8. PŘÍLOHA I

VOLTAMMETRIC DETERMINATION OF 8-NITROQUINOLINE USING A SILVER SOLID ELECTRODE AND ITS APPLICATION TO MODEL SAMPLES OF DRINKING AND RIVER WATER

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Voltammetric Determination of 8-Nitroquinoline Using a Silver Solid Electrode and Its Application to Model Samples of Drinking and River Water

Tereza Rumlova,*[a] Jiri Barek,*[a] and Frank-Michael Matysik*[b]

Abstract: This work is focused on the application of a silver solid electrode (AgE) for the development of modern voltammetric methods for the determination of submicromolar concentrations of biologically active compounds present in the environment. 8-Nitroquinoline (8-NQ), a well-known chemical carcinogen, was chosen as a model substance. Differential pulse voltammetry (DPV) was used to study electrochemical behavior of 8-NQ in different aqueous matrices. The following optimal conditions for determination of 8-NQ in the concentration ranges from 2 to 100 μmol L^{-1} were used: Britton–Robinson (BR) buffer of pH 3.0, the regeneration potentials cycles ($E_{in} = -1000$ mV, $E_{fin} = -100$ mV) and constant cleaning potential −2000 mV. Practical applicability of AgE for the determination of micromolar concentrations of 8-NQ was verified on model samples of drinking and river water.

Keywords: Silver solid electrode · Differential pulse voltammetry · 8-Nitroquinoline · Drinking water · River water

1 Introduction

Monitoring of organic compounds in the environment is one of the most important tasks of modern analytical chemistry. Electroanalytical methods are especially suitable for large scale environmental monitoring of electrochemically active organic pollutants because they are inexpensive, extremely sensitive and they present an independent alternative to so far prevalent spectrometric and separation techniques [1]. Development of sufficiently sensitive and selective voltammetric and amperometric methods for the determination of various environmentally important biologically active substances is the main task of our UNESCO Laboratory of Environmental Electrochemistry [2–4]. Quinolines and its nitroderivatives are among substances suspected of carcinogenity and mutagenity [5–7]. 8-Nitroquinoline (8-NQ, for structural formula see Figure 1) belongs to the group of nitrated aromatic heterocyclic compounds and is known for its carcinogenic properties [8]. Electrocatalytic hydrogenation of 8-NQ has been studied on a copper cathode using skeleton catalyst (Ni, Cu, Zn, Fe) [9]. The electrochemical reduction of quinolines is possible, but more complicated than reduction of its nitroderivatives such as 5-NQ or 8-NQ [10–15]. At first, there is reduction to dihydroquinoline and in the next step to tetrahydroquinoline in two two-electron waves. Quinolines and their derivatives are usually used as catalysts and as corrosion inhibitors [16,17]. It has been proved that quinoline is inhibiting the photosynthesis of seaweed and causes degenerating changes in the retina [18] and in the eye lens [19,20]. The electrochemical determination of nitroquinolines and their electrochemical behavior was described in [7]. Silver solid electrode (AgE) was studied for the sake of comparison with silver solid amalgam electrodes [21] and it has been already tested for voltammetric determination of other nitro-compounds [22]. The advantages of AgE are primarily its wide potential window in cathodic region, relatively high signals obtained and low noise of measurements. Another advantage of AgE is also non-toxicity compared to mercury electrodes. The usability of AgE for electrochemical determinations of inorganic ions (e.g. lead, cadmium), organic compounds (e.g. 6-mercaptopurine, 2-mercaptopyrimidine) and drugs has been proved recently [22–27]. AgE was also successfully used for investigation of electrochemical behavior of DNA [28,29]. In our work with silver amalgam electrodes we

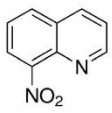

Fig. 1. Structural formula of 8-nitroquinoline.

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have got better results with DPV than SWV. Usually the problems with passivation are lower for DPV because the electrode is for relatively shorter fraction of total time at potential at which electrode reaction producing possibly passivating products proceeds. This is because time between pulses in the case of DPV is longer than the pulse width while in SWV the time between pulses is equal to pulse width. Therefore, we have used DPV at AgE as well in this paper.

2 Experimental

2.1 Apparatus

All DPV measurements in deionized water were carried out using potentiostat 797 VA Computrace for trace analysis (Metrohm AG, Switzerland). The software (VA Computrace software, Metrohm AG, Switzerland) worked under the operating system Microsoft Windows 7 (Microsoft Corp., USA). Measurements in model samples of drinking and river water were carried out using μAutolab type III potentiostat (Metrohm Autolab, Netherland) and the software (NOVA 1.10, Metrohm Autolab, Netherland) under the operating system Microsoft Windows 8 (Mircrosoft Corp., USA). All measurements were carried out in a three-electrode system with platinum wire (Elektrochemické detektory, s.r.o., Czech Republic) as an auxiliary electrode, silver/silver chloride reference electrode Type 10-20+polaro (1 mol L^{-1} KCl, Elektrochemické detektory, spol. s.r.o., Czech Republic) and AgE (disk diameter 2 mm, Metrohm, Switzerland) as a working electrode. Unless stated otherwise, the scan rate 20 mV s^{-1}, the pulse amplitude −50 mV, pulse width 80 ms, and interval between pulses 250 ms were used. The best repeatability and reproducibility of voltammetric measurements at AgE were obtained using electrochemical regeneration of electrode surface by the application of 150 potential cycles between −1000 mV and −100 mV, each for 50 ms followed by the application of constant cleaning potential −2000 mV on working electrode for 60 s.

2.2 Reagents

The stock solution of 8-NQ (1×10^{-3} mol L^{-1}) was prepared by dissolving of 0.0174 g of 8-NQ (98% Aldrich Chem. Co., CAS reg. Number 607-35-2) in deionized water and filling up to 100 mL. More dilute solutions were prepared by serial dilution of this stock solution with deionized water. All solutions were kept in dark and at laboratory temperature. The other chemicals used, boric acid, phosphoric acid, acetic acid, sodium hydroxide and potassium chloride, were of p.a. purity (Lachner, Czech Republic). BR buffers were prepared in a usual way by mixing 0.2 mol L^{-1} sodium hydroxide with the mixture of 0.04 mol L^{-1} of boric, phosphoric, and acetic acid. The pH was measured by pH meter Jenway with combined glass electrode (type 924005, Jenway, UK). Deionized water (Millipore Q plus system, Millipore, USA) was used.

2.3 Procedures

An appropriate volume of the stock solution of 8-NQ (1×10^{-3} mol L^{-1}) was filled up to 10.0 mL with BR buffer of appropriate pH and then transfered into the voltammetric cell. Oxygen was removed by purging with nitrogen (purity class 4.0, Linde Gas, Czech Republic) for 5 minutes and then the DP voltammogram was recorded. The DPV peaks were evaluated from the straight line connecting the minima before and after the peaks.

The limits of quantification (*LOQ*) were calculated as the concentration of the analyte corresponding to the tenfold standard deviation of the analyte's response from ten consecutive determinations at the lowest attainable concentration range [30].

For the preparation of model samples of drinking water, the water from water pipeline in the building of Faculty of Science, Charles University in Prague, was used. The river water from river Vltava, sampled in the locality of Výtoň, was used. The samples of drinking and river water were spiked with standard solutions of 8-NQ. 9 mL of thus prepared model samples of 8-NQ inappropriate matrix were filled up to 10 mL by BR buffer of appropriate pH and their voltammograms were recorded after removal of oxygen.

3 Results and Discussion

3.1 Optimization

At first, the dependence of DPV behavior of 8-NQ (1×10^{-4} mol L^{-1}) on pH of BR buffer from 2 to 12 was investigated (see Figure 2). Observed signal obviously corresponds to four electron reduction of the nitro group to the hydroxylamino group, analogously to reduction on mercury electrodes [32]. The highest and the best developed peak was obtained in BR buffer pH 3.0.

Furthermore, the influence of electrochemical regeneration of the electrode surface before each curve was tested to minimize the influence of electrode passivation which resulted in the shift of peak potential to more negative values and in certain decrease of peak height. The regeneration potentials (initial potential before and final potential after the peak or both initial and final potential before the peak) were applied to the electrode surface in 150 cycles with frequency 10 cycles per second. After imposing the regeneration potentials, the height of the peaks became more stable and the decreasing tendency was eliminated. The best repeatable and the best developed peaks were obtained using initial potential E_{in}= −1000 mV and final potential E_{fin}=−100 mV. The influence of various regeneration potentials on the height of the peak is depicted in Figure 3.

