

A.S. Gashevskaya<sup>1</sup>, A.O. Gusar<sup>1</sup>, Ye.V. Dorozhko<sup>1</sup>, K.V. Dyorina<sup>1</sup>, S.O. Kenzhetayeva<sup>2</sup>

<sup>1</sup>*Tomsk Polytechnic University, Russia;*

<sup>2</sup>*Ye.A. Buketov Karaganda State University, Kazakhstan*

*(E-mail: asg30@tpu.ru)*

### **Voltammetric determination of carbaryl in some cereals on an impregnated graphite electrode modified with carbon ink**

Nowadays, pesticides are an integral part of our lives. These compounds are contained in food, water, soil. Consequently people consume them constantly in significant amounts. Therefore, the control of pesticides content in various objects is the most important problem for human health maintaining. In the present work, the electrochemical oxidation of carbaryl on an impregnated graphite electrode modified with carbon ink was studied for the first time. The optimal conditions of carbaryl extraction from some grain crops were selected, followed by its determination on an impregnated graphite electrode modified with carbon ink by linear sweep anodic voltammetry. A number of cereals, such as wheat, oats and corn, were selected as the objects of study. The determination of carbaryl in the objects was carried out after chromatographic separation by TLC. It is revealed that carbon ink increases the electroactive surface of the impregnated graphite electrode. As a result, the sensitivity of carbaryl determination increases. Therefore, the accuracy of carbaryl trace amounts determination increases. The range of linear dependence of  $dI/dE$  on the concentration of carbaryl was from  $0 \cdot 10^{-8}$  M to  $1.6 \cdot 10^{-8}$  M, the detection limit was  $1.2 \cdot 10^{-9}$  M.

*Keywords:* carbaryl, linear sweep anodic voltammetry, impregnated graphite electrode, carbon ink, food, pesticides, thin-layer chromatography, crops.

#### *Introduction*

Today, the problem of pesticide residues determination in food, drinking water and soil is relevant to safety and well being of society. Even a small amount of pesticides in food, water and soil can cause significant harm to human health. Therefore, the monitoring of these residues is one of the most important steps to minimize the potential risks to the health of not only humans, but also animals [1]. In order to avoid hazards to human and animal health caused by pesticide residues, governments of various countries regulate the maximum level of pesticide residues in fruits and vegetables, in drinking water, and in the soil, seeking to limit their effects on the population [2].

Carbamates are a group of pesticides, the derivatives of carbamic acid. All pesticides of this group are known as active insectoacaricides, fungicides, and herbicides [3]. The mechanism of carbamates toxic effect on the living organism has been poorly studied. However, it is known that the effect of carbamates on the body disrupts redox processes; there are signs of hypoxia and damage to the central nervous system. In persons working with carbamates, there are lesions of the upper respiratory tract. In contact with the skin there is a pronounced irritant effect. In case of acute intoxication, hemolytic anemia may develop. There is a strong irritant effect of carbamic acid derivatives on mucous membranes [3].

The maximum level of pesticide residues values of carbamates in food products, as established by regulatory authorities, range from 0.01 to 10 mg/kg in relation to acceptable daily intake. In addition, for drinking

water and soil, values were given as indicative limits from 10 µg/l to 90 µg/l [1]. According to the literature, mainly carbamates, namely carbaryl, are determined using chromatographic methods of investigation, such as gas and liquid chromatography, thin layer chromatography [4]. Along with the above methods for the determination of carbamates, inverse voltammetry is also used [5–8]. The advantages of this method are high sensitivity, a wide range of defined elements, and simplicity of measurement techniques, reliability, and low costs [9].

