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Article

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Study of the Methionine Electrooxidation at an Electrode Modified with Vitamin B_{12} and Multi-Walled Carbon Nanotubes

The electrochemical behavior of methionine at an electrode modified with vitamin B_{12} and multi-walled carbon nanotubes has been studied in this work. A possible mechanism of redox processes occurring on the modified electrode is proposed. When the electrode is formed, vitamin B_{12} is fixed on the surface of a carbon-containing electrode modified with multi-walled carbon nanotubes due to adsorption. In the process of cathodic polarization, cobalt(III) in cobalamin is reduced to cobalt(II) to which a partially negatively-charged sulfur atom in the methionine molecule is attached due to electrostatic interactions. During anodic polarization, cobalt(II) in the complex is oxidized up to Co^{3+}, the methyl group from methionine is transferred to cobalamin, and homocysteine passes into the solution, which is proved by Raman spectra. Based on the study of the dependence of current and potential on the sweep speed, it was found that the oxidation process is not reversible, the limiting stage is adsorption, and one proton and one electron participate in the electrochemical stage. The following optimal conditions for recording an analytical signal were selected: the background electrolyte is a tartrate buffer solution with pH = 4.01; the electrolysis potential is 1.6 V; the accumulation time is up to 180 s. The metrological characteristics of the procedure for determining methionine were estimated. The accuracy index did not exceed 29 %, the repeatability and intermediate precision indices did not exceed 14 % and 16 %, respectively. The range of detectable contents was $(1–50)\times10^{-7}$; the detection limit was 5.0×10^{-8} M. It was shown that a 10-fold excess of ascorbic acid, tryptophan, glycine, cysteine and tyrosine does not have a noticeable distorting effect on the procedure for determining methionine.

Keywords: methionine, modified electrode, vitamin B_{12}, electrooxidation, cobalamin, electron, proton, stripping voltammetry, multi-walled carbon nanotubes.

Introduction

Methionine is an essential amino acid that plays an important role as a precursor for all other sulfur-bearing amino acids and their derivatives in living organisms. It involves in the regulation of metabolic processes of the immune system and has antioxidant activity. The methionine concentration in the range of 5–15 μmol/l is considered normal for men and women. The increased content of methionine is associated with damage caused to nucleic acids, with various types of cancer and cardiovascular diseases. The reduced methionine concentration leads to neurodegenerative diseases [1–6]. In this regard, the determination of the methionine content in foodstuff and biological fluids is a relevant task. Electrochemical methods of analysis are promising for this purpose.

The mechanism of methionine electrooxidation remains ambiguous. In 1960, dehydro-methionine was proposed in [7] as an intermediate of the product of anodic oxidation of methionine at a platinum wire electrode with pH =7.0. Dehydro-methionine was also identified as a by-product of methionine oxidation using various analytical methods [8–10]. A few years later, voltammetric determination of methionine at platinum electrodes was reported in [11]. The authors observed a voltammetric wave between +0.7 and +1.0 V (calomel electrode), which manifested itself only in acidic media and only in the presence of hydrogen and chloride ions [11]. Later, owing to the development of new electrode materials, more detailed studies were carried out. In [12] the authors demonstrated methionine oxidation at a graphite electrode, which is an irreversible process controlled by diffusion. In [13], the authors reported that the oxidation potential of methionine at a glassy-carbon electrode remains constant in the pH range from 3 to 7. The authors also noted that the voltammetric wave of methionine oxidation strongly resembles cystine obtained in similar experimental conditions [12] at the glassy-carbon electrode. In 1994, the authors [14] showed that the neighboring carboxylate and amino groups of thioester, which modifies the electrode, play an important role in the methionine elec-

trooxidation at the carbon electrode, even if these groups are not rigidly held in a fixed position relatively the function of thioester in the molecular skeleton. Later, in 2011, glassy-carbon and diamond electrodes doped with boron were used to study the electrochemical oxidation of methionine in a wide pH range using cyclic and differential pulse voltammetry [15]. The results conform fully to the conclusions of the work [13]. In [15] the oxidation reaction proceeds in two stages at the glassy-carbon electrode and in one stage at boron-doped diamond electrodes, where, probably, the high oxidation current of the second peak is superimposed on the first one. Oxidation reactions have been found to be irreversible, diffusion-controlled, and one-electron processes, independent of pH at pH> 3.

