Voltammetric determination of naphthalene, fluorene and anthracene using mixed water-organic solvent media

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The voltammetric method for the determination of naphthalene, fluorene and anthracene by their anodic oxidation at a glassy carbon or carbon paste electrode using the mixed water-organic solvent media is described. The compositions of mixed media are the following: 0.1 mol l^{-1} H$_2$SO$_4$ as an aqueous component with 20% (by volume) of methanol for naphthalene or 25% of acetonitrile for fluorene and anthracene. The detection limits using the glassy carbon electrode for naphthalene, fluorene and anthracene are 12, 6.4 and 1.2 μmol l^{-1}, respectively. The oxidation peak potentials vs. saturated Ag/AgCl electrode are the following: +1.54 ± 0.01 V for naphthalene, +1.61 ± 0.01 V for fluorene and +1.21 ± 0.01 V for anthracene. The adsorptive accumulation using the carbon paste electrode decreases the detection limit of anthracene to 0.2 μmol l^{-1}. Very close oxidation peak potentials of naphthalene and fluorene do not allow the simultaneous determination of all three analytes. However, due to its high volatility naphthalene can be removed quantitatively during the process of the evaporation of hexane extract. The results of the determination of anthracene and fluorene in spiked environmental samples are presented.

Key words: voltammetry, anthracene, fluorene, naphthalene, organic solvent-water

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the components of crude oil, coal and wood tar, creosotes and are formed during the incomplete combustion of almost any organic material [1]. Several hundred of different PAHs are emitted by natural and anthropogenic sources to the environment where they undergo various chemical and microbiological transformations. PAHs and their numerous derivatives are of great environmental concern because of their ubiquitous distribution in the environment and well-known toxic, mutagenic and carcinogenic properties [2]. In the 1970s, US Environmental Protection Agency included sixteen individual polycyclic aromatic hydrocarbons (16 PAH) in the general list of priority pollutants on the basis that they are more harmful than other PAHs and there is a greater possibility of people being exposed to them [3]. The list of 16 PAH includes the aromatic hydrocarbons containing from two to six condensed rings, however, PAHs with 2–3 rings dominate in the emissions to the atmosphere. For example, according to the UK National Atmospheric Emissions Inventory for 2005 the emissions of 16 PAH were comprised of 73% naphthalene and 20% three-ring PAHs [4]. Although, generally the 5–6 ring PAHs are more toxic, the 2–3 ring PAHs are of similar environmental importance due to their higher emissions and better volatility and solubility in water.

The advantages of the chromatographic analysis in the determination of PAHs are unquestionable, however, the low cost voltammetric techniques can be also successfully used for the determination of the electroactive PAHs derivatives if they are relatively soluble in the aqueous media [5, 6]. The aim of this work was to develop a simple and re-

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liable voltammetric method for the determination of sparingly soluble in water naphthalene, fluorene and anthracene by their anodic oxidation using the mixed water-organic solvent media.

EXPERIMENTAL

The voltammetric measurements were performed using a polarograph PU-1 in a square wave voltammetry mode (amplitude 100 mV, frequency 25 Hz, scan rate 100 mV s^{-1}) with an x–y recorder N307/1 (all ZIP, Russia) or computerized equipment for registration of the voltammograms.

Glassy carbon (GCE) and carbon paste (CPE) electrodes were used as the working electrodes. The glassy carbon electrode was F 3500 (Radiometer, Denmark). Its surface was thoroughly polished by 3 μm diamond paste and then re-polished by 0.05 μm alumina slurry before each run. The carbon paste electrode was a Teflon tube with a 2 mm hole filled by carbon paste with a contact through the threaded stainless steel piston. The carbon paste was prepared by thorough mixing of 250 mg of carbon powder with 100 μl of paraffin oil Uvasol (Merck). The carbon powder used was the mixture of 200 mg of spherical glassy carbon particles of 0.4–12 μm diameter type 2 (Alfa Aesar, Ward Hill, MA, USA) and 50 mg of graphite powder Acheson 38 (Fisher, USA).

A saturated Ag/AgCl electrode and a platinum wire were used as reference and auxiliary electrodes, respectively. The volume of the solution in the cell was 20 ml.

Naphthalene, fluorene, anthracene and organic solvents were obtained from Aldrich.

