

Voltametrické stanovení stopových množství 2-aminofluorenu pomocí adsorpční rozpouštěcí voltametrie na uhlíkové pastové elektrodě

S teoretickými základy moderních polarografických a voltametrických metod jsou posluchači seznámeni během přednášky „Elektrochemické metody“ a během přednášky „Organická polarografie a voltametrie“. Optimalizace podmínek pro stanovení 2-aminofluorenu adsorpční rozpouštěcí voltametrií na uhlíkové pastové elektrodě je popsána v poslední části tohoto návodu. Z didaktických důvodů je příloha v originále, tj. v anglickém jazyce.

Aparatura: Počítačem řízený EkoTribo Polarograf se softwarem PolarPro verze 2.0 (Polarosensors, Praha). Pracováno bude vždy v tříelektrodovém zapojení s nasycenou argentchloridovou referenční elektrodou a platinovou drátkovou pomocnou elektrodou. Jako pracovní elektroda bude použita uhlíková pastová elektroda.

Ovládací program

Popis programu: PolarPro je program pro měření a vyhodnocení koncentrace látek ve vzorcích analyzovaných na EkoTribo Polarografu. Program ve verzi Pro umožňuje též návrh a úpravu metod měření. Tento uživatelsky přívětivý program pracuje v operačním prostředí Windows a jeho ovládání je názorné a jednoduché. Zvládnutí tohoto programu usnadňuje snadno dostupná rozsáhlá nápověda.

Požadavky programu: EkoTribo Polarograf; stojánek + převodníková karta

Polaro 4 (vše Polarosensors Praha)

Windows 3.1 CE nebo Windows 95, volné 2 MB na disku, myš.

Minimální doporučená sestava: procesor 486, RAM paměť 8 MB.

Omezení programu: maximální počet křivek v jednom souboru – 24; maximální počet vyhodnocovaných látek v jednom souboru - 8

Pracovní postup:

1. Příprava uhlíkové pastové elektrody
250 mg grafitového prášku CR-5 (Tesla Lanškroun, velikost částic 5 μm) se pečlivě smísí se 100 μL parafinového oleje Uvasol (Merck). Takto připravenou pastou se naplní tělo používané elektrody. Před každým měřením se povrch uhlíkové pastové elektrody obnoví otřením tenké vrstvy pasty vlhkým filtračním papírem.
2. Sestrojení kalibrační křivky
Kalibrační křivka se proměří v prostředí Brittonova-Robinsonova pufru o pH 12 v koncentračním rozmezí 2-10 $\mu\text{mol/L}$ při době akumulace 20 s v míchném roztoku při potenciálu akumulace 0 V.
3. Statisticky vyhodnoťte sestavenou kalibrační závislost a vypočtete odpovídající mez stanovitelnosti.
4. Pomocí sestavené kalibrační křivky určete koncentraci 2-aminofluorenu v neznámém vzorku.

Metoda: DP voltametrie

Potenciál		Parametry metody	
počáteční E_{in}	-50 mV	počet měření	3
konečný E_{fin}	+550 mV	výška pulsu	- 50 mV
rychlost	20 mV/s	šířka pulsu	80 ms

Vyhodnocení se provede pomocí podprogramu „HODNOCENÍ“, který je součástí používaného programu Polar Pro, verze 2.0.

Upozornění: Do jednoho souboru lze uložit maximálně 24 křivek

VOLTAMMETRIC DETERMINATION OF 2-AMINOFLUORENE AND 2,7-DIAMINOFLUORENE USING CARBON PASTE ELECTRODE

KEY WORDS: 2-aminofluorene, 2,7-diaminofluorene; carbon paste electrode; differential pulse voltammetry; adsorptive stripping voltammetry

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ABSTRACT

The voltammetric determination of 2-aminofluorene (2-AF) and 2,7-diaminofluorene (2,7-DAF) based on their oxidation on carbon paste electrode is described. Britton-Robinson buffer and pH ranges 1-3 and 10-12 are recommended for the simultaneous determination of 2-AF and 2,7-DAF. The sensitivity of determination can be enhanced substantially by adsorptive accumulation of analytes on carbon paste electrode in the pH range 10-12. The detection limits for the accumulation time 200 s were evaluated as $2 \cdot 10^{-7}$ and $1 \cdot 10^{-7}$ mol l⁻¹ for 2-AF and 2,7-DAF, respectively. Relative standard deviations for the concentration range $(1-10) \cdot 10^{-7}$ mol l⁻¹ do not exceed 10 %.

