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Voltammetric Determination of Nitrophenols at a Silver Solid Amalgam Electrode*

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of 85th anniversary of the invention of polarography.

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The voltammetric behavior of 2-nitrophenol, 4-nitrophenol and 2,4-dinitrophenol was investigated by differential pulse voltammetry (DPV) at a mercury meniscus-modified silver solid amalgam electrode (m-AgSAE) and liquid mercury free polished silver solid amalgam electrode (p-AgSAE). Conditions have been found for their determination by DPV at m-AgSAE and p-AgSAE in Britton-Robinson buffer in the concentration range from 2 to 100 $\mu mol.L^{-1}$. The applicability of these methods in combination with solid phase extraction (SPE) for determination 2-nitrophenol in drinking water with limit of determination around 20 $nmol.L^{-1}$ was verified.

Keywords: Solid amalgam electrodes; Voltammetry; Nitrophenols; Growth stimulators; Solid phase extraction (SPE).

1. INTRODUCTION

Nitrophenols coming from pesticide degradation products, car exhausts, and industrial wastes are listed as priority pollutants by the US Environmental Protection Agency [1, 2]. Pesticides based on simple nitrophenols are generally not allowed today but some of than are still used as growth stimulators in agriculture [3]. They are potential carcinogens, teratogens, and mutagens [4]. Because of their toxicity and vast scale distribution in the environment, their determinations have become one of the important goals of environmental analysis.

The easy electrochemical reduction of nitro groups at the aromatic ring, whose mechanism is discussed in monographs [5, 6] permits the very sensitive determination of a number of nitrophenols using modern techniques such as polarography at a classical dropping mercury electrode [7] or differential pulse voltammetry and adsorptive stripping voltammetry at a hanging mercury drop electrode [8].

It is obvious that mercury is the best electrode material for these determinations. However, because of fears of mercury toxicity (although unsubstantiated according to our opinion), there is a tendency to substitute mercury with other non-toxic materials. For that reason, new types of non-traditional electrode materials are being investigated [9]. Non-toxic dental amalgam electrode developed by Trondheim research group was found to be suitable for voltammetric determination of zinc, cadmium, lead, thallium, copper, nickel, and cobalt [10]. The same research group has shown that non-toxic silver-based electrode containing 4% of bismuth, mercury, or lead dioxide exhibit high hydrogen overvoltage making them suitable for voltammetric determination of electrochemically reducible metals [11]. Bismuth-coated carbon electrodes were shown to be attractive alternatives to common mercury electrodes for voltammetric measurements and could address possible restrictions on the use of mercury electrodes [12, 13]. They were used for direct cathodic electrochemical detection of organic compounds [14] and for potentiometric stripping determination of heavy metals [15, 16]. Bismuth-coated screen-printed carbon paste electrode represent a new, disposable and mercury-free electrode with negligible toxicity [17] and bismuth-film-plated carbon paste electrodes [18] exhibit a good performance in stripping voltammetry of some heavy metals.

Practically non-toxic mercury meniscus-modified silver solid amalgam electrode (m-AgSAE), which has a good mechanical stability, simple handling and regeneration including an electrochemical pre-treatment of its surface, was developed by Prague research group [19-23]. In absence of specific interactions between the analyte and silver, the DPV peak potentials on m-AgSAE and hanging mercury drop electrode (HMDE) are nearly the same [19]. This electrode was found suitable for the determination of submicromolar concentrations of selected nitrated polycyclic aromatic hydrocarbons, which are typical representatives of polarographically active environmental carcinogens [24]. Moreover, it was used for adsorptive stripping voltammetry of denaturated DNA [25]. The aim of this work was to develop a differential pulse voltammetric (DPV) method for the determination of trace amounts of nitrophenols as model agriculturally important compounds, using a non-toxic silver solid amalgam electrode in common mercury meniscus modification and in completely mercury free polished modification to compare the advantages and disadvantages of these electrodes with those of a classical hanging mercury drop electrode.

2. EXPERIMENTAL

2.1. Reagents

The stock solutions of 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) in deionized water (c = 1 mmol.L^{-1}) was prepared by dissolving 0.0139 g of the substance (C. A. S. Registry Numbers: [88-75-5 and 100-02-7]; 98%, Sigma-Aldrich, Germany) in 100 mL of the solvent by sonication. The stock solution of 2,4-dinitrophenol (DNP) in deionized water (c = 1 mmol.L^{-1}) was prepared by dissolving

0,0184 g of the substance (C. A. S. Registry Number: [51-28-5]; 97%, Reachim, Russia) in 100 mL of the solvent by sonication.

