ (mol L}^{-1}\text{)}$	Slope ( $\text{mA mol}^{-1} \text{L}$ )	Intercept (nA)	Correlation coefficient	$L_{\text{Q}} \text{ (mol L}^{-1}\text{)}$
$(2-10) \cdot 10^{-6}$	21.1	10.9	0.9999	----
$(2-10) \cdot 10^{-7}$	24.4	1.4	0.9961	----
$(2-10) \cdot 10^{-8}$	25.8	0.1	0.9965	$2.5 \cdot 10^{-8}$



**Figure 8.** DP voltammograms of 4-NBP at HMDE in the lowest attainable concentration range. Britton-Robinson buffer – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0. Concentration of 4-NBP ( $\text{mol}\cdot\text{L}^{-1}$ ): 0 (1),  $2\cdot 10^{-8}$  (2),  $4\cdot 10^{-8}$  (3),  $6\cdot 10^{-8}$  (4),  $8\cdot 10^{-8}$  (5),  $10\cdot 10^{-8}$  (6).

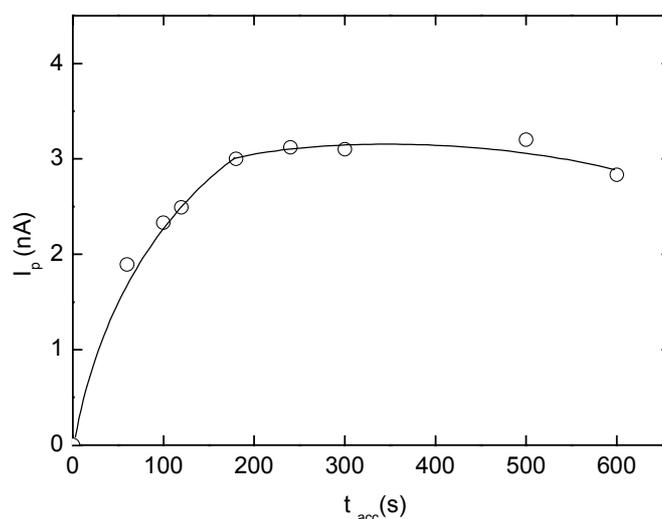


**Figure 9.** The influence of the accumulation time  $t_{\text{acc}}$  on the peak height  $I_p$  of 2-NBP ( $c = 1\cdot 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ ). Measured by AdSV at HMDE in the  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH – methanol (100:1) mixture. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ .

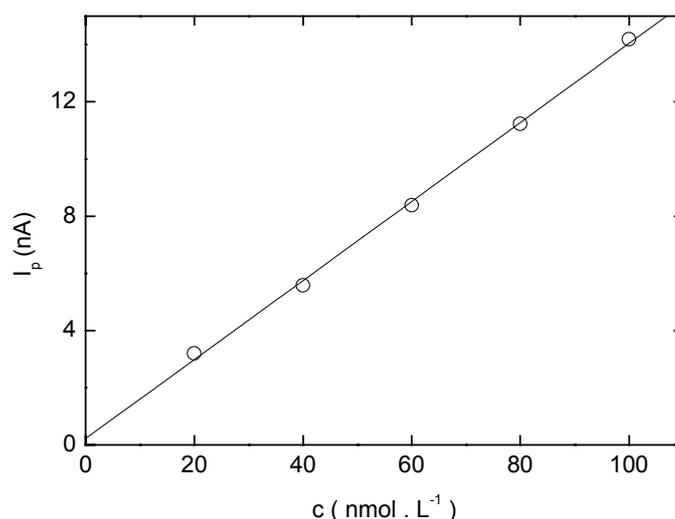
#### *Adsorptive Stripping Voltammetry of 2-Nitrobiphenyl at HMDE*