In [16], we proposed a technique for determining methionine at an electrode modified with cyanocobalamin (vitamin B_{12}). When choosing the technique for electrode modification, we proceeded from the following assumptions: methionine entering the human body, when interacting with enzymes, and is reduced to homocysteine [17]. Such reaction can serve as a prototype of the corresponding electrode process. We proposed the use of cyanocobalamin as an auxiliary substance. It is an electroactive substance due to the presence of cobalt(III) in the corrin ring. The process of vitamin B_{12} chemisorption on mesoporous carbon is known [18]. By attaching vitamin B_{12} to the surface of the electrode due to adsorption, it is possible to create conditions allowing the binding of methionine from the solution to form an electroactive compound at the electrode. The purpose of this work is to establish the mechanism of methionine oxidation at the modified electrode to optimize the conditions for the determination of methionine by stripping voltammetry.

Experimental

Equipment and reagents

Methionine (Sigma, USA), multi-walled carbon nanotubes produced by "Graphen" (USA), vitamin B_{12} (Belarus) were used in the work. All measurements were taken using standard pH solutions purchased from "Merck" (Germany). The solutions were prepared using deionized water obtained from "Sartorius" of the arium® pro brand. All the experiments were carried out at room temperature. Electrochemical measurements were performed using a TA-LAB voltammetric analyzer (NPO "Tomanalit") in direct-current mode in a three-electrode cell. The indicator electrode was a modified carbon-containing electrode; silver-chloride electrodes in the 3 M KCl solution were used as an auxiliary electrode and a reference electrode. Multi-walled carbon nanotubes (MCNT) were applied to the surface of the carbon-containing electrode by electrolysis from a MCNT aqueous suspension by means of a universal power source UIP-2.

Modification of the carbon-containing electrode

MCNT were moistened with a small amount of ethyl alcohol; then water was added. After it MCNT were placed into the ultrasound bath for 3 hours. The ready-to-use suspension was used to apply nanotubes to the surface of the carbon-containing electrode by anodic polarization. A stainless-steel plate was used as the cathode (counter electrode). After 8 s of the electrolysis, the applied MCNT were dried and vitamin B_{12} was deposited. Vitamin B_{12} was deposited at the electrode modified with MCNT by cycling the potential in the range of –1.4... +1.0 V. The modification of the electrode is described in more detail in [18].

Results and Discussion

The choice of optimal conditions for the oxidation and/ or reduction processes of the substance is the essential task in the development of a quantitative technique. Suitable conditions lead to an increase in the sensitivity of the analysis. The effect of a number of factors, such as the pH of the background electrolyte, accumulation parameters, and the potential sweep rate on the anode signal of methionine, was studied to select the optimal conditions for obtaining an analytical signal.

The effect of pH

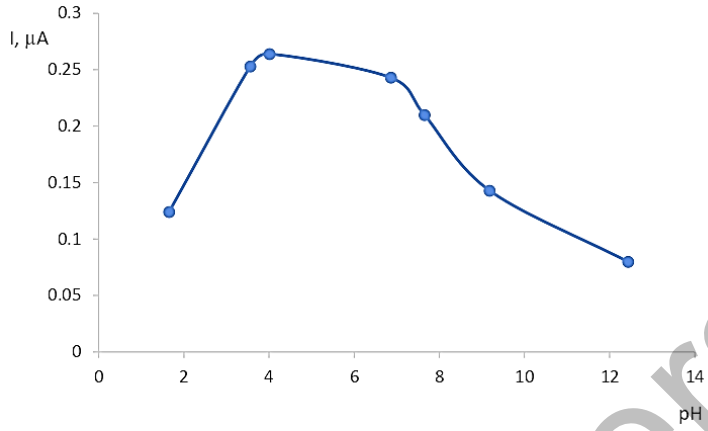
The pH of the background electrolyte has a significant effect on the mechanism of redox processes in voltammetric analysis. Standard buffer solutions from 1.65 to 12.43 were used to establish the optimal value of the hydrogen ion concentration during methionine oxidation at the modified electrode.

