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Quantum point-contact sensors: state of the art and prospects

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Abstract

In this review, we present generalized information on the new type of universal quantum detectors operating on the basis of Yanson point contacts. The fundamental properties of these unique nanoobjects shape the behaviour of quantum sensing elements based on them. The properties and capabilities of quantum point-contact detectors are totally different from those of conventional sensors based on the principle of changing electric conductance. To give an idea of the nature of these differences, we examine the spectral properties of Yanson point contacts, which are fundamental for understanding the operation mechanisms of quantum point-contact sensors. Along with the classical methods for creating Yanson point contacts proposed in the Yanson point-contact spectroscopy, a description of the original developments made in the process of sensor research is given. The prerequisites that contributed to the discovery of the point-contact gas-sensitive effect are discussed. One of the most important features that determine the functioning of point-contact sensing elements is the quantum detection mechanisms discovered during the study of the point-contact gas-sensitive effect. The detection mechanisms based on the energy principles of analysis and conductance quantization are considered. The innovative methods developed using breath analysis with quantum point-contact sensors made it possible for the first time to detect in real time carcinogenic strains of the bacterium *Helicobacter pylori* and the hormonal background of the human body. The future work will be focused on universalizing the technology of quantum point-contact sensors, addressing various problems including evaluation of the general state of the human body and solutions to global ecological problems.

Keywords

quantum sensor, Yanson point-contact spectroscopy, conductance quantization, cyclic switchover effect, quantum mechanism of selective detection, breath analysis

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1. Introduction

In 2023, it has been 50 years since the original pioneering experiments that led to the development of the Yanson point-contact spectroscopy (Yanson PCS). Almost throughout the entire period of its existence, the Yanson PCS has demonstrated unique innovative opportunities to study a wide range of objects and phenomena [1-3]. Originally proposed as a method for studying electron-phonon interaction in metals [4], the Yanson PCS technology subsequently became a methodological and theoretical basis for a large number of studies that resulted in many discoveries and led to the development of new areas of research. At the initial stage of its application, the Yanson PCS and its techniques were developed exclusively in the framework of the low-temperature approach. However, after 2006, the temperature range of this technology has expanded significantly thanks to the discovery of the point-contact gas-sensitive effect [5, 6]. These works have led to the creation of a new promising area of study and development of quantum point-contact sensors, which is rooted in the fundamentals of the Yanson PCS [7, 8].

The operation principle of quantum point-contact sensors is essentially different from that of the conventional sensors and nanosensors based on electrical conductance changing under the action of external agents. The operation of quantum sensors abides by the laws of quantum mechanics. This is what has shaped the detection mechanisms which underlie their operation, and, accordingly, their advantages. The conventional, electrically conductive, sensors operate in accordance with the postulates of classical physics. This imposes a number of limitations on their capabilities, in particular, when it comes to selective detection in a complex gaseous environment.

The originality of the point-contact gas-sensitive effect came into light immediately after its discovery [5, 6]. It became obvious after the comparison of the characteristics of point-contact sensing elements and the parameters of the conventional sensors based on the principle of changing electrical conductance [7, 8]. The reason for this is easily understood: point-contact sensors were, in fact, the first example of quantum conductive sensors functioning at room temperature. Already in the first experiments, the sensing element of a point-contact sensor in the form of a Yanson point contact almost instantly showed not only its ultra-high sensitivity to the action of various gases, but also its ability to relax to the initial state in real time, even when dealing with such complex materials as carbon nanotubes [5, 6]. The short relaxation times of point-contact sensors [6] looked especially impressive if compared to the many hours of relaxation of the sensors based on a single nanotube, which were then considered the golden standard of the conventional sensors using the principle of changing electrical conductance [9]. Thus, the advantages of the quantum approach in sensorics were displayed in the first sensor experiments with Yanson point contacts.

Modern sensor research is mainly focused on the development and study of nanostructured sensing elements [10-12]. This follows from the operation principles of the conventional electrically conductive sensors. The sensitivity of such devices is largely determined by the geometric factor: the higher the surface-to-volume ratio of the sensing element, the higher its sensitivity. Reducing the size of nanostructured sensors should eventually lead to overcoming the threshold for observing the effects of quantum confinement. However, thermal effects in the conventional sensors suppress the quantum phenomena in their electrical conduction and do not allow developing a quantum approach to detecting and analysing the objects under study. The uniqueness of the Yanson point contact, when compared to other nanostructured elements, lies in

the fact that it provides spatial separation of the non-equilibrium and thermal phenomena, which creates the necessary conditions for the implementation of the quantum mechanisms of detection in gaseous and liquid media. Thus, the property that makes it possible to implement the Yanson PCS [4] at low temperatures also turns out to be a key factor for the operation of quantum point-contact sensing elements at room temperature.

Another important property of the Yanson point contact which reflects its uniqueness is the potential distribution in the contact [4]. In the Yanson PCS, the original potential distribution in the contact plays a fundamental role for the observation of spectral effects at low temperatures [2, 3]. At room temperature, the potential distribution in the Yanson point contact is the key to both the point-contact gas-sensitive effect itself and the new original effects that are not observed in the conventional electrically conductive systems. One of them is the electrochemical cyclic switchover effect caused by the appearance of a gapless electrochemical electrode system in the conduction channel of a point contact placed in a liquid medium [13]. The electrochemical cyclic switchover effect and the gapless electrochemical electrode system have become a source of new sensory capabilities of the quantum point-contact sensors based on conductance quantization.

Conductance quantization is one of the important properties of Yanson point contacts [14-16]. This purely fundamental phenomenon has acquired practical importance in the sensor research after the discovery of the electrochemical cyclic switchover effect and new quantum mechanism for detection in gaseous and liquid media [13, 17]. With their help, the quantum nature of electrical conductance in the Yanson point contact becomes an effective tool for probing the quantum states of the analysed systems, thereby ensuring the absolute selectivity of quantum point-contact sensors.

A distinctive feature of the operation of point-contact sensors is the focus on the fundamental characteristics of the object under study and, in the first place, on the energy parameters that characterize its nature. The quantum mechanisms of detection, which underlie the principles of operation of point-contact sensors, make it possible to register the energy of the metastable quantum states of the analysed objects (or the parameters which characterize it) and work with a wide range of gaseous and liquid media.

The development of an innovative technology for creating unique sensing elements based on Yanson point contacts was made possible by the numerous “know-how” of the Yanson PCS [8]. The quantum nature of their electrical conduction became the basis for the discovery and study of new detection mechanisms that cannot be implemented in the conventional sensors with the operation principle of changing electrical conductance [17, 18]. This feature predetermined the universality of point-contact sensors and allowed using them to work with various media and objects [19]. In particular, point-contact sensors have demonstrated their innovative capabilities in the development of medical technologies, which allows us to speak of them as a universal tool for non-invasive diagnostics of the states of the human body [18, 20, 21]. The results obtained in these studies demonstrate significant prospects for practical use of the quantum point-contact sensor technology.

In this review, we present a brief summary of the main aspects of the research into quantum point-contact sensing elements, methods for their creation, new quantum detection mechanisms discovered using Yanson point contacts, and some of the possible applications tested in real conditions.

2. Yanson point contact as a basic element of Yanson point-contact spectroscopy and quantum point-contact sensors

The Yanson point contact is the main object of research in the field of Yanson PCS and point-contact gas-sensitive effect, as well as an effective multifunctional tool employed in quantum point-contact sensors. It is an electrical contact created over a small area between two bulk metal electrodes which meets a series of specific Yanson PCS criteria [2]. It is characterized by direct conduction, that is it does not contain tunnelling barriers. Yanson point contact *per se* is

the simplest electrophysical structure and can be presented as an “electrode - point contact - electrode” system. It should be noted that the Yanson point contact is a real nanosized object, whose design is based on the numerous “know-how” of the Yanson PCS. The development of this technique entailed creation of the technology and original "know-how" based on simple but highly technological solutions, which now make it possible to use available tools to easily produce nanoobjects with unique quantum properties.

