POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF TRACE AMOUNTS OF 3-NITROFLUORANTHENE

Karel Čížek[1], Jiří Barek[2,*] and Jiří Zima[3]

UNESCO Laboratory of Environmental Electrochemistry, Department of Analytical Chemistry, Charles University, 128 43 Prague 2, Czech Republic; e-mail: [1] karel.cizek@email.cz, [2] barek@natur.cuni.cz, [3] zima@natur.cuni.cz

Received August 3, 2006
Accepted September 26, 2006

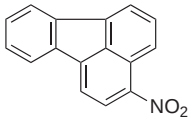
The polarographic behavior of 3-nitrofluoranthene was investigated by DC tast polarography (DCTP) and differential pulse polarography (DPP), both at a dropping mercury electrode, differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV), both at a hanging mercury drop electrode. Optimum conditions have been found for its determination by the given methods in the concentration ranges of 1×10^{-6}–1×10^{-4} mol l^{-1} (DCTP), 1×10^{-7}–1×10^{-4} mol l^{-1} (DPP), 1×10^{-8}–1×10^{-6} mol l^{-1} (DPV) and 1×10^{-9}–1×10^{-7} mol l^{-1} (AdSV), respectively. Practical applicability of these techniques was demonstrated on the determination of 3-nitrofluoranthene in drinking and river water after its preliminary separation and preconcentration using liquid–liquid and solid phase extraction with the limits of determination 4×10^{-10} mol l^{-1} (drinking water) and 2×10^{-9} mol l^{-1} (river water).

Keywords: DC tast polarography; Differential pulse voltammetry; Adsorptive stripping voltammetry; Nitro compounds; Solid phase extraction; Water; Electrochemistry.

Nitrated polycyclic aromatic hydrocarbons (NPAH) rank among the substances whose occurrence in the environment can be causally associated with an increased cancer rate[1]. The interest in them increased in 1978 when Jäger[2] and Pitts et al.[3] independently found out that polycyclic aromatic hydrocarbons (PAH) might react with nitrogen oxides to form NPAH under conditions that can be expected in polluted atmosphere and/or in combustion processes[4]. A higher occurrence of NPAH was proved in urban areas compared to rural areas[5]. Nevertheless, the transport of NPAH in vapour phase or bound to atmospheric particles has an impact in remote areas such as Antarctica[6]. 3-Nitrofluoranthene (3-NF) as a typical representative of this class of compounds was found especially in diesel and petrol exhausts, in ambient and urban air, in products of coal combustion, fly ash, river and wastewater[7]. 3-NF is generated during incinerating processes which is in contrast to 2-nitrofluoranthene formed mainly by atmospheric

doi:10.1135/cccc20061571

reactions[8]. Low accumulation of NPAH in water is expected due to its low aqueous solubility. However, strong adsorption of these compounds in the organic fractions of soil and sediments can be a source of water pollution[9]. The solubility of NPAH in water is estimated in the range 0.01–10 mg l^{-1} and for 3-NF a value of 0.0195 mg l^{-1} was found[10].



So far, mostly chromatographic methods have been used for the determination of NPAH. About one quarter of all chromatographic analysis employed for the determination of NPAH has been done by HPLC [11]. Most of the analyses have been performed in reversed-phase mode with octadecyl-modified silica as the stationary phase. The presence of a reducible nitro group in 3-NF enables the application of electrochemical detectors in thin-layer arrangement with gold amalgam electrode[4]. The fluorescent detector, a favourite one for detection of APAH, cannot be used for NPAH with sufficient sensitivity. The preliminary reduction of the nitro to amino group is required. Some examples of determination of 3-NF with on-line reduction have been described[4,12]. Current use of GC is combined with a MS detector in different modes[13,14], thermionic nitrogen-phosphorus detector (NPD)[15] and chemiluminescent detector (also known as TEA – thermal energy analyzer)[16,17]. Spectrophotometric methods are established as well, e.g. determination of 3-NF by Linder et al.[18]

The reduction mechanism of NPAH was studied earlier[19,20]. For the aromatic nitro compounds the reduction occurs in principle in two steps: A four-electron reduction of the nitro group to an arylhydroxylamine (*1*) followed in acid media by a two-electron reduction of a protonated form of the arylhydroxylamine, resulting in a formation of a amino derivative (*2*).

$$ArNO_2 + 5\ H^+ + 4\ e \rightarrow ArNHOH_2^+ + H_2O \qquad (1)$$

$$ArNHOH_2^+ + 2\ e + 2\ H^+ \rightarrow ArNH_3^+ + H_2O \qquad (2)$$

Modern electroanalytical methods can meet high demands on determination of NPAH due to their high sensitivity[21]. Nevertheless, the use of these methods for the determination of nitroarenes is not too frequent in spite of the easy reducibility of the nitro group and the fact that polarographic

and voltammetric methods are much cheaper as far as investment and operating costs are concerned. Moreover, the knowledge of reduction mechanism aids to understand metabolic transformation of these compounds[22]. In some cases, electrochemical behavior of NPAH can be correlated with their mutagenic effects[23,24].

The only determination of 3-NF by an electrochemical method was at a solid silver amalgam electrode in ref.[25] The results presented here are a part of a systematic study of NPAH determination by modern polarographic and voltammetric techniques. DC tast polarography, differential pulse polarography, differential pulse voltammetry and adsorptive stripping voltammetry were applied to the determination of 3-NF at mercury electrodes. Practical applicability of the newly developed methods in combination with solid phase or liquid–liquid extraction was verified using model samples of drinking and river water.

