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MATHEMATICAL AND PHYSICAL MODELS OF DEVICES FOR DETECTION OF SOME CHEMICAL SUBSTANCES IN THE ENVIRONMENT

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Abstract—In contemporary world there is a real need to detect harmful chemicals in polluted environment. The development of detector devices for the registration of chemical environmental pollution is really necessary – as separate devices, as well as parts of devices already developed for the fire control and fire extinguishing systems, and etc. A necessary and essential subsystem of such detectors are their sensory elements, including chemosensitive ones that are the membrane systems with selectivity to ions. The purpose of present work is the development of some models of sensory elements in devices for detecting of chemical environmental pollutants, especially those that are released during fires and other emergencies, in particular at chemical plants, industrial enterprises of oil and gas cycles, and etc. In present article the theoretical bases for such practical elaborations are suggested as well as some physical models with primary mathematic background suitable for such tasks solutions.

Index Terms—Physical model; mathematical model; detector device; sensor; chemical substances; chemical pollution of environment.

I. INTRODUCTION

In contemporary world there is an urgent need to detect harmful chemicals in the environment in order to save the Nature, as well as to preserve the life and health of people and other living organisms. In industrial regions this situation is the most dangerous due to the fires and destruction of chemical polluted objects, in the regions influenced by Chernobyl accident, etc. So, the development of detector devices for the registration of chemical environmental pollution is really necessary – as separate devices, and as parts of devices already developed for the fire extinguishing systems [1] – [3].

A necessary and essential subsystem of such detectors are their sensory elements: chemosensitive membranes (artificial and/or natural origin), specific coverings and layers of substances that after the contact with certain environmental chemicals are able to form the signals about pollutants present and/or to perform their initial identification [1] – [3]. The latter is the most desirable for the development of multi-functional portable sensors. Studies aimed on the construction of devices for the detecting various environmental pollutants are based on a detailed study of membrane systems that simulate the main physicochemical properties of artificial and natural membranes, including their selectivity to ions; and such studies are becoming increasingly important.

II. PROBLEM STATEMENT

Simulation of development of some devices related to fire extinguishing is really necessary in contemporary reality. If environmental pollution occurs as a result of fire with the release of chemicals harmful to living organisms, to successfully develop fire extinguishing algorithms, it is necessary to study, using methods of mathematical modeling, the processes of fire initiation and development in different protected areas in order to determine the optimal extinguishing tactics – the order of functioning of devices, modules and their groups.

This is especially necessary during a fire extinguishing and eliminating of other consequences of accidents, catastrophes at large industrial enterprises and objects of energetic, when extinguishing algorithms have to be linked quickly with current state of the object. The automated system that control the processes of extinguishing and liquidation of emergency situation have to work in real time, limited by the specifics of the controlled process and corresponding to the transition of the fire or emergency situation into an uncontrolled fire or techno gene disaster. In any modern enterprise it is very important to ensure quick, effective and reliable extinguishing with strictly metered commissioning of extinguishing means and thereby ensuring the lowest possible changes of technological regimes. The currently used

automatic fire extinguishing systems based on traditional executive inertial devices and installations for supplying fire extinguishing compositions are not adapted to changes in the degree of fire hazard of the protected area, the intensity and scale of the fire. These systems extinguish equally regardless of the options for the occurrence of fires and fire development schemes [1] – [3].

The *purpose* of present work is the development of physical models of devices for detecting of chemical environmental pollutants, especially those that are released during fires and other emergencies, in particular, at chemical plants, enterprises of oil and gas cycles, and etc.

III. PROBLEM SOLUTION

A. Physical models of some sensor elements for detectors of chemical pollution of artificial or natural origin

The analyzing unit for such systems was already developed by the authors earlier [3]. It allows to estimate objectively the scale of ignition from the indications of the sensors; and according to the information from automatic control system for an object or a technological process — the real degree of fire danger in the area where the fire occurred, and respectively development of the fire and to initiate the necessary for this case, incorporated in the control algorithm, the number of acting devices. Reliability, speed of executive system initiation and reduction of probability of false actions can be achieved by following ways: increasing of the resistance of sensors to noises due to the spatial structure of the sensor network, their duplication or introduction of additional blocks for detecting of the false signals and noises from the fire, using of sensors that operate on logic schemes that confirm the reliability of the fire signal, the use of a centralized collection of information about the changes in parameters of the object or environment state, and others.