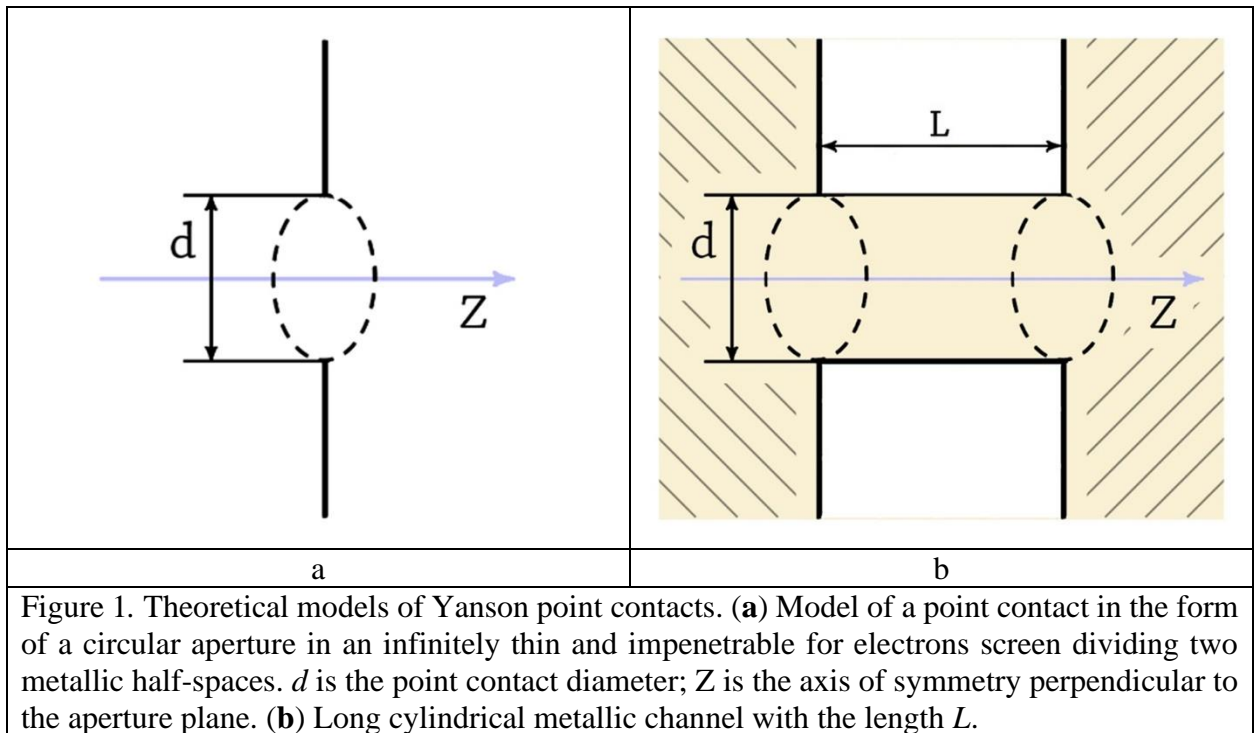
In contrast to the various types of electrical contacts widely used in engineering and scientific research, the Yanson point contact is characterized by a predetermined or predictable behaviour. Among the original characteristics of these objects is the possibility of observing the spectral nature of interactions with various types of quasiparticles, the quantum nature of electrical conductance, the point-contact gas-sensitive effect, the cyclic switchover effect, etc. [8]. Meeting the Yanson PCS criteria allows putting the mentioned qualities into these nanoobjects in the process of their production. The many years of studies of Yanson point contacts have permitted researchers to formulate the basic principles of architectural design and technology for manufacturing sensing elements of quantum point-contact sensors. Some elements of this technological process have become the basis of an inexpensive but highly efficient technology of production of innovative sensor devices with unique parameters.

When applied to sensory analysis, one of the most important Yanson PCS criteria to be met in Yanson point contacts is fulfilment of the inequality $d \ll l$, where d is the contact diameter and l is the mean free path of electrons in the contact material [2, 4, 22]. This criterion defines the Yanson point contact as a nanostructure with a size ranging from the size of an atom to several tens of nanometers. In practice, dimensions of Yanson point contacts are always smaller than those of the conventional electrical contacts used in the electric technologies or those of thin films or nanowires used in the sensor techniques. This criterion is also responsible for one of the main differences between the Yanson point contact and the conventional electrical contact – the absence of thermal effects that could affect its behaviour. The long mean free path of charge carriers in the Yanson point contact (in comparison with the contact dimension) make it possible to avoid influence of the thermal effects. The more strictly the inequality $d \ll l$ is fulfilled, the more reliably the possible influence of the thermal effects on the processes occurring in the contact under various unfavourable factors is excluded. A necessary condition for achieving a long mean free path of electrons is a defect-free and uniform crystalline structure of the sample. This can be realized in highly perfect single crystals, which are used to create Yanson point contacts.

The properties of real Yanson point contacts can be well described within several theoretical models. One of them is the model of an orifice in an infinitely thin and impenetrable for electrons interface dividing two metallic half-spaces [4] (Fig. 1a). The orifice can come in various shapes: a circle, an ellipse, or a rectangle. In the case of a circular orifice, the characteristic dimension of the point contact is its diameter d . To discuss the sensory properties of point-contact sensing elements, it is preferable to consider the model of a long cylindrical metallic channel with the length $L \gg d$ [23] (Fig. 1b). It should be noted that, in principle, variation in the contact shape has no effect on the nature of the physical processes inside the contact and does not lead to any qualitative change in the results of the Yanson PCS [2, 3]. As a consequence, the current-voltage characteristics (IVC) of a point contact do not depend qualitatively on the geometric parameters of the object.

When the inequality $d \ll l$ is fulfilled, a ballistic mode of current flow is realized in the point contact. In this case, the elastic l_i and inelastic l_e mean free paths of charge carriers exceed significantly the point-contact length and diameter. This is the so-called pure limit [2, 22]. In this regime, the trajectories of electrons are straight lines if the applied bias eV (e is the electron charge, V is the voltage) is much smaller than the Fermi energy ε_F of electrons. With a decrease in the mean free path of electrons, a transition to the diffusion mode of current flow occurs. This takes place when the condition $d \ll \lambda$ is fulfilled, where λ is the energy relaxation diffusion length. In the diffusion regime, the trajectories of electrons appear as broken lines. They are similar to the paths of particles in the Brownian motion which preserve their energy during the multiple

collisions. Yanson point contacts in which the inequality $l_i \ll d < \lambda$ is fulfilled also possess spectral properties and can be efficiently used as sensor sensing elements.



A transition from the ballistic mode of current flow to the diffusion mode within one analytical act plays an important role in the operation of the point-contact sensor. Electric current distribution in the Yanson point contact depends on the ratio of the electron mean free path l to the point contact diameter d . In the pure limit, the current distribution is uniform, while in the diffusion mode with a small mean free path the current is concentrated near the aperture edges [24, 25]. The lower the l -to- d ratio, the more pronounced the effect. Adsorption of gas molecules on the surface of a point contact creates additional scattering centres in the contact material. As a result, the current density in a superficial layer of the point-contact material can significantly exceed the high current density observed in the ballistic regime with a uniform distribution of current across the whole contact. In Yanson point contacts with a uniform distribution of current across the whole contact, the current density can reach 10^9 - 10^{10} A/cm² at liquid helium temperatures [22] and 10^7 A/cm² at room temperature [5]. Redistribution of current during the transition from the ballistic regime to the diffusion one leads to a current density significantly exceeding these values along the contact surface. At the same time, it should be noted that such an extreme current regime has absolutely no effect on the mechanical stability of the point contact, since all thermal energy is effectively removed from the contact area.

It should also add that the appearance of defects in the crystalline structure of the contact during the adsorption of molecules and the reduction in the mean free path of electrons also play an important role. The shortening of the mean free path leads to an increase in the residence time of electrons in the region of distortion of the crystalline structure. This increases the probability of electron scattering at the sites of the adsorbed molecules. As a result, the number of cases of interaction between electrons and the gas molecules increases, so does the transfer to the latter of the excess energy acquired by electrons in the electric field of the contact during the current flow. The ultrahigh current density guarantees the transfer of energy needed for molecule desorption. In this case, after receiving an energy comparable to that of adsorption, the molecules desorb from the surface of the conduction channel of the Yanson point contact, thereby carrying away the excessive thermal energy into the surrounding space.

A characteristic feature of Yanson point contacts operating in the ballistic and diffusion modes of current flow is the absence of lattice heating effects, with the electron system of the point contact being in a non-equilibrium state [2-4]. The possibility of separating the thermal and nonlinear current effects in point contacts is their distinctive feature, which homogeneous conductors and nanostructured sensors do not possess. In the case of a homogeneous conductor, the processes of electron inelastic scattering, which are responsible for the electric resistance in the conductor, and energy relaxation processes are combined and occur uniformly in the entire volume of the sample. As a result, a homogeneous sample melts before the electron gas is able to gain an excess energy of the lattice vibration level. The current density at which a metal melts is $10^2 - 10^3$ A/cm² [26] [24], that is it is much lower than the current densities in the Yanson point contact observed in spectral and sensor experiments. This means that if the physical properties of the point contact corresponded to those of a homogeneous conductor, the metal softening would destroy this nanoobject even before it can reach the current densities required for the research. However, point-contact sensors demonstrate an effective heat discharge by the bulk electrodes [2, 3] and keep their mechanical stability for a long period. An ordinary electrical contact, similarly to a homogeneous conductor, cannot function as a quantum sensor and, at best, could match the conventional sensors and nanosensors, taking into account its geometric parameters. It is the situation taking place in the case of point contacts in the thermal regime of current flow with $d \gg l_i$, $d \gg \lambda$ [27, 28]. In this regime, a point contact behaves almost like a homogeneous conductor. The small values of inelastic mean free path of phonons result in a deviation of the phonon system from equilibrium, which plays a significant role. The excitation gas in the contact becomes non-equilibrium, thereby changing the effective temperature of the material in the constriction area. As a result, an increase in the applied voltage leads to significant Joule heating of the metal and an increase in the temperature of the contact, which ultimately causes rapid destruction of the sensing element.

