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Bismuth film electrode at a silver solid amalgam substrate as a new tool for voltammetric determination of electrochemically reducible organic compounds

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Dedicated to Professor Yuri Zolotov on the occasion of his 80th birthday.

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ABSTRACT

New type of bismuth film electrode prepared by electrodeposition of bismuth film on a silver solid amalgam substrate (BiF–AgSAE) was tested as a sensor for voltammetric determination of electrochemically reducible organic substances using 2-amino-6-nitrobenzothiazole (ANBT) as a model analyte. Using the optimized conditions (a 9:1 (v/v) mixture of aqueous Britton–Robinson buffer solution (pH 10.0) and methanol), the limits of quantification are 0.16 μmol L^{-1} for direct current voltammetry (DCV) and 0.22 μmol L^{-1} for differential pulse voltammetry (DPV). The obtained calibration dependences are linear in the concentration range from 0.2 to 100 μmol L^{-1} and the practical applicability of the newly developed electrode for the direct determination of ANBT in tap and mineral water model samples was confirmed in the concentration range from 0.2 to 10 μmol L^{-1}.

1. Introduction

Mercury is obviously the best available electrode material for voltammetric determination of electrochemically reducible organic compounds because of easily renewable and atomically smooth surface and large cathodic potential window [1]. However, due to increasing fears of liquid mercury toxicity resulting in somewhat unsubstantiated “mercurophobia” [2], considerable attention is paid to the search for new electrode materials applicable for cathodic voltammetry. Boron-doped diamond film electrodes [3,4], various types of non-toxic solid [5–8], paste [9–11] or composite [12,13] silver amalgam electrodes and, quite recently, solid bismuth electrodes [14] or bismuth film electrodes [15] are typical examples of this approach. In the case of silver solid amalgam, our recent results showed that the mercury vapor pressure of such amalgam containing no liquid mercury is far lower than the mercury vapor pressure of liquid mercury (about two orders of signal magnitude) and comparable with mercury vapor pressure of dental amalgams [16]. A number of papers deal with the bismuth film deposited on a glassy carbon (BiF–GCE) or carbon paste (BiF–CPE) substrate [17–23]. However, silver solid amalgam, which was found useful for deposition of a uniform mercury film [24,25], was not tested as a substrate for bismuth film so far. Therefore, we have investigated the possibility of electrochemical preparation of uniform bismuth film at this substrate and practical application of thus-prepared bismuth film electrode at the silver solid amalgam substrate (BiF–AgSAE) for voltammetric determination of electrochemically reducible organic compounds.

We have used 2-amino-6-nitrobenzothiazole (ANBT, see Fig. 1) as a model substance. This compound (used, e.g., in the dye industry) is known for its genotoxic and mutagenic properties [26] and, thus, it is desirable to develop inexpensive and sensitive electroanalytical methods for its determination in the environment. It contains cathodically reducible nitro-group and its investigation using direct current polarography [27,28], oscillopolarography [27], cyclic voltammetry [28] and coulometry [28] at mercury electrodes and DC voltammetry (DCV) and differential pulse voltammetry (DPV) at a polished silver solid amalgam electrode (p-AgSAE) and a mercury meniscus modified silver solid amalgam electrode (m-AgSAE) [29] confirmed a four-electron reduction of the nitro-group to the hydroxyamino-group followed by its two-electron reduction to the amino-group. In addition, to testing the possibility to prepare and use the BiF–AgSAE, we have verified its application for the direct determination of the target compound in model samples of tap and mineral water. We have used these model matrices because of the potential hazard of surface and ground waters contamination by ANBT during the industrial production of dyes and pigments [30].

2. Experimental

2.1. Reagents

A 1×10^{-3} mol L^{-1} stock solution of 2-amino-6-nitrobenzothiazole (ANBT) was prepared by dissolving an exactly weighed

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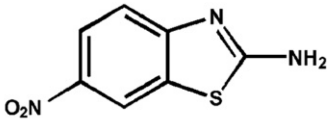

Fig. 1. Structural formula of 2-amino-6-nitrobenzothiazole (ANBT).

amount of the substance supplied by Sigma-Aldrich, Prague, Czech Republic, in methanol (99.9%, Merck, Darmstadt, Germany). The stock solution was stored in refrigerator at 4 °C and the dilute solutions were prepared freshly before use.

