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MATHEMATICAL MODELING OF THE ELECTROCHEMICAL DETERMINATION OF FIPRONIL USING A COMPOSITE SENSOR BASED ON TRIAZOLIC SCHIFF BASES AND VANADIUM(III) OXYHYDROXIDE

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This study explores the electrochemical determination of the phenylpyrazole insecticide fipronil using a novel composite sensing material based on triazolic Schiff bases and vanadium(III) oxyhydroxide, VO(OH). Fipronil is among the most extensively used insecticides in agriculture and veterinary medicine, and its environmental persistence, bioaccumulation potential, and toxicity toward non-target organisms underscore the need for sensitive, selective, and rapid analytical methods for its detection in environmental matrices.

The proposed sensing platform incorporates VO(OH) as the electroactive component of the modified electrode, while the synthesized triazolic Schiff bases serve a dual role by facilitating electron transfer and stabilizing the composite architecture. This synergistic combination enhances the electrocatalytic activity, operational stability, and reproducibility of the analytical response.

A mathematical model describing the electrochemical behavior of the sensor was developed by considering fipronil adsorption, interfacial charge-transfer reactions, mediator regeneration, and analyte interactions with the composite surface. The model was analyzed using linear stability theory and bifurcation analysis to elucidate the dynamic behavior of the sensing system over a broad range of kinetic and physicochemical conditions. Particular emphasis was placed on identifying the parameter domain that ensures stable sensor operation and optimal analytical performance.

The theoretical investigation demonstrates that the cathodic electrochemical process occurring at the electrode modified with the triazolic Schiff base–VO(OH) composite provides a favorable mechanism for the determination of fipronil in mildly acidic media. Under these conditions, the sensor is predicted to generate a well-defined, highly reproducible electrochemical response exhibiting a linear dependence on analyte concentration, thereby enabling reliable quantitative determination.

The dynamic behavior of the sensing system was also evaluated. The analysis predicts that both oscillatory and monotonic instabilities may arise under specific kinetic conditions; however, these regimes are confined to a narrow parameter range and are therefore unlikely to affect sensor performance under practical analytical conditions.

Overall, the obtained results provide a solid theoretical foundation for the development of highly sensitive electrochemical sensors for monitoring fipronil in environmental and agricultural samples. Moreover, the proposed modeling approach offers valuable insights for the rational design of advanced composite sensing materials intended for the electrochemical detection of persistent organic pollutants. *Key words:* intoxication prevention, fipronil, vanadium (III) oxyhydroxide, Schiff bases, electrochemical sensors, stable steady-state.

Математичне моделювання електрохімічного визначення фіпронілу із застосуванням композитного сенсорного матеріалу на основі триазольних основ Шиффа та оксигідроксиду ванадію(III). Ткач В.В., Морозова Т.В., Ізабель Гайван О'Нілл, да Пайва Мартінш Ж.І.Ф.

Окреслено електрохімічне визначення інсектициду фіпронілу із застосуванням нового композитного сенсорного матеріалу на основі триазольних основ Шиффа та оксигідроксиду ванадію(III) VO(OH). Фіпроніл є одним із найпоширеніших інсектицидів фенілпіразольної групи, який широко використовується у сільському господарстві та ветеринарній практиці. Висока персистентність цієї сполуки в навколишньому середовищі, її здатність до накопичення та токсичний вплив на нецільові організми зумовлюють потребу у створенні чутливих, селективних, швидких і надійних методів контролю її вмісту в об'єктах довкілля.

Запропонований сенсорний матеріал містить оксигідроксид ванадію(III) як електроактивний компонент модифікованого електрода, тоді як синтезовані триазольні основи Шиффа виконують подвійну функцію: забезпечують ефективне перенесення електронів та стабілізують структуру композиту. Така організація сенсорного шару сприяє підвищенню електрокаталітичної активності, стабільності функціонування та відтворюваності аналітичного сигналу.