It followed from preliminary experiments [11], that the best developed and most easily evaluated adsorptive stripping voltammograms were obtained in the  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH – MeOH (100:1) mixture. The influence of  $\text{pH}^m$  on the height and the position of the peak is shown in Table 7. The best-developed and best repeatable voltammograms were obtained at  $E_{\text{acc}} = -400 \text{ mV}$ . (At  $-450 \text{ mV}$  the peaks were higher but less reproducible and not so easy to evaluate). Afterwards, the influence of the accumulation time on the peak height was investigated (see Fig. 9 and Fig. 10). Optimum time of accumulation was found to be 60 s for the concentration range  $(2\text{--}10)\cdot 10^{-8} \text{ mol}\cdot\text{L}^{-1}$  and 180 s for the

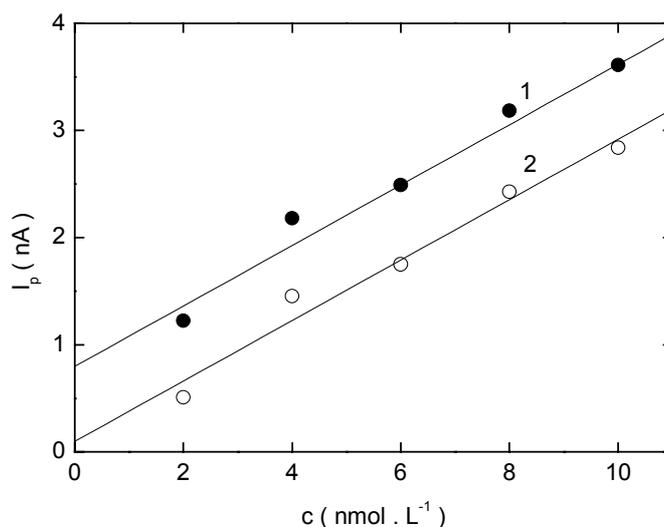
range  $(2-10) \cdot 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ . Under these conditions, linear calibration curves were obtained (see Fig. 11 and Fig. 12). In the lowest attainable concentration range, the calibration dependence is linear with relatively high intercept (curve 1 in Fig. 12), which is again caused by an interfering peak in the base electrolyte. By subtracting the height of this peak from the peaks of 2-NBP, a corrected calibration straight line (see curve 2 in Fig. 12) was obtained passing practically through the origin. The parameters of these calibration curves are given in Table 7.



**Figure 10.** The influence of the accumulation time  $t_{\text{acc}}$  on the peak height  $I_p$  of 2-NBP ( $c = 1 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ ). Measured by AdSV at HMDE in the  $0.01 \text{ mol} \cdot \text{L}^{-1}$  NaOH – methanol (100:1) mixture. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ .



**Figure 11.** The dependence of the peak current ( $I_p$ ) on the concentration of 2-NBP ( $c = (2 - 10) \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ ). Measured by AdSV at HMDE in the  $0.01 \text{ mol} \cdot \text{L}^{-1}$  NaOH – methanol (100:1) mixture with resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Time of accumulation  $t_{\text{acc}} = 60 \text{ s}$ .



**Figure 12.** The dependence of the peak current ( $I_p$ ) on the concentration of 2-NBP ( $c = (2 - 10) \cdot 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ ). Measured by AdSV at HMDE in the  $0.01 \text{ mol L}^{-1}$  NaOH – methanol (100:1) mixture with resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Time of accumulation  $t_{\text{acc}} = 180 \text{ s}$ . Curve 1 is calibration curve with an interfering peak in the base electrolyte. Curve 2 is corrected calibration line.

**Table 7.** The dependence of the peak potential ( $E_p$ ) and peak current ( $I_p$ ) of 2-NBP measured by AdSV at HMDE on resulting  $\text{pH}^m$  of the Britton-Robinson buffer – methanol (100:1) mixture at various potentials of accumulation ( $E_{\text{acc}}$ ).