In the framework of optimization, the cleaning of the electrode surface using various constant cleaning potentials for certain time was tested to solve the problem with shifting of the peak potential to more negative values caused by electrode passivation. The best reproducibility

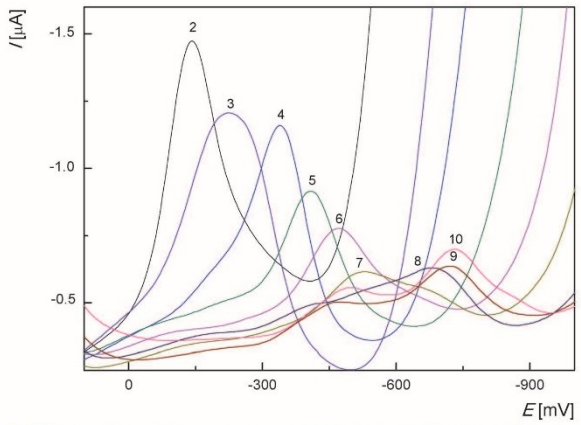

Fig. 2. DP voltammograms of 8-NQ (1×10^{-4} mol L^{-1}) at AgE in the BR buffer pH 2.0 (2), 3.0 (3), 4.0 (4), 5.0 (5), 6.0 (6), 7.0 (7), 8.0 (8), 9.0 (9), 10.0 (10). Polarization rate 20 mV s^{-1}.

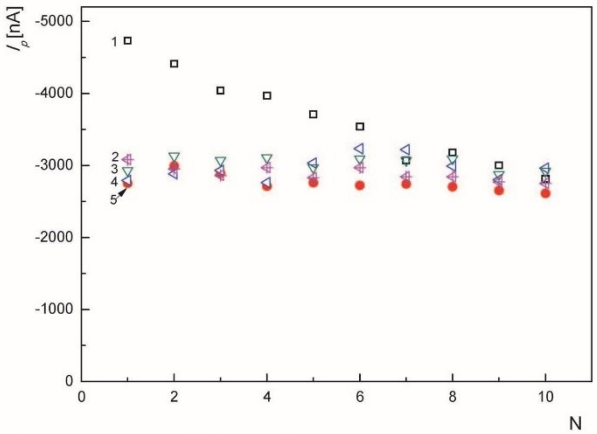

Fig. 3. Dependence of the DPV peak current I_p of 8-NQ (1×10^{-4} mol L^{-1}) at AgE in BR buffer pH 3.0 on the serial number of measurement (N) for chosen regeneration potentials (E_{in}, E_{fin}): without regeneration (1), −400; +100 (2), +100; −400 (3), −100; −1000 (4), −1000; −100 (5) mV.

and repeatability of measurements was achieved using a constant cleaning potential of $E_{const}=-2000$ mV for 60 s. The influence of inserted constant cleaning potential on the working electrode used for consecutive DPV measurements is depicted in Figure 4.

3.2 Determination of 8-Nitroquinoline in Deionized Water

The DPV calibration dependences of 8-NQ in BR buffer pH 3.0 in the concentration ranges of $(2–10)\times10^{-7}$ mol L^{-1}, $(2–10)\times10^{-6}$ mol L^{-1}, and $(2–10)\times10^{-5}$ mol L^{-1} are linear and their parameters and limits of quantification are summarized in Table 1. For the sake of illustration corresponding DP voltammograms are depicted in Figures 5–7.

3.3 Determination of 8-Nitroquinoline in Drinking and River Water

The practical applicability of newly developed DPV was tested on the determination of 8-NQ in model spiked samples of drinking and river water. Because of relatively simple matrix of drinking and river water, the possibility

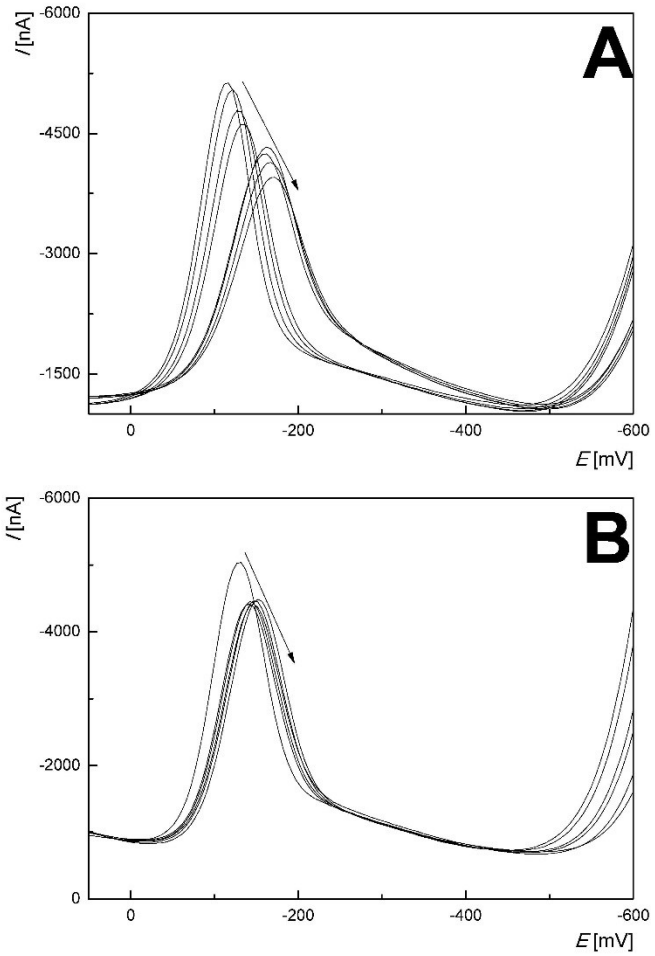

Fig. 4. DP voltammograms of consecutive measurements of 8-NQ (1×10^{-4} mol L^{-1}) at AgE in BR buffer pH 3.0 with regeneration potentials $E_{in}=-1000$ mV, $E_{fin}=-100$ mV and with various constant cleaning potentials: −900 mV (A), −2000 mV (B), for 60 s before each curve.

Table 1. Parameters of the calibration curves for DPV determination of 8-NQ at AgE.

Matrix	Concentration range (mol L^{-1})	Slope (nA mol^{-1} L)	Intercept (nA)	R [a]	LOQ [b] (mol L^{-1})
deionized water	$(2–10)\times10^{-5}$	-3.91×10^{-7}	−868	0.9793	–
	$(2–10)\times10^{-6}$	-5.33×10^{-7}	0.4	0.9958	–
	$(2–10)\times10^{-7}$	-7.86×10^{-7}	−4.7	0.9975	6.0×10^{-7}
drinking water	$(2–10)\times10^{-5}$	-7.16×10^{-6}	−61.7	0.9989	–
	$(2–10)\times10^{-6}$	-1.57×10^{-7}	−29.6	0.9938	9.7×10^{-7}
river water	$(2–10)\times10^{-5}$	-7.46×10^{-6}	−71.4	0.9985	–
	$(4–10)\times10^{-6}$	-1.00×10^{-7}	−30.3	0.9950	2.2×10^{-6}

[a] Correlation coefficient, [b] limit of quantification (10σ; $\alpha=0.05$)

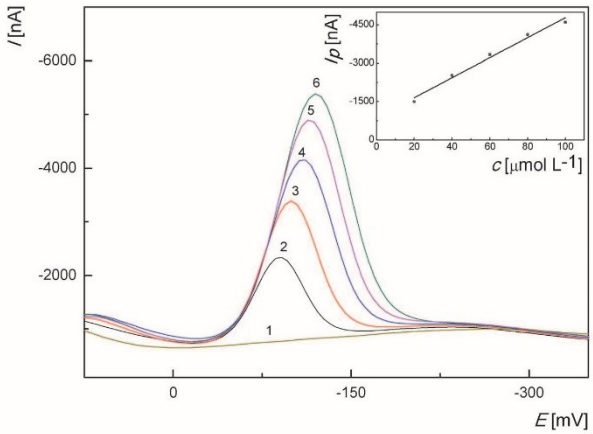

Fig. 5. DP voltammograms of 8-NQ at AgE in the BR buffer of pH 3.0 corresponding to the concentrations: 0 (1); 20 (2); 40 (3); 60 (4); 80 (5); and 100 (6) µmol L^{-1}. Inset: Corresponding calibration curve.

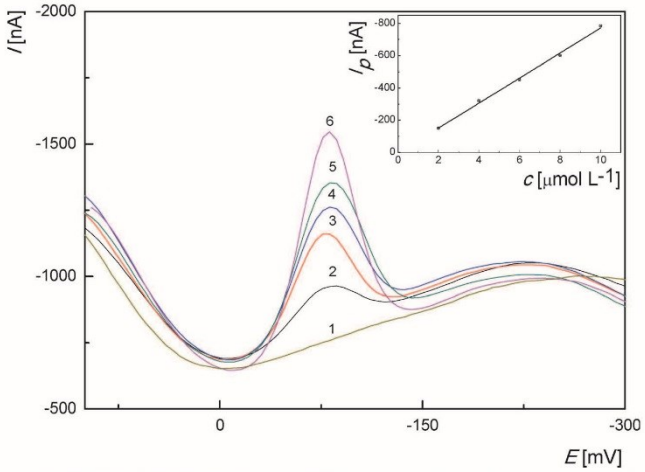

Fig. 6. DP voltammograms of 8-NQ at AgE in the BR buffer pH 3.0 corresponding to the concentrations: 0 (1); 2 (2); 4 (4); 6 (6); 8 (8); and 10 (10) µmol L^{-1}. Inset: Corresponding calibration curve.

of direct determination was tested and verified. The measured solutions were prepared by mixing 9.0 mL of tap or river water sample containing given added concentration of 8-NQ and 1.0 mL of the BR buffer pH 3.0. The concentration range from 2×10^{-6} mol L^{-1} to 1×10^{-5} mol L^{-1} was measured. DP voltammograms of 8-NQ in drinking and river water are depicted in Figures 8 and 9. All parameters of quantification are summarized in Table 1.

