POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF GENOTOXIC NITRO DERIVATIVES OF QUINOLINE USING MERCURY ELECTRODES

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Dedicated to Professor Petr Zuman on the occasion of his 85th birthday.

Electrochemical behavior of genotoxic nitro derivatives of quinoline, namely 5-nitroquinoline (5-NQ), 6-nitroquinoline (6-NQ) and 8-nitroquinoline (8-NQ), was investigated by DC tast polarography (DCTP) and differential pulse polarography (DPP), both at a classical dropping mercury electrode (DME), and by differential pulse voltammetry (DPV) and adsorptive stripping differential pulse voltammetry (AdSDPV), both at a miniaturized hanging mercury drop minielectrode (HMDmE), in buffered aqueous (for 5-NQ) or aqueous-methanolic (for 6-NQ and 8-NQ) solutions. Optimum conditions were found for the determination of 5-NQ, 6-NQ and 8-NQ by DCTP at DME (with limits of quantification, $L_Q \approx 9 \times 10^{-7}$, 3×10^{-7} and 2×10^{-6} mol l^{-1}, respectively), by DPP at DME ($L_Q \approx 1 \times 10^{-8}$, 9×10^{-8} and 1×10^{-7} mol l^{-1}, respectively), by DPV at HMDmE ($L_Q \approx 2 \times 10^{-8}$, 1×10^{-7} and 1×10^{-7} mol l^{-1}, respectively), and by AdSDPV at HMDmE ($L_Q \approx 1 \times 10^{-8}$ mol l^{-1} for 8-NQ; an attempt at increasing the sensitivity using AdSDPV at HMDmE was not successful for 5-NQ and 6-NQ). Practical applicability of the developed methods was verified on the direct determination of the studied compounds in model samples of drinking and river water in submicromolar concentrations and on the determination in model samples of drinking and river water using preliminary separation and preconcentration by solid phase extraction (SPE) in nanomolar concentrations.

Keywords: Analytical methods; Electrochemistry; Polarography; Voltammetry; Mercury electrodes; 5-Nitroquinoline; 6-Nitroquinoline; 8-Nitroquinoline; Spiked water samples; Solid phase extraction.

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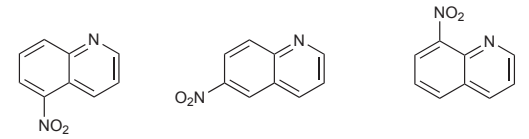
Nitrated polycyclic aromatic compounds constitute a group of chemicals of environmental concern which display a broad spectrum of mutagenic, genotoxic, and carcinogenic properties[1]. Among them, nitro derivatives of quinoline (NQs) represent a unique group of nitro compounds with a structure containing one nitrogen heteroatom. As well as structurally similar nitronaphthalenes, NQs are formed during the incomplete combustion of both gasoline and diesel fuel and during the biomass pyrolysis process[2]. Although the content of NQs in particulate matter of diesel exhaust is significantly lower in contrast to carcinogenic mononitrated polycyclic aromatic hydrocarbons (e.g., 2-nitronaphthalene, 4-nitrobiphenyl, 2-nitrofluorene, 3-nitrofluoranthene, or 1-nitropyrene)[3], it is necessary to consider the genotoxic NQs to be hazardous substances in the environment because the majority of nitroaromatic compounds in the biosphere are at least genotoxic[4,5], some of them act as mutagens and/or carcinogens[6]. On the other hand, nitroaromatic compounds are widely used in medicine, often as anticancer drugs[7].

In this paper, mercury electrodes, which are believed to be the most suitable working electrodes for the determination of polarographically reducible substances[4,8–13], were used. In the sixties of the last century, Tachibana et al.[14] have studied polarographic behavior of NQs and their derivatives. The reduction half-wave potentials ($E_{1/2}$), corresponding to the reduction of the nitro group to the hydroxyamino group, have been measured for 35 representative compounds in buffered aqueous media of pH 3.78, 6.98 and 9.85. Discussions have been made on the $E_{1/2}$ values in connection with their chemical structures. It has been found for all the NQs measured that the first well-defined polarographic wave, observable in the potential range from –0.1 to –0.5 V (E vs saturated calomel electrode), corresponded to the 4-electron reduction of the nitro group to the hydroxyamino group. Another polarographic wave, which was observed at more negative potentials, was connected with a subsequent 2-electron reduction step corresponding to the reduction of the previously formed hydroxyamino group to the amino group. All the $E_{1/2}$ values measured have been found to be strongly dependent on pH [14].