EXPERIMENTAL

Reagents

The stock solution of 3-nitrofluoranthene ($c = 1 \times 10^{-3}$ mol l^{-1}) was prepared by dissolving 0.0247 g of the substance (90% Sigma–Aldrich, Czech Republic) in 100 ml of methanol. More dilute solutions were prepared by exact dilution of the stock solution with methanol. All the solutions were stored in the dark. It followed from a spectrophotometric study of stability of the stock solution[26] that the methanolic solution is stable for at least 120 days. Methanol, sodium hydroxide, glacial acetic acid, boric acid, phosphoric acid, hexane, toluene and ethyl acetate were of analytical grade purity (Lachema, Brno, Czech Republic). Dichloromethane and ether (all p.a. purity) were supplied by Merck (Germany). Britton–Robinson (BR) buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 mol l^{-1} in phosphoric acid, 0.04 mol l^{-1} in acetic acid and 0.04 mol l^{-1} in boric acid with an appropriate amount of 0.2 M sodium hydroxide solution. Deionized water was produced by Milli-Q_{plus} system (Millipore, U.S.A.).

Apparatus

Measurements were carried out using a computer-driven Eco-Tribo Polarograph with PolarPro software, v. 2.0 (both Polaro Sensors, Prague, Czech Republic) in combination with a classical dropping mercury electrode (DME) or a hanging mercury drop electrode (HMDE) of the UMμE (Ultra-mini and micro-electrode) type (Polaro Sensors, Prague), a platinum wire auxiliary electrode and silver/silver chloride (1 M KCl) reference electrode (type RAE 113) (both Monokrystaly, Czech Republic), to which all the potential values are referred. The parameters of the classical DME used in DC tast polarography (DCTP) and differential pulse polarography (DPP) were as follows: mercury reservoir height h = 25 cm, the flow rate m = 4.25 mg s^{-1} and the drop time τ = 3.3 s (at an applied voltage of 0 V in 0.1 M KCl). Experiments with the DME were carried out at a polarization rate of 4 mV s^{-1}, controlled drop time of 1 s, and modulation amplitude in DPP of –50 mV. For differential pulse

voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) at HMDE, the maximum attainable drop size obtained by opening the valve for 300 ms, with a surface of 2.01 mm^2, a polarization rate of 20 mV s^{-1}, and the modulation amplitude –50 mV were used. Following devices were used: universal shaker type 327 (Premed, Poland) and vacuum evaporator Rotavapor R-114 equipped with a water bath B-480 (both Büchi, Switzerland), vacuum manifold (Burdick & Jackson, U.S.A.) and mini-shaker (Vortex, Germany). pH was measured using a conductivity and pH meter Jenway 4330 with a combined glass electrode (type 924 005) (all Jenway, U.K.). Spectrophotometric measurements were made with a diode array spectrophotometer HP 8453 (Hewlett–Packard) in silica cuvettes (optical path length 10 mm). Coulometric experiments using Autolab Potentiostat/Galvanostat PGSTAT30 with software GPES v. 4.8 (all Eco Chemie, Netherlands) were made in a 10-ml cell under argon atmosphere with mercury pool as cathode, platinum sheet as anode and saturated calomel electrode (SCE) as a reference electrode. Sintered glass was used to separate the cathodic and anodic compartments.

Procedures

The general procedure to obtain polarograms or voltammograms was as follows: the required amount of the stock solution of the test substance in methanol was placed in a 10-ml volumetric flask, an appropriate volume of methanol was added and the system was diluted with BR buffer of the required pH or with 0.01 M NaOH. Oxygen was removed from the measured solutions by bubbling with nitrogen for 5 min. A prebubbler containing a water–methanol mixture in the same ratio as in the polarographed solution was placed prior to the polarographic vessel. The calibration curves were measured in triplicate and their statistical parameters (e.g., slope, intercept, limit of determination) were calculated according to Oppenhelmer[27], Schwartz[28] and Ebel[29] using statistic software Adstat v. 2.0 (Trilobyte, Czech Republic).

For the determination of 3-NF in drinking and river water samples after liquid–liquid extraction (LLE) with hexane, the procedure was as follows: A model sample of drinking or river water containing an appropriate amount of added 3-NF was extracted with 2 or 5 ml of hexane, the organic phase was evaporated to dryness using a rotating vacuum evaporator, the residue was dissolved in 9 ml of methanol with sonication, 1 ml of BR buffer pH 3 was added and a DP voltammogram was recorded. The procedure for voltammetric determination of 3-NF in drinking or river water after solid phase extraction (SPE) was as follows: an SPE column LiChrolut® RP-18e (catalog number L989050, Merck, Germany), which is filled with 500 mg of RP-18 phases bonded to silica gel, was connected to a suction pump and activated by washing with 3 ml of ether and 3 ml of deionized water. Afterwards, the sample of drinking or river water spiked with different amounts of 3-NF was sucked through the column. Adsorbed 3-NF was then eluted with 2 × 3 ml of ether, the solvent was evaporated to dryness using a rotating vacuum evaporator and final procedure was the same as mentioned above. The river water used for extraction was taken from the Rokytka creek 400 m before its estuary to the Vltava river in Prague.

