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INFORMATION SYSTEMS WITH CHEMOSENSITIVE DETECTORS FOR ENVIRONMENT PROTECTION

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Abstract*—Nature protections from large-scale fires in different countries of contemporary world become critically necessary and the development of novel electronic information systems with detectors of substances emanated during fires become an urgent problem. Progress of such detectors recording the presence of chemical substances - environmental pollutants becoming now an important task, and the article proposes the theoretical bases for its solution. Such detectors have to contain sensory elements with chemo-sensitive membranes, coatings and/or layers of specific substances. Being in contact with chemicals, such detectors have to demonstrate chemo-sensitivity and, preferably, ability for preliminary identification of these substances. Conducted studies were focused on further development of devices for the detection of various environmental pollutants as well as combustion products. This publication can form the theoretical basis for the development of artificial detectors with chemo-sensitive surfaces. The purpose of present work was to form the theoretical basis for the development of devices for the detection of some harmful chemical substances in environment, including ones emanated during fires and other emergencies, in particular, during accidents at enterprises of oil and gas cycle, chemical enterprises, other industries.*

Index Terms—Information system; mathematical model; detector; sensor device; fires; chemical substances.

I. INTRODUCTION

Large-scale fires in different countries, other disasters caused by natural or antropogenic factors – such challenges have been periodically faced by humankind in recent years [1] – [3]. Among them there were great fires in Ukraine (Chernobyl and Polissya regions, April 2020), Australia (2019), regularly happened fires in the USA and Siberia (Russia). Large amounts of chemical substances were emanated in atmosphere during such disasters; a lot of them are harmful for the Nature in whole, and for the people and animals in particular. Urgent necessity of the Nature, our environment and human lives protection stimulated the engineering creativity for new technical means invention and perfection of prototypes. The development of novel devices and systems are necessary now – robots, drones with chemo sensitive detectors, others; as well as information systems (ISs) [2] with detectors for the registration of chemical pollution of the environment [4], [5]. In present article the description of information system (IS) with chemo sensitive detectors is presented as well as theoretical bases for these novel detectors elaboration.

II. PROBLEM STATEMENT

The version of automated information system (AIS) developed with the participation of Prof. V. D. Zakhmatov was described below [2]. This electronic AIS was developed for the control of fire prevention and extinguishing system. It is enough perfect, used in practice and has a number of facilities. An attractive idea was to supplement such AIS with novel chemo sensitive detectors, forming AIS detector subsystem. The required AIS detector subsystem have to contain sensory elements for combustion products and other chemicals, for which novel chemo-sensitive membranes, specific coatings and layers of substances have to be elaborated. Such detectors, being in contact with specific chemical ssubstances, demonstrate chemo-sensitivity effects for various chemicals, including harmful substances emanated in fires. Contemporary investigations are focused now on detailed study of membrane systems simulating the basic physical and chemical

properties of artificial and natural membranes, including their selectivity to various chemicals predominantly in ionic form. In present paper the theoretical bases for the development of such sensors with chemo-sensitive surface is suggested in continuation of our previous publications [4], [5].

The aim of the performed work was to give a brief description of electronic automated information system with detectors for the control of fires prevention and extinguishing system, and to suggest theoretical bases for the elaboration of sensory elements for such system – detectors of chemical environmental pollutants, especially for combustion products and other ones emanated during fires and other emergencies.

III. PROBLEM SOLUTION

A. Description of suggested electronic information system for the control of fire prevention and extinguishing system

The functional structure of fires extinguishing can effectively use rapidly developing technology of electronic information systems [1] – [3]. Its structure can include several pulsed spray devices and automated information system (AIS) controlling their work with a network of sensors for the reveal of flame and smoke, as well as thermal imager ("teplovisors") and video cameras. These ISs with sensors can show, record and analyze the reliability of the data of fires current parameters, can predict the trends in its further development based on the data from the zone of fire surroundings. First of all, the factor of wind at the open space is important for such ISs operation as well as presence of ventilation in case of enclosed spaces (with directivity and strength of the air flows from this ventilation). Beside of this, the direction of fire development determines the presence of flammable substances and materials around it, primarily self-igniting ones. AIS can obtain these data from automated controlled system of the objects: production, warehouse, office, skyscraper, and etc. AIS have to analyze them to predict the development of intensive Fire, fixing simultaneously the real process of its development.

