# CRITERIA FOR THE SELECTING PARAMETERS ANODE POLARIZATION PROCESS OF SUBSTANCES ON THE ION-SELECTIVE ELECTRODES SURFACE 

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#### Abstract

The methods of making solid-phase ion-selective electrodes, as primary converters for controlling the concentration of harmful substances during environmental monitoring of natural and technological waters, have been analyzed. The algorithm of the method of creating an ion-selective electrode with a sulfide function (IESF) is developed. The results of processes of anodic polarization of an electrode-active substance on the surface of an ion-selective electrode are given. The dependences of the time of application of the electrode-active material Ag2S at a constant current density of $6,10,20,30,40 \mu \mathrm{~A} / \mathrm{mm}^{2}$ are obtained. The mathematical models of creation of the IESF with the help of one-parametric regression analysis are developed. Key words: ecological safety, ion-selective electrode, anodic polarization, regression analysis, model.


Критерії вибору параметрів процесу анодної поляризації речовин на поверхні іон-селективних електродів. Тичков В.В., Трембовецька Р.В., Гальченко В.Я. Проаналізовані методи виготовлення твердофазних іон-селективних електродів як первинних перетворювачів для контроля концентрації шкідливих речовин при екологічному моніторингу природної та технологічної води. Розроблений алгоритм методу виготовлення іон-селективного електроду з сульфідною функцією (ІСЕСФ). Наведено результати процесів анодної поляризації електродно-активної речовини на поверхню іон-селективного електроду. Отримані залежності часу нанесення електродно-активного матеріалу Ag 2 S при постійній щільності струму 6,10 , $20,30,40$ мкА/мм². Розроблені математичні моделі створення ІСЕСФ за допомогою однопараметричного регресійного аналізу. Ключові слова: екологічна безпека, іон-селективний електрод, анодна поляризація, регресійний аналіз, модель.

Критерии выбора параметров процесса анодной поляризации веществ на поверхности ион-селективных электродов. Тычков В.В., Трембовецкая Р.В., Гальченко В.Я. Проанализированы методы изготовления твердофазных ион-селективных электродов как первичных преобразователей контроля концентрации вредных веществ при экологическом мониторинге природной и технологической воды. Разработанный алгоритм метода изготовления ион-селективного электрода с сульфидной функцией (ИСЕСФ). Приведены результаты процессов анодной поляризации электродно-активного вещества на поверхность ион-селективного электрода. Получены зависимости времени нанесения электродно-активного материала Ag 2 S при постоянной плотности тока $6,10,20,30,40$ мкА/мм². Разработаны математические модели изготовления ИСЕСФ с помощью однопараметрического регрессионного анализа. Ключевые слова: экологическая безопасность, ион-селективный электрод, анодная поляризация, регрессионный анализ, модель.

Formulation of the problem. The water of rivers and seas is polluted by industrial discharges, sewage from urban sewers, livestock complexes, as well as toxic chemicals and mineral fertilizers washed off the fields. Almost $40 \%$ of wastewater is only partially purified or not cleaned at all. At the same time, the condition of many treatment plants is in such a state that most chemical compounds pass unhindered through them. For modern objects of automation of industrial production there are quite a variety of functional tasks that put forward stringent requirements to the level of automation, methods and means of ensuring the efficiency and reliability of measuring control systems. One of the systems elements are the primary information converters, whose task is to determine the composition and concentration of substances, pressure, temperature and other parameters in automatic control systems of industrial production, in chemical, ecological studies, in agriculture and in a number of other areas. Thus, the varieties of technological parameters require the development of
reliable operating automatic control systems, where an operative measurement of physical and chemical quantities is required, based on different principles. Particular importance of measuring concentration is acquired for labor protection, solving the problem of environmental protection, in crisis, emergency and technogeny situations. Usually in such cases, fast and accurate measuring instruments are required as part of automated process control systems that ensure the measurement of parameters, while directly determining the composition and properties of process water.

The relevance of research. The most important technological parameter for automatic control systems (ACS) is the composition of processing materials; therefore measuring analytical control is an obligatory element of any ACS of process water, which is carried out directly in the production stream. The term technological water (or process water) means water, which is used to provide the technological process at all stages of production and operation of the enterprise, as a
whole, and directly contacts raw materials and intermediate products in the technological process [1]: from selection, washing and use in the process itself and ending with aqueous solutions that form waste water. The quality of process water is determined by the complex of its chemical components and physical properties that determine the suitability of water for certain types of water use. The main factors that affect the quality of the technological process include, for example, water composition, pressure and temperature in process units and units.

