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Renewable Silver-Amalgam Film Electrode for Direct Cathodic SWV Determination of Clothianidin, Nitenpyram and Thiacloprid Neonicotinoid Insecticides Reducible in a Fairly Negative Potential Range

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A voltammetric characterization of three commercial neonicotinoid insecticides, thiacloprid (TCL), clothianidin (CLO), and nitenpyram (NIT), was carried out to optimize the procedure of their determination using the renewable silver-amalgam film electrode (Hg(Ag)FE) in the aqueous solution of Britton-Robinson supporting electrolyte. The characterization measurements in the pH range between 2.0 and 8.0 showed two reduction peaks of NIT and CLO, and one of TCL, which appeared in a fairly negative potential range (approximately from -0.8 to -1.6 V), and whose shapes strongly depended on the pH of the supporting electrolyte. For the analytical purpose, the selected pH was 7.0 for NIT and TCL, and 7.5 for CLO. The analytes were determined by the optimized direct square wave voltammetry (SWV) in the concentration ranges (μg mL^{-1}) of 0.58–5.96 for the first and 0.61–5.96 for second peak for NIT, 0.91–5.62 for TCL, and 1.51–54.08 for CLO. The reproducibility of the analytical signals was characterized by a relative standard deviation smaller than 1.0%. The procedure was applied for the determination of the insecticides in spiked river water samples, and TCL in its commercial formulation Calypso® 480-SC.

Keywords: Thiacloprid, clothianidin, nitenpyram, renewable silver-amalgam film electrode, square wave voltammetry, determination

1. INTRODUCTION

Today, neonicotinoids are one of the most important categories of insecticides introduced to the global market since the synthetic pyrethroids. They are registered in more than 120 countries, being

generally regarded as the most powerful insecticides for control of sucking insect pests like aphids, whiteflies, leaf- and plant-hoppers, thrips, some micro-Lepidoptera, or some other coleopteran pests [1-3]. Thus, massive and still expanding application of neonicotinoids requires also new analytical measurements that can be operated in very diverse samples, including the reliable monitoring of the photodegradation processes.

The methods of choice for the determination of neonicotinoids are being based on high- and ultra-performance liquid chromatography (HPLC and UPLC), combined with the sensitive detection by a diode-array (DAD) [4,5], mass spectrometry [6-9], or thermal-lens spectrometry [10].

As is well known, voltammetric techniques, as a good alternative to the above methods, can be used in the analysis of neonicotinoids with different electroactive fragments like nitroguanidine (imidacloprid (IMI), thiamethoxam (TIA), clotianidin (CLO)), nitromethylene (nitenpyrame (NIT)), and methylamine (acetamiprid, (ACT) and thiacloprid (TCL)) [11-26]. A common denominator for all the mentioned compounds is that their reduction signals are observed in a fairly negative range of potentials. The measurements can be performed using several techniques such as cyclic voltammetry (CV) [11], differential pulse polarography / voltammetry (DPP / DPV) [12−14, 19-22, 26], or square-wave voltammetry (SWV) [20-26]. Regarding this specific group of insecticides, the individual methods proposed for their determination have employed the mercury-based working electrodes [12-17, 23-26] or various unmodified and modified carbonaceous electrodes [11, 18-22, 26].

Modern voltammetric methods are fast, sensitive and inexpensive, and thus suitable for a large-scale monitoring of electrochemically active environmental pollutants [27, 28] often easily adaptable for in field work. Mercury electrodes are obviously the best sensors for the voltammetric determination of electrochemically reducible compounds [27], especially those that are electroactive in a fairly negative potential range, like NIT and TCL [26]. However, because of the fears of mercury toxicity, the tendency is to replace mercury with other nontoxic or less toxic electrode materials [27, 28].

One of the promising alternatives to the family of mercury electrodes are the group of different solid amalgam electrodes [23-25, 27-44] such as dental amalgam electrodes (DAEs) [28-31] and metal solid amalgam electrodes (MeSAEs) [23-25, 32-44]. The wide potential window, low noise, ease of electrochemical renewal of the surface, and mechanical robustness, all this makes them applicable in flow liquid systems. Besides, simple preparation and regeneration make amalgam electrodes a very promising electroanalytical tool [27, 28] compatible with the concepts of green analytical chemistry. The DAEs was used mainly for the determination of metals [28-31], but their application in the analysis of biologically active organic compounds has also been reported [27]. MeSAEs are widely used and fully compatible with both centralized and decentralized testing of electrochemically reducible pollutants [32-44]. An important feature of these electrodes is their mechanical stability, so that they can be used for the measuring in flowing systems such as HPLC-ED or FIA-ED. The problem of limiting the amount of mercury or its soluble salts in the analytical procedures can be solved with the help of a renewable silver amalgam-film electrode (Hg(Ag)FE) [35-44], which is in fact an MeSAE. The electrode is designed in such a way that the thin amalgam sensor layer can easily be regenerated before each measurement / or measurement cycle, which ensures a good reproducibility of the results. The first proposal for the construction of an Hg(Ag)FE and the principles of its operation were described in [36, 37]. The main rationale behind the electrode is the replacement of the toxic