In this work, the electrochemical properties of a carbaryl model compound from the class of carbamates were studied by linear sweep anodic voltammetry on an impregnated graphite electrode modified with carbon ink. The working conditions for the determination of carbaryl in working solutions were the following: the background electrolyte was an alcohol solution of sodium perchlorate, the working electrode was an impregnated graphite electrode, the auxiliary and reference electrode were platinum and silver chloride electrodes. It has been established that the application of carbon ink as an electrode modifier improves the sensitivity of its determination, which is especially important when determining the trace amounts of carbaryl in cereals. The dependence of  $dI/dE$  on the carbaryl concentration was linear from  $0 \cdot 10^{-8}$  to  $1.6 \cdot 10^{-8}$  M, the detection limit was  $1.2 \cdot 10^{-9}$  M. The approbation of the method for carbaryl determination in corn, oats, and wheat was carried out.

### Experimental

Carbaryl is an organic compound, a carbamate, the  $\alpha$ -naphthyl ester of N-methylcarbamic acid, the highly effective insecticide (Fig. 1). It is a solid crystalline substance with a white or slightly yellowish tinge; it has no odor, is poorly soluble in water, and well in organic solvents. Carbaryl is approved to be used in Russia.

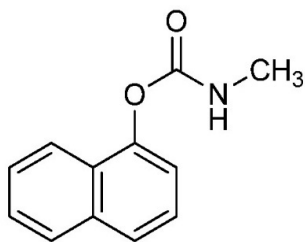


Figure 1. The structural formula of carbaryl

The following reagents were used to study the electrochemical properties of carbaryl, namely sulfuric acid  $H_2SO_4$  (Reahim, Russia), purified ethyl alcohol 96 %  $C_2H_5OH$  (Labtech, Russia), potassium chloride KCl (Uralkali, Russia), sodium perchlorate  $NaClO_4$  (Merk, Germany), carbaryl  $C_{12}H_{11}NO_2$  (Sigma-Aldrich, USA), microcrystalline graphite ( $<20\mu m$ , Sigma-Aldrich, USA), polystyrene (Sigma-Aldrich, USA), 1,2-dichloroethane  $C_2H_4Cl_2$  (Sigma-Aldrich, USA).

All necessary experiments were carried out on a TA — Lab voltammetric station (manufactured by Tomanalit Research and Production Enterprise, Tomsk).

The currents recorded on the anodic voltammogram in the form of a wave were transformed in the mode of the first derivative  $dI/dE - E$ , where the analytical signals were observed in the form of peaks.

A sodium perchlorate alcohol solution of 0.1 M was used as the background electrolyte. An impregnated graphite electrode was used as a working electrode, which was obtained by vacuum impregnation of blanks from spectral coal with epoxy resins (Mikroprimesi LLC, Tomsk), the auxiliary and reference electrode were silver and silver chloride electrodes, respectively. Working solutions of carbaryl were prepared by dissolving a certain sample of state standard sample in ethanol.

Modifying carbon ink was a mixture of 0.09 g of microcrystalline graphite and 0.01 g of polystyrene dissolved in  $0.5\text{ cm}^3$  of 1,2-dichloroethane. To create a homogeneous suspension, the mixture was vigorously stirred for 3 minutes using an ElmySkyline shaker.  $1\ \mu l$  of the resulting suspension was placed on the surface of the working electrode and dried in air for 2–3 minutes.

The electrochemical properties of carbaryl on an unmodified and modified carbon ink impregnated graphite electrode were carried out in the potential range from  $-2.5$  to  $+2.5$  V under scan rate  $v = 70$  mV/s.

### Isolation of carbaryl in food

A weighed portion of crushed grain weighing 100 g was filled in with 200 cm<sup>3</sup> *n*-hexane and left overnight with constant stirring under a fume hood. Then, the resulting mass was filtered into a vacuum cup, washing the contents of the flask several times with *n*-hexane, 20 cm<sup>3</sup> each. The filter was also washed with *n*-hexane several times 15 cm<sup>3</sup> each. The contents of the cup were left under a fume hood, to completely volatilize the solvent at room temperature. To extract the carbaryl and remove impurities, 10 ml of 96 % ethanol was added to the dry residue and the residue was triturated with a glass rod. The resulting mixture was filtered through a «Blue Ribbon» filter paper. The filtrate was used to detect carbaryl.