The purpose of this work is to develop a model of primary information converters for flow injection ACS and to assess the effect of their application on the quality of process water control, depending on the proposed methods for manufacturing ion-selective electrodes based on anodic polarization.

Communication of author's development with important scientific and practical tasks. Research and innovation in the development of environmental monitoring techniques were performed according to the international study on the project Tempus NETCENG "The new model of the third cycle in the field of engineering education in connection with the Bologna process in the BY, RU, UA" at the Department Instrument Making, Mechatronics and Computerized Technologies of Cherkasy State Technological University [2].

Analysis of recent research and publications. Solid membrane ion-selective electrodes, as a rule, are made of homogeneous and heterogeneous materials [3-6]. As homogeneous materials, single crystals, solidified salt melts, pressed powdered salts or ceramic materials pressed into the pellets, which are obtained by sintering or pressing at high temperature, vanadium and tungsten bronze oxides, stoichiometric compounds with cationic disordering (such as halides and silver chalcogenides), non-stoichiometric compounds with a high intrinsic disorder (such as $\mathrm{Al}_{2} \mathrm{O}_{3}$ ), a compound with a high concentration of anionic vacancies, which realized due to disordering impurity (such as a stabilized $\mathrm{Zr}_{2}$ ). Heterogeneous materials are powdered precipitates of sparingly soluble salts that are embedded in an inert matrix.

The main methods of manufacturing solid ion-selective electrodes are [3-6]:

- pressing under pressure $-2500 \mathrm{~kg} / \mathrm{cm}^{2}$ at a temperature of $1000-1100^{\circ} \mathrm{C}$ for 20-30 hours; 1400-20000 atm. at a temperature of $150-200^{\circ} \mathrm{C} ; 250-300 \mathrm{~kg} / \mathrm{cm}^{3}$; $120 \mathrm{kgf} / \mathrm{cm}^{2}$ at a temperature of $120 \pm 5^{\circ} \mathrm{C}$ for 90 minutes; $120-130 \mathrm{~kg} / \mathrm{cm}^{2}$ under a vacuum of $10-2-10-3 \mathrm{~mm} . \mathrm{rt}$. st. at a temperature of $800-1000^{\circ} \mathrm{C}$ for $1.5-2$ hours; $50.5 \mathrm{~kg} / \mathrm{mm}^{2} ; 10 \mathrm{~atm} / \mathrm{cm}^{2}$ at a temperature of $500^{\circ} \mathrm{C}$; $7.5 \mathrm{t} / \mathrm{cm}^{2}$ at $150{ }^{\circ} \mathrm{C}$ for several hours; $9000 \mathrm{~kg} / \mathrm{cm}^{2}$ for 3 minutes at an annealing of $25-180{ }^{\circ} \mathrm{C} ; 20 \mathrm{t} / \mathrm{cm}^{2}$ at room temperature for 24 hours; $3000-5000 \mathrm{kgf} / \mathrm{cm}^{2}$ at $90-210^{\circ} \mathrm{C}$ for $5-15$ minutes;
- anodic polarization $-0.75 \mathrm{~A} / \mathrm{dm}^{2} ; 400 \mathrm{Cl} / \mathrm{dm}^{2}$; $0.2 \mathrm{~A} / \mathrm{dm}^{2}$ for 30 minutes and $0.3 \mathrm{~A} / \mathrm{dm}^{2}$ for 10 min -
utes; $0.21-0.25 \mathrm{~V}$ pulsed sinusoidal voltage in for 10-15 seconds;
- cathodic polarization $-0.5-0.6 \mathrm{~A} / \mathrm{dm}^{2} ; 300-360$ $\mathrm{Cl} / \mathrm{dm}^{2} ; 0.25 \div-0.21 \mathrm{~V}$ pulsed sinusoidal voltage for 50-60 seconds;
- vacuum deposition - deposition rate $0.5 \mathrm{~nm} / \mathrm{s}$ at a temperature of $200-350^{\circ} \mathrm{C} ; 4000 \mathrm{~A} / \mathrm{min}$ at a temperature of $1700^{\circ} \mathrm{C}$ for 2 hours and at a temperature of $2000^{\circ} \mathrm{C}$ for 5 minutes,
- mixing with organic material - polystyrene, epoxy and silicone compound, paraffin, polytetrafluoroethylene, graphite and polystyrene, fluoroplastic emulsion, rubber, polyvinyl chloride, graft polymer-based copolymer with acrylonitrile, BF glue.

