DETERMINATION OF TRINITROTOLUENE AT *EX-SITU* PREPARED BISMUTH FILM ELECTRODE: AN INITIAL STUDY

Hanna SOPHA and Ivan ŠVANCARA[1]
Department of Analytical Chemistry,
The University of Pardubice, CZ–532 10 Pardubice

A bismuth film electrode prepared ex-situ on a glassy carbon powder substrate (BiF-GCPE) was applied to the determination of trinitrotoluene (TNT) in combination with square-wave adsorptive stripping voltammetry. The electroanalytical performance of the BiF-GCPE was studied in Britton-Robinson buffers in the range of pH 4-9, revealing the most favourable stripping signals in mild alkaline solutions (pH 9.0). For calibration, linear responses could be obtained in the concentration range of 0.5-5.0 ppm TNT, when using a deposition time of 60 s (R^2 = 0.9999), and within 0.1-1.5 ppm TNT after deposition for 120 s (R^2 = 0.9983). The LOD (3σ) was estimated to be about 7 ppb (for deposition time of 240 s), and the BiF-GCPE exhibited a very good repeatability (RSD = ±2.3 %; n = 10, c_i = 0.5 ppm). Finally, possible determination of TNT in the presence of nitrobenzene was also shown.

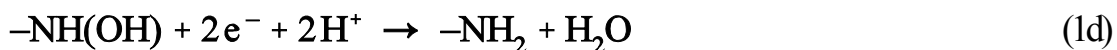[1] To whom correspondence should be addressed.

Introduction

Over the last decade, bismuth has been shown to be a promising alternative to mercury in electroanalytical chemistry due to its non-toxic character [1] and its similar electrochemical behaviour, including a wide operational potential range [2]. By now, this environmentally friendly metal is applied as electrode material in electroanalytical laboratories worldwide [3]. Since the introduction of bismuth-coated electrode into electrochemical stripping analysis [2], many different modifications of bismuth based electrodes were proposed, including *in-* and *ex-situ* prepared bismuth film electrodes (BiFEs [4]), and when using the electrode support from glassy carbon (GC [2]), carbon paste (CP [5]), carbon fibre [6], screen-printed inks (e.g., Ref. [7]) or boron-doped diamond (BDD [8]) substrate electrodes for the determination of heavy metal ions [9-11] and some organic compounds [12,13].

Also, there have been reports on carbon pastes modified with bismuth powder (the Bi-CPE type [14]) or bismuth precursors, such as bismuth trioxide or ammonium tetrafluorobismuthate (Bi_2O_3-CPE and NH_4BiF_4-CPE, respectively [15,16]), as well as a bismuth bulk electrode (BiBE) made of compact metal [17]. Among this spectrum of the working electrodes and their use in organic analysis, only a few were employed in the stripping voltammetric mode with pre-concentration; namely, in the case of determination of *Daunomycin* [18] at the BiBE or for *Sildenafil* citrate (Viagra®) with a BiFE [19]. Otherwise, organic compounds were detected directly, without accumulation.

Concerning organic nitro derivatives and except some preliminary assays, none of BiFEs has hitherto been employed to determine dangerous polynitro aromatic compounds, such as 2,4,6-trinitrotoluene ($C_7H_5N_3O_6$, "TNT"), being notoriously known for their toxic properties with serious impact on humans and environment [20]. Moreover, these substances are massively used as the secondary explosives in the army and mine industry, which both may lead to a severe ground-water contamination and a threat to public safety [21,22].

Due to these reasons, fast and precise detection of TNT is highly desirable. In the last decade, electroanalytical determinations of TNT have been accomplished using different types of electrodes, such as mercury electrodes, carbon-nanotube modified glassy carbon electrodes or carbon fibre electrodes, and the respective procedures became soon attractive thanks to low-priced and potable instrumentation on one hand and fast and accurate measurements on the other, resulting in a series of interesting publications [23-27].

