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Selection of point-contact sensors for analysis of complex gas media

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The criterion for selection of point-contact sensors in the laboratory batches of samples to improve the reliability of the results in the study of complex gas media was proposed for the first time. The electrical conductivity of point-contact sensors in a multi-component gas, which was exhaled by a person, was studied. Cluster analysis method was used for selection of transducers with similar parameters in the studied sample batch of sensors. Group of samples with similar parameters of sensory images was selected on the basis of the received data. Correct application of the approach to the development of criteria for the selection of point-contact sensors was confirmed in medical investigations of gas which was exhaled by patients.
Keywords: Yanson point contact spectroscopy; point contact; sensor; breath gas; cluster analysis.

У даній роботі вперше запропонований критерій відбору точково-контактних сенсорів в лабораторних партіях зразків для підвищення достовірності результатів при дослідженні складних газових середовищ. Вивчена електропровідність точково-контактних сенсорів в складному багатокомпонентному середовищі газу, що видихається людиною. Для відбору близьких по параметрах зразків в досліджeній партії сенсорів застосований метод кластерного аналізу. На основі отриманих даних була виділена група зразків з однорідними параметрами сенсорних образів. Коректність застосованого підходу при розробці критерію для вибору точково-контактних сенсорів підтверджена в медичних експериментах по дослідженню газу пацієнтів, що видихається.
Ключові слова: мікроконтактна спектроскопія Янсона; точковий контакт; сенсор; газ, що видихається; кластерний аналіз.

В данной работе впервые предложен критерий отбора точечно-контактных сенсоров в лабораторных партиях образцов для повышения достоверности результатов при исследовании сложных газовых сред. Изучена электропроводность точечно-контактных сенсоров в сложной многокомпонентной среде газа, выдыхаемого человеком. Для отбора близких по параметрам образцов в исследованной партии сенсоров применен метод кластерного анализа. На основе полученных данных была выделена группа образцов с однородными параметрами сенсорных образов. Корректность примененного подхода при разработке критерия для выбора точечно-контактных сенсоров подтверждена в медицинских экспериментах по исследованию выдыхаемого газа пациентов.
Ключевые слова: микроконтактная спектроскопия Янсона; точечный контакт; сенсор; выдыхаемый газ; кластерный анализ.

Introduction

Sensor research is a rapidly progressing field of scientific and technological activities at the present time. They are performed at the edge of such fundamental sciences as physics, chemistry, biology, medicine, and materials science. The possibilities of these sciences provide a solid foundation for advanced development in all spheres of human activity, including electronics, biomedical engineering, agricultural and food industries, monitoring of industrial processes, computer engineering, communications, and others. One of the most promising trends in the creation of sensor devices is nanotechnology. The involvement of nanotechnology unveils new unlimited possibilities for the development of various types of sensitive elements with unique parameters. Yanson point-contact spectroscopy [1, 2], which is one of modern nanotechnology directions in the areas of sensor technique, can be used as an example that confirms this

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statement. Recently, a new method of creating the sensing elements [3, 4], which is based on the Yanson point-contact spectroscopy and unique nonlinear properties of point contacts, has been proposed. It provides the possibility of obtaining physical data for the different areas of research [4]. Point-contact sensors are a fundamentally new type of nanosensors. They have excellent, unprecedented features and their parameters exceed significantly the parameters of the known analogues [4, 5].

Sensors based on TCNQ (tetracyanoquinodimethane) compounds [6-8] are one of the types of point contact sensors that have serious prospects for the development methods of non-invasive medical diagnostics. The sensing elements based on TCNQ compounds consist of a set of large number of point contacts that are located randomly with respect to each other [7]. These samples represent the original version of the point-contact sensor array, which essentially is a point-contact mesoscopic multistructure and includes up to 200-300 point contacts that are arranged on a general substrate with a surface area of 0.5 mm^2. Sensor samples based on the point-contact multistructure are used for research and analysis of complex gas media. The large amount of interactions continuously occurring among the components in complex gas media may cause variations in composition and component concentration of these media. Significant variability of experimental conditions in multicomponent gas media sets the high quality requirements to sensitive elements which are used in these experiments. It is caused primarily by the need to provide good reproducibility of the results. Therefore there is a need to develop new approaches to the selection of samples which have similar parameters in the batches of sensors that are produced under laboratory conditions. This problem can be solved by developing criteria for selection of point-contact sensors, which are similar to the criteria [1] that are known in the Yanson point-contact spectroscopy. In the Yanson point-contact spectroscopy, these criteria help to select the point contacts with the best characteristics that guarantee obtaining of high-quality information about the test material. The purpose of this study was to analyze the parameters of the response curves of point contacts and search for criteria to select the point-contact sensors that can provide high reliability of results in the study of complex gas media.