Allocation of previously unresolved parts of the general problem to which this article is devoted. There remain a number of unresolved problems that play an important role in the development of automatic control systems (ACS). One of such tasks is to improve the quality of primary information converters, in particular for control of process water. The quality of process water is determined by the complex of its chemical components and physical properties that determine the suitability of water for certain types of water use; therefore it is very important to determine these parameters in real time. At the moment, automatic operational control of technological parameters in the ACS is performed with insufficient accuracy, and for some technological processes it is not realized at all.

To assess the effect of the use of ion-selective electrodes on the quality of process water control, the main task is to develop methods for manufacturing primary information converters for flow-injection systems for automatic control of process water [7-8].

The main criteria for limiting anodic polarization in the manufacture of an ion-selective electrode include the thickness of the electrode-active membrane, the resistance of the electrode, and the polarization time.

The thickness of the electrode-active material affects the overall resistance of the ion-selective electrode. The larger the thickness, the greater the resistance of the ion-selective electrode, which affects the characteristics of the ion-selective electrode itself, namely: the response time increases, which entails the need to increase the input resistance of the measuring device, which reaches several gigaOm.

Currently, these criteria are not sufficiently developed.
Novelty. The novelty of the study is the formulation of rational criteria for the anodic polarization of an electrode active substance on the surface of ion-selective electrodes.

Methodological or general scientific value. A unified methodology for the formation of an electrode active substance on the surface of ion-selective electrodes

Statement of the main material. The formation of an electrode-active element of an ion-selective electrode is carried out using the example of a sulfide-silver electrode according to the algorithm [9] (Fig. 1).


Fig. 1. Algorithm for forming an electrode-active element of an ion-selective electrode by the example of a sulfide-silver electrode

Calculation of the thickness of the Ag 2 S layer deposition on the silver substrate is carried out according to the Faraday law:

$$
\begin{equation*}
\mathrm{m}=\mathrm{k} \cdot \mathrm{q}=\mathrm{k} \cdot \mathrm{I} \cdot \mathrm{t} \tag{1}
\end{equation*}
$$

where m - the mass of the substance released on the electrode, kg;
k - the coefficient associated with the atomic mass of substance $A, k=\frac{1}{F} \frac{A}{n}$;
q - the electric charge, Cl ;
I - the strength of the direct current passing through the solution, A ;
t - the reaction time, s ;
F - Faraday number, $9.648 \cdot 10^{4} \mathrm{Cl} / \mathrm{mol}$;
n - the valence of the ion.
The weight of the electrode-active substance deposited on the electrode material is related to the geometry of the electrode itself:

$$
\begin{equation*}
\mathrm{m}=\mathrm{S} \cdot \mathrm{~h} \cdot \mathrm{~A}, \tag{2}
\end{equation*}
$$

where $S$ - the cross-sectional area of the electrode surface, $\mathrm{m}^{2}$;
h - thickness of the deposited layer of electrode-active material, m;
$\rho$ - the density of the material, $\mathrm{kg} / \mathrm{m}^{3}$.
Further, applying formulas 1 and 2, the thickness of deposition of electrode-active material Ag 2 S as an ion-selective electrode of circular cross-section is calculated by the formula:

$$
\begin{equation*}
\mathrm{h}=\frac{4 \mathrm{~A} \cdot \mathrm{I} \cdot \mathrm{t}}{\dot{\mathrm{~A}} \cdot \mathrm{~d}^{2} \cdot \dot{\mathrm{~A}} \cdot \mathrm{~F} \cdot \mathrm{n}} \tag{3}
\end{equation*}
$$

To compare the electrical characteristics of an ion-selective electrode, calculations are made of the thickness of deposition of electrode-active material on two types of electrodes:

- newly developed by the authors heterogeneous electrode of the 2 nd kind $\mathrm{d}=3.3 \mathrm{~mm}, \mathrm{U}=4 \mathrm{~V}, \mathrm{I}=$ $1.5525 \cdot 10^{-3} \mathrm{~A} \cdot \mathrm{~s}$;
- silver wire from a standard factory-made electrode $\mathrm{d}=1.8 \mathrm{~mm} ; \mathrm{U}=1 \mathrm{~V} ; \mathrm{I}=7.56 \cdot 10-2 \mathrm{~A} \cdot \mathrm{~s}$.