The stock solutions of 2 mmol l^{-1} of anthracene, and 10 mmol l^{-1} of naphthalene or fluorene were prepared by dissolving precisely weighed amounts of the substances in methanol. Working solutions of lower concentrations were prepared by further dilution of the stock solutions with aqueous media. The Britton-Robinson buffers were prepared from a mixture of H$_3$BO$_3$, H$_3$PO$_4$ and CH$_3$COOH solutions at 0.04 mol l^{-1} concentration each by adding 0.2 mol l^{-1} solution of NaOH to the desired pH. The salts and acids used to prepare the aqueous media were of analytical grade (Reachim, Russia). The distilled water was used throughout the experiments.

RESULTS AND DISCUSSION

The water solubilities of naphthalene, fluorene and anthracene at 25 °C are very low: $2.4 \cdot 10^{-4}$, $1.1 \cdot 10^{-5}$ and $2.5 \cdot 10^{-7}$ mol l^{-1}, respectively [7]. Although these hydrocarbons can be electrochemically oxidized at the carbonaceous electrodes, such water solubilities do not allow their voltammetric determination. Therefore, the mixtures of aqueous solutions and organic solvents were investigated as the possible determination media. The organic solutions used for this purpose cannot be electroactive in the poten-

tial range of interest, should be miscible well with water solutions and, of course, dissolve the organic analytes. Furthermore, to maintain the sufficient electrical conductivity of the mixed medium the proportion of the organic solvent cannot be very high.

It has been found that after the addition of 20% (by volume) of methanol to the aqueous media, well-defined naphthalene anodic oxidation peaks can be obtained at the glassy carbon electrode for naphthalene concentrations up to 1 mmol l^{-1}. Using the lower content of methanol in the methanol / water mixture, the oxidation peaks are less reproducible while the higher content decreases the conductivity of the solution.

Preliminary experiments have shown that in comparison with naphthalene the solubilities of fluorene and athracene in 20% methanol / water mixture are about ten and hundred times lower, respectively. Moreover, the anodic oxidation peaks of fluorene and anthracene in methanol / water mixture are of an irregular shape and poorly reproducible. However, the substitution of methanol by acetonitrile increased the solubilities of the analytes substantially and allowed to obtain well-defined oxidation peaks. Thus, the 25% acetonitrile / water mixture is a suitable medium for the determination of the concentrations of fluorene and anthracene up to 0.5 mmol l^{-1} and 9 μmol l^{-1}, respectively. The range of anthracene concentrations can be expanded up to 0.7 mmol l^{-1} if the content of acetonitrile is increased to 50%.

It should be noted that possibly the oxidation of acetonitrile occurs in some extent at positive potentials and this negatively influences the shape of background voltammogram – it is important especially when the heights of small oxidation peaks of analytes are evaluated. Therefore, the methanol / water mixture is preferable for the determination of naphthalene.

The typical voltammograms with oxidation peaks of the analytes using the media consisting of 0.1 mol l^{-1} H$_2$SO$_4$ in water and organic solvent are shown in Fig. 1. The oxidation peak potentials vs. saturated Ag/AgCl electrode under the conditions of Fig. 1 are the following: +1.54 ± 0.01 V for naphthalene, +1.61 ± 0.01 V for fluorene and +1.21 ± 0.01 V for anthracene.

Various compositions of the aqueous component have been tested to choose the optimal mixed solvent. It has been found that the oxidation peaks obtained using Britton-Robinson buffers in the pH range 1–10 were 1.5–2 times lower than using 0.1 mol l^{-1} H$_2$SO$_4$ solution. Only slight dependence of the oxidation peaks on the acid concentration has been noted, therefore the 0.1 mol l^{-1} H$_2$SO$_4$ solution has been chosen as the best aqueous component.