$\text{pH}^m$	$E_{\text{acc}}(\text{mV})$	$E_p(\text{mV})$	$I_p(\text{nA})$	$\text{pH}^m$	$E_{\text{acc}}(\text{mV})$	$E_p(\text{mV})$	$I_p(\text{nA})$
2.0	100	-52	4.1	8.0	-100	-434	3.9
3.0	100	-122	0.9	9.0	-100	-484	5.0
4.0	0	-193	2.1	10.0	-100	-534	5.6
5.0	0	-243	8.9	11.0	-300	-574	7.6
6.0	0	-314	1.1	12.0	-400	-614	10.2
7.0	-100	-384	2.8				

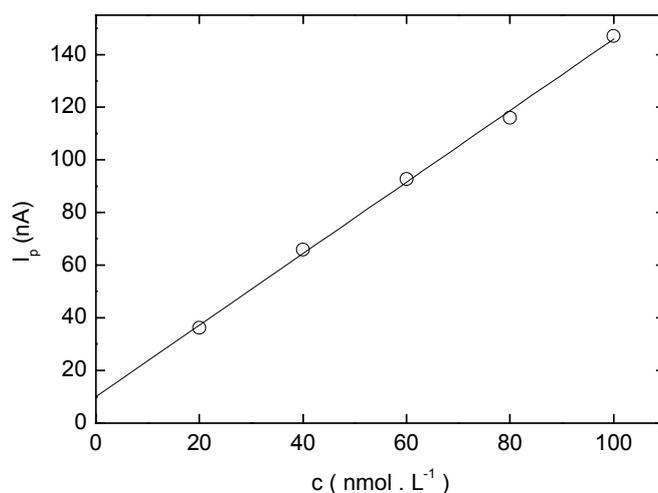
**Table 8.** Parameters of calibration curves for the determination of 2-NBP by AdSV at HMDE in  $0.01 \text{ mol} \cdot \text{L}^{-1}$  NaOH - methanol (100:1) mixture of resulting  $\text{pH}^m$  12. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ .

$c \text{ (mol L}^{-1}\text{)}$	Slope ( $\text{mA mol}^{-1} \text{L}$ )	Intercept ( $\text{nA}$ )	Correlation coefficient	$L_Q \text{ (mol L}^{-1}\text{)}$
$(2-10) \cdot 10^{-8} \text{ }^a$	138.1	0.24	0.9991	$2.2 \cdot 10^{-8}$
$(2-10) \cdot 10^{-9} \text{ }^b$	282.3	0.08	0.9842	$2.9 \cdot 10^{-9}$

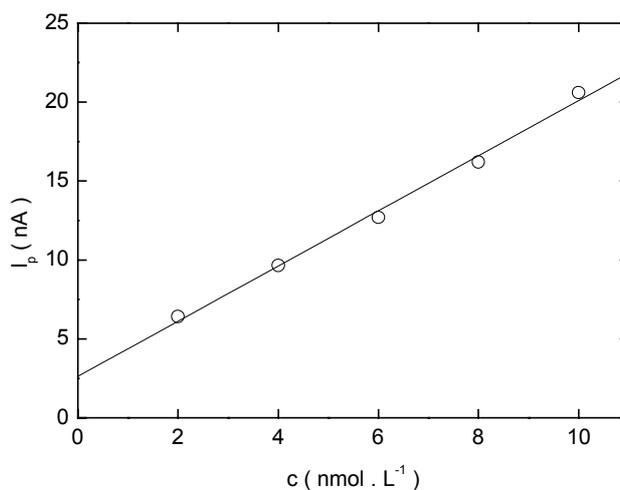
<sup>a</sup> time of accumulation  $t_{\text{acc}} = 60 \text{ s}$ ; <sup>b</sup> time of accumulation  $t_{\text{acc}} = 180 \text{ s}$ ;