reagent, miniaturization, and a dramatic reduction in the amounts of reagents consumed and waste generated, thus reducing/avoiding the side effects of the analytical method [38]. The application of the electrode well corresponds to the definition of "green chemistry", that is, "the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc. that are hazardous to human health or the environment" [38]. Hg(Ag)FEs have been successfully used in the determination of several elements (Pb, Zn, Cd, Cu, Cr, Co, Ni, elemental S, Mn, Mo, Se, U, Pd, Sc) in water, snow, sediment samples, and chemical reagents [36,37, 39-42]. A first example of the application of Hg(Ag)FE for the determination of organic compounds was the determination of B_1 vitamin by SWV [43]. There are three procedures concerning the dinotefuran, moroxydine, and Blasticidine S compounds for adsoprtive stripping analysis [25, 38, 44] of their traces in different samples. Recently, a renewable Hg(Ag)FE-based SWV method was successfully applied for the monitoring of solar photodegradation of the imidacloprid insecticide in the presence of the Fe/TiO_2 and TiO_2 catalysts [23] and determination of thiamethoxam contents in different samples like river water, commercial formulation and honey samples [24].

Relying on our previous experiences with the Hg(Ag)FE-based SWV determination of IMI [23] and TIA [24] we continue the voltammetric investigations of another neonicotinoid with the same nitroguanidine moiety (CLO, Fig. 1A), as well as with methylamine (TCL, Fig. 1B) and nitromethylene (NIT, Fig. 1C) electroactive pharmacophores.

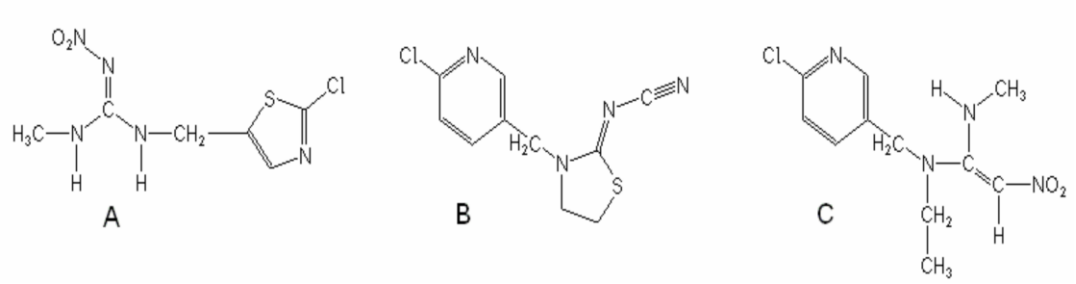

Figure 1. Chemical structures of the investigated neonicotinoids: CLO (A), TCL (B) and NIT (C)

After investigating their voltammetric behavior in the Britton-Robinson buffer supporting electrolyte, the optimized Hg(Ag)FE-based SWV method was used to determine these three neonicotinoids in river water samples and in a selected commercial formulation of TCL (Calypso® 480-SC). The obtained results were compared with corresponding HPLC-DAD measurements.

2. MATERIALS AND METHODS

2.1. Chemicals and Solutions

All chemicals used were of analytical reagent grade and the solutions were prepared in doubly distilled water. Analytical standards (Sigma-Aldrich Laborchemikalien GmbH, Germany, PESTANAL®) of the neonicotinoids were of 99.9% purity. The concentrations of the stock solutions were 100.0, 120.0 and 266.0 μg mL^{-1} for CLO, TCL and NIT, respectively, and they were further diluted as required.

The Britton-Robinson buffer solution were prepared from a stock solution containing 0.04 mol L^{-1} phosphoric (Merck, Germany), boric (Merck) and acetic (Merck) acids, by adding 0.2 mol L^{-1} sodium hydroxide (Merck) to obtain the required pH value. For the preparation of the mobile phase in the HPLC experiments, acetonitrile (J. T. Baker, Netherlands, purity 99.8%) and 0.2% phosphoric acid (made by diluting phosphoric acid (Centrohem, Serbia)) were used.

The river water sample was collected from the Danube River (Novi Sad, Republic of Serbia) and stored in the dark at 4°C for one week before analysis. Commercial formulation of TCL was Calypso® 480-SC (Syngenta Crop Protection AG, Switzerland).

2.2. Apparatus

Voltammetric experiments were performed on an AUTOLAB PGSTAT12 electrochemical analyzer operated via GPES 4.9 software (Ecochemie, The Netherlands). The cell stand included a three-electrode system with a Hg(Ag)FE as working, a saturated calomel electrode (SCE) (Amel, Italy) as reference, and a platinum (Amel) auxiliary electrode. All potentials are quoted vs. the SCE reference electrode. Comparative HPLC measurements were performed using an Agilent 1100 liquid chromatograph (Agilent Technologies Inc., USA), Zorbax Eclipse XDB-C18 (250 mm × 4.6 mm, 3.5 μm) column, and DA-detector.

