Differential Pulse Voltammetric Determination of 4-Nitrophenol Using a Glassy Carbon Electrode: Comparative Study between Cathodic and Anodic Quantification

Rene Pfeifer[1,3,], Priscila Tamiasso Martinhon[1], Célia Sousa[1], Josino C. Moreira[2],
Marco Antonio Chaer do Nascimento[1], Jiří Barek[3]*

[1]Federal University of Rio de Janeiro, Chemistry Institute, Departament of Physical Chemistry, Grupo Interdisciplinar de Educação, Eletroquímica, Saúde, Ambiente e Arte, Avenida Athos da Silveira Ramos, 149, Bloco A – 4ª andar, Sala 411, 21941-909, Cidade Universitária, Rio de Janeiro, RJ, Brazil.
[2]Fundação Oswaldo Cruz (FIOCRUZ), Centro de Estudos da Saúde do Trabalhador e Ecologia Humana, ENSP, Rua Leopoldo Bulhões, 1480, 21041-210, Manguinhos, Rio de Janeiro, RJ, Brazil.
[3]Charles University in Prague, Faculty of Science, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ-128 43 Prague 2, Czech Republic
[*]E-mail: renepfeifer18@yahoo.com.br

Differential pulse voltammetry (DPV) at a glassy carbon electrode (GCE) was used for the determination of trace amounts of US EPA priority pollutant 4-nitrophenol (4NP) in Britton-Robinson buffer (BR) of pH 2.0 as an optimal base electrolyte. 4NP can be determined by DPV directly using either its electrochemical oxidation or reduction. The calibration curve was measured for both reactions in the same concentration range from 2 to 100 $\mu mol.L^{-1}$. The calculated limits of detection and quantification are 0.17 and 0.56 $\mu mol.L^{-1}$ (RSD = 2.3 % and R^2 = 0.9987 for n = 5) for cathodic reduction and 0.39 and 1.29 $\mu mol.L^{-1}$ (RSD = 5.3 %, R^2 = 0.9928 for n = 5) for anodic oxidation.

1. INTRODUCTION

Nitro aromatic and phenolic compounds are important intermediates in the production of fungicides, pesticides, dyes, pharmaceuticals (i.e. aminophenol) and explosives. The U.S.A Environmental Production Agency (EPA) categorize p-nitrophenol (4NP) as a priority pollutant and its

exposure can lead to significant increase of methemoglobin, serum glutamic oxaloacetic transaminase (SGOT) and corneal opacity. [1-2] Moreover, oral exposition above 920 mg/kg can lead to human dermatological effects. [3]

Different techniques were used to detect low concentrations of this substance in water, e.g. gas and liquid chromatograph, capillary electrophoresis and voltammetry. [4-6] The advantage of electrochemical methods are low cost per analysis, high selectivity, reasonable sensitivity and easy miniaturization. 4-NP can be detected and quantified electrochemically either by the irreversible reduction of the nitro group or by irreversible oxidation of the hydroxyl group. The elimination of the effect of dissolved oxygen is a vital step to obtain a reasonable quantification of 4NP using cathodic reduction. Meanwhile, the main problem of quantification of 4NP by anodic oxidation is the strong passivation of the surface of working electrode. Attempts to eliminate this passivation have been made by Avaca et al. and Zhao et al. using boron doped diamond electrodes. [7-9] Several types of modified glassy carbon electrodes were presented as alternatives for the detection of 4NP. Tang et al. used a modified glassy carbon with a reduced graphene oxide/gold nanoparticle composite. [10] Yin et. al. used Cupper(I) oxide nanoparticles modified glassy carbon. [11] Even zeolites were used for modification of this type of electrode. [12] Nevertheless, the boron doped diamond and amalgams electrodes are still the best alternative to quantification of this substance by cathodic reduction. [7, 8, 13-15]

This work aim is to study 4NP quantification using differential pulse voltammetry (DPV) at glassy carbon electrode as a model to understand the quantification of hydroxyl and nitro derivatives of aromatic compounds which are inexpensive and easily obtainable models of various cancer biomarkers.

2. EXPERIMENTAL

2.1. Reagents

Aqueous stock solutions of $1\,mmol\,L^{-1}$ 4-nitrophenol (99%, Sigma-Aldrich, Steinheim, Germany) were prepared freshly every week by dissolving 0.14099 g of pure substance in 1 L of deionized water. Previous study demonstrated that the stock solution is stable for at least two month [13]. More dilute 4NP solutions were prepared by exact dilution of the stock solution with buffer solution.

Boric acid, acetic acid, phosphoric acid, and sodium hydroxide (all p.a. purity, Chemapol, Prague, Czech Republic) were used to prepare appropriate Britton-Robinson (BR) buffers by titration of a mixture of $0.04\,mol\,L^{-1}$ boric acid, $0.04\,mol\,L^{-1}$ phosphoric acid, and $0.04\,mol\,L^{-1}$ acetic acid with $0.2\,mol\,L^{-1}$ sodium hydroxide.

Deionized water produced by a Milli-Q Plus system (Millipore, Billerica, MA, USA) was used in all cases. All solutions were stored in glass vessels in the dark at the laboratory temperature.

2.2. Apparatus

Voltammetric measurements were performed with a computer controlled FRA2 µAUTOLAB TYPE III, µ3AUT71265 with General Purpose Electrochemical System (GPES) 4.9 software for Microsoft Windows operating systems (both Metrohm®, Prague, Czech Republic). Measurements were carried out in the three-electrode arrangement with glassy carbon electrode (GCE, 3 mm diameter, Metrohm®, Prague, Czech Republic) working electrode, a platinum wire auxiliary electrode, and a Ag|AgCl (1.0 mol L^{-1} KCl) reference electrode (both Monokrystaly, Turnov, Czech Republic). All potentials in this paper are given with respect to this reference electrode.