Figure 1 shows the dependence of the anode peak value of methionine on the pH of the background electrolyte. With an increase in the pH from 1.65 to 4.01, the peak current of methionine oxidation increases. The decrease in the signal at pH<4 is associated with the protonation of the amino groups of methionine and cobalamin; the adsorption of methionine on the electrode is hindered as a result of electrostatic repulsion. The signal intensity decreases when the pH shifts to the neutral and alkaline regions, which is due to the lack

of protons required for methionine oxidation. The peak shift towards more negative values as the pH of the buffer solution increases. A linear dependence can be observed between the peak potential and the pH:

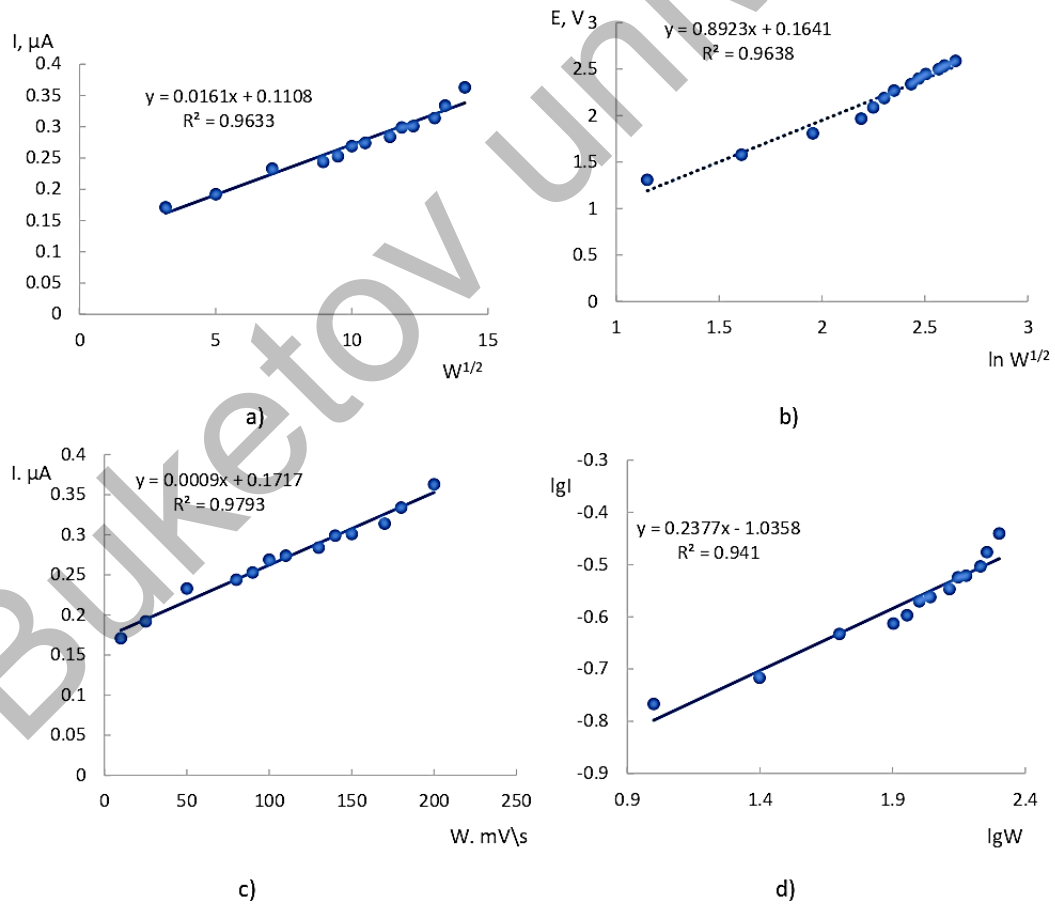
$$Y = -0.0492X + 0.6930. \quad (1)$$

The slope value of 49.2 mV/pH is close to the Nernst slope (59.0 mV/pH), which indicates an equal number of electrons and protons participating in the electrochemical process.