The modular technology was used for the formation of algorithmic component of described AIS structure, taking into account its specifics. A set of three information and analytical modules of AIS was formed and tested as computer programs: the module for documentation of the organization of communication and management, the module for automated formation of communication organization schemes, the module for remote monitoring of fire state at protected object, and the module for commands generation to operate the system of pulse devices in various versions from one to the whole system simultaneously.

The system controls simultaneously the initiation and spraying parameters of extinguishing agents according to traditional technique, the system of pulsed spray devices, and at least one rescue unit during the fighting of massive fires. At the same time, the data on device parameters can be recorded in system's memory - the type of fire extinguishing composition or compositions mixtures charged into these devices, and about the range and area of extinguishing. The problem of control of tasks' ranking in AIS have been formulated and analytically solved. The algorithms and methodology of ordering in query of preference of control problems for practical implementation in described system were proposed by its developers [1] – [3]. Basing on the above described it is possible to predict further development and improvement of this AIS in terms of increasing of its adaptability for the use of simple pulse devices or complex multi-barrel modules for the fighting with massive fires.

B. Theoretical bases for the development of chemo censoring surfaces in detectors of electronic information system for the detecting of chemicals – combustion products

Below we would like to suggest the theoretical bases for the development of chemo sensitive detector surfaces, primarily for the detector subsystem in above described automated information system. We suppose that the works of research groups which studied the properties of the glass and other surfaces contacting with water solutions and gases may be selected as such theoretical base [6]. According to our modification of such ideas [4], [5], developed primarily by B. P. Nikolsky [6], the surface of detecting element (detector) can be covered with detecting material (glass covering, or film, or membrane etc.) being in contact with water solution with dissolved chemicals (or in some cases with gas phase if water was dropped inside). During the description of the differences in electrical potentials which appeared on the thin glass membranes (like ones in case of glass electrodes) following approaches by Nikolsky about the ion-exchange equilibrium on the boundaries glass-solution could be taken as theoretical base. According to ion-exchange theory of glass electrode [6], there were supposed the existence of ion-exchange sites and ion exchange processes in glass materials:

$$i + \overline{j} \rightleftarrows \overline{i} + j. \qquad (1)$$

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

Difference in potentials in this case can be represented by Nikolsky equation [6]:

$$\varphi = \frac{RT}{F} \ln \frac{a_i^{'} + \sum^{n} k_{ij} a_j^{'}}{a_i^{''} + \sum^{n} k_{ij} a_j^{''}}, \qquad (2)$$

where *k* is the ion exchange constant. The approach that the ion exchange sites in the glass material were available for any of exchanging cations were done. The cation activities in the glass were assumed to be proportional to their molar fractions, and the transmembrane potential difference was determined on whole by the sum of two boundary potential step-like changes (so, the contribution of the diffusion potential could be neglected). Equation (2) predicts strictly defined form of transition from one cationic function of membranes to another when the cation composition of one of the media separated by membrane changes. Further the theoretically explained equations were obtained; these equations describe satisfactory the complex forms of transitions from one cationic function of glasses to another one [6]. The equation (3) below describes the extended transition; the result is shown at the plot on Fig. 1 [6].

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

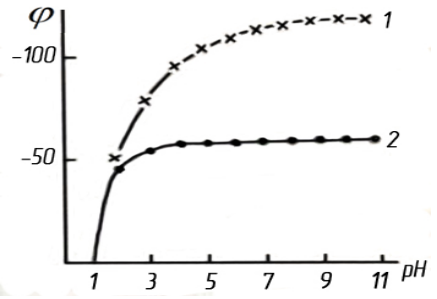

Fig. 1. The dependence of the difference of potential on the membrane for electrode glass NAS 17.5-10 in KCl solutions with pH 0.1 M (curve 1) and NaCl solutions (curve 2) [5] (explanations see in text)

On Figure 1 the abscissa axis shows the pH of external solution into which the glass electrode is immersed. On the ordinate axis is the potential difference in the glass electrode circuit, inside of which there was 0.1 M HCl solution. The transitions from the hydrogen to the metal (sodium) electrode function for curve 2 was described by the equation of ion-exchange theory by Nikolsky. More extended transition from hydrogen to metal (potassium) function, represented by curve 1, can be described by equation (3).