The aim of this study was to find optimum conditions for the determination of trace amounts of selected genotoxic nitro derivatives of quinoline – 5-nitroquinoline (5-NQ), 6-nitroquinoline (6-NQ) and 8-nitroquinoline (8-NQ) (structures in Fig. 1) – using modern polarographic and voltammetric methods, namely DC tast polarography (DCTP) and differential pulse polarography (DPP) at a classical dropping mercury electrode (DME), differential pulse voltammetry (DPV) and adsorptive stripping differential

pulse voltammetry (AdSDPV) at a miniaturized hanging mercury drop minielectrode (HMDmE), and to verify their practical applicability on model samples of drinking and river water or on these samples preconcentrated by solid phase extraction (SPE).

All the used electroanalytical techniques are well described in monographs[15–17]. Great sensitivity, especially of DPP, DPV and AdSDPV [18], and a relatively low price of instrumentation, in comparison with LC-MS or GC-MS instrumentation, are the most important advantages of these methods[19,20].



5-Nitroquinoline 6-Nitroquinoline 8-Nitroquinoline

FIG. 1
Structural formulae of tested compounds

EXPERIMENTAL

Reagents

Stock solutions of 5-nitroquinoline (5-NQ; 99%, Sigma–Aldrich, Prague, Czech Republic) in deionized water ($c = 1 \times 10^{-3}$ mol l^{-1}) and of 6-nitroquinoline (6-NQ; 98%, Sigma–Aldrich) and 8-nitroquinoline (8-NQ; 98%, Sigma–Aldrich) in methanol (both of $c = 1 \times 10^{-3}$ mol l^{-1}) were prepared by dissolving 0.01742 g of the pure substances in 100 ml of deionized water or methanol (MeOH; 99.9%, p.a. purity, Merck, Darmstadt, Germany), respectively. Methanol was used as a solvent in the case of 6-NQ and 8-NQ due to their limited solubility in deionized water. UV-Vis spectrophotometric studies demonstrated that the stock solutions are stable for at least three months[21–23]. Dilute solutions were prepared by dilution of the stock solutions with deionized water (for 5-NQ) or MeOH (for 6-NQ and 8-NQ). Britton–Robinson (BR) buffers were prepared in a usual way[10]; boric acid, phosphoric acid (85%), acetic acid (99%), and sodium hydroxide, all of p.a. purity, were supplied by Lachema, Brno, Czech Republic. Lithium hydroxide (p.a. purity) was supplied by Lachema. Deionized water produced by a Milli-Q Plus system (Millipore, Billerica, MA, USA) was used. All the solutions were stored in glass vessels in the dark at laboratory temperature.

Apparatus

All electrochemical measurements were carried out using an Eco-Tribo electrochemical analyzer driven by Polar Pro 5.1 software (all Polaro-Sensors, Prague, Czech Republic). The software worked under the operational system Microsoft Windows XP Professional (Microsoft Corporation, Redmond, WA, USA). The measurements were carried out in a three-electrode system – platinum wire auxiliary electrode (type PPE), silver|silver chloride reference electrode (Ag|AgCl; type RAE 113, 1 M KCl) (both from Monokrystaly, Turnov, Czech Republic), and an appropriate working mercury electrode.

For DCTP and DPP, classical DME was used as the working electrode – the electronically controlled mercury drop lifetime was 1.0 s and the height of the mercury reservoir was 49 cm (mercury drop lifetime was 2.4 s at this height, measured in 0.1 M KCl at 0 V vs Ag|AgCl (1 M KCl), and the flow rate of mercury through the capillary was 3.90 mg s^{-1}); the scan rate 4 mV s^{-1} was used. For DPP, the pulse amplitude –50 mV and the pulse width 100 ms (with current sampling for the last 20 ms) were used.

For DPV and AdSDPV, miniaturized HMDmE of the UMμE (ultra-mini and micro-electrode) type (Polaro-Sensors) was used as the working electrode – the valve opening time was 200 ms, the mercury drop surface was 0.77 mm^2, and the flow rate of mercury through the capillary was 5.32 mg s^{-1}; the scan rate 20 mV s^{-1}, the pulse amplitude –50 mV, and the pulse width 100 ms (with current sampling for the last 20 ms) were used.

The pH was measured using digital Conductivity & pH Meter Jenway 4330 (Jenway, Chelmsford, UK) with a combined glass electrode. For SPE techniques, LiChrolut® columns RP-18 E (1000 mg; Merck, Darmstadt, Germany) and a 12-port SPE vacuum manifold (model BJ9400, Honeywell Burdick & Jackson, Morristown, NJ, USA) were used.

