POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF GENOTOXIC 4-NITROINDAN USING MERCURY AND SILVER SOLID AMALGAM ELECTRODES

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Introduction

❖ Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) – including studied **4-nitroindan** – can be either directly emitted from combustion sources such as diesel or gasoline engines, or formed from their parent PAH by atmospheric OH or NO_3 radical initiated reactions. Since it has been shown that nitro-PAH can be many times more mutagenic and/or carcinogenic than their parent PAH, the analysis of nitro-PAH in emission sources and living environment becomes to be important [1]. Due to the presence of electrochemically easily reducible nitro group on aromatic ring, polarographic and/or voltammetric methods can be successfully used for the determination of trace amounts of 4-nitroindan.
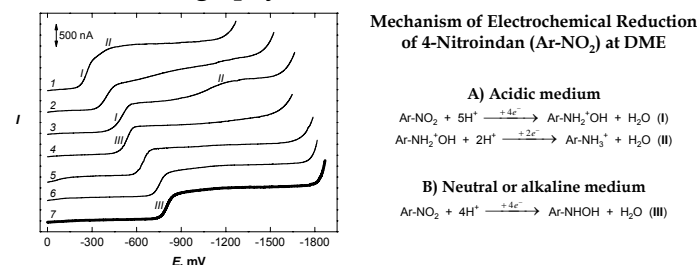
❖ Analyte:
4-nitroindan, nitro-PAH with non-full aromatic structure and with structural [2] and toxicological [3] properties similar to 1-nitronaphthalene (*IARC group 3*), has been electrochemically determined at a **classical mercury dropping electrode (DME)** [4] and at a **mercury meniscus modified silver solid amalgam electrode (m-AgSAE)** [5] – a non-toxic alternative to traditional mercury electrodes. The stock solution of 4-nitroindan ($c = 1 \times 10^{-3}$ mol L^{-1}) was prepared in methanol due to the lower solubility of 4-nitroindan in water. Optimal conditions for the determination of 4-nitroindan have been investigated in buffered aqueous-methanolic solutions; **optimal medium: methanol – Britton-Robinson (BR) buffer (1:1)**. Obtained results have been compared with UV-VIS spectrophotometric determination of 4-nitroindan in methanol.

❖ Polarographic and voltammetric techniques used for the determination of 4-nitroindan:
 - **DC tast polarography (DCTP) at DME**,
 - **differential pulse polarography (DPP) at DME**,
 - **DC voltammetry (DCV) at m-AgSAE**,
 - **differential pulse voltammetry (DPV) at m-AgSAE**.
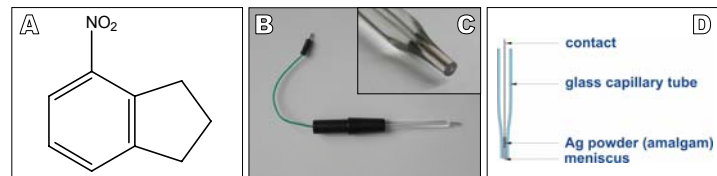
4-Nitroindan (**A**), meniscus modified silver solid amalgam electrode (**B**), detailed picture of meniscus (**C**), and scheme of electrode (**D**).

DC Tast Polarography of 4-Nitroindan at DME

Mechanism of Electrochemical Reduction of 4-Nitroindan (Ar-NO$_2$) at DME

A) Acidic medium

$$Ar\text{-}NO_2 + 5H^+ \xrightarrow{+4e^-} Ar\text{-}NH_2^+OH + H_2O \ (\mathbf{I})$$
$$Ar\text{-}NH_2^+OH + 2H^+ \xrightarrow{+2e^-} Ar\text{-}NH_3^+ + H_2O \ (\mathbf{II})$$

B) Neutral or alkaline medium

$$Ar\text{-}NO_2 + 4H^+ \xrightarrow{+4e^-} Ar\text{-}NHOH + H_2O \ (\mathbf{III})$$