4 Conclusion

A new method for voltammetric determination of genotoxic 8-nitroquinoline (8-NQ) at a silver solid electrode (AgE) based on cathodic reduction of present nitrogroup was developed. The best results were obtained using differential pulse voltammetry (DPV) in Britton-Robinson buffer of pH 3.0 and the optimum regeneration potentials (E_{in} = −1000 mV, E_{fin} = −100 mV). After regeneration potentials the constant cleaning potential E_{const} = −2000 mV for 60 s was applied to the electrode to counteract shifting of peak potential to more negative values. In the whole

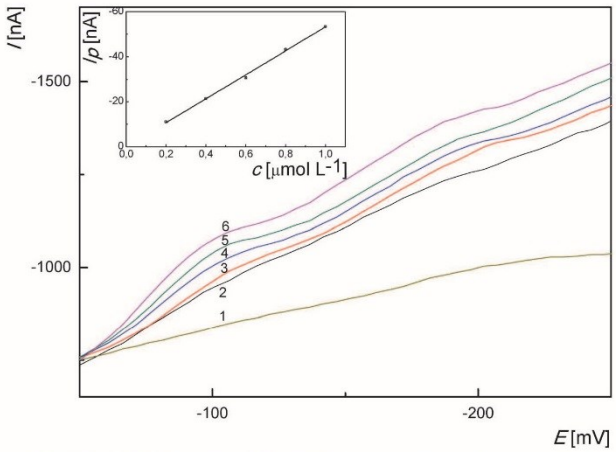

Fig. 7. DP voltammograms of 8-NQ at AgE in the BR buffer pH 3.0 corresponding to the concentrations: 0 (1); 0.2 (2); 0.4 (4); 0.6 (6); 0.8 (8); and 1.0 (10) μmol L^{-1}. Inset: Corresponding calibration curve.

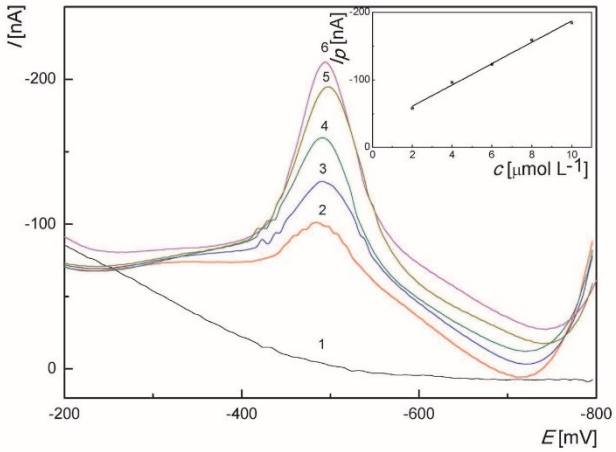

Fig. 8. DP voltammograms of 8-NQ at AgE in drinking water model samples (9 mL of spiked water was filled up to 10 mL by BR buffer pH 3.0). The curves are corresponding to the concentrations of 8-NQ in 9 mL of drinking water model sample: 0 (1); 2 (2); 4 (3); 6 (4); 8 (5); and 10 (6) μmol L^{-1}. Inset: Corresponding calibration curve.

tested range of pH 2–12 the substance provided only one peak. The linear calibration dependences of 8-NQ in deionized water with the limits of quantification $LOQ = 6.0\times10^{-7}$ mol L^{-1} for DPV were obtained. The practical applicability of DPV for direct determination of 8-NQ in drinking and river water model samples has been verified. Limit of quantification was $LOQ = 9.7\times10^{-7}$ mol L^{-1} for drinking water and $LOQ = 2.2\times10^{-6}$ mol L^{-1} for river water. The applicability of silver solid electrode for DPV determination of micromolar concentration of genotoxic 8-NQ in drinking and river water samples was confirmed.

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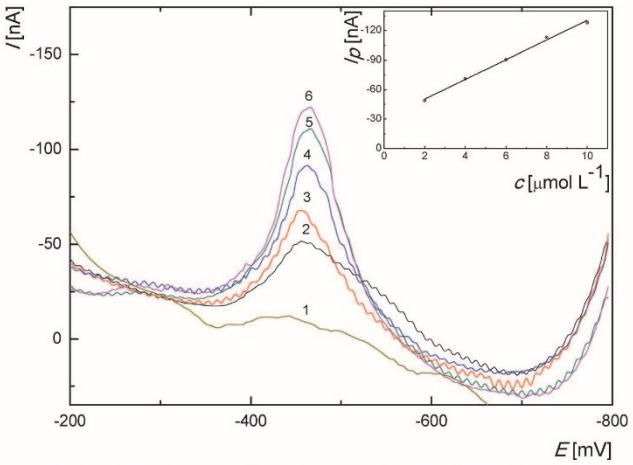

Fig. 9. DP voltammograms of 8-NQ at AgE in river water model samples (9 mL of spiked water was filled up to 10 mL with BR buffer pH 3.0). The curves are corresponding to the concentrations of 8-NQ in 9 mL of river water model sample: 0 (1); 2 (2); 4 (3); 6 (4); 8 (5); and 10 (6) μmol L^{-1}. Inset: Corresponding calibration curve.

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9. PŘÍLOHA II

DETERMINATION OF 2-NITROPHENOL USING CARBON FILM ELECTRODE

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ORIGINAL PAPER

Determination of 2-nitrophenol using carbon film electrode

Tereza Rumlová[1] · Anežka Kabátová[1] · Miroslav Fojta[2,3] · Jiří Barek[1]

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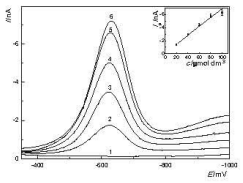
Abstract This study is focused on the application of a carbon film electrode for the determination of micromolar concentrations of pesticide 2-nitrophenol using modern voltammetric methods. For the determination of 2-nitrophenol, direct current (DCV) and differential pulse (DPV) voltammetry were chosen. The following optimal conditions for the determination of 2-nitrophenol were found: Britton–Robinson buffer of pH 5.0 for DCV and pH 6.0 for DPV, and the regeneration potential cycles ($E_{in} = 0$ mV, $E_{fin} = 0$ mV). Under these conditions, limit of quantification was found to be 1.2×10^{-6} mol dm^{-3} for DCV and 2.0×10^{-6} mol dm^{-3} for DPV in deionized water. The limit of quantification for model samples of drinking water was 3.0×10^{-7} mol dm^{-3} for DCV and 1.0×10^{-6} mol dm^{-3} for DPV. The applicability of carbon film electrode for the determination of micromolar concentrations of 2-nitrophenol based on cathodic reduction of present nitro group and in model samples of drinking water was confirmed.

Graphical abstract



Keywords Electrochemistry · Reductions · Voltammetry · Nitrophenols · Drinking water

Introduction

There is an ever increasing amount of various ecotoxic organic compounds in environment resulting from increasing industrial and agricultural activities [1]. Therefore, the monitoring of those organic compounds in the environment is necessary. Electroanalytical methods are suitable for such purpose because of their low cost, reasonable selectivity and sensitivity, portability, and easy miniaturization of corresponding instrumentation [2]. Nitrophenols are plenteous environmental pollutants, which come mainly from industrial processes, especially from production of pesticides, pharmaceuticals, explosives, and dyes [3]. Moreover, they are used as growth stimulators in agriculture [4]. Nitrophenols are potentially carcinogenic, mutagenic, and teratogenic [5], and 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol are listed in EPA Priority Pollutants List [6]. They were already determined using modern voltammetric methods at silver

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solid amalgam electrode [5, 7], silver amalgam paste electrode [8], boron-doped diamond film electrode [9], screen printed electrode [10], and hanging mercury drop electrode [11] and also using different electroanalytical methods [12–14]. Other analytical methods used for determination of nitrophenols involve HPLC, UPLC, GC, etc. [15–19].