Procedures

The general procedure to obtain polarograms or voltammograms was as follows: An appropriate amount of 5-NQ, 6-NQ or 8-NQ stock solution was measured into a voltammetric cell, deionized water (in the case of 5-NQ) or MeOH (in the case of 6-NQ and 8-NQ) was added, if necessary, to the total volume 1.0 ml (for 5-NQ and 6-NQ) or 5.0 ml (for 8-NQ) and the solution was filled up to 10.0 ml with BR buffer of appropriate pH. Before each polarographic and/or voltammetric measurement, oxygen was removed from the measured solutions by bubbling with nitrogen (purity 4.0, Linde, Prague, Czech Republic) for 5 min. Before entering the voltammetric cell, nitrogen was first passed through a bubbler containing a MeOH–deionized water mixture in the same ratio as in the measured solution or deionized water alone (if no MeOH was present in the measured solution).

All the curves were measured three times and all the measurements were carried out at laboratory temperature. The wave heights, i.e., limiting diffusion currents (I_{lim}), recorded using DCTP were evaluated from the extrapolated linear portions of the currents. The peak heights (I_p) recorded using DPP, DPV and AdSDPV were evaluated from the straight lines connecting the minima before and after the peak. The parameters of calibration curves (i.e., slope, intercept, correlation coefficient, and confidence intervals) and other mathematical and statistical quantities (all for the significance level $\alpha = 0.05$)[24] were calculated using software Origin Pro 8.0 (OriginLab Corporation, Northampton, MA, USA). The limit of quantification (L_Q) was calculated as the analyte concentration corresponding to a tenfold standard deviation of the respective response from ten consecutive determinations at the lowest measurable concentration[25].

Model Samples

The drinking water from the public water pipeline in the building of Faculty of Science of Charles University in Prague, Prague, Czech Republic and the river water from the Vltava river (sampling locality Výtoň) in Prague, Czech Republic (filtered through a glass frit funnel of porosity S4), spiked with an appropriate amount of 5-NQ, 6-NQ or 8-NQ stock solution, were used for model samples.

The procedure for the direct DPV determination of studied compounds in the model samples of drinking or river water was as follows: 9.0 ml of a model water sample, spiked with an appropriate amount of 5-NQ, 6-NQ or 8-NQ, were filled up to 10.0 ml with the BR buffer of appropriate optimum pH and, after deaeration with nitrogen, DP voltammograms at HMDmE were recorded.

The procedure for the DPV determination of studied compounds in the model samples of deionized, drinking, or river water after SPE was as follows: Each SPE column was connected to the SPE vacuum manifold and activated by washing with 5 ml of MeOH and 5 ml of deionized water. Afterwards, the model water samples, spiked with different amounts of 5-NQ, 6-NQ or 8-NQ, were sucked through the column using volumetric flasks as sample reservoirs and polytetrafluoroethylene tubing for connecting the reservoirs and SPE columns. The adsorbed analyte was then eluted with 1.0 ml (for 5-NQ) or 5.0 ml (for 6-NQ and 8-NQ) of MeOH, the solution was filled up to 10.0 ml with the BR buffer of appropriate optimum pH and, after deaeration with nitrogen, DP voltammograms at HMDmE were recorded. The percent recoveries were calculated from the ratio I_{pI}/I_{p0}, where I_{pI} is the peak height of the analyte after SPE and I_{p0} is the peak height of a reference solution prepared by addition of a standard solution of the studied analyte to the blank solution.

RESULTS AND DISCUSSION

DC Tast Polarography and Differential Pulse Polarography at Dropping Mercury Electrode

The influence of pH on polarographic behavior of 5-NQ, 6-NQ and 8-NQ was investigated using DCTP and DPP at DME in the solutions of BR buffer (for 5-NQ), MeOH–BR buffer (1:9) (for 6-NQ), or MeOH–BR buffer (1:1) (for 8-NQ). It can be seen in Fig. 2 that 5-NQ and 8-NQ gave one well-developed irreversible polarographic wave in the whole investigated pH region; 6-NQ exhibited very similar polarographic behavior. The half-wave potentials shifted towards more negative values with increasing pH or pH* (resulting pH of the MeOH–BR buffer medium) according to the relationships: $E_{1/2}$ [mV] = –44.5 pH – 0.4 (in the pH range 2.0–13.0; correlation coefficient, R = –0.9990), $E_{1/2}$ [mV] = –49.2 pH* – 20.6 (in the pH* range 2.1–12.0; R = –0.9985), and $E_{1/2}$ [mV] = –48.2 pH* – 23.1 (in the pH* range 2.8–9.3; R = –0.9990) for 5-NQ, 6-NQ and 8-NQ, respectively. Other strongly irreversible and badly developed waves were obtained at more negative potentials but they are not suitable for analytical purposes. The best developed waves were obtained in the BR buffer pH 3.0 medium (for 5-NQ), in the MeOH–BR buffer pH 12.0 (1:9) medium (for 6-NQ) and in the MeOH–BR buffer pH 5.0 (1:1) medium (for 8-NQ), which were used for measuring of calibration curves. Parameters of the calibration straight lines are summarized in Table I.