The resulting sample was applied to a Sorbfil chromatographic (aluminum) plate. Chloroform (97.4 %) was chosen as the mobile phase, which is not electrochemically active. The spots were dried in air, and then the plate was introduced into the chamber for chromatography. Then the plate was removed from the chamber, dried in air and irradiated with UV light. When the plate was irradiated with UV light, the spots acquired a red color.  $R_f$  for carbaryl was 0.57, the time of chromatography was 3 hours.

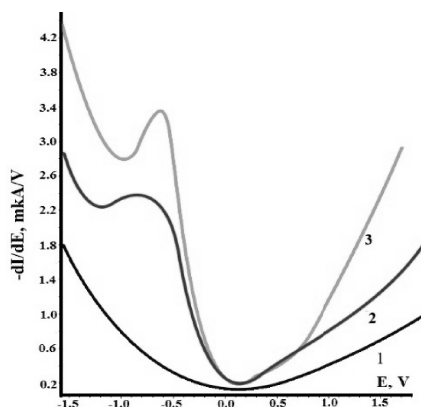
Carbaryl was washed off by a method of washing a fixed spot of the development of a spot with ethyl alcohol, in an amount of 3 cm<sup>3</sup> in a glass container. The operation was repeated twice.

### Results and Discussion

#### The voltammetric determination of carbaryl

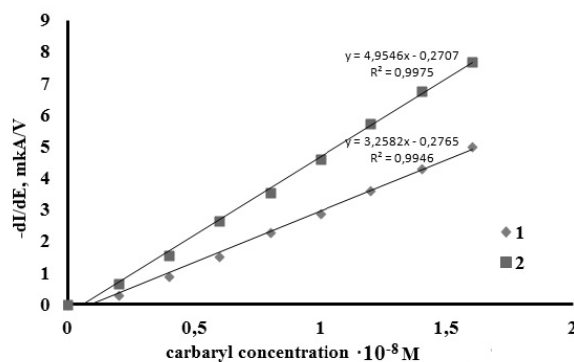
When studying the electrochemical properties of carbaryl, cyclic voltammograms was recorded on different electrodes (carbon-containing, mercury-film, platinum, modified carbon-containing electrode with carbon ink, impregnated graphite, impregnated graphite electrode, modified with carbon ink) under  $v=70$  mV/s sodium perchlorate is in the background electrolyte. The analytical signal of carbaryl was detected only on the impregnated graphite electrode in the anodic region of the potentials -2.5V to +2.5V (Fig. 2). When carbon ink was applied to the surface of an impregnated graphite electrode, the sensitivity of the determination of carbaryl in model solutions increased 10 fold.

Figure 2 shows voltammograms of carbaryl oxidation (concentration  $0.4 \cdot 10^{-8}$  M) on unmodified and modified graphite carbon ink in electrodes (Fig. 2a) and the range of linear dependence of the oxidation current on the concentration of carbaryl (Fig. 2b), which amounted to  $0 \cdot 10^{-8}$  to  $1.6 \cdot 10^{-8}$  M.



1 — background curve of sodium perchlorate alcohol solution 0.1 M; 2 — carbaryl ( $0.4 \cdot 10^{-8}$  M) on the unmodified graphite electrode; 3 — carbaryl ( $0.4 \cdot 10^{-8}$  M) on a graphite electrode modified with carbon ink

Figure 2a. Anodic voltammograms of carbaryl



1 — unmodified graphite electrode;  
2 — carbon graphite-modified carbon ink

Figure 2b. Linear dependence of the carbaryl oxidation current in the concentration range from  $0 \cdot 10^{-8}$  to  $1.6 \cdot 10^{-8}$  M

According to the literature data, the electrochemical oxidation of carbaryl can occur through the oxidation of a carbamate group [7]. The modification of an impregnated graphite electrode with carbon ink leads to the sensitivity increase of carbaryl determination in model solutions due to the possible increase in the area of the electroactive surface of the electrode. A standard technique for evaluating the effectiveness of an electrode modifier is the usage of redox  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  as a standard (Fig. 3).

