

Bismuth Powder-Bulk-Modified Carbon Paste Electrode for the Voltammetric Determination of *Nitenpyram* Insecticide

Valéria Guzsvány^{1*}, Zsigmond Papp¹, Ivan Švancara², and Karel Vytřas²

¹ Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, RS-21000 Novi Sad, Republic of Serbia;

² Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic.

Abstract: In this article, voltammetric investigation of a commercial neonicotinoid insecticide, *Nitenpyram* (*Nit*), was carried out using a bismuth powder-bulk-modified tricresyl phosphate-based carbon paste electrode (Bi-TCP-CPE). The effect of the content of bismuth and of the electrode pretreatment are evaluated. The surface structure of the working electrodes was tested using scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS). Then, a new method employing the (direct) differential pulse voltammetry and the Bi_{5%}-TCP-CPE (*i.e.*, with 5% Bi, w/w) has been proposed for the determination of *Nit* at the low $\mu\text{g mL}^{-1}$ concentration level.

Keywords: Carbon paste electrode; tricresyl phosphate; bismuth powder, bulk modification; voltammetric determination, *Nitenpyram*.

*) Author to whom correspondence should be addressed. E-mail: valeria.guzsvany@dh.uns.ac.rs

Introduction

Nowadays, modern voltammetric methods in combination with a large variety of electrodes / detection systems, are usually simple, inexpensive, rapid, as well as sufficiently sensitive and selective to be employed for a large-scale monitoring of electrochemically active environmental pollutants [1,2].

Carbon paste electrodes (CPEs [3-5]), as a biggest group of the heterogeneous carbon electrodes enjoy wide popularity in the electrochemical and electroanalytical science, mostly because of their advantageous features, namely, simple preparation (often in labs in a wide range of various configurations, including very special mixtures), minimal costs (usually incomparable to those of commercially available carbon solid electrodes), favorable signal-to-noise characteristics (in both faradic and non-faradic measurements), unique surface characteristics (of hydrophobic nature given by the presence of lipophilic pasting liquid), and, mainly, almost unlimited possibilities of being chemically and biologically modified. And when one considers also their environmentally friendly character, wide adaptability to the latest trends, or a full compatibility with miniaturised detection systems and modern technologies, it is not so surprising that these electrodes are so frequently employed in the present day's electroanalysis, including the determination of various pesticides and related substances (see [6] and refs. therein).

While surface modification of carbon-based electrodes (normally, including also CPEs) with bismuth is well studied, bulk modification with the same element has, at the moment, a limited scope of applicability [7]. Bismuth powder-bulk-modified carbon paste electrodes were applied for the determination of selected metal ions [8], cysteine [9], 4-amino-3-nitrophenol [10], and also for *Imidacloprid* [7] – as a first example of application of such electrode for the analysis of a neonicotinoid insecticides.

Today, the neonicotinoids represent the fastest-growing class of insecticides introduced on market since the commercialization of pyrethroids [11,12]. *Nitenpyram* (*Nit*) represents one of the seven commercialized neonicotinoids (Fig. 1). Developed jointly by Takeda and Syngenta in 1995, *Nit* is mostly used in flea control in the animal health domain [13,14]. However, additional uses for the control of sucking insects capable of largely damaging the important field crops like rice, tea, or various vegetables and fruits were tested in Japan, having resulted in a new product with commercial name *Bestguard* [13].

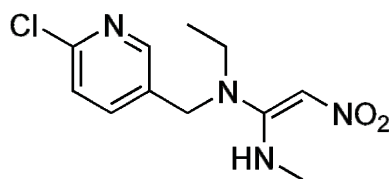


Fig. 1: Structural formula of *Nitenpyram* [*Nit*; (E)-N-(6-Chloro-3-pyridylmethyl)-N-ethyl-N'-methyl-2-nitrovinylidene-diamine].

In this article, an attempt was made in the use of the bismuth bulk modified tricresyl phosphate-based carbon based electrode (Bi-TCP-CPE) for voltammetric determination of a commercial neonicotinoid insecticide *Nit*. All the important results and observations from the development and testing of the respective method are described below.

Experimental

Chemicals, Reagents, Stock, and Standard Solutions

All chemicals used were of analytical reagent grade and the solutions were prepared in doubly distilled water. Analytical standard of *Nit* (*Sigma-Aldrich Laborchemikalien GmbH*, Germany, PESTANAL[®]) of neonicotinoids was of 99.9% purity. The concentration of the *Nit* stock solution was 176.0 $\mu\text{g mL}^{-1}$ ($6.5 \times 10^{-4} \text{ mol L}^{-1}$), and it was further diluted as required.

Britton-Robinson buffer (BRB) with pH 7.0 was prepared from a stock solution containing 0.04 M phosphoric, boric, and acetic acids, by adding of 0.2 M sodium hydroxide (all four chemicals purchased from *Merck*) in order to obtain the required pH value.