E_{el} = –1.6 V; t = 120 s; W = 50 mV/s; $C = 2\times10^{-6}$ mol/dm^3

Figure 1. Dependence of the electrooxidation current of methionine at the modified electrode on the pH



E_{el} = –1.6 V; t =120 s, $C = 2\times10^{-6}$ mol/dm^3

Figure 2. Dependence of the methionine oxidation current on the square root of the potential sweep rate (*a*), the dependence of the potential on $lnW^{1/2}$ (*b*), the dependences of the current on the potential sweep rate (*c*) and lg$I$ on lg$W$ (*d*)

The effect of the potential sweep rate on the current and potential of the anode peak

The dependences of the anode peak current and potential on the potential sweep rate allow us to estimate the mechanism of the electrochemical reaction. In this regard, the influence of the potential sweep rate on the anode current of methionine was studied. To establish the mechanism of methionine electrooxidation at the modified electrode, the dependences of the current on the square root of the sweep rate (Fig. 2a) and the peak potential on $\ln(W^{1/2})$ were plotted in Figure 2b.

The linear dependence for the current (Fig. 2a) is typical of both reversible and irreversible processes while the linear dependence of the peak potential of methionine on $\ln W^{1/2}$ evidences the irreversibility of the process (Figure 2b). Figure 2b presents the dependence of the current on the sweep rate and a similar dependence in logarithmic coordinates (Fig. 2d). The linearity of the logarithmic dependence (Fig. 2d) indicates that diffusion is not a limiting stage of the process. The Semerano criterion (the slope of the dependence of lg*I* on lg*W*) was 0.24, which indicates the absence of the effect of the diffusion process during the oxidation of methionine on the electrode surface. The Semerano criterion should be 0.5 for the processes limited by diffusion [19]. A similar dependence of the current on the sweep rate demonstrates that adsorption is the limiting stage of the process.

The transfer coefficient of the irreversible process (methionine oxidation) was calculated based on the Tafel dependence. The value of the transfer coefficient was 0.44. The obtained value shows that the first electron participates in the limiting stage of the process.

The following formula was used to calculate the electrons in the case of an irreversible process:

$$\left|E_P - E_{\frac{P}{2}}\right| = \frac{47.7}{\alpha n}, \qquad (2)$$

where E_P is the peak potential; $E_{P/2}$ is the half-peak potential.

The value of n = 1.08 indicates that one electron takes part in the oxidation reaction.

Earlier in [16] we proposed a possible reaction mechanism based on the Raman spectra of pure methionine and its oxidation products from the electrode. Homocysteine has been shown to be the oxidation product of the methionine complex with cyanocobalomine. Based on the study of the above-mentioned kinetics, it is possible to conclude that one electron and one proton participate in the oxidation process of the complex. This may be conditioned by the fact that cobalt, being in the corrin ring of vitamin B_{12}, is oxidized to Co(III) during the anodic potential sweep. During cathodic polarization of the electrode, cobalt in cyanocobalamin is first reduced to +2, and then it is the reduced complex that interacts with methionine. The reverse process of cobalt oxidation occurs during anodic sweep: the methyl group of methionine is transferred to cobalamin and passes into the homocysteine solution (Figure 3).