DCT polarograms of 4-nitroindan ($c = 1 \times 10^{-4}$ mol L^{-1}) measured at DME (*drop lifetime* = 1.0 s, *height of the mercury reservoir* = 64 cm, *mass flow rate of mercury through the capillary* = 2.63 mg s^{-1}) in methanol – BR buffer (1:1) medium; pH of used BR buffer = 2.0 (1), 4.0 (2), 5.0 (3), 6.0 (4), 8.0 (5), 10.0 (6) and 12.0 (7); *polarization rate* = 4 mV s^{-1}. Roman numerals represent individual steps of polarographic reduction of 4-nitroindan at DME. Bold DCT polarogram represents optimal conditions selected for subsequent DCT polarographic determination of 4-nitroindan at DME.

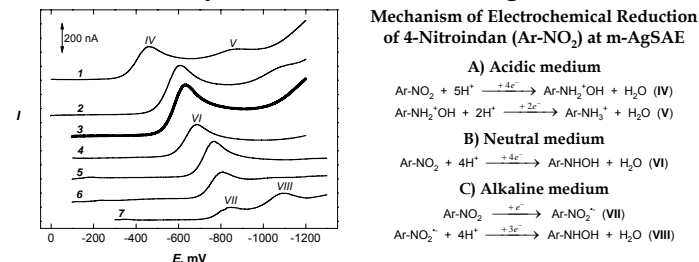## Differential Pulse Polarography of 4-Nitroindan at DME
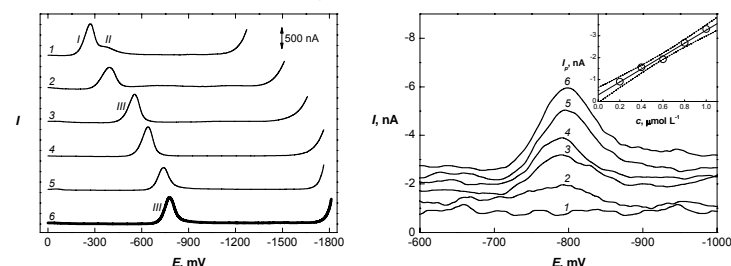
DP polarograms of 4-nitroindan ($c = 1 \times 10^{-4}$ mol L^{-1}) measured at DME (*drop lifetime* = 1.0 s, *height of the mercury reservoir* = 64 cm, *mass flow rate of mercury through the capillary* = 2.63 mg s^{-1}) in methanol – BR buffer (1:1) medium; pH of used BR buffer = 2.0 (1), 4.0 (2), 6.0 (3), 8.0 (4), 10.0 (5) and 12.0 (6). Roman numerals represent individual steps of polarographic reduction of 4-nitroindan at DME. Bold DP polarogram represents optimal conditions selected for subsequent DP polarographic determination of 4-nitroindan at DME.

DP polarograms of 4-nitroindan measured at DME (*drop lifetime* = 1.0 s, *height of the mercury reservoir* = 64 cm, *mass flow rate of mercury through the capillary* = 2.63 mg s^{-1}) in methanol – BR buffer pH 12.0 (1:1) medium; c(4-nitroindan) = 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5) and 1.0 (6) μmol L^{-1}; *polarization rate* = 4 mV s^{-1}. The corresponding calibration straight line is in the inset; confidence bands (- - -) are constructed for significance level α = 0.05.