The thickness of the ion-selective electrode of the first type is $\mathrm{h} 1=0.05 \cdot 10^{-6} \mathrm{~m}$, and in the second $-\mathrm{h} 2=$ $6.43 \cdot 10^{-6} \mathrm{~m}$. The current density $\mathrm{i}_{01}=1.8 \cdot 10-2 \mathrm{~A} / \mathrm{mm}^{2}$, and $\mathrm{i}_{02}=2.4 \mathrm{~A} / \mathrm{mm}^{2}$.

When optimizing the thickness of deposition of elec-trode-active material, the following formula for determining the application time is recommended:

$$
\begin{equation*}
\mathrm{t}=\frac{\mathrm{S} \cdot \mathrm{~A} \cdot \mathrm{~F} \cdot \mathrm{~h}}{\mathrm{~A} \cdot \mathrm{I}}, \tag{4}
\end{equation*}
$$

For example, to obtain the electrode-active material of an ion-selective electrode of the first type with a thickness of $1 \mu \mathrm{~m}$ and $\mathrm{I}=10^{-5} \mathrm{~A} \cdot \mathrm{~h}$, the application lasts about 30 minutes. With the increment of the current to I $=10^{-3} \mathrm{~A} \cdot \mathrm{~h}$ the application time is sharply reduced to 32 s .

To a powder of silver with a particle size of $1-3 \mu \mathrm{~m}$, thoroughly washed and dried, ED-20 epoxy resin with a curing agent was added in a ratio of $70 \%$ silver powder and $30 \%$ ED-20 by weight, thoroughly mixed until an electrically conductive mixture was obtained. The resulting mixture was formed into an electrode of the required size and the mixture solidified at $60^{\circ} \mathrm{C}$. After solidification, the electrode surface was ground and washed with distilled water. The electrode was immersed in a 0.1 M solution of $\mathrm{Na}_{2} \mathrm{~S}$ and anodically polarized at a current density of $1.16 \cdot 10^{-7} \mathrm{~A} / \mathrm{mm}^{2}$ at normal temperature. In the process of polarization, the volume of the electrode-active substance of the electrode increases in comparison with the volume of the metal and a dense layer of elec-trode-active material forms in the pores of the matrix, which has the properties of an impermeable membrane for electrolyte.

The current density was chosen in such a way that a dense membrane was formed, the presence of which is indicated by the dependence of $\mathrm{U}(\mathrm{t})$ at a constant current strength (Fig. 2).

The obtained electrode has the following characteristics: a membrane thickness of about $10 \mu \mathrm{~m}$, a membrane resistance of $1.4 \mathrm{M} \Omega$.

Figure 2 shows the time dependence of deposition of electrode-active material with Ag 2 S -function at a constant current density of $6,10,20,30,40 \mu \mathrm{~A} / \mathrm{mm}^{2}$. With a low current density, the formation of a dense layer of electrode active substance in the pores of the matrix, which has the properties of an impermeable membrane, occurs slowly without detachment. With increasing current density, the formation of a dense layer occurs quickly and there is the possibility of detachment of the electrode active substance. Jumps on linear sections

Table 1
Comparative characteristics of electrodes

| Electrode parameter | Analog | Prototype | In accordance with the <br> developed criteria |
| :---: | :---: | :---: | :---: |
| Heating temperature of <br> electrode material | $100-350^{\circ} \mathrm{C}$, sintering at <br> $500^{\circ} \mathrm{C}$ | $600-700^{\circ} \mathrm{C}$, cooling at <br> $450^{\circ} \mathrm{C}$ | hardening at $60^{\circ} \mathrm{C}$ <br> Current Density$\quad 10 \mathrm{~mA} / \mathrm{cm}^{2}$ |

arise due to a sharp decrease in the local resistance of the pores of the matrix.

After each application of the electrode active substance, the electrode was ground, washed with distilled water and a new layer was applied.

In the manufacture of an ion-selective electrode, the thickness of the electrode-active substance, the resistance of the electrode, and the polarization time can be classified as the main criteria for the parameters of anodic polarization.

The main developed mathematical models for manufacturing an ion-selective electrode using the example of a sulfide-selective measuring primary transducer are presented in Tables 2-6.