Reportedly, the electrochemical detection of TNT and related compounds in aqueous solutions at higher pHs (see, e.g., Refs [24,28,29]) takes place *via* a consecutive reduction pathway, giving rise to a cascade of three stripping signals that reflect the four-step transformation of each nitro group involving six electrons

$$-NO_2 + 2e^- + 2H^+ \rightarrow -N(OH)_2 \tag{1a}$$

$$-N(OH)_2 \rightarrow -N=O + H_2O \tag{1b}$$

$$-N=O + 2e^- + 2H^+ \rightarrow -NH(OH) \tag{1c}$$

$$-NH(OH) + 2e^- + 2H^+ \rightarrow -NH_2 + H_2O \tag{1d}$$

therefore, the overall scheme can be formulated as follows

$$-NO_2 + 6e^- + 6H^+ \rightarrow -NH_2 + 2H_2O \tag{1e}$$
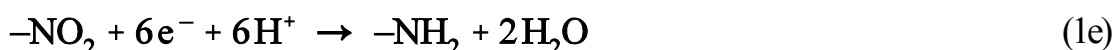
When considering the molecule of TNT as a whole, the full reduction corresponds to the involvement of 18 e$^-$ + 18 H$^+$ [29], which is rather surprising if one imagines that specialised text-books (see, e.g., Ref. [30]), as well as some scientific reports [24,31] quote that this is possible only for reduction of poly nitro derivatives in (highly) acidic media.

Concerning the electrode reduction of TNT at pH ≥ 7, the maximal number of electrons exchanged in scheme (1e) can be explained by the existence of intermediate functional group, $-N(OH)_2$, being relatively stable in (mild) alkaline media [29] and promoting the initial reduction of nitro group; see scheme (1a). The following dehydration toward nitroso group, $-N=O$, is then a spontaneous process, followed by immediate reduction to $-NH(OH)$ and final transformation into the amino group, $-NH_2$; see sequences (1b-d). Furthermore, it can be deemed that specific constellation of the TNT molecule with high symmetry of all three nitro groups and minimal participation of the fourth substituent, $-CH_3$ group, with respect to its steric or electrophile effect(s) seem to be beneficial also in the straightforward reduction involving $3 \times 6 = 18$ electrons [29,30,32].

Nevertheless, depending on actual conditions including the electrode itself, some authors admit [22,24,28] that the reduction of the nitro group(s) may be incomplete and terminated ,e.g., in the stage of hydroxylamine, $-NH(OH)$, which would lead to adequately lesser number of totally involved electrons. In any case, coulometric study or other special experiments — e.g., isolation of electrode products with the aid of preparative electrolysis and their identification by NMR and/or MS [33] — should be performed in order to verify such hypotheses and define the ultimate mechanism of the reduction pathway.

In this article, two types of carbon paste electrode and the corresponding *ex-situ* prepared BiFEs have for the first time been employed and tested as the working electrodes of choice to detect low concentrations of TNT by using adsorptive stripping voltammetry (AdSV) with the cathodically scanned stripping step. As shown in the following sections, a very fine reduction with three stripping

Sopha H., Švancara I./Sci. Pap. Univ. Pardubice, Ser. A **20** (2014) 7–22

9

signals has been confirmed for both carbon paste-based and Bi-film plated electrodes; moreover, being found to be distinguishable from the reduction of the single nitrobenzene (NB), allowing us to examine also the simultaneous determination of TNT and NB.

Experimental

Chemicals and Reagents

All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich or Merck. A stock solution of 1000 mg l^{-1} 2,4,6-trinitrotoluene was prepared by dissolving the appropriate amount of this substance in pure acetonitrile.

To prepare the *ex-situ* (pre-plated) bismuth film, an AAS standard solution of Bi(III) salt (with $c_{Bi} = 1000 \pm 0.1$ mg l^{-1}) was chosen and diluted as required. Throughout the work, doubly distilled water was used.

Apparatus and Instrumentation

Voltammetric measurements were carried out using the modular electrochemical system AUTOLAB (model "PGSTAT 30", Ecochemie, Utrecht, Holland) operated with Nova 1.10 software (Metrohm Autolab B.V.). A usual three-electrode configuration was employed with the bare or a bismuth-film modified carbon paste electrode (CPE) or glassy carbon paste electrode (GCPE) as the working electrode, an Ag/AgCl/KCl(satd.) as the reference, and a Pt-plate (3×5 mm) counter electrode, completing the cell. During the deposition and cleaning steps, the solutions were stirred using a PC-controlled magnetic stirrer rotated at ca. 300 rpm. All the experiments were carried out at room temperature of 23 ± 1 °C in an ordinary voltammetric cell ($V_{tot} = 20$ ml).