All measurements were carried out using DPV with the following parameters: scan rate 10 mV s^{-1}, modulation amplitude 50 mV and pulse duration 50 ms.

The pH measurements were carried out by the pH meter Jenway 4330 (Jenway, Chelmsford, UK) with a combined glass electrode by the same producer. The pH meter was calibrated with standard aqueous calibration buffers of pH 4.00, 7.00, and 10.00 (Sigma-Aldrich, Steinheim, Germany).

2.3. Procedures

2.3.1. Pretreatment of the working electrode

The GCE electrode was polished before measurement with alumina powder (grain size 1.0 µm) followed by rinsing with deionized water. For cathodic reduction no additional treatment of the electrode was needed between individual measurements. However, previous studies reported passivation of the surface of GCE during anodic oxidation of aromatic hydroxyl compounds. Polishing with alumina powder and cleaning in an ultrasonic bath with ultra-pure water between individual measurements was proposed and tested as an option to remove negative influence of this passivation.

2.3.2. Measurement procedures

An appropriate volume of the aqueous stock solution of the investigated compound was added into a 10 mL volumetric flask and the solution was then filled up with the buffer of an appropriate pH to the mark and transferred into a voltammetric cell. For cathodic reductions, oxygen was removed by bubbling with nitrogen (purity class 4.0, Linde, Prague, Czech Republic) for 5 min before each measurement, and a nitrogen atmosphere was then maintained above the solution in the cell. All measurements were carried out at laboratory temperature.

All voltammetric curves were measured five times. The DPV peak heights (I_p) were evaluated from the straight lines connecting the minima before and after the peak. The calibration curves were treated by linear regression. The parameters of the calibration curves (*i.e.*, slope, intercept, coefficient of determination (R^2), and confidence intervals) and other mathematical and statistical quantities (all for the significance level $\alpha = 0.05$) [15] were calculated using Origin Pro 8.0 software (OriginLab Corporation, Northampton, MA, USA). The limit of quantification (L_Q) was calculated using the

equation: $L_Q = 10s/b$, where s is the standard deviation of 5 repetitive determinations at the lowest measurable concentration of the analyte and b is the slope of the calibration curve [17].

3. RESULTS AND DISCUSSION

3.1. Anodic Differential Pulse Voltammetry of 4-Nitrophenol at Glassy Carbon Electrode

3.1.1. Pretreatment of the electrode

Initially, the effect of passivation of GCE electrode surface was investigated. Five DP voltammograms of 4NP (100 µmol.L^{-1} in BR buffer pH 2.0) were recorded without any cleaning procedure of the electrode between individual measurements. Strong passivation of the surface was observed, leading to a fast decrease of peak height (E_p = 1200 mV) (see Figure 1a). This passivation is commonly encountered when working with solid electrodes [27-29].
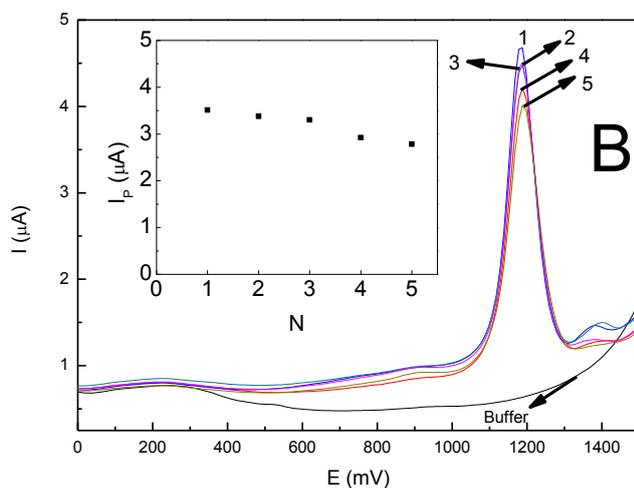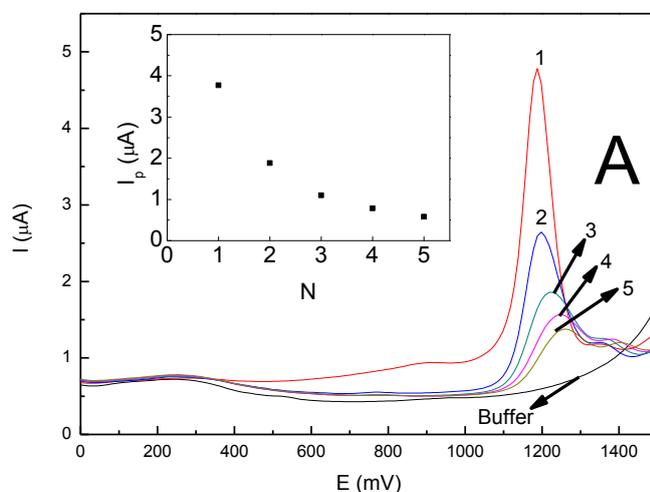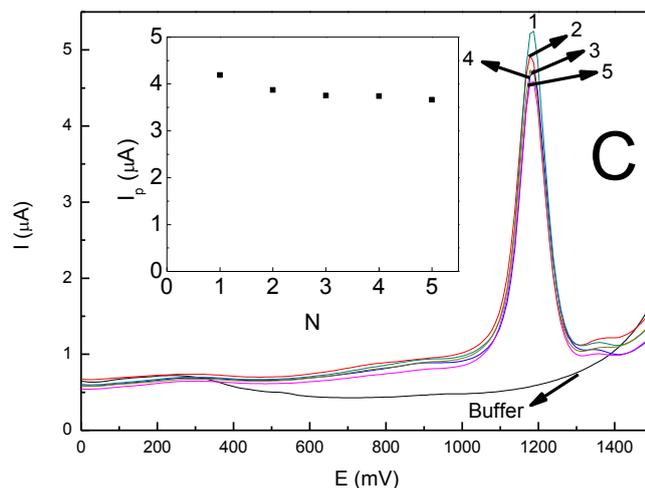
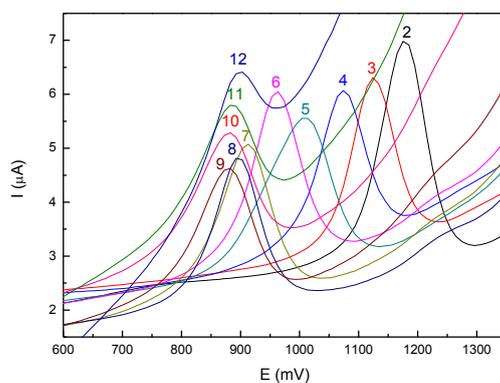**Figure 1.** DP anodic voltammograms of 4-NP (100 µmol.L^{-1}) at GCE in BR buffer pH 2.0. Five measurements without any cleaning process (A), with polishing with alumina powder before each measurement (B) and polishing with alumina powder followed by sonication in an ultrasonic bath with ultra-pure water before each measurement (C). The numbers next to each curve correspond to serial number of measurement. Polarization rate 10 mV.s^{-1}. Insets correspond of the dependency of anodic peak current (I$_p$) on serial number of measurement (N).