Electrochemical Apparatus and Other Instrumentation

In all voltammetric measurements an electrochemical system AUTOLAB PGSTAT12 (*Eco Chemie*; The Netherlands) was used in combination with GPES software (the same manufacturer). The cell stand included a three-electrode system with a CPE as working, a saturated calomel electrode (SCE) (*Amel*, Italy) as reference, and a platinum (*Amel*) auxiliary electrode. All potentials are quoted vs. SCE reference electrode.

The surface of the bulk modified electrodes were examined on a *JEOL* (Japan) scanning electron microscope with an accelerating voltage of 20 kV in low vacuum mode at the working distance of 20 mm, using a secondary electron detector. The surface microanalyses using an energy dispersive spectrometry (EDS) were carried on a representative surface area. The electrodes were measured directly without any surface pretreatment.

Carbon Paste Electrode

Carbon Paste. The unmodified TCP-CPE was prepared by hand-mixing of 0.25 g graphite powder (*Graphite Týn*, Czech Republic) with 0.1 mL tricresyl phosphate (mixture of isomers, *Sigma-Aldrich*); the detailed procedure of the electrode preparation being described earlier [15].

The bismuth powder-bulk modified pastes were prepared by replacing 5 or 20 % (w/w) of the carbon powder with bismuth powder (99.99%, 100 mesh, *Aldrich Chem*) [7], when the mixing procedure was otherwise identical to that for the native carbon paste.

Carbon Paste Electrodes (CPEs). The prepared pastes were packed into the piston-driven holder [16,17] with the surface diameter of 2 mm. Whenever needed, the CPE surface was renewed mechanically – by wiping off the used CP-layer, when extruding and smoothing the new one.

Voltammetric Measurements

Nit was measured in 5.00 mL of the solution of different concentration, to which 5.00 mL BRB pH 7.0 was added. Scan rate in cyclic voltammetry was $v_{CV} = 25 \text{ mV s}^{-1}$. Operational parameters in differential pulse voltammetry (DPV) were as follows: the pulse amplitude, $\Delta E = 50 \text{ mV}$, pulse width, $w = 50 \text{ ms}$, and the scan rate, $v_{DPV} = 25 \text{ mV s}^{-1}$ [15]. Otherwise, the solutions were measured without filtering, at ambient temperature.

Results and Discussion

Characterization of the Electrodes

As our previous experiments showed, that the TCP is a convenient binder because imparts polar behavior to the carbon paste, allowing sensitive determination of neonicotinoids [15,18-22]. In this work we tried to compare the behavior of unmodified TCP-CPE with the bismuth powder modified ones in the determination of *Nit*.

Firstly, there was a need for the morphological characterization of the modified electrodes, similarly to earlier investigations concerning the unmodified TCP-CPE [15]. Fig. 2 shows the typical morphology of the Bi-TCP-CPE modified with 5% (w/w) powdered bismuth (further denoted as “Bi_{5%}-TCP-CPE”; see images A, C, and E) or 20%, respectively (“Bi_{20%}-TCP-CPE” type; see B, D, and F). It can be seen that the basic carbon matrix contains random distributed non-homogeneities which are — as expected — more frequent in the case of the TCP-CPE modified with 20% bismuth powder. The EDS measurements performed on two different parts of the representative Bi_{5%}-TCP-CPE surface, selected so that one of them contains the above-mentioned non-homogeneity, proving that these irregularities are, in fact, “bismuth islands” in the tricresyl phosphate-based carbon paste matrix – see Fig. 3.