2.3. Procedures

Voltammetry on Hg(Ag)FE. In the model systems, the neonicotinoids were measured in 5.00 mL of the solution of different concentration, to which 5.00 mL of Britton–Robinson buffer was added. In the case of real samples, the solutions for the analysis were prepared from a mixture of aqueous solution of analyte and Britton–Robinson buffer (1:1, V/V). The measurement parameters in SWV were as follows: the pulse amplitude, 20 mV, step potential 5 mV, and step frequency 30 Hz. The deaerated solutions (nitrogen stream, 10 min) were measured without filtering, at ambient temperature.

HPLC-DAD. For the comparative analysis, all aliquots were filtered through the Millex 0.22 μm syringe filters. The mobile phase was a mixture of water (0.2% phosphoric acid) and acetonitrile (85:15, v/v). The reversed phase separation was performed at the isocratic regime, the flow rate was 0.8 mL min^{-1}, and the column temperature was held at 25 °C. The neonicotinoids were detected at their main absorption maxima 242, 266, and 270 nm, respectively for TCL, CLO, and NIT. Concentrations of the investigated compound were determined from the area of the corresponding peak.

3. RESULTS AND DISCUSSION

The experiments encompassed the SWV characterization of CLO, NIT and TCL model solutions in the Britton-Robinson supporting electrolyte (pH 2.0-9.0) using Hg(Ag)FE, optimization of the corresponding analytical procedure for their determination by direct cathodic SWV in model

solutions, and testing of the developed method for the determination of CLO, NIT and TCL in spiked river water samples, as well as for the determination of the active ingrediant TCL in its commercial formulation Calypso® 480-SC.

3.1 Voltammetric investigation of NIT, TCL, and CLO at Hg(Ag)FE

In view of the fact that the electroanalytical behavior of neonicotinoids is significantly influenced by the pH of the solution [18-24, 26], the SWV curves were recorded in the range of pH 2.0-9.0 in order to study the effect of the hydronium ion concentration on the neonicotinoid reduction signals and to define the optimal pH for the determination.

Like IMI and TIA, the CLO molecule contains an electroactive nitro group in its nitroguanidine pharmacophore which can be readily reduced at the Hg(Ag)FE, (Fig. 2A). In the investigated potential range between -0.4 V and -1.6 V, there are two reduction signals which are well separated in the pH range from 6.0 to 8.0. At lower pH values, the second peak is overlapped with the peak of hydrogen evaluation. The current of the first peak I_p is 20 times higher compared to that of the second peak. The SWV curves for all three analytes and the corresponding E_p-pH dependence are presented in Fig. 2. Generally, both peaks obtained at Hg(Ag)FE shift cathodically with the increase in the pH, the first from -0.8 to -1.0 V, and the second from -1.1 to -1.5 V. This behavior is in accordance with the previous findings with dropping mercury electrode for IMI, TMO and CLO [12,14,16,26]. The E_p–pH plots for the first peak (Fig. 2B) exhibit two linear parts with a break at approximately pH 5; the slope of the first part being 142 mV pH^{-1} (not shown) and that of the second one 29 mV pH^{-1} (r = 0.992). The E_p–pH correlation of second peak was described with linear function which slope was 91 mV pH-1 (r = 0.997). Such behavior indicates the involvement of protons and that the proton-transfer reaction precedes the electrode process proper, indicating a complex electrode process [12,14,16,26]. Based on the literature data and the similarity of the SWV signals obtained for IMI and TMO, it may be supposed that in a medium with the pH $\geq$ 5, the first step is the reduction of the nitro group to hydroxylamine, while the second step is the reduction of hydroxylamine to amine, involving four and two protons in the two reactions [12,14,16,26].

The reduction of NIT, occurring at the potentials that are more negative than –1.3 V, takes place at two peaks which are best pronounced in the pH range from 7.0 and 8.0 (Fig. 2C). At the lower pH values, the second peak is overlapped with the signal of hydrogen evaluation (not shown). In contrast to CLO, the reduction peaks of NIT have very similar I_p values (e.g. -3.0 μA and -3.1 μA at pH 7.0 and at c = 5.3 μg mL^{-1}). This can be ascribed to the fact that, instead at the nitroguanidine group, the reduction takes place at the nitromethylene functional group. Like in the previous case, the reduction peaks shift to the negative direction with the increase in the pH, the first from -1.3 to -1.5 V (between pH 6.0 and 8.0), and the second from -1.5 to -1.7 V (between pH 7.0 and 8.0). The peaks are characterized by the very similar E_p-pH dependence, the slope for the first peak being 56 mV pH^{-1} (r = 0.972) and for the second 64 mV pH^{-1} (r = 0.983), which means that the number of the exchanged electrons and protons are the same.