RESULTS AND DISCUSSION

Tast Polarography and Differential Pulse Polarography at DME

The influence of pH on DC tast polarograms of 3-NF was investigated in a mixed methanol–BR buffer (9:1) medium with resulting pH from 4.0 to 11.7. The high percentage of methanol in a measured solution was due to limited solubility of 3-NF in water[26]. The obtained half-wave potentials ($E_{1/2}$) and limiting currents (I_{lim}) in dependence on pH are given in Table I and selected polarograms are depicted in Fig. 1. Under these conditions the tast polarogram exhibits a single, well developed irreversible wave in the whole investigated pH range. This wave corresponds to the reduction of 3-NF to 3-(hydroxyamino)fluoranthene. The half-wave potential of this first wave varies with pH in the range 5.1–10.4 according to the relationship $E_{1/2}$ (V) = –0.070 pH + 0.057 (R = 0.9886). Moreover, a more negative second wave is observed, the nature of which changes with pH. At pH 4.0–7.0, a much lower, poorly developed irreversible wave is observed, the $E_{1/2}$ of which shifts to more negative potentials with increasing pH. At pH 8.3–11.7 another wave at a more negative potential can be seen. Neither its

TABLE I
The effect of pH on tast polarograms of 3-NF (c = 1 × 10^{-4} mol l^{-1}) at DME in mixed methanol– BR buffer (9:1)

pH[a]	pH[b]	$E_{1/2}{}^1$, mV	$-I_{lim}{}^1$, nA	$E_{1/2}{}^2$, mV	$-I_{lim}{}^2$, nA
2.0	4.0	–300	2159	–784	1084
3.0	5.1	–323	2056	–824	812
4.0	6.0	–358	2065	–917	1202
5.0	7.0	–417	2029	–1019	1019
6.0	8.3	–496	2186	–1640	844
7.0	8.9	–538	2054	–1654	888
8.0	9.5	–623	2088	–1630	850
9.0	9.6	–637	2106	–1616	930
10.0	10.2	–660	2151	–1639	932
11.0	10.4	–665	2106	–1635	865
12.0	11.7	–679	2042	–1630	809

[a] pH of BR buffer; [b] resulting pH of methanol–BR buffer (9:1) medium; [1] first wave, [2] second wave.

$E_{1/2}$ nor I_{lim} is dependent on pH. Both waves obviously correspond to further reduction of 3-(hydroxyamino)fluoranthene to 3-aminofluoranthene. The phenomenon of reduction of nitroaromatics through hydroxyamino derivatives to amino analogs is well described in acid medium[19,20]. However, a similar behavior was also proved in alkaline medium for 3-NF in potentiostatic coulometry. The experiments were carried out in a mixture methanol–0.1 M NaOH (9:1). Applying a more negative potential (E_{app}), –1.9 V vs SCE, a six-electron reduction of 3-nitrofluoranthene to 3-aminofluoranthene was observed. At a less negative potential (–1.4 V vs SCE), only a four-electron reduction corresponding to the formation of 3-(hydroxyamino)fluoranthene was proved. In acid medium of methanol–BR buffer pH 3 (9:1), at –1 V vs SCE, a six-electron reduction of 3-NF was observed as well. Products of constant potential coulometric reductions were monitored by spectrophotometry (Fig. 2). The figure depicts the spectra of 3-NF, 3-AF and their mixture along with the spectra obtained after coulometric experiments with 3-NF in alkaline media. The similarity of the 3-NF spectrum after its potentiostatic reduction at –1.9 V vs SCE to that of 3-NF and 3-AF standard mixture proved the formation of 3-AF. Moreover, the numbers of exchanged electrons in the reduction of 3-NF are in agree-

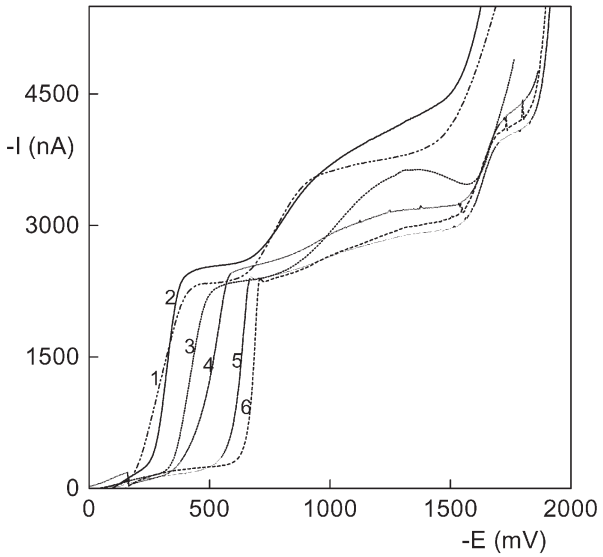


FIG. 1
Selected DC tast polarograms of 3-NF ($c = 1 \times 10^{-4}$ mol l^{-1}) in a methanol–BR buffer (9:1) mixture; resulting pH: 4.0 (*1*), 5.1 (*2*), 7.0 (*3*), 8.3 (*4*), 9.5 (*5*) and 11.7 (*6*)

ment with the first- and second-wave limiting current ratio (I_{lim}^1/I_{lim}^2 = 2:1) measured by DCTP (see Table I). The second wave is not suited for analytical purposes because it is low and poorly developed. The highest and best developed first waves were obtained in mixed media of methanol–BR buffer pH 3.0 and 12.0 (9:1) (pH of the mixture 5.1 and 11.7, respectively), where calibration dependences were measured. The height of the first wave is a linear function of 3-NF concentration within the concentration range of 3×10^{-6}–1×10^{-4} mol l^{-1} (Table II). However, the limit of determination (LOD ~ 3×10^{-6} mol l^{-1}) is not sufficient for environmental applications (see Table II).