To enhance the sensitivity of determination, the adsorptive accumulation at the carbon paste electrode was investigated. Since the oxidation potentials of anthracene, fluorene and naphthalene are quite positive, the carbon paste prepared from the mixture of glassy carbon powder (80%) and graphite powder (20%) was applied [8]. The adsorptive accumulation
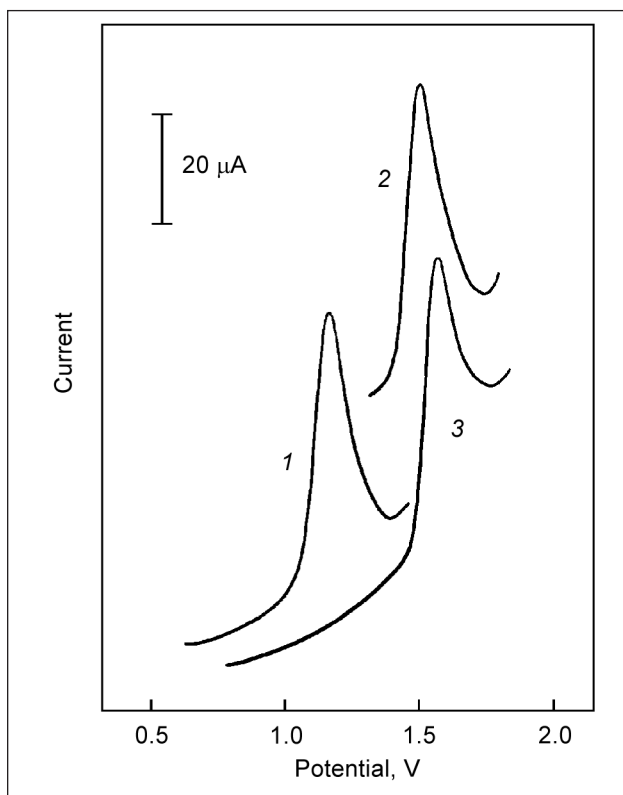
Fig. 1. Voltammograms of the oxidation of anthracene, naphthalene and fluorene at GCE. *1* – 0.2 mmol l⁻¹ anthracene, *2* – 0.2 mmol l⁻¹ naphthalene, *3* – 0.1 mmol l⁻¹ fluorene. Conditions: 0.1 mol l⁻¹ H_2SO_4 with 50 and 25% of CH_3CN for anthracene and fluorene, respectively, and 20% of CH_3OH for naphthalene

Fig. 2. Influence of adsorptive accumulation time on analytical signals using the carbon paste electrode. *1* – 0.04 mmol l⁻¹ anthracene, *2* – 0.2 mmol l⁻¹ naphthalene, *3* – 0.2 mmol l⁻¹ fluorene. Conditions: as in Fig. 1

was performed at room temperature and with intensive stirring of the solution by a magnetic stirrer. The effect of the adsorptive accumulation on analytical signals is shown in Fig. 2. It is clearly seen that the analytical signals depend on the accumulation time – e. g., after 12 min of accumulation the anthracene, fluorene and naphthalene oxidation peaks increase 13, 8 and 21 times, respectively. The accumulation potential has only a slight influence on the analytical signals in the potential range 0–1.0 V tested what confirms the chemical nature of interaction between adsorbates and the surface. The open-circuit potential about +0.5 V vs. saturated Ag/AgCl has been chosen for the convenience in the experiments with the adsorptive accumulation of the analytes at CPE.

The dependencies of the oxidation peak heights on the concentrations up to 100 μmol l⁻¹ (or 10 μmol l⁻¹ for anthracene) using both GCE and CPE electrodes are very close to linear (correlation coefficients 0.993–0.997) without significant intercepts on x- or y-axis. Due to the low solubility
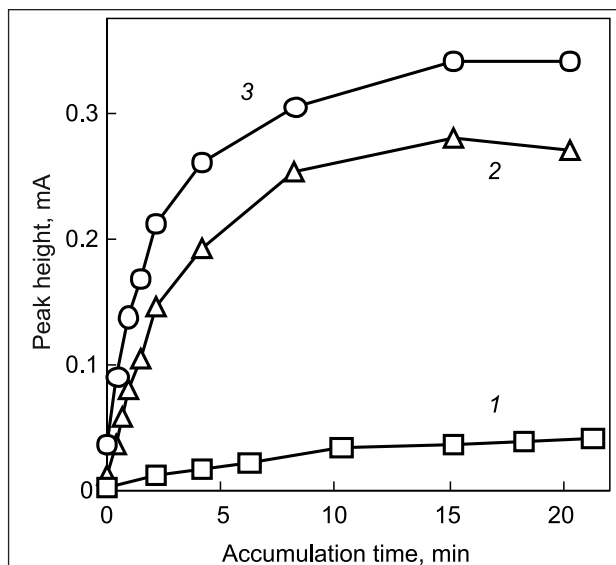
of the analytes the deviations from the linearity become significant at higher concentrations. The concentration ranges tested and the slopes of the calibration lines are shown in Table 1. It can be seen from the values of the slopes that the oxidation currents using the CPE in spite of their lower geometric surface area are 4–9 times higher than at GCE. However, the background currents at the carbon paste electrodes are also very high and this high sensitivity is only apparent. Therefore, from the analytical point of view CPE have advantages against GCE only in the case of much easier oxidizable anthracene.