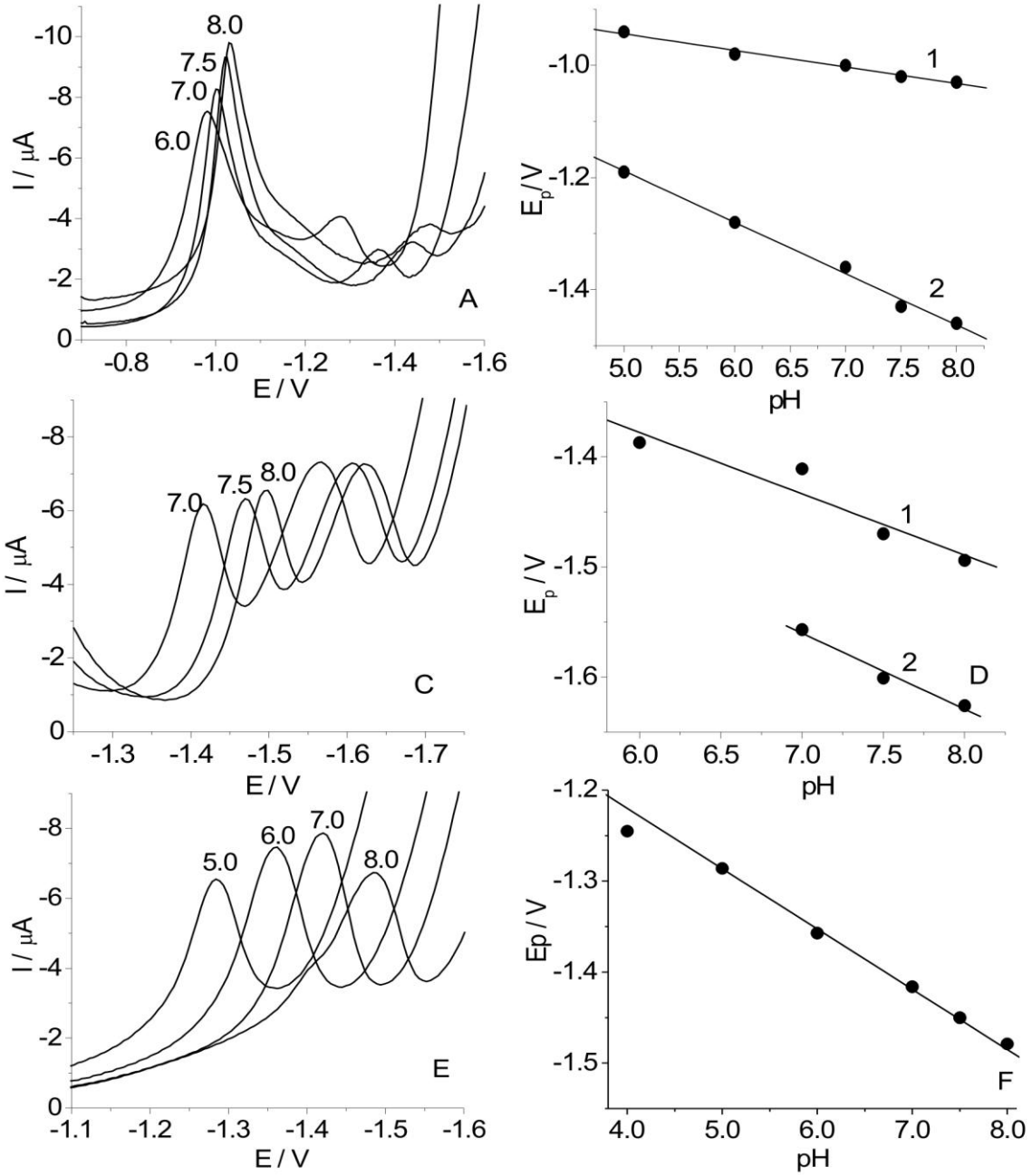

Figure 2. Influence of the pH (values indicated at the curves) on the shape of the SWV curves for CLO (A), NIT (C) and TCL (E) and the corresponding E_p-pH dependences (B, D and F)

In the investigated region of potentials, TCL shows only one reduction peak which is observed in the range of pH 4.0-8.0. The *Ep*-pH dependence can be described as linear, whose slope of 67 mV pH^{-1} (r = 0.997) indicates that the ratio of the exchanged electrons and protons is most probably one. Like in the case of CLO and NIT, the I_p values are also influenced by the pH of the medium.

Like every solid working electrode, the Hg(Ag)FE also requires renewal and/or conditioning of the sensor surface. In accordance with the previous findings [23,24], the procedure for renewing the mercury film on the Hg(Ag)FE was carried out before each set of measurements. Besides, Hg(Ag)FE

was activated electrochemically by cycling its potential in the range from -0.20 to -1.60 V in the corresponding Britton-Robinson supporting electrolyte. In the case of need (which is recognized as the loss of the electrode sensitivity), chemical activation in 2% V/V HNO_3 was applied to clean the sensor surface. The cleaned electrode was again covered with amalgam by dipping into the attached mercury pool [36,39] and subjected to electrochemical conditioning.

3.2 Direct cathodic SWV determination of NIT, CLO and TCL

As first, the signal stability at the Hg(Ag)FE was checked by replicated recording of the SWV reduction curves for CLO, NIT and TCL at the levels of 16.67, 3.46 and 2.93 μg mL^{-1}, at pH 7.0 (for NIT and TCL) and 7.5 (for CLO), respectively, in an interval of 30 min (Fig. 3). No significant changes in the electrode response were observed during the measurements.