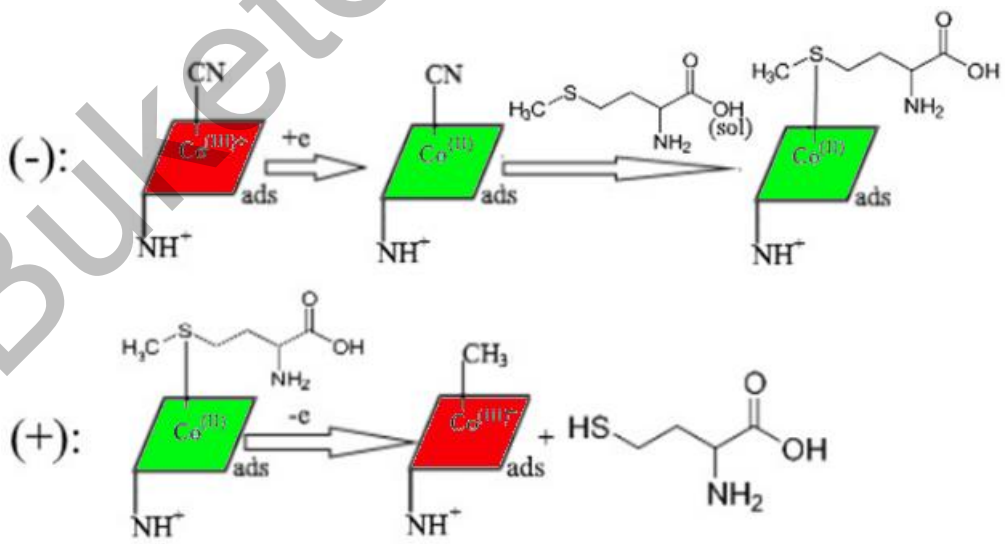


Figure 3. Blank drawing of the methionine oxidation process

The effect of accumulation parameters on the intensity of the electrooxidation signal

The range of values from –1.9 V to –1.1 V was studied when choosing the electrolysis potential (Figure 4*a*). The dependence of the anode peak current on the electrolysis potential passes through the maximum. The anode peaks decrease when the potential is shifted to the negative region, which is most likely due to the release of hydrogen that prevents the formation of the complex on the electrode surface. Therefore, the potential of –1.6 V was chosen as optimal for concentrating methionine at the modified electrode. As can be seen from Figure 4*b*, after accumulation for more than 300 s, the signal intensity changes slightly, which may be conditioned by the complete filling of the electrode surface with a monolayer of the deposited methionine. Therefore, during subsequent studies, the accumulation was carried out no more than 180 s.

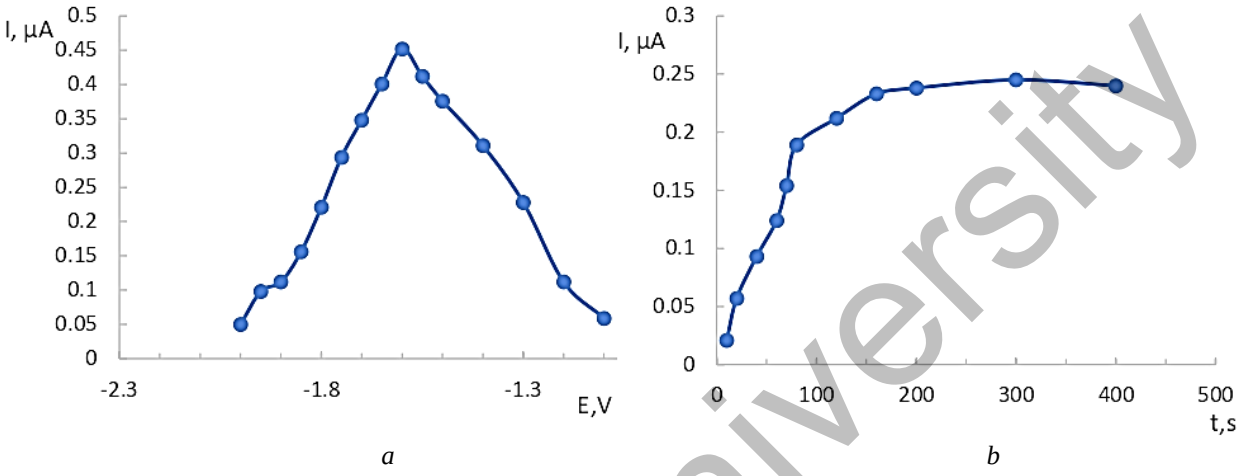


Figure 4. Dependence of the methionine electrooxidation current on the accumulation potential at the modified electrode (t = 120 s, W = 80 mV/s, $C = 5\times10^{-6}$ mol/dm^3) (*a*) and the dependence of the methionine electrooxidation current on the accumulation time (E_{el} = –1.6 V, W = 80 mV/s, $C = 2\times10^{-6}$ mol/dm^3) (*b*)