The detection limits were estimated by performing the repetitive measurements at the lowest concentrations of the analytes for glassy carbon and carbon paste electrodes. The results of the measurements are presented in Table 2. The low detection limit for anthracene can be explained by its more negative potential of the oxidation and location of the oxidation peaks on the background voltammogram. As a result, the evaluation of the peak height is easier and more precise. Moreover, using the adsorptive accumulation at CPE, the detection limit for anthracene can be reduced substantially. The detection limits for fluorene and naphthalene are almost the same using the accumulation at CPE or direct anodic oxidation at GCE. Therefore, in order to reduce the total duration of determination in this case the GCE electrode is recommended.

Table 1. **Concentration ranges and slopes of the calibration lines for anthracene, fluorene and naphthalene**

Analyte	Concentration range, μmol l⁻¹	Slope of the calibration line, μA (μmol l⁻¹)⁻¹	
		CPE (accumulation time)	GCE
Anthracene	0.5–10	1.5 (12 min)	0.36
Fluorene	10–100	2.4 (8 min)	0.36
Naphthalene	20–100	1.5 (8 min)	0.17

Table 2. Reproducibility of the analytical signals of anthracene, fluorene and naphthalene and their detection limits

| Analyte | Electrode (accumulation time) | Concentration, µmol l⁻¹ | Statistical parameter | | Detection limit, µmol l⁻¹ |
			n	RSD	
Anthracene	GCE	2	8	0.14	1.2
	CPE (12 min)	0.5	4	0.13	0.2
Fluorene	GCE	10	10	0.15	6.4
	CPE (8 min)	10	8	0.10	6.2
Naphthalene	GCE	20	10	0.18	12
	CPE (8 min)	20	9	0.14	14

The extensive study of the simultaneous determination of all three analytes has been carried out. It has been shown that simultaneous determination is possible only in the case of anthracene and fluorene or anthracene and naphthalene. The difference between the potentials of oxidation of fluorene and naphthalene is only 70 mV and such measures as changing of voltammetric parameters and media composition or addition of metal ions to form molecular complexes with the analytes did not allow separating the analytical peaks. Also, all three analytes appeared to be sensitive to photochemical oxidation by UV radiation, and this fact excluded the possibility to remove one of the interfering components.

However, it has been found that naphthalene can be removed from the mixture employing its high volatility in comparison with fluorene and anthracene. The saturated vapour pressures at 25 °C for naphthalene, fluorene and anthracene are 10.4 Pa, 0.09 Pa and 0.001 Pa, respectively [7], therefore the process of evaporation of hexane extracts of all three analytes was investigated. It has been shown that during the evaporation of the extracts at room temperature the naphthalene evaporates quantitatively together with the solvent, whereas recovery of fluorene after such procedure is 94–98%. No loses of anthracene have been detected during evaporation. Consequently, the procedure of extraction / evaporation with further dissolving of the analytes in the mixed water-organic solvent medium enable to determine fluorene in the presence of naphthalene.

The voltammetric determination of anthracene and fluorene has been tested using environmental matrices – sand, soil and bottom sediments. The dry weighted samples of about 3 g mass were extracted by 30 ml of hexane, and then 10 ml of the extract was evaporated using heated water bath directly in the beaker of the electrochemical cell. After the
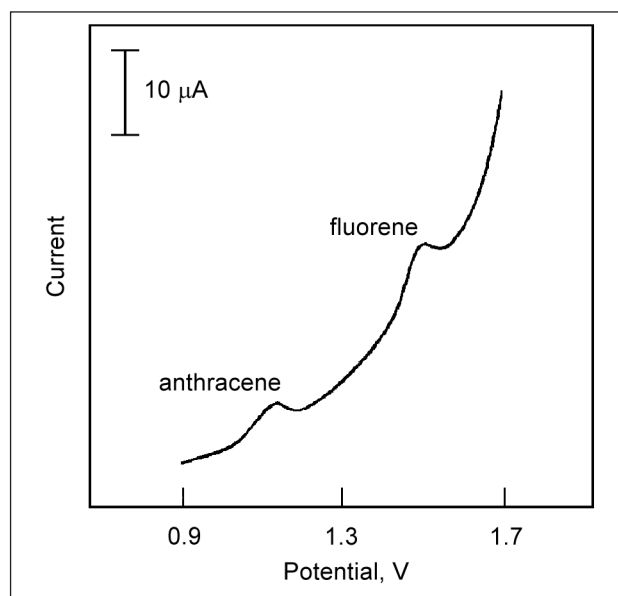