Working Electrodes

Carbon Paste Electrodes. Two types of mixtures of (standard) carbon paste and glassy carbon paste were prepared by thoroughly hand-mixing of graphite powder ("CR-5" type; Maziva Týn, the Czech Republic) with 30 % (w/w) paraffin oil (Merck) or glassy carbon powder ("Sigradur-G", HTW Maitingen, Germany) with 20 % (w/w) paraffin oil (Merck), resp. Both mixtures were homogenized using a pestle and mortar and subsequently dosed into two identical piston-driven electrode holders with a diameter of 3 mm [34]. Prior to each set of measurements,

the surface of (G)CPE was renewed by extruding about 0.5 mm thin layer of carbon paste mixture out of holder with the subsequent smoothing with a wet filter paper.

Bismuth Film Modified Carbon Paste Electrodes. The metallic film was generated *ex-situ* onto the surface of either CPE or GCPE. If not stated otherwise, the bare paste electrodes were plated in a solution of 0.1 M acetate buffer (pH 4.5), containing 5 mg l^{-1} Bi(III) by applying a potential of –1.0 V vs ref for 60 s. Before the film preparation, the electrode surface was regenerated electro-chemically at +0.3 V vs ref for a period of 30 s.

Procedures

Determination of TNT by Adsorptive Stripping Voltammetry (AdSV). Typical measurements were carried out in Britton–Robinson buffer (pH 7.0 or pH 9.0, respectively) as a sample solution. Following the pre-concentration step at –0.3 V vs Ag/AgCl (in further text, abbreviated as "ref") for 60 s, the stirring was stopped for 10 s during the equilibrium period and the stripping curve recorded in the cathodic voltammetric mode within a potential range from –0.3 V to –1.3 V vs ref and when using the square-wave potential ramp (with a frequency, $f_{SW} = 25$ Hz; step potential, $E_i = 4$ mV; and the pulse height, $\Delta E = 50$ mV). No electrochemical cleaning of the electrode surface was needed between the individual measurements; nevertheless, the sample had to be purged with argon to remove dissolved oxygen interfering when being reduced in the cathodic mode used.

Evaluation of the Measurements. All the stripping signals were measured as the current intensities — typically, in μA — with the aid of the manufacturer's software and using the ordinary procedure for the peak height computation.

Results and Discussion

Choice of Working Electrode

Figure 1 brings a comparison of the SWV behaviour of TNT at four different electrodes made of two carbonaceous substrates and being tested either bare — i.e., CPE (curve "a") and GCPE ("c") —, or as the bismuth film plated configurations: BiF-CPE ("b") and BiF-GCPE ("d").

In all the cases, the reduction of TNT had resulted in three consecutive signals, however, the second and the third ones remaining almost undeveloped at the CPE and BiF-CPE (within sensitivity range being chosen identical for all four records) — see negligible or very small plateaus upon the voltammograms "a" and "b". The poorest response in the set with a single peak also confirms some previous observations [35] that the standard carbon paste (made of common gra-

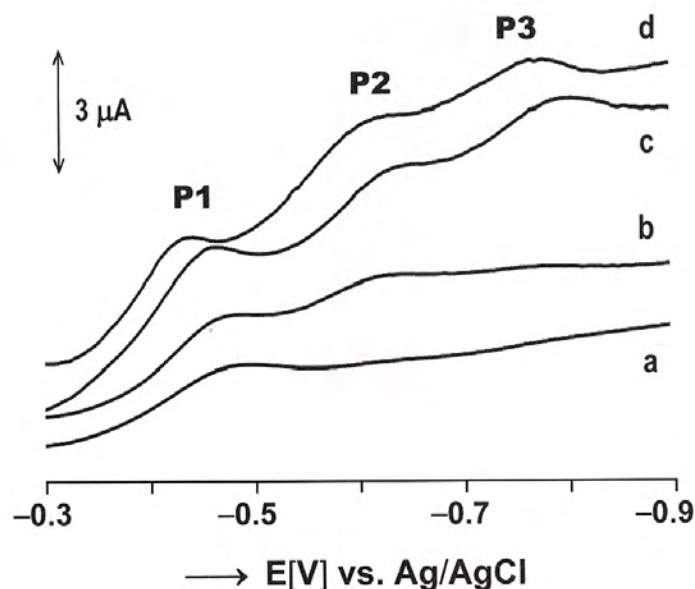Sopha H., Švancara I./Sci. Pap. Univ. Pardubice, Ser. A **20** (2014) 7–22