The Britton–Robinson (BR) buffer solutions were prepared in a usual way, by mixing a solution containing 0.04 mol L^{-1} solution of phosphoric acid (p.a. purity, Merck), acetic acid (p.a. purity, Panreac, Barcelona, Spain) and boric acid (p.a. purity, Lach-Ner, Neratovice, Czech Republic) with an appropriate amount of 0.2 mol L^{-1} sodium hydroxide (p.a. purity, Merck). Sodium acetate trihydrate (p.a. purity, Lach-Ner) and ethylenediaminetetraacetic acid (EDTA, p.a. purity, Panreac) were also used. Deionized water was produced by Milli-Q Plus system (Millipore, Billerica, MA, USA).

2.2. Instrumentation

2.2.1. Apparatus

Voltammetric measurements were carried out using a PalmSens electrochemical analyzer driven by PSTrace 2.1 software (both Palm Instruments, Houten, The Netherlands). The software worked under the operational system Microsoft Windows XP (Microsoft Corporation, Redmond, WA, USA). All measurements were carried out in a three-electrode system using platinum electrode (type PPE, Monokrystaly, Turnov, Czech Republic) as an auxiliary electrode and silver|silver chloride electrode (type RAE 113, 3 mol L^{-1} KCl, Monokrystaly) as a reference electrode. The BiF–AgSAE (the disc diameter 0.50 mm) was used as a working electrode. The scan rate 20 mV s^{-1} was used for both DCV and DPV, the pulse amplitude −50 mV and the pulse width 100 ms, with current sampling for the last 20 ms, were used in DPV.

The solution pH was measured by a Jenway digital pH meter (type 3510, Jenway, Chelmsford, UK) with a combined glass electrode (of the same producer) calibrated with standard aqueous buffers at laboratory temperature.

2.2.2. Preparation of bismuth film electrode on silver solid amalgam substrate (BiF–AgSAE)

The BiF–AgSAE was prepared *ex situ* by deposition of the bismuth film on the AgSAE at constant potential of −1.2 V (vs. Ag|AgCl) for selected time (t_{dep}) under stirring in 10 mL of plating solution (after deaeration of the solution for 5 min with pure nitrogen) containing 0.5 mL of bismuth standard solution (1000 mg L^{-1} Bi(III), Darmstadt, Merck, Germany) and 9.5 mL of 1.0 mol L^{-1} acetate buffer pH 4.75. The BiF–AgSAE was plated every day with new bismuth film because the lifetime of the electrode surface was relatively short, namely just a few hours. No mechanical, electrochemical or chemical cleaning or activation was performed, since such procedures damaged the bismuth film coating leading to less reproducible results.

The AgSAE used as a substrate consisted of a drawn-out glass tube, whose tip was packed with a fine silver powder (2–3.5 μm, 99.9%, Sigma-Aldrich, Prague, Czech Republic), amalgamated by liquid mercury (triply distilled polarographic mercury, 99.999%, Polarografie, Prague, Czech Republic), polished on the alumina with particle size 1.1 μm (Monokrystaly, Turnov, Czech Republic) and connected to an electric contact [5].

2.3. Procedures

An appropriate amount of ANBT stock solution in methanol was measured into a voltammetric cell, methanol was added, if necessary, to a total volume of 1.0 mL and filled up to 10.0 mL with a BR buffer of appropriate pH. Oxygen was removed from the measured solutions by bubbling with pure nitrogen for 5 min. Unless stated otherwise, all curves were measured three times, and all the measurements were carried out at laboratory temperature.

The DCV peak height (I_p) was evaluated from the extrapolated linear portion of the voltammogram before the onset of the peak. DPV peaks were evaluated from the straight line connecting the minima before and after the peak. The parameters of calibration curves (such as slope, intercept, correlation coefficient, limit of quantification) were calculated with statistic software Adstat 2.0 (TriloByte, Pardubice, Czech Republic) [31].

2.4. Model samples

The tap water from the public water pipeline in the building of National and Kapodistrian University, Athens, Greece, and natural mineral water (Spring Olympos, Katerini, Greece), spiked with appropriate amounts of ANBT stock solution, were used as model samples. Both tap and mineral water were either used without further pretreatment/purification or solid EDTA was added (1 g per 50 mL of water) for masking of cations present in solution. The procedure for DCV or DPV determination of ANBT in model samples was as follows: 9.0 mL of the model water sample were diluted to 10.0 mL with the BR buffer pH 10.0 and, after deaeration with nitrogen, DC or DP voltammograms at the BiF–AgSAE were recorded.