Despite the fact that the participation of adsorption during electrooxidation of methionine at the electrode has been established, it can be concluded that the mentioned factor does not prevent quantitative assessment in the specified concentration range. The dependence of current on concentration is linear in the range of $(1–50)\times10^{-7}$ and obeys the equation:

$$I = 0.024C + 0.003 \ (E_{el} = –1.6 \text{ V}, t = 150 \text{ s}, W = 80 \text{ mV/s}). \quad (3)$$

The effect of other amino acids on the results of the determination of methionine was studied. The ultimate transferable concentration was defined as the maximum concentration of a hindrance substance, causing an error in the determination of amino acids of no more than 5 % [19, 20]. The 10-fold excess of ascorbic acid, tryptophan, histidine, glycine, arginine, cysteine and tyrosine does not have a noticeable distorting effect on the procedure for methionine determination.

Some metrological characteristics of the procedure for tryptophan and 5-hydroxytryptophan determination

According to ISR 61-2010, the indices of repeatability, intermediate precision, and accuracy were calculated (Table 1).

Table 1

Metrological characteristics of the procedure for methionine determination (p = 0.95, n = 2, l = 15)

Concentration$\times10^{-7}$, mol/dm^3	Repeatability index, σ_r^*, %	Intermediate precision index, σ_{Rl}^*, %	Accuracy index (relative accuracy limits at P = 0.95), ±Δ, %
1	13.9	15.2	29.0
10	13.3	14.7	28.4
20	12.9	14.3	27.3
30	12.5	13.9	26.9
40	12.0	13.5	25.5
50	11.7	13.3	25.4

Based on the obtained metrological characteristics of the developed procedure for methionine determination, it is possible to conclude that the accuracy index does not exceed 29 %, the repeatability and intermediate precision indices do not exceed 14 % and 16 %, respectively.

The modified electrode makes it possible to obtain stable analytical signals for at least 25 cycles (blank experiment, analyzed assay, spiked sample). Further, the electrode sensitivity decreases and the electrode surface renewal is required. The electrode surface is cleansed by electrolysis for 300 s with a potential of –0.5 V. Then a new film of vitamin B_{12} is applied to the surface by cyclic potential scanning.

Conclusions

One proton and one electron take part in the process of oxidation of methionine complex with cobalamin. During oxidation, methionine takes one proton and one electron. In the process of cathodic polarization, cobalt(III) in cobalamin is reduced to cobalt(II) to which a partially negatively-charged sulfur atom in the methionine molecule is attached due to electrostatic interactions. In case of anodic polarization, cobalt(II) in the complex is oxidized to Co(III), the methyl group is transferred from methionine to cobalamin, while homocysteine passes into solution. The process is controlled by adsorption. The following optimal conditions for methionine determination have been selected: the background electrolyte is the tartrate buffer solution with pH = 4.01; the electrolysis potential is 1.6 V; the accumulation time is up to 180 s. A number of metrological indices have been established for the procedure of methionine determination: accuracy. repeatability and intermediate precision indices. The range of detectable contents was $(1–50)\times10^{-7}$; the detection limit was 5.0×10^{-8} M.

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В.В. Шелковников, А.М. Алтыев, М.С. Фрянова

B_{12} дәрумені мен көпқабырғалы көміртекті нанотүтікшелермен модификацияланған электродта метионинніңэлектр тотығуын зерттеу