11

Fig. 1 Square-wave adsorptive stripping voltammograms of 1 ppm trinitrotoluene (TNT) at four different electrodes. Legend: a) bare CPE, b) BiF-CPE, c) bare GCPE, d) BiF-GCPE. Experimental conditions: supporting electrolyte: Britton–Robinson buffer (BRB, pH 7.0); accumulation potential, $E_{ACC} = -0.3$ V vs ref; accumulation time, $t_{ACC} = 60$ s; equilibration time, $t_{EQ} = 10$ s; Square-wave potential ramp: frequency, $f_{SW} = 25$ Hz; step potential, $E_{SW} = 4$ mV; pulse height, $\Delta E_{SW} = 50$ mV. BiFE preparation: plating solution: 0.1 M acetate buffer + 5 ppm Bi(III); deposition / generating potential, $E_G = -1.0$ V vs ref and time, $t_G = 60$ s. Note: Arrow depicts difference of current intensity, ΔI_{SWV} (in µA)

phite) is not very suitable for detection of polynitro compounds.

Somewhat better response could be obtained for the plated variant (curve "b"), revealing already all three signals, but with the last one still badly developed. Compared to these measurements, the electrodes based on the CP-mixture with glassy carbon powder "Sigradur" had offered much better function, exhibiting all three peaks during the cathodic scanning ("c" and "d"); the respective responses being positioned at approximately $E_{P(1)} = -0.45$ V, $E_{P(2)} = -0.60$ V, and $E_{P(3)} = -0.75$ V vs ref. According to the scheme (1a-d), each peak appears to correspond to the sequential reduction of one nitro group [22,29].

Concerning the eventual analytical use, the first response(s), "P1" at lowest negative potentials, exhibited the most favourable characteristics, including the highest absolute current and repeatability (of about ±3-7 %). Finally, when considering the individual four electrodes and their performance reflected in the peak P1, the highest stripping signals of TNT could be attributed to the (bare) GCPE type. Nevertheless, in this case, the resultant repeatability was worse compared to its bismuth-plated variant and hence, the BiF-GCPE type was the ultimate choice for further experimentation.

Optimization of the Method

All the basic optimization measurements with TNT at the BiF-GCPE were carried out in a series of Britton–Robinson buffers, representing apparently the most popular supporting media in organic electrochemistry of aqueous solutions [32,36] as being able to provide the different pH within a sufficiently wide range.

In this study, the respective interval was from pH 4.0 to pH 9.0 and the corresponding voltammograms are shown in Fig. 2, while the dependence of all three stripping signals, "P1, P2 and P3", upon the pH value is illustrated in Fig. 3. It is evident that the current intensities of all three signals increase with the decreasing acidity. Moreover, higher pH values give rise to a shift in the peak potentials, of all three signals, $E_{P(i)}$, towards more negative potentials.

As pointed out in literature [22,25,29,36], this behaviour is expected for the reduction involving protons, including the step-wise transformation like that for TNT and similar structures (see again above, scheme 1a-d). Since the most developed peaks and the highest current intensities were achieved in the Britton–Robinson buffer with pH 9.0, this solution was chosen as the optimum in all the subsequent experiments.
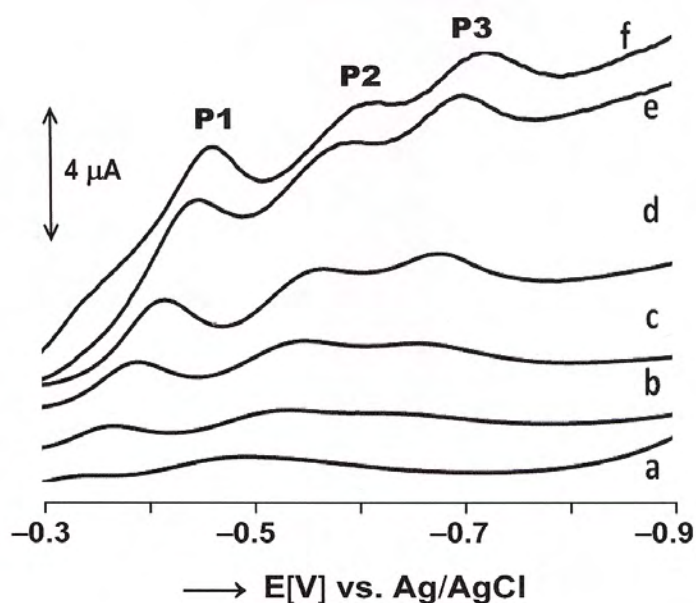

Fig. 2   Square-wave adsorptive stripping voltammograms of 2 ppm TNT at *ex-situ* prepared BiF-GCPE in Britton–Robinson buffers of different pH. Legend: a-f) pH 4.0, 5.0, … 9.0. For experimental conditions, see Fig. 1