Experimental technique

We have created samples of point-contact gas-sensitive nanosensors based on the organic conductive compound [N-C_4H_9-iso-Qn](TCNQ)$_2$, which is synthesized from TCNQ and N-alkylquinolinium (N Alk-iso-Qn). During the manufacturing process, the used materials make a significant contribution to ensuring functionality of the sensitive elements. Organic conductors are materials that are promising for the development of new high-sensitivity sensor devices. Molecules packed in stacks are a characteristic feature of their crystalline structure [9]. The three-dimensional crystals of TCNQ complexes are composed of linear chains which are formed from stacks and are a typical part of their structure. Distances between TCNQ molecules within a stack are significantly shorter than the distances between the different stacks. The electrical conductivity of the crystal is provided by overlapping of the wave functions of π-electrons of the neighbouring molecules in a stack. Consequently, the transport properties of these compounds are mainly determined by the nature of quasi-one-dimensional motion of electric charge carriers along the molecular stacks. A high anisotropy of electrical conductivity of TCNQ compounds lies in the basis of sensory properties of these materials [10]. As a result, absorption of a small amount of gas atoms on the surface of the organic conductor is able to cause significant changes in its conductive properties.

The sensitive element is a mesoscopic point-contact multistructure which is composed of stable elements that are formed by lateral faces of needle-like TCNQ crystals [7]. Point contacts of this structure are similar to the point contacts obtained by shifting one electrode along the other in accordance with the Chubov displacement technique [11], which is the most effective and reliable technique to make contacts in Yanson point-contact spectroscopy [1, 2]. Samples were created on a dielectric glass-cloth-base laminate substrate with the size of 5x10 mm^2. The substrate was covered with copper foil, which was used as a conductive electrode. Part of the foil with a size of 0.15x5 mm^2 was removed from the substrate. A point-contact sample of TCNQ compound was formed in the created gap as a flat mesostructure with a thickness of 10-30 microns. Using a number of original technological methods we prepared samples of active-type sensors. Their structure contains a source of electrical energy, which transforms the changes in the physicochemical properties of the gas sensitive material occurring in the process of interaction with the gaseous medium into the sensor output. The source of accumulated energy of the active sensor element was created by using electrochemical synthesis [6].

The gas breathed out by the man was selected as the complex gas media. The exhaled gas is a multicomponent mixture of various endogenous and exogenous substances [12]. The source of components of these substances, in particular, is the respiratory tract, gastrointestinal digestive tract and the oral cavity. The composition of the breath gas is also dependent on environmental and behavioural factors such as smoking or pollution of the environment [13]. There are up to 2000 known components in the exhaled mixture at the present time. Among them 400-600 volatile organic compounds are already characterized as markers of the human organism state [14, 15]. This fact causes an extra interest in the study of breath and determines the great prospects of these studies for the development of non-invasive medical diagnostics. Analysis of the exhaled gas is at the forefront of the new diagnostic methods, whose realization occurs without any external intervention in the human organism.

There was produced a laboratory batch of 49 point-contact sensors. The study of the created sensitive samples was carried out by means of measuring their electric resistance dependency on time in the exhaled gas media. A significant change in the electrical conductivity of the sensor occurs under the action of the gas medium. This allows us to record the process easily using traditional measurement equipment such as Keithley 2000 and Keithley 2100 multimeters (USA). In this case, the recorded value is the signal of sensor response. In our studies we used a portable measurement system specially designed for this purpose. Its working principle was described in detail in Ref. [16]. The measured signal was fed automatically to a personal computer. Registration and processing of the results was performed using the original software developed at B. Verkin ILTPE of the NAS of Ukraine.