The electrochemical behavior of 3-nitrofluoranthene using DPP at DME was studied under the same conditions as above. It reflects its behavior in DC tast polarography. 3-NF gives a well developed peak in the pH range 4.0–11.7, which shifts towards more negative potentials with increasing pH. At pH 4.0–7.0, a second, much lower and poorly developed peak appears which shifts to more negative potentials with increasing pH as well. At pH 8.3–11.7, another more negative peak is observed with a roughly constant peak potential and peak current. The best developed and most easily evaluated peaks of 3-NF were again obtained in mixed medium of methanol–BR buffer pH 3.0 and 12.0 (9:1). The height of the peak was measured from the straight line connecting the minima before and after

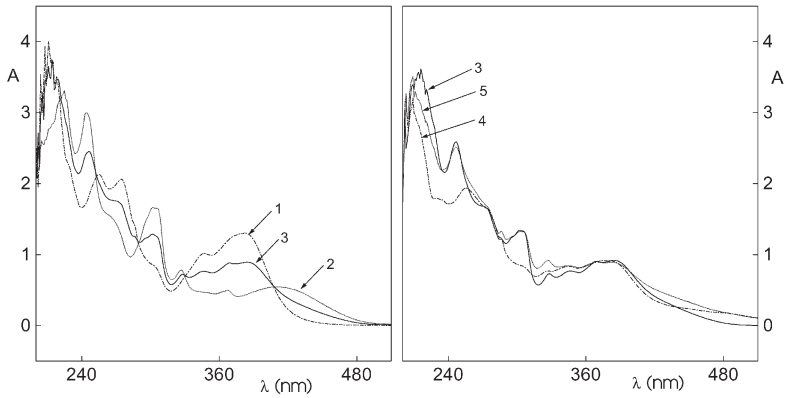


FIG. 2

UV-VIS spectra of 3-NF and 3-AF in methanol–0.1 M NaOH (9:1): 3-NF ($c = 1 \times 10^{-4}$ mol l^{-1}) (*1*), 3-AF ($c = 1 \times 10^{-4}$ mol l^{-1}) (*2*), 3-NF and 3-AF (each $c = 5 \times 10^{-5}$ mol l^{-1}) (*3*), 3-NF ($c = 1 \times 10^{-4}$ mol l^{-1}) after 10 min of constant potential coulometry at applied potential –1.4 V vs SCE (passed charge 261 mC) (*4*), 3-NF ($c = 1 \times 10^{-4}$ mol l^{-1}) after 6 min of constant potential coulometry at applied potential –1.9 V vs SCE (passed charge 389 mC) (*5*)

the peak. The calibration curves are linear within the concentration range of 1×10^{-7}–1×10^{-5} mol l^{-1} and their parameters are given in Table II. The calibration dependence for concentrations of (2–10) $\times 10^{-5}$ mol l^{-1} was not linear and thus is not included in Table II.

Differential Pulse Voltammetry at HMDE

As in the previous case, the substance gives two peaks (Fig. 3 and Table III) and the behavior of 3-NF at the electrode was similar to that of DPP at DME. The highest and well developed peaks were obtained in mixtures of methanol–BR buffer pH 3.0 and 12.0 (9:1) with resulting pH 5.2 and 11.4.

TABLE II
Optimum conditions and parameters of the calibration straight lines for the polarographic and voltammetric determination of 3-NF

Technique/ Electrode	pH[a]	*c*(3-NF) μmol l^{-1}	Slope A l mol^{-1}	Intercept nA	Correlation coefficient	LOD[b] μmol l^{-1}
DCTP/DME[c]	3.0	20–100	0.0200	145.2	0.9995	–
DCTP/DME[c]	3.0	1–10	0.0254	10.1	0.9971	3
DCTP/DME[c]	12.0	20–100	0.0212	40.0	0.9997	–
DCTP/DME[c]	12.0	1–10	0.0192	–1.2	0.9953	5
DPP/DME[c]	3.0	2–10	0.0448	26.8	0.9999	–
DPP/DME[c]	3.0	0.1–1	0.0463	8.6	0.9985	0.1
DPP/DME[c]	12.0	2–10	0.0505	–22.1	0.9953	–
DPP/DME[c]	12.0	0.1–1	0.0460	–2.2	0.9972	0.4
DPV/HDME[c]	3.0	0.2–1	0.0862	0.2	0.9998	–
DPV/HDME[c]	3.0	0.01–0.1	0.0793	0.1	0.9985	0.03
DPV/HDME[c]	3.0	0.2–1	0.0844	–0.9	0.9988	–
DPV/HDME[c]	12.0	0.02–0.1	0.0721	0.2	0.9976	0.03
DPV/HDME[d]	12.0	0.02–0.1	0.0445	0.1	0.9975	0.03
AdSV/HDME[e]	12.0	0.02–0.1	2.02	–5.9	0.9984	0.02
AdSV/HDME[f]	12.0	0.02–0.1	1.16	0.8	0.9990	0.02
AdSV/HDME[g]	12.0	0.002–0.01	4.79	0.2	0.9948	0.005

[a] pH of the BR buffer or sodium hydroxide solution; [b] limit of determination; [c] methanol–BR buffer (9:1); [d] methanol–0.01 M NaOH (9:1); [e] methanol–BR buffer (1:1), E_{acc} = –200 mV, t_{acc} = 500 s; [f] methanol–0.01 M NaOH (1:1), E_{acc} = –200 mV, t_{acc} = 500 s; [g] methanol–0.01 M NaOH (1:9), E_{acc} = –200 mV, t_{acc} = 1200 s.