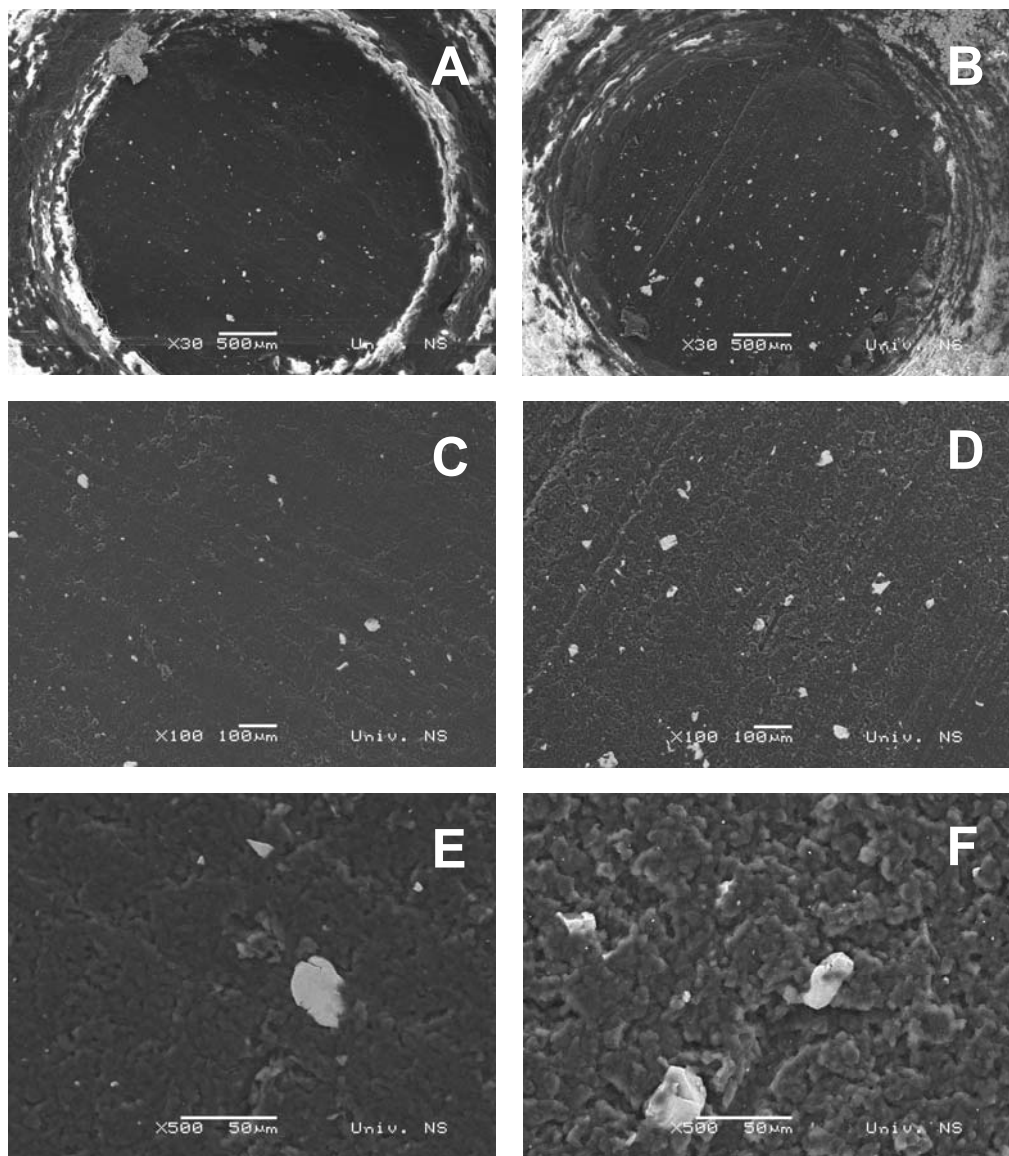


Fig. 2: SEM micrographs of the $Bi_{5\%}$ -TCP-CPE (A,C,E) and $Bi_{20\%}$ -TCP-CPE (B,D,F) at magnifications of 30x (A,B), 100x (C,D) i 500x (E,F).

In the next step the effect of the potential cycling – as an electrode conditioning step – on the basic characteristics of the Bi-TCP-CPEs was tested and compared to the results achieved with the unmodified TCP-CPE (Fig. 4). It was earlier proved that the unmodified TCP-CPE shows a significant sensitivity to the presence of the dissolved oxygen in the

cathodic range [15], opposite to the bismuth powder modified ones [7]. Because of that, the measurements using a bare TCP-CPE were carried out after removing of the oxygen by purging the solutions with inert gas (nitrogen).