3. Results and discussion

3.1. Bismuth film deposition

At first, parameters for the deposition of the bismuth film on the AgSAE surface were optimized. The times of deposition (t_{dep}) 60, 120, 180, 240, 300 and 600 s were tested. The $t_{dep}=300$ s was selected as the optimum one because shorter times of deposition resulted in unstable bismuth films, leading to low repeatability of twenty consecutive DPV measurements of ANBT. At $t_{dep}=600$ s, the results were very similar to those obtained at 300 s.

The reproducibility of the bismuth film deposition was also investigated because the new film had to be prepared every day. The relative standard deviation (RSD) of DPV determination of ANBT ($c=1\times10^{-4}$ mol L^{-1}) in the BR buffer pH 10.0–methanol (9:1) medium (this medium was selected on the basis of initial experiments conducted at different pH values; see below) at ten different BiF–AgSAEs was 16% (Fig. 2A); this value was assumed to be satisfactory. Moreover, the repeatability of twenty consecutive DPV measurements of ANBT (also expressed as RSD), performed under the conditions mentioned above at a single freshly prepared bismuth film, was 4.5% (Fig. 2B), which also represents a satisfactory value for this type of electrode [19]. It can be seen in Fig. 2B that the I_p value decreased with the serial number of DPV scan performed. Nevertheless, such decrease usually stopped after about thirty to fifty DPV scans, resulting in RSD about 2% for another following twenty consecutive measurements.

3.2. Voltammetric behavior of 2-amino-6-nitrobenzothiazole at the BiF–AgSAE

The influence of pH on the DC and DP voltammetric behavior of 1×10^{-4} mol L^{-1} ANBT at the BiF–AgSAE was investigated in

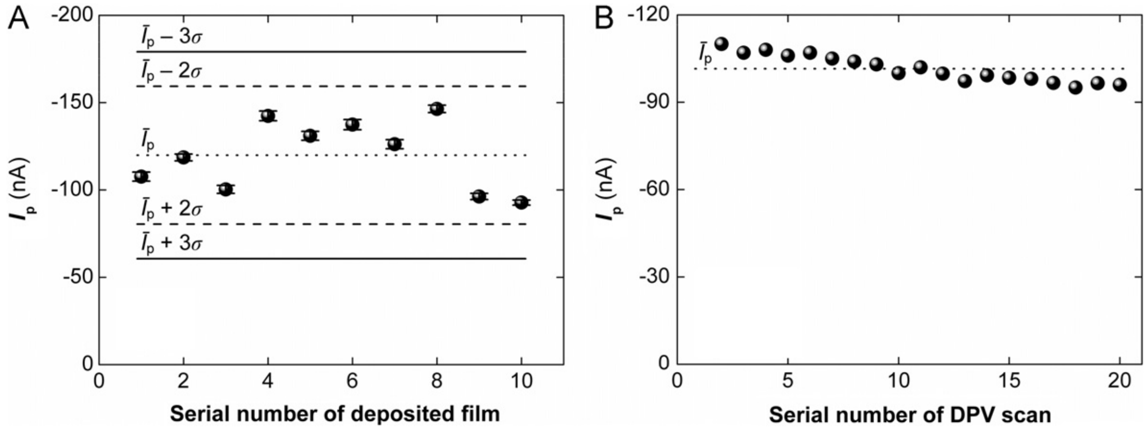

Fig. 2. (A) Reproducibility of the bismuth film deposition shown as the control chart (average value (dotted line), warning limits (dashed lines), control limits (solid lines)) of the DPV peak height of ANBT ($c = 1 \times 10^{-4}$ mol L^{-1}), recorded at ten different BiF–AgSAEs ($t_{dep} = 300$ s) in the BR buffer pH 10.0–methanol (9:1) medium; the error bars are constructed for $\alpha = 0.05$ ($n = 3$). (B) Repeatability of twenty consecutive DPV determinations of ANBT ($c = 1 \times 10^{-4}$ mol L^{-1}) at a single BiF–AgSAE ($t_{dep} = 300$ s) in the BR buffer pH 10.0–methanol (9:1) medium; the first measured value was discarded as an outlier; the average peak height is marked by the dotted line ($n = 19$).