A new approach to eliminate this passivation was proposed in this paper based upon the cleaning of the electrode surface by polishing with alumina powder followed by ultrasonic bath treatment in with ultra-pure water before each measurement. These results are presented in Figure 1b and 1c. It was observed that polishing the surface with alumina powder followed by cleaning at an ultrasonic bath gave much more reproducible results than just polishing the surface electrode with alumina powder.

3.1.2. Influence of pH

Figure 2. DP anodic voltammograms of 4-NP (100 µmol.L^{-1}) at GCE in BR buffer pH 2.0 (2), 3.0 (3), 4.0 (4), 5.0 (5), 6.0 (6), 7.0 (7), 8.0 (8), 9.0 (9), 10.0 (10), 11.0 (11), 12.0 (12), Polarization rate 10 mV.s^{-1}. Numbers above voltammograms correspond to pH values.
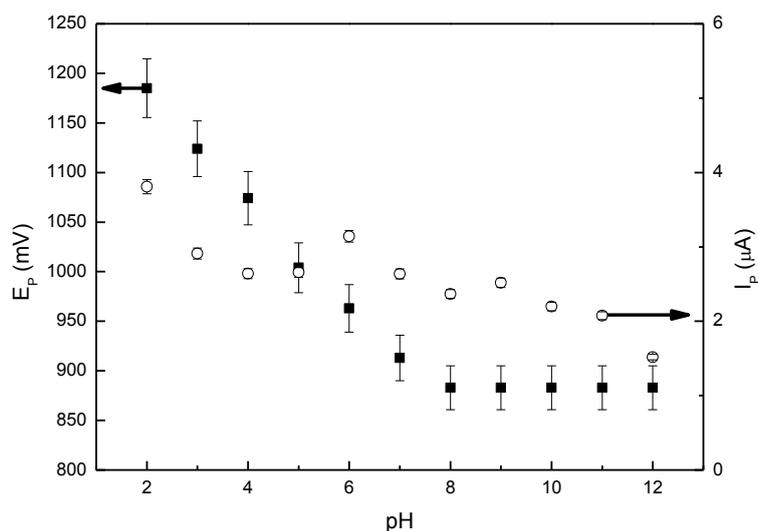
Figure 3. A dependence of the DPV anodic peak current (I_p, ○) and anodic peak potential (E_p, ▪) of 4-NP, c = 100 µmol.L^{-1} in BR buffer, on pH from 2 to 12. Polarization rate 10 mV.s^{-1}.

The influence of pH on the voltammetric behavior of 4NP at GCE was investigated using DPV in BR buffer from pH 2 to 12. The dependency of the peak current (I_p) and peak potential (E_p) on pH is presented in Figure 3. It was found that 4NP peak shifts towards less positive potentials with increasing pH. This is common effect connected with participation of protons in electrode process and with pronation and or deprotonation of electrochemically oxidized species. Parameters of the measured linear dependence of the peak potential of 4NP on pH are given in Table 1.

Table 1. Parameters of measured linear dependences of DPV anodic peak potential of 4NP on pH.

| Analyte	method	*Slope* [mV/pH]	*Intercept* [mV]	R^2
4NP (2<pH<8)	DPV	−54.8	1290	0.9947
4NP (8<pH<12)	DPV	0.00	893	0.9987

The obtained slopes suggest irreversible nature of the studied redox process corresponding to the oxidation of the present hydroxyl group. The calculated pKa value of 4NP, obtained from peak potential dependency on pH, was 7.26 which is in good agreement with value of 7.20 presented in literature [7]. The highest peak was obtained at pH 2.0 which was used for further measurements.