TABLE III
The effect of pH on DP voltammograms of 3-NF (c = 1 × 10^{-4} mol l^{-1}) at HMDE in mixed methanol–BR buffer (9:1)

pH[a]	pH[b]	E_p^1, mV	$-I_p^1$, nA	E_p^2, mV	$-I_p^2$, nA
2.0	3.9	–241	579	–617	273
3.0	5.2	–271	1228	–742	201
4.0	6.0	–312	1278	–808	187
5.0	6.9	–373	1125	–956	115
6.0	8.0	–493	1256	–1572	233
7.0	8.9	–529	1567	–1564	266
8.0	9.3	–542	1733	–1560	273
9.0	9.6	–555	1824	–1564	288
10.0	10.0	–584	1779	–1568	302
11.0	10.5	–601	1962	–1568	312
12.0	11.4	–610	2270	–1560	303

[a] pH of BR buffer; [b] resulting pH of methanol–BR buffer (9:1) medium; [1] first peak, [2] second peak.

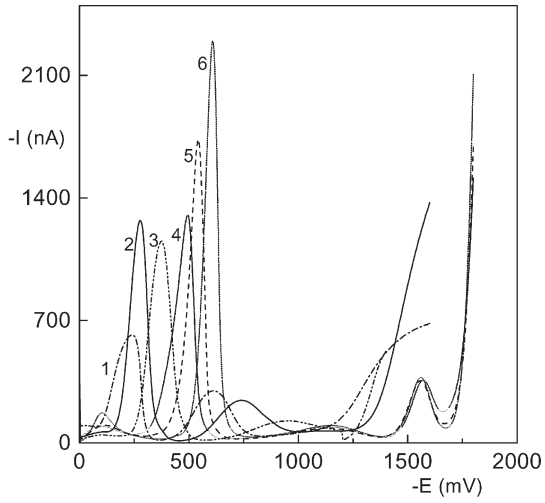


FIG. 3
Selected DP voltammograms of 3-NF (c = 1 × 10^{-4} mol l^{-1}) in a methanol–BR buffer (9:1) mixture; resulting pH: 3.9 (*1*), 5.2 (*2*), 6.9 (*3*), 8.0 (*4*), 9.3 (*5*) and 11.4 (*6*)

0.01 M NaOH was also used instead of BR buffer pH 12 to decrease the content of potential impurities in the supporting electrolyte in measurements of calibration curves. The calibration curves were measured in the range 1×10^{-8}–1×10^{-5} mol l^{-1} of 3-NF but the calibration dependence deviates from the linear course at higher concentrations ($(1–10) \times 10^{-6}$ mol l^{-1}). The height of the first peak (I_p^1) was evaluated; the concentrations lower than 1×10^{-8} mol l^{-1} were not detectable. The straight line parameters of the calibration dependences are summarized in Table II.

Adsorptive Stripping Voltammetry at HMDE

To lower the limit of detection obtained by DP voltammetry, we carried out the adsorptive accumulation of 3-NF on the electrode surface. With respect to previous results of DPV, BR buffer pH 12 and/or 0.01 M NaOH were selected as aqueous parts of the base electrolyte. First, we examined the methanol content because its presence in the supporting electrolyte can have a negative effect on the accumulation. With decreasing content of methanol, the height of the 3-NF first peak increased in dependence on accumulation time (t_{acc}) (Fig. 4). Afterwards, the influence of the accumulation potential (E_{acc}) on the peak height was investigated in methanol–BR buffer pH 12

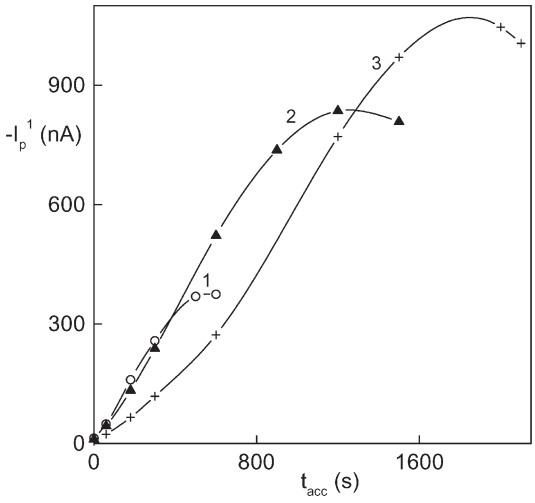


FIG. 4

The dependence of the height of the first peak of 3-NF ($c = 2 \times 10^{-7}$ mol l^{-1}) on accumulation time t_{acc} for E_{acc} = –200 mV in methanol–BR buffer pH 12 mixture, measured by AdSV at HMDE in the ratio: 1:1 (*1*), 1:9 (*2*) and 1:99 (*3*)

(1:1) with t_{acc} = 60 s. No significant influence was observed; however, the best developed and reproducible peaks were obtained at E_{acc} = –200 mV. Therefore, the determination of 3-NF in concentrations (2–10) × 10^{-8} mol l^{-1} was carried out in methanol–BR buffer pH 12 and methanol–0.01 M NaOH (1:1) mixtures with E_{acc} = –200 mV and t_{acc} = 500 s. For even lower concentrations, the calibration curves in the concentration range (1–10) × 10^{-9} mol l^{-1} were measured in a methanol–0.01 M NaOH (1:9) mixture with E_{acc} = –200 mV and t_{acc} = 1200 s (Fig. 5). The parameters of concentration dependences are given in Table II.

Practical Applications

For the determination of 3-NF in samples of drinking and river water, DPV at HMDE with the supporting electrolyte MeOH–BR buffer pH 3 (9:1) was chosen, because it is sufficiently sensitive to the analyzed compound, fast and the adsorption of impurities contained in matrix does not influence the determination as in the case of AdSV.