*Adsorptive Stripping Voltammetry of 3-Nitrobiphenyl at HMDE*

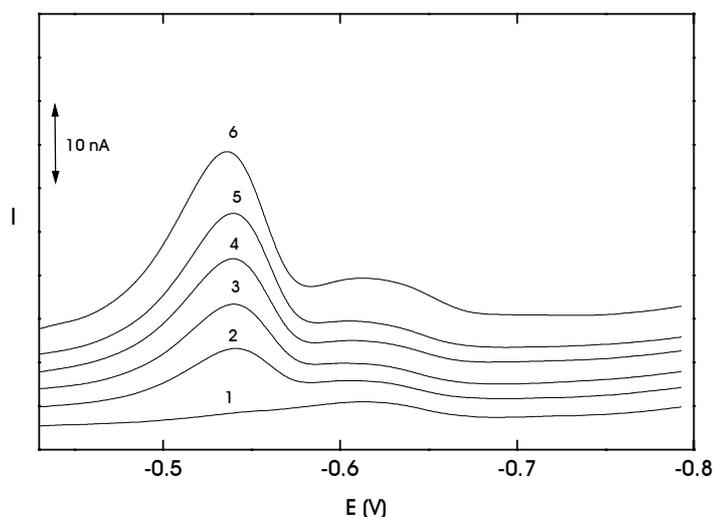
In this case, the following optimum conditions were found based on detailed investigations of the influence of various parameters on the height, position, and shape of the peak [11]: medium  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH – MeOH (100:1) mixture, accumulation potential  $E_{\text{acc}} = -400 \text{ mV}$ , accumulation time  $t_{\text{acc}} = 300 \text{ s}$  for the concentrations  $(2-10) \cdot 10^{-8} \text{ mol}\cdot\text{L}^{-1}$  and  $t_{\text{acc}} = 600 \text{ s}$  for the range  $(2-10) \cdot 10^{-9} \text{ mol}\cdot\text{L}^{-1}$ . Linear calibration curves obtained under these conditions are in Fig. 13 and Fig. 14. DP voltammograms corresponding to the lowest attainable concentration range are depicted in Fig. 15. The parameters of these calibration curves are summarized in Table 8.



**Figure 13.** The dependence of the peak current ( $I_p$ ) on the concentration of 3-NBP ( $c = (2 - 10) \cdot 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ ). Measured by AdSV at HMDE in the  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH – methanol (100:1) mixture of resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Time of accumulation  $t_{\text{acc}} = 300 \text{ s}$ .



**Figure 14.** The dependence of the peak current ( $I_p$ ) on the concentration of 3-NBP ( $c = (2 - 10) \cdot 10^{-9} \text{ mol}\cdot\text{L}^{-1}$ ) measured by AdSV at HMDE in the  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaOH – methanol (100:1) mixture of resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Time of accumulation  $t_{\text{acc}} = 600 \text{ s}$ .



**Figure 15.** Voltammograms of 3-NBP measured by AdSV at HMDE in the lowest attainable concentration range. 0.01 mol L<sup>-1</sup> NaOH – methanol (100:1) mixture with resulting pH<sup>m</sup> 12.0. Time of accumulation  $t_{acc} = 300$  s and potential of accumulation  $E_{acc} = -400$  mV. Concentration of 3-NBP (mol L<sup>-1</sup>): 0 (1),  $2 \cdot 10^{-9}$  (2),  $4 \cdot 10^{-9}$  (3),  $6 \cdot 10^{-9}$  (4),  $8 \cdot 10^{-9}$  (5),  $10 \cdot 10^{-9}$  (6).

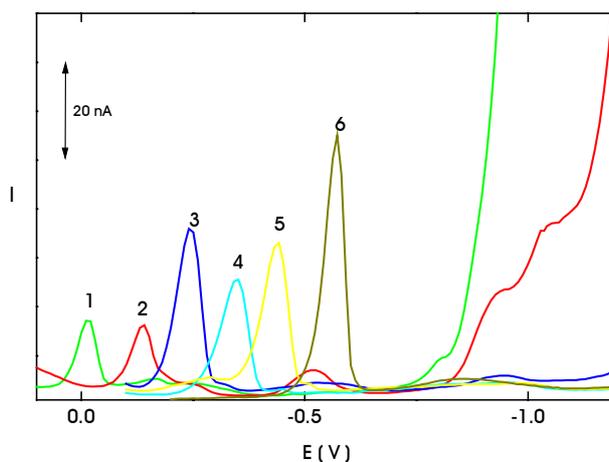
#### Adsorptive Stripping Voltammetry of 4-Nitrobiphenyl at HMDE

