VOLTAMMETRIC DETERMINATION OF 1,2-DIAMINOANTHRAQUINONE USING CARBON PASTE ELECTRODE

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Dedicated to Professor Karel Štulík on the occasion of his 70th birthday.

Direct current (DC) voltammetry and differential pulse (DP) voltammetry using a carbon paste electrode (CPE) have been used for the determination of trace amounts of ecotoxic 1,2-diaminoanthraquinone (DAAQ). The limit of determination (L_D) of DAAQ for DC voltammetry was 2×10^{-6} mol l^{-1}, and for DP voltammetry 2×10^{-7} mol l^{-1} under the optimized conditions in a mixed Britton–Robinson buffer pH 12 and methanol (1:9) medium. Adsorptive accummulation of the analyte on the surface of CPE decreased the limit of determination to 2×10^{-8} mol l^{-1} for DP voltammetry. Practical applicability of these newly developed methods was verified on model samples of river water.

Keywords: Analytical methods; Electrochemistry; Voltammetry; Carbon paste electrode; 1,2-Diaminoanthraquinone; Differential pulse voltammetry; Direct current voltammetry; Adsorptive stripping voltammetry.

Amino-substituted anthraquinones belong among ecotoxic and mutagenic compounds[1] polluting the environment. Due to their prolonged use in the industry they are occurring in soil, sediments, water and food products[2]. These substances are used as chemical intermediates in production of azo dyes and azo pigments[3–8], polyimides[9], and also antineoplastic agents[10–11]. Methods of determination of amino-substituted anthraquinones include optical, electrochemical and separation methods. Anthraquinone molecule contains two conjugated systems separated by carbonyl groups so that the absorption maximum of lies in UV region, with slight overlap into a visible reagion resulting in pale yellow colour. By the substitution of electron do-

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nor amino group into the anthraquinone ring the colour intensifies and becomes darker as a consequence of the interaction of amino groups with carbonyl groups through the conjugated double bond system. Thus, the amino anthraquinones can be easily determined by spectrophotometry and by amperometry utilizing both their reducibility and oxidizability by electrochemical detectors in HPLC or electrophoresis. Another feature of amino anthraquinones is the existence of intramolecular hydrogen bonds which are quite strong in aprotic solvents and which on one hand contribute to increased chemical stability of amino anthraquinone derivatives and on the other hand shift both oxidation and reduction potential to higher values. 1,2-Diaminoanthraquinone (DAAQ) was determined by e.g. RP HPLC with fluorescent detection with the L_D at the nanomolar level[12], by normal phase liquid chromatography, again with fluorescent detection with $L_D = 2 \times 10^{-8}$ mol l^{-1} [13]. Chronopotentiometry was used for the determination of DAAQ by DNA modified screen-printed electrode with $L_D = 5 \times 10^{-8}$ mol l^{-1} [14]. DAAQ was also tested as fluorescent probe during the study of the mechanism of nitric oxide imaging in living cells[15]. The solid-state colorimetric sensors for nitrite anion and both aqueous and gaseous nitric oxide were described. They are based on cross-linked poly(2-hydroxyethylmethacrylate) films doped with 1,2-diaminoanthraquinone (DAQ). The sensors show no appreciable leaching of DAAQ even after six months of storage in water[16].

Carbon paste constitute for already more than 60 years a very useful tool in analytical electrochemistry. Carbon pastes electrodes are valued for their composition variability, the possibility for chemical and biological modification with tayloring their properties according to the problems to be solved, high sensitivity, low baseline currents, etc. With adsorptive accumulation of the analyte on the working electrode surface sub-nanomolar limits of detection can be quite frequently reached. Nevertheless, carbon pastes are better suited for oxidizable analytes as the adsorbed oxygen on carbon particles often interferes with the signal of reducible analytes. The utilization of carbon paste electrodes in modern electroanalysis is described in several newer reviews[17–20] or book chapters[21,22]. In this contribution, we have developed new methods of DAAQ determination by direct current (DC) voltammetry and differential pulse (DP) voltammetry using bare carbon paste electrodes and verified their applicability on model samples of river water.