First, the possibility of separation and preconcentration of 3-NF from a model sample of deionized water by liquid–liquid extraction with hexane was investigated. The recovery was calculated for the highest concentration

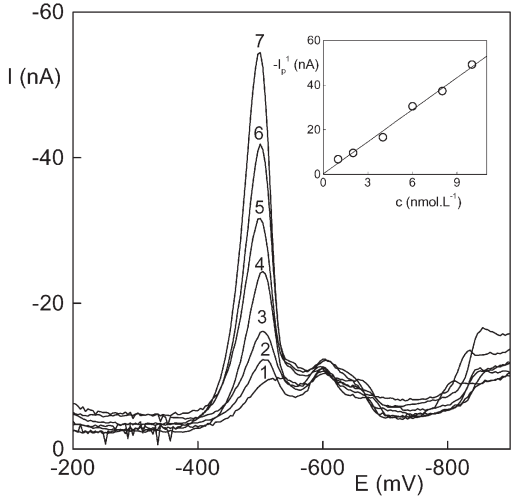


FIG. 5
AdS voltamograms of 3-NF in methanol–0.01 M NaOH (1:9) medium, measured by AdSV at HMDE for t_{acc} = 1200 s and E_{acc} = –200 mV; c(3-NF) in nmol l^{-1}: 0 (*1*), 1 (*2*), 2 (*3*), 4 (*4*), 6 (*5*), 8 (*6*) and 10 (*7*). The corresponding calibration straight line is in the inset

of 3-NF of the given concentration range from the ratio I_p/I_p^o, where I_p is the peak height of 3-NF after extraction with hexane and I_p^o is the peak height of 3-NF in a reference solution prepared by an addition of standard solution of 3-NF to the blank solution. The recovery was found to be 75 and 97% for the extraction with 2 and 5 ml of hexane from 10 and 100 ml of water, respectively (Table IV). A model extraction was carried out to determine 3-NF in 10 ml of deionized water containing (2–10) × 10^{-8} mol l^{-1} of the analyte using 2 ml of hexane and in 100 ml of deionized water containing (2–10) × 10^{-9} mol l^{-1} of 3-NF using 5 ml of hexane. The parameters of the straight lines are given in Table V. It was also observed that increasing the volume of hexane used for extraction influences negatively the height of 3-NF peak. The obtained DPV peak of 3-NF was much lower when we used more than 20 ml of hexane for extraction. This can be explained by some surfactants presented in hexane. Calibration measurement of 3-NF

TABLE IV
The results of liquid–liquid extraction of 3-NF from deionized water, measured by DPV at HMDE in methanol–BR buffer pH 3 (9:1)

Solvent	V_{sample} ml	c(3-NF) 10^8 mol l^{-1}	Recovery %	RSD %
Hexane (2 ml)	10	10	74.9	9
Hexane (5 ml)	100	1	96.7	10

TABLE V
Parameters of calibration straight lines for the determination of 3-NF by DPV at HMDE in methanol–BR buffer pH 3 (9:1) after liquid–liquid extraction of 3-NF from water

c(3-NF)[a] nmol l^{-1}	Slope A l mol^{-1}	Intercept nA	Correlation coefficient	LOD nmol l^{-1}
20–100[b]	0.0445	–0.1	0.9981	40
2–10[c]	0.465	–0.8	0.9992	4
2–10[d]	0.466	–0.8	0.9963	4
20–100[c]	0.0280	0.0	0.9967	30

[a] Concentration of 3-NF in water; [b] extraction from 10 ml of deionized water with 2 ml of hexane; [c] extraction from 100 ml of deionized water with 5 ml of hexane; [d] extraction from 100 ml of drinking water with 5 ml of hexane; [e] extraction from 10 ml of river water with 2 ml of hexane.

in the range of (2–10) × 10^{-9} mol l^{-1} in drinking water was carried out under the conditions used for the same concentration range in deionized water. The parameters of the concentration dependence are summarized in Table V. The determination in river water was done only in the concentration range (2–10) × 10^{-8} mol l^{-1} (see Table V) because the present impurities interfered with the signal of 3-NF at lower concentrations.

To decrease LOD for the determination of 3-NF in river water, solid phase extraction was used for preliminary separation and preconcentration. First, we applied SPE on the spiked samples (1 × 10^{-7} M 3-NF) of deionized water (50 ml), using the procedure described in Experimental, to investigate the extraction recovery and repeatability. Six different elution agents were compared (Table VI). The best recovery 72% and the lowest relative standard deviation (RSD) 4% were found for ether. Thus calibration measurements for determination of 3-NF in deionized water as a model sample were carried

TABLE VI
The results of solid phase extraction of 3-NF (1 × 10^{-7} mol l^{-1}) from 50 ml of deionized water, measured by DPV at HMDE in methanol–BR buffer pH 3 (9:1)

Elution agent	Methanol	Ethyl acetate	CH_2Cl_2	Toluene	Ether
Recovery, %	42	54	60	65	72
RSD, %	10	6	9	10	4

TABLE VII
Parameters of calibration straight lines for the determination of 3-NF by DPV at HMDE in methanol–BR buffer pH 3 (9:1) after solid phase extraction

c(3-NF)[a] nmol l^{-1}	Slope A l mol^{-1}	Intercept nA	Correlation coefficient	LOD nmol l^{-1}
20–100[b]	0.124	–1.9	0.9972	20
2–10[c]	1.23	–1.4	0.9974	2
2–10[d]	1.18	–1.1	0.9925	2
2–10[e]	1.32	–1.1	0.9961	2
0.2–1[d]	7.01	–1.2	0.9956	0.4