These assays involved optimization of two key parameters for the accumulation step: the studies of "$I_{P(i)}$ vs E_{ACC}" and "$I_{P(i)}$ vs t_{ACC}" dependences plus some associated phenomena. Because the stripping signals "P1" had appeared already at a potential of ca. –0.45 V vs ref and the bismuth film — i.e., the electrode proper — started to dissolve at potentials more positive than — 0.3 V, this limit

value was set as the accumulation potential of choice. Otherwise, the dependence of each stripping signal, $I_{P(1)}$, $I_{P(2)}$, and $I_{P(3)}$, upon the accumulation time is given together in the set of the corresponding plots in Fig. 4; in all the cases, for model concentration of 800 µg l^{-1} TNT).
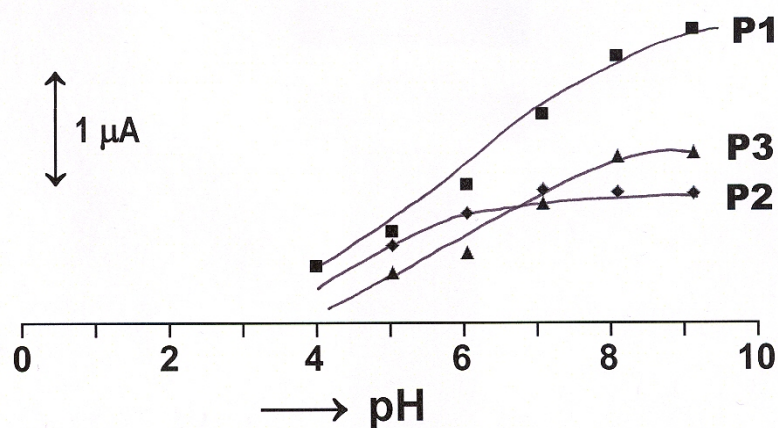

Fig. 3 SWAdSV of 2 ppm TNT at *ex-situ* prepared BiF-GCPE. Actual intensity of three stripping peaks vs pH dependence(s). For legend and experimental conditions, see Figs 1 and 2
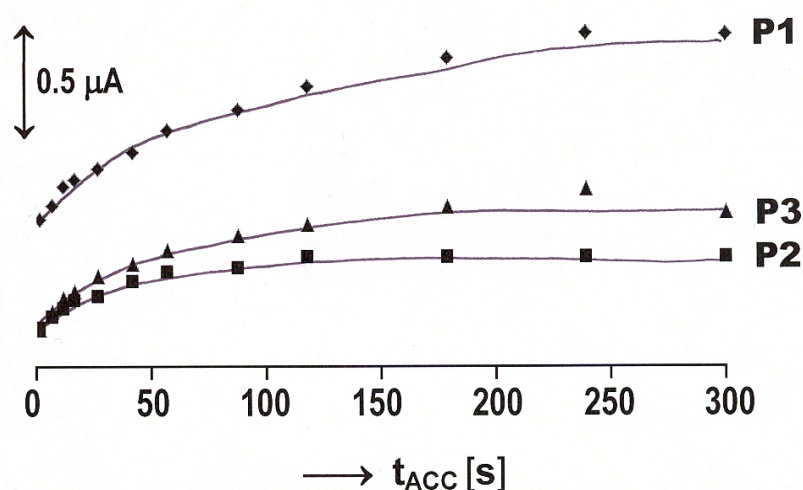

Fig. 4 Optimization of deposition time for determination of TNT at low ppm level with *ex-situ* prepared BiF-GCPE. Experimental conditions: Britton–Robinson buffer, pH 9.0; $c_{(TNT)}$ = 0.8 ppm. For other conditions, see Fig. 1

Evidently, all three stripping signals $I_{P(i)}$ increased markedly with the accumulation time until 45 s; afterwards, from 45 to 90 s, the current intensities still increased but less notably. Application of higher values of t_{ACC} led to yet another increase in the signal "P1"; however, other two plots for the stripping signals "P2" and "P3" already suggested the starting saturation of the electrode surface. To prevent this undesirable effect, the setting of t_{ACC} = 60 s seems to be maximum; at least, for the low ppm concentration level used in this assay. (For lower concentrations, the accumulation period could still be prolonged.)

Thus, according to the actual concentration level in the sample, the accumulation time $t_{ACC} = 60$ s or 120 s, or even 240 s was used in further measurements; always, with the respective specification.