Для теоретичного опису роботи сенсора розроблено математичну модель, яка враховує адсорбцію фіпронілу на поверхні електрода, перебіг електродних реакцій, регенерацію медіатора та взаємодію аналіту з композитним модифікатором. Аналіз

моделі виконано із застосуванням методів теорії лінійної стійкості та біфуркаційного аналізу, що дало змогу встановити закономірності функціонування електрохімічної системи за різних кінетичних і фізико-хімічних умов, а також визначити діапазони параметрів, у межах яких забезпечується її стійкий аналітичний режим.

Результати теоретичного дослідження свідчать, що катодний електрохімічний процес на електроді, модифікованому композитом на основі триазольної основи Шиффа та VO(OH), є перспективним для визначення фіпронілу у слабкокислому середовищі. За цих умов формується чіткий, відтворюваний електрохімічний сигнал, величина якого лінійно залежить від концентрації аналіту, що створює передумови для його кількісного визначення.

Окрему увагу приділено аналізу динамічної поведінки електрохімічної системи. Встановлено, що за певних співвідношень кінетичних параметрів можливе виникнення як осциляторних, так і монотонних нестійкостей. Водночас результати моделювання показали, що такі режими реалізуються лише за вузького діапазону параметрів і не повинні істотно впливати на роботу сенсора в умовах практичного аналізу.

Отримані результати формують теоретичне підґрунтя для конструювання високочутливих електрохімічних сенсорів нового покоління, призначених для моніторингу фіпронілу в природних водах, ґрунтах, сільськогосподарській продукції та інших складних об'єктах аналізу. *Ключові слова:* профілактика інтоксикації; фіпроніл; оксигідроксид ванадію(III); основи Шиффа; електрохімічні сенсори; стійкий стаціонарний стан.

Introduction. In July and August 2017, more than 50 egg poisoning cases outbroke throughout the 15 member states of European Union plus Switzerland and Hong Kong [1–2]. Most of the people hospitalized during this outbreak were Dutch, German, French and Belgian citizens and the outbreak forced to shut down temporarily about 180 farms in the Netherlands.

An investigation was carried on and it revealed that the overdose of fipronil (Fig. 1), used as a vet drug to protect the poultry from parasite infections had caused the poisoning.

Fipronil (Fig. 1) (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile) is used as a broad-spectrum insecticide, employed to control the population of insects, harmful to man [1–5]. It is also used as drug for treatment and prevention of parasitic infections, generally for veterinary use [2]. Its mechanism of action includes disruption of chloride passage through GABA–mediated channels in nerve cell membranes, resulting in terminal neurologic malfunction [2]. It is an active substance of different commercial formulations like Regent®, Frontline®, Termidor®, 4fleas®, Activo®, Alfamed® among others [3–5].

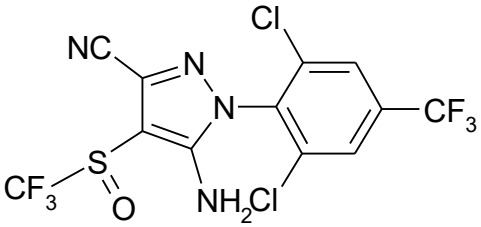

Fig. 1. Fipronil

It is used against beetles, ticks, seas, termites and other pests. It is currently registered in more than 70 countries for the control of insect pests in more than hundred crops like corn, soybean, sugar cane and wheat [3–5].

Fipronil is classed by World Health Organization as Class II moderately hazardous pesticide [6].

The major metabolite of fipronil (Figure 2) [7] in vertebrates and invertebrates appears to be fipronil sulfone [8]. On plants and in soils, fipronil undergoes a photoextrusion reaction, yielding a desulfinyl derivative [8]. There have been limited studies of the degradation of fipronil on the surface (skin) of domestic species, particularly dogs and cats. It has been reported that basic conditions (pH > 7) and increased temperatures will induce hydrolysis of fipronil [9], conditions, that may occur on the skin surface of mammals.