Жұмыста B_{12} витаминімен және көпқабырғалы көміртекті нанотүтіктермен модификацияланған электродтағы метионинніңэлектрохимиялық тәртібі зерттелген. Модификацияланған электродта болатын тотығу-тотықсыздану процестерінің ықтимал механизмі ұсынылған. Электродты қалыптастыру кезінде B_{12} дәрумені адсорбция есебінен көпқабатты көміртекті нанотүтікшелермен модификацияланған көміртегі бар электродтың бетіне бекітіледі. Катодты поляризация кезінде кобаламиндегі кобальт (III) кобальт (II) дейін азаяды, оған электростатикалық өзара әрекеттесулер есебінен метионин молекуласындағы жартылай теріс зарядталған күкірт атомы қосылады. Анодты поляризация кезінде кешендегі кобальт (II) Co^{3+} дейін тотығады, метионинненметил тобы кобаламинге ауысады, бұл ретте гомоцистеин ерітіндіге өтеді, яғни бұл комбинациялық шашырау спектрлерімен дәлелденген. Ток пен потенциалдың жаймалау жылдамдығына тәуелділігін зерттеу негізінде тотығу процесі қайтымсыз екендігі анықталды. Шектеу сатысы адсорбция болып табылады, ал бір протон мен бір электрон электрохимиялық сатыға қатысады. Аналитикалық сигналды тіркеудің келесі оңтайлы шарттары таңдалды: фондық электролит-тартраттық буферлік ерітінді pH = 4.01; электролиз потенциалы — 1.6 В; жинақтау уақыты — 180 с дейін. Метионинді анықтау әдісінің метрологиялық сипаттамаларына бағалау жүргізілді. Дәлдік көрсеткіші 29 %-дан аспайды. Қайталану және аралық дәлдік көрсеткіштері сәйкесінше 14% және 16% құрады. Анықталған құрамдардың диапазоны $(1–50)\times10^{-7}$; анықтау шегі — 5.0×10^{-8} М. Аскорбин қышқылының, триптофанның, глициннің, цистеиннің және тирозиннің 10 есе артық болуы метионинді анықтау әдісіне айтарлықтай бұрмалаушы әсер етпейтіні көрсетілген.

Кілт сөздер: метионин, модификацияланған электрод, B_{12} витамині, электр тотығу, кобаламин, электрон, протон, инверсиялы вольтамперметрлеу, көпқабырғалы көміртекті нанотүтіктер.

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Изучение процесса электроокисления метионина на модифицированном витамином B_{12} и многостенными углеродными нанотрубками электроде

В статье изучено электрохимическое поведение метионина на электроде, модифицированном витамином B_{12} и многостенными углеродными нанотрубками. Предложен возможный механизм окислительно-восстановительных процессов, протекающих на модифицированном электроде. При формировании электрода витамин B12 закрепляется на поверхности углеродсодержащего электрода модифицированного многостенными углеродными нанотрубками за счет адсорбции. При катодной поляризации кобальт (III) в кобаламине восстанавливается до кобальта (II), на который, за счет электростатических взаимодействий, присоединяется частично отрицательно заряженный атом серы в молекуле метионина. При анодной поляризации кобальт (II) в комплексе окисляется до Co^{3+}, метильная группа с метионина переносится на кобаламин, при этом в раствор переходит гомоцистеин, что доказано спектрами комбинационного рассеяния. На основании изучения зависимости тока и потенциала от скорости развертки было установлено, что процесс окисления необратим. Лимитирующей стадией является адсорбция, а в электрохимической стадии участвуют один протон и один электрон. Были подобраны следующие оптимальные условия регистрации аналитического сигнала: фоновый электролит — тартратный буферный раствор pH = 4,01; потенциал электролиза — 1,6 В; время накопления — до 180 с. Проведена оценка метрологических характеристик методики определения метионина. Показатель точности не превышал 29 %. Показатели повторяемости и промежуточной прецизионности не превы-

шали 14 и 16 % соответственно. Диапазон определяемых содержаний составил (1–50)×10^{-7}; предел обнаружения — 5,0×10^{-8} М. Показано, что 10-кратный избыток аскорбиновой кислоты, триптофана, глицина, цистеина и тирозина не оказывает заметного искажающего влияния на методику определения метионина.

Ключевые слова: метионин, модифицированный электрод, витамин B_{12}, электроокисление, кобаламин, электрон, протон, инверсионная вольтамперометрия, многостенные углеродные нанотрубки.

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