The ranking of mathematical models based on the correlation coefficient of experimental and calculated
data on models based on one-parameter regression analysis is made. The standard error did not exceed $1.33 \%$.

The main conclusions. The obtained results made it possible to solve an important scientific and technical problem of improving the quality of process water control by improving ionometric primary converters for automated control and measurement systems and to reveal a number of regularities in the course of anodic polarization of an electrode active substance on the surface of ion-selective electrodes in order to obtain rational parameters.

The developed methods of manufacturing an ion-selective electrode, mathematical and computer models have expanded the scientific and technical base for the design of ionometric primary converters.


Fig. 2. Dependences of the voltage in the function versus time for depositing an electrode active material with an Ag2S function at a constant current density

Table 2
Regression models for current density of $6 \mu \mathrm{~A} / \mathrm{mm}^{2}$,
which are ranked by the correlation coefficient. No weighting used

| Rank | Model family | Model equation | Coefficient Data | Standard Error | Correlation Coefficient | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 3rd degree Polynomial Fit | $y=a+b x+c x^{2}+d x^{3}+\ldots$ | $\begin{aligned} & \mathrm{a}=-0.01586116 \\ & \mathrm{~b}=0.86107566 \\ & \mathrm{c}=-0.058806944 \\ & \mathrm{~d}=0.0016020452 \end{aligned}$ | 0.0948107 | 0.9985689 | Linear regression completed successfully. |
| 2 | MMF Model | $y=\frac{a b+c x^{d}}{b+x^{d}}$ | $\begin{aligned} & \mathrm{a}=0.019879606 \\ & \mathrm{~b}=8.1890173 \\ & \mathrm{c}=6.9249312 \\ & \mathrm{~d}=1.1387493 \\ & \hline \end{aligned}$ | 0.0951351 | 0.9985591 | The fit converged to a tolerance of $10^{-6}$ in 5 iterations |
| 3 | Rational Function | $y=\frac{a+b x}{1+c x+d x^{2}}$ | $\begin{aligned} & \mathrm{a}=-0.055183972 \\ & \mathrm{~b}=0.96626574 \\ & \mathrm{c}=0.11753196 \\ & \mathrm{~d}=0.00039517782 \end{aligned}$ | 0.1015502 | 0.9983581 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations |
| 4 | Exponential Association | $y=a\left(1-e^{-b x}\right)$ | $\begin{aligned} & a=5.5742239 \\ & b=0.15396517 \end{aligned}$ | 0.1024378 | 0.9981620 | The fit converged to a tolerance of $10^{-6}$ in 4 iterations |
| 5 | Exponential Association (3) | $y=a\left(b-e^{-c x}\right)$ | $\begin{aligned} & a=5.5740591 \\ & b=1.0001888 \\ & c=0.15387804 \end{aligned}$ | 0.1048476 | 0.9981620 | The fit converged to a tolerance of $10^{-6}$ in 4 iterations |
| 6 | Quadratic Fit | $y=a+b x+c x^{2}$ | $\mathrm{a}=0.20088066$ $\mathrm{~b}=0.64874041$ $\mathrm{c}=-0.022001894$ | 0.1782984 | 0.9946755 | Linear regression completed successfully |
| 7 | Sinusoidal Fit | $y=a+b \cos (c x+d)$ | $\begin{aligned} & \mathrm{a}=-21.290935 \\ & \mathrm{~b}=26.272677 \\ & \mathrm{c}=0.041880654 \\ & \mathrm{~d}=-0.61153839 \end{aligned}$ | 0.1903512 | 0.9942190 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$ |
| 8 | Logistic Model | $y=\frac{a}{\left(1+b e^{-c x}\right)}$ | $\begin{aligned} & \mathrm{a}=4.8023304 \\ & \mathrm{~b}=6.9645473 \\ & \mathrm{c}=0.48498216 \end{aligned}$ | 0.3002328 | 0.9848278 | The fit converged to a tolerance of $10^{-6}$ in 10 iterations |
| 9 | Harris Model | $y=\frac{1}{\left(a+b x^{c}\right)}$ | $\begin{aligned} & \mathrm{a}=9.8218183 \\ & \mathrm{~b}=-9.1914979 \\ & \mathrm{c}=0.017465265 \end{aligned}$ | 0.4949634 | 0.9582030 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$. |
| 10 | Linear Fit | $y=a+b x$ | $\begin{aligned} & \mathrm{a}=0.90896838 \\ & \mathrm{~b}=0.31497412 \end{aligned}$ | 0.5088212 | 0.9536179 | Linear regression completed successfully |