In good agreement with DCT polarographic behavior of studied compounds, 5-NQ, 6-NQ and 8-NQ gave one well-developed cathodic peak in the whole investigated pH region upon the DPP at DME. Other worse developed peaks obtained at more negative potentials are not analytically useful.

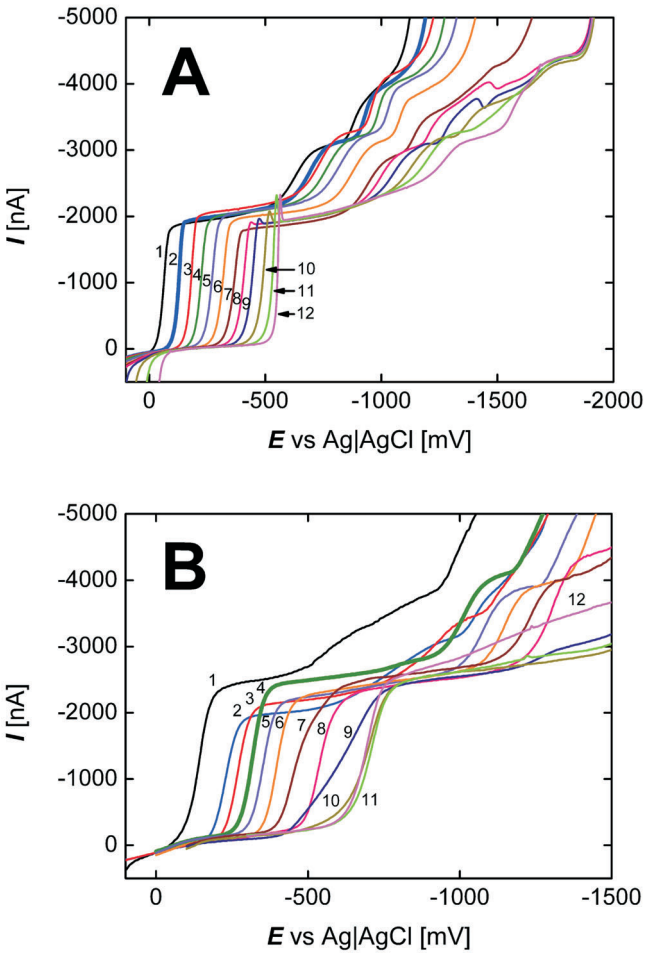


FIG. 2
DCT polarograms of 5-NQ (A) and 8-NQ (B) (both $c = 1 \times 10^{-4}$ mol l^{-1}) at DME, recorded in the BR buffer (A) or in the MeOH–BR buffer (1:1) medium (B) with the BR buffer of pH: 2.0 (1), 3.0 (2), 4.0 (3), 5.0 (4), 6.0 (5), 7.0 (6), 8.0 (7), 9.0 (8), 10.0 (9), 11.0 (10), 12.0 (11), and 13.0 (12). Polarograms recorded under optimum conditions for the determination of 5-NQ and 8-NQ are in bold

TABLE I

Parameters of the calibration straight lines for the determination of studied compounds using various polarographic and voltammetric techniques (R, correlation coefficient; L_Q, limit of quantification (10σ; $\alpha = 0.05$))