For Yanson point contacts to display their spectral and sensory properties, it is necessary to provide the possibility of current carriers acquiring an excess energy comparable with the energy of lattice vibrations and energy of adsorption of gas molecules on the surface of the contact material. This situation can be realized if the voltage applied to the contact satisfies the condition $eV \leq \hbar\omega_D$, where \hbar is the reduced Planck constant, ω_D is the Debye frequency of phonons; that is, when the applied voltage bias eV is much smaller than the Fermi energy ε_F . Electrons are capable of acquiring excess energy of this level when accelerated in an electric field. In the Yanson point contact, the electric field is concentrated in the constriction area which covers a space with a characteristic dimension of the order of d . This is due to the potential distribution. As was shown in Ref. [4], the potential $\varphi(r)$ reaches its constant value equal to $\pm V/2$ at a distance r of the order of a from the contact centre following the law $\sim a^2/r^2$, where a is the radius of the hole. Therefore, the electric field in the Yanson point contact is concentrated in the constriction area and covers a space with a characteristic size of the order of $d = 2a$. In the pure limit, the dependence of electrostatic potential φ on coordinate z from the contact centre along the symmetry axis passing through the contact can be presented as [2, 4]:

$$\varphi(z) = \frac{V}{2} \left(\sqrt{1 + \frac{a^2}{z^2}} \right)^{-1} \text{sign}z$$

A similar situation is observed in the diffusion regime [2, 25, 29].

The original potential distribution forms an electric field which leads to another important fundamental property of the Yanson point contact. As electrons pass through the contact, they are accelerated by the strong electric field in the contact constriction area over a distance $\sim d$ and get an excess energy [4, 23]. The value of this energy is determined by the voltage applied to the contact. As a result, electron states with a non-equilibrium energy distribution function appear in the contact area [4]. For points on the contact plate, it has the following form:

$$f(\varepsilon_p) = f_0 \left(\varepsilon_p + \frac{eV}{2} \text{sign } v_z \right),$$

where ε_p is the energy of an electron with the momentum p , $f_0(\varepsilon_p) = \{[\exp(\varepsilon_p - \mu)/k_B T] + 1\}^{-1}$ is the equilibrium electron distribution function (Fermi-Dirac distribution function), v_z is the electron velocity projection on the contact axes, μ is the chemical potential, and k_B is the Boltzmann constant. The function of electron distribution over momenta in the Yanson point contact area reflects the presence of a group of electrons with an excess energy eV . It is this group of electrons that is responsible for the unique spectral and sensory capabilities of the Yanson point contacts. After receiving an excess energy, electrons tend to relax to their initial state. Relaxation can proceed through interaction with various groups of quasiparticles, for example, phonons or magnons, or with molecules of external agents adsorbed on the surface of the conduction channel of the Yanson point contact. This interaction is quite effective thanks to the ultrahigh current density. Electrons transfer their excess energy during the interaction with quasiparticle excitations, which leads to a change in the electrical conductance of the point contact. This process is recorded in the IVC of the contact when its spectral characteristics are studied or in the temporal dependence of its electrical resistance in the case of sensor experiments.

The specific voltage distribution in the Yanson point contact is an important prerequisite for this nanoobject to be used and studied as a new type of electrochemically active nanostructure. A Yanson point contact can serve as a nanostructured instrument to control chemical processes at the nanoscale level thanks to the voltage distribution in the narrow part of the contact, since the conduction channel of a point contact immersed in electrolyte transforms into an electrochemical gapless electrode system (GES) [30, 31]. Formation of the GES is a necessary condition for the cyclic switchover effect to occur [13]. This effect reflects the quantum processes of synthesis and dissolution of dendritic Yanson point contacts, which proceed automatically in the "needle-anvil" system immersed in the electrolyte. The quantum nature of the ongoing transformations and the cyclic nature of the process make it possible to implement new quantum mechanisms, concepts, and detection modes.

3. Methods of creating Yanson point contacts and technological solutions for development of quantum point-contact sensing elements

An important element of the Yanson PCS and point-contact sensorics is the technology for creating Yanson point contacts and point-contact sensors. This technology includes a significant number of original high-tech solutions which allow creation of unique nanostructured objects without involving perfect but very expensive devices, such as, for example, various types of electron microscopes. The simplicity, reliability, and high economic efficiency of the methods for creating Yanson point contacts are the most significant advantages of the technology of quantum point-contact sensors. However, simplicity is combined in the point-contact technology with innovation brought by original "know-how".

Point-contact sensing elements are a new type of modern transducers. This refers to the novelty not only in their work, but also in the methods of their creation. New sensors, the operation of which is based on the quantum nature of nanostructures, require new approaches to the technology of their manufacture. This task was largely facilitated by the technological developments that had already existed in the Yanson PCS by the time of the discovery of the point-contact gas-sensitive effect [5, 6]. The requirements to be met in the point-contact sensor technology and the main strategy in the development of point-contact sensing elements have already been partly formulated in the Yanson PCS. First of all, the Yanson PCS criteria must be

fulfilled when creating Yanson point contacts for point-contact sensors [2]. Their implementation determines the manufacture of quantum sensing elements with reproducible properties. Dominance of thermal effects is excluded in such sensing elements and quantum sensory phenomena are displayed without distortion.

One of the distinctive features of the Yanson point-contact technology is the unique methodology for creating nanosized structures using ordinary macroscopic electrodes. This allows avoiding the use of additional, complicated, costly equipment and components. In addition, the mass of the electrodes used to produce point-contact sensing elements can be reduced to a minimum, scaling the electrodes down to a micrometer range [32]. In this case, consumption of the material for the manufacture of a quantum point-contact sensor is minimized. This approach has proven itself in the Yanson PCS and sensor research [2, 3, 8]. Another feature of quantum point-contact sensing elements is a pretty high response signal that allows using simple techniques for its registration. As a result, very simple electronic circuits can be used in portable point-contact sensor devices [33].

An important role in the operation of quantum point-contact sensors is played by the choice of the contact material. A Yanson point contact can be made of almost any conductive substance. The choice of the material is mostly determined by the nature of the target analyte and service conditions of the sensor device. The techniques used to produce point-contact structures are rather simple [7] and in many cases do not need high-precision processing. Very often, copper is used to produce Yanson point contacts. However, at the time of the discovery of the point-contact gas-sensitive effect, the use of this metal in the development of conventional sensors was limited. Activation of the quantum sensor mechanisms and principles of detection made it possible to raise the technologies and choice of material for point-contact sensing elements to a qualitatively new level compared to the traditional sensor technology [8]. In particular, with this approach, unlimited possibilities have been created for the use of the most ordinary and easily accessible materials to solve detection problems. For example, traditional metals, which previously were of no interest to the sensor developers or rarely used by them, have turned into a high-tech object and an inexhaustible source of raw materials for the new generation of quantum sensors. Copper, which proved itself in the creation of dendritic Yanson point contacts [13, 17], is a characteristic example of that. It also is chosen because of both its low cost and the large number of technological methods and techniques for using it in the fundamental studies. When creating a point-contact sensor, in order to make it able to operate in complex multicomponent environments, such as, for example, human breath, it is necessary to choose a material with which highly-reactive gas molecules do not enter into a chemical interaction and from which they can desorb easily. The anion-radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) are an example of such materials [34].

In the Yanson PCS, special attention is paid to the mechanical stability of Yanson point contacts. It is necessary, however, to bear in mind that there are approaches to producing contacts for short-term Yanson PCS studies and long-term studies of quantum point-contact sensors and their operation. The higher the mechanical stability of Yanson point contacts, the more durable the contact and the lower the level of electrical noise in the measured signal. This rule is especially valid when the "needle-anvil" method [35] and the Chubov displacement technique [36] are used. To ensure a high mechanical stability of Yanson point contacts in the spectral studies, various damping elements are used [2]. In point-contact sensor experiments, in addition to the mentioned techniques and methods, original technologies, developments, and "know-how" are also used. These include the Fisun twist method [7, 37], which provides an increased mechanical stability of Yanson point contacts and a high durability of point-contact sensors. The technology for creating point-contact sensor multistuctures (matrices) [38] allows creation of Yanson point contacts in a film configuration, which are completely resistant to mechanical oscillations and vibrations.

An important role in the preparation for Yanson PCS studies is played by the surface treatment of electrodes used to create contacts. To produce Yanson point contacts that satisfy the pure limit condition using such classical methods as the "anvil-needle" and the Chubov displacement technique, electrodes need to be covered with a layer of dielectric or poorly

conductive material of a certain thickness, which is important role for the formation of the contact and its mechanical stability. Therefore, the main task that usually arises during the preparation of the contact surface is the creation of an oxide film of optimal thickness.