3.1.3. Anodic Differential Pulse Voltammetric Determination of 4-Nitrophenol at a Glassy Carbon Electrode

The concentration dependence of 4NP in BR buffer solution pH 2.0 were measures in the range of 2 − 100 µmol.L^{-1} and they are depicted in Figures 4 and 5. The limits of detection and quantification are summarized in Table 2.
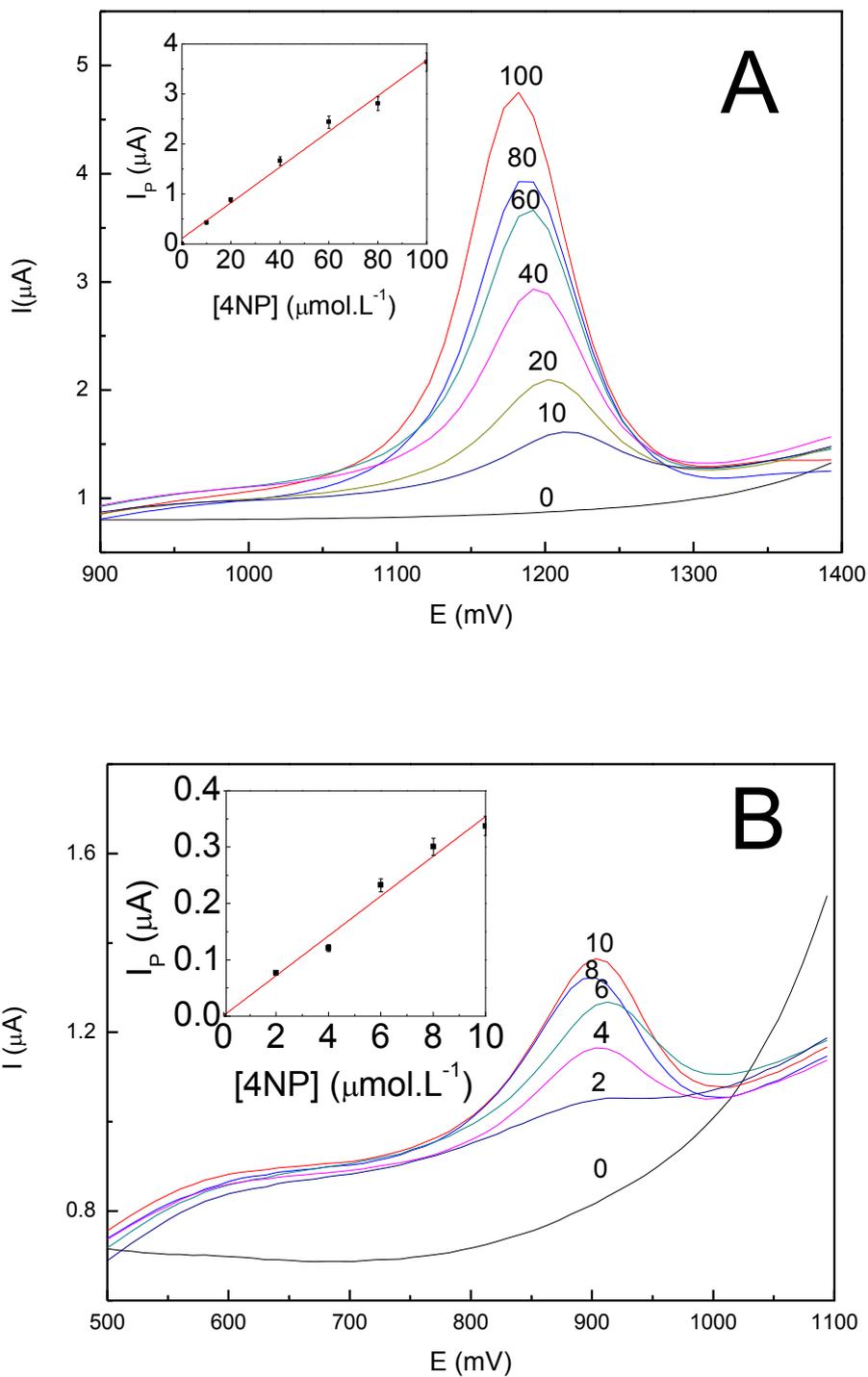
Figure 4. DP anodic voltammograms of 4-NP at GCE in the BR buffer of pH 2.0 in the concentration range of $10 - 100$ μmol.L^{-1} (A) and $2 - 10$ μmol.L^{-1} (B); numbers above voltammograms correspond to actual concentration of 4-NP in μmol.L^{-1}. Insets correspond to concentrations dependence of 4-NP for each range. Polarization rate 10 mV.s^{-1}.
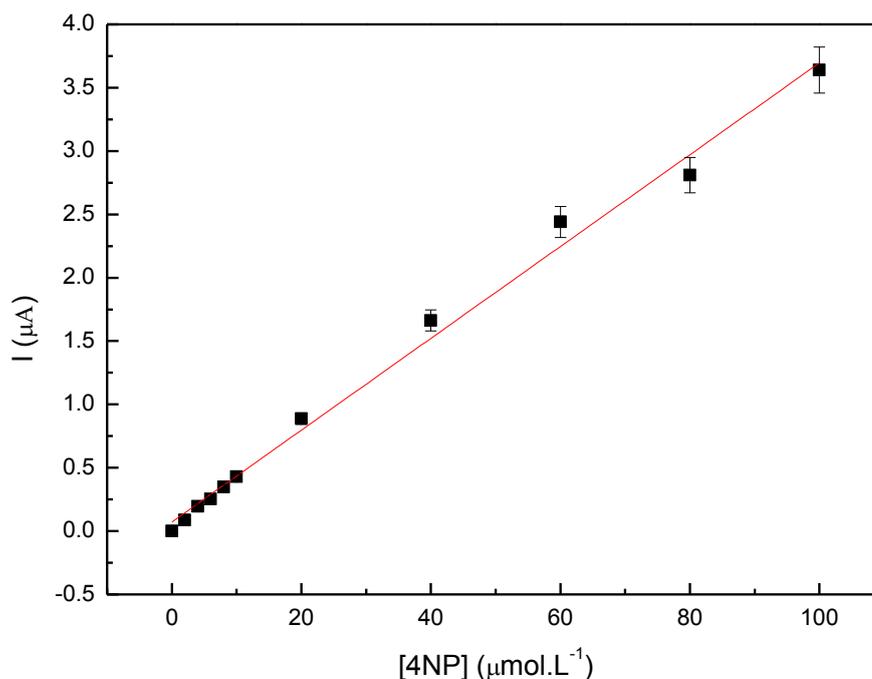
Figure 5. Anodic DPV concentration dependence of 4-NP in the range of 2 – 100 μmol.L^{-1}. Polarization rate 10 mV.s^{-1}.