The spectrophotometric study at wave length of absorption maximum (278 nm, 316 nm and 356 nm for 2-NP, 4-NP and DNP, respectively) confirmed that the stock solutions are stable for at least 2 months when kept in dark. Britton–Robinson buffers were used as a base electrolyte. De-ionized water was produced by a Milli-Q plus system. Other chemicals were obtained from Lachema Brno (Czech Republic) in p.a. purity. All the chemicals were used without any further purification.

2.2. Apparatus

DPV measurements were carried out using computer controlled Eco-Tribo Polarograph with Polar Pro software, version 5.1 for Windows XP (both Polaro-Sensors, Prague, Czech Republic) in combination with a three electrode arrangement with a platinum foil auxiliary electrode and silver/silver chloride (1M-KCl) reference electrode RAE 113 (Monokrystaly, Turnov, Czech Republic), to which all the potential values are referred. The working electrode was silver solid amalgam electrode (AgSAE) with the disc diameter 0.565 mm. The way of preparation of AgSAE was described in previous papers [19, 26] . The electrode consisted of a drawn-out glass tube, the bore of which near the tip was filled with silver solid amalgam which was connected to an electric contact. Afterwards, it was immersed into a small volume of liquid mercury and agitated for 15 seconds to form mercury meniscus modified silver solid amalgam electrode (m-AgSAE). This process, denoted as amalgamation, was repeated every week. Alternatively, polished AgSAE (p-AgSAE) was prepared by polishing at polyurethane pad with 1 μm alumina suspension. The solution pH was measured with digital a Conductivity & pH meter 4330 (Jenway Ltd., Essex, Great Britain) using combined glass electrode (type 924 005).

2.3. Procedures

Before starting the work, as well as after electrode passivation or every pause longer than one hour, the electrochemical activation of AgSAE was carried out in 0.2 M KCl at -2200 mV under stirring of the solution for 300 seconds followed by rinsing with distilled water. Where not stated otherwise, work with AgSAE was carried out at a scan rate of 20 $mV.s^{-1}$, the pulse amplitude of -50 mV, pulse duration of 100 ms, sampling time of 20 ms beginning 80 ms after the onset of the pulse and interval between pulses of 100 ms. A short electrochemical regeneration of AgSAE lasting about 30 s preceded each measurement. The regeneration was carried out by periodical switching every 0.1 s between potentials 100 mV more negative than the potential of amalgam dissolution ($E_{reg\ 1}$) and 100 mV more positive than the potential of hydrogen evolution ($E_{reg\ 2}$) in the given base electrolyte, for optimal values see Table 1. Regeneration always ended at more negative potential. The appropriate values of the potential and the time of regeneration were inserted in the program of the used computer-controlled instrument so that the regeneration of AgSAE was always carried out automatically. For solid phase extraction polymeric SPE Lichrolut EN cartridges purchased from (Merck, Darmstadt, Germany) were used. These cartridges contain 200 mg of sorbent based on an ethylvinylbenzene–divinylbenzene copolymer with a large specific area. Cartridge was conditioned by 3 mL methanol and 3 mL water. Sample was

applied at flow rate 1000 mL per 1 hour. After washing the cartridge with 1 mL of deionized water and drying by air for 10 minutes sample was eluted by 2x 3 mL of methanol and filled by Britton-Robinson buffer pH 8 up to 10 mL.

Table 1. Experimentally found optimal values of regeneration potentials of AgSAE in Britton-Robinson buffer.

	m-AgSAE		p-AgSAE	
pH	$E_{reg\ 1}$ [mV]	$E_{reg\ 2}$ [mV]	$E_{reg\ 1}$ [mV]	$E_{reg\ 2}$ [mV]
2.0	200	-750	0	-700
3.0	100	-1100	0	-1000
4.0	100	-1100	-100	-800
5.0	100	-1200	-100	-900
6.0	0	-1200	-100	-900
7.0	0	-1200	-200	-1000
8.0	-100	-1300	-150	-1300
9.0	-100	-1300	-100	-1300
10.0	-200	-1400	-200	-1400
11.0	-200	-1500	-300	-1300
12.0	-200	-1600	-300	-1400

The general procedure to obtain voltammograms was as follows: Appropriate amount (1-1000 μL) of the stock solution of given nitrophenol (c = 0.1 mmol.L^{-1}) in deionized water was measured into a 10-mL volumetric flask, deionized water was added to the total volume of 1 mL, the solution was filled up to the mark with corresponding Britton-Robinson buffer and transferred into an electrochemical cell. Oxygen was removed from measured solutions by purging with nitrogen for 5 minutes under stirring. The calibration curves were measured in triplicate and evaluated by the least squares linear regression method. The limits of determination were calculated as the tenfold standard deviation from 7 analyte determinations at the concentration corresponding to the lowest point on the appropriate calibration straight line [27] . All the measurements were carried out at laboratory temperature.