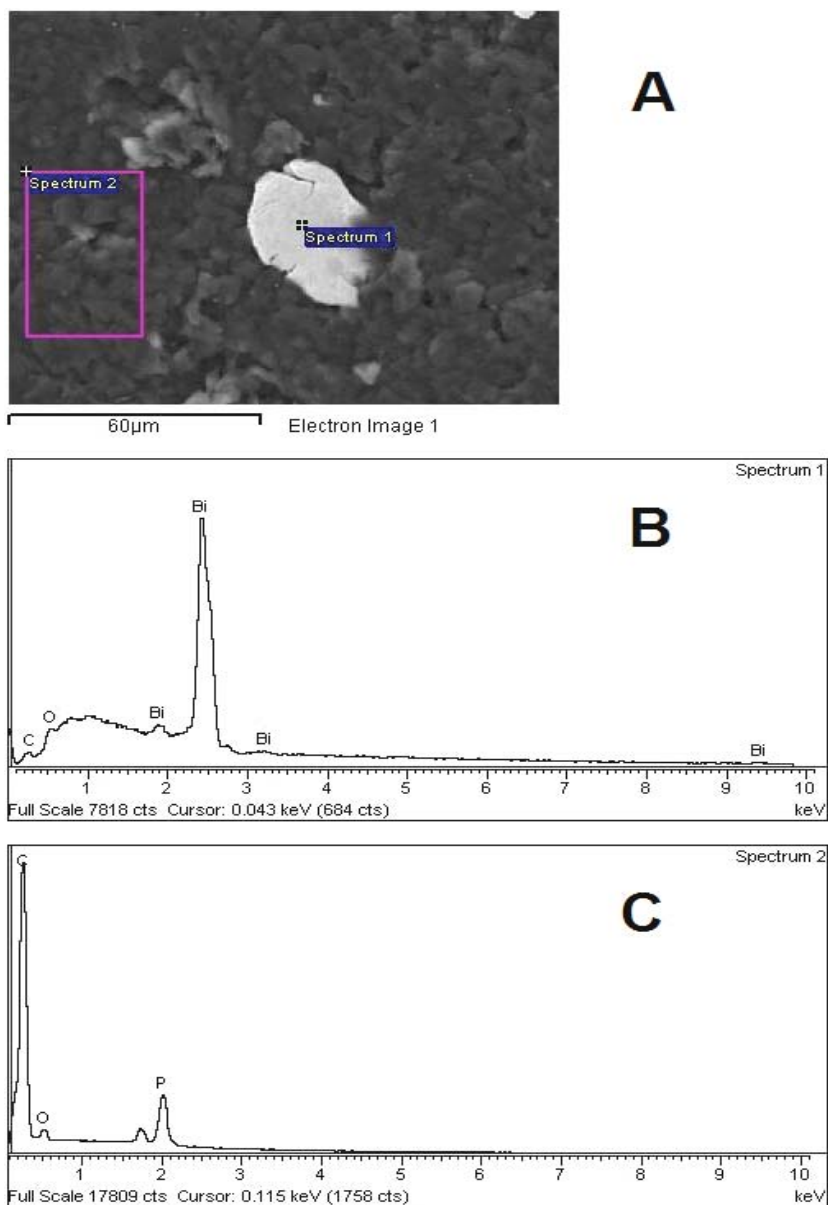


Fig. 3: Representative part of the Bi_{5%}-TCP-CPE surface (A). EDS-microanalysis spectra of the bismuth-rich surface area (B) and of the carbon paste matrix (C) (assembled after cit. [7]).

The bismuth powder modified electrodes were investigated in the presence of the dissolved oxygen. As can be seen in Fig. 4, the voltammograms show a very distinct effect of the potential cycling in the investigated potential range (from -0.6 to -1.5 V vs. ref.). In all cases, a significant signal stabilization and residual current decrease was achieved after ten cycles. Further treatment of the electrodes did not lead to significant improvements.

On the other hand, it is also clearly visible, that the presence of the elementary bismuth in the TCP-CPE matrix led to appearance of spiky noises on the CV signals. The frequency of these noises is directly correlated with the amount of the bismuth modifier. It is also clear that the modification led to a bit higher background currents in the investigated range, which was also directly connected with the amount of the bismuth powder in the TCP-CPE matrix.

The DPV investigation of the baselines by applying the potential cycling on Bi_{5%}-TCP-CPE and Bi_{20%}-TCP-CPE (Fig. 5) also confirmed that the frequency of the spiky noises is directly correlated with the amount of the modifier. On the other hand, the intensity of the peak appearing on the DPV signals in the potential range between -0.60 and -0.85 V vs. ref. is also directly dependent on the bismuth content. Coincidentally, the position of this peak, did not make any difficulties or troubles in the analysis of *Nit* whose reduction took place at a potential of about -1.3 V vs. ref. (see Fig. 6).

Voltammetric Determinations Using the Bi_{5%}-TCP-CPE and Bi_{20%}-TCP-CPE

After detailed characterization of the electrode surface and the overall electrode properties in the investigated potential range, it was tried to develop a quantitative DPV method for the determination of *Nit*. Earlier experiments [20-22] showed that the electrochemical reduction of *Nit* at TCP-CPE is an irreversible reduction process; see Fig. 6. Also, it was shown that the optimal conditions for its determination requires pH 7.0. Bearing in mind all these data, no additional characterization of the target compound was done in this work.

The reproducibility of the analytical signal in DPV measurements for both Bi_{5%}-TCP-CPE (Fig. 7A) and Bi_{20%}-TCP-CPE (Fig. 7B) was determined by obtaining eight records for a *Nit* concentration of $9.96 \mu\text{g mL}^{-1}$ in the time interval around 30 min. As clearly evident, the signal of the investigated compound showed no significant changes during the time, so apart from high reproducibility, it also confirms that no unwanted adsorption / absorption processes occur during these direct voltammetric measurements.