Regression models for current density of $10 \mu \mathrm{~A} / \mathrm{mm}^{2}$,
which are ranked by the correlation coefficient. No weighting used.

| Rank | Model family | Model equation | Coefficient Data | Standard Error | Correlation Coefficient | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | MMF Model | $y=\frac{a b+c x^{d}}{b+x^{d}}$ | $\begin{aligned} & \mathrm{a}=-0.16394022 \\ & \mathrm{~b}=17.188845 \\ & \mathrm{c}=37.147937 \\ & \mathrm{~d}=0.71799244 \end{aligned}$ | 0.2207596 | 0.9980936 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations. |
| 2 | Rational Function | $y=\frac{a+b x}{1+c x+d x^{2}}$ | $\begin{aligned} & \mathrm{a}=0.036261843 \\ & \mathrm{~b}=2.0483837 \\ & \mathrm{c}=0.17644637 \\ & \mathrm{~d}=-0.0033832081 \end{aligned}$ | 0.2363993 | 0.9978136 | The fit converged to a tolerance of $10^{-6}$ in 7 iterations. |
| 3 | $\begin{array}{\|l\|} \hline \text { 3rd degree } \\ \text { Polynomial Fit } \end{array}$ | $y=a+b x+c x^{2}+d x^{3}+\ldots$ | $\mathrm{a}=0.32933613$ $\mathrm{~b}=1.4560054$ $\mathrm{c}=-0.087617579$ $\mathrm{~d}=0.002415726$ | 0.2896300 | 0.9967163 | Limear regression completed successfully. |
| 4 | Exponential Association (3) | $y=a\left(b-e^{-c x}\right)$ | $\begin{aligned} & a=12.511854 \\ & b=1.0335835 \\ & c=0.1085052 \end{aligned}$ | 0.3021628 | 0.9962464 | The fit converged to a tolerance of $10^{-6}$ in 5 iterations. |
| 5 | Exponential Association | $y=a\left(1-e^{-b x}\right)$ | $\begin{aligned} & a=12.238764 \\ & b=0.12602876 \end{aligned}$ | 0.3391006 | 0.9950444 | The fit converged to a tolerance of $10^{-6}$ in 4 iterations. |
| 6 | Quadratic Fit | $y=a+b x+c x^{2}$ | $\begin{aligned} & a=0.6561614 \\ & b=1.1358248 \\ & c=-0.032119198 \end{aligned}$ | 0.3642924 | 0.9945394 | Linear regression completed successfully. |
| 7 | Sinusoidal Fit | $y=a+b \cos (c x+d)$ | $\begin{aligned} & \mathrm{a}=-30.328437 \\ & \mathrm{~b}=40.969299 \\ & \mathrm{c}=0.041213847 \\ & \mathrm{~d}=-0.71169611 \end{aligned}$ | 0.3854227 | 0.9941775 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$. |
| 8 | Logistic Model | $y=\frac{a}{\left(1+b e^{-c x}\right)}$ | $\begin{aligned} & a=10.424018 \\ & b=5.8725011 \\ & c=0.36596637 \end{aligned}$ | 0.6405118 | 0.9830210 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations. |
| 9 | Linear Fit | $y=a+b x$ | $\begin{aligned} & a=1.6898547 \\ & b=0.64858015 \end{aligned}$ | 0.7834244 | 0.9732577 | Linear regression completed successfully. |
| 10 | Harris Model | $y=\frac{1}{\left(a+b x^{c}\right)}$ | $\begin{aligned} & \mathrm{a}=4.8361121 \\ & \mathrm{~b}=-4.5075667 \\ & \mathrm{c}=0.019039133 \end{aligned}$ | 0.7838855 | 0.9744587 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$. |