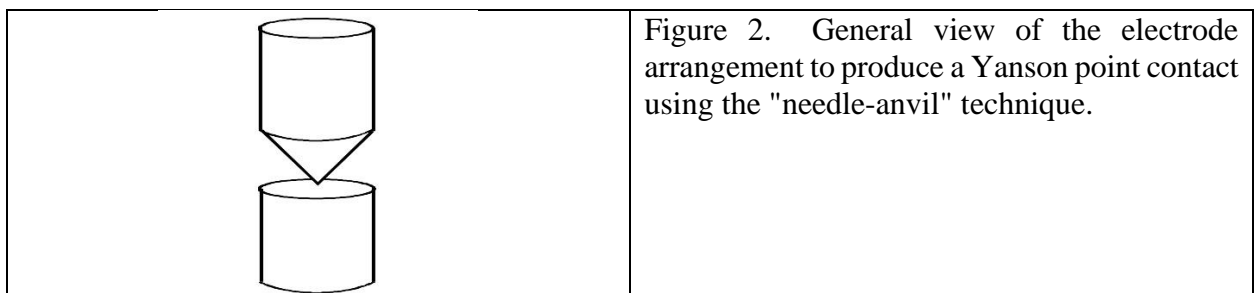
Normally, for each contact material, the resistance of Yanson point contacts which most often exhibit spectral properties lies in a certain range. Since the power dissipated in the contact decreases with an increase in the contact resistance, it is convenient, from the viewpoint of experiments, to create samples with higher resistance within the registered range. The resistance of the manufactured Yanson point contacts depends on the composition and thickness of the dielectric layer on the electrode surface and the electrode pressing force. Most frequently, point contacts with higher resistance correspond to a greater thickness of the dielectric layer and a weaker pressing force between the electrodes. However, it should be taken into account that too large a decrease in the pressing force results in mechanical instability of the contacts, while a significant increase in the thickness of the dielectric layer leads to contacts with direct conduction only being formed when the electrodes are strongly pressed to each other, which causes plastic deformation of the metal in the contact area.

The surface treatment of the electrodes used to create Yanson point contacts is carried out taking into account the chemical activity, structure, and composition of the conductor under study [2]. It includes mechanical polishing, chemical etching, and electrochemical polishing. The compositions of electrolytes and mixtures for chemical etching are selected in accordance with the standard recommendations for specific materials and taking into account the "know-how" of the Yanson PCS. The methods for processing electrode surface tested in the Yanson PCS are also highly effective in the sensor studies.

Devices for making point contacts for the Yanson PCS evolved with the experimental research. Their design fully reflected the requirements of the low-temperature experiment. This resulted in a high-tech device invented by Bobrov and coauthors [39] that, at the same time, was easy to manufacture and operate. Most of the later devices used it as a prototype. A distinctive feature of the created Bobrov device is its ability to produce Yanson point contacts using several methods without the need to modify the device in order to switch from one method to another. The methodological solutions of the Bobrov device later served as the basis for the development of some of the sensor devices [17, 40-42].

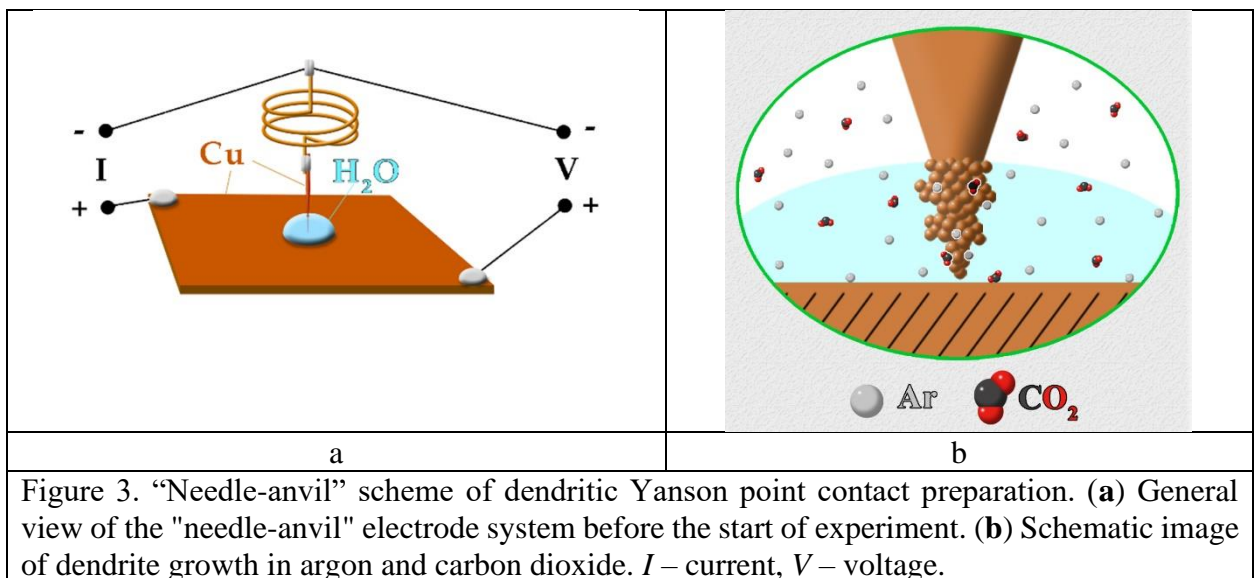
There are several ways to make point contacts for Yanson PCS research that are also highly effective in sensor experiments. The most commonly used methods for obtaining point contacts, as a rule, are based on pressing two electrodes to each other. Each of them is characterized by a certain configuration of the electrodes. The choice of an appropriate method for creating point contacts for specific experiments is made taking into account its advantages and the peculiarities of the task. The first experiments that led to the discovery of the point-contact gas-sensitive effect [5] were performed using the "needle-anvil" technique [35] and the "break-junction" method [43]. Now let us take a closer look at how they work.

The "needle-anvil" method is traditionally widely used in the Yanson PCS. It has proven to be a simple but highly effective technique for working with various materials and under various experimental conditions [2, 3]. The operation principle of this method is based on bringing two electrodes, a needle-shaped and flat one, close to each other, and then making the surface of the flat electrode gently touch the tip of the needle (Fig. 2).



Typically, the needle electrode is made in the form of a needle with a tip radius of about 1 μm , while the anvil electrode has a well processed and polished area. Before a contact is made, the metal electrodes are coated with a thin layer of oxide. Electrical resistance of the manufactured Yanson point contacts depends essentially on its composition and thickness. When the needle is pressed against the anvil, the oxide layer cracks, and a contact with direct conduction is formed. The oxide fulfils an important basic function in the process of mechanical stabilization of the direct metallic contact. It should be noted that when creating “needle-anvil” contacts, the pressing force between the electrodes must be balanced so that it ensures the mechanical stability of the Yanson point contact and, at the same time, does not cause deformation of the contact material, which can essentially affect the quality of the obtained point contacts. Deformation can be avoided by reducing the electrode pressing force. However, it must be remembered that excessive reduction may lead to mechanical instability of the point contacts.

The "needle-anvil" method served as a prototype for the creation of dendritic Yanson point contacts, which demonstrated a number of original sensor effects [13, 17]. In this case, the contact between the needle and the anvil is formed in a drop of pure (distilled) water used as a weak electrolyte (Fig. 3a). Before starting the experiment, the electrodes undergo chemical and electrochemical treatment in order to remove oxides from their surface [44]. Once a certain current flows in the “needle electrode-electrolyte-anvil electrode” system, two areas emerge at the phase interface: the cathode area, at the negative pole of the voltage source, and the anode area on the opposite side. This means that a standard electrochemical system is formed. A dendrite starts to grow on the cathode electrode, which, as a rule, is the needle (Fig. 3b). A Yanson point contact is formed at the moment the counterelectrode surface is reached by the dendrite tip. The crucial difference between dendritic Yanson point contacts and the other types of point contacts is that, as the contact is formed, there is no mechanical influence of the researcher on the movement of the electrodes. The researcher only sets the parameters of dendrite growth and waits for a contact with direct electronic conduction to appear. Dendritic contacts are characterized by a perfect crystalline structure formed during their growth, as well as by quantum properties.



The process of production of dendritic Yanson point contacts is characterized by significant innovative possibilities. In particular, a method was proposed on its basis for creating contact nanostructures with programmable atomic sizes [13]. The idea of the method is to stop the process of the cyclic switchover effect at a certain energy level of the dendritic point-contact structure. This allows one to obtain a dendritic Yanson point contact with a predetermined electrical conductance and a certain atomic size. This method is of great potential for sensor applications.

The high innovative potential of dendritic Yanson point contacts is supported by the discovery of new quantum sensor effects [13, 17, 44]. They include the quantum cyclic switchover effect (to be considered in section 6.1), which is launched during the synthesis of dendritic point-contact nanostructures [13]. This effect displays its rich quantum nature, which serves as a prerequisite for the development of new methods for quantum detection in complex gaseous and liquid media [8, 19]. Conductance quantization in dendritic Yanson point contacts became an example of new mechanism for selective detection in gases and liquids [17]. These original fundamental properties of dendritic point contacts open the door for developing novel quantum sensor technologies which currently have no analogue.