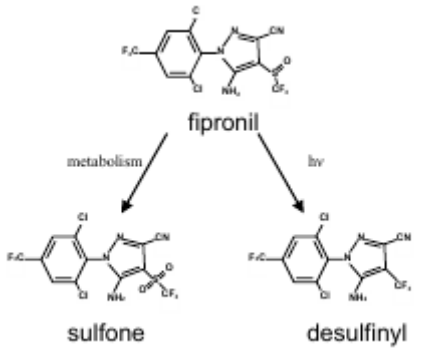

Fig. 2. Fipronil metabolism. Reproduced from [7]

The selective toxicity of fipronil will therefore depend on the relative rate of conversion to the more persistent and less selective sulfone metabolite and desulfinyl photoproduct [10]. The desulfinyl photoproduct, in particular, has a 10 fold greater selectivity for mammalian GABA chloride channels than the parent compound [8]. No directly applicable data are available on the influence of degradation products on the toxicity of Fipronil applied to target animals.

The intoxication symptoms include sweating, nausea, vomiting, headache, abdominal pain, dizziness, agitation, weakness, and tonic-clonic seizures [11, 12]. The U.S. EPA has classified fipronil as a group C (possible human) carcinogen based on an increase in thyroid follicular cell tumors in both sexes of the rat [12].

Its ecotoxicity for crustaceans, insects and zooplankton is very high [13]. Its half-life lasts four months to one year

depending on the media. It is relatively stable in water, but it´s not so stable in soil, due to its photolysis. Thus, the development of a precise, exact, rapid and efficient method of its quantification is really actual task [14–16].

For now, three works concerning fipronil electrochemical determination are known. Two of them are authored by Brazilian groups [17, 18], and the third one is our theoretical investigation, in which the CoO(OH)-assisted fipronil electrochemical determination is foreseen [19]. Either cathodical or anodical processes may be applied. Nevertheless, the cathodical process is more efficient in energetical terms, due to the presence of the acceptor groups in fipronil molecule.

One of the cathode modifiers, capable to be used for this purpose is vanadium(III)oxyhydroxide [20, 21], a compound with the possibility of semiconducting properties and flexible electrochemical behavior, but more inclined to be reducent. In order to enhance the vanadium (III) oxyhydroxyde stability in acidic medium, the triazolic derivatives like those described in [22, 23] may be used as stabilizers.

The electroanalytical behavior of VO(OH) hasn't been described experimentally, due to the relative novelty of the proper material. However, it is theoretically predicted in our previous works [24–26].

It is important to consider that the development of a principally new electrode modifier for a new analyte may confront some problems, like:

– the indecision about the mechanism of electrochemical action of the electrode modifier with the analyte;

– the possibility of the appearance of electrochemical instabilities, characteristic for the electrosynthesis and action of CoO(OH), a similar compound [19, 27, 28].

These problems may be solved, if the experimental essays are preceded by an *a priori* theoretical investigation of the electroanalytical system. So, in this work, the theoretical mechanistic investigation of fipronil electrochemical determination, assisted by VO(OH), stabilized by a novel Schiff base, is given. Also the behavior of this system is compared with that of the similar electroanalytical processes [24–28].

System and its modeling.

Experimental. 5-adamantyl-4-amino-1,2,4-triazole-3-thiol has been provided as a courtesy by Zaporizhzhya state medical university. 9-formylanthracene aldehyde has been used from the stores of Chernivtsi National University. Acetic acid has been acquired from Sfera Sim (Lviv) and used without further purification. The ^{1}H NMR experiment has been carried out in Enamin (Kiev, Ukraine) by Varian Mercury 400 spectrometer (400 MHz) in DMSO-d_6. The reaction has been realized as in the Fig. 3.