Carbon film electrode (CFE) can be fabricated from any solid electrode on which it is possible to prepare the carbon film sufficiently adhering to its surface. In this case, polished silver solid amalgam electrode (p-AgSAE) [20, 21] was used. The solid electrode substrate serves only as a conductive part, and electrochemical behavior is controlled by carbon film prepared on its surface. Carbon film is prepared by dipping the electrode into the carbon ink, which is made from carbon powder dispersed in a solution of suitable polymer in a solvent with high vapor tensions. When the solvent evaporates from the surface, the CFE is ready to use. The advantages of this electrode (CFE) are dictated by merits of the surface material, wide potential windows in both cathodic and anodic regions (cca from +1.5 to −1.5 V), high sensitivity, and low background current. Moreover, CFE can be easily prepared, its surface can be easily renewed, it is easy to fabricate its micro version and it is inexpensive and compatible with "green analytical chemistry" approach [22]. Voltammetric determination of oxidisable organic compounds (impossible at mercury electrodes because of their narrow anodic potential window) can be carried out at CFE as demonstrated by the determination of selected drugs (e.g., paracetamol) [23], various nitro-substituted oxidizable compounds (e.g., 2-amino-6-nitrobenzthiazole) [24], and guanine and adenine [25].

This work is focused on voltammetric determination of genotoxic priority pollutant 2-nitrophenol (2-NP) based on cathodic reduction of its nitro group on CFE.

Results and discussion

Preliminary investigations

At first, the influence of pH on direct current (DC) and differential pulse (DP) voltammograms of 2-NP (1×10^{-4} mol dm^{-3}) was investigated (see Fig. 1). The signal observed by both methods had decreasing tendency from pH 6 (DCV) and pH 7 (DPV) to higher pH. We

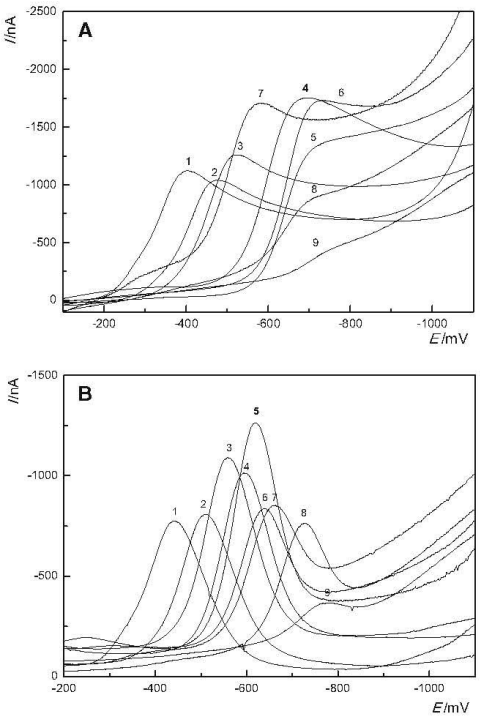
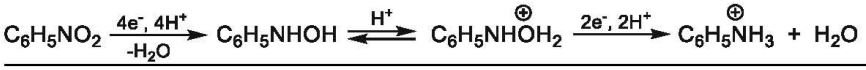


Fig. 1 DC (**a**) and DP (**b**) voltammograms of 2-NP (1×10^{-4} mol dm^{-3}) at CFE in BR buffer pH 2.0 (*1*); 3.0 (*2*); 4.0 (*3*); 5.0 (*4*); 6.0 (*5*); 7.0 (*6*); 8.0 (*7*); 9.0 (*8*); 10.0 (*9*). Polarization rate 20 mV s^{-1}

suppose that the observed decreasing tendency of 2-NP signal can be connected with increased electrode passivation at higher pH. The highest and the best developed waves/peaks were obtained in Britton–Robinson (BR) buffer pH 5.0 for DCV and pH 6.0 for DPV method. The difference between optimum pH for DCV and DPV is connected with different potential program and current sampling, and it is quite frequent in voltammetry of organic compounds.

We assume that under these conditions, the electrochemical reduction of present nitro group corresponds to the reduction of aromatic nitro compounds by the following mechanism [26]:



Afterwards, insertion of cleaning electrochemical regeneration cycles on the electrode surface before each curve was tested to minimize the undesirable influence of electrode passivation, which contributes to the certain decrease of peak height. The regeneration potential cycles (initial potential before and final potential after the peak or both initial and final potential before the peak) were put on the electrode surface in 150 cycles with frequency 10 cycles per second. After application of the regeneration potentials, the height of the waves and peaks became more stable and the decreasing tendency was eliminated. The best results (the best repeatability and the best developed peaks) were obtained using hypothetical cycling of initial regeneration potential $E_{in} = 0$ mV and final regeneration potential $E_{fin} = 0$ mV, which is equal to keeping the constant potential on the working electrode. The influence of chosen regeneration potential cycles on the height of the DPV peak is depicted in Fig. 2.

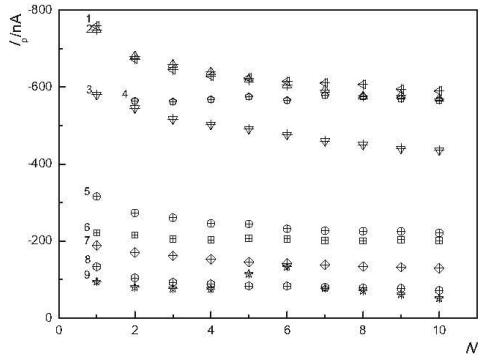


Fig. 2 Dependence of the DPV peak current I_p of 2-NP (1×10^{-4} mol dm^{-3}) at CFE in BR buffer pH 6.0 on the serial number of measurement (N) for chosen regeneration potentials (E_{in}, E_{fin}): −400; −500 (*1*); −800, −400 (*2*); −400, −800 (*3*); 0, 0 (*4*); −100, −1100 (*5*); −1100, −100 (*6*); −500, −400 (*7*); −400, −1000 (*8*); −1000, −400 (*9*) mV

DC voltammetry of 2-nitrophenol in deionized water

The DCV calibration dependences of 2-NP determination in deionized water as the simplest model matrix using BR buffer of pH 5.0 as supporting electrolyte in the concentration ranges of $(2–10) \times 10^{-6}$ and $(2–10) \times 10^{-5}$ mol dm^{-3} are linear and their parameters and limits of quantification are summarized in Table 1. For the sake of illustration, corresponding DC voltammograms are depicted in Figs. 3 and 4.

DP voltammetry of 2-nitrophenol in deionized water

The DPV calibration dependences of 2-NP determination in deionized water using BR buffer of pH 6.0 in the concentration ranges of $(2–10) \times 10^{-6}$ and $(2–10) \times 10^{-5}$ mol dm^{-3} are linear and their parameters and limits of quantification are summarized in Table 1. For the sake of illustration, corresponding DP voltammograms are depicted in Figs. 5 and 6.

DC voltammetry of 2-nitrophenol in drinking water

The practical applicability of the newly developed method was tested on the determination of 2-NP in model samples of drinking water. Because of relatively simple matrix, the possibility of direct determination was first tested and verified. The model samples of 2-NP were prepared by mixing 9.0 cm^3 of tap water sample containing the exact amount of 2-NP stock solution and 1.0 cm^3 of the BR buffer of pH 5.0. The concentration range from 2×10^{-6} to 1×10^{-4} mol dm^{-3} was measured. The deviation of the highest concentration from linearity is typical for higher concentration (usually for concentration ranges from

Table 1 Parameters of the calibration curves for determination of 2-NP at CFE

Technique/matrix	Concentration range/mol dm^{-3}	Slope/nA mol^{-1} dm^3	Intercept/nA	R^a	LOQ^b/mol dm^{-3}
DCV/deionized water	$(2–10) \times 10^{-5}$	-6.03×10^5	5.59	0.9848	–
	$(2–10) \times 10^{-6}$	-1.89×10^5	0.01	0.9554	1.2×10^{-6}
DPV/deionized water	$(2–10) \times 10^{-5}$	-1.23×10^5	−3.68	0.9907	–
	$(2–10) \times 10^{-6}$	-2.40×10^5	−0.01	0.9990	2.0×10^{-6}
DCV/drinking water	$(2–10) \times 10^{-5}$	-5.30×10^4	−0.17	0.9829	–
	$(2–10) \times 10^{-6}$	-1.71×10^5	0.16	0.9996	3.7×10^{-7}
DPV/drinking water	$(2–10) \times 10^{-5}$	-6.98×10^4	0.03	0.9906	–
	$(2–10) \times 10^{-6}$	-1.23×10^5	−0.03	0.9980	1.0×10^{-6}

[a] Correlation coefficient

[b] Limit of quantification (10σ; $\alpha = 0.05$)