To create Yanson point contacts with a high mechanical stability, the “break-junction” technique is used [43]. This method allows obtaining atomic-sized contacts suitable for both spectral and sensor studies. The method consists in breaking a specially prepared electrode and then bringing the broken parts together to make a contact. The most common electrode for creating Yanson point contacts using the “break-junction” method is a wire of small diameter. A schematic view of a point contact obtained using this technique is shown in Fig. 4.

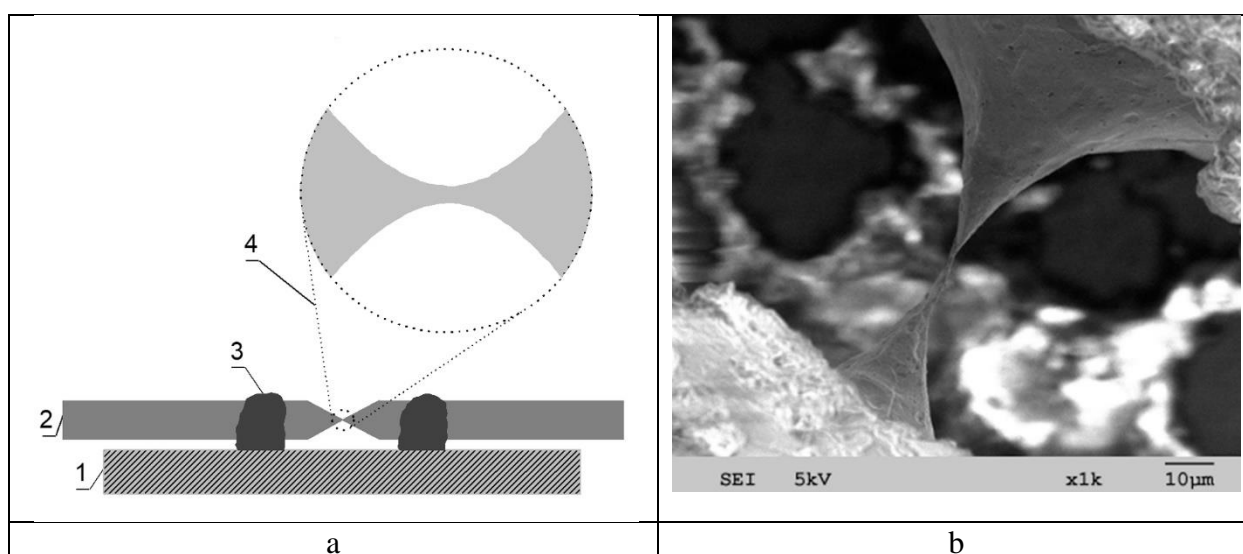


Figure 4. Elements of the technique for creating point contacts using the “break-junction” method. **(a)** Scheme of arrangement of the electrode on the substrate. 1 – substrate, 2 – wire, 3 – drop of glue, 4 – notch with a point contact. **(b)** Result of chemical treatment of the notched area of the sample prepared for making point contacts using the “break-junction” method.

Before a point contact is made, the electrode undergoes a special preparation. First, an incision is made on the wire (Fig. 4a). It is in the narrow area of the notch that point contacts are created when the electrode is stretched and then broken, the dimensions of the contacts can be reduced down to monoatomic structures. Quite strict requirements are imposed on the process of creating a notch: the diameter of the sample at the place of the notch must be small enough, but not so small that the wire loses its mechanical strength. To get rid of the effects of deformation and defects, the wire electrode is annealed at a temperature specific for each material, which, as a rule, is half its melting temperature. All annealing manipulations are made in a vacuum or rare gas environment. The annealing process takes several hours. The notched wire is then cleaned by chemical treatment in a special solution. The cleaned sample is fixed with a special adhesive on the substrate (Fig. 4a). After the glue hardens, the resulting structure is placed in a special device for creating contacts, in which the wire can be broken very smoothly by bending the substrate at the incision point. The diameter of the wire is gradually changed to the required size. The process of substrate bending can be stopped when the required point contact resistance is reached or continued until the wire is completely broken. By changing the degree of substrate bending, it is possible to change in a reversible manner the diameter of the contact and, as a consequence, its

resistance. Another way to change the diameter of the wire in the notch area is chemical etching. An example of chemically processed sample is shown in Fig. 4b.

The main advantage of the “break-junction” technique is the possibility of creating contacts of ultrasmall size, down to an atomic size, and a rather high mechanical stability of the obtained nanoobjects. However, this method also has some disadvantages. With repeatedly bringing together and moving away the parts of the electrode at the point of rupture, plastic deformation of the material occurs, accompanied by an increase in the concentration of defects and a decrease in the mean free path of current carriers in the newly created point contact. Sensors based on Yanson point contacts obtained using this method are highly durable. For example, the sensor whose results are used in Ref. [5] kept its sensory properties for more than one year under environmental conditions.

One of the most efficient (if not the most efficient) method for creating Yanson point contacts for spectral studies is the Chubov displacement technique [36]. This method was invented by Pavel Chubov in 1979 and immediately became the basic technique of the point contact preparation for Yanson PCS studies. It allows obtaining ballistic Yanson point contacts under the most complicated conditions, when spectroscopy of samples is impossible with other methods of point contact preparation. In particular, the Chubov technique has demonstrated high efficiency for layered materials. It is with the help of this method that it became possible to obtain high-quality electron-phonon interaction spectra in organic conductors and transition metal dichalcogenides [45-47]. In this method, point contacts are produced between bulk metallic electrodes of high purity by means of making the electrodes contact each other and then shifting one of them with respect to the other (Fig. 5a). For this reason, samples obtained by this method are also referred to as “sliding-type” point contacts [2, 3].

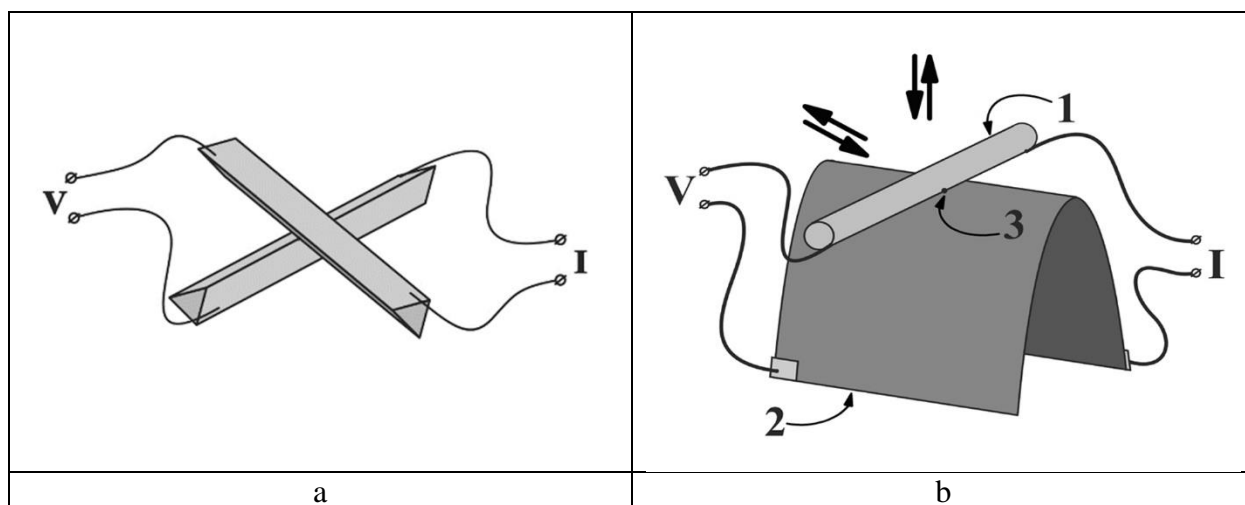


Figure 5. Scheme for creating Yanson point contacts using the Chubov method. (a) Traditional prism-shaped electrode arrangement. (b) General scheme of Au/SWNT heterocontact fabricated by the Chubov displacement method [6]. 1 – Au wire; 2 – folded SWNT film on Nafion membrane; 3 – Yanson point contact. Arrows show the directions of the electrode displacement. I – current, V – voltage.

The electrodes used in the Chubov technique to create Yanson point contacts can be a prism or a cylinder with a linear size of 5-15 mm and a cross-section of 0.5-2 mm. However, the types of electrodes that can be used in the Chubov method are not limited to these forms. An original approach to the creation of point-contact sensing elements using the Chubov displacement technique was applied in Ref. [6], where one of the electrodes was a Nafion membrane onto which a film of single-walled carbon nanotubes (SWNT) was deposited. The elastic Nafion membrane made it possible to bend the SWNT film without damaging it and create a film electrode to be effectively used in the Chubov displacement technique (Fig. 5b).