Fig. 3. Voltammogram of the oxidation of anthracene and fluorene from the hexane extract of spiked bottom sediment. Conditions: 0.2 µmol of anthracene and fluorene added to 1 g of dry sediment; medium – 0.1 mol l⁻¹ H_2SO_4 with 25% of CH_3CN; GCE

addition of 0.1 mol l⁻¹ H_2SO_4 and acetonitrile mixed medium, the determination of anthracene and fluorene by the standard additions method has been carried out. Since no analytical signals of the analytes were detected, the solid samples before the extraction were spiked by anthracene and fluorene. The voltammogram of a spiked sample of bottom sediments is shown in Fig. 3. The results of anthracene and fluorene determinations are presented in Table 3. It can be seen that the

Table 3. Determination of anthracene and fluorene in spiked environmental matrices after extraction with hexane

| Sample | Anthracene | | Fluorene | |
	Spiked / determined, µmol g⁻¹	Recovery, %	Spiked / determined, µmol g⁻¹	Recovery, %
Sand from sand quarry	–	–	0.50/0.47	94
Soil from suburban garden	0.50/0.49	98	0.50/0.47	94
	0.20/0.18	90	0.20/0.17	85
Urban soil (yard of the Faculty of Chemistry)	0.50/0.49	98	0.50/0.47	94
Bottom sediments (Venta River in Western Lithuania)	0.20/0.19	95	0.20/0.16	80

recoveries are generally higher for anthracene, and this can be explained by its lower volatility in comparison with fluorene. Also, there are no indications that such a complex matrix as soil influences the results of the determinations.

CONCLUSIONS

Consequently, the employment of mixed water-organic solvent media allows the voltammetric determination of sparingly soluble in water compounds – naphthalene, fluorene and anthracene at 10^{-6}–10^{-5} mol l^{-1} concentration range. The problem of the mutual naphthalene / fluorene interference due to their close oxidation potentials can be partially solved by quantitative removal of volatile naphthalene during the evaporation of hexane extracts of the analytes.

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VOLTAMPEROMETRINIS NAFTALENO, FLUORENO IR ANTRACENO NUSTATYMAS NAUDOJANT MIŠRIĄ VANDENS IR ORGANINIO TIRPIKLIO TERPĘ

S a n t r a u k a

Straipsnyje aprašytas voltamperometrinis metodas naftalenui, fluorenui ir antracenui nustatyti anodiškai oksiduojant juos ant stikliškosios anglies arba anglies pastos elektrodo paviršiaus mišrioje vandens ir organinio tirpiklio terpėje. Mišrios terpės sudėtis: 0,1 mol l^{-1} H_2SO_4 ir 20 % (tūrio) metanolio naftalenui arba 25 % acetonitrilo fluorenui ir antracenui. Naftaleno, fluoreno ir antraceno aptikimo ribos naudojant stikliškąją anglį yra atitinkamai 12, 6,4 ir 1,2 μmol l^{-1}. Oksidacijos smailių potencialai sočiojo Ag/AgCl elektrodo atžvilgiu yra +1,54 ± 0,01 V naftalenui, +1,61 ± 0,01 V fluorenui ir +1,21 ± 0,01 V antracenui. Naudojant adsorbcinį kaupimą ant anglies pastos elektrodo antraceno aptikimo riba gali būti sumažinta iki 0,2 μmol l^{-1}. Dėl labai artimų naftaleno ir fluoreno oksidacijos smailių potencialų neįmanoma vienu metu nustatyti visų trijų analičių. Tačiau didelis naftaleno lakumas leidžia jį kiekybiškai pašalinti iš analičių mišinio garinant jų ekstraktą heksane. Pateikiami antraceno ir fluoreno nustatymo aplinkos objektuose rezultatai.