Calibration of Analytical Signal

Figure 5 illustrates the first set of voltammograms for consecutive additions of 0.5 mg l^{-1} TNT within a concentration range of 0.5-5.0 mg l^{-1} and in combination with accumulation for 60 s; the corresponding calibration plots for all three signals being shown as well.
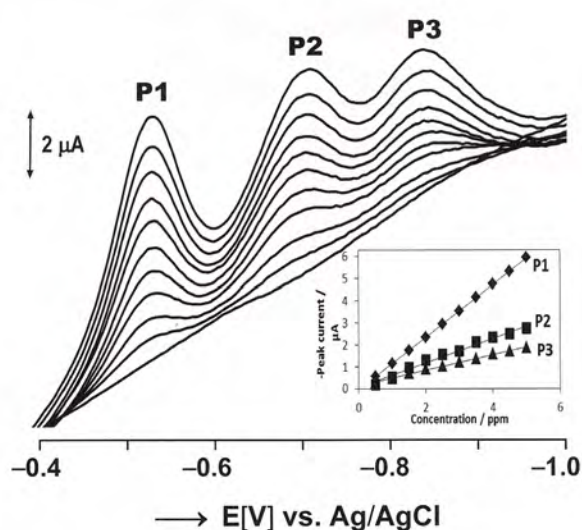

Fig. 5   SWAdSV with repeated additions of TNT at *ex-situ* prepared BiF-GCPE. Set I. Legend: successive additions of 0.5 mg l^{-1} in range of 0.5-5 mg l^{-1} TNT. Experimental conditions: Britton–Robinson buffer, pH 9.0; $t_{ACC} = 60$ s. For other conditions, see Fig. 1. Note: Inset shows the corresponding calibrations

In this concentration range tested, an excellent correlation could be achieved as documented by the respective correlation coefficients for the stripping signals; namely, $R^2(P1) = 0.9999$ and $R^2(P3) = 0.9970$. The linearity for the stripping signal "P2" was somewhat poorer, with the correlation $R^2(P2) = 0.9859$.

Figure 6 illustrates the second set of the stripping voltammograms recorded after the subsequent additions of 100 µg l^{-1} TNT in the concentration range of 100-1500 µg l^{-1}; now, with a longer accumulation period, $t_{ACC} = 120$ s. Also, for these conditions, linear calibration curves were obtained for all three stripping signals "P1, P2 and P3" with correlation coefficients $R^2(Pi)$ of 0.9983, 0.9963, and 0.9913, respectively.

Another important analytical parameter, the limit of detection (LOD) was calculated next as a 3σ-estimate and found to be ca. 7 µg l^{-1} TNT for the stripping
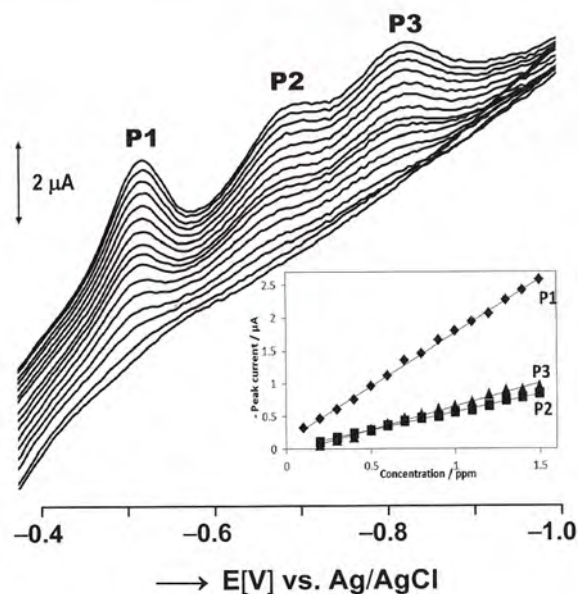
Fig. 6　SWAdSV with repeated additions of TNT at *ex-situ* prepared BiF-GCPE. Set II. Legend: successive additions of 0.1 mg l^{-1} in range of 0.1-1.5 mg l^{-1} TNT. Experimental conditions: Britton–Robinson buffer, pH 9.0; t_{ACC} = 120 s. For other conditions, see Fig. 1

signal "P1", when analysing model concentration of 200 μg l^{-1} TNT and after applying t_{ACC} = 240 s. Concerning the remaining two signals, their LODs were one-order higher; specifically: 83 μg l^{-1} for "P2": and 56 μg l^{-1} TNT for "P3". Last but not least, ten replicate measurements of 0.5 mg l^{-1} TNT (here, with accumulation for 60 s) have resulted in still acceptable relative error expressed as RSD(P1) = ±2.3 %, RSD(P2) = ±7.3 %, and RSD(P3) = ±6.4 %.