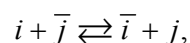
The scientific basis for such devices with sensor elements could be the set of works on the selective chemically sensitive surfaces of various types of glass, various samples of which have specific chemical sensitivity either by themselves or acting as a substrate – the basis for covering them by the layers of some specific substances. Previous studies have demonstrated that even for solving relatively simple tasks (for example, for the registration of current-voltage characteristics), one has to be faced real difficulties in studying of the selective membranes in living and artificial objects. These difficulties could be overcome in case if adequate physical and/or mathematical models are found. An equally important task for such simulation is to

establish the physicochemical nature of the phenomenon of the ionic selectivity of membranes either artificial or biological ones. According to the studies of ionic selectivity of membranes in stationary conditions, it is also important a problem of modelling the transient processes that occur on them during contacts of the membranes with molecules of harmful chemicals. Concerning this the attempts to model structural and functional disorders of artificial and cell membranes are also of great interest [4]. Both circles of these phenomena are closely interrelated and the consequences of their changes can be recorded in the experiment. Obviously, the most interesting are the searches for model systems that, firstly, reveal high ionic selectivity and, secondly, are characterized by the following permeability sequences for ions that could be seen as characteristic ones of some artificial and biological (protoplasmic) membranes. The latter, in particular, refers to the so-called biological range of permeabilities of the surface membranes of cells at nonexcited state for cations of alkali metals. Sometimes biosensors are seen as prospective ones for such purposes [5].

B. The theoretical basis for the inventing of physical models

As a theoretical basis for the development of the studied physical models, there were chosen a complex of works on the study of the interaction of ions of various substances with glass surfaces. Extremely high specificity of membranes made of glasses of a certain composition with respect to H^+ ions is known from the time of Kremer's research and such membranes have found widespread laboratory and technological applications [4]. Changes in glasses' composition leads to significant changes in the ion selectivity of membrane glass electrodes, determined under the stationary conditions, as well as changes in the kinetic parameters of such selective membranes.

When describing the difference of electric potentials that appear on thin glass membranes (glass electrode) in cases where the latter separate media with different ionic composition, the concepts of ion-exchange equilibrium established at the glass-solution interfaces are most often used. According to the ion-exchange theory of the glass electrode, developed by B. P. Nikolsky [4], there were supposed the existence of ion-exchange sites and ion exchange processes in the glass material



where i and j are cations in the solution contacting with the glass, \bar{j} and \bar{i} are the same cations bound by fixed negative charges of the glass matrix.

Difference in potentials in this case can be represented by the Nikolsky equation [4]:

$$\varphi = \frac{RT}{F} \ln \frac{a_i' + \sum^n k_{ij} a_j'}{a_i'' + \sum^n k_{ij} a_j''}, \quad (1)$$

where k is the ion exchange constant. There were done the assumptions that the ion exchange sites in the glass material are available for any of the exchanging cations, the cation activities in glass are proportional to their molar fractions, and the transmembrane potential difference is determined entirely by the sum of two boundary potential jumps, i.e. the contribution of the diffusion potential can be neglected. The Nikol'skii equation predicts a strictly defined form of transition from one cationic function of membranes to another when the cation composition of one of the media separated by a membrane changes. The experimentally obtained dependence for the region of the transition from one cationic function to another often differs significantly from that predicted by simple ion-exchange theory [4]. To explain this kind of anomaly by Eisenman and co-workers an empirical equation was suggested [4]:

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \left[a_i^{1/n} + \sum^n (K_{ij} a_j)^{1/n} \right]^n, \quad (2)$$

where the value of n is a parameter that determines the degree of nonideality of the ion-exchange properties of glass.

The classic in this sphere B. P. Nikolsky and his collaborators obtained theoretically based equations that satisfactorily describe the complex forms of transitions from one cationic function of glasses to another [4]. In particular, the extended transition is well described by the equation

$$\varphi = \varphi^0 + \frac{RT}{2F} \ln (a_i + K_{ij}' a_j) + \frac{RT}{2F} \ln (a_i + a_{ij} K_{ij}' a_j). \quad (3)$$

This equation corresponds to the conditions of low dissociation of ionogenic glass groups in their i th and j th forms.

The constant in this case differs from the constant of Nikol'skii in the equation (1), but it is linked with the latter one by the relation:

$$K_{ij}' = K_{ij} a_{ij}^{-1/2}, \quad (4)$$

where $a_{ij} = k_i / k_j$ is additional coefficient characterizing the difference in bond strengths of ionogenic groups of the glass with ions i and j .

Equation (3) can also be extended to the case when three types of cations are present in the solutions [5]:

$$\varphi = \varphi^0 + \frac{RT}{2F} \ln (a_i + K_{ij}' a_j + K_{ik}' a_k) + \frac{RT}{2F} \ln (a_i + a_{ij} K_{ij}' a_j + a_{ik} K_{ik}' a_k). \quad (5)$$

Unlike the empirical Eisenmann equation, this equation can be successfully used to describe the electrode behavior of glasses in solutions containing three types of cations in cases where a slow transition from one electrode function to another is detected. The latter was registered experimentally during the study of the concentration dependences of the potentials of glass electrodes prepared from sodium aluminum silicate glass (NAS 27.5-4.5) and potassium-gallium glass (KGaS 22-0.7)

These studies have shown that at constant ionic strength of solutions and variable concentrations of H^+ , Na^+ and K^+ ions, the constants K'_{HNa} and K'_{HK} as well as a_{HNa} and a_{HK} can be considered as really constant. However, it should be noted that with relatively small ionic forces (10^{-2} – 10^{-3}), the same constants are no longer more could be the constants.