3. RESULTS AND DISCUSSION

The influence of pH on the differential pulse voltammograms of tested nitrophenols is documented by Fig. 1. The parameters of linear dependences of peak potentials (E_p) at pH, calculated by linear regression method, are summarized in Table 2. The pH, at which the highest, best developed and therefore most easily evaluated peaks were obtained, were used for the construction of calibration

dependences (see Table 3).

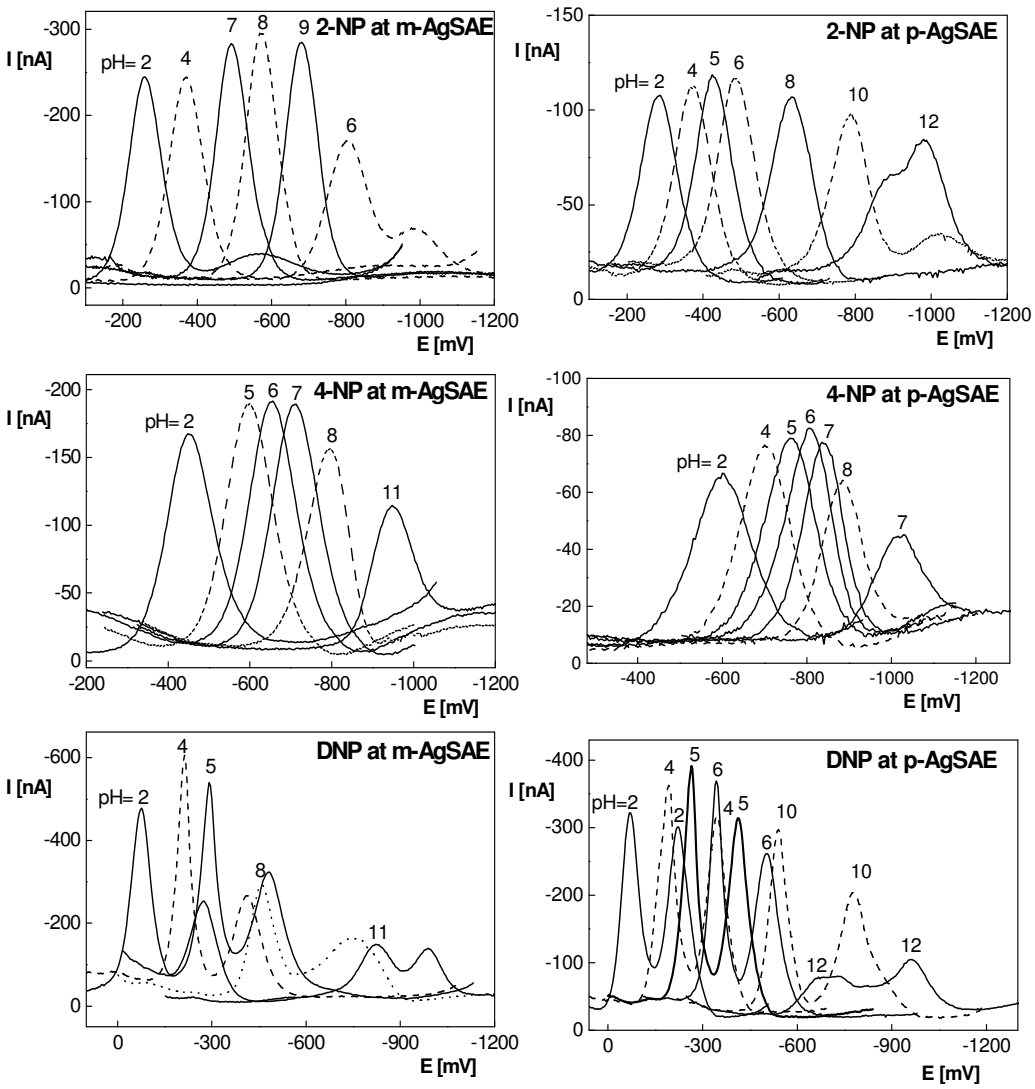

Figure 1. Differential pulse voltammograms of 2-NP, 4-NP and DNP at m-AgSAE and p-AgSAE in Britton-Robinson buffer pH from 2 to 12 (numbers above curves correspond to given pH), concentration of analytes 100 μmol.L^{-1}.