A distinctive feature of the Chubov displacement method is shearing microprotrusions and displacing the non-conductive surface layer of the electrodes. This occurs when the electrodes are mutually moved in the plane of their contact. As a result, the surface layer of the material is significantly less deformed compared to the “needle-anvil” contacts. In addition, when samples are created by the displacement technique, the dielectric layer is efficiently removed from the point contact area. In the case of the Chubov method, the metal in the formed contact can be in the same good condition as it is in the homogeneous electrodes, that is, the state of the metal in the contact practically does not differ from the state of the metal in the depth of the electrodes. This increases the yield of Yanson point contacts corresponding to the ballistic current flow regime. The ideal case of creating Yanson point contacts with an absolutely perfect crystalline structure can be achieved using the electrochemical synthesis method proposed in Ref. [38]. A soft electrochemical synthesis allows synthesis of films consisting of layered crystals of the Cu-TCNQ compound. Yanson point contacts are formed at the points of contact of the lateral faces of such crystals in accordance with the mechanism employed in the Chubov displacement technique [48]. As a result, a sensor matrix is formed with an ultra-high density of quantum point-contact sensing elements – more than 5×10^5 contacts per mm^2 (Fig. 6).

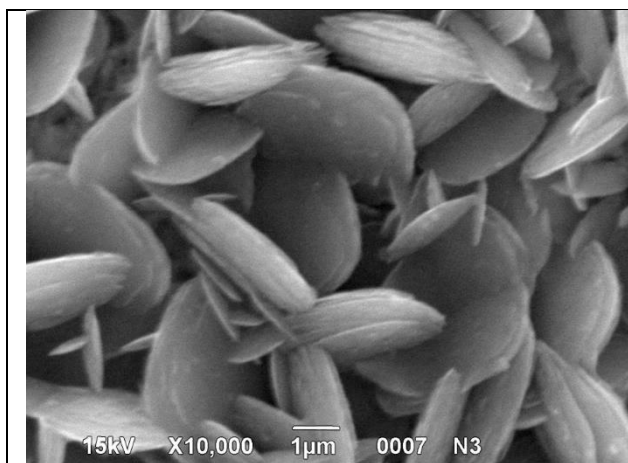


Figure 6. General view of the surface of point-contact sensing matrix based on the TCNQ compound. Reprinted with permission from Ref. [48].

The methods for production of Yanson point contacts and the mechanisms of operation of quantum point-contact sensors make it possible to avoid one of the very serious problems that affect the operation of conventional sensors with the operation principle based on changing electrical conductance. Chemical sensors of all types undergo changes caused by the irreversible processes in the surface layers of the sensing element under the action of the analysed gases. This effect leads to a drift in the sensor parameters and reduction of the reproducibility of results. This decreases the lifetime of the sensing element, which ultimately results in its replacement. The problem can be solved by employing the Chubov displacement technique in the process of sensor studies, since this method ensures removal of a "contaminated" or degraded surface layer of electrodes and allows creation of a large number of Yanson point contacts on a clean surface during one experimental cycle. Ultra-high current densities in point-contact sensing elements favour an effective removal of the gas molecules physically adsorbed on the surface of the conduction channel of the Yanson point contact. In combination with this property of point-contact sensing elements, the choice of highly functional materials such as, for example, TCNQ compounds, provides a high durability of quantum point-contact sensors.

4. Point-contact gas-sensitive effect. Comparison of point-contact sensors with known analogues

The concept of development of quantum point-contact sensors is based on the discovery of the point-contact gas-sensitive effect [5, 6] and the unique nonlinear properties of Yanson point contacts [8]. The point-contact gas-sensitive effect manifests itself at room temperature as a change

in the point contact electrical conductance by 2-3 orders of magnitude when exposed to gases of concentration of a few ppm units and less which exhibit either donor or acceptor properties with respect to electron transfer from the gas molecules to the gas-sensitive material of the samples, as well as give rise to a shift in the density of electron states in the point-contact area.

The point-contact gas-sensitive effect was discovered during the study of copper Yanson point contacts [5]. The prerequisite for making these experiments was the general idea of the operation of conventional sensors with the operation principle based on changing electrical conductance. A conductor in a gaseous medium undergoes a modification of its surface layer and a change in its conductive properties under the action of the gas molecules adsorbed on its surface. The adsorption process results in a redistribution of the electron density of states in the surface layer, and the local electrical conductance changes proportionally to the gas amount. Since the depth of the layer influenced by the adsorbed gas molecules is small, the thickness of the surface layer of the sample with a changed electrical conductance is also insignificant. It follows that in order to see a noticeable change in the electrical conductance of the entire sample caused by interaction with the gaseous medium, it is necessary to reduce its size. It's obvious that a conductive sample will demonstrate a significant response to the action of an external agent if the thickness of its surface layer, whose conductance changes after the interaction, is close or equal to the cross-section area of the sample. This conclusion underlies the dominant trend in the development of conventional sensors with the operation principle based on changing electrical conductance. Initially, this led to using film samples for the development of sensing elements [49-51], and then to widely involving a large number of different nanostructures in this process [52-55].

If we assess the operation of a conductive sensor from the point of view of its geometric factor, then the Yanson point contact as a sensing element has undeniable advantages over many types of nanostructures. Fulfilment of the criterion $d \ll l$, as has already been mentioned, specifies the size of a point contact in the range from that of one atom to several tens of nanometers. At the same time, the Yanson point contact is a highly perfect crystalline object due to the original technology of its manufacture. Of course, such a nanostructure, based on general ideas, should be very promising for the development of sensors.

In addition to the geometric factor, the original electrophysical and quantum properties of Yanson point contacts serve as a prerequisite for the existence of the point-contact gas-sensitive effect. Let us consider them in more detail in the context of their manifestation during interaction of the point contact with a gaseous medium. One of the basic properties of Yanson point contacts which are responsible for their excellent performance is the potential distribution. When a current flows through the contact, its electric field is concentrated in the constriction area and covers a space of the order of magnitude of the point-contact diameter d . For contacts corresponding to the model of long conduction channel [23], the potential distribution defines the area of voltage drop over a distance of the order of magnitude of the conduction channel length. This means that the resistance of this small area determines the resistance of the entire "bulk electrode - point contact - bulk electrode" structure. Thanks to the potential distribution, the contribution of the bulk electrodes to the resistance of the entire structure is negligible. As a result, a tiny region of the conductor becomes a key element that determines the electrical properties of the entire system of electrodes involved in the formation of a Yanson point contact. An external action will lead to a change in the electrical resistance of this system as a whole only if the electrical conductance of the Yanson point contact itself changes. Therefore, the possible interaction of the electrodes that form the Yanson point contact or current-feeding wires with the gas molecules will practically not affect the character of the electrical conductance of the entire system. This means that if we observe a change in the electrical conductance of a point-contact structure under the action of a gaseous medium, then it is the Yanson point contact which is the source of this change.

The prerequisites for the high sensitivity of a point-contact sensor, along with the geometric factor, are the features of the current state of the Yanson point contact. The ultrahigh current density of the order of 10^7 A/cm² increases significantly the probability of interaction of the current carriers in the point contact with the gas molecules adsorbed on its surface [5]. In this aspect,

Yanson point contacts significantly outperform traditional conductors, since a current density higher than 10^3 A/cm^2 cannot be reached in the latter without destroying the sample. Thanks to the ultrahigh current density, the response of the point contact to the adsorption of gas molecules is almost instantaneous. And since the surface-to-volume ratio in the point contact is very large, the magnitude of the response signal to the action of an external agent is also significant. The considerable levels of magnitude of the resistance response are due to the commensurability between the channel and the analyte molecules. This is clearly seen in the example of the first observation of the point-contact gas-sensitive effect using copper Yanson point contacts [5] (Fig. 7). In these experiments, point contacts displayed an instant response to the action of a

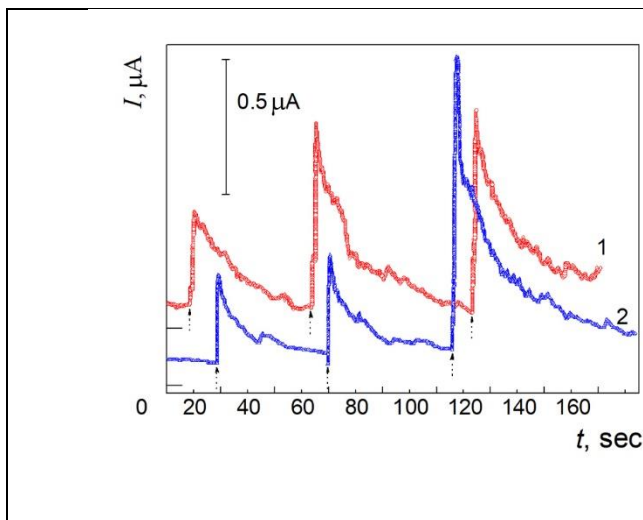


Figure 7. Response of copper Yanson point contact to a pulsed action of gases. Curve 1 is related to the multiple interrupting action of NO_x with a concentration of 0.1 ppm; curve 2 – HCl with a concentration of 50 ppm. Resistance of the Yanson point contact in the equilibrium state before exposure is $R_0 = 50 \ \Omega$; current in the equilibrium state is $I_0 = 0.1 \ \mu\text{A}$. Dotted arrows indicate gas pulses. Reprinted with permission from Ref. [5].

gaseous medium and an ultrahigh sensitivity to the studied gases, as evidenced by a 300-1000% increase in the current flowing in the contact under the action of a pulse of gas of low concentration.