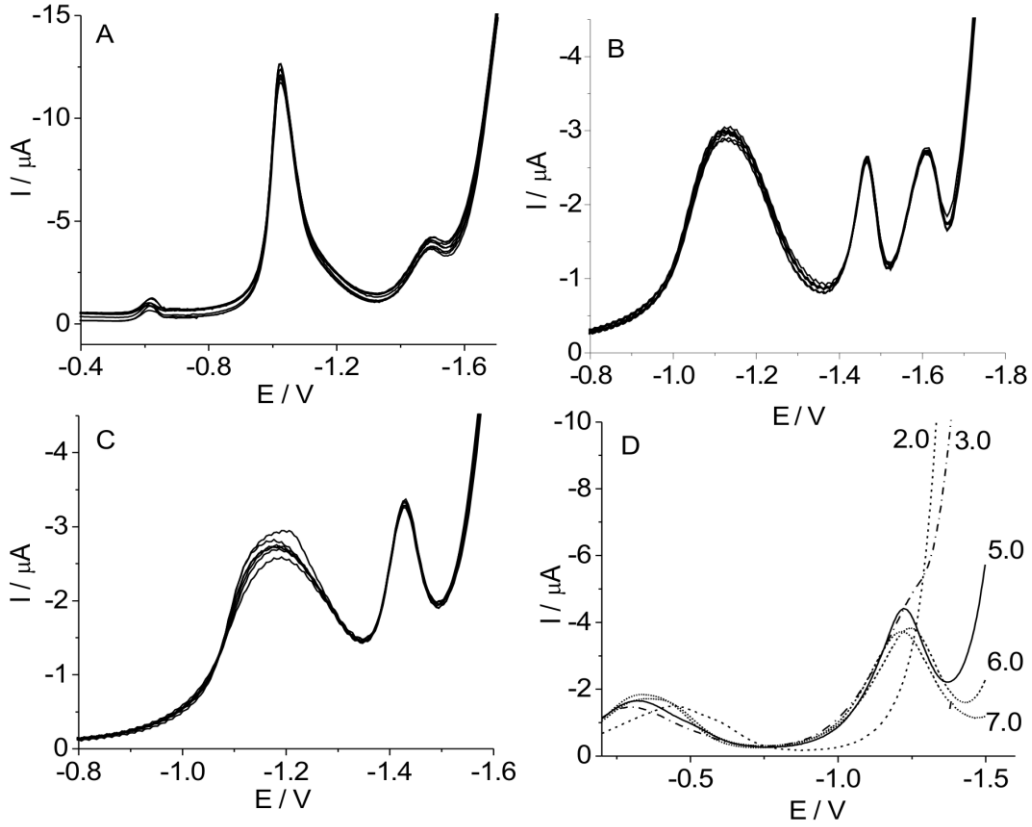

Figure 3. The reproducibility of the analytical signals (9 repetitions) for CLO (A), NIT (B) and TCL (C) in the model solutions (at the levels of 16.67, 3.46 and 2.93 μg mL^{-1}, respectively), and the baselines (D) between pH 2.0 and 7.0

As was pointed out in our previous papers [23,24], an unexpected peak is registered on the baselines for the supporting electrolytes of the pH > 3.0, which is most intense at the pH 5.0 (Fig. 3D). This peak was also observed for the acetate buffer pH 4.5 and phosphate buffer pH 7.5. Since a well defined baseline is a prerequisite for a good analytical method, the best choice would be to record the

voltammograms for the solution of the optimal pH (7.0 and 8.0 (see later Fig. 6A)), as the analytical signal is well shaped and separated most from the undesirable baseline signal. At the same time, the baseline signal, registered at about -1.20 V, is characterized by a reproducible shape and intensity (Fig. 3 D and C). Although the baseline recorded for the solution pH 2.0 does not contain the unexpected peak (Fig. 3D), the peaks of the reduction of the investigated compounds mainly overlap with the hydrogene evolution signal. On the other hand, in the alkaline supporting electrolyte (pH ≥ 9.0), the electrode surface is chemically passivated, probably by the formation of an oxide layer which spoils its sensitivity and gives poorly reproducible signals. Because of that, the electrode is preferably applied in neutral supporting electrolytes.

The dependences of the I_p values on the pH for all three analytes are presented in Fig. 4. For CLO (curve 1), the *Ip* values are shown only for the first reduction peak, while for NIT, both peaks (curves 3 and 4) were taken into account. As can be seen, in the case of TCL (curve 2) and NIT, the peak currents are highest at the pH 7.0, and this pH was chosen for their determination. In the case of CLO, the pH 7.5 was selected as the optimal bearing in mind the position of the undesired baseline peak, and appropriate I_p intensity of analytical signal.