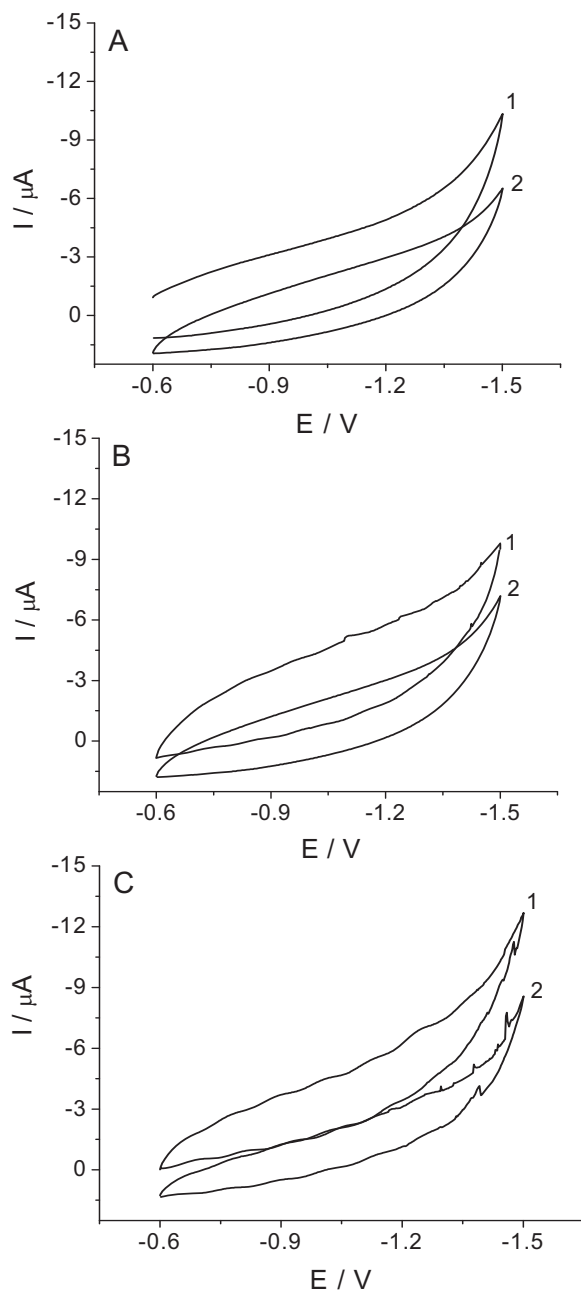


Fig. 4: Typical cyclic voltammograms obtained during the potential cycling of bare TCP-CPE (A), $\text{Bi}_{5\%}$ -TCP-CPE (B), $\text{Bi}_{20\%}$ -TCP-CPE (C) in Britton-Robinson buffer (pH 7); $\nu = 25 \text{ mV s}^{-1}$: Legend: The first cyclic voltammogram (1) and the tenth replicate (2).

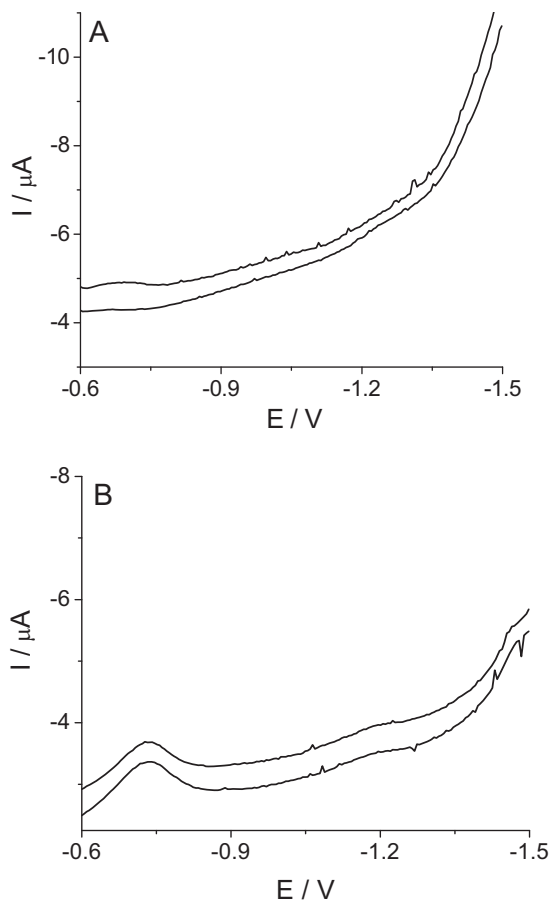


Fig. 5: Typical DPV-baselines (blank) for $\text{Bi}_{5\%}\text{-TCP-CPE}$ (A) and for $\text{Bi}_{20\%}\text{-TCP-CPE}$ (B) obtained in Britton-Robinson buffer (pH 7.0). Presented in two replicates.

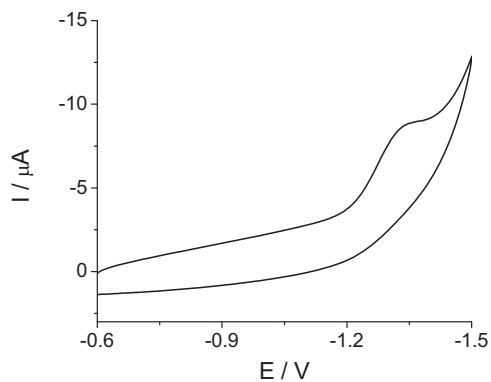


Fig. 6:
CV signal of $29.33 \mu\text{g mL}^{-1}$ Nit at the bare TCP-CPE and obtained in Britton-Robinson buffer with pH 7.