EXPERIMENTAL

Reagents

1,2-Diaminoanthraquinone was purchased from Sigma-Aldrich, Germany. The 1×10^{-3} M 1,2-diaminoanthraquinone stock solution was prepared by dissolving 23.87 mg of the analyte in methanol (Lach-Ner, Czech Republic) in 100 ml volumetric flask. The solutions of lower concentrations were prepared daily by proper dilution of the stock solution with methanol. Britton–Robinson (BR) buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 M phosphoric acid, 0.04 M acetic acid and 0.04 M boric acid with the appropriate amount of 0.2 M sodium hydroxide solution. Chemicals for the preparation of the BR buffers (all p.a. purity) were obtained from Sigma Aldrich, Germany. Deionized water from Millipore Q-plus System, Millipore, USA was used for all experiments. Carbon paste was prepared from 250 mg of glassy carbon spherical microparticles type 2, 0.4–12 μm (Alfa Aesar, USA) and 90 μl of mineral oil Nujol (Fluka, Germany). River water samples were collected from river Vltava, right bank, 20 m downstream the railway bridge near Vyšehrad.

Apparatus

Direct current and differential pulse voltammograms were obtained with Eco-Tribo Polarograph controlled by Polar Pro version 5 software (both Polaro-Sensors, Czech Republic) working under operation system Windows XP (Microsoft Corp., USA). The measurements were carried out in a three-electrode system consisting of a working carbon paste electrode (University of Pardubice, Czech Republic)[19], a silver/silver chloride (3 M KCl) reference electrode RAE 113 and a platinum wire auxiliary electrode PRE (both Monokrystaly, Czech Republic). Applied parameters for DP voltammetry were: potential range from 0 to +1300 mV, scan rate 20 mV s^{-1}, pulse amplitude +50 mV, pulse width 80 mV, 10 s quiet period.

A 4330 Conductivity & pH Meter (Jenway Ltd., UK) fitted with the combined glass electrode was employed to measure the pH of the solutions. The pH meter was calibrated with aqueous buffers at a laboratory temperature. The spectrophotometric measurements were performed using UV/Vis spectrophotometer Pye Unicam PU 8800 (Philips, Cambridge, Great Britain) in 1 mm quartz cuvettes.

Procedures

Prepared carbon paste was packed using 2 mm stainless steel rod into the teflon electrode body with 2 mm inner diameter (geometric area 3.1 mm^2). Carbon paste was allowed to homogenize till the next day when the measurements were started. The composition of carbon paste was chosen on the basis of previous measurements. Prior to each new voltammetric measurement, the surface of the electrode was mechanically renewed by wiping with wet filter paper. The voltammetric measurements were performed in an unstirred and not deaerated mixed medium of BR buffer and methanol. Adsorptive accumulations were performed always in stirred (1000 rpm) medium for different time periods. The calibration curves were measured in triplicate and their statistical parameters (e.g. slope, intercept, limit of determination) were calculated using the least squares linear regression method[23]. L_D corresponds to the lowest signal for which the relative standard deviation is equal 0.1 [24]. All measurements were performed at laboratory temperature. The stability of DAAQ stock solution was controlled spectrophotometrically by measuring the absorbance at 263 and 518 nm.

Model samples of river water were prepared by mixing 1 ml of DAAQ of appropriate concentration with 5 ml of filtered river water and adjusted to 10 ml by BR buffer of pH 12.