IV. CONCLUSION

The preliminary work suggests that the systems of glass surfaces that we selected as model of the system with selectively interaction with various chemicals are enough well for the solution of stated problems.

At the same time, a number of conditions during the real practical application of our developed devices limit sharply the range of systems that could be applied as models. In this regard, it is also necessary to observe in future such model systems as glass electrode, Boytner chains, including layers of nonpolar solvents, some samples of ion-selective bilayer phospholipid membranes, as well as some other model membranes.

The study of the latter is important for understanding of the physico-chemical nature of ion selectivity and specificity in the broad sense of the term, since the approximation of such non-isomorphic systems is important in the development of sensory groups for detecting of harmful chemicals in the environment.

REFERENCES

- [1] V. D. Zachmatov, "Ecological and information systems and new technique for the struggle with high molecular organic pollutants flow on the water,"

Materials of RAN, no. 3, 2013, pp. 73–78. (in Russian)

- [2] V. D. Zachmatov, “Wave-attack mechanisms of impulse fire extinguishing of high molecular organic substances,” *Materials of reports of 3-d Minsk international colloquium in physics of wave attacks, fire and detonation*. Minsk, A.V. Likov Institute of Warm and Mass Exchange, November 12-15, 2013, pp. 100–101. (in Russian)
- [3] V. D. Zachmatov, “Ecological and information systems for decision making support for automated, universal subsystem of impulse and multistage defense,” *Materials of Conference “Intellectual systems for decision making and problems of computational complex, ISDVCI’2012,”* Cherson: ChNTU, 2012, pp. 257–263. (in Russian)
- [4] A. A. Lev, *Simulation of ionic selectivity of cell membranes*. Leningrad: Science. 1976, 210 p. (in Russian)
- [5] D. Yu. Kucherenko, I. S. Kucherenko, O. O. Soldatkin, and A. P. Soldatkin, “Application of glutamate-sensitive biosensor for analysis of foodstuff,” *Biotechnologia Acta*. 11(4), 2018, pp. 57–67.

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В. М. Шутко, В. Д. Захматов, О. О. Шутко, А. М. Миколушко. Математичні та фізичні моделі пристроїв для детектування деяких хімічних речовин у довкіллі

У сучасному світі існує реальна необхідність детектувати шкідливі хімічні речовини у забрудненому середовищі. Розробка пристроїв-детекторів для реєстрації хімічних забруднювачів довкілля є дійсно необхідною – як окремих пристроїв, так і частин пристроїв, що вже були розроблені для систем пожежного контролю та систем пожежогасіння. Необхідною та важливою підсистемою таких детекторів є їх сенсорні елементи, включаючи і їх хемосенсорні елементи, які є мембранними іонселективними системами. Метою роботи є розробка деяких моделей сенсорних елементів у пристроях для детектування хімічних забруднювачів довкілля, особливо тих, що виділяються під час пожеж та інших надзвичайних ситуацій зокрема на хімічних заводах, промислових виробництвах нафтогазового комплексу та ін. У статті запропоновано теоретичні основи для таких практичних розробок, а також деякі фізичні моделі з першим математичним обґрунтуванням, яке підходить для вирішення таких проблем.

Ключові слова: фізична модель; математична модель; детектуючий пристрій; сенсор; хімічні речовини; хімічне забруднення довкілля.

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В. Н. Шутко, В. Д. Захматов, Е. О. Шутко, А. Н. Миколушко. Математические и физические модели устройств для детектирования некоторых химических веществ в окружающей среде

В современном мире существует реальная необходимость детектировать вредные химические вещества в загрязненной среде. Разработка устройств-детекторов для регистрации химических загрязнителей окружающей среды действительно является необходимой – как отдельных устройств, так и частей устройств, которые уже были разработаны для систем пожарного контроля и систем тушения пожаров. Необходимой и важной подсистемой таких детекторов являются их сенсорные элементы, включая и их хемосенсорные элементы, которые являются мембранными ионселективными системами. Целью работы является разработка некоторых моделей сенсорных элементов в устройствах для детектирования химических загрязнителей окружающей среды, особенно таких, которые выделяются во время пожаров и других чрезвычайных ситуаций в частности на химических заводах, промышленных производствах нефтегазового комплекса и др. В статье предложены теоретические основы для таких практических разработок, а также некоторые физические модели с первым математическим обоснованием, которое подходит для решения таких проблем.

Ключевые слова: физическая модель; математическая модель; детектирующее устройство; сенсор; химические вещества; химическое загрязнение окружающей среды.

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Направление научной деятельности: обработка сигналов, компьютерное проектирование.

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