Again, using usual optimization procedures [11], the following conditions were found: medium 0.01 mol L<sup>-1</sup> NaOH – MeOH (100:1) mixture, accumulation potential  $E_{acc} = -400$  mV, accumulation time  $t_{acc} = 300$  s for the concentrations  $(2-10) \cdot 10^{-8}$  mol L<sup>-1</sup> and  $t_{acc} = 600$  s for the range  $(2-10) \cdot 10^{-9}$  mol L<sup>-1</sup>. For the sake of illustration, the influence of pH on AdSV recordings of 4-NBP is demonstrated by Fig. 16, calibration curves are depicted in Fig. 17 and Fig. 18 and their parameters are given in Table 9. Relatively high intercept in Fig. 18, curve 1, is again caused by a coinciding peak of an impurity in the base electrolyte (see Fig. 19). After subtraction of the current corresponding to this coinciding peak, a corrected calibration straight line (see curve 2 in Fig. 19) was obtained with lower intercept.

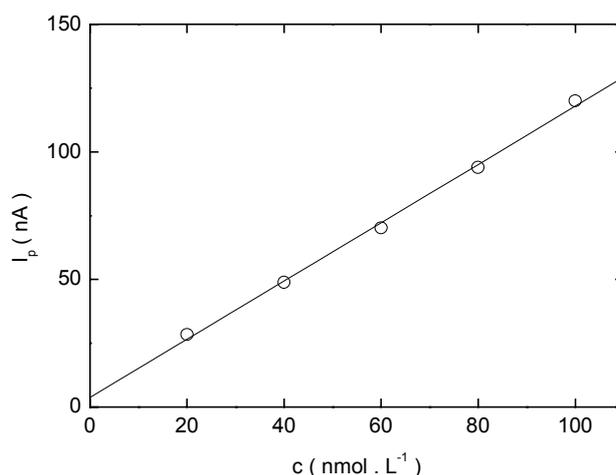
**Table 9.** Parameters of calibration curves for the determination of 3-NBP by AdSV at HMDE in 0.01 mol L<sup>-1</sup> NaOH – methanol (100:1) mixture of resulting pH<sup>m</sup> 12. Potential of accumulation  $E_{acc} = -400$  mV.

c (mol L <sup>-1</sup> )	Slope (nA mol <sup>-1</sup> L)	Intercept (nA)	Correlation coefficient	L <sub>Q</sub> (mol L <sup>-1</sup> )
$(2-10) \cdot 10^{-8}$ <sup>a</sup>	$1.32 \cdot 10^9$	10.3	0.9991	$2.1 \cdot 10^{-8}$
$(2-10) \cdot 10^{-9}$ <sup>b</sup>	$2.39 \cdot 10^9$	2.64	0.9872	$2.4 \cdot 10^{-9}$

<sup>a</sup> time of accumulation  $t_{acc} = 300$  s; <sup>b</sup> time of accumulation  $t_{acc} = 600$  s;



**Figure 16.** AdSV voltammograms of 4-NBP at HMDE in the Britton-Robinson buffer – methanol (100:1) mixture at resulting  $\text{pH}^m$  2.0 (1), 4.0 (2), 6.0 (3), 8.0 (4), 10.0 (5), 12.0 (6). Time of accumulation  $t_{\text{acc}} = 60$  s.

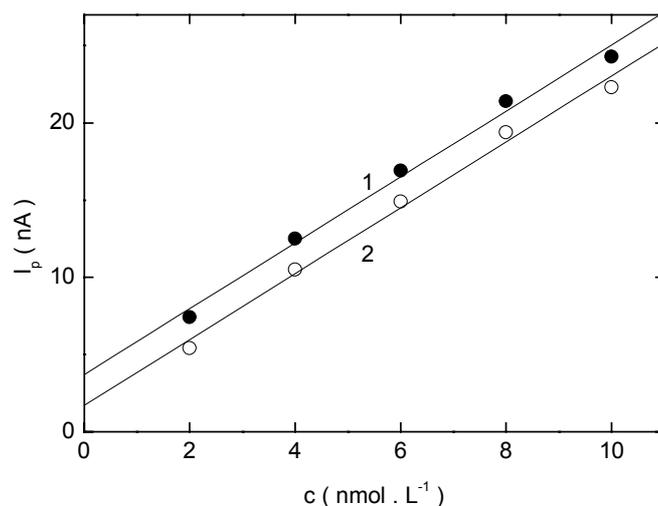


**Figure 17.** The dependence of the peak current ( $I_p$ ) on the concentration of 4-NBP ( $c = (2 - 10) \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ ) measured by AdSV at HMDE in the  $0.01 \text{ mol L}^{-1}$  NaOH – methanol (100:1) mixture with resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400$  mV. Time of accumulation  $t_{\text{acc}} = 300$  s.