Results and discussion

The point-contact gas-sensitive sensors based on TCNQ compounds demonstrate a unique response to the action of a complex gas medium, which was not observed in sensor technology earlier [4]. Typical responses of conventional semiconductor sensors have a stepped or monotonous domed shape [17, 18]. Such curves are characterized by a monotonic increase of the signal during the exposure and a smooth relaxation after the action of the external agent ceases. The response of point-contact sensitive elements to the action of the human breath gas has a complicated structure in contrast to the response of conventional sensors. The dependence of the electric conductivity of point-contact sensor on time could be considered as a spectrum-like profile of the gas breathed out by a man [8]. The point-contact samples reproduce the signal in numerous experiments and demonstrate a response that is specific for each researcher (volunteer) and depends on his/her individual condition. Medical studies demonstrate the point-contact spectroscopic profile of the breath gas to accurately describe the internal state of the organism [4, 19].

A typical response curve of point-contact sensors based on TCNQ compounds under the action of the breath gas is shown in Fig. 1.

The left section of the response curve in the range of 0-60 seconds characterizes the exposure period (t_1) of the sensor in the breath gas medium. The right section is obtained after the gas stops acting on the sensor and it is placed in the ambient air. At this point a relaxation of the sensor to its original equilibrium state starts (relaxation period t_2). As can be seen from the presented dependence, the point contact responses curves are characterized by a nonmonotonic structure reflecting the individual profile of the breath gas

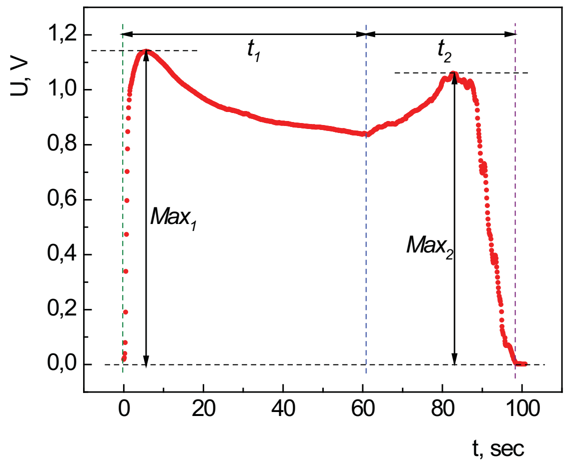

Fig. 1. Dependence of electric conductivity of a point-contact sensor based on TCNQ compound on time in the environment of gas breathed out by a man. U – voltage, t – time, t_1 – time of exposure, t_2 – time of relaxation.

(see also Ref. [5, 8]). Response curves of point-contact sensors are characterized by a set of parameters [7], which not only can be used for analysis of the breath gas, but also can serve as criteria for evaluating the reproducibility of the sensor device's data.

Achieving a high reproducibility of properties and parameters of the created sensory object is one of the researcher's main tasks in the process of development of a new method to diagnose the state of human body. Fulfilment of the task will allow us to be sure that any discrepancy observed in the response curves is due to a change in the characteristics of the breath gas and is not related to possible variations in properties of the sensor device. In this case, the parameters of the response curves will reflect with high accuracy the profile of the breath gas of a specific person and thus provide a high selectivity and specificity in diagnosing the states of organism.

To select samples with similar parameters in a studied batch of sensors we used the method of cluster analysis [20, 21]. The procedure of cluster analysis is based upon allows one to ignore the nature of the objects to which it is applied. This makes it a universal tool in almost all disciplines of human knowledge with focus placed only on properties of the analyzed objects, thus converting the problem into a purely mathematical one. The task of this method is to divide a set of objects of similar nature but with slightly different properties within those to be studied into groups (clusters), each comprising those objects that are most similar among themselves but different from the objects from the other groups. Most visibly the results of this approach manifest themselves if it is applied in psychology when a huge group of people united by the same productive activity is divided into several natural groups (according to the age, interests, skills, salary or any other property characterizing a person).

In our case, we had to divide a batch of sensors produced in laboratory into groups in which each pair of sensor devices showed the most similar response values under the action of the gas under study.