Analyte	Technique	Medium	Concentration mol l^{-1}	Slope[a] mA mol^{-1} l	Intercept[a,b] nA	R	L_Q mol l^{-1}
5-NQ	DCTP at DME	BR buffer pH 3.0	2×10^{-5} – 1×10^{-4}	–20.05 ± 0.21	–20 ± 14	–0.9998	–
			1×10^{-6} – 1×10^{-5}	–19.44 ± 0.10	1.73 ± 0.98	–0.9998	9×10^{-7}
	DPP at DME	BR buffer pH 3.0	2×10^{-5} – 1×10^{-4}	–61.9 ± 1.2	–0.9 ± 7.7	–0.9993	–
			2×10^{-6} – 1×10^{-5}	–55.8 ± 1.3	–0.1 ± 1.8	–0.9999	–
			1×10^{-7} – 1×10^{-6}	–53.5 ± 1.1	–1.16 ± 0.38	–0.9997	9×10^{-8}
		0.2 M NaOH	2×10^{-5} – 1×10^{-4}	–93.3 ± 4.8	960 ± 320	–0.9948	–
			2×10^{-6} – 1×10^{-5}	–61.3 ± 1.4	16.7 ± 9.3	–0.9990	–
			2×10^{-7} – 1×10^{-6}	–54.0 ± 1.0	–1.89 ± 0.65	–0.9993	–
			2×10^{-8} – 1×10^{-7}	–59.0 ± 1.2	–0.36 ± 0.25	–0.9997	1×10^{-8}
	DPV at HMDmE	0.2 M NaOH	2×10^{-5} – 1×10^{-4}	–26.98 ± 0.46	–82 ± 31	–0.9994	–
			2×10^{-6} – 1×10^{-5}	–30.88 ± 0.68	–1.9 ± 4.5	–0.9990	–
			2×10^{-7} – 1×10^{-6}	–28.15 ± 0.42	0.48 ± 0.28	–0.9996	–
			2×10^{-8} – 1×10^{-7}	–27.35 ± 0.29	–0.12 ± 0.10	–0.9998	2×10^{-8}
6-NQ	DCTP at DME	MeOH–BR buffer pH 12.0 (1:9)	2×10^{-5} – 1×10^{-4}	–3.93 ± 0.43	4.7 ± 1.2	–0.9999	–
			2×10^{-6} – 1×10^{-5}	–3.86 ± 0.36	0.46 ± 0.21	–0.9999	3×10^{-7}
	DPP at DME	MeOH–BR buffer pH 12.0 (1:9)	2×10^{-5} – 1×10^{-4}	–24.11 ± 0.27	308 ± 33	–0.9957	–
			2×10^{-6} – 1×10^{-5}	–11.96 ± 0.18	4.3 ± 1.2	–0.9997	–
			2×10^{-7} – 1×10^{-6}	–10.15 ± 0.13	–0.41 ± 0.17	–0.9993	9×10^{-8}
	DPV at HMDmE	MeOH–BR buffer pH 12.0 (1:9)	2×10^{-5} – 1×10^{-4}	–44.46 ± 0.88	–17 ± 11	–0.9988	–
			2×10^{-6} – 1×10^{-5}	–43.61 ± 0.52	5.4 ± 3.3	–0.9993	–
			2×10^{-7} – 1×10^{-6}	–44.51 ± 0.24	0.69 ± 0.41	–0.9964	1×10^{-7}
8-NQ	DCTP at DME	MeOH–BR buffer pH 5.0 (1:1)	2×10^{-5} – 1×10^{-4}	–21.32 ± 0.17	32 ± 11	–0.9999	–
			2×10^{-6} – 1×10^{-5}	–20.46 ± 0.31	6.5 ± 2.1	–0.9995	2×10^{-6}
	DPP at DME	MeOH–BR buffer pH 5.0 (1:1)	2×10^{-5} – 1×10^{-4}	–27.44 ± 0.68	–33 ± 45	–0.9988	–
			2×10^{-6} – 1×10^{-5}	–31.80 ± 0.79	15.6 ± 5.3	–0.9988	–
			1×10^{-7} – 1×10^{-6}	–61.09 ± 0.61	0.77 ± 0.37	–0.9998	1×10^{-7}
	DPV at HMDmE	MeOH–BR buffer pH 4.0 (1:1)	2×10^{-5} – 1×10^{-4}	–9.88 ± 0.15	–22 ± 12	–0.9994	–
			2×10^{-6} – 1×10^{-5}	–9.91 ± 0.16	0.2 ± 1.1	–0.9995	–
			2×10^{-7} – 1×10^{-6}	–9.41 ± 0.12	–0.13 ± 0.17	–0.9997	1×10^{-7}
	AdSDPV at HMDmE	MeOH–BR buffer pH 10.7 (1:9)[c]	2×10^{-8} – 1×10^{-7}	–48.4 ± 1.2	0.12 ± 0.10	–0.9989	1×10^{-8}

[a] Intervals represent the lower and upper confidence limits ($\alpha = 0.05$); [b] all intercepts are not statistically significantly different from zero at the significance level $\alpha = 0.05$; [c] LiOH was used instead of NaOH in the BR buffer.

For 5-NQ, the highest and best developed peaks were obtained in the BR buffer pH 3.0 and 13.0 medium, which was further used to measure calibration curves. The BR buffer pH 13.0 medium was substituted by 0.2 M NaOH medium for simplification. For 6-NQ and 8-NQ, the optimum media found were MeOH–BR buffer pH 12.0 (1:9) (for 6-NQ) and MeOH–BR buffer pH 5.0 (1:1) (for 8-NQ). Parameters of the obtained calibration curves are also summarized in Table I.

Differential Pulse Voltammetry at Hanging Mercury Drop Minielectrode

Electrochemical behavior of 5-NQ, 6-NQ and 8-NQ was further characterized using DPV at HMDmE. It follows from DP voltammograms that, e.g., 5-NQ (Fig. 3) gave one well-developed cathodic peak in the whole investigated pH region. Other strongly irreversible and badly developed peaks were observed at more negative potentials but they are not, as in the case of DPP at DME, analytically useful. The best developed peaks were obtained under the similar conditions as for DPP at DME. Parameters of the calibration curves obtained are presented in Table I.