EXPERIMENTAL

Materials and Apparatus

All measurements were performed using a computerized voltammetric analyzer EkoTriboPolarograoph with UM μ E stand(PolaroSensors, Czech Republic) at a differential pulse voltammetry mode. The scan rate was 20 mV s⁻¹, pulse amplitude 50 mV, pulse duration and frequency were 80 ms and *ca.* 8 Hz, respectively.

Carbon paste electrode was prepared by thorough mixing of 250 mg graphite powder CR-5 (particle size *ca.* 5 μ m; Tesla Lanškroun, Czech Republic) with 100 μ l paraffin oil Uvasol (Merck). The reference electrode was RAE 113 (Monokrystaly, Turnov, Czech Republic) - Ag/AgCl electrode filled by 1 mol l⁻¹ KCl. Platinum wire served as an auxiliary electrode.

2-aminofluorene and 2,7-diaminofluorene were obtained from Aldrich. The stock solutions were prepared by dissolving of these substances in 0.1 mol l⁻¹ hydrochloric acid. Britton - Robinson buffers were used as the media for voltammetric measurements. Other reagents used were of analytical grade (Lachema, Brno, Czech Republic). All solutions were prepared using water obtained from a MilliQ Plus unit (Millipore).

Procedures

Before every measurement the surface of the carbon paste electrode was renewed by removing of thin layer of the paste by wet filter paper. The 2-AF and 2,7-DAF determination was performed in Britton-Robinson buffer pH 12 medium. After the immersion of the CPE to 10 ml volume of test solution the stirring by motor driven stirrer was switched on for accumulation time (e.g., for 20-200 s). Since adsorptive accumulation does not require external potential it starts immediately after the immersion of the electrode. Stirring was stopped for a rest time 5 s before the end of accumulation. After the accumulation step the potential scan from -50 mV to 550 mV *versus* Ag/AgCl was started to obtain analytical peaks of the 2-AF and 2,7-DAF. To achieve better reproducibility of the results it is recommended to repeat the measurement cycle 2-3 times. Method of standard additions was used for quantification of the measurement results.

RESULTS AND DISCUSSION

It has been found that well-defined and not overlapping peaks are characteristic for oxidation of 2-aminofluorene and 2,7-diaminofluorene on the carbon paste electrode in Britton-Robinson buffer (Fig. 1). Both 2-AF and 2,7-DAF peak potentials depend on pH – the shift is about 0.4 V to negative side when pH changes from 1 to 12.

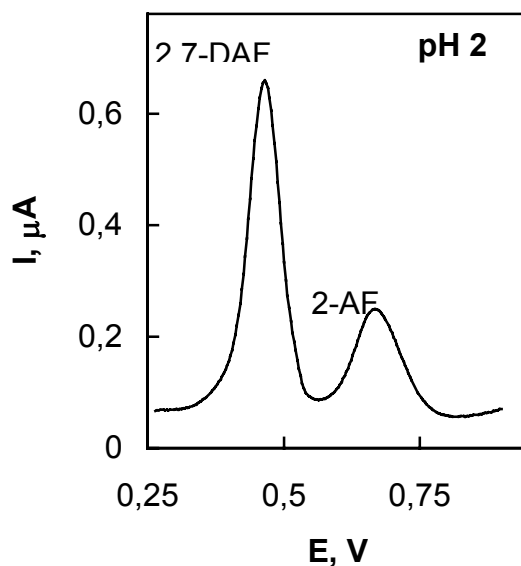


FIG. 1. Examples of voltammograms of 2-AF and 2,7-DAF oxidation on carbon paste electrode in Robinson-Britton buffer ($20 \mu\text{mol l}^{-1}$ 2-AF and 2,7-DAF).