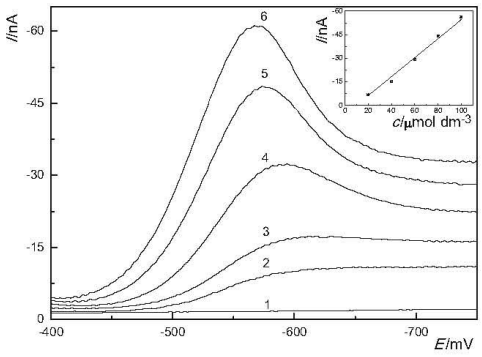


Fig. 3 DC voltammograms of 2-NP at CFE in deionized water using BR buffer of pH 5.0 as supporting electrolyte (9 cm^3 of sample in deionized water was filled up to 10 cm^3 by BR buffer of pH 5.0). Concentrations of 2-NP in deionized water: 0 (*1*); 20 (*2*); 40 (*3*); 60 (*4*); 80 (*5*); and 100 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

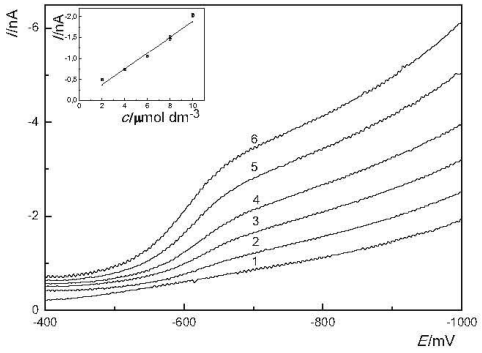


Fig. 4 DC voltammograms of 2-NP at CFE in deionized water using BR buffer of pH 5.0 as supporting electrolyte (9 cm^3 of sample in deionized water was filled up to 10 cm^3 by BR buffer of pH 5.0). Concentrations of 2-NP in deionized water: 0 (*1*); 2 (*2*); 4 (*3*); 6 (*4*); 8 (*5*); and 10 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

10^{-5} mol dm^{-3} upwards). DC voltammograms of 2-NP in drinking water are depicted in Figs. 7 and 8.

DP voltammetry of 2-nitrophenol in drinking water

The model samp[1]es of 2-NP were prepared in the same way as for DCV determination, by mixing 9.0 cm^3 of tap water sample containing exact amount of 2-NP stock solution and 1.0 cm^3 of the BR buffer of pH 6.0. The concentration range from 2×10^{-6} to 1×10^{-5} mol dm^{-3} was measured. DP

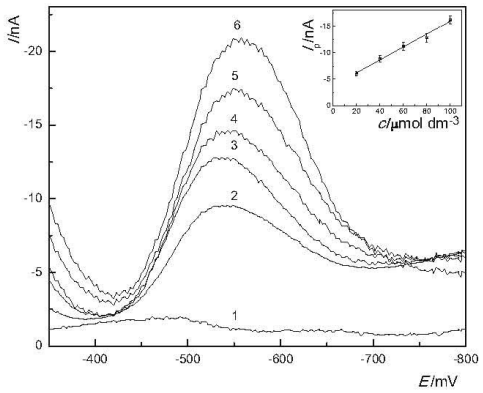


Fig. 5 DP voltammograms of 2-NP at CFE in deionized water using BR buffer of pH 6.0 as supporting electrolyte (9 cm^3 of sample in deionized water was filled up to 10 cm^3 by BR buffer of pH 6.0). Concentrations of 2-NP in deionized water: 0 (*1*); 20 (*2*); 40 (*3*); 60 (*4*); 80 (*5*); and 100 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

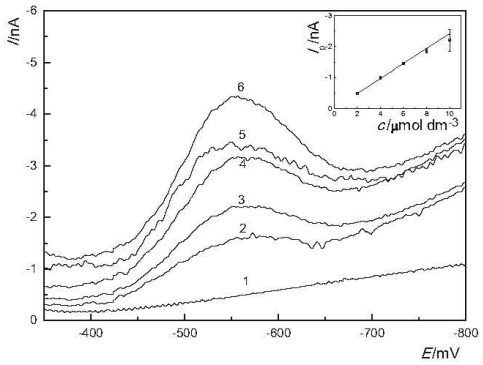


Fig. 6 DP voltammograms of 2-NP at CFE in deionized water using the BR buffer of pH 6.0 as supporting electrolyte (9 cm^3 of sample in deionized water was filled up to 10 cm^3 by BR buffer of pH 6.0). Concentrations of 2-NP in deionized water: 0 (*1*); 2 (*2*); 4 (*3*); 6 (*4*); 8 (*5*); and 10 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

voltammograms of 2-NP in drinking water are depicted in Figs. 9 and 10.

All parameters of the above-obtained calibration curves are summarized in Table 1. The rather unusual fact that in this specific case the limit of quantification (LOQ) for DCV is lower than for DPV can be connected with electrode passivation which influence more DPV than DCV and with resulting higher noise of DPV.

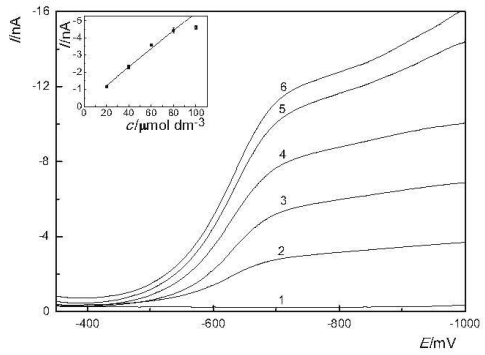


Fig. 7 DC voltammograms of 2-NP at CFE in drinking water model samples (9 cm^3 of spiked drinking water was filled up to 10 cm^3 by BR buffer of pH 5.0). The *curves* correspond to the concentrations of 2-NP in 9 cm^3 of drinking water model sample: 0 (*1*); 20 (*2*); 40 (*3*); 60 (*4*); 80 (*5*); and 100 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

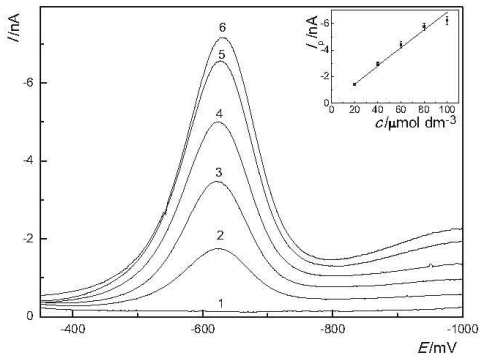


Fig. 9 DP voltammograms of 2-NP at CFE in drinking water model samples (9 cm^3 of spiked water was filled up to 10 cm^3 with BR buffer of pH 6.0). The *curves* correspond to the concentrations of 2-NP in 9 cm^3 of drinking water model sample: 0 (*1*); 20 (*2*); 40 (*3*); 60 (*4*); 80 (*5*); and 100 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

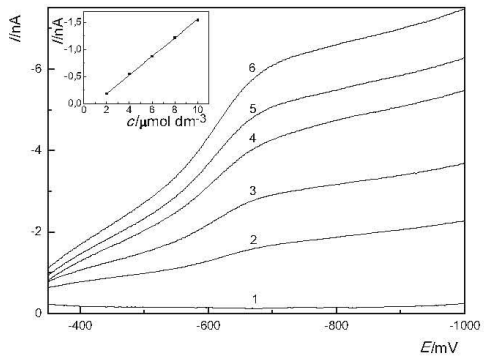


Fig. 8 DC voltammograms of 2-NP at CFE in drinking water model samples (9 cm^3 of spiked water was filled up to 10 cm^3 with BR buffer of pH 5.0). The *curves* correspond to the concentrations of 2-NP in 9 cm^3 of drinking water model sample: 0 (*1*); 2 (*2*); 4 (*3*); 6 (*4*); 8 (*5*); and 10 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

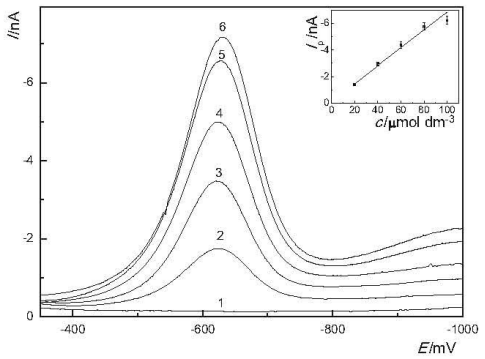


Fig. 10 DP voltammograms of 2-NP at CFE in drinking water model samples (9 cm^3 of spiked water was filled up to 10 cm^3 with BR buffer of pH 6.0). The *curves* correspond to the concentrations of 2-NP in 9 cm^3 of drinking water model sample: 0 (*1*); 2 (*2*); 4 (*3*); 6 (*4*); 8 (*5*); and 10 (*6*) μmol dm^{-3}. The corresponding *calibration curve* is given in the *inset*

The possibility of measuring lower concentrations ranges of 2-NP at CFE was tested; unfortunately, the results were not satisfying because of increasing noise.