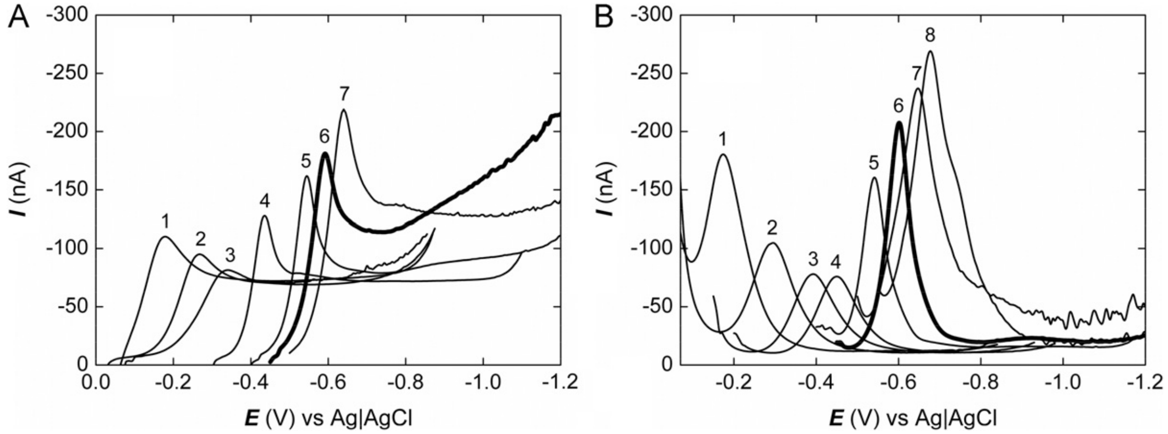

Fig. 3. DC (A) and DP (B) voltammograms of ANBT ($c = 1 \times 10^{-4}$ mol L^{-1}) at the BiF–AgSAE ($t_{dep} = 300$ s) in BR buffer–methanol (9:1) media; polarization rate 20 mV s^{-1}. The BR buffer pH values for A: 2.0 (1), 4.0 (2), 5.0 (3), 7.0 (4), 9.0 (5), 10.0 (6), 11.0 (7); and for B: 2.0 (1), 3.0 (2), 4.0 (3), 5.0 (4), 8.0 (5), 10.0 (6), 11.0 (7), 12.0 (8). The voltammograms recorded under optimum conditions for the determination of ANBT are in bold.

the BR buffer–methanol (9:1) media in the pH range of 2.0–12.0. Fig. 3 illustrates that ANBT gives one well-developed cathodic DCV or DPV peak, corresponding to the four-electron reduction of the nitro-group to the hydroxyamino-group, over the whole pH range explored. The second peak, which can be observed at more negative potentials at mercury [28] and silver solid amalgam [29] working electrodes and which corresponds to a two-electron reduction of the hydroxyamino-group to the amino-group, is not observable at the BiF–AgSAE.

The difference in voltammetric behavior of ANBT in acidic, neutral and alkaline media is evident from the peak shapes and peak height values (Fig. 3). The peak potential shifted towards more negative potentials with increasing pH, which can be explained by a preceding protonation of the nitro-group in ANBT, leading to a decrease in the electron density at the nitro-group and resulting in easier electron acceptance at low pH values [32].

3.3. Voltammetric determination of 2-amino-6-nitrobenzothiazole

The highest and best developed DCV and DPV peaks were obtained in the BR buffer pH 10.0–methanol (9:1) medium. This medium was then used for measuring the calibration curves in a concentration range from 0.2 to 100 μmol L^{-1} of ANBT; DP voltammograms of ANBT at the BiF–AgSAE in the concentration range 2–10 μmol L^{-1} and 0.2–1.0 μmol L^{-1} are depicted in Fig. 4A and B, respectively. The parameters of all the calibration straight lines are summarized in Table 1.