The solution of 0,26 g (0,00125 mol) of 9-formylanthracene in 5 ml of acetic acid was added to the hot solution of 0,33 g (0,00125 mol) of 5-adamantyl-4-amino-1,2,4-triazole-3-thiol in 10 ml of acetic acid. Furtherly, it was kept for 12 hours in the room temperature. The brightly yellow fluorescent crystalline compound has been filtered out, rinsed by water and dried. Yield 0,40 g (66⅔%). Chrystallized by water from DMF solution. M.p. 238 ^{0}C. Found: C: 73,75%, H: 5,75%, N: 12,52%. $C_{27}H_{26}N_4S$. Calculated: C: 73,94%, H: 5,97%, N: 12,77%.

The ^{1}H NMR shifts of the Schiff base may be given as on the Fig. 4.

Fipronil is reduced on the first stage by vanadium (III) oxyhydroxide in aqueous media as on the Fig. 5.

The reduction product is also capable to be reduced in the presence of VO(OH) either by sulfur atom (Fig. 6) or by heterocyclic ring scission (Fig. 7).

Both of the processes include rearrangements in the double electric layer (DEL), capable to cause the oscillatory behavior and other dynamic phenomena.

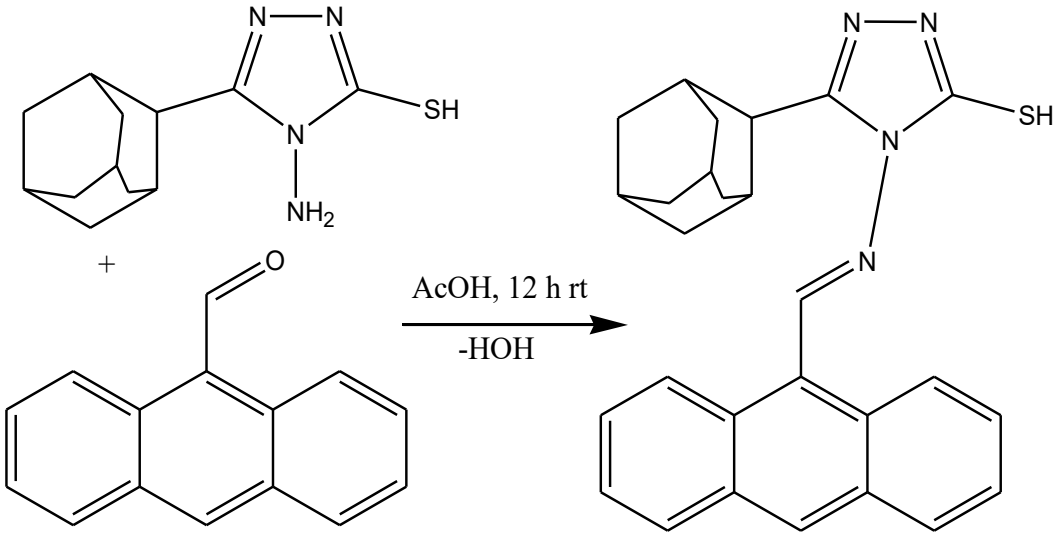

Fig. 3. Synthesis of the triazolic Schiff base

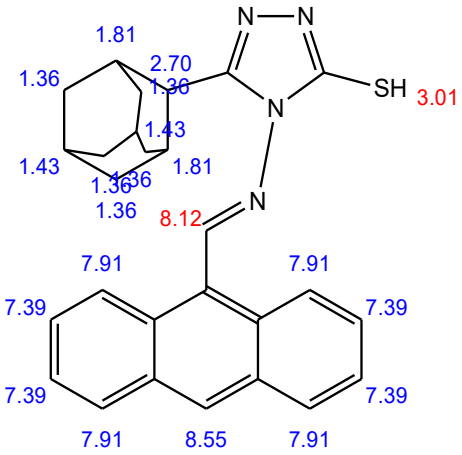

Fig. 4. The PMR shifts of the Schiff base

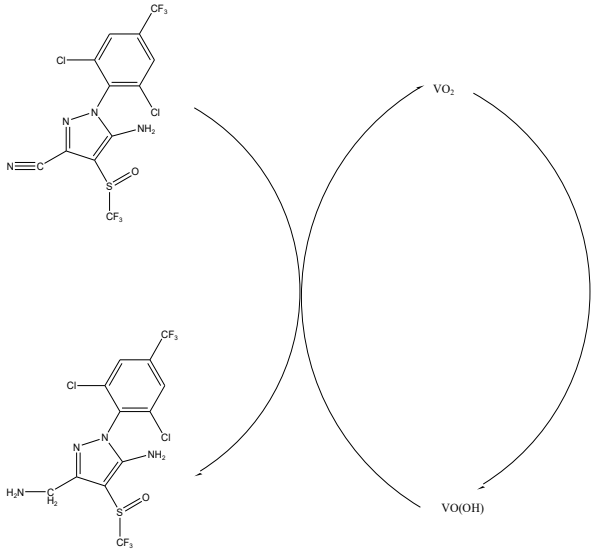

Fig. 5. VO(OH)-assisted fipronil reduction

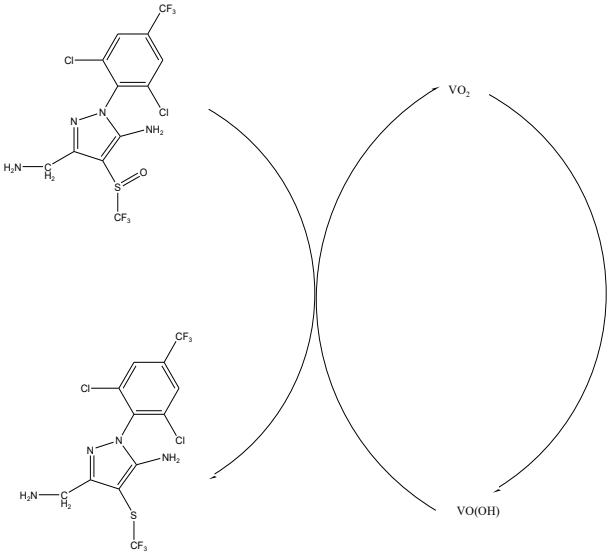

Fig. 6. Sulfur atom reduction by VO(OH)

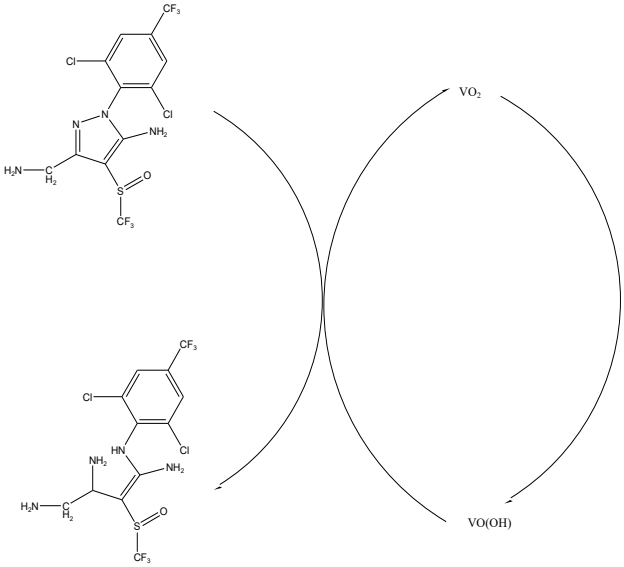

Fig. 7. VO(OH)-assisted ring scission

So, in order to describe the gyromitrin electrochemical determination, we introduce three variables:

f – fipronil concentration in the pre-surface layer;

n – nitrile reduction product concentration in the pre-surface layer;

θ – vanadium dioxide triazolic complex surface coverage degree.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte is in excess, so we can neglect the migration flow. The pre-surface layer thickness is assumed to be constant, equal to δ, and the concentration profile of the analyte to be linear.