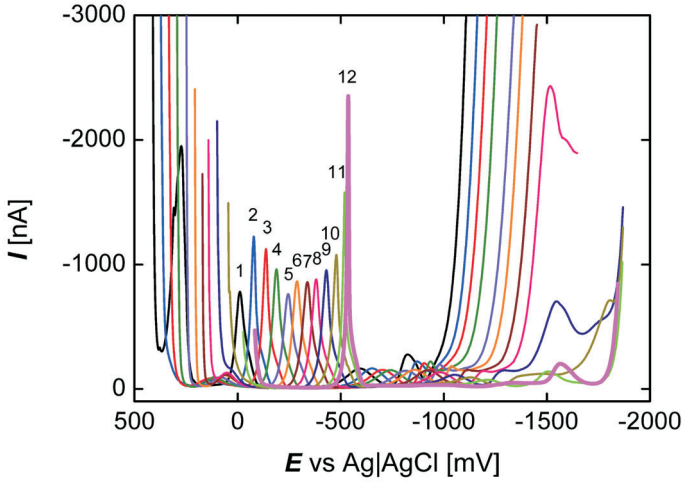


FIG. 3
DP voltamograms of 5-NQ ($c = 1 \times 10^{-4}$ mol l^{-1}) recorded at HMDE in BR buffer of pH: 2.0 (1), 3.0 (2), 4.0 (3), 5.0 (4), 6.0 (5), 7.0 (6), 8.0 (7), 9.0 (8), 10.0 (9), 11.0 (10), 12.0 (11), and 13.0 (12). Voltammogram recorded under optimum conditions for the determination of 5-NQ is in bold

Adsorptive Stripping Differential Pulse Voltammetry at Hanging Mercury Drop Minielectrode

For further decrease of the limit of quantification obtained for 5-NQ, 6-NQ and 8-NQ by DPV at HMDmE ($L_Q \approx 2 \times 10^{-8}$, 1×10^{-7} and 1×10^{-7} mol l^{-1}, respectively), a possible utilization of the adsorption of the analytes on the electrode surface was tested using AdSDPV at HMDmE. It has been previously found that the presence of MeOH decreases the adsorption of the test substance on the surface of HMDmE [8,18]. Therefore, the determinations of selected NQs using AdSDPV were carried out with the lowest possible content of MeOH in the supporting electrolyte.

The influence of pH on voltammetric behavior of NQs ($c = 1 \times 10^{-7}$ mol l^{-1}) was investigated using AdSDPV at HMDmE in BR buffers from pH 2.0 to 13.0. The accumulation potential (E_{acc}) was changed from +200 mV at pH 2.0 to –400 mV at pH 12.0, always before the onset of corresponding voltammetric peak, and the accumulation time (t_{acc}) was 60 s. Unfortunately, the attempt at increasing the sensitivity using AdSDPV at HMDmE was not successful for 5-NQ and 6-NQ – it has been proved that 5-NQ and 6-NQ did not significantly increased their voltammetric responses in dependence on the t_{acc}.

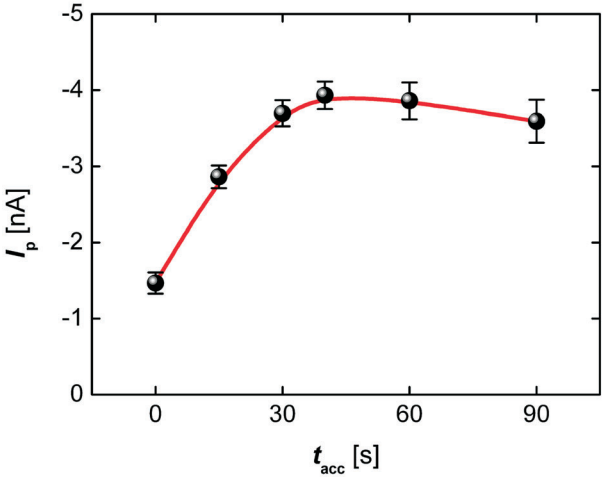


FIG. 4
Influence of accumulation time (AdSDPV with E_{acc} = –250 mV) on the peak current of 8-NQ ($c = 1 \times 10^{-7}$ mol l^{-1}) at HMDmE in the MeOH–BR buffer pH 10.7 (1:9) medium, where LiOH was used instead of NaOH. The error bars are constructed for $\alpha = 0.05$ ($n = 3$)

On the other hand, the best developed AdSDP voltammograms of 8-NQ were obtained in the MeOH–BR buffer pH 10.7 (1:9) medium, where LiOH was used instead of NaOH because of its greater purity, at the optimum E_{acc} = –250 mV. Under these conditions, the optimum t_{acc} was chosen to be 40 s (Fig. 4); peaks were well-developed and longer accumulation times were not useful, probably because of concurrent adsorption of other substances present in very low concentrations in the supporting electrolyte.