Effect of Surfactants

In electroanalysis of organic compounds, the presence of surface-active substances in the sample may lead to serious problems from a deteriorated reproducibility of the electrode up to its total fouling [32,37]. Therefore, some representatives of surfactants were included into optimization measurements also in this work. Namely, a trio of typical and widely used surfactants was selected: (i) Triton X-100®, a non-ionic surfactant; (ii) cetyltrimethyl-ammonium bromide (CTAB), a cationic surfactant; and (iii) sodium dodecyl sulphonate (DDS), an anionic surfactant. Their effect upon the stripping signal(s) of TNT was examined in detail and the principal results are summarized in Table I (see overleaf).

As expected, when adding Triton X-100 or DDS to the model sample, all three stripping signals of TNT decreased rapidly due to the firm entrapment of their lipophilic molecules onto the electrode surface [32,37]. At the same time, the

peak potentials of all three signals moved more negatively in relation with the increasing content of surfactants.

However, the third surfactant tested, CTAB, had exhibited a completely different behaviour; if being present at lower concentrations (max. 0.5 mmol l^{-1}), it caused the abrupt increase in the current intensity for all three signals. In the case of peak "P2", such enhancement could achieve up to 140 % (see Table I), with a marked shift of its potential, $E_{P(2)}$, towards less negative values.

Table I   Actual intensities and signal decrease of all three signals of 1 ppm TNT after addition of respective surfactant at *ex-situ* prepared BiF-GCPE

Reagent Concentration mM		P1		P2		P3	
		Peak current μA	Peak decline %	Peak current μA	Peak decline %	Peak current μA	Peak decline %
Triton X-100	-	−1.448	-	−0.594	-	−0.831	-
	0.5	−0.917	−36.7	−0.617	−3.9	−0.133	−84.0
	1	−0.427	−70.5	−0.371	−37.5	−0.072	−91.3
	1.5	−0.261	−82.0	−0.247	−58.4	−0.047	−94.3
	2	−0.167	−88.6	−0.166	−72.1	−0.074	−91.1
CTAB	-	−1.144	-	−0.541	-	−0.637	-
	0.5	−1.466	28.2	−1.286	137.7	−0.796	24.9
	1	−1.061	−7.3	−0.844	56	−0.457	−28.3
	1.5	−0.722	−36.8	−0.616	13.8	−0.307	−51.8
	2	−0.505	−55.8	−0.443	−18.1	−0.228	−64.2
DDS	-	−1.274	-	−0.620	-	−0.623	-
	0.5	−1.012	−20.6	−0.313	−49.5	−0.423	−32.1
	1	−0.508	−60.2	−0.226	−63.6	−0.290	−46.5
	1.5	−0.356	−72.1	−0.158	−74.6	−0.182	−70.7
	2	−0.326	−74.4	−0.155	−75.1	−0.161	−74.1

Experimental conditions: Britton–Robinson buffer, pH 9.0. For other conditions, see Fig 1.

Almost the same phenomenon was noticed for nitrobenzene reducible at a BiF-CPE and the authors of this study [38] have concluded on intensive adsorption

of CTAB at the electrode surface, changing the actual electrode overpotential, as well as influencing the electrode kinetics towards moderated reaction rates.

Unfortunately, the enhancement after adding CTAB at the millimolar level had no analytical use because the whole process was found unstable and the amplified voltammetric responses decreased rapidly with each subsequent scan. Also, in this case, the CTAB molecules showed their primary effect — the rapid occupation of the active sites at the electrode surface and the resultant fouling of the electrode [32,37].

Detection of TNT in the Presence of Nitrobenzene

As already mentioned, bismuth film electrodes have already been employed in fundamental studies with nitrobenzene (NB, $C_6H_5NO_2$ [38]) which can be considered as the simplest representative of (poly)nitro derivatives.