It is possible to show that the system´s behavior will be described by the following trivariant equation set:

$$\begin{cases} \dfrac{df}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}\left(f_0 - f\right) - r_{15}\right) \\ \dfrac{dn}{dt} = \dfrac{2}{\delta}\left(r_{15} - r_{16} - r_{17}\right) \\ \dfrac{d\theta}{dt} = \dfrac{1}{G}\left(r_{14} + r_{15} + r_{17} - r_2\right) \end{cases} \quad (1)$$

In which f_0 is the fipronil bulk concentration, Δ is the diffusion coefficients, G is the VO_2 complex maximal surface concentration, and the parameters r are the chemical and electrochemical stages rates, capable to be calculated as:

$$r_{15} = k_{15} f\left(1-\theta\right)^6 \exp\left(-\alpha\theta\right) \quad (2)$$

$$r_{16} = k_{16} n\left(1-\theta\right)^4 \exp\left(-\alpha\theta\right) \quad (3)$$

$$r_{17} = k_{17} n\left(1-\theta\right)^4 \exp\left(-\alpha\theta\right) \quad (4)$$

$$r_2 = k_2 \theta \exp\left(-\frac{F\varphi_0}{RT}\right). \quad (5)$$

Here, the parameters k stand for the correspondent rate constants, α and β are parameters, relating DEL capacitance to the coverage degree, F is the Faraday number, φ_0 is the potential slope related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

The DEL influences of the complex configuration changes make the system´s behavior more dynamic. Moreover, as the reduction process is "branched", all of its stages are capable to alter the DEL capacitance, conductivity and ionic composition. Even though, the electroanalytical process will be efficient, as shown below.

Results and discussion. In order to describe the fipronil electrochemical detection, assisted by vanadium(III)oxyhydroxide, stabilized by triazolic derivatives, we analyze the equation-set (1) by means of the linear stability theory. The steady-state Jacobian functional matrix members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (6)$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_{15}(1-\theta)^6 \exp(-\alpha\theta)\right) \quad (7)$$

$$a_{12} = 0 \quad (8)$$

$$a_{13} = \frac{2}{\delta}\left(6k_{15}f(1-\theta)^5 \exp(-\alpha\theta) - \alpha k_{15}f(1-\theta)^6 \exp(-\alpha\theta)\right) \quad (9)$$

$$a_{21} = \frac{2}{\delta}\left(k_{15}(1-\theta)^6 \exp(-\alpha\theta)\right) \quad (10)$$

$$a_{22} = \frac{2}{\delta}\left(-k_{16}(1-\theta)^4 \exp(-\alpha\theta) - k_{17}(1-\theta)^4 \exp(-\alpha\theta)\right) \quad (11)$$

$$a_{23} = \frac{2}{\delta}\begin{pmatrix} -6k_{15}f(1-\theta)^5 \exp(-\alpha\theta) + \alpha k_{15}f(1-\theta)^6 \exp(-\alpha\theta) + \\ 4k_{16}n(1-\theta)^3 \exp(-\alpha\theta) - \alpha k_{16}n(1-\theta)^4 \exp(-\alpha\theta) + \\ 4k_{17}n(1-\theta)^3 \exp(-\alpha\theta) - \alpha k_{17}n(1-\theta)^4 \exp(-\alpha\theta) \end{pmatrix} \quad (12)$$

$$a_{31} = \frac{1}{G}\left(k_{15}(1-\theta)^6 \exp(-\alpha\theta)\right) \quad (13)$$

$$a_{32} = \frac{1}{G}\left(k_{16}(1-\theta)^4 \exp(-\alpha\theta) + k_{17}(1-\theta)^4 \exp(-\alpha\theta)\right) \quad (14)$$

$$a_{33} = \frac{1}{G}\begin{pmatrix} -6k_{15}f(1-\theta)^5 \exp(-\alpha\theta) + \alpha k_{15}f(1-\theta)^6 \exp(-\alpha\theta) - \\ 4k_{16}n(1-\theta)^3 \exp(-\alpha\theta) + \alpha k_{16}n(1-\theta)^4 \exp(-\alpha\theta) - \\ 4k_{17}n(1-\theta)^3 \exp(-\alpha\theta) + \alpha k_{17}n(1-\theta)^4 \exp(-\alpha\theta) - \\ k_2 \exp\left(-\frac{F\varphi_0}{RT}\right) - jk_2\theta \exp\left(-\frac{F\varphi_0}{RT}\right) \end{pmatrix} \quad (15)$$