Equation (3) can be successfully used for the description of electrode behavior of glasses in solutions containing three types of cations in cases when the slow transition from one electrode function to another was detected. The latter one was registered experimentally during the study of concentration dependences for 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 demonstrated 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} could 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 [6].

In some cases it was possible to register the changes in the potential of the glass electrode with the changes of ionic composition of the solutions, that could be attributed to the variability of the cation specificity constants (Fig. 2). Besides of this, the cationic selectivity of glass electrodes, which was determined under the steady-state conditions, depends on what solutions were prepared previously (or stored) examined glass electrodes.

Although the question of the cation selectivity dependence of glass electrodes on the concentration of salts in solutions or their ionic strength can not yet be considered sufficiently investigated, it seems that the specificity decreases significantly with the decreasing of ionic strength to the value 10^{-3}.

One of the most interesting features of electrode glasses is the ability to obtain different values of cationic selectivity coefficients by varying of their composition (Fig. 2). The systems of aluminosilicate glasses (Na_2O (or K_2O) – Al_2O_3 – SiO_2) and alumino-borosilicate (Na_2O (or K_2O) – Al_2O_3 – B_2O_3 – SiO_2) glasses have been studied in this regard the most comprehensively [6]. The isotherms were found for the first system; they characterized the dependence of K_{ij} constants for alkali metal cations on the fraction of oxides in the glass. One of such diagrams characterizing the dependence of K_{KNa} on the composition of sodium aluminosilicate glasses obtained in experimental conditions was represented on Fig. 2.

Systematic studies of such systems and a number of other electrode glass systems, carried out by

Eisenman [6] demonstrated that K_{Ki} values and the sequence of alkali metal cations were possible to arrange in the sequences according to the increase of studied coefficients. And these coefficients were linked, consequently, with the function of glass composition. Concerning the latter, from the total 120 possible rearrangements, only 11 different sequences were experimentally detected [6].

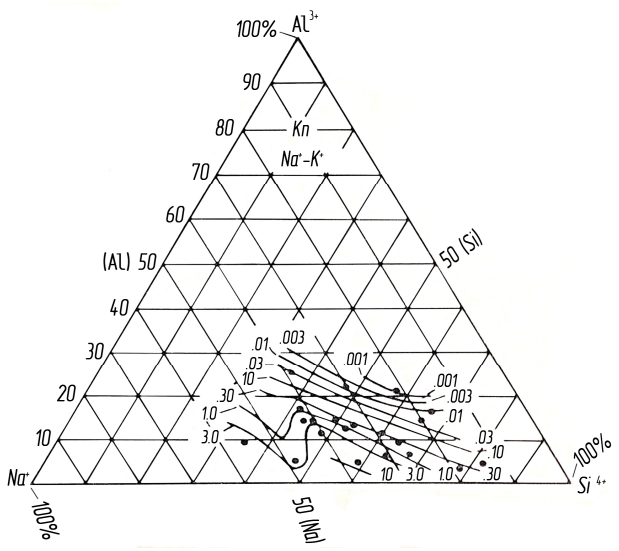

Fig. 2. Diagram of the contour of isospecificity (constant values of coefficient of specificity for K_{KNa}) for the system of sodium-aluminosilicate glass [6]. The atomic percentages of Na, Al, and Si are indicated on the sides of the three-coordinate diagram of the glass composition. The curves make connections between the diagram points with equal values of K_{KNa}, which were specified for each curve [6]