However, while the shape of the 2-AF oxidation peaks do not change significantly in the pH range 1-12, those for 2,7-DAF split to two overlapped peaks for pH values between 4 and 9. Dependencies of peak potentials on pH presented in Fig. 2 show that the useful range of pH values for simultaneous determination of 2-AF and 2,7-DAF are pH 1-3 and pH 10-12. It can be seen from the curves that the difference between 2-AF and 2,7-DAF oxidation peak potentials is about 30 % higher at pH 12 in comparison with those in the pH range 1-3. Only slight increase of the heights of the oxidation peaks was observed increasing pH in the ranges of interest.

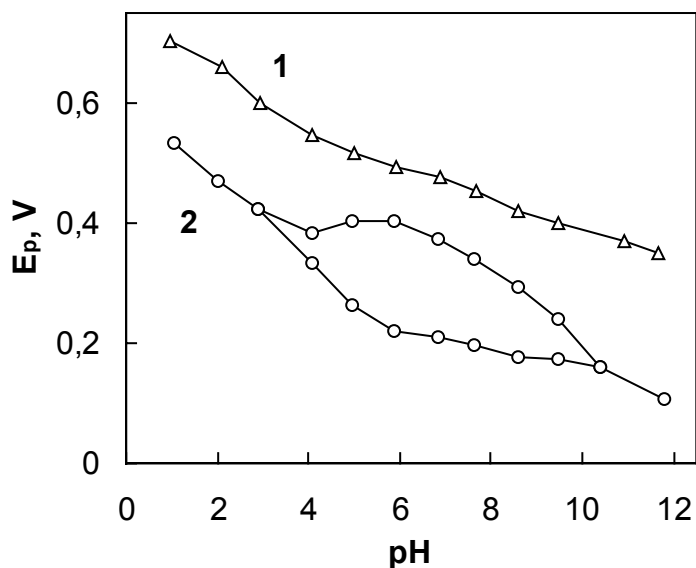


FIG. 2. Effect of pH on oxidation peak potentials of aminofluorenes. 1 – 2-AF, 2 – 2,7-DAF. Conditions as in Fig. 1.

It was found that the sensitivity of 2-AF and 2,7-DAF determination can be enhanced by introducing of accumulation step before the potential scan. The accumulation does not depend on electrode potential and can be performed even without external potential. The effect of accumulation depends on pH – the higher the pH the higher analytical peaks can be obtained using the accumulation step. Table 1 illustrates the effect of accumulation time on peak heights of 2-AF and 2,7-DAF oxidation at pH 2 and pH 12. Possibly, increased fraction of deprotonized species of 2-AF and 2,7-DAF at higher pH values results in adsorptive accumulation of analytes on the carbon paste electrode.

Fig. 3 shows the effect of accumulation time on analytical peaks at pH 12 for $1 \mu\text{mol l}^{-1}$ concentrations of 2-AF and 2,7-DAF. It can be seen from the comparison of the data in the Table 1 and Fig. 3 that in the case of low concentrations analytical peaks increase substantially at least up to 5 min whereas . for $20 \mu\text{mol l}^{-1}$ concentrations this range is only about 1 min. This indicates also on the adsorptive mechanism of accumulation.

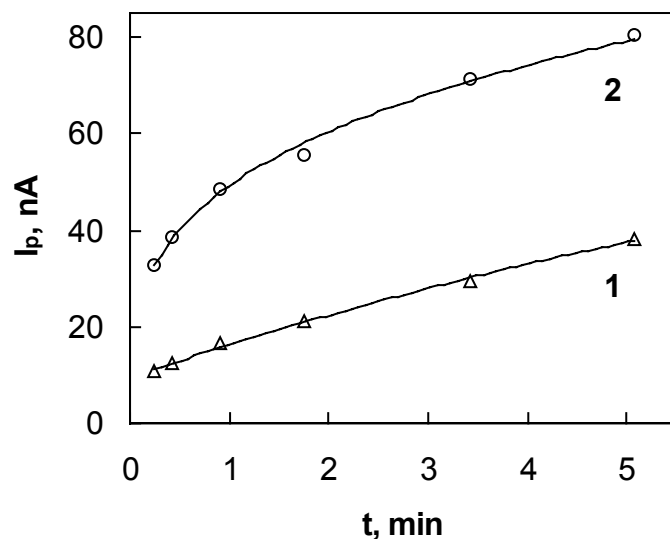


FIG. 3. Dependencies of 2-AF and 2,7-DAF oxidation peaks on adsorptive accumulation time. 1 – 2-AF, 2 – 2,7-DAF. Conditions: $1 \mu\text{mol l}^{-1}$ 2-AF and 2,7-DAF; pH 12.