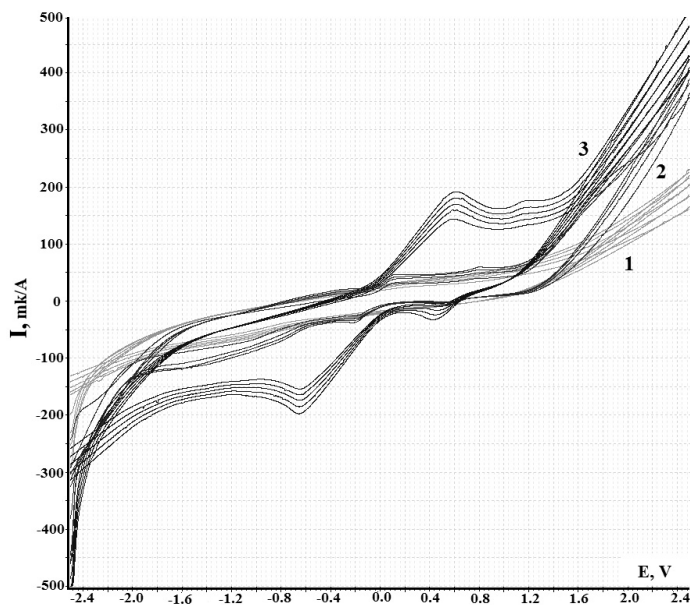


Figure 3. Cyclic voltammograms  $1 \cdot 10^{-4}$  M  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  on unmodified graphite (2) and graphite electrode modified with carbon ink in graphite electrode (3) at  $\text{pH}=6.86$ ,  $v = 70\text{mV/s}$  (1) is the background curve

The Randles-Shevchik equation (1) was used to calculate the electroactive surface area:

$$I_p = 2.69 \times 10^5 Z^{3/2} A D^{1/2} C V^{1/2}, \tag{1}$$

where  $I_p$  is peak current, A;  $Z$  is the number of electrons ( $n = 1$ );  $A$  is the area of the electroactive surface,  $\text{cm}^2$ ;  $D$  is diffusion coefficient ( $7.60 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ), [10];  $C$  is concentration of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  in solution ( $1 \cdot 10^{-4}$  M);  $V$  is the sweep speed,  $\text{mV/s}$ .

The calculated electroactive surface area of the unmodified graphite electrode was  $0.013 \text{ cm}^2$ , while, after modification, it became 10 times large as  $0.103 \text{ cm}^2$ . Thus, the efficiency of using carbon ink as a modifier of an impregnated graphite electrode for the voltammetric determination of carbaryl is shown. All further determinations of carbaryl, both in model solutions and in grain crops, were carried out on an impregnated graphite electrode modified with carbon ink.

As a method for isolating carbaryl from the analyzed mixture of components obtained from grain crops, the method of thin layer chromatography was used (the technique is presented in the «experimental part» section). The verification of proposed determination method for carbaryl in model solutions was carried out using the «introduced-found» method. The results are presented in Table 1.

Table 1

**Check the correctness of the definition of carbaryl using the «entered-found» method**

No.	Is entered, $10^{-8}$ M	Found, $10^{-8}$ M	$\Delta$ , %
1	0.4	0.33	$\pm 4.5$
2	0.8	0.79	$\pm 4.3$
3	1.2	1.12	$\pm 4.0$

Thus, in the indicated range of carbaryl concentrations, the standard deviation of the found results from the accepted reference values does not exceed 4.5 %.