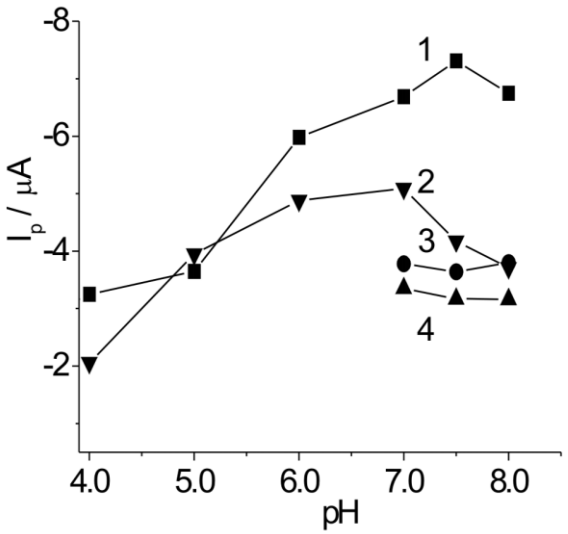

Figure 4. Dependence of the I_p on the pH for CLO (curve 1), TCL (curve 2), NIT (curve 3, first peak, and curve 4, second peak).

Under the optimal conditions, there is a linear relationship between the reduction peak height and the neonicotinoid concentration (μg mL^{-1}) over the range of 0.91-5.62, 0.58-5.96 (0.61-5.96, E_{p2}), and 1.51-54.08 for TCL, NIT, and CLO, respectively (Fig. 5). The analytical parameters for the determinations are summarized in Table 1. Using the optimized conditions, there is a linear relationship between the I_p and the concentration (Fig. 5). In the case of NIT, both reduction peaks are suitable for the analytical purposes. As can be seen from the Table 1, the linear concentration range for CLO is much wider than for the other two neonicotinoids. This could be ascribed to the difference in the electroactive functional groups. However, it could be speculated that some influence might have the nature of the Hg(Ag)FE surface after the baseline reduction peak at -1.2 V.