Table 2. Parameters of the calibration straight line of 4-NP anodic determination using DPV at GCE in BR buffer pH 2.0 in the concentration range from 2 to 100 μmol.L^{-1}.

Range of concentration, μmol.L^{-1}	10 – 100	2 – 10	2 – 100
Slope, μA μmol^{-1} L	0.0366	0.0433	0.0362
Intercept, μA	0.118	0.00659	0.0723
Correlation coefficient	0.9895	0.9952	0.9928
L$_D$, μmol.L^{-1}	2.3	0.39	0.39
L$_Q$, μmol.L^{-1}	7.7	1.29	1.29
RSD (n=5) , %	6.6	5.3	5.3

Table 3. Limits of determination (L$_D$) of 4-NP using voltammetric methods.

Working Electrode	method	Range of Concentration [μmol L^{-1}]	L$_D$ [mol L^{-1}]	R^2	Reference
BDD	SWV	3.0 - 30	8.7 x 10^{-8}	0.9985	7
	Sono-SWV	3.0 – 48.7	1.8 x 10^{-8}	0.9995	8
m-AgSAE	DPV	2.0 - 100	1.1 x 10^{-7}	0.9992	13
p-AgSAE	DPV	2.0 - 100	2.8 x 10^{-7}	0.9932	13
AuNP/RGO/GCE	DPV	0.05 – 2.0	1.0 x 10^{-8}	0.9981	18
	SWW	0.05– 2.0	2.0 x 10^{-8}	0.9961	

MMIPs/Au-NPs/AuE	DPV	0.1 - 1400	1.0×10^{-7}	0.9999	19
m-HAp/ECG/ GCE	DPV	0.2 - 994	2.7×10^{-7}	0.9913	20
PdNPs/CPM /GCE	DPV	0.3 – 1500	7.0×10^{-8}	0.9937	21
CS/PTMS/AuNPs/GCE	DPV	0.03 - 350	2.7×10^{-9}	0.9987	22
nano-Cu2O GCE	DPV	1.0 - 400	5.0×10^{-7}	0.9985	11
SWCNT/PyCD/GCE	DPV	0.2 – 2.4	8.6×10^{-10}	0.9993	23
C/p-NiTSPc CFME	DPV	0.00072 - 3.6	7.2×10^{-10}		24
AgA-PE	DPV	0.2 – 100	3.2×10^{-7}	0.9991	14
HDME	DPV	0.2 – 10	1.3×10^{-7}	0.9992	14
m-AgSAE	DPV	2.0 - 100	6.2×10^{-7}	0.9995	14
LiTCNE/PLL/GCE	DPV	0.027 – 23.2	7.5×10^{-9}		25
SWy-2-AQ CCE	DPV	2.1 - 323	1.4×10^{-7}		26
Zeolite CPE	DPV	1.4 – 71.8	2.9×10^{-7}		12
GCE	DPV	2 - 100	1.7×10^{-7}	0.9987	This Work

* SWV - Square Wave Voltammetry, Sono- SWV – Sono Square Wave Voltammetry, DPV – Differential Pulse Voltammetry, BDD – Boron Doped Diamond Electrode, p-AgSAE – Polished Silver Solid Amalgam Electrode, m-AgSAE – Meniscus Modified Silver Solid Amalgam Electrode, AuNP/RGO/GCE - Au Nanoparticles Reduced Graphene Oxide Modified Glassy Carbon Electrode, MMIPs/Au-NPs/AuE – Molecularly Imprinted Polymers with Gold Nanoparticles Modified Au Electrode, m-HAp/ECG/ GCE - Magnetite-Hydroxyapatite Edge-Carboxylated Graphene Modified Glassy Carbon Electrode PdNPs/CPM /GCE - Palladium Nanoparticles Carbon Porous Materials Modified Glassy Carbon Electrode, CS/PTMS/AuNPs/GCE - Imprinted Chitosan/Phenyltrimethoxysilane/Au Nanoparticles hybrid modified Glassy Carbon Electrode, nano-Cu2O GCE- nano-Cu2O modified Glassy Carbon Electrode, SWCNT/PyCD/GCE - Single-Walled Carbon Nanotube/Pyrenecyclodextrin Nanohybrids modified Glassy Carbon Electrode, C/p-NiTSPc CFME - Para-phenylenediamine Tetrasulfonated Nickel Phtalocyanine outer-Coating modified Carbon Fiber Microelectrode, AgA-PE - Silver Amalgam Paste Electrode, HDME - Hanging Mercury Drop Electrode, LiTCNE/PLL/CME - Lithium Tetracyanoethylenide Poly-L-Lysine hydrochloride Chemically Modified electrodes, SWy-2-AQ GCE - Na-montmorillonite(SWy-2) and Anthraquione (AQ) modified Glassy Carbon Electrode, Zeolite CPE - Zeolite modified Carbon Paste Electrode and GCE - Glassy Carbon Electrode.