Generally, the measurement sensitivity slightly varies between the individual concentration orders (see Table 1). This behavior, typical for voltammetry at solid electrodes, is usually caused by the passivation of the working electrode surface by electrode reaction products or by adsorption of the analyte [33]. However, within the individual concentration orders, the concentration dependences obtained are linear. For the concentration range from 2 to 100 μmol L^{-1} of ANBT, the sensitivity of both DCV and DPV determinations achieved at the BiF–AgSAE is approximately two times higher, on average, than that at the bare p-AgSAE [29], whereas, for the concentration range from 0.2 to 1.0 μmol L^{-1} of ANBT, the determination sensitivity is approximately 1.6–1.7 times higher at the p-AgSAE [29]. These differences can probably be related to the different morphology of working electrode surfaces (p-AgSAE vs. BiF–AgSAE), which is under our current investigation. Nevertheless, the limits of quantification (L_Qs) reached at the BiF–AgSAE and p-AgSAE are comparable (see Table 1 and Ref. [29], respectively).

A further increase in the sensitivity of the determination could be achieved by adsorptive accumulation of the analyte on the surface of the working electrode [34]. The aqueous component of the optimum medium found for DCV and DPV determination of ANBT (BR buffer pH 10.0) has been used for investigating the possible accumulation.

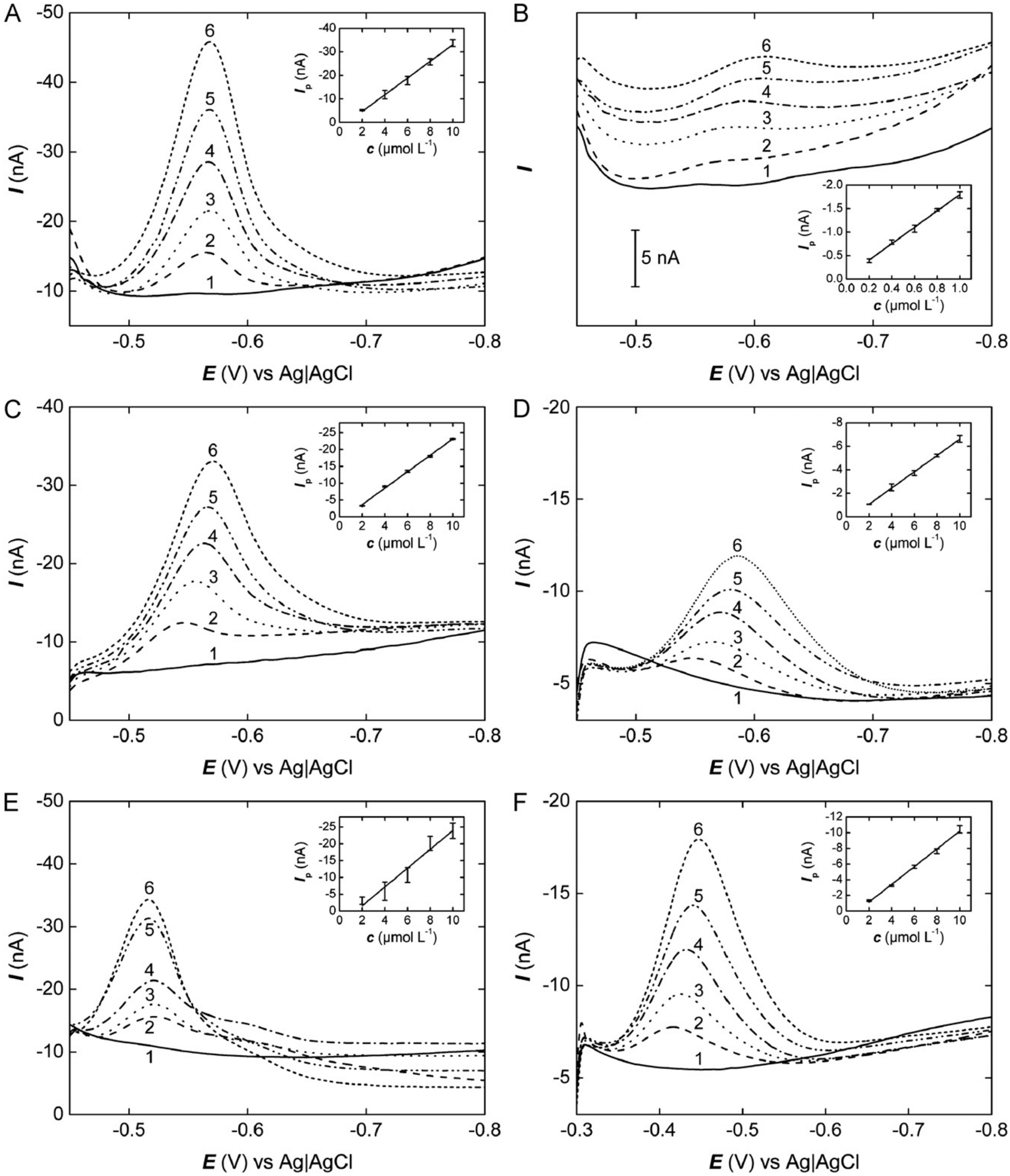

Fig. 4. (A and B) DP voltammograms of ANBT at the BiF–AgSAE ($t_{\mathrm{dep}}=300$ s) in the BR buffer pH 10.0–methanol (9:1) medium; concentrations of ANBT (μmol L^{-1}) for A: 0 (1), 2 (2), 4 (3), 6 (4), 8 (5), 10 (6); and for B: 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), 1.0 (6). (C–F) DP voltammograms of ANBT at the BiF–AgSAE ($t_{\mathrm{dep}}=300$ s) in model samples of tap (C and D) and mineral (E and F) water; measured in 9 mL of spiked waters diluted by BR buffer pH 10.0 to 10 mL (dilution factor 0.9) without (C and E) and with the addition of EDTA (D and F) to tap or mineral water; concentrations of ANBT (μmol L^{-1}) in waters: 0 (1), 2 (2), 4 (3), 6 (4), 8 (5), 10 (6). Polarization rate 20 mV s^{-1}; the corresponding calibration straight lines are given in the insets; the error bars are constructed for $\alpha=0.05$ ($n=3$).