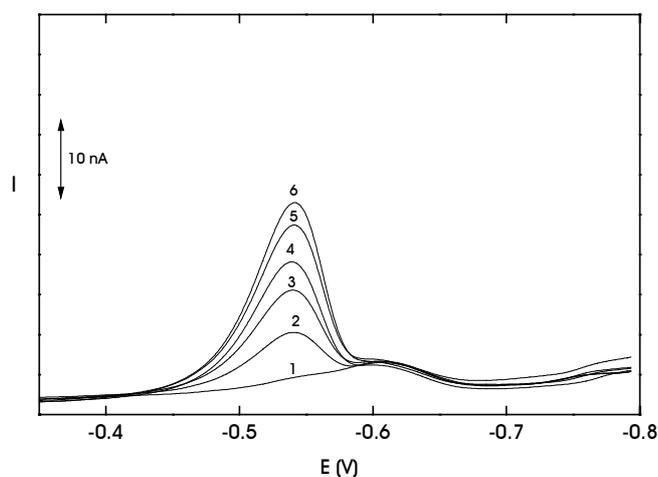
**Table 10.** Parameters of calibration curves for the determination of 4-NBP by AdSV at HMDE in  $0.01 \text{ mol} \cdot \text{L}^{-1}$  NaOH - methanol (100:1) medium of resulting  $\text{pH}^m$  12. Potential of accumulation  $E_{\text{acc}} = -400$  mV.

$c \text{ (mol} \cdot \text{L}^{-1})$	Slope ( $\text{nA mol}^{-1} \text{ L}$ )	Intercept ( $\text{nA}$ )	Correlation coefficient	$L_Q \text{ (mol} \cdot \text{L}^{-1})$
$(2-10) \cdot 10^{-8}^a$	$1.27 \cdot 10^9$	0.51	0.9973	----
$(2-10) \cdot 10^{-9}^b$	$2.36 \cdot 10^9$	1.40	0.9876	$3.3 \cdot 10^{-9}$

<sup>a</sup> time of accumulation  $t_{\text{acc}} = 300$  s; <sup>b</sup> time of accumulation  $t_{\text{acc}} = 600$  s;



**Figure 18.** The dependence of the peak current ( $I_p$ ) on the concentration of 4-NBP ( $c = (2 - 10) \cdot 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ ) measured by AdSV at HMDE in the  $0.01 \text{ mol L}^{-1}$  NaOH – methanol (100:1) mixture of resulting  $\text{pH}^m$  12.0. Potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Time of accumulation  $t_{\text{acc}} = 600 \text{ s}$ . Curve 1 is calibration curve with an interfering peak in the base electrolyte. Curve 2 is corrected calibration line.