In our work, it was tested how this compound behaves in the presence of a polynitro compound, — i.e., whether or not it is possible to determine TNT simultaneously with (the single) nitrobenzene. The result of such a test is shown in Fig. 7, illustrating analysis of a model mixture of TNT + NB at the BiF-GCPE in 0.1 M phosphate buffer (pH 6.6).
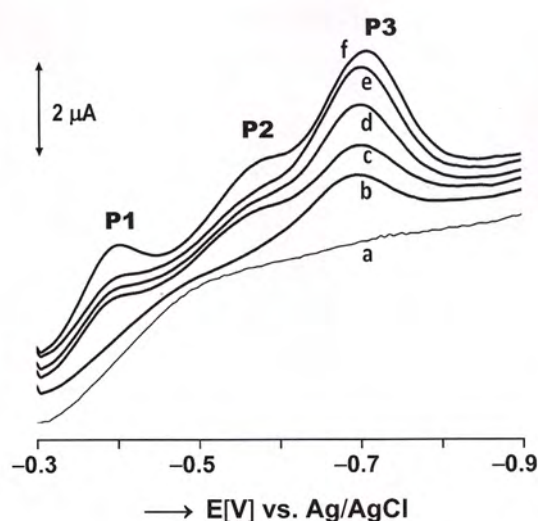

Fig. 7 SWAdSV of NB and TNT in model mixtures at *ex-situ* prepared BiF-GCPE. Legend: a) baseline, b) 4.4 µM nitrobenzene (NB), c) 4.4 µM NB + 4.4 µM TNT, d) 8.8 µM NB + 4.4 µM TNT, e) 13.2 µM NB + 4.4 µM TNT, and f) 13.2 µM NB + 8.8 µM TNT. Experimental conditions: 0.1 M phosphate buffer (pH 6.6). For other conditions, see Fig. 1

As can be seen, the reduction of NB gives rise to a single stripping signal only (curve "b"), being positioned at ca. –0.7 V vs ref. After adding the equimolar amount of TNT — when 4.4 µM TNT corresponds to 1 ppm TNT — a cascade of three consecutive signals are again obtained: "P1" ... ca. 0.4 V, "P2" ... 0.56 V, and

"P3" ... 0.7 V vs ref.; for all, see curve "c".

From the overall character of the individual voltammograms, it can be deemed that the signals "P1" and "P2" are related to TNT, whereas the signal "P3" tends to both nitro derivatives examined. This is also evident after addition of higher concentrations of NB into the solutions with constant content of TNT, where the signal P3 increases while the signals "P1" and "P2" are practically unaffected (curves "d" and "e"). And *vice versa* — another addition of 4.4 µM TNT to the solution leads to an increase in both "P1" and "P2", while the third peak remains unchanged, thus enabling to calibrate the NB response lying coincidentally — at nearly the same potential like "P3" (see again Fig. 7).

Herein, it can be stated that such behaviour can be exploited and rearranged into a selective determination of TNT in the presence of NB by means of detecting, evaluating, and computing the stripping signal "P1".

Conclusion

In this contribution, the applicability of *ex-situ* pre-plated bismuth film on a glassy carbon paste electrode — the BiF-GCPE configuration — is reported in association with the determination of trinitrotoluene (TNT) in Britton–Robinson buffer (pH 9.0) and when using square-wave adsorptive stripping voltammetry. The analyte of interest proved itself to be highly electroactive, giving rise to a trio of well-developed stripping peaks, from which one could further be utilised as well-reproducible analytical signal. After its calibration, linear responses were obtained in the concentration ranges of 0.5-5.0 ppm and 0.1-1.5 ppm TNT, when using accumulation time of 60 s and 120 s, respectively.

A special study with the use of surfactants showed that particularly CTAB could markedly enhance the stripping signal(s) of TNT, but the behaviour of so-pretreated electrode surface was poorly reproducible and analytically inapplicable.

Finally, regarding possible determination of TNT in the presence of NB (see, e.g., Refs [39,40]) or, eventually, their simultaneous analysis, it is necessary to have roughly the same concentration level of these two analytes; otherwise, too significant differences in their concentration ratio would already lead to mutual overlaps of the corresponding peaks "NB" and "P3" with complicated or even impossible evaluation.

In perspective, highly attractive electrode behaviour of TNT at the bismuth film plated carbon paste electrodes could be subjected to some advanced investigations in order to establish definitely the complete reduction pathway and, mainly, the number of electrons involved. Also, the individual reaction products should unambiguously be identified, which could also help in further improvement of electroanalytical performance. As shown in our previous research of similar interest [33], the above-mentioned controlled electrolysis in combination with

powerful identification techniques of NMR and MS enables to characterize in this respect even more complicated organic structures and processes than those exhibited by TNT and related compounds.

Acknowledgement

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Sopha H., Švancara I./Sci. Pap. Univ. Pardubice, Ser. A **20** (2014) 7–22

21

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