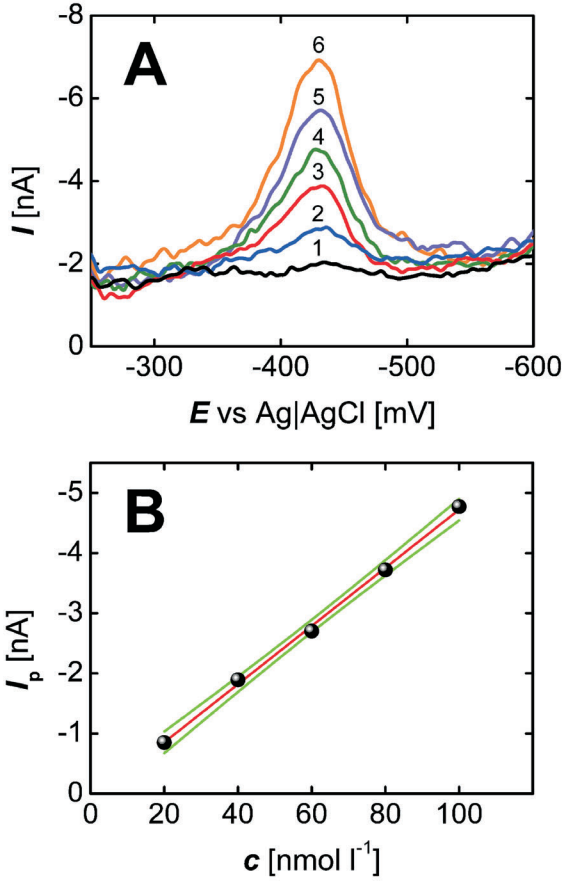


FIG. 5

A AdSDP voltammograms of 8-NQ recorded at HMDmE in the MeOH–BR buffer pH 10.7 (1:9) medium; t_{acc} = 40 s, E_{acc} = –250 mV. Concentrations of 8-NQ [mol l^{-1}]: 0 (1), 2×10^{-8} (2), 4×10^{-8} (3), 6×10^{-8} (4), 8×10^{-8} (5), and 1×10^{-7} (6). B The corresponding calibration straight line; the confidence bands are constructed for $\alpha = 0.05$ ($n = 3$)

TABLE II

Parameters of the calibration straight lines for the determination of studied compounds in model samples of water using DPV at HMDmE (R, correlation coefficient; L_Q, limit of quantification (10σ; α = 0.05); DeW, deionized water; DW, drinking water; RW, river water)

Analyte	Technique	Medium	Concentration mol l^{-1}	Slope[a] mA mol^{-1} l	Intercept[a,b] nA	R	L_Q mol l^{-1}
5-NQ	Direct determination in spiked DW	Spiked DW–0.2 M NaOH (9:1)	$2 \times 10^{-7} - 1 \times 10^{-6}$ $2 \times 10^{-8} - 1 \times 10^{-7}$	–28.25 ± 0.33 –27.24 ± 0.43	1.24 ± 0.22 0.11 ± 0.10	–0.9997 –0.9995	– 2×10^{-8}
	Direct determination in spiked RW	Spiked RW–0.2 M NaOH (9:1)	$2 \times 10^{-7} - 1 \times 10^{-6}$ $2 \times 10^{-8} - 1 \times 10^{-7}$	–24.84 ± 0.17 –23.82 ± 0.24	0.34 ± 0.11 –0.01 ± 0.10	–0.9999 –0.9998	– 7×10^{-9}
	SPE from 100 ml of spiked DeW	MeOH–0.2 M NaOH (1:9)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–172.2 ± 2.5	–0.33 ± 0.16	–0.9983	2×10^{-9}
	SPE from 100 ml of spiked DW	MeOH–0.2 M NaOH (1:9)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–130.6 ± 4.4	0.02 ± 0.10	–0.9978	3×10^{-9}
	SPE from 100 ml of spiked RW	MeOH–0.2 M NaOH (1:9)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–111.7 ± 2.3	–0.04 ± 0.10	–0.9992	1×10^{-9}
6-NQ	Direct determination in spiked DW	Spiked DW–BR buffer pH 12.0 (9:1)	$2 \times 10^{-7} - 1 \times 10^{-6}$	–43.28 ± 0.22	–0.25 ± 0.21	–0.9999	2×10^{-7}
	Direct determination in spiked RW	Spiked RW–BR buffer pH 12.0 (9:1)	$2 \times 10^{-7} - 1 \times 10^{-6}$	–41.22 ± 0.15	–0.32 ± 0.12	–0.9998	2×10^{-7}
	SPE from 100 ml of spiked DeW	MeOH–BR buffer pH 12.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–185.1 ± 3.1	–0.23 ± 0.15	–0.9988	2×10^{-9}
	SPE from 100 ml of spiked DW	MeOH–BR buffer pH 12.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–176.2 ± 3.5	–0.07 ± 0.12	–0.9987	2×10^{-9}
	SPE from 100 ml of spiked RW	MeOH–BR buffer pH 12.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–174.5 ± 2.1	–0.05 ± 0.11	–0.9985	3×10^{-9}