RESULTS AND DISCUSSION

DC Voltammetry of 1,2-Diaminoanthraquinone

The composition of the supporting electrolyte for studying the influence of pH on the oxidation of DAAQ on CPE was determined on the basis of preliminary experiments involving changing of methanol content as the analyte is slightly soluble in water. It was found that 10% methanol (v/v) was sufficient to ensure the solubility of DAAQ as no cloud or even precipitate appeared during one hour, giving rise to stable and homogenous solutions with $c \leq 1 \times 10^{-4}$ mol l^{-1} of DAAQ. Therefore, the influence of pH on DC voltammograms of 1×10^{-4} M DAAQ was studied in a mixed media of methanol and BR buffers pH 2–12 (1:9). The DC voltammetric curves had a peak-like shape which was apparently connected with the combination of electrode surface passivation and unfavorable mass transport and charge transfer characteristics. The DAAQ signal moved with increasing pH to less positive potential values which was connected with the protonation of amino group in acidic medium. The protonation of amino groups in acidic medium further endorses the formation of intra- and intermolecular hydrogen bonds. Therefore, the oxidation of active amino group is much easier in alkaline medium. The influence of DAAQ peak potential on pH could be described by the equation E_p(mV) = –53.5 pH + 812.0 with the correlation coefficient of linear regression –0.9989. The highest and best developed DAAQ signals were obtained in a medium of methanol–BR buffer pH 12 (1:9) at which the calibration dependences were measured in the concentration range from 1×10^{-4} to 2×10^{-6} mol l^{-1}. The parameters of DC calibration lines are summarized in Table I. The calculated limit of determination of DAAQ for DC voltammetry was 2×10^{-6} mol l^{-1}. The limited solubility of the analyte in aqueous medium can be used to lower its limit of determination by means of adsorptive accumulation of the analyzed substance on the surface of hydrophobic carbon paste electrode. At first, the influence of the accumulation time on the peak current of DAAQ in methanol–BR buffer pH 12 (1:9) medium was studied. As the accumulation potential, only E_{acc} = 0 V was utilized because DAAQ oxidizes at low potential values in this medium. In Fig. 1, the influence of accumulation time under stirring with 1000 rpm on DAAQ current signal is depicted. The accumulation time of 180 s was chosen as the optimum for measuring the calibration

TABLE I
Parameters of calibration straight lines for voltammetric determination of 1,2-diaminoanthraquinone in methanol–BR buffer pH 12 (1:9) medium on CPE

Concentration μmol l^{-1}	Slope mA mol^{-1}	Intercept nA	Correlation coefficient	L_D μmol l^{-1}
DCV				
20–100	1.3	210	0.9934	–
2–10	11.6	6.2	0.9944	0.2
Adsorptive stripping DCV, t_{acc} = 180 s				
0.2–1	108	8.2	0.9915	0.2
DPV				
20–100	2.2	409	0.9919	–
0.6–10	23.8	65	0.9971	0.6
Adsorptive stripping DPV, t_{acc} = 180 s				
0.2–1	43.1	40	0.9959	–
0.02–0.1	127	1.6	0.9994	0.02

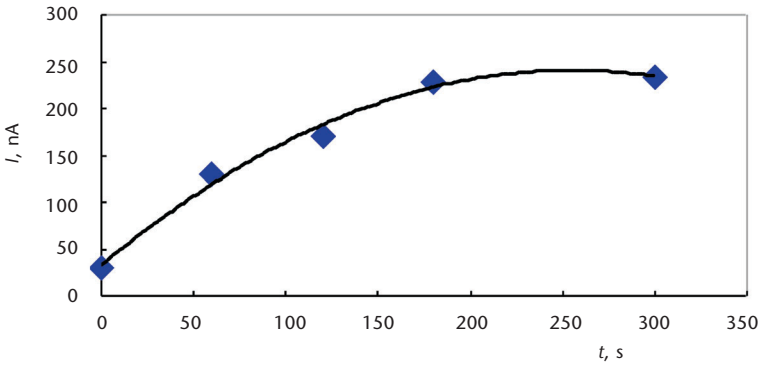

FIG. 1
The influence of accumulation time on signal current of 2 × 10^{-6} M DAAQ, under stirring (1000 rpm). Measured by DC voltammetry using CPE in methanol–BR buffer pH 12 (1:9) medium

dependences using adsorptive stripping DC voltammetry. The approximately tenfold increase in analyte current resulted in approximately tenfold decrease in calculated limit of DAAQ determination which was about 2×10^{-7} mol l^{-1}. The parameters of calibration lines are summarized in Table I.