In the work, the carbaryl was determined by voltammetry on a carbon ink impregnated graphite electrode modified in carbon in corn, oats, and wheat. Sample preparation and chromatographic isolation of carbaryl from grain crops was performed according to the method presented in the section «experimental part». Quantitative determination of carbaryl in the resulting washes was carried out under the following conditions: the anodic region of the signal at a potential of  $-0.8\text{V}$ ,  $v=70 \text{ mV/s}$ , the background electrolyte was an alcohol solution of sodium perchlorate 0.1 M. The concentration of carbaryl was calculated by the method of calibration curve. The results of the voltammetric determination of carbaryl are presented in Table 2. These results are calculated using the equations presented in Figure 2b.

**The results of the determination of carbaryl in food ( $n = 3$ )**

Object of study	Found, M	$\Delta$ , %
Corn	$0.84 \cdot 10^{-8}$	$\pm 0.13$
Oats	$0.36 \cdot 10^{-8}$	$\pm 0.054$
Wheat	—	—

Thus, the selected voltammetric conditions for the determination of carbaryl in model solutions allow the determination of its trace amounts in corn and oats. Carbaryl was not detected in wheat.

### Conclusions

In this work, the electrochemical properties of a carbaryl model compound from the class of carbamates were studied by anodic voltammetry on an impregnated graphite electrode modified with carbon ink. The working conditions for the determination of carbaryl in working solutions were selected, namely the background electrolyte is an alcohol solution of sodium perchlorate, the working electrode is an impregnated graphite electrode, the auxiliary and reference electrode is platinum and silver chloride electrodes. It is revealed that when using carbon ink as an electrode modifier, it increases the sensitivity of its determination, which is especially important when determining the trace amounts of carbaryl in grain crops. The range of linear dependence of  $dI/dE$  on the concentration of carbaryl was from  $0 \cdot 10^{-8}$  to  $1.6 \cdot 10^{-8}$  M, the detection limit was  $1.2 \cdot 10^{-9}$  M. The approbation of the carbaryl determination method in corn, oats and wheat was carried out.

### References

- 1 ГН 1.2.1323–03 Гигиенические нормативы содержания пестицидов в объектах окружающей среды.
- 2 Alamgir Zaman Chowdhury M. Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography-mass spectrometry / Alamgir Zaman Chowdhury M., A.M. Fakhrudin, Nazrul Islam M., M. Moniruzzaman, S.H. Gan, Khorshed Alam M. // *Food Control*. — 2013. — Vol. 34. — P. 457–465.
- 3 Çelebi M.S. Electrochemical oxidation of carbaryl on platinum and boron-doped diamond anodes using electro-Fenton technology / M.S. Çelebi, N. Oturan, H. Zazou, M. Hamdani, M.A. Oturan // *Separation and Purification Technology*. — 2015. — Vol. 156. — P. 996–1002.
- 4 Fan Y. Determination of carbaryl pesticide in Fuji apples using surface-enhanced Raman spectroscopy coupled with multivariate analysis. LWT / Y. Fan, K. Lai, B.A. Rasco, Y. Huang // *Food Science and Technology*. — 2015. — Vol. 60. — P. 352–357.
- 5 Van Dyk J.S. Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment / J.S. Van Dyk, B. Pletschke // *Chemosphere*. — 2011. — Vol. 82. — P. 291–307.
- 6 Cesarino I. Electrochemical detection of carbamate pesticides in fruit and vegetables with a biosensor based on acetylcholinesterase immobilised on a composite of polyaniline-carbon nanotubes / I. Cesarino, F.C. Moraes, M.V. Lanza, S.S. Machado // *Food Chemistry*. — 2012. — Vol. 135. — P. 873–879.
- 7 Moraes F.C. Direct electrochemical determination of carbaryl using a multi-walled carbon nanotube/cobalt phthalocyanine modified electrode / F.C. Moraes, L.H. Mascaro, S.S. Machado, C.A. Brett // *Talanta*. — 2009. — Vol. 79. — P. 1406–1411.
- 8 Wei H. Rapid hydrolysis and electrochemical detection of trace carbofuran at a disposable heated screen-printed carbon electrode / H. Wei, J.J. Sun, Y.M. Wang, X. Li, G.N. Chen // *Analyst*. — 2008. — Vol. 133. — P. 1619–1624.
- 9 Liu B. Electrochemical analysis of carbaryl in fruit samples on grapheme oxide-ionic liquid composite modified electrode / B. Liu, B. Xiao and L. Cui // *Journal of Food Composition and Analysis*. — 2015. — Vol. 40. — P. 14–18.
- 10 Липских О.И. Определение кармуазина в безалкогольных напитках методом вольтамперометрии / О.И. Липских, Е.И. Короткова, Е.В. Дорожко, К.В. Дёрина, О.А. Воронова // *Заводская лаборатория. Диагностика материалов*. — 2016. — Т. 82, № 6. — С. 22–26.