| Rank | Model family | Model equation | Coefficient Data | Standard Error | Correlation Coefficient | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | MMF Model | $y=\frac{a b+c x^{d}}{b+x^{d}}$ | $\begin{aligned} & \mathrm{a}=1.9039411 \cdot 10^{-6} \\ & \mathrm{~b}=0.26773449 \\ & \mathrm{c}=6.3371565 \\ & \mathrm{~d}=2.2921148 \end{aligned}$ | 0.0089030 | 0.9999957 | The fit converged to a tolerance of $10^{-6} \mathrm{in} 29$ iterations. |
| 2 | Exponential Association | $y=a\left(1-e^{-b x}\right)$ | $\begin{aligned} & \mathrm{a}=6.2921151 \\ & \mathrm{~b}=1.5731967 \end{aligned}$ | 0.0107500 | 0.9999931 | The fit converged to a tolerance of $10^{-6}$ in 5 iterations. |
| 3 | Exponential Association (3) | $y=a\left(b-e^{-c x}\right)$ | $\begin{aligned} & a=6.2920312 \\ & b=1.0000135 \\ & c=1.5731839 \end{aligned}$ | 0.0110027 | 0.9999931 | The fit converged to a tolerance of $10^{-6}$ in 5 iterations. |
| 4 | Rational Function | $y=\frac{a+b x}{1+c x+d x^{2}}$ | $\begin{aligned} & a=-6.1226843 \cdot 10^{-5} \\ & b=15.216919 \\ & c=1.981808 \\ & d=0.043803703 \end{aligned}$ | 0.0234908 | 0.9999699 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations. |
| 5 | Logistic Model | $y=\frac{a}{\left(1+b e^{-c x}\right)}$ | $\begin{aligned} & a=6.233345 \\ & b=7459.6947 \\ & c=10.316956 \end{aligned}$ | 0.0590889 | 0.9998000 | The fit converged to a tolerance of $10^{-6}$ in 17 iterations. |
| 6 | $\begin{array}{\|l\|} \hline \text { 4th Degree } \\ \text { Polynomial Fit } \end{array}$ | $y=a+b x+c x^{2}+d x^{3}+\ldots$ | $\begin{aligned} & \mathrm{a}=0.0044789762 \\ & \mathrm{~b}=7.1048486 \\ & \mathrm{c}=-2.80422 \\ & \mathrm{~d}=0.45741233 \\ & \mathrm{e}=-0.026232619 \end{aligned}$ | 0.1072546 | 0.9994036 | Linear regression completed successfully |
| 7 | Quadratic Fit | $y=a+b x+c x^{2}$ | $\begin{aligned} & a=0.10675676 \\ & b=3.0881596 \\ & c=-0.33307593 \end{aligned}$ | 0.6308206 | 0.9769383 | Linear regression completed successfully. |
| 8 | Sinusoidal Fit | $y=a+b \cos (c x+d)$ | $\begin{aligned} & \mathrm{a}=-47.61032 \\ & \mathrm{~b}=54.88472 \\ & \mathrm{c}=0.11134534 \\ & \mathrm{~d}=-0.51661143 \end{aligned}$ | 0.6568767 | 0.9761754 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$. |
| 9 | Linear Fit | $y=a+b x$ | $\begin{aligned} & \mathrm{a}=0.41086957 \\ & \mathrm{~b}=1.1621118 \end{aligned}$ | 1.3201111 | 0.8892869 | Linear regression completed successfully |

Table 6
Regression models for current density of $40 \mu \mathrm{~A} / \mathrm{mm}^{2}$,
which are ranked by the correlation coefficient. No weighting used