Repeated measurements revealed quite pronounced passivation of the electrode, probably by products of the electrode reaction, resulting in decreasing peaks moving toward more negative potentials. Effect of passivation of the electrode surface was reduced by the above described electrochemical activation but settings of regeneration potentials have strong impact on signal stability (see Fig. 2) and therefore, regeneration potentials had to be found for each of nitrophenol individually. Optimal regeneration potentials are listed in Table 3. Linear calibration curves were obtained in the

concentration range 2-100 μmol.L^{-1}. Their parameters are also summarized in Table 3. Although the sensitivity of methods using m-AgSAE and p-AgSAE were similar, better reproducibility and simpler handling prefers the application of m-AgSAE as compared to p-AgSAE.

Table 2. Parameters of dependences of peak potentials of tested nitrophenols (E_p) on pH of Britton-Robinson buffer. Measured by DPV at m-AgSAE and p-AgSAE.

Substance	m-AgSAE	p-AgSAE
2-NP, 1. peak	E_p (mV) = -60.07 pH – 118.76 R=0.9917 for pH from 2 to 12	E_p (mV) = -64.37 pH – 124.3 R = 0.9952 for pH from 2 to 12
4-NP, 1. peak	E_p (mV) = -53.56 pH - 347.75 R=0.9891 for pH from 2 to 12	E_p (mV) = -41.78 pH – 540.15 R = 0.9959 for pH from 2 to 12
DNP, 1. peak	E_p^1 (mV) = -67.31 pH + 53.21 R=0.9972 for pH from 2 to 9	E_p^1 (mV) = -59.15 pH + 85.38 R = 0.9965 for pH from 2 to 12
DNP, 2. peak	E_p^2 (mV) = -79.11 pH – 117.05 R=0.9918 for pH from 2 to 12	E_p^2 (mV) = -74.08 pH – 6.52 R = 0.9961 for pH from 2 to 12

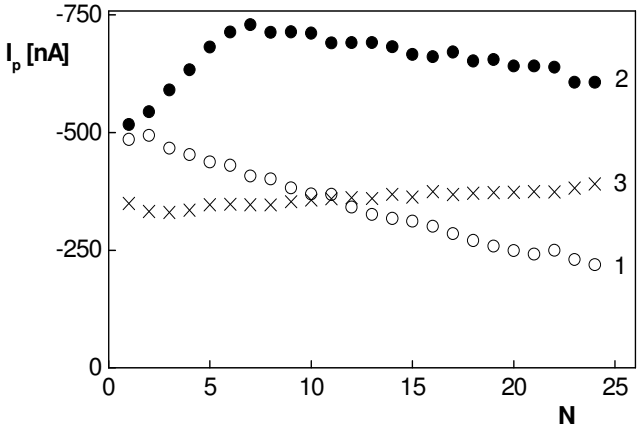

Figure 2. The dependence of first peak current of 2,4-dinitrophenol (c = 100 μmol.L^{-1}) at m-AgSAE in a Britton-Robinson buffer of pH 4 on the number of measurements N. Potentials for regeneration: (1, ○) E_{reg1} = 100 mV, E_{reg2} = -1100 mV; (2, ●) E_{reg1} = 100 mV, E_{reg2} = -1400 mV; (3, ×) E_{reg1} = 0 mV, E_{reg2} = -1400 mV.

The practical applicability of these methods after model experiments with deionized water was confirmed by determination of 2-NP in drinking water as a simple environmental matrix. To improve limit of determination, preconcentration by solid phase extraction (SPE) from 100 mL and 1000 mL samples was used. Lichrolut EN cartridges containing polymeric sorbent with large specific surface and the adsorption capacity for polar organic substances (like e. g. nitrophenols [28]) were used. Recovery of 2-nitrophenol using SPE was calculated from the ratio of the peak height of the substance

after SPE and peak height of 2-nitrophenol standard solution at concentration corresponding to expected concentration after extraction. Parameters of calibration dependences are summarized in Table 4.

Table 3. Parameters of the calibration straight lines for the determination of tested nitrophenols in the concentration range 2-100 μmol.L^{-1} using DPV at m-AgSAE and p-AgSAE in a Britton-Robinson buffer.