The obtained limit of detection (LD) and quantification (LQ) are 0.39 and 1.29 µmol.L^{-1} (RSD =5.3 %, R^2 = 0.99283 for n = 5), respectively. A summary of the limits of detection using different electrode materials is presented in Table 3. It can be seen that limits of detection obtained with the GCE are better than those obtained with the nano-Cu$_2$O modified GCE (nano-Cu$_2$O GCE), Na-montmorillonite (SWy-2) and anthraquione (AQ) modified GCE (SWy-2-AQ GCE) and Zeolite CPE - Zeolite modified carbon paste electrode . The results of obtained with molecularly imprinted polymers with gold nanoparticles modified Au electrode (MMIPs/Au-NPs/AuE) are slighty better than those obtained with GCE electrode. The lowest limits of detection of 4NP, using the anodic oxidation can be obtained with the single-wall carbon nanotube/pyrenecyclodextrin nanohybrids modified GCE (SWCNT/PyCD/GCE) and with p-phenylenediamine tetrasulfonated nickel phtalocyanine outer-coating modified carbon fiber microelectrode (C/p-NiTSPc CFME). However, our commercially available GCE does not require complex and time consuming modification.

3.2. Cathodic Differential Pulse Voltammetry of 4-Nitrophenol at a Glassy Carbon Electrode

3.2.1. Influence of pH

Table 4. Parameters of measured linear dependences of DPV cathodic peak potential of 4NP on pH.

Analyte	method	*slope* [mV/pH]	*Intercept* [mV]	R^2
4NP (2<pH<8)	DPV	−46.2	−477.	0.9688
4NP (8<pH<12)	DPV	−57.1	−398	0.9101
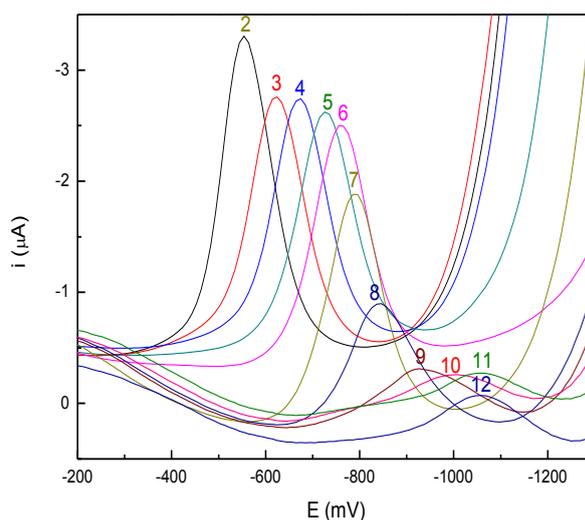

Figure 6. DP cathodic voltammograms of 4-NP (100 μmol.L^{-1}) at GCE in BR buffer pH 2.0 (2), 3.0 (3), 4.0 (4), 5.0 (5), 6.0 (6), 7.0 (7), 8.0 (8), 9.0 (9), 10.0 (10), 11.0 (11), 12.0 (12), Polarization rate 10 mV.s^{-1}.Numbers above voltammograms correspond to pH values.
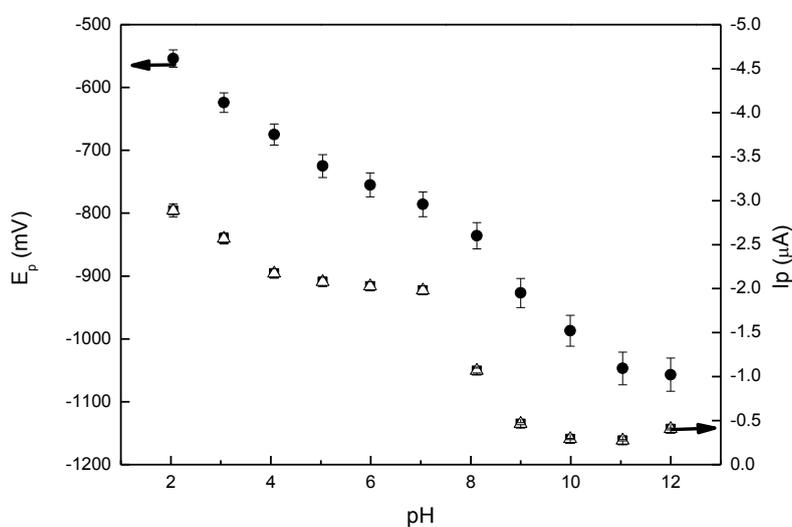
Figure 7. Dependence of the DPV cathodic peak current (I_p, Δ) and cathodic peak potential (E_p, ●) of 4-NP, c = 100 μmol.L^{-1} , in BR buffer on pH from 2 to 12. Polarization rate 10 mV.s^{-1}.

The influence of pH on cathodic DPV behavior of 4NP at GCE was investigated in BR buffer from pH 2 to 12. The dependency of the peaks current (I_p) and potential (E_p) on pH is presented in Figure 7. It was found that 4NP peak shifts towards more negative potentials with increasing pH. Parameters of the measured linear dependence of the peak potential of 4NP on pH are given in Table 4. The obtained slopes suggest an irreversible nature of the studied redox process corresponding to the four-electron reduction of the present nitro group to corresponding hydroxylamino group [24]. The calculate pKa of 4NP, obtained from peak potential dependency on pH, was 7.16 which is in good agreement with value of 7.20 presented in literature. [7] The highest and best developed peak was obtained at pH 2.0 which was used for further measurements.