| Rank | Model family | Model equation | Coefficient Data | Standard Error | Correlation Coefficient | Comments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Rational Function | $y=\frac{a+b x}{1+c x+d x^{2}}$ | $\begin{aligned} & a=-2.9852183 \cdot 10^{-8} \\ & b=78.516962 \\ & c=12.199357 \\ & d=-0.11467602 \end{aligned}$ | 0.0182087 | 0.9999823 | The fit converged to a tolerance of $10^{-6}$ in 7 iterations. |
| 2 | Exponential Association | $y=a\left(1-e^{-b x}\right)$ | $\begin{aligned} & a=6.5486868 \\ & b=2.4133497 \end{aligned}$ | 0.0663580 | 0.9997411 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations. |
| 3 | Exponential Association (3) | $y=a\left(b-e^{-c x}\right)$ | $\begin{aligned} & a=6.5485862 \\ & b=1.0000145 \\ & c=2.4133849 \\ & \hline \end{aligned}$ | 0.0679195 | 0.9997411 | The fit converged to a tolerance of $10^{-6}$ in 6 iterations. |
| 4 | 4th Degree Polynomial Fit | $y=a+b x+c x^{2}+d x^{3}+\ldots$ | $\begin{aligned} & \mathrm{a}=0.0036766496 \\ & \mathrm{~b}=9.6037025 \\ & \mathrm{c}=-4.777796 \\ & \mathrm{~d}=0.95773409 \\ & \mathrm{e}=-0.066240565 \end{aligned}$ | 0.1329116 | 0.9991025 | Linear regression completed successfully. |
| 5 | Quadratic Fit | $y=a+b x+c x^{2}$ | $\begin{aligned} & \mathrm{a}=0.098122867 \\ & \mathrm{~b}=3.7423269 \\ & \mathrm{c}=-0.46476719 \end{aligned}$ | 0.6957476 | 0.9724521 | Linear regression completed successfully. |
| 6 | Sinusoidal Fit | $y=a+b \cos (c x+d)$ | $\begin{aligned} & \mathrm{a}=-48.773534 \\ & \mathrm{~b}=56.41432 \\ & \mathrm{c}=0.12974353 \\ & \mathrm{~d}=-0.52288064 \end{aligned}$ | 0.7232289 | 0.9716386 | The iteration count of 100 was exceeded. The fit failed to converge to tolerance of $10^{-6}$. |
| 7 | Linear Fit | $y=a+b x$ | $\begin{aligned} & \mathrm{a}=0.35943775 \\ & \mathrm{~b}=1.4296902 \end{aligned}$ | 1.3251651 | 0.8907820 | Linear regression completed successfully. |

A new method for manufacturing an ion-selective electrode was developed by applying an electrode active substance to a metal substrate, which was a current-conducting mixture of silver powder with a solid bonding dielectric, and an electrode-active substance was formed on the surface of the base by immersing the substrate in an electrolyte solution and anodic polarization at
the current density in the range from $10-7 \mathrm{~A} / \mathrm{mm}^{2}$ to $10-8 \mathrm{~A} / \mathrm{mm}^{2}$.

Prospects for using the research results. The practical value of the work is to ensure the improvement of the accuracy of the process water quality monitoring by using the flow-injection analysis method, the development and improvement of the primary converters.

## References

1. Tychkov, V.V. Methods for Improving Primary Transducers Quality in the Systems of Automatic Process Water Control: thesis for the degree of candidate of technical sciences, specialty 05.13 .05 - computer systems and components; Cherkasy State Technological University. Cherkasy, 2017. 20 p. (in Ukrainian).
2. Tychkov, V.V., Trembovetskaya, R.V. Kisil, T.Yu., Bondarenko, Yu.Yu. Using Ion-selective Electrodes in Environmental Monitoring. 10th International Conference "Environmental Engineering": 10th ICEE. - Selected papers. April 27-28, 2017. Vilnius, Lithuania. P. 1-8. URL: https://doi.org/10.3846/enviro.2017.052.
3. Camman, K. Working with Ion-Selective Electrodes: Chemical Laboratory Practice. Springer Science \& Business Media. 2012. 226 p. DOI: 10.1007/978-3-642-67276-7.
4. Lindner, E. Dynamic Characteristics Of Ion Selective Electrodes. CRC Press, 2018. 146 p.
5. Thomas, J. D. R. Ion-Selective Electrode Reviews. Volume 7. Elsevier, 2017. 324 p.
6. Covington, A.K. Ion Selective Electrode Method. Volume 2. CRC Press, 2018. 137 p.
7. Tychkov, V.V.; Trembovetskaya, R.V. 2015. Strategy of steady development of injection analysis methods. Theses of XIV of the International scientific and technical conference of «DEVICE-MAKING: the state and prospects», 22-23 April 2015, Kyiv, NTUU «KPI»: 124-125. URL: http://pbf.kpi.ua/arch/scientific/PB/2015/conf_PB_s5_2015.pdf.
8. Tychkov, V.V.; Trembovetskaya, R.V. 2015. A Device for Successive Injection Analysis, Materials Science Conference «Informatics, Mathematics and Automation. IMA: 2015», 20-25 April 2015, Sumy: 169. URL: http://essuir.sumdu.edu.ua/ handle/123456789/41216.
9. Tychkov, V.V.; Stepanenko, V.Ye. 2004. The method of ion-selective electrode making. Patent Ukraine No 3914. IPC 7G01N27/30, application No 2004042421, 01.04.2004, Publ. 01.04.2004, Bul. No 12. URL: http://uapatents.com/3-3914-sposib-vigotovlenn-ya-ionselektivnogo-elektroda.html