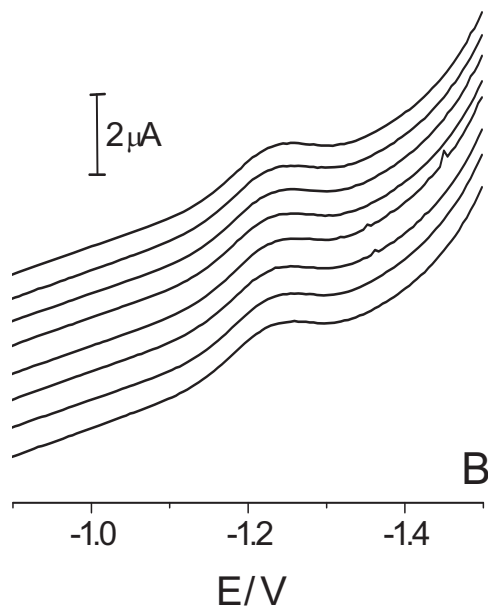
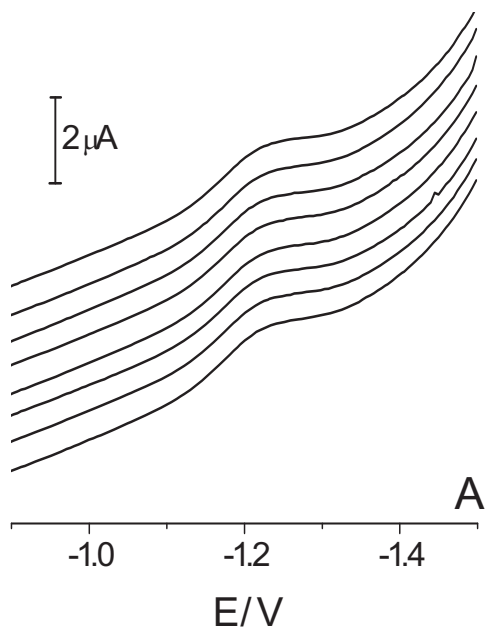


Fig. 7: Reproducibility of the signal of interest for $9.96\ \mu\text{g mL}^{-1}$ Nit at $\text{Bi}_{5\%}\text{-TCP-CPE}$ (A) and at $\text{Bi}_{20\%}\text{-TCP-CPE}$ (B) in the time interval for 30 min. Both in eight replicates

At the end, DPV signals for the low ppm concentration level of *Nit* at Bi_{5%}-TCP-CPE (see Fig. 8A) and Bi_{20%}-TCP-CPE (Fig. 9A), both obtained in the BR-buffer (pH 7.0) could be calibrated, giving fine linear plots (Figs. 8B, 9B).

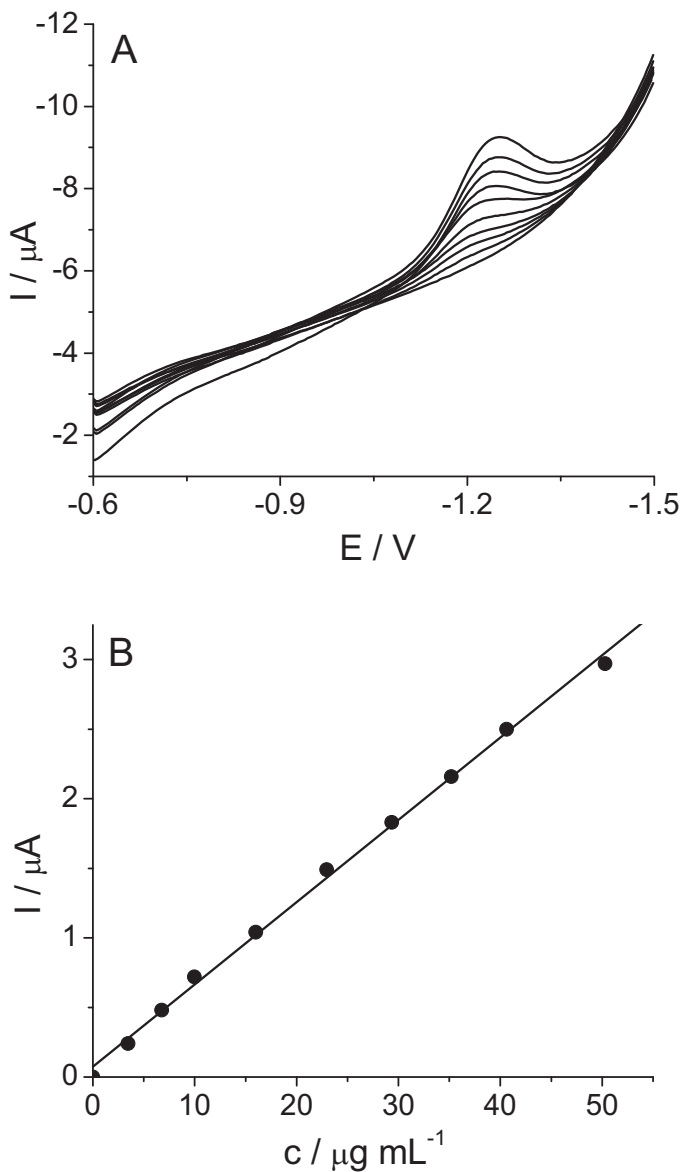


Fig. 8: DPV signals recorded at Bi_{5%}-TCP-CPE (A) in Britton-Robinson buffer (with pH 7.0) together with the corresponding calibration curve (B) for the low $\mu\text{g mL}^{-1}$ concentration level.