3.2.2 Cathodic Differential Pulse Voltammetric Determination of 4-Nitrophenol at a Glassy Carbon Electrode
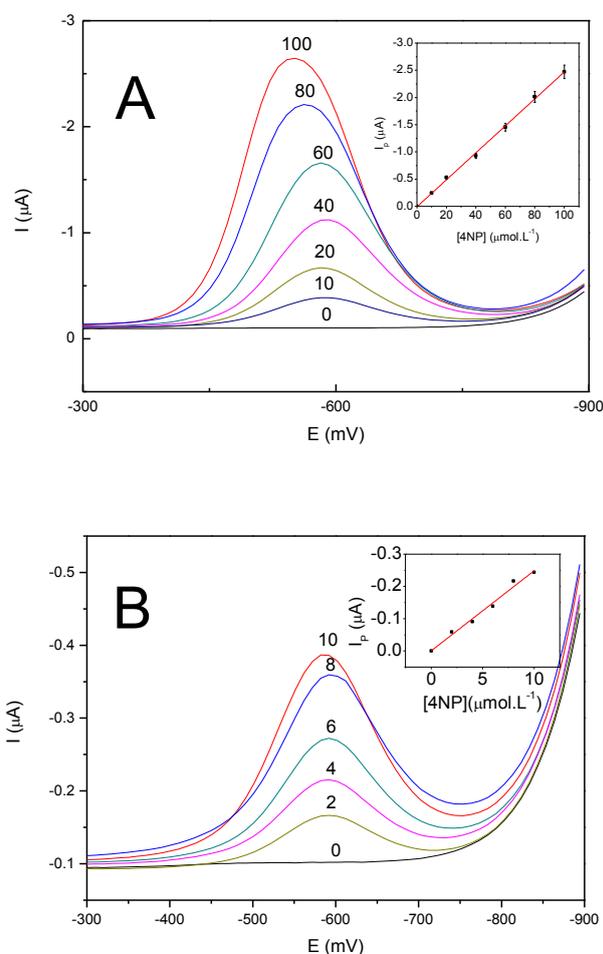
Figure 8. DP cathodic voltammograms of 4-NP at GCE in the BR buffer of pH 2.0 in the concentration range of 10 – 100 μmol.L^{-1} (A) and 2 – 10 μmol.L^{-1} (B); numbers next to curves correspond to actual concentration of 4-NP in μmol.L^{-1}. Insets correspond to concentrations dependence of 4-NP for each range. Polarization rate 10 mV.s^{-1}.
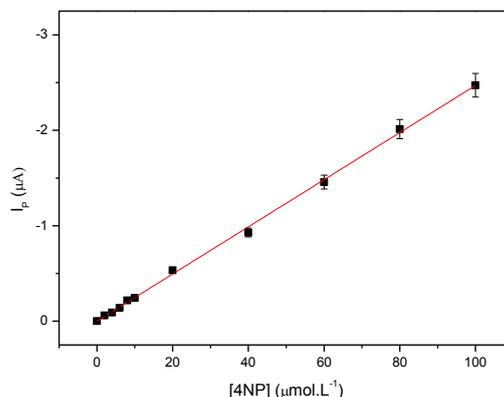
Figure 9. Cathodic DPV concentration dependence of 4-NP in the concentration range of 2 – 100 μmol.L^{-1} . Polarization rate 10 mV.s^{-1}.

The concentration dependences of 4NP in BR buffer pH 2.0 were measured in the range of 2 – 100 μmol.L^{-1} and are depicted in Figures 8 and 9. The limits of detection and quantification are summarized in Table 5.

Table 5. Parameters of the calibration straight line of 4-NP cathodic determination using DPV at GCE in BR buffer pH 2.0 in the concentration range from 2 to 100 μmol.L^{-1}.

Range of concentration, μmol.L^{-1}	10 – 100	2 – 10	2 – 100
Slope, μA μmol^{-1} L	-0.024	-0.024	-0.024
Intercept, μA	0.0041	-0.0007	0.0001
Correlation coefficient	0.9983	0.9824	0.9987
L$_D$, μmol.L^{-1}	0.39	0.17	0.17
L$_Q$, μmol.L^{-1}	1.3	0.56	0.56
RSD (n=5) , %	1.3	2.3	2.3

The obtained limit of detection (LD) and quantification (LQ) are 0.17 and 0.56 μmol.L^{-1}(RSD = 2.3 % and R^2 = 0.9987 for n = 5), respectively. According to the comparative limits of detection presented at Table 5, the results obtained at this work are slightly higher than those obtained at the silver amalgam paste electrode (AgA-PE), hanging mercury drop electrode (HDME), polished silver solid amalgam electrode (p-AgSAE), and meniscus modified silver solid amalgam electrode (m-AgSAE). The lowest limits of cathodic detection of 4NP were obtained with boron doped diamond electrode (BDD). However, our simple and commercially available glassy carbon electrode is more environmentally friendly than mercury based electrodes and more common than BDDE.