[a] Concentration of 3-NF in water; [b] extraction from 50 ml of deionized water; [c] extraction from 500 ml of deionized water; [d] extraction from 500 ml of drinking water; [e] extraction from 500 ml of river water.

out using SPE with ether as an eluent. The parameters of the straight lines for two orders of magnitude of concentrations are summarized in Table VII. High intercepts of both straight lines led us to investigation of the recovery of 3-NF in dependence on its concentration in water. A DPV experiment was performed measuring five concentrations in the range (2–10) × 10^{-9} M 3-NF in 500 ml of deionized, drinking and river water after SPE (Fig. 6). It is clear that recovery decreases with decreasing 3-NF concentration in water, which could explain negative intercepts observed in all calibration dependences gained after SPE from water. Nevertheless, a calibration measurement for (2–10) × 10^{-9} M 3-NF was carried out in drinking water. The parameters of the straight line are given in Table VII. LOD was found to be 2 × 10^{-9} mol l^{-1}. Measurements at lower concentrations require using a larger volume of extracted water (5 liter) or an extraction with evaporation followed by dissolution of a residue in a smaller volume of supporting electrolyte. We chose the latter approach and used a 1-ml polarographic vessel. First, the set-up was tested without previous extraction. Good results were obtained when oxygen was removed by purging with nitrogen for 1 min. The whole measurement did not take more than 10 min. Longer times of purging resulted in a decrease in the supporting electrolyte volume caused by evaporation of methanol thus leading to positive errors. The optimized conditions for SPE were applied to the determination of 3-NF in drinking

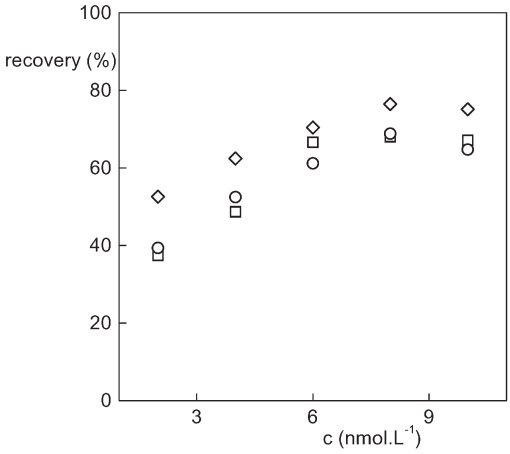


Fig. 6
The dependence of recovery of 3-NF on its concentration after SPE from 500 ml of water, measured by DPV at HMDE in methanol–BR buffer pH 3 (9:1) medium; deionized water (□), drinking water (○) and river water (◇)

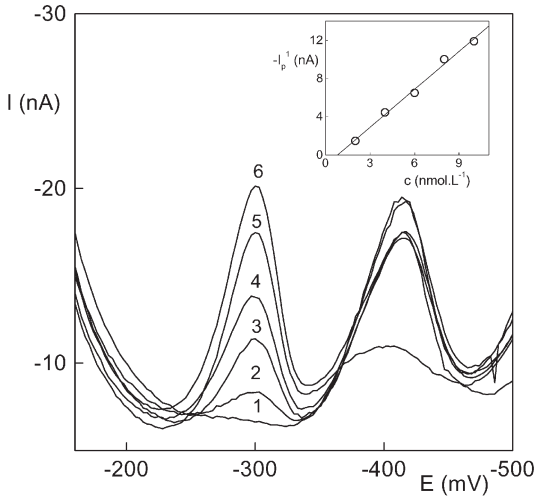


FIG. 7

DP voltamograms of 3-NF after SPE from 500 ml of drinking water, measured by DPV at HMDE in methanol–BR buffer pH 3 (9:1) medium; c(3-NF) in nmol l^{-1}: 0 (*1*), 0.2 (*2*), 0.4 (*3*), 0.6 (*4*), 0.8 (*5*) and 1 (*6*). The corresponding calibration straight line is in the inset

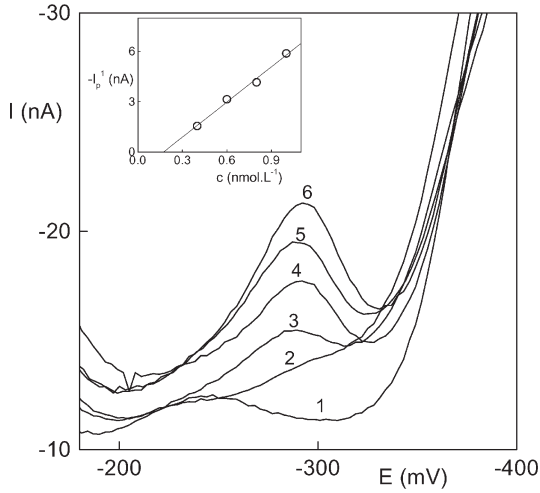


FIG. 8

DP voltamograms of 3-NF after SPE from 500 ml of river water, measured by DPV at HMDE in methanol–BR buffer pH 3 (9:1) medium; c(3-NF) in nmol l^{-1}: 0 (*1*), 2 (*2*), 4 (*3*), 6 (*4*), 8 (*5*) and 10 (*6*). The corresponding calibration straight line is in the inset

water in the concentration range (2–10) × 10^{-10} mol l^{-1} (Fig. 7). The parameters are summarized in Table VII. LOD was calculated as 4 × 10^{-10} mol l^{-1}. The calibration measurement of 3-NF in river water after SPE was carried out in the concentration range (2–10) × 10^{-9} mol l^{-1} (Fig. 8) with parameters given in Table VII. Detection of lower concentrations was not successful due to the impurities present in river water. Reached LODs for determination of 3-NF in drinking and river water were similar as ones already published for different NPAH measured by voltammetric methods[30,31].