IV. Conclusions

The brief description of developed electronic information system for the control of intensive fires prevention and extinguishing system was done in present publication. For such information system AIS chemo sensitive subsystem with detectors with specific covering was suggested as continuation of biosensor concept development [7]. Such detecting chemo sensory elements were supposed to be covered with specific chemo-sensitive membranes, other specific coatings or layers of substances. Suggested coverings, being in contact with certain chemicals, demonstrate chemo-sensitivity to some chemical substances. Theoretical bases for the elaboration of such detectors with chemo sensitive covering surface were suggested in present article. Also the theoretical bases for the development of detector surfaces for the detection of chemical pollutants in environment, especially those released during fires and other emergencies, in particular, at chemical enterprises, enterprises of oil and gas cycle, etc. were suggested. Present study we see as important for the understanding of physico-chemical nature of ion selectivity and specificity in the broad sense of these terms as well, since it is important for the development of sensory groups for detecting of harmful chemicals, including combustion products in the environment.

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В. М. Шутко, В. Д. Захматов, О. О. Колганова, Д. А. Навроцький, А. М. Миколушко. Інформаційні системи з хемочутливими детекторами для захисту оточуючого середовища

Захист природи від масштабних пожеж у різних країнах сучасного світу є критично необхідним і нагальною проблемою є розробка нових електронних інформаційних систем з детекторами речовин, що виділяються при пожежах. Винахід таких детекторів, що реєструють наявність хімічних речовин – забруднювачів оточуючого середовища натепер є важливою задачею, і у статті запропоновано для цього теоретичні основи. Такі детектори повинні містити сенсорні елементи з хімічно чутливими мембранами, покриттями та / або шарами специфічних речовин. Перебуваючи у контакті з хімічними речовинами, такі детектори мають демонструвати хімічну чутливість і, бажано, здатність до попередньої ідентифікації таких речовин. Проведені дослідження були спрямовані на подальшу розробку пристроїв для виявлення різних забруднювачів оточуючого середовища, а також продуктів горіння. Дана публікація може слугувати теоретичною основою для розробки штучних детекторів з хімічно чутливою поверхнею. Метою представленої роботи було формування теоретичної бази для розробки пристроїв для виявлення деяких шкідливих хімічних речовин в оточуючому середовищі. У тому числі речовин, які виділяються при пожежах і в інших надзвичайних ситуаціях, зокрема, при аваріях на підприємствах нафтогазового циклу, хімічної промисловості, підприємствах у інших галузях.
Ключові слова: інформаційна система; математична модель; детектор; сенсорний пристрій; пожежі; хімічні речовини.

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В. Н. Шутко, В. Д. Захматов, Е. О. Колганова, Д. А. Навроцкий, А. Н. Миколушко. Информационные системы с хемочувствительными детекторами для защиты окружающей среды

Защита природы от масштабных пожаров в разных странах современного мира стала критически необходимой и насущной проблемой является разработка новых электронных информационных систем с детекторами веществ, выделяемых при пожарах. Изобретение таких детекторов, регистрирующих наличие химических веществ - загрязнителей окружающей среды в настоящее время становится важной задачей, и в статье предлагаются для этого теоретические основы. Такие детекторы должны содержать сенсорные элементы с химически чувствительными мембранами, покрытиями и / или слоями конкретных веществ. Находясь в контакте с химическими веществами, такие детекторы должны демонстрировать химическую чувствительность и, предпочтительно, способность к предварительной идентификации этих веществ. Проведенные исследования были направлены на дальнейшую разработку устройств для обнаружения различных загрязнителей окружающей среды, а также продуктов сгорания. Данная публикация может послужить теоретической основой для разработки искусственных детекторов с химически чувствительной поверхностью. Целью представленной работы было формирование теоретической базы для разработки устройств для обнаружения некоторых вредных химических веществ в окружающей среде. В том числе веществ, которые выделяются при пожарах и других чрезвычайных ситуациях, в частности, при авариях на предприятиях нефтегазового цикла, химической промышленности, предприятиях в других отраслях.
Ключевые слова: информационная система; математическая модель; детектор; сенсорное устройство; пожары; химические вещества.

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