TABLE 1

Effect of Accumulation Time on Analytical Peaks of 2-aminofluorene and 2,7-diaminofluorene at Various pH Values ($c = 20 \mu\text{mol l}^{-1}$)

Accumulation time, s	2-AF, nA		2,7-DAF, nA	
	pH 2	pH 12	pH 2	pH 12
10	158	151	647	521
35	173	256	648	665
60	174	294	619	704
85	171	308	667	709
110	171	324	633	719

The dependencies of 2-AF and 2,7-DAF oxidation peaks on concentration are linear at least up to concentrations $80\text{-}100 \mu\text{mol l}^{-1}$ if the accumulation time for higher concentrations is decreased properly. Otherwise the saturation of electrode surface by adsorbed analyte results

in deviation from linearity. Parameters of linear dependencies of analytical signals of 2-AF and 2,7-DAF on concentration are presented in Table 2. The fact that intercepts are characteristic only for the concentration range 10-80 $\mu\text{mol l}^{-1}$ can be explained by lower sensitivity of determination at higher concentrations.

TABLE 2

Parameters of Linear Dependencies of Analytical Signals of 2-aminofluorene and 2,7-diaminofluorene on Concentration at pH 12 (P=0.95)

Concentration range, $\mu\text{mol l}^{-1}$	Analyte	Accumulation time, s	Slope, nA ($\mu\text{mol l}^{-1}$) ⁻¹	Intercept, nA	Correlation coefficient
10-80	2-AF	20	9.1±0.6	42±30	0.9989
	2,7-DAF	20	28±3	180±140	0.9973
1-10	2-AF	20	11±0.8	–	0.9924
	2,7-DAF	20	37±2	–	0.9967
0.2-1.0	2-AF	200	37±2	–	0.9982
0.1-0.5	2,7-DAF	200	78±6	–	0.9938

The reproducibility of 2-AF and 2,7-DAF oxidation peak potentials is very high – relative standard deviation is less than 1%. The relative standard deviations of analytical signals depend on the concentration – they do not exceed 5% and 10% for the concentration ranges 10-80 and 1-10 $\mu\text{mol l}^{-1}$, respectively. However, for the concentration range 0.1-1.0 $\mu\text{mol l}^{-1}$ the reproducibility is lower – about 12-15%. Lower reproducibility of peak heights and noise on voltammograms leads to a conclusion that for the accumulation time 200 s limits of detection for 2-AF and 2,7-DAF are 0.2 and 0.1 $\mu\text{mol l}^{-1}$, respectively. Fig. 4 shows the voltammograms of oxidation of 2-AF and 2,7-DAF at the limit of detection.

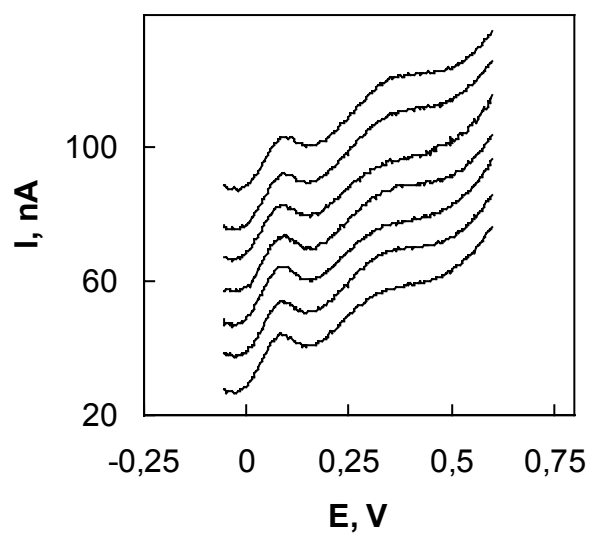


FIG. 4. Voltammograms of 2-AF and 2,7-DAF oxidation on carbon paste electrode. Conditions: $0.2 \mu\text{mol l}^{-1}$ 2-AF and $0.1 \mu\text{mol l}^{-1}$ 2,7-DAF; pH 12; accumulation – 200 s.