Already in the first studies, it was noticed that the sensor properties of Yanson point contacts are fundamentally different from those of the conventional sensing elements. In particular, a decrease in the gas concentration does not lead to a symmetrical drop in the intensity of the response signal of a point-contact sensing element, as is the case in the conventional sensors. In Ref. [6], sensors based on point heterocontacts Au/SWNT exhibited a strongly nonlinear dependence on NH_3 concentration. The dilution of gas by two orders of magnitude resulted in only halving the signal amplitude. This implies that point-contact sensor properties are fundamentally distinctive from those of the conventional chemical gas sensors.

Taking into account the ultras-small dimensions of the Yanson point contact ranging from ångströms to nanometers, one gas atom can be enough to react with the constriction area material and cause measurable changes in the electrical conductance of the contact. This results in an incomparably high sensitivity of the point-contact sensing element. Thus, the lowest detection limit at the level of one gas molecule is achievable with point-contact sensors. Adsorption of even one atom leads to a significant change in the electrical resistance of the point contact, which can be easily registered. For example, in the case of a Yanson point contact formed by one atom, interaction with just one gas molecule results in a resistance change as high as at least $12.9/n \text{ k}\Omega$, n being the number of atoms in the contact [13, 17]. This value can easily be registered with ordinary measuring instruments. As a result, the quantum point-contact sensor response to the exposure to a gas medium is always stronger than that of any other equally small homogeneous nanosensor because the latter cannot operate in the quantum registration mode with an ultrahigh current density. This means that less complicated and cheaper equipment is needed to register the response signal of the quantum Yanson point contact. Larger transducers are *a priori* far less sensitive than quantum point-contact sensors.

The ultrahigh current density in the Yanson point contact also ensures very short relaxation times of point-contact sensing elements. Before the adsorption starts, the current state in the Yanson point contact is determined by the perfect crystalline structure in the entire conduction channel of the point contact with an electric current distributed uniformly over the entire volume of the sample. The adsorption process immediately results in a change in the current state of the point contact because adsorbed gas molecules cause structural defects in the surface layer of the conduction channel. And since the cross section of the conduction channel has atomic dimensions, this process affects almost the entire volume of the point contact. This leads to a transition from the ballistic regime of current flow to the diffusion one. In the diffusion mode, a decrease in the mean free path of electrons results in the concentration of the current near the edges of the orifice [24, 25]. The smaller the ratio of the mean free path of electrons l to the contact diameter d , the stronger the effect. The result is a unique surface current state with a current density which is even higher than the huge current density of a Yanson point contact in the ballistic mode. This further increases the already significant probability of scattering of conduction electrons at the sites of adsorbed gas molecules, thus creating favourable conditions for the transfer of the excess electron energy to these molecules and their subsequent desorption. As a consequence of this, the process of relaxation of the point contact takes a very short time. It can be 20-30 seconds, as in Fig. 7, or several minutes, depending on the conditions of the experiment. The character of relaxation of the point contact conductance depends on both the nature of the conduction channel and the nature of the gas agent.

To assess the prospects of research into the point-contact gas-sensitive effect, the parameters of point-contact sensing elements and popular conventional sensors and nanosensors based on the principle of changing electrical conductance were compared in Refs. [6, 7]. It is not a simple task to ensure the correctness of such a comparison, because the information that can be found in the literature is often not transparent, when, for example, the parameters of sensing elements are given as those of sensor devices, in which sensors can be connected with amplifiers or even spectrometers. It is not rare that during the relaxation of a sensing element, the recorded results are obtained using heating devices, vacuum equipment, or various irradiation procedures. Of course, this can significantly improve the results. However, it is necessary to remember that such results do not characterize the sensing element itself. To ensure the purity of the experiment and the reliability of the data obtained, Yanson point contacts are always studied as an independent quantum sensing element without involving any additional amplifying equipment. The use of Yanson point contacts in connection with a point-contact spectrometer can immediately lead to an increase in their sensitivity by 3-6 orders of magnitude. So, a direct comparison with the published data will only be correct and accurate if different techniques are compared at the approximately same stages of their development. For this purpose, it is necessary to use the original general parameters of point-contact sensors and their nanosized analogues without any special treatment or using complex structures such as sensor arrays, artificial amplification of the signal, etc.

Comparison of the parameters of point-contact sensing elements published in Refs. [5, 6] and other nanosensors [9, 56-60] selected taking into account the above criteria demonstrated significant superiority and high competitiveness of the former. The analysed data show that the performance of point-contact samples has a great competitive advantage over other sensors. Moreover, Yanson point contacts have excellent and unprecedented characteristics and their performance exceeds significantly that of their analogues. In particular, the response time of a point-contact sensing element to the action of 0.1 ppm of gaseous NO_x was less than 1 second, while the reaction of the nanostructured analogues was hundreds of times slower even to significantly higher gas concentrations. The sensitivity of point-contact sensors exceeded the results of their analogues by a factor of 100 or more. Observation of a very high and fast 1000% response of point-contact sensors to their exposure to 0.1 ppm NO_x allows setting the lower limit of detection for point-contact sensors at a value essentially lower than 0.1 ppm NO_x . The relaxation time of a point-contact sensing element after the action of 0.1 ppm NO_x was 20-30 seconds. For its nanostructured analogues, this parameter was at best 1200 seconds [57] or required a very long

time without special treatment. These facts evidence the superiority of the quantum point-contact sensor approach.

The selectivity of Yanson point contacts cannot be considered and evaluated employing the standard approaches used for the conventional sensors with the operation principle based on changing electrical conductance. Selective detection using conventional chemical sensors is based on the principle of “a key and a lock” [61, 62]. Any effect or property of the material of the sensing element can act as a key to determine the analysed agent. The purpose of this approach is to ensure that the sensor displays a maximum change in its electrical conductance under the action of a certain gas and does not respond to other substances, or responds weakly. This situation can be achieved, for example, through functionalization of the material by adding an element already existing in nature or created artificially [63-66]. A typical example of this kind of solution is the use of proteins on the surface of the sensing element [67, 68]. Such sensors are able to solve the problem of detecting a particular substance. However, this approach leads to a narrow specialization of the sensor and allows using it for one purpose only. Since nature has an infinite number of keys, locks, and their combinations, such a strategy leads to extensification of the sensor development, and search for acceptable matches becomes a long and costly procedure, development of which requires many years of efforts of a large number of specialists.

In contrast to the conventional selective sensors exploiting the principle of changing electrical conductance, Yanson point contacts can provide response to almost any gas, including both chemically active and completely inert substances. At the same time, a point-contact sensing element has absolute selectivity to any component of a complex gas mixture or liquid medium [17, 18]. The difference from the conventional chemical sensors is that the interactions in the Yanson point contact are characterized by quantum processes which involve conversion of energy (for example, between electrons and phonons). In the conventional sensors, this scenario is impossible for a number of reasons, which we have already discussed and will continue discussing in more detail in the next section. The energy nature of the interaction in the Yanson point contact is most clearly manifested in complex gaseous and liquid media. In the case of a one-component gaseous medium, the contact response is similar to the response signal shown in Fig. 7. In this case, as noted above, the change in the electrical conductance of the point contact is quite significant and occurs over a very short period of time. The amplitude of the response signal may depend on the material or condition of the contact [28]. In the general case, the quantum detection mechanisms, on which the operation of point-contact sensing elements is based, make it possible to observe a response to the action of any substance.

The key property which characterizes the nature of the analysed gaseous agent is its activity with respect to electrons, in other words, the balance between its donor and acceptor properties. It makes it possible to see the nature of the charge transfer in the analysed gas (donor or acceptor) using metal-semiconductor point-contact sensing elements. The impact on the contact exerted by gases of different nature leads to a change of the sign of the response signal. This effect was demonstrated using Au/SWNT heterocontacts for gaseous ammonia NH_3 and nitrogen dioxide NO_2 taken as examples [6]. The action of ammonia led to an increase in the resistance of the heterocontact. However, in contrast to the NH_3 case, exposure of the contact to NO_2 decreased the sample resistance. Since SWNTs have p-type conductivity, sorption of a strong oxidant such as NO_2 should increase the hole concentration. In contrast, the electron donating properties of NH_3 should reduce the hole concentration in SWNTs. So, we can conclude that the interaction of SWNT with gases of different nature (oxidizing or reducing) dominates the device functionality and Au/SWNT heterocontact sensors demonstrate selective response inherited from SWNTs.

If a Yanson point contact is placed in a complex gaseous medium, it responds with a change in its electrical conductance caused by spectral-type interactions. In this regard, the result of detection in human breath using Au/SWNT point contacts [8] is very illustrative. It reflects the complex pattern of changes in electrical conductance initiated by the quantum interactions of charge carriers with gas molecules adsorbed on the surface of the conduction channel of the point contact (Fig. 8). Despite the large number of studies with carbon nanotubes used as sensing

elements in the conventional sensors, we are not aware of any results of such behaviour demonstrated by them. Some of the reasons for this have already been mentioned. This issue will be discussed in more detail in the next section. In the general case, this is because the quantum detection mechanisms cannot be implemented in the conventional sensors whose operation principle is based on changing electrical conductance.