Conclusion

New modern voltammetric methods for the determination of 2-nitrophenol using carbon film electrode (CFE) based on cathodic reduction of the present nitro group were developed. The best results were obtained using direct current voltammetry (DCV) in BR buffer of pH 5.0 with optimum regeneration potentials ($E_{in} = 0$ mV, $E_{fin} = 0$ mV) and differential pulse voltammetry (DPV) in BR buffer of pH 6.0 with the same optimum regeneration potentials ($E_{in} = 0$ mV, $E_{fin} = 0$ mV). The linear calibration dependences of 2-NP in deionized water with the limits of quantification LOQ $= 1.2 \times 10^{-6}$ mol dm^{-3} for DCV and LOQ $= 2.0 \times 10^{-6}$ mol dm^{-3} for DPV were obtained. Limit of quantification in model samples of

drinking water was LOQ = 3.0×10^{-7} mol dm^{-3} for DCV and LOQ = 1.0×10^{-6} mol dm^{-3} for DPV. The practical applicability of both methods, DCV and DPV, for direct determination of 2-NP at CFE in drinking water has been verified.

Experimental

Apparatus

DCV and DPV measurements were carried out using potenciostat Eco-Tribo Polarograph (EcoTrend Plus, Czech Republic) with PolarPro 5.1 software (Polaro-Sensors, Czech Republic). The software worked under the operating system Microsoft Windows XP (Microsoft Corp., USA). All measurements were carried out in a three-electrode system with platinum wire (Elektrochemické detektory, s r. o., Czech Republic) as an auxiliary electrode, silver/silver chloride reference electrode (1 mol dm^{-3} KCl, Elektrochemické detektory, spol. s r. o., Czech Republic), and carbon film electrode (CFE on p-AgSAE substrate, disk diameter 0.413 mm, EcoTrend Plus, Czech Republic) as an working electrode. The scan rate 20 mV s^{-1}, the pulse amplitude −50 mV, and pulse width 80 ms were used. The best repeatability and reproducibility of voltammetric measurements at CFE were obtained using electrochemical regeneration of the electrode surface by the application of equal initial regeneration potential E_{in} = 0 mV and final regeneration potential E_{fin} = 0 mV, each for 50 ms.

Reagents

The stock solution of 2-NP (1×10^{-3} mol dm^{-3}) was prepared by dissolving 0.0139 g of the substance (Sigma-Aldrich Chemie, Germany, CAS Reg. No. 88-75-5) in deionized water and filling up to 100 cm^3. More diluted solutions were prepared by serial dilution of stock solution with deionized water. All solutions were kept in dark and at laboratory temperature. Boric acid, phosphoric acid, acetic acid, sodium hydroxide, and potassium chloride were of p.a. purity (Lachner, Czech Republic). BR buffers were prepared in a usual way by mixing of 0.2 mol dm^{-3} sodium hydroxide with the mixture of 0.04 mol dm^{-3} of boric, phosphoric, and acetic acid. The pH was measured by pH meter Jenway with combined glass electrode (type 924005, Jenway, UK), and deionized water (Millipore Q plus system, Millipore, USA) was used.

Procedures

An appropriate volume of the stock solution of 2-NP (1×10^{-3} mol dm^{-3}) was diluted in deionized water and filled up to 10.0 cm^3 with BR buffer solution of appropriate pH and then transferred into the voltammetric cell. Oxygen was eliminated by purging with nitrogen (purity class 4.0, Linde Gas, Czech Republic) for 5 min and then the voltammograms were recorded. DCV wave heights were evaluated from the extrapolated linear portion of the voltammogram before the onset of the wave. DPV peaks were evaluated from the straight line connecting the minima before and after the peaks.

The limits of quantification (LOQ) were calculated as the concentration of the analyte corresponding to the tenfold standard deviation of the analyte response from ten consecutive determinations at the lowest attainable concentration range [27].

For the preparation of model samples of drinking water, the water from water pipeline in the chemistry building (Faculty of Science, Charles University in Prague) after 5 min of outflowing was used. The samples of drinking water were spiked with standard solutions of 2-NP. 9 cm^3 of thus prepared model samples of 2-NP in drinking water were filled up to 10 cm^3 by BR buffer of appropriate pH, and voltammograms were recorded after bubbling with nitrogen for 5 min.

Carbon film electrode

The conductive carbon ink was prepared by mixing 0.01 g of polystyrene, 0.09 g of carbon powder (microcrystalline graphite 2 μm, CR 2, Maziva Týn, Czech Republic), and 0.5 cm^3 of 1,2-dichloroethane (MERCK, Germany). Then, the mixture was thoroughly homogenized by intensive agitation for 3 min at Vortex-Genie 2 (Scientific industries, Inc., USA).

CFE was fabricated by covering p-AgSAE's surface with a carbon film. The film was formed by immersing electrode's surface into the conductive ink (the active part of the electrode just touches the surface of the ink). One minute after immersing, 1,2-dichloroethane evaporates and thus prepared CFE is ready to use. According to our experiences, CFE prepared using this way is keeping its properties and is usable for at least 30 consecutive measurements. When it is necessary to renew the old film (e.g., because of the passivation of the electrode surface), it can be easily removed by wiping it off with a filter paper and a new film is created by the same procedure as described above.

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10. PŘÍLOHA III

ANODIC DIFFERENTIAL PULSE VOLTAMMETRIC DETERMINATION OF 2-NITROPHENOL AT A NON-TRADITIONAL CARBON FILM COMPOSITE ELECTRODE

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Anodic Differential Pulse Voltammetric Determination of 2-Nitrophenol at a Non-Traditional Carbon Film Composite Electrode

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Abstract

A new method was developed for the determination of 2-nitrophenol (2-NP) by differential pulse voltammetry (DPV) employing the anodic oxidation of the present hydroxyl group using a non-traditional carbon film composite electrode (CFCE) based on a microcrystalline natural graphite-polystyrene composite film. Britton-Robinson (BR) buffer of pH 6.0 was found to be an optimal supporting electrolyte. Cleaning regeneration potentials E_{in} = +1300 mV and E_{fin} = 0 mV had to be applied before each measurement to get rid of problems connected with electrode passivation. Linear calibration curves were obtained in the concentration range from 0.2 to 10 μmol L^{-1} of 2-NP for both tested matrices (deionized and drinking water). Limit of quantification (*LOQ*) for DPV at CFCE was found to be 0.2 μmol L^{-1} and 0.1 μmol L^{-1} for deionized and drinking water, respectively.

Keywords: Carbon film composite electrode, Electrode passivation, Electrode electrochemical cleaning, Drinking water, 2-Nitrophenol, Anodic oxidation

1. Introduction

Nitrophenols are often used in industry, especially in manufacturing of pesticides, pigments, explosives, dyes, etc. [1]. Many of them are also listed on the List of Authorized Plant Protection Products and are often used as plant growth stimulators [2]. Nitrophenols are well known for their toxicity in general and have significant detrimental effects on environment quality, and especially on water quality, because of their toxicity to aquatics [3]. Moreover, they are suspected from carcinogenicity, mutagenicity and teratogenicity [4] and 2-nitrophenol (2-NP) and many others are on EPA Priority Pollutants List [5]. The

concentration of 2-NP in natural water has been restricted by US EPA to be lower than 10 μg L^{-1}, i.e. 7 μmol L^{-1} [6]. 2-NP was detected in rainwater samples in California and Germany which was probably caused by tropospheric transformation of corresponding alkyl benzene [7]. For the above given reasons, it is necessary to develop new sensitive and environmentally friendly methods for 2-NP determination.

Nitrophenols are easily electrochemically oxidizable and reducible as proved by comparative electrochemical study of 4-NP at a glassy carbon electrode (GCE) [8]. Modern voltammetric methods have been already used for voltammetric determinations of several nitrophenols at a silver solid amalgam electrode [4,9], a silver amalgam paste electrode [10], a boron-doped diamond film electrode [11], a bismuth film modified screen-printed carbon electrode [12], a hanging mercury drop electrode [13], and a carbon film electrode [14]. Differential pulse voltammetry (DPV) at a highly dispersed silver particles modified GCE [15], square-wave voltammetry and amperometry at a bismuth film modified GCE [16], or single-walled carbon nanotubes based sensor [17] were applied for monitoring of nitrophenols as well. Moreover, modern separation methods (HPLC/MS [18], HPLC/UV [19, 20], GC/PND and GC/MS [21], etc.) and spectrophotometric methods (e.g. fibre-optic spectrophotometry [22]) have been also described for the determination of nitrophenols. For comparison of voltammetric determinations of 2-NP using different working electrodes in deionized water, see Table 1.