DC Voltammetry of 4-Nitroindan at m-AgSAE

Mechanism of Electrochemical Reduction of 4-Nitroindan (Ar-NO$_2$) at m-AgSAE

A) Acidic medium

$$Ar\text{-}NO_2 + 5H^+ \xrightarrow{+4e^-} Ar\text{-}NH_2^+OH + H_2O \ (\mathbf{IV})$$
$$Ar\text{-}NH_2^+OH + 2H^+ \xrightarrow{+2e^-} Ar\text{-}NH_3^+ + H_2O \ (\mathbf{V})$$

B) Neutral medium

$$Ar\text{-}NO_2 + 4H^+ \xrightarrow{+4e^-} Ar\text{-}NHOH + H_2O \ (\mathbf{VI})$$

C) Alkaline medium

$$Ar\text{-}NO_2 \xrightarrow{+e^-} Ar\text{-}NO_2^{\cdot -} \ (\mathbf{VII})$$
$$Ar\text{-}NO_2^{\cdot -} + 4H^+ \xrightarrow{+3e^-} Ar\text{-}NHOH + H_2O \ (\mathbf{VIII})$$

DC voltammograms of 4-nitroindan ($c = 1 \times 10^{-4}$ mol L^{-1}) measured at m-AgSAE (*disc diameter* = 0.52 mm) in methanol – BR buffer (1:1) medium; pH of used BR buffer = 2.0 (1), 4.0 (2), 5.0 (3), 6.0 (4), 8.0 (5), 10.0 (6) and 12.0 (7); *polarization rate* = 20 mV s^{-1}. Roman numerals represent individual steps of voltammetric reduction of 4-nitroindan at m-AgSAE. Bold DC voltammogram represents optimal conditions selected for subsequent DC voltammetric determination of 4-nitroindan at m-AgSAE.

DP Voltammetry of 4-Nitroindan at m-AgSAE
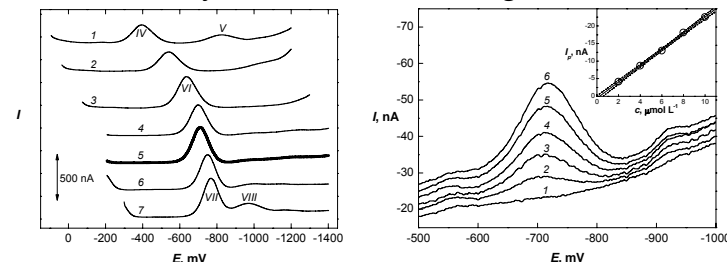
DP voltammograms of 4-nitroindan ($c = 1 \times 10^{-4}$ mol L^{-1}) measured at m-AgSAE (*disc diameter* = 0.52 mm) in methanol – BR buffer (1:1) medium; pH of used BR buffer = 2.0 (1), 4.0 (2), 6.0 (3), 8.0 (4), 9.0 (5), 10.0 (6) and 12.0 (7); *polarization rate* = 20 mV s^{-1}. Roman numerals represent individual steps of voltammetric reduction of 4-nitroindan at m-AgSAE. Bold DP voltammogram represents optimal conditions selected for subsequent DP voltammetric determination of 4-nitroindan at m-AgSAE.

DP voltammograms of 4-nitroindan measured at m-AgSAE (*disc diameter* = 0.52 mm) in methanol – BR buffer pH 9.0 (1:1) medium; c(4-nitroindan) = 0 (1), 2.0 (2), 4.0 (3), 6.0 (4), 8.0 (5) and 10.0 (6) μmol L^{-1}; *polarization rate* = 20 mV s^{-1}; regeneration potentials $E_{1,reg}$ = -300 mV, $E_{2,reg}$ = -1300 mV. The corresponding calibration straight line is in the inset; confidence bands (- - -) are constructed for significance level α = 0.05.