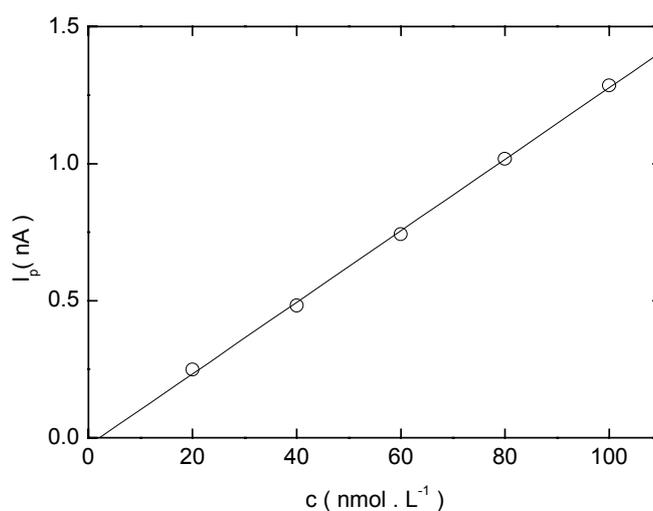


**Figure 19.** Voltammograms of 4-NBP measured by AdSV at HMDE in the lowest attainable concentration range.  $0.01 \text{ mol L}^{-1}$  NaOH – methanol (100:1) mixture of resulting  $\text{pH}^m$  12.0. Time of accumulation  $t_{\text{acc}} = 300 \text{ s}$  and potential of accumulation  $E_{\text{acc}} = -400 \text{ mV}$ . Concentration of 4-NBP ( $\text{mol L}^{-1}$ ): 0 (1),  $2 \cdot 10^{-9}$  (2),  $4 \cdot 10^{-9}$  (3),  $6 \cdot 10^{-9}$  (4),  $8 \cdot 10^{-9}$  (5),  $10 \cdot 10^{-9}$  (6).

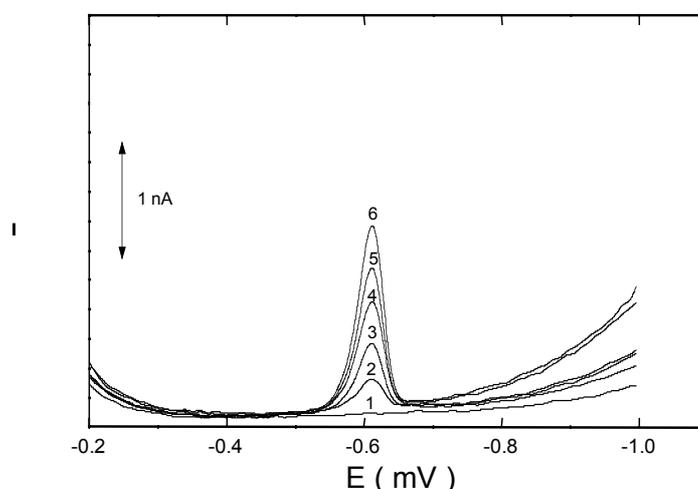
### *Analysis of Model Samples of Drinking Water*

The following procedure was used: 5.00 mL of drinking water was spiked with standard solutions of 3-NBP to obtain model samples containing  $(2-10) \cdot 10^{-8} \text{ mol L}^{-1}$  of 3-NBP, 100  $\mu\text{L}$  of  $1 \text{ mol} \cdot \text{L}^{-1}$  NaOH was added and the solution was filled up to 10 mL with methanol. The resulting calibration curve (see Fig. 20) and corresponding voltammograms (Fig. 21) confirm the applicability of DPV at

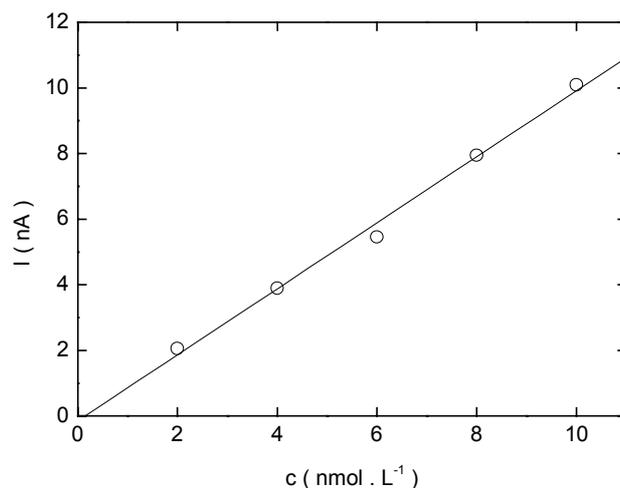
HMDE in this concentration range. To determine even lower concentrations, a preliminary separation and preconcentration must be included. The following procedure can be used [11]: 100 mL of model solutions of drinking water containing  $(2-10) \cdot 10^{-9} \text{ mol} \cdot \text{L}^{-1}$  of 3-NBP were extracted with 5 mL of hexane, the extract was evaporated to dryness using a rotating vacuum evaporator and the residue was dissolved in 1 mL of methanol using sonication. Afterwards, 1 mL of Britton-Robinson buffer pH 12 was added and DP voltammogram was recorded. The recovery was found to be 65.8 %. The calibration curves thus constructed are depicted in Fig. 22 and corresponding DP voltammograms in Fig. 23. It can be seen that this approach is suitable for the determination of nanomolar concentrations of 3-NBP in drinking water.