TABLE II
(*Continued*)

Analyte	Technique	Medium	Concentration mol l^{-1}	Slope[a] mA mol^{-1} l	Intercept[a,b] nA	R	L_Q mol l^{-1}
8-NQ	Direct determination in spiked DW	Spiked DW–BR buffer pH 4.0 (9:1)	$1 \times 10^{-7} - 1 \times 10^{-6}$	–8.10 ± 0.17	–0.64 ± 0.11	–0.9991	9×10^{-8}
	Direct determination in spiked RW	Spiked RW–BR buffer pH 4.0 (9:1)	$1 \times 10^{-7} - 1 \times 10^{-6}$	–8.87 ± 0.20	–0.04 ± 0.13	–0.9990	1×10^{-7}
	SPE from 100 ml of spiked DeW	MeOH–BR buffer pH 4.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–148.8 ± 1.8	0.18 ± 0.12	–0.9989	2×10^{-9}
	SPE from 100 ml of spiked DW	MeOH–BR buffer pH 4.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–175.2 ± 3.4	0.16 ± 0.11	–0.9993	2×10^{-9}
	SPE from 100 ml of spiked RW	MeOH–BR buffer pH 4.0 (1:1)	$2 \times 10^{-9} - 1 \times 10^{-8}$	–176.1 ± 1.5	0.16 ± 0.10	–0.9996	2×10^{-9}

[a] Intervals represent the lower and upper confidence limits ($\alpha = 0.05$); [b] all intercepts are not statistically significantly different from zero at the significance level $\alpha = 0.05$.

The calibration curves were constructed for the concentration range from 2×10^{-8} to 1×10^{-7} mol l^{-1}. The I_p value is proportional to the concentration of 8-NQ in the whole investigated concentration range (see Table I). Corresponding AdSDP voltammograms are depicted in Fig. 5. Higher concentrations of 8-NQ were not measured due to the possibility of using DPV or DPP technique.

Determination of the Studied Compounds in Drinking and River Water

The optimum conditions found above for DPV determination of 5-NQ, 6-NQ and 8-NQ were used for direct determination of studied compounds in model samples of drinking and river water. 9.0 ml of spiked drinking or river water were filled up to 10.0 ml with 0.2 M NaOH, BR buffer pH 12.0, and BR buffer pH 4.0 for 5-NQ, 6-NQ and 8-NQ, respectively. The parameters of obtained calibration dependences, measured in the concentration range from zero to 10^{-6} mol l^{-1}, are presented in Table II.

Furthermore, we tried to preconcentrate the studied compounds using SPE. Recovery parameters were measured using samples of spiked deionized water and MeOH as eluent. Recoveries of SPE from 100 ml ($c = 5 \times 10^{-8}$ mol l^{-1}) of deionized water were evaluated using DPV at HMDmE. The values were 85, 90 and 92% for 5-NQ, 6-NQ and 8-NQ, respectively. The studied compounds were then extracted from 100 ml of spiked drinking water ($c = 1 \times 10^{-8}$ mol l^{-1}) with recoveries 80, 91 and 96% and of spiked river water ($c = 1 \times 10^{-8}$ mol l^{-1}) with recoveries 97, 94 and 93% for 5-NQ, 6-NQ and 8-NQ, respectively. Parameters of extractions and parameters of the obtained regression dependences are presented in Table II (the differences in digit places of slopes are due to the use of original values of concentrations of the order 10^{-9} mol l^{-1} before the tenfold SPE preconcentration).

CONCLUSIONS

Electrochemical reduction of the nitro group of genotoxic 5-nitroquinoline, 6-nitroquinoline and 8-nitroquinoline at mercury electrodes has been studied in buffered aqueous or aqueous-methanolic solutions of pH 2–12 and the studied compounds have been determined under optimum conditions using polarographic and voltammetric techniques. Nanomolar concentrations of these compounds can be determined not only in deionized water but also in model matrix of drinking or river water (using differential pulse voltammetry at the miniaturized hanging mercury drop minielectrode with preliminary separation and preconcentration of the analytes by solid phase

extraction). Thus, the presented sensitivity of determination of these genotoxic nitro derivatives of quinoline illustrates the usefulness of mercury electrodes in current analytical chemistry and confirms that mercury electrodes are still useful electrochemical sensors.

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