А.С. Гашевская, А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, С.О. Кенжетаева

### **Кейбір дәнді дақылдарда ерітінді сіңірілген, көміртектік сиялармен модификацияланған, графит электродында карбарилді вольтамперометриялық анықтау**

Пестицидтер бұл күнде біздің өміріміздің ажырамайтын бөлігі болды. Олар күнде біздің ағзамызға тағамдармен, сумен, топырақпен түседі. Сондықтан әртүрлі нысандарда пестицидтердің құрамын бақылау адам өмірі үшін ең маңызды мәселе болды. Мақалада алғаш рет карбарилдің ерітіндісі сіңірілген, көміртек сияларымен модификацияланған, графит электродында электрохимиялық

тотығуы зерттелген. Карбарилдің кейбір дәнді дақылдардан бөліп алудың оңтайлы жағдайлары табылды, сонынан көміртек сияларымен модификацияланған, ерітінді сіңірілген графит электродында анодтық вольтамперометрия әдісімен анықталды. Зерттеу нысандары болып бидай, сұлы, жүгері сияқты дәнді дақылдар таңдалған. Таңдалған нысандарда карбарилдің анықталуы ЖҚХ әдісімен хроматографиялық бөлуден кейін жүргізілді. Электродтық модификатор ретінде көміртек сияларын қолданғанда ерітінді сіңірілген графит электродының электробелсенді беттерінің аумағы артатыны анықталды. Сол мезгілде карбарилді анықтау сезімталдығы да жоғарлайтыны анықталды, әсіресе бұл карбарилдің дәнді дақылдардағы іздік мөлшерлерін анықтау барысында маңызды. Карбарил концентрациясынан сызықтық тәуелділік диапазоны  $dI/dE$  —  $0 \cdot 10^{-8}$  М-ден  $1,6 \cdot 10^{-8}$  М дейін, ал табу шекарасы  $1,2 \cdot 10^{-9}$  М құрады.

*Кілт сөздер:* карбарил, анодтық вольтамперометрия, ерітінді сіңірілген электрод, көміртектік сиялар, тағамдар, пестицидтер, жұқақабатты хроматография, дәнді дақылдар.

А.С. Гашевская, А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, С.О. Кенжетаева

## **Вольтамперометрическое определение карбарила в некоторых зерновых культурах на импрегнированном графитовом электроде, модифицированном углеродными чернилами**