The biggest problem connected with anodic voltammetric determination of phenolic compounds is frequent passivation of working electrode caused be deposition of electrode reaction products (namely dimers and polymers formed from free radicals generated in the first step of the electrode reaction). One possibility to minimize this problem is to use electrodes with easily renewable surface, e.g. carbon film electrodes (CFEs). As a CFE, any solid electrode is denoted on which the carbon film is deposited [23]. In this paper, the CFE developed in our laboratory and based on polished silver solid amalgam as a conductive substrate covered by a microcrystalline natural graphite-polystyrene composite film [24], further denoted as carbon film composite electrode (CFCE), was applied. The electrochemical behaviour of this CFCE is governed solely by the carbon composite film deposited on the substrate which forms just conductive contact with no influence on CFCE electrochemical properties. The main advantages of this CFCE are simple, fast, and inexpensive fabrication, easy renewal of the carbon composite film (made simply by wiping the electrode surface off by a filter paper and creating a new film by immersing the electrode surface into the carbon ink), wide potential window (ca. from –1.5 V to +1.5 V), and relatively high sensitivity and low noise of measurements. Both oxidizable organic compounds (e.g. paracetamol [24], and guanine and adenine [25]) and reducible organic compounds (e.g. 4-nitrophenol [26], 5-nitrobenzimidazole [27], and 5-nitroquinoline [28]) were so far determined at this CFCE.

The purpose of this work is to prove practical applicability of the CFCE on a polished silver solid amalgam substrate (p-AgSAE) for the determination of anodically oxidizable phenolic organic compounds in simple aquatic samples, taking 2-NP as a model compound, and to prove that this approach can eliminate or at least minimize problems connected with working electrode passivation which frequently complicates voltammetric determination of phenolic compounds. Moreover, the possibility to use more simple electrochemical cleaning of the electrode to minimize problems with its passivation was tested and verified.

2. Experimental

2.1. Reagents

2-Nitrophenol (2-NP, CAS Registry Number 88-75-5, Sigma-Aldrich, Germany); 1 mmol L^{-1} stock solution was prepared in deionized water; solutions with lower concentrations were prepared by its precise dilution with deionized water. Britton-Robinson (BR) buffers of required pH were prepared in a usual way by mixing of 0.2 mol L^{-1} sodium hydroxide (Lach-Ner, Czech Republic) with the mixture of boric, phosphoric, and acetic acid (all 0.04 mol L^{-1}, Lach-Ner, Czech Republic). All solutions were stored in dark and at room temperature. Deionized water from Millipore Milli-Q Plus system (Millipore, USA) was used.

2.2. Apparatus

A μAutolab type III potentiostat (Metrohm Autolab, The Netherlands) was used for all measurements. The potentiostat worked under a Microsoft Windows 8 software (Microsoft Corporation, USA), and all voltammograms were recorded and evaluated using a NOVA 1.10 software (Metrohm Autolab, The Netherlands). All measurements were carried out using a three-electrode system with a platinum wire (Elektrochemicke Detektory, Czech Republic) as an auxiliary electrode, a Ag|AgCl (3 mol L^{-1} KCl) as a reference electrode, and the CFCE (a p-AgSAE surface covered by a carbon composite film prepared as described further, disk diameter 0.413 mm, Eco-Trend Plus, Czech Republic) as a working electrode. DPV with following parameters was used: scan rate of 20 mV s^{-1}, pulse amplitude of +50 mV, pulse width of 100 ms, and sampling time of 20 ms. pH was measured with pH meter Jenway with a combined glass electrode (type 924 005, Jenway, UK) calibrated with standard aqueous buffers (Sigma-Aldrich, Germany).

2.3. Procedures

2.3.1. Preparation of carbon film composite electrode

The previously described procedure was used [23]. Briefly: to 0.01 g of polystyrene dissolved in 0.5 mL of 1,2-dichloroethane (Merck, Germany), 0.09 g of carbon powder (microcrystalline graphite with a grain size of 3.5-5.5 μm, CR 2 995, Graphite Týn, Czech Republic) was added and homogenized by 3 min stirring at Vortex-Genie 2 (Scientific Industries, USA). Thus prepared carbon ink was used to cover the p-AgSAE surface with a carbon composite film by simple immersing the end of the electrode into the conductive ink. When 1,2-dichloroethane evaporates (after ca. 1 min), the CFCE is ready to use. In the case of the electrode surface passivation, the carbon composite film can be easily renewed by wiping the surface off with a filter paper and by simple preparing a new carbon composite film by the above described procedure.

2.3.2. Sample and data treatment

9.0 mL of a 2-NP solution (of exactly known concentration) in deionized water were diluted up to 10.0 mL with a BR buffer solution of required pH. Model samples of drinking water were prepared in the same way as samples in deionized water. Tap water from the Chemistry Building at the Faculty of Science, Charles University, Prague, Czech Republic, used for preparation of model samples was at first outflowed for 5 min. All thus prepared solutions were used immediately for DPV determination.

DPV peak height was evaluated from the straight line connecting minimum before and after the peak. The limit of quantification (*LOQ*)/detection (*LOD*) was calculated as a 2-NP concentration corresponding to the tenfold/threefold of the standard deviation from ten consecutive measurements at the lowest attainable concentration range divided by the slope of the calibration curve [29].

3. Results and discussion

3.1. Optimization of DPV

At first, the influence of pH in the range of 2.0-12.0 on DPV of 2-NP (0.1 mmol L^{-1}) at the CFCE has been investigated. In the whole tested range, 2-NP gave one well developed peak. The highest and the best developed peak was obtained at pH 6.0 (see Fig. 1). However, 10 consecutive voltammograms recorded on the same electrode without film renewal and without any electrochemical cleaning have shown a pronounce decrease of voltammetric peaks connected with their broadening and a shift to more positive potentials as the result of obvious electrode passivation by electrode reaction products (see Fig. 2). This negative effect can be eliminated by using a new film for each voltammogram registration. However, this approach is more laborious, more time consuming, and results in larger standard deviation connected with film renewal. Therefore, the possibility of inserting the regeneration potential cycles to eliminate the negative influence of the proved electrode passivation was investigated. Before recording each voltammogram, 150 regeneration potential cycles (10 cycles per second) were inserted on the CFCE to clean the electrode surface and eliminate decreasing height of peaks resulting from electrode passivation. During the search for the best conditions, various values of the initial potential (E_{in}) were inserted before and of the final potential (E_{fin}) after the 2-NP peak potential, or both initial and final potentials were inserted before the 2-NP peak potential. The optimal results were obtained using regeneration potential cycles between E_{in} = 1300 mV and E_{fin} = 0 mV giving somewhat lower but better reproducible peaks. Under these conditions, the 30 consecutive DP voltammograms were recorded (see Fig. 3). It can be seen that the decrease of DPV peaks is rather small (by 15.5% after 30 recordings, *RSD* of the 30 recordings being 10.9%), confirming efficient minimization of electrode passivation. The same holds for the shape of voltammograms with practically constant peak potential, again confirming negligible effective minimization of the electrode passivation under these conditions.

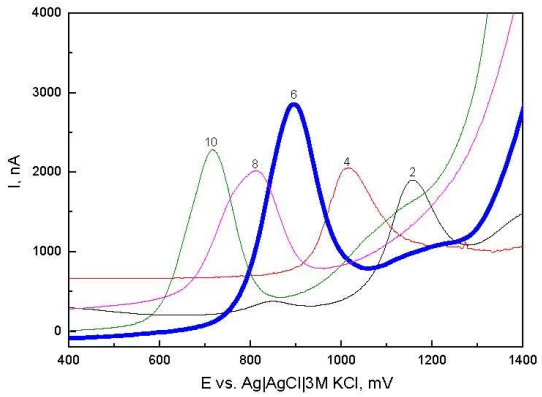

Fig. 1. DP voltammograms of 2-NP (0.1 mmol L^{-1}) at the CFCE in the BR buffer medium of pH 2.0 (2), 4.0 (4), 6.0 (6), 8.0 (8), and 10.0 (10). The best developed voltammogram is in bold.

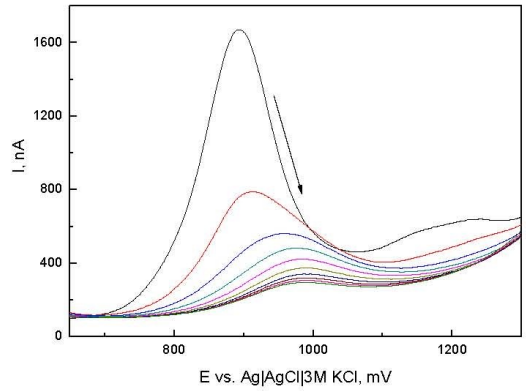

Fig. 2. DP voltammograms of 10 consecutive determinations of 2-NP (0.1 mmol L^{-1}) at the CFCE. Supporting electrolyte: BR buffer of pH 6.0, recorded without film renewal and without application of regeneration potentials.