DP Voltammetry of 1,2-Diaminoanthraquinone

DP voltammetry of organic compounds gives often better evaluable signals than DC voltammetry which frequently results in lower limits of determination. Nevertheless, the dependence of analyte peak potentials on pH of supporting electrolyte follows the same trend reflecting preliminary protonation of the analyte. At lower pH values the peaks are broader and worse developed. With usually very small charging current contribution to peak current and flat background currents better sensitivities and better resolutions are often reached with DP voltammetry than with DC voltammetry.

The dependence of DPV peak currents of DAAQ on pH of the supporting electrolyte was very similar to DC voltammetry and could be described by the equation E_p(mV) = –49.2 pH + 762, correlation coefficient –0.9960, selected DP voltammograms are depicted in Fig. 2.

It follows from Fig. 2 that the peak height of DAAQ increased with increasing pH and the same holds for peak symmetry and evaluability. Therefore, for measuring the calibration dependences, methanol–BR buffer pH 12

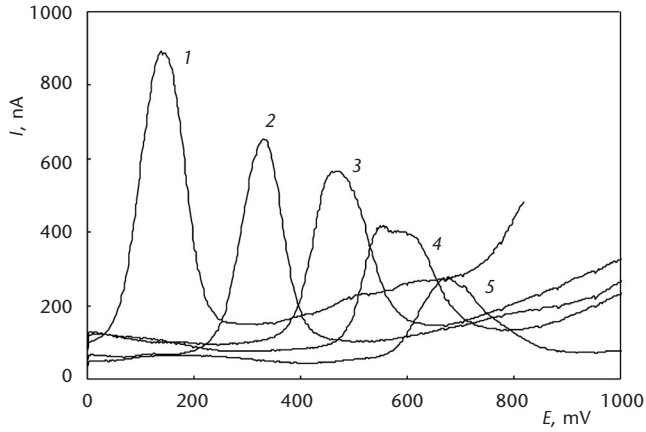

FIG. 2
DP voltammograms of 1×10^{-4} M DAAQ at CPE in methanol–BR buffers pH 12 (*1*), 10 (*2*), 7 (*3*) 4 (*4*) and 2 (*5*) (1:9) media

(1:9) medium was selected. The concentration range from 2×10^{-6} to 1×10^{-4} mol l^{-1} was investigated. The calculated slopes of calibration dependences (2–10) $\times 10^{-6}$ and (2–10) $\times 10^{-5}$ mol l^{-1}) differed significantly. The lower slope value for higher concentration range indicated probable passivation of the electrode surface reaction products. Adsorption of DAAQ increases the signal at lower concentrations and decreases the signal at higher concentrations. As in case of DC voltammetric study, the influence of accumulation time on DPV peak height of 2×10^{-6} M DAAQ on CPE in methanol–BR buffer pH 12 (1:9) medium was studied. Almost tenfold increase in DAAQ peak current with 180 s accumulation time led to almost tenfold decrease in the limit of determination of DAAQ to 2×10^{-8} mol l^{-1} using the accumulation of the analyte in a stirred (1000 rpm) solution, see Fig. 3. The parameters of calibration lines are summarized in Table I.

DCV and DPV Determinations of DAAQ in Model Samples of River Water

The practical applicability of newly developed voltammetric methods of DAAQ determination was tested on model samples of river water with standard additions of the analyte. The prepared samples were analysed by both DC and DP voltammetry (see Fig. 3) in the concentration range from 2 ×