Moreover, media representing acidic (BR buffer pH 3.0) and neutral (BR buffer pH 7.0) pH values have also been tested to cover the whole pH range. Because methanol is also usually adsorbed on the electrode surface [34], it was avoided from the supporting electrolyte. Suitable accumulation potentials were tested with the accumulation time varying from 0 to 5 min. Unfortunately, it has been found that the voltammetric peak of ANBT did not significantly increase with prolonging accumulation time under any conditions tested. Similar negative results have also been obtained for adsorptive accumulation of ANBT at the p-AgSAE and m-AgSAE [29].

Table 1
Parameters of the calibration straight lines (including standard deviations) for DCV and DPV determination of ANBT at the BiF–AgSAE in the BR buffer pH 10.0–methanol (9:1) medium.

Method	Concentration (μmol L^{-1})	Slope (nA L μmol^{-1})	Intercept (nA)	R	L_Q (μmol L^{-1})
DCV	20–100	−2.81 ± 0.11	14.6 ± 7.1[a]	−0.9978	–
	2–10	−2.74 ± 0.10	−1.25 ± 0.68[a]	−0.9979	–
	0.2–1	−3.029 ± 0.034	−0.186 ± 0.022	−0.9998	0.16
DPV	20–100	−3.21 ± 0.11	6.0 ± 7.5[a]	−0.9981	–
	2–10	−3.54 ± 0.13	2.43 ± 0.84[a]	−0.9974	–
	0.2–1	−1.739 ± 0.048	−0.058 ± 0.032[a]	−0.9984	0.22

R, correlation coefficient; L_Q, limit of quantification (10σ; $\alpha=0.05$).

[a] Intercepts are not statistically significantly different from zero at the significance level $\alpha=0.05$.

Table 2
Parameters of the calibration straight lines (including standard deviations) for DCV and DPV determination of ANBT at the BiF–AgSAE in model samples of water, i.e., in the mixture of spiked water sample–BR buffer pH 10.0 (9:1).

Water	Method	Concentration (μmol L^{-1})	Slope (nA L μmol^{-1})	Intercept (nA)	R	L_Q (μmol L^{-1})
Tap	DCV	2–10	–1.595 ± 0.049	1.46 ± 0.33	–0.9986	–
		0.2–1	–2.055 ± 0.086	0.130 ± 0.057[a]	–0.9974	0.45
	DPV	2–10	–2.440 ± 0.062	1.26 ± 0.41[a]	–0.9987	–
		0.2–1	–2.002 ± 0.063	0.236 ± 0.042	–0.9985	0.40
Tap with EDTA	DCV	2–10	–0.713 ± 0.081	0.447 ± 0.053	–0.9998	–
		0.2–1	–0.920 ± 0.017	0.166 ± 0.011	–0.9995	0.35
	DPV	2–10	–0.690 ± 0.012	0.321 ± 0.077	–0.9994	–
		0.2–1	–0.291 ± 0.016	0.058 ± 0.011	–0.9938	0.31
Mineral with EDTA	DCV	2–10	–0.528 ± 0.046	0.25 ± 0.31[a]	–0.9934	–
		0.2–1	–0.612 ± 0.077	−0.32 ± 0.12[a]	–0.9964	0.40
	DPV	2–10	–1.130 ± 0.042	1.12 ± 0.28[a]	–0.9972	–
		0.2–1	–0.638 ± 0.080	0.171 ± 0.053[a]	–0.9696	0.44

R, correlation coefficient; L_Q, limit of quantification (10σ; $\alpha=0.05$).