CONCLUSIONS

It has been shown that mercury electrodes, namely the classical dropping mercury electrode and hanging mercury drop electrode in combination with modern polarographic and voltammetric techniques are suitable sensors for the determination of submicromolar and nanomolar concentrations of 3-nitrofluoranthene. The most sensitive method is AdSV, the limit of determination reached by this method being 5 × 10^{-9} mol l^{-1}. However, this method is not suitable for the determination of the compound in more complex matrices because of the influence of surface-active substances and other impurities on the AdSV signal. Therefore, DPV at HMDE was chosen for the determination of 3-nitrofluoranthene in drinking and river water. It was verified that it is a useful method together with a preliminary liquid–liquid or solid phase extraction, the letter one being more effective. Thus, it can be concluded that polarographic and voltammetric methods are useful alternative tools for the determination of 3-nitrofluoranthene. Of course, other NPAH reduced at similar potential will interfere with determination of 3-nitrofluoranthene. In such cases, their preliminary separation using e.g., HPLC is necessary. On the other hand, presented determination of 3-nitrofluoranthene represents an independent method to its detection.

The authors thank Dr J. Ludvík (J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic) for help with coulometry experiments. This research was supported by the Ministry of Education, Youth and Sports of the Czech Republic (project No. LC 06035).

REFERENCES

1. O'Neil I. K., Fishbein L.: *Int. J. Environ. Anal. Chem.* **1986**, *26*, 229.
2. Jager J.: *J. Chromatogr.* **1978**, *152*, 575.
3. Pitts J. N., Van Cauwenberge K. A., Grosjean D., Schmid J. P., Fitz D. R., Belser W. L., Knudson G. B.: *Science* **1978**, *202*, 515.
4. MacCrehan W. A., May W. E., Yang S. D., Benner B. A.: *Anal. Chem.* **1988**, *60*, 194.

5. Gbson T. L. J.: *Air Pollut. Control Assoc*. **1986**, *36*, 1022.
6. Vincenti M., Maurino V., Minero C., Pelizzetti E.: *Int. J. Environ. Anal. Chem*. **2001**, *79*, 257.
7. Jacob J., Karcher W., Belliardo J. J., Dumler R., Boenke A.: *Fresenius J. Anal. Chem*. **1991**, *340*, 755.
8. Arey J., Zielinska B., Atkinson R., Winer A. M., Ramdahl T., Pitts J. N.: *Atmos. Environ*. **1986**, *20*, 2339.
9. URL: http://www.who.int/ipcs/publications/part_1.pdf, downloaded June 8th, 2006.
10. Yu G., Xu X. B.: *Chemosphere* **1992**, *24*, 1699.
11. Barek J., Cvačka J., Moreira J. C., Zima J.: *Chem. Listy* **1996**, *90*, 805.
12. Kamiura T., Kawaraya T., Tanaka M., Nakadoi T.: *Anal. Chim. Acta* **1991**, *254*, 27.
13. Ramdahl T., Becher G., Bjorseth A.: *Environ. Sci. Technol*. **1982**, *16*, 861.
14. Nielsen T., Seitz B., Ramdahl T.: *Atmos. Environ*. **1984**, *18*, 2159.
15. Paputa-Peck M. C., Marano R. S., Schuetzle D., Riley T. L., Hampton C. V., Prater T. J., Skewens L. M., Jensen T. E., Ruehle P. H., Bosch L. C., Duncan W. P.: *Anal. Chem*. **1983**, *55*, 1946.
16. Niles R., Tan Y. L.: *Anal. Chim. Acta* **1989**, *221*, 53.
17. Robbat A., Corso N. P., Doherty P. J., Wolf M. H.: *Anal. Chem*. **1986**, *58*, 2078.
18. Lindner W., Posch W., Wolbeis O. S., Tritthart P.: *Chromatographia* **1985**, *20*, 213.
19. Zuman P.: *Collect. Czech. Chem. Commun*. **1993**, *58*, 41.
20. Zuman P., Fijalek Z., Dumanovic D., Suznjevic D.: *Electroanalysis* **1992**, *4*, 783.
21. Fry A. M.: *Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, p. 319. Wiley, Chichester 1982.
22. Palmer B. D., Wilson W. R., Cliffe S., Denny W. A.: *J. Med. Chem*. **1992**, *35*, 3214.
23. Klopman G., Tonucci D. A., Holloway M., Rosenkranz H. S.: *Mutat. Res*. **1984**, *126*, 139.
24. Lopes W. A., Pereira P. A. D., Viertler H., de Andrade J. B.: *J. Braz. Chem. Soc*. **2005**, *16*, 1099.
25. Barek J., Fischer J., Navrátil T., Pecková K., Yosypchuk B.: *Sensors* **2006**, *6*, 445.
26. Čížek K.: *M.S. Thesis*. Charles University, Prague 2003.
27. Oppenheimer L., Cappizi T. P., Weppelmann R. M., Metha H.: *Anal. Chem*. **1983**, *55*, 638.
28. Schwartz L. M.: *Anal. Chem*. **1983**, *55*, 1424.
29. Ebel S., Kamm U.: *Fresenius J. Anal. Chem*. **1984**, *318*, 293.
30. Pecková J., Barek J., Moreira J. C., Zima J.: *Anal. Bioanal. Chem*. **2005**, *381*, 520.
31. Barek J., Kadeřábková M., Moreira J. C., Zima J.: *Chem. Anal*. **2005**, *50*, 37.