Electrode	Substance	pH	E_{reg1} [mV]	E_{reg2} [mV]	Concentration [mol.L^{-1}]	Slope [nA.mol^{-1}.L]	Intercept [nA]	R	L_Q [mol.L^{-1}]
m-AgSAE	2-NP	8.0	-100	-1300	(2-10)·10^{-5}	-1.26·10^{6}	-4.1	0.9999	-
					(2-10)·10^{-6}	-1.49·10^{6}	-1.3	0.9992	1.1·10^{-6}
	4-NP	6.0	0	-1200	(2-10)·10^{-5}	-1.90·10^{6}	-6.9	0.9985	-
					(2-10)·10^{-6}	-2.15·10^{6}	-2.5	0.999	1.1·10^{-6}
	DNP 1.peak	4.0	0	-1400	(2-10)·10^{-5}	-2.66·10^{6}	-18.3	0.9964	-
					(2-10)·10^{-6}	-3.89·10^{6}	-5.7	0.9969	2.4·10^{-6}
	DNP 2.peak	4.0	0	-1400	(2-10)·10^{-5}	-0.86·10^{6}	-3.1	0.9891	-
					(2-10)·10^{-6}	-0.97·10^{6}	-2	0.9969	1.8·10^{-6}
p-AgSAE	2-NP	5.0	-100	-900	(2-10)·10^{-5}	-1.11·10^{6}	-0.4	0.9997	-
					(2-10)·10^{-6}	-0.98·10^{6}	-0.5	0.9996	1.0·10^{-6}
	4-NP	6.0	-100	-900	(2-10)·10^{-5}	-8.11·10^{5}	-0.03	0.9992	-
					(2-10)·10^{-6}	-7.49·10^{5}	-2.56	0.9932	2.8·10^{-6}
	DNP 1.peak	5.0	-200	-1200	(2-10)·10^{-5}	-1.88·10^{6}	-11.6	0.9998	-
					(2-10)·10^{-6}	-1.50·10^{6}	-3.7	0.9954	2.7·10^{-6}
	DNP 2.peak	5.0	-200	-1200	(2-10)·10^{-5}	-0.74·10^{6}	1.2	0.9961	-
					(2-10)·10^{-6}	-0.48·10^{6}	-1.9	0.9832	5.8·10^{-6}

Table 4. Parameters of the calibration straight lines for the determination of 2-nitrophenol in drinking water after solid phase extraction using DPV at m-AgSAE. Concentrations range 20-1000 nmol.L^{-1}. After SPE, the sample was eluted with 6 mL of methanol and filled up to 10 mL by Britton-Robinson buffer pH 8. Potentials for regeneration were E_{reg1} = -100 mV and E_{reg2} = -1300 mV.

Matrix	Volume [mL]	Recovery [%]	Concentration [mol.L^{-1}]	Slope [nA.mol^{-1}.L]	Intercept [nA]	R	L_Q [mol.L^{-1}]
Deonized	100	98.0	(2-10)·10^{-7}	-1.04·10^{7}	-0.6	0.9987	2.1·10^{-7}
water	1000	95.1	(2-10)·10^{-8}	-1.05·10^{8}	-0.2	0.9989	2.2·10^{-8}
Drinking	100	96.2	(2-10)·10^{-7}	-0.95·10^{8}	-0.4	0.9983	2.7·10^{-7}
water	1000	95.1	(2-10)·10^{-8}	-1.05·10^{8}	-1.2	0.9987	2.1·10^{-8}

4. CONCLUSIONS

It has been proved that m-AgSAE is a suitable sensor for the determination of micromolar concentrations of nitrophenols. The limits of determination of nitrophenols using DPV at m-AgSAE and p-AgSAE are around 2 $\mu mol.L^{-1}$, but for m-AgSAE larger signal stability given by lower pasivation of electrode was observed. Furthermore, m-AgSAE has a better reproducibility and thus in many cases it represents an effective and simpler alternative to the HMDE. Therefore, for coupling with solid phase extraction (SPE) more reliable m-AgSAE was used. It was shown that in combination with a preliminary separation and preconcentration by SPE it is possible to determine concentration of 2-nitrophenol down to 20 $nmol.L^{-1}$**.** For methods without precontration, limits of determination are similar as for differential pulse polarography on a dropping mercury electrode (2 $\mu mol.L^{-1}$, [7]) and higher than for differential pulse voltammetry on a hanging mercury drop electrode (0.1 $\mu mol.L^{-1}$, [8]). As with polarographic and voltammetric methods on mercury electrodes, substances reducible at the same potential will interfere. Among other aspects, the solid amalgam electrodes provide good mechanical stability, simple handling and thus new fields of application in electrochemical techniques can be envisaged.

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