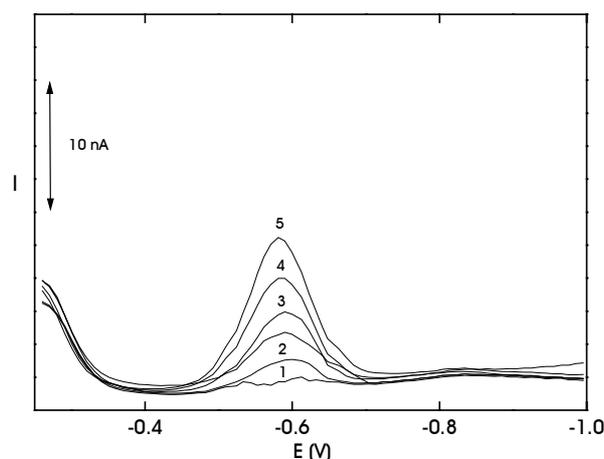
**Figure 20.** The dependence of the peak current ( $I_p$ ) on the concentration of 3-NBP measured by DPV at HMDE in the mixture drinking water – methanol (1 : 1) with resulting  $\text{pH}^m$  12.0 (Adjusted by  $100 \mu\text{L}$  of  $1 \text{ mol} \cdot \text{L}^{-1}$  NaOH). Concentration of 3-NBP in drinking water  $(2 - 10) \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ .



**Figure 21.** DP voltammograms of 3-NBP at HMDE in the drinking water – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0 (Adjusted by  $100 \mu\text{L}$  of  $1 \text{ mol} \cdot \text{L}^{-1}$  NaOH). Concentration of 3-NBP in drinking water ( $\text{mol} \cdot \text{L}^{-1}$ ): 0 (1),  $2 \cdot 10^{-8}$  (2),  $4 \cdot 10^{-8}$  (3),  $6 \cdot 10^{-8}$  (4),  $8 \cdot 10^{-8}$  (5),  $10 \cdot 10^{-8}$  (6).



**Figure 22.** The dependence of the peak current ( $I_p$ ) on the concentration of 3-NBP measured by DPV at HMDE in the Britton-Robinson buffer – methanol (1:1) mixture with resulting  $\text{pH}^m$  12.0. 100 mL of model solutions of drinking water containing  $(2-10) \cdot 10^{-9}$  mol·L<sup>-1</sup> of 3-NBP extracted with 5 mL of hexane.



**Figure 23.** DP voltammograms of 3-NBP at HMDE in the Britton-Robinson buffer – methanol (1:1) medium with resulting  $\text{pH}^m$  12.0. 100 mL of model solutions of drinking water containing 0 (1),  $2 \cdot 10^{-9}$  (2),  $4 \cdot 10^{-9}$  (3),  $6 \cdot 10^{-9}$  (4),  $8 \cdot 10^{-9}$  (5),  $10 \cdot 10^{-9}$  (6) mol·L<sup>-1</sup> of 3-NBP extracted with 5 mL of hexane.

## Conclusions

It has been shown that hanging mercury drop electrode is a suitable sensor for the determination of submicromolar and nanomolar concentrations of nitro substituted biphenyls in simple matrices, such as drinking water, using DPV or AdSV. For more complicated matrices, such as surface or waste waters, classical dropping mercury electrode should be preferred because of periodical renewal of its surface preventing problems with passivation of the electrode or fouling of its surface, which can be the case with HMDE, the surface of which is not renewed in the course of registration of a voltammetric curve.

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*Sample Availability:* Available from the authors.