4. CONCLUSIONS

The quantification of 4NP was carried out with differential pulse voltammetry at glassy carbon electrode. Strong passivation of the surface was observed for anodic oxidation. However, ultrasonic

bath cleaning after alumina polishing was found to be an efficient step in the elimination of passivation of the electrode surface after each measurement. The dependency of potential peak on pH for both cathodic reduction and anodic oxidation was measured. The values of pKa for 4-NP obtained from DPV measurements are in good agreement with the experimental values of 7.20 presented in literature. The calculated limits of detection and quantification for cathodic reduction are 0.17 and 0.56 μmol L^{-1} (RSD = 2.3 % and R^2 = 0.9987 for n = 5) and for anodic oxidation are 0.39 and 1.29 μmol L^{-1}(RSD =5.3 %, R^2 = 0.9928 for n = 5). Comparison of limits of detection obtained in this work reveal that anodic oxidation reaction can be used for the quantification of submicromolar concentrations of 4NP. However, the passivation of the electrode surface must effectively eliminated by the developed combination of mechanical cleaning with alumina followed by sonication The limits of detection based on anodic oxidation are slightly higher than those obtained with cathodic reduction. The advantage of GCE used in this work is the complete absence of mercury.

References

1. National Toxicology Program. *Toxicology and Carcinogenesis Studies of p-Nitrophenol (CAS No. 100-02-7) in Swiss Webster Mice (Dermal Studies).* TR-417. 1993.
2. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Nitrophenols* (Draft). Public Health Service, U.S. Departamente of Health and Human Services, Atlanta, GA, 1990.
3. U.S. Environmental Protection Agency. *Integrated Risk Information System (IRIS) on p-Nitrophenol.* National Center for Environmental Assessement, Office of Research and development, Washington, DC. 1999.
4. R. Wissiak, E. Rosenberg, *J. Chromatogr. A.* 963 (2002) 149.
5. S. F. Y Li, C. P. Ong, C. L. Ng, N. C. Chang, N. K. Lee, *J. Chromatogr. A.* 216 (1990) 263.
6. A. Brega ,P. Prandini,; C. Amaglio, E. Pafuni, *J. Chromatogr. A.* 535 (1990) 313.
7. V. A. Pedrosa, L. Codognoto, L. A. Avaca, *J. Braz. Chem. Soc.* 14 (2003) 530.
8. G. S. Garbellini, G. R. Salazar-Banda, L. A. Avaca, *J. Braz. Chem. Soc.* 18 (2007) 1095.
9. G. H. Zhao, Y. T. Tang, ; M. C. Liu, Y. Z. Lei, X. Xiao, *Chin. J. Chem.* 25 (2007) 1445.
10. Y. Tang, R. Huang, C. Liu, S. Yang, Z. Lua, S. Luo, *Anal. Methods* 5 (2013) 5508.
11. H. Yin, Y. Zhou , S. Ai, Q. Ma , L. Zhu, L. Lu, *Intern. J. Environ. Anal. Chem.* 92 (2012) 15.
12. M. M. C. Rando, M. B. Zamora, J. M. B. Salvador, I. N. Rodríguez, J. A. M. Leyva, J. L. H. Cisneros, *Mikrochim. Acta* 132 (1999) 7.
13. J. Fischer, L. Vanourkova, A. Danhel, V. Vyskocil, K. Cizek, J. Barek, K. Peckova, B. Yosypchuk, T. Navratil, *Int. J. Electrochem. Sci.* 2 (2007) 226.
14. A. Niaz, J. Fischer, J. Barek, B. Yosypchuk, S. M. I. Bhanger, *Electroanalysis* 21 (2009) 1786.
15. J. Barek, J. Fischer, T. Navratil, K. Peckova and B. Yosypchuk, *Sensors* 6 (2006) 445.
16. J.N. Miller and J.C. Miller, *Statistics and Chemometrics for Analytical Chemistry* (Fifth Edition), Pearson Education, Harlow, 2005.
17. J. Inczedy, T. Lengyel and A.M. Ure, *Compendium of Analytical Nomenclature: Definitve Rules 1997* (Third Edition), Blackwell Science, Malden, MA, 1998.

18. Y. Tang, R.Huang, C. Liu, S. Yang, Z. Lua, S. Luo, *Anal. Methods*, 5 (2013) 5508.
19. G. Xu , L. Yang , M. Z. C. Li , X. Lu, X. Kan, *Microchim. Acta*, 180 (2013) 1461.
20. G. Bharath, V. Veeramani, S. M. Chen, R. Madhu, M. M. Raja, A. Balamurugan, D. Mangalaraj, C. Viswanathana, N. Ponpandian, *RSC Advances*, 5 (2015) 13392.
21. P. V. R. Madhu, S. M. Chen, V. Veeramani, C T. Hung, P. H. Tang, C. B. Wang, S. B. Liu, *J. Mater. Chem A*, 2 (2014) 16015.
22. S. Li, D.Du, J. Huang, H. Tu, Y. Yang. A. Zhang, *Analyst*, 777 (2013) 63.
23. Y. W. L. T. Kong, R. Yang, L. Wang, J. H. Liu, X. J. Huang, *Langmuir*, 27 (2011) 10295.
24. M. Ponti, L. Sikpo, G. Thouand, R. Lahan, I. Tapsoba, R. Mallet, T. Feng, *Electroanalysis* 23 (2009) 433.
25. R C. S. Luz, F. S. Damos, A. B. Oliveira, J. Beck, L.T. Kubota, *Talanta*, 64 (2004) 935.
26. S. Hu, C. Xu, G.Wang, D. Cui, *Talanta*, 54 (2001) 115.
27. T. Navratil, J. Barek, *Crit. Rev. Anal. Chem.* , 39 (2009) 131.
28. B. Yosypchuk, J. Barek, *Crit. Rev. Anal. Chem.*, 39 (2009) 189.
29. A. Danhel, J. Barek, *Curr. Org. Chem.* 15 (2011) 2957.