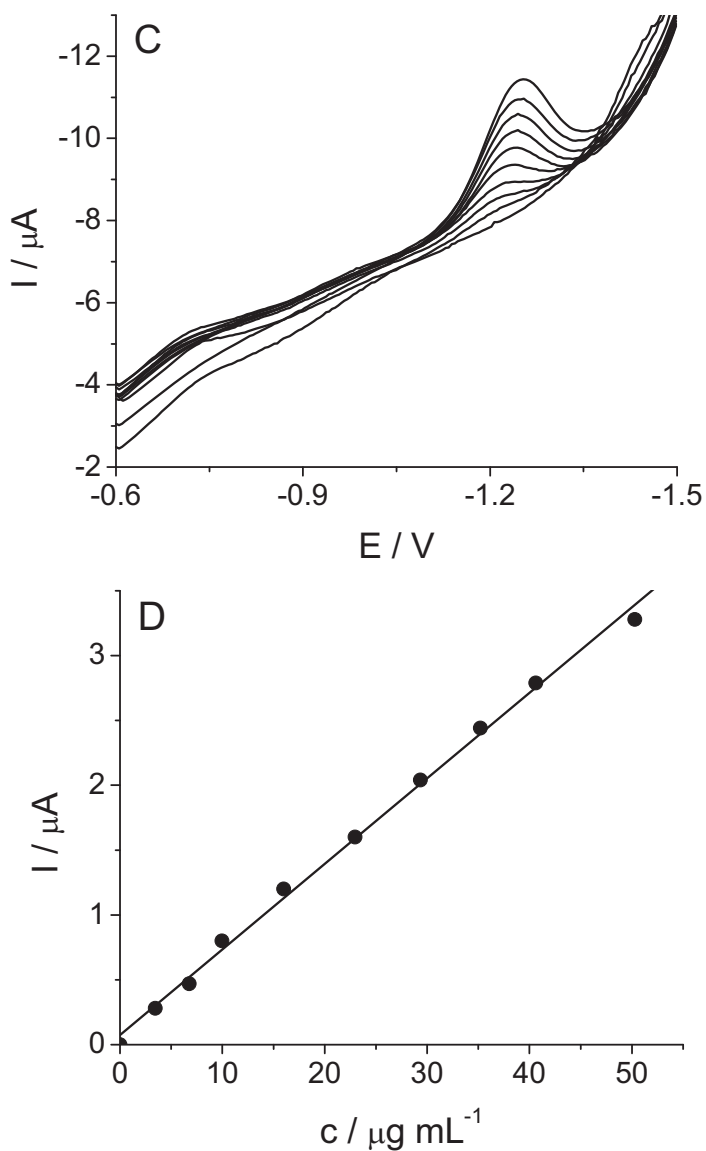


Fig. 9: DPV signals recorded at $Bi_{20\%}$ -TCP-CPE (A) in Britton-Robinson buffer (with pH 7.0) together with the corresponding calibration curve (B) for the low $\mu g \cdot mL^{-1}$ concentration level.

Thanks to a high signal-to-noise ratio when considered *via* the absolute current intensities, both calibration dependences were practically unaffected by somewhat enhanced background, which is a typical feature of experiments with the CPE-TCP [4,5].

The comparison of the data obtained at the bulk modified electrodes in the presence of the oxygen with the data of the unmodified TCP-CPE after oxygen removal have resulted in similar values, confirming again the applicability of the bismuth-powder modified electrodes in practical analyses focused on the determination of *Nit*.

The linearity of the calibration plot was checked in the range of 2.7–50.3 $\mu\text{g mL}^{-1}$. The calculated values of the limit of detection (LOD) (3σ) were 0.89 and 0.81 $\mu\text{g mL}^{-1}$ for Bi_{5%}-TCP-CPE and Bi_{20%}-TCP-CPE, respectively. The analytical data for the all investigated electrodes are shown in Table I.

Table I: Analytical parameters for the direct DPV determination of *Nitenpyram* at the bare TCP-CPE, Bi_{5%}-TCP-CPE, and Bi_{20%}-TCP-CPE.