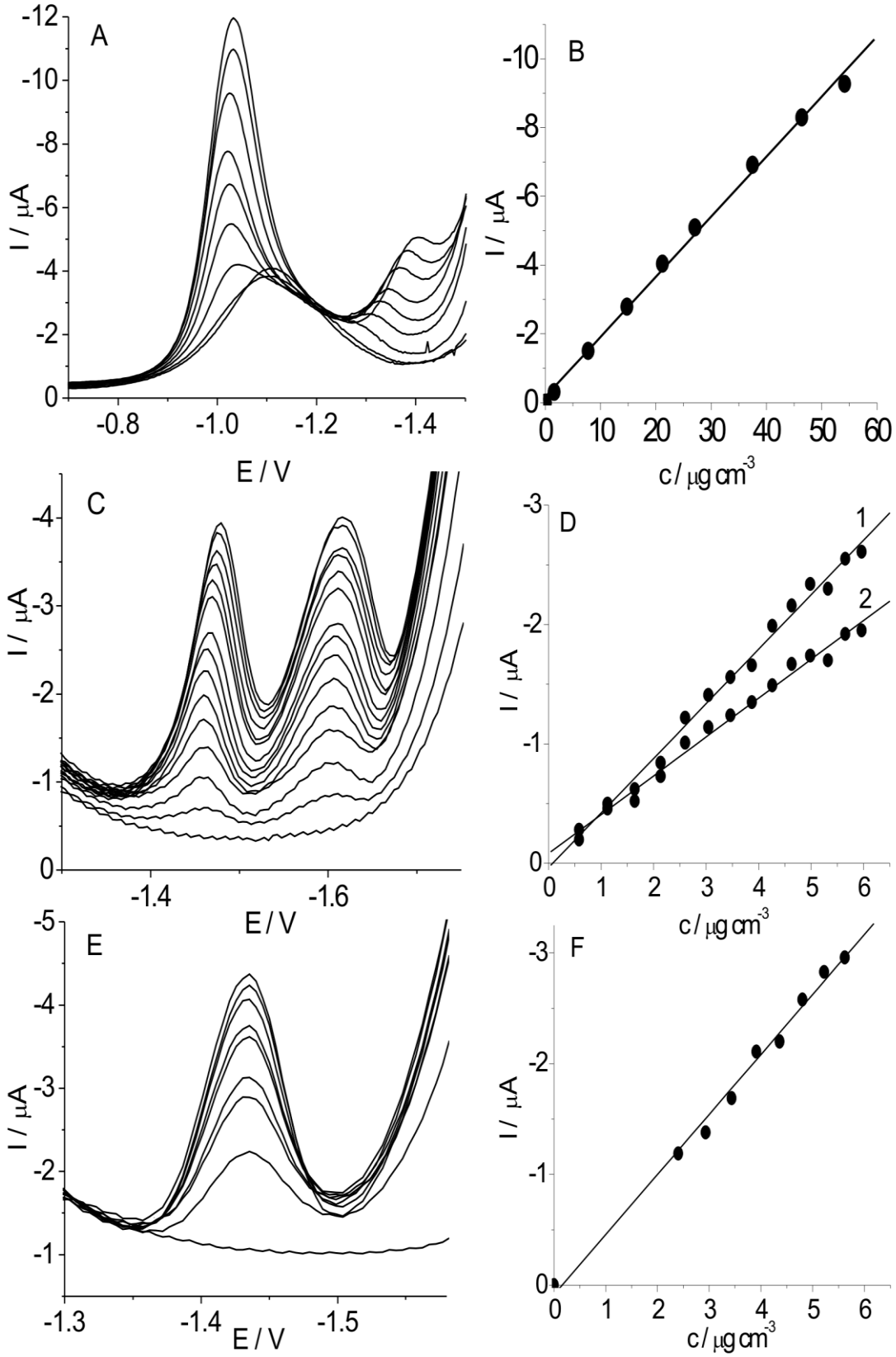

Figure 5. SWV curves recorded for different concentrations of CLO, NIT and TCL in the Britton-Robinson buffer solution pH 7.5 for CLO (A) and NIT (C) and pH 7.0 for TCL (E) and the corresponding I_p-c dependences B, D and F

Table 1. Analytical parameters for the determination of NIT, CLO and TCL. r: linear regression coefficient; LOD: limit of detection; LOQ: limit of quantitation.

Parameter	Compound			
	TCL	CLO	NIT, E_{p1}	NIT, E_{p2}
Concentration range [μg mL^{-1}]	0.91-5.62	1.51-54.08	0.58-5.96	0.61-5.96
Intercept [μA]	0.081	0.168	0.043	0.081
Slope [μA mL μg^{-1}]	0.54	0.18	0.46	0.31
r	0.996	0.998	0.997	0.993
LOD [μg mL^{-1}]	0.27	0.52	0.18	0.20
LOQ [μg mL^{-1}]	0.91	1.51	0.58	0.61
RSD [%] (n = 9)	0.47	0.78	0.51	0.55

Generally, the comparative HPLC-DAD method was applicable in a wider concentration range of 0.75 – 5.0 μg mL^{-1}, but the developed SWV method has some other advantages. Namely, it is suitable for in field analysis, and the sample preparation is not complex as it is usual in chromatography. Besides, the Hg(Ag)FE-based SWV method is less costly and is suitable for rapid measurements.

3.3 Determination of NIT, CLO and TCL in selected samples

The Hg(Ag)FE-based SWV method was applied for the determination of NIT, CLO and TCL in the spiked Danube river water samples, and in the commercial formulation Calypso® 480-SC in the case of TCL.

It appeared that the matrix of Danube water and that of the commercial formulation Calypso® 480-SC did not block the electrode surface, to interfere with the voltammetric determination. All three neonicotinoids were determined by standard addition method (Fig. 6).

The Danube river water samples were spiked with all investigated neonicotinoids (each sample with one insecticide, while the spiked concentration in the samples were 2.4, 2.13, and 9.2 μg mL^{-1} for TCL, NIT and CLO, respectively), and the results obtained, together with the parallel HPLC-DAD measurements are presented in Table 2. The determination of lower concentrations of the target compound, especially in the case of river water samples, can be achieved, e.g. by applying different preconcentration or extraction methods before the analysis. In the case of NIT, both peaks could be successfully used for its determination.

The Hg(Ag)FE-based SWV curves of TCL contained in the Calypso® 480-SC sample, along with that of the blank, are shown in Fig. 6E. The analysis result (Fig. 6F), are in good agreement with those of the comparative HPLC-DAD method (Table 2) and with the nominal value indicated by the supplier (3.07 μg mL^{-1} in the measured aliquote).