As in other systems with the use of vanadium oxyhydroxide as electrode modifier [24–26], the oscillatory behavior will be possible. Moreover, even though the surface instabilities are absent in this system, the oscillatory behavior will be relatively probable, as there are more than one process influencing the double electric layer (DEL) capacitances.

Beside of the element $-jk_2\theta \exp\left(-\frac{F\varphi_0}{RT}\right) > 0$, if j<0, typical for all similar systems and describing the DEL influences of the electrochemical stage, the elements containing the parameter α outside the exponent are possible, if α>0 describe the DEL influences of the complex compound rearrangement on the chemical stages. All of there influences become more intensive beyond the detection limit, so they do not interfere significantly to the electroanalytical process. The oscillations are frequent and of small amplitude.

In order to investigate the *steady-state stability*, we apply the Routh-Hurwitz criterion to the equation-set (1). By this, avoiding the cumbersome expressions, we introduce new variables, rewriting the determinant as:

$$\frac{4}{\delta^2 G}\begin{vmatrix} -\kappa - \Xi & 0 & \Omega \\ \Xi & -X & -\Omega + \Lambda \\ \Xi & X & -\Omega - \Lambda - P \end{vmatrix} \quad (16)$$

Opening the straight brackets of the determinant, applying to it the inequity, salient from the criterion, we may obtain the steady-state stability condition, described as:

$$(-\kappa - \Xi)(2X\Omega + XP) + 2\Xi X\Omega < 0. \quad (17)$$

Which may be rearranged into:

$$-2\kappa X\Omega - (\kappa + \Xi)XP < 0. \quad (18)$$

Depicting an electroanalytically efficient diffusion-controlled system. This is realized, if the parameters, describing the system's behavior during the chemical and electrochemical stages Ξ, X, Ω and P are positive. Really, if we suppose them to be positive, the left side of the inequation (18) will be more negative, stabilizing the steady-state. Taking into account the inexistence of side reactions in the pH chosen for this system (neutral or lightly acidic), the steady-state will be electroanalytically efficient, correspondent to the linearity of the dependence between concentration and electrochemical parameter (in this case, current).

The monotonic instability, related to the detection limit, will be realized in the point of:

$$-2\kappa X\Omega - (\kappa + \Xi)XP = 0. \quad (19)$$

In this point, correspondent to the saddle-node bifurcation, the limit between stable steady-states and unstable states is posed. It is correspondent to the equity between the stabilizing and destabilizing influences.

This electrode may be used for fipronil determination either in vitro, or in vivo (in plant and animal organisms). The selectivity is achieved, due to the difference in the reaction of fipronil and other pesticides used for plant protections with vanadium (III) oxyhydroxide. It

is possible to substitute triazoles by other basic organic compounds, capable to stabilize vanadium (III) oxyhydroxide. The compounds may be either micro or macromolecular, and the behavior of this system will also be described by this model.

Conclusions. From the theoretical investigation of the possibility of the fipronil electrochemical detection, assisted by vanadium(III) oxyhydroxide, stabilized by triazoles, it is possible to conclude that:

– VO(OH) may serve as an excellent modifier for fipronil electrochemical determination. The system is electroanalytically efficient, although the pesticide reduction process is ramified;

– The electroanalytical process tends to be diffusion-controlled;

– The oscillatory behavior in this system is possible, being more probable than in similar systems. The amplitude is expected to be small and the oscillations to be frequent.

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