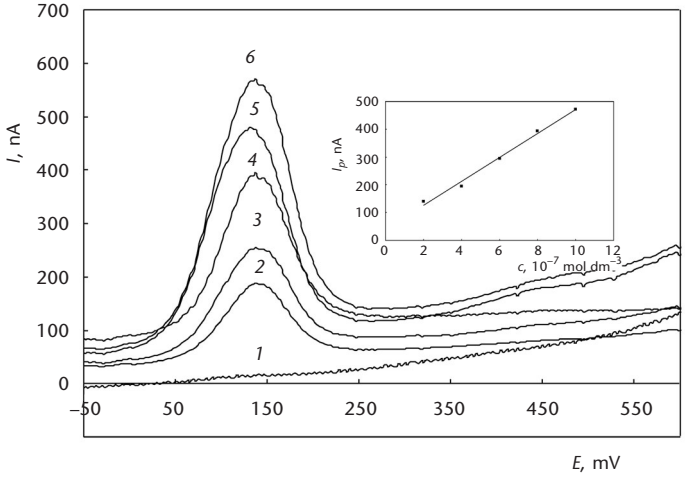

FIG. 3
Adsorptive stripping DP voltammograms of DAAQ in methanol–BR buffer pH 12 (1:9) medium. *c*(DAAQ): 0 (*1*), 2×10^{-7} (*2*), 4×10^{-7} (*3*), 6×10^{-7} (*4*), 8×10^{-7} (*5*) and 10×10^{-8} (*6*) mol l^{-1}. E_{acc} = 0 V, t_{acc} = 180 s, 1000 rpm. Calibration line in the inset

10^{-7} to 1×10^{-5} mol l^{-1}. The calculated slopes of calibration dependences of DAAQ (for DPV curves, see the inset of Fig. 4) measured in river water matrix were not significantly different from slopes measured in clean supporting electrolyte. The observed shift in DAAQ peak potential in river water is attributed to the presence of active surface substances in this matrix. The evaluation of spiked samples proved that both methods are useful in the determination of 1,2-diaminoanthraquinone in river samples so that they can be used for monitoring purposes in environmental analysis. Nevertheless, it can be expected that structurally similar compounds would interfere, however, their simultaneous occurence with tested analyte in one matrix is not probable.

It has been shown that DC voltammetry and DP voltammetry using bare carbon paste electrode could be used for the determination of 1,2-diaminoanthraquinone. When utilizing adsorptive accumulation of the analyte on the surface of the carbon paste electrode the limits of DAAQ determination of 2×10^{-8} mol l^{-1} for adsorptive stripping differential pulse voltammetry and 2×10^{-7} mol l^{-1} for adsorptive stripping direct current voltammetry were reached, the relative standard deviations < 5% (n = 7) for the concentration of 1×10^{-7} mol l^{-1}. For model samples of DAAQ spiked river water DC and DP voltammetry were successfully used.

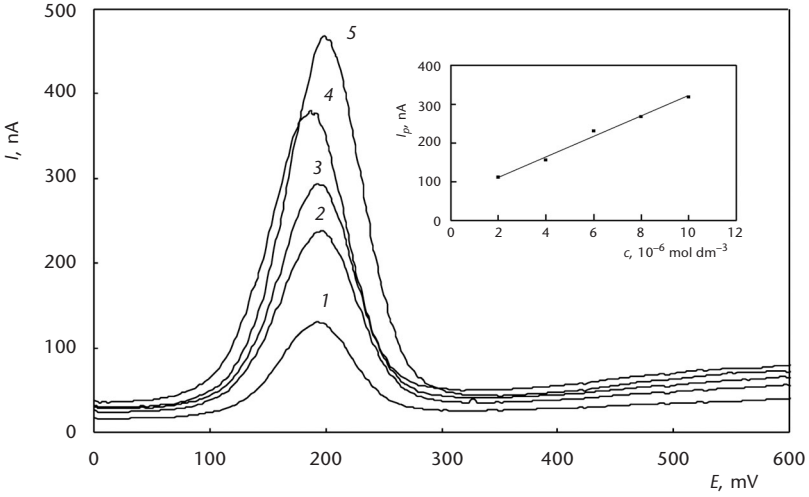

FIG. 4
Voltammograms of DAAQ in model samples of river water. Measured by DP voltammetry using CPE in methanol–BR buffer pH 12 (1:9) medium. c(DAAQ): 2×10^{-6} (*1*), 4×10^{-6} (*2*), 6×10^{-6} (*3*), 8×10^{-6} (*4*) and 10×10^{-6} (*5*) mol l^{-1}

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