Parameter \ Electrode	Bare TCP-CPE*	Bi _{5%} -TCP-CPE	Bi _{20%} -TCP-CPE
Concentration interval [$\mu\text{g mL}^{-1}$]	2.51-29.33	2.97–50.28	2.70–50.28
Intercept [μA]	0.0452	0.0743	0.0752
Slope [$\mu\text{A mL } \mu\text{g}^{-1}$]	0.0714	0.0591	0.0659
Correlation coefficient, r^2	0.998	0.999	0.998
LOD [$\mu\text{g mL}^{-1}$]	0.75	0.89	0.81
LOQ [$\mu\text{g mL}^{-1}$]	2.51	2.97	2.70
RSD [\pm , %] ($n=8$)	0.83	1.93	1.13

Legend: LOD: limit of detection; LOQ: limit of quantification; *) made after [20-22].

On the other hand, markedly higher level of the oscillation noise in the case of Bi_{20%}-TCP-CPE may negatively affect the analysis, which does not seem to be the case of Bi_{5%}-counterpart that could be reliably used also for the determination of *Nit* in the presence of dissolved molecular oxygen, O₂. As discussed in detail in our previous reports [4,5] and newly illustrated in Fig. 10 overleaf, the parasitic (double) signal for the two-step reduction of dioxygen, O₂ → HO₂⁻ → H₂O, is much less pronounced at the TCP-CPE substrate than any other carbon paste-based electrode.

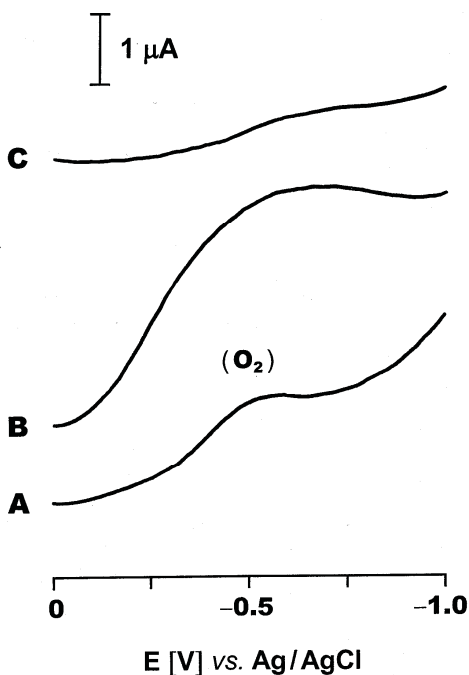


Fig. 10:

Cathodic polarization of carbon pastes and the respective reduction responses of dioxygen

Legend: **A)** typical reduction signal (ordinary carbon paste mixture of the mineral-oil type), **B)** atypically large signal (carbon paste made of a graphite with enhanced adsorption capabilities), **C)** the lowered signal at the CPE-TCP.

(Redrawn from [5] and re-edited by extending the original legend)

In fact, this effect of suppressing the undesirable response of oxygen is one of the atypical features of the TCP-CPE which — as such — has been of particular interest in our newest review [6]. Herein, the respective information about this rather unusual carbon paste can be extended by interpreting this anomaly *via* a series of microscopic studies performed within the last decade and focused exclusively on the carbon paste microstructure (see *e.g.* [15,23-25]). The individual (scanning electron) microscopic observations with the TCP-containing carbon paste mixtures indicate clearly that this mixture forms relatively large and tightly arranged aggregates that fill up the normally occurring air-gaps inside the carbon pastes [4]. Otherwise speaking, in the TCP-based carbon paste, the graphite particles are so thoroughly covered with highly lipophilic molecules of tricresyl phosphate (see the respective SEM images in refs. [4] and [23]) that there is only minimal interior space for entrapping air oxygen — readily reducible species that subsequently make troubles during the cathodic scanning. And, with respect to the bismuth-modified configuration used in this study, it can be deduced that the electrochemical properties of the substrate — *i.e.*, of the TCP-CPE itself — are being reflected in behavior of the resultant Bi-TCP-CPE configuration, giving to this electrode its favorable polarization / depolarization characteristics [4,5,25].

Conclusions

In this contribution, a new voltammetric method has been developed for the determination of *Nit*, using a tricresyl-phosphate based carbon paste electrodes bulk modified with two different amounts of bismuth powder (with 5% and 20% Bi, respectively) in aqueous Britton-Robinson buffer (pH 7.0) as the supporting electrolyte.

As found, the electrode with 5% Bi has been superior to the second one tested, because the experimentation in the DPV mode has less suffered from the higher background and/or electrical noise, as typical feature of each TCP-based CPE. Also, the Bi_{5%}-TCP-CPE has enabled the employment in the presence of dissolved oxygen in the sample.

It can be stated that the method developed and described above can be recommended for orientation measurements as inexpensive tool for obtaining a rapid information about the content of the pollutant — herein, insecticide *Nit* — in the sample or any other material to be analysed. Otherwise, most of measurements performed have suggested us that further experiments are still needed to confirm fully the applicability of the bismuth-modified TCP-CPE in analysis of real samples.

Acknowledgements

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