Пестициды на сегодняшний день являются неотъемлемой частью нашей жизни. Каждый день они попадают в наш организм с продуктами питания, водой, почвой. Поэтому контроль содержания пестицидов в различных объектах является наиболее важной проблемой для жизни человека. В настоящей работе впервые изучено электрохимическое окисление карбарила на импрегнированном графитовом электроде, модифицированном углеродными чернилами. Подобраны оптимальные условия выделения карбарила из некоторых зерновых культур, с последующим его определением на импрегнированном графитовом электроде, модифицированном углеродными чернилами, методом анодной вольтамперометрии. Объектами исследования были выбраны зерновые культуры, такие как пшеница, овес и кукуруза. Определение карбарила в выбранных объектах исследования проводилось после хроматографического разделения методом ТСХ. Выявлено, что при использовании углеродных чернил в качестве электроодного модификатора происходит увеличение площади электроактивной поверхности импрегнированного графитового электрода. При этом увеличивается чувствительность определения карбарила, что особенно важно при определении следовых количеств карбарила в зерновых культурах. Диапазон линейной зависимости  $dI/dE$  от концентрации карбарила составил от  $0 \cdot 10^{-8}$  М до  $1,6 \cdot 10^{-8}$  М, предел обнаружения —  $1,2 \cdot 10^{-9}$  М.

*Ключевые слова:* карбарил, анодная вольтамперометрия, импрегнированный электрод, углеродные чернила, продукты питания, пестициды, тонкослойная хроматография, зерновые культуры.

### References

- 1 GN 1.2.1323–03 *Hihienicheskie normativy sodержaniia pestitsidov v obektakh okruzhaiushchei sredy* [Hygienic standards for the content of pesticides in environmental objects] [in Russian].
- 2 Alamgir Zaman Chowdhury M., Fakhruddin, A.M., Nazrul Islam M., Moniruzzaman M., Gan S.H., & Khorshed Alam M. (2013). Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography–mass spectrometry. *Food Control*, 34, 457–465.
- 3 Çelebi, M.S., Oturan, N., Zazou, H., Hamdani, M., & Oturan, M.A. (2015). Electrochemical oxidation of carbaryl on platinum and boron-doped diamond anodes using electro-Fenton technology. *Separation and Purification Technology*, 156, 996–1002.
- 4 Fan, Y., Lai, K., Rasco, B.A., & Huang, Y. (2015). Determination of carbaryl pesticide in Fuji apples using surface-enhanced Raman spectroscopy coupled with multivariate analysis. *LWT — Food Science and Technology*, 60, 352–357.
- 5 Van Dyk, J.S., & Pletschke, B. (2011). Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment. *Chemosphere*, 82, 291–307.
- 6 Cesarino, I., Moraes, F.C., Lanza, M.V., & Machado, S.S. (2012). Electrochemical detection of carbamate pesticides in fruit and vegetables with a biosensor based on acetylcholinesterase immobilised on a composite of polyaniline-carbon nanotubes. *Food Chemistry*, 135, 873–879.
- 7 Moraes, F.C., Mascaro, L.H., Machado, S.S., & Brett, C.A. (2009). Direct electrochemical determination of carbaryl using a multi-walled carbon nanotube/cobalt phthalocyanine modified electrode. *Talanta*, 79, 1406–1411.
- 8 Wei, H., Sun, J.J., Wang, Y.M., Li, X., & Chen, G.N. (2008). Rapid hydrolysis and electrochemical detection of trace carbofuran at a disposable heated screen-printed carbon electrode. *Analyst*, 133, 1619–1624.
- 9 Liu, B., Xiao, B. & Cui, L. (2015). Electrochemical analysis of carbaryl in fruit samples on grapheme oxide-ionic liquid composite modified electrode. *Journal of Food Composition and Analysis*, 40, 14–18.
- 10 Lipskikh, O.I., Korotkova, E.I., Dorozhko, E.V., Derina, K.V., Voronova, O.A. (2016). Opredelenie karmuazina v bezalkoholnykh napitkakh metodom voltamperometrii [Determination of carmoisin in soft drinks by voltammetry]. *Zavodskaiia laboratoriia. Diahnostika materialov — Factory laboratory. Diagnostics of materials*, 82, 6, 22–26 [in Russian].