[a] Intercepts are not statistically significantly different from zero at the significance level $\alpha=0.05$.

3.4. Model samples of tap and mineral water

In order to verify practical applicability of the developed DCV and DPV methods, the determination of ANBT was carried out in model samples of tap and mineral water in a submicromolar concentration range under optimum conditions. Calibration curves were measured using a mixture of 9.0 mL of spiked model water sample and 1.0 mL of the BR buffer pH 10.0. DP voltammograms of ANBT at the BiF–AgSAE representing its direct determination in spiked tap (Fig. 4C and D) and mineral (Fig. 4E and F) water, in the concentration range 2–10 μmol L^{-1}, are depicted in Fig. 4.

During the preparation of model samples of waters, both tap and mineral water were either used without further pretreatment/purification or solid EDTA was added (1 g per 50 mL of water) for masking of cations (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}) present in solution to eliminate their negative effect. The effect of the addition of EDTA on voltammetric determination of ANBT is demonstrated in Fig. 4D and F and Table 2. Upon the addition of EDTA to tap water, the sensitivity of determination decreased, however, the L_Qs attained are rather lower. Therefore, the addition of EDTA to samples containing the tap water contaminated with ANBT could be considered for individual cases. On the other hand, in the case of the addition of EDTA to mineral water, the better results were obtained. Although the sensitivity of the determination after the addition of EDTA also decreased, calibration dependences with better linearity were obtained and the repeatability of the determination was better as well. Thus, it is advisable to add EDTA always upon the determination of ANBT in water samples with higher content of mineral cations. DPV voltammograms corresponding to the lowest attainable concentration range are illustrated in Fig. 5 for both tap and mineral water model samples with the addition of EDTA. The obtained parameters of the calibration curves are summarized in Table 2. These results confirm the possible application of tested electrode for the determination of submicromolar concentrations of ANBT in both tap and mineral waters.

3.5. Possibilities of the newly introduced BiF–AgSAE

The area, in which bismuth film electrodes (BiFEs) find most applications, is trace analysis of metals by electrochemical stripping techniques [18]. However, determinations of low-molecular-weight organic compounds by adsorptive stripping analysis at the BiFEs have not been reported so far [19]. There are only sporadic reports on voltammetric or amperometric determinations of some genotoxic nitro-compounds (e.g., nitrobenzene [35], 2-nitrophenol [15,36], 4-nitrophenol [15] and 2,4-dinitrophenol [15]) and some pesticides (e.g., paraquat [37], thiamethoxam, acetamiprid, nitenpyram [38], imidacloprid [38,39] and clothianidin [39]). Therefore, the BiF–AgSAE presented in this paper represents valuable alternative to previously reported BiFEs, moreover, with one of the lowest L_Qs achieved in organic electroanalysis (this is probably thanks to the property of bismuth to form “fused alloys” with heavy metals, which is analogous to the amalgams that mercury forms [19,40]).

We suppose that the p-AgSAE substrate also plays important role in the observed benefits of BiF–AgSAE. In our recent comparative studies [41,42], the BiF–AgSAE has been confronted with BiFEs based on glassy carbon (BiF–GCE) and gold (BiF–AuE) substrates upon the voltammetric determination of 5-nitrobenzimidazole (a compound structurally very similar to ANBT). The L_Q