Concentration Dependences of 4-Nitroindan Determination

Technique and Electrode [Medium / Regeneration Potentials]	Concentration Range [mol L^{-1}]	Slope [a] [mA mol^{-1} L^{-1}]	Intercept [a,b] [nA]	Correlation Coefficient	Repeatability (n = 20) [%]	L_Q [c] [mol L^{-1}]
DCTP at DME [methanol – BR buffer pH 12.0 (1:1)]	$(2-10) \times 10^{-5}$	-6.50 ± 0.58	21.7 ± 38.6	-0.9988	— [d]	—
	$(2-10) \times 10^{-6}$	-4.29 ± 0.36	**-1.2 ± 2.4**	-0.9990	2.96 [e]	6.5×10^{-7}
DPP at DME [methanol – BR buffer pH 12.0 (1:1)]	$(2-10) \times 10^{-5}$	-6.54 ± 0.59	5.3 ± 39.1	-0.9988	— [d]	—
	$(2-10) \times 10^{-6}$	-4.45 ± 0.66	**-2.9 ± 4.4**	-0.9968	— [d]	—
	$(2-10) \times 10^{-7}$	-2.95 ± 0.46	**-0.3 ± 0.3**	-0.9964	3.89 [e]	1.0×10^{-7}
DCV at m-AgSAE [methanol – BR buffer pH 5.0 (1:1)] [$E_{1,reg}$ = -200 mV, $E_{2,reg}$ = -1100 mV]	$(2-10) \times 10^{-5}$	-2.71 ± 0.19	6.1 ± 12.6	-0.9993	0.95 [f]	—
	$(2-10) \times 10^{-6}$	-2.44 ± 0.19	**0.3 ± 1.3**	-0.9991	— [d]	—
	$(1-10) \times 10^{-7}$	-1.65 ± 0.18	**-0.8 ± 0.1**	-0.9970	5.36 [e]	1.2×10^{-7}
DPV at m-AgSAE [methanol – BR buffer pH 9.0 (1:1)] [$E_{1,reg}$ = -300 mV, $E_{2,reg}$ = -1300 mV]	$(2-10) \times 10^{-5}$	-2.71 ± 0.46	14.6 ± 30.6	-0.9957	0.94 [f]	—
	$(2-10) \times 10^{-6}$	-2.31 ± 0.12	**0.6 ± 0.8**	-0.9996	— [d]	—
	$(1-10) \times 10^{-7}$	-1.22 ± 0.23	**0.0 ± 0.1**	-0.9912	4.90 [e]	1.4×10^{-7}
UV-VIS spectrophotometry [methanol, λ_{max} = 267 nm]	$(2-10) \times 10^{-5}$	7.47 ± 0.46 [g]	**-10.7 ± 30.1** [h]	0.9995	— [d]	—
	$(2-10) \times 10^{-6}$	6.65 ± 4.33 [g]	3.6 ± 28.7 [h]	0.9425	1.21 [e]	3.7×10^{-7}

[a] – intervals represent lower and upper confidence limits, [b] – intercepts which are not statistically significantly different from zero value (allowing use of the method of standard addition) are in bold, [c] – limit of quantification (10σ; α = 0.05), [d] – repeatability was not measured, [e] – repeatability for lowest equidistant measurable concentration of 4-nitroindan ($c = 2 \times 10^{-7}$ mol L^{-1}), [f] – repeatability for highest measurable concentration of 4-nitroindan ($c = 4 \times 10^{-4}$ mol L^{-1}), [g] – the unit of slope is mAU mol^{-1} L, [h] – the unit of intercept is mAU

Conclusion

❖ Following methods of determination of 4-nitroindan have been developed:
 – DCTP at DME in concentration range 2 – 100 μmol L^{-1} in methanol – BR buffer pH 12.0 (1:1),
 – DPP at DME in concentration range 0.2 – 100 μmol L^{-1} in methanol – BR buffer pH 12.0 (1:1).
 – DCV at m-AgSAE in concentration range 0.1 – 100 μmol L^{-1} in methanol – BR buffer pH 5.0 (1:1),
 – DPV at m-AgSAE in concentration range 0.1 – 100 μmol L^{-1} in methanol – BR buffer pH 9.0 (1:1).

❖ The limits of quantification (L_Q) of newly developed polarographic and voltammetric methods of 4-nitroindan determination at DME and m-AgSAE are comparable or lower than the L_Q's reached by UV-VIS spectrophotometry. The sensitivity of newly developed polarographic and/or voltammetric methods of determination of 4-nitroindan can be further increased by using analyte preconcentration, e.g. solid phase extraction.

Acknowledgement

References

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