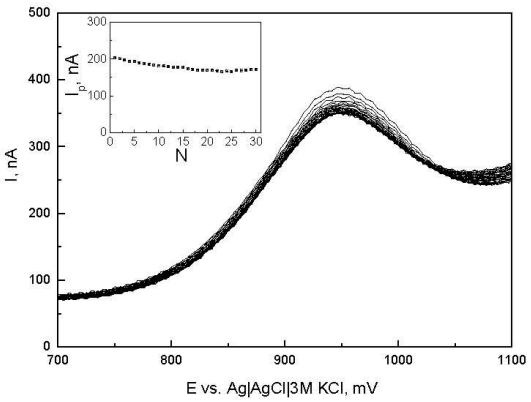

Fig. 3. DP voltammograms of 30 consecutive determinations of 2-NP (0.1 mmol L^{-1}) at the CFCE. Supporting electrolyte: BR buffer of pH 6.0, measured with regeneration potentials E_{in} = 1300 mV and E_{fin} = 0 mV. The corresponding peak currents evaluated from obtained signals are given in the inset, where N is the consecutive number of the voltammogram.

3.2. DPV determination of 2-nitrophenol at carbon film composite electrode in deionized water

The DPV calibration dependences were constructed using the above obtained optimum conditions (BR buffer of pH 6.0, E_{in} = 1300 mV, E_{fin} = 0 mV). The calibration dependences were linear in the concentration range from 0.2 to 10 μmol L^{-1}. Parameters of the calibration dependences are shown in Table 2. The respective DP voltammograms with corresponding calibration dependences are shown in Fig. 4.

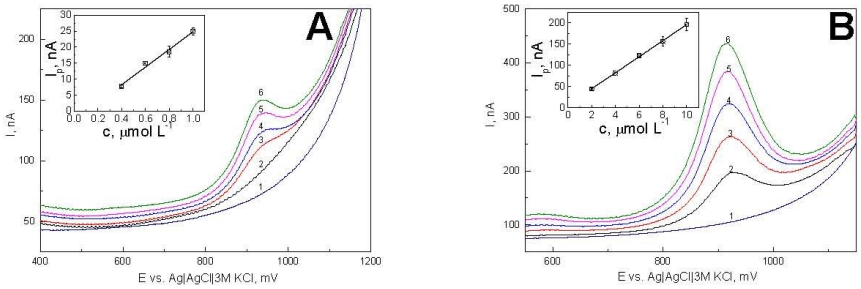

Fig. 4. DP voltammograms of 2-NP at the CFCE in deionized water and BR buffer of pH 6.0. Concentration of 2-NP in deionized water (*A*): 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), and 1.0 (6) μmol L^{-1}; (*B*): 0 (1), 2 (2), 4 (3), 6 (4), 8 (5), and 10 (6) μmol L^{-1}. Corresponding calibration dependences are in the insets (error bars for n = 4).

3.3. DPV determination of 2-nitrophenol at carbon film composite electrode in drinking water

The applicability of the DPV method developed in this work was verified by the direct determination of 2-NP in drinking water. The preparation of model samples has been described above in the Section 2.3.2.

Again, BR buffer of pH 6.0 was used in this case as a supporting electrolyte for all model samples, and optimized regeneration potentials E_{in} = 1300 mV and E_{fin} = 0 mV were used as well. The linearity of the calibration dependences was observed in the concentration range from 0.2 to 10 μmol L^{-1}. The corresponding DP voltammograms of 2-NP at the CFCE are shown in Fig. 5.

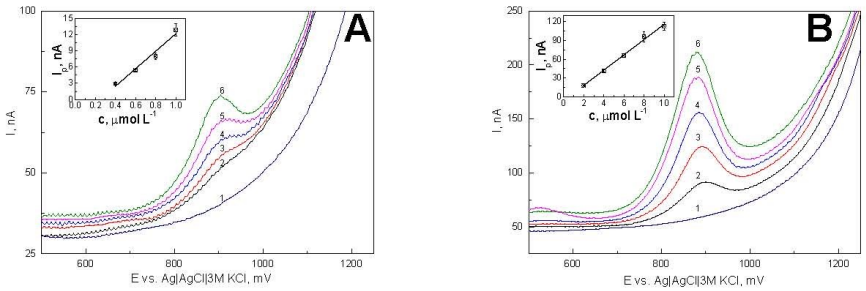

Fig. 5. DP voltammograms of 2-NP at the CFCE of model samples of drinking water using BR buffer of pH 6.0 as a supporting electrolyte. The concentrations of 2-NP in 9.0 mL of model samples of drinking water (A): 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), and 1.0 (6) μmol L^{-1}; (B): 0 (1), 2 (2), 4 (3), 6 (4), 8 (5), and 10 (6) μmol L^{-1}. Corresponding calibration dependences are shown in the insets (error bars for n = 4).

It is obvious from the comparison of Fig. 4 and Fig. 5 that the change of matrix results in the change of both background current and peak current and peak potential, which can be explained by the presence of some surfactants in the analyzed samples of drinking water. This fact is also reflected in somewhat different slopes of linear calibration dependences in Table 2, which can be also affected by the way of peak height evaluation in connection with different relative contribution of background current at different sensitivities.

Table 1

Comparison of *LOD*s of so far published voltammetric determinations of 2-NP in aquatic samples using different types of electrodes.

Electrode	Method	*LOD*[a] (μmol L^{-1})	Ref.
p-AgSAE	DPV	1.0	[4]
BDDE	DPV	0.3	[11]
BiFE	DPV	5.4	[1]
DME	DPP	0.05	[30]
GCE/AgNDs	LSV	1.8	[31]
GCE/Au (nano)	DPV	75	[32]
GCE/BMIMPF$_6$-SWCNT	DPAdSV	0.005	[33]
GCE/MWCNT	derDCV	0.5	[34]
GCE/OMC	DPV	0.8	[35]
GCE/SDS-HTLC	DPAdSV	0.5	[36]
HMDE	DPV	0.2	[13]
HMDE	AdSV	0.02	[13]
HMDE	DPV	0.02	[37]
CFCE	DPV	0.06	This work

[a] Limit of detection; p-AgSAE, polished silver solid amalgam electrode; BDDE, boron-doped diamond electrode; BiFE, bismuth film electrode; DME, dropping mercury electrode; GCE/AgNDs, silver nanodendrites modified glassy carbon electrode; GCE/Au (nano), nano-gold modified glassy carbon electrode; GCE/BMIMPF$_6$/SWCNT, 1-butyl-3-methylimidazolium hexafluorophosphate-single-walled carbon nanotube gel modified glassy carbon electrode; GCE/MWCNT, multi-walled carbon nanotubes modified glassy carbon electrode; GCE/OMC, ordered mesoporous carbon modified glassy carbon electrode; GCE/SDS-HTLC, sodium dodecylsulphate hydrotalcite-like clay modified glassy carbon electrode; HMDE, hanging mercury drop electrode; CFCE, carbon film composite electrode; AdSV, adsorptive stripping voltammetry; derDCV, derivative direct current voltammetry; DPP, differential pulse polarography; DPV, differential pulse voltammetry; DPAdSV, differential pulse adsorptive stripping voltammetry; LSV, linear sweep voltammetry.

Table 2

Parameters of the calibration dependences for the DPV determination of 2-NP at the CFCE. BR buffer of pH 6.0 was used as a supporting electrolyte, and electrochemical cleaning of the working electrode described above was applied before each determination.

Matrix	Concentration range, μmol L^{-1}	Slope, nA L moL^{-1}	Intercept, nA	r[a]	*LOQ*[b], μmol L^{-1}	*LOD*[c], μmol L^{-1}
Deionized	2-10	1.89×10^7	6.87	0.9911	–	–
water	0.2-1	2.77×10^7	–2.86	0.9786	0.2	0.06
Drinking	2-10	1.22×10^7	–6.44	0.9925	–	–
water	0.2-1	1.62×10^7	–4.01	0.9535	0.1	0.03

[a] Correlation coefficient; [b] limit of quantification (10σ); [c] limit of detection

4. Conclusion

8

The new differential pulse voltammetric (DPV) method for the determination of 2-nitrophenol (2-NP) in aquatic samples using carbon film composite electrode (CFCE) with microcrystalline natural graphite-polystyrene composite film was developed. The method is based on simple anodic oxidation of the hydroxyl group of 2-NP. The optimal conditions for all measurements were found to be: BR buffer of pH 6.0 and regeneration potentials E_{in} = 1300 mV and E_{fin} = 0 mV. Under these conditions, the negative influence of electrode passivation was minimized. The calibration dependences of 2-NP were linear both in deionized water and in drinking water in the concentration range from 0.2 to 10 μmol L^{-1} with the limit of quantification (*LOQ*) of 0.2 μmol L^{-1} and 0.1 μmol L^{-1} for deionized and drinking water, respectively.

Authors contribution

Tereza Birhanzlová - Rumlová – Investigation, Methodology, Validation, Writing – original draft.
Jiří Barek – Conceptualization, Supervision, Writing & editing.
Jan Fischer – Methodology, Supervision.
Vlastimil Vyskočil – Conceptualization, Supervision, Writing & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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