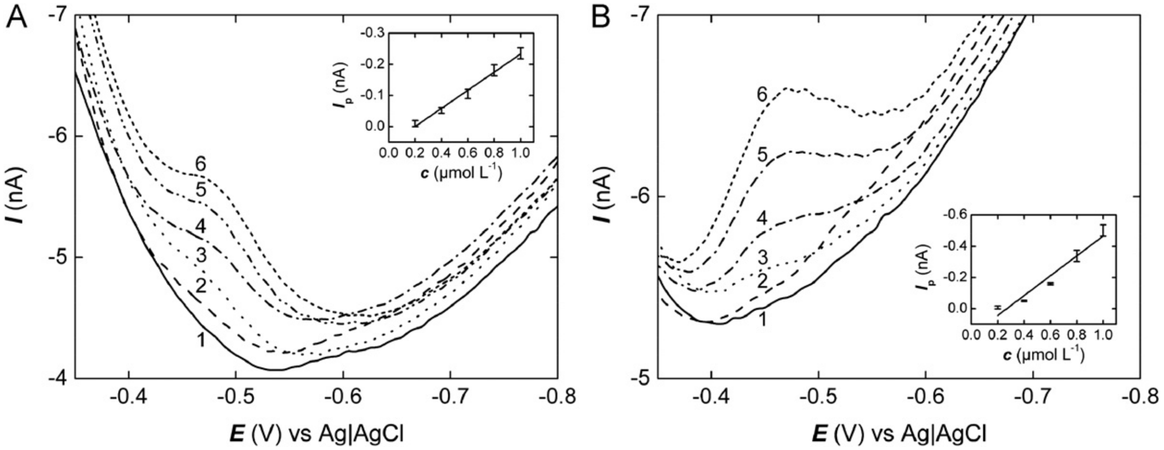

Fig. 5. DP voltammograms of ANBT at the BiF–AgSAE ($t_{dep}=300$ s) in model samples of tap (A) and mineral (B) water; measured in 9 mL of spiked waters diluted by BR buffer pH 10.0 to 10 mL (dilution factor 0.9) with the addition of EDTA to tap or mineral water; polarization rate 20 mV s^{-1}; concentrations of ANBT (μmol L^{-1}) in waters: 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), 1.0 (6); the corresponding calibration straight lines are given in the insets; the error bars are constructed for $\alpha=0.05$ ($n=3$).

in the concentration order of 10^{-8} mol L^{-1} was achieved for 5-nitrobenzimidazole at the BiF–AgSAE [41], whereas, at both BiF–GCE and BiF–AuE, the L_Qs were about two orders of magnitude higher [42]. In addition, the repeatabilities of twenty consecutive DPV measurements of 5-nitrobenzimidazole ($c=1\times10^{-4}$ mol L^{-1}) were 3%, > 5% and 1% at the BiF–AgSAE, BiF–GCE and BiF–AuE, respectively.

Simple mechanical renewal of the BiF–AgSAE surface, good reproducibility of measurements and elimination of problems connected with "electrode history" confirm practical usefulness of this electrode. Its major drawback is collective for all the BiFEs, i.e., its limited anodic range that prevents the use of this electrode for the determination or accumulation of species at more positive potentials [19].

4. Conclusions

It has been proved that newly developed bismuth film electrode on a silver solid amalgam support can be used as a working electrode for cathodic voltammetry. Both DC voltammetry (DCV) and differential pulse voltammetry (DPV) at the bismuth film modified silver solid amalgam electrode (BiF–AgSAE) can be used for the determination of submicromolar concentrations of genotoxic 2-amino-6-nitrobenzothiazole (ANBT). The sensitivity of this determination is ca. two times higher than that in the determination at the substrate electrode. The optimum time of the bismuth film deposition on the silver solid amalgam substrate (disc diameter 0.50 mm) was found to be 300 s. In the optimum medium found (BR buffer pH 10.0–methanol (9:1)), the measurable concentration range was 0.2–100 μmol L^{-1} of ANBT for both DCV (the limit of quantification, $L_Q\approx0.16$ μmol L^{-1}) and DPV ($L_Q\approx0.22$ μmol L^{-1}) determination at the BiF–AgSAE. The attempt to increase the sensitivity using adsorptive stripping DCV or DPV at the BiF–AgSAE was not successful.

The applicability of the tested electrode for DCV and DPV determination of ANBT in model samples of tap and mineral water (in the concentration range from 0.2 to 10 μmol L^{-1} of ANBT) has also been verified, with the L_Qs in the concentration order of 10^{-7} mol L^{-1}. Therefore, it can be concluded that the BiF–AgSAE can be successfully used for the determination of trace amounts of ANBT as suitable non-toxic and environmentally friendly alternative to electrodes containing metallic mercury.

Acknowledgments

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