The characteristic variables Max_1, Max_2, and t_2 (see Fig. 1), which describe the shape and behaviour of the response curves under the action of the gas, were chosen as the parameters to be analyzed within the proposed approach. The entire set of sensors was considered as the objects of the three-dimensional Euclidean space of their properties (those described by the above parameters: X = Max_1; Y = Max_2; Z = t_2).

The Euclidean distance between objects of the space was used to assess their similarity (proximity):

$$d^{[i,j]} = \sqrt{(X^{[i]} - X^{[j]})^2 + (Y^{[i]} - Y^{[j]})^2 + (Z^{[i]} - Z^{[j]})^2},$$

where i and j are the numbers of the objects the distance $d^{[i,j]}$ between which is calculated.

It should be noted that to ensure correct final results the methods of mathematical statistics require that each variable should be scaled in such a way as to convert the so called non-uniformly scaled random variables P (X, Y and Z in our case) into their standardized analogues by means of the centering and normalization procedures. As a result of these transformations, our set of objects will be analyzed in the Euclidean space of normalized random variables U according to the principle described above.

To convert a random variable P into the normalized random variable U, it is necessary to additionally calculate the mathematical expectation M and dispersion σ for P for the given group of objects. Mathematical expectation is the average value of the variable under study:

$$M_P = \frac{\sum_{n=1}^{N} P_n}{N},$$

where N is the number of objects.

Dispersion can be calculated using the following relation:

$$\sigma_P = \sqrt{\frac{\sum_{n=1}^{N} (P_n - M_P)^2}{(N-1)}}.$$

Then, to convert the random values P into the normalized analogues U we need to perform the following transformation for all the variables used to describe the sensor properties:

$$X^{(n)} \to U_X^{(n)} = \frac{(X^{(n)} - M_X)}{\sigma_X};$$

$$Y^{(n)} \to U_Y^{(n)} = \frac{(Y^{(n)} - M_Y)}{\sigma_Y};$$

$$Z^{(n)} \to U_Z^{(n)} = \frac{(Z^{(n)} - M_Z)}{\sigma_Z}.$$

It should be noted that in order to simplify the calculation and minimize the eventual variability of the gas medium acting on the sensor during the measurement we chose the three parameters of the response curves of the analyzed point-contact sensors that had already been successfully tested medically and thus proven to be good markers of the states of human organism [5, 7, 19]. The parameters include the amplitudes of the main exposure and relaxation peaks (Max_1 and Max_2) and the relaxation time t_2 (Fig. 1). We measured response of all the 49 samples of point-contact sensors to the action of the exhaled gas. The measurements were performed under the standardized conditions following the procedure [7] developed for medical research. The parameter values Max1, Max2, and t2 used in cluster analysis were determined for the recorded curves. Calculation performed in the three-dimensional Euclidean space of sensors properties constructed in the coordinates of exposure maximum, relaxation maximum, and relaxation time values allowed us to find the Euclidean distances needed to select the most similar samples. On the basis of the obtained data a set of sensors forming a cluster with a boundary Euclidean distance of 0.27 was selected.

The calculations have shown that sensory samples of the selected sensitive elements should demonstrate a good correlation within the experimental error. This allows us to consider the selected group of samples as similar objects and use them to study the composition of complex gas media in clinical practice, in particular, for the non-invasive diagnosis based on the analysis of the human breath gas. We used these sensors in medical experiments [8], which confirmed the correctness of the approach applied to develop the criteria for the selection of point-contact sensing elements able to provide a high reliability of the results in the study of complex gas media. As a result, a new basis for the breath test for detecting carcinogenic strains of the bacterium *Helicobacter pylori* was developed [8]. The sensor samples used in these studies demonstrated a high selectivity (93.1%) and specificity (89.9%) of the new diagnosis method.

Thus, a new criterion for selecting point-contact sensors from laboratory batches of samples was proposed which can provide a high reliability of the results in the study of complex gas media. The electrical conductivity of point-contact sensors in complex multi-component gas media exhaled by a human was studied. Cluster analysis method was used to select samples with similar parameters from the studied batch of samples. On the basis of the obtained data, a group of samples with sensory images demonstrating good reproducibility was selected. The correctness of the approach applied to select the point-contact sensors was confirmed in experimental medical studies of human breath gas.

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