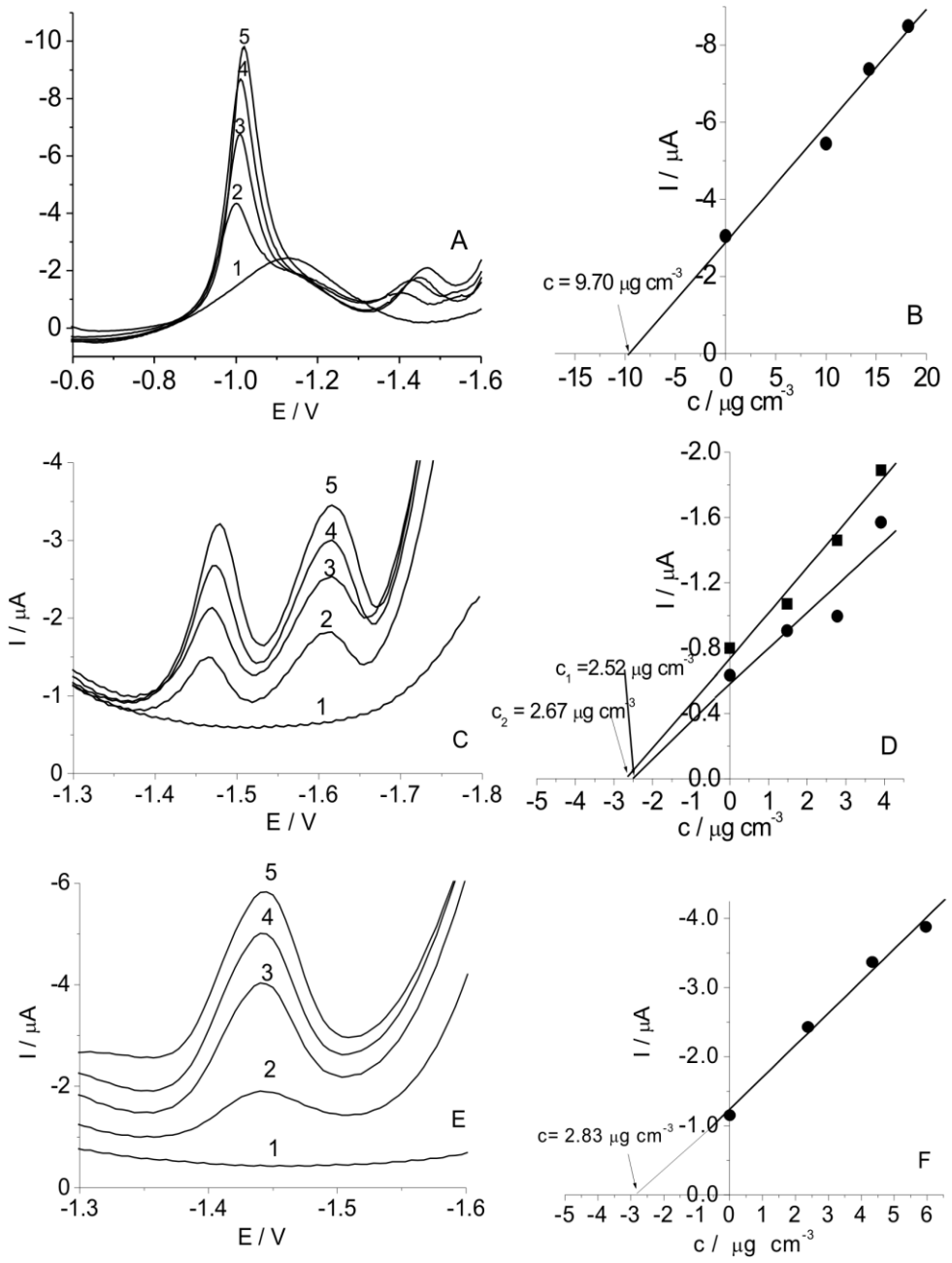

Figure 6. Determination of neonicotinoids in different real samples by standard addition method: CLO (A) and NIT (C) in spiked river water samples, and of TCL (E) in the commercial formulation Calypso® 480-SC. The curves: baseline (1), sample (2), and successive standard additions (3-5). The corresponding analytical curves are: B, D and F

A good correlation between the determined and declared/added amounts of the insecticides, as well as the low RSDs and good agreement with the results of the comparative HPLC-DAD method reflect the high accuracy and precision of the proposed SWV method (Table 2).

Table 2. Assay of TCL[a], NIT[b] and CLO[c] in selected samples (n = 5)

Sample	Method of determination				
	Hg(Ag)FE –SWV			HPLC-DAD	
	Found / μg mL^{-1}	RSD / %		Found / μg mL^{-1}	RSD / %
Calypso® 480-SC [a]	2.83	4.9		2.97	3.2
Danube water[a]	2.17	2.3		2.57	0.5
Danube water[b]	2.52 (2.67)	4.1		2.33	1.2
Danube water[c]	9.70	2.5		9.91	1.4

The developed Hg(Ag)FE–based SWV method is especially suitable for large scale environmental monitoring of electrochemically active organic pollutants. The method is inexpensive, gives a rapid and reliable response, and can be used for in field measurements. Besides, the amount of mercury is limited, so that the Hg(Ag)FE electrode is more environment-friendly than any other Hg electrode. Further experiments will be performed to enhance the sensitivity of the metode and expand the spectrum of its application.

4. CONCLUSION

It can be stated that the study has demonstrated the applicability of the Hg(Ag)FE-based SWV method for the determination of the three neonicotinoid insecticides, CLO, NIT and TCL, which are reducible in a fairly negative potential range. The sensitivity of the procedure was found to depend considerably upon the pH of the supporting electrolyte and the Hg(Ag)FE condition. The linear response was obtained in the concentration range (μg mL^{-1}) of 0.91-5.62; 1.51-54.08, and 0.58-5.96 (0.61-5.96, E_{p2}) for TCL, CLO and NIT (for both peaks given), respectively. The relative standard deviation did not exceed 1.0%.

Moreover, the developed voltammetric procedure was also found to be effective for the determination of the same neonicotinoids in selected real samples, river water, and commercial formulation Calypso® 480-SC in the case of TCL. To the authors' knowledge, the method described herein is the first application of the Hg(Ag)FE for the determination of the widely used TCL and among the very first for NIT.

Although the commonly used HPLC analyses provide undoubtedly richer information about the examined system, the voltammetric alternative with the Hg(Ag)FE detection offers a rapid, simple, and inexpensive tool that is applicable for the basic screening, capable of providing the actual concentration profile(s) of the insecticides. Hence, the method may find further application in the field of the analysis of real samples.

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