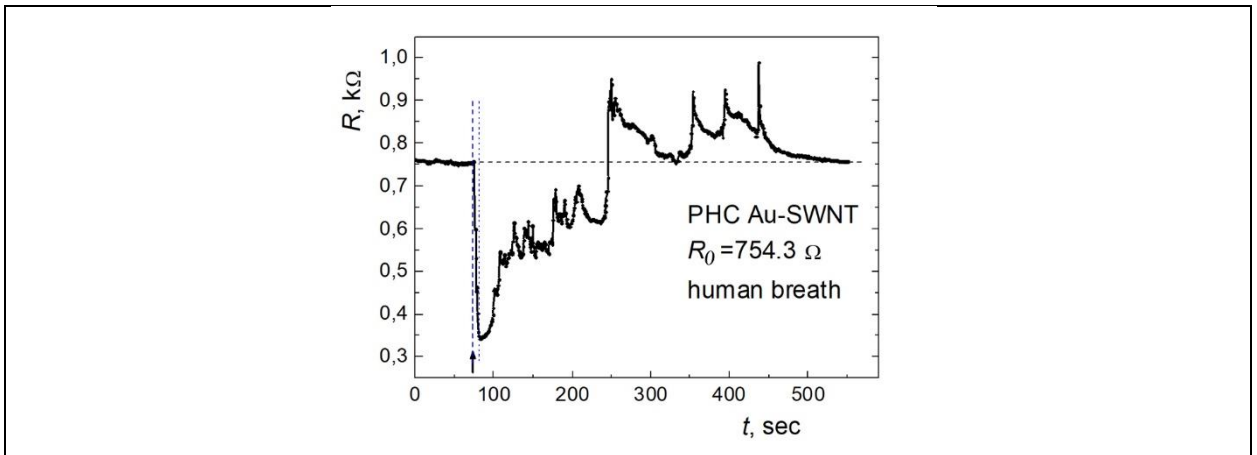


Figure 8. Spectral response of Au/SWNT point heterocontact to the action of human breath. Arrow marks the onset of the gas action. Vertical dashed and dotted lines show duration of exposure. Reprinted with permission from Ref. [8].

5. Quantum mechanisms of selective detection in complex gaseous media. Analysis of human breath

Quantum sensors are fundamentally new detectors, the operation principle of which is based on fundamental quantum mechanisms. The concepts of quantum detection provide the basis for the development of innovative models that are impossible to implement practically in the conventional sensors and nanosensors. The legitimacy of this statement is confirmed by the point-contact sensing elements based on Yanson point contacts. In the previous sections, the unique quantum properties of these nanoobjects were mentioned. In this section, we consider how they make it possible to implement new quantum mechanisms for detection in gaseous and liquid media.

Reducing the size of nanostructures creates the prerequisites for the manifestation of quantum confinement of charge carriers and emergence of quantum size effects [69, 70]. Quantum confinement arises when the size of the free electron localization region (for example, one of the characteristic dimensions of the sensing element of a sensor or particles of its material), becomes comparable to the de Broglie wavelength

$$\lambda_D = \hbar / (2mE)^{1/2},$$

where \hbar is the reduced Planck constant, m is the electron effective mass, and E is the electron energy. For semiconductors, the Bohr radius of the exciton

$$a_0 = (4\pi\epsilon_0\hbar^2) / (e^2m)$$

serves as such a criterion. Here ϵ_0 is the permittivity of free space, e is the charge of an electron. As a rule, the de Broglie wavelength in metals is in the range of 0.1-10 nm, while the value of the Bohr exciton radius in semiconductors is 1-10 nm.

The small size of nanostructures can limit the free motion of electrons in these objects to one, two, or three directions. With a decrease in the characteristic dimensions of a nanosized sample, the exciton binding energy increases, as a result of which quantum limitations can be seen

even at room temperature. Quantum confinement results in electrons being only able to occupy discrete energy levels in a limited region of space. The limitation to the free motion of electrons and the discreteness of their energy states, in contrast to the case of free motion in bulk objects, leads to a difference in the properties of nanostructured sensing elements from those of their bulk analogues. For example, nanostructured sensors exhibit chemical activity that is significantly different from that of bulk objects [71]. In nanocrystalline materials, the charge transfer rate is mainly determined by the effects of quantum confinement and differs significantly from the situation in classical homogeneous samples characterized by the free motion of electrons. As a result, unconventional detection mechanisms may appear in nanostructured sensing elements. This allows developing new principles and directions of operation of sensor devices.

One of these new areas is the search and development of quantum detection mechanisms based on the energy principles of analysis [17, 18, 20]. The general ideas about quantum objects served as a stimulus for conducting research in this direction. A quantum system has a set of metastable energy states that form its unique energy portrait. The knowledge of the energy portrait of the system provides unlimited possibilities for its recognition and analysis. This leads to a simple conclusion: for effective detection and analysis of the system, it is sufficient to determine the energies of the metastable quantum states [17].

An appropriate tool is needed to implement this idea. Nanostructured objects that satisfy the condition of quantum confinement could become such a tool. Following the general ideas, nanostructures are direct candidates for being used as quantum sensing elements with the operation principle based on changing conductance. However, at room temperature there is an obstacle to this approach. At room temperature, thermal phenomena play a significant role, hiding the manifestation of quantum effects, and the creation of quantum tools becomes much more complicated. In electrical conductors, the competing influence of thermally induced processes can lead to a complete neutralization of the object's quantum nature. As a result, at room temperature, electrically conductive materials used to create chemical sensors and nanosensors become unsuitable for implementing quantum detection mechanisms within the conventional sensor approaches. In addition, in traditional sensorics, the operation of a large class of objects is focused on the use of heat to increase their efficiency. These include, for example, sensors based on carbon nanotubes and graphene [65]. The operation of sensors based on metal oxides also requires the use of high temperatures because of their significant band gap [53, 57]. At the same time, an attempt to cool a semiconductor sensor in order to reduce the contribution of thermal fluctuations can lead to its transition to the insulator state at low temperatures.

To implement the energy concept of quantum detection, one needs to have a method for determining the energy of specific states of the objects under study. One of the ways to solve this problem can be using the interaction energy of the systems of quasiparticle excitations that characterize the sensor material and the analysed object. Gas molecules adsorbed on the surface of the sensing element can be a source of information about the analysed object, for example, a complex gaseous medium. The energy information about the quantum states of the "sensing element - analysed object" system can be obtained using quasi-particle excitations in the sensor material. Systems of electrons and phonons in a metal can serve as a tool for selective detection of various external agents [8, 18]. The interaction of electrons and phonons with each other or with atoms and molecules adsorbed from the outside on the surface of the sensing element of the sensor makes it possible to obtain all necessary energy information about the sensor material, as well as data for identification of the analysed agent [18].

The energy approach proposed in the works dedicated to the study of point-contact sensing elements is a universal principle that ensures the absolute selectivity of quantum sensors [17, 20]. However, its implementation at room temperature using conventional nanosensors with an operation principle based on changing electrical conductance encounters significant difficulties, the biggest being the thermal effects. They can dominate at room temperature and, as a result, hide any non-linear non-equilibrium processes in the material and lead to suppression of the quantum phenomena. One of the ways to eliminate the negative influence of the thermal effects is to separate

in space the non-equilibrium processes that characterize the quasiparticle interactions accompanied by a change in energy and the thermal ones. Currently, we know only one example of an instrument capable of solving this problem. It is the Yanson point contact. Apparently, in the framework of a homogeneous conductor, it is hardly possible to implement such an approach even at low temperatures.

In the Yanson point contact, the non-equilibrium state of its electron system makes it possible to use electrons to probe and record the phonon energies which characterize the vibrations of atoms in the crystal lattice or natural vibrations of atoms adsorbed on the surface of the conduction channel of the sensing element. In the electric current state, the non-equilibrium of the electron system in the contact could be brought to the level of the adsorption energy of the gas molecules without letting the effects of heating of the crystal lattice manifest themselves [5, 6]. As a result, electrons possess a sufficient excess energy to be transferred to phonons in the contact or adsorbed molecules with a subsequent change in their energy state. This transfer becomes possible in the Yanson point contact because the energy processes resulting from the interaction and the thermal processes that cause chaotic vibrations of atoms and disrupt the interaction of the quasiparticle systems in their pure form are reliably separated in space [4]. Hypothetically, in the case of a homogeneous conductive sensing element, even if it were possible to obtain electrons with excess energies sufficient to excite lattice vibrations, it would be extremely hard to obtain a nonlinear IVC with information about the quantum processes. That's because already at the initial stage of recording the I–V characteristics at current densities of the order of 10^2 – 10^3 A/cm², destruction (melting, sublimation) of the sensor material would occur. The reason for the destruction of a homogeneous conductor in this case is the spatial combination of the processes of inelastic scattering of electrons forming the electrical resistance of the conductor and the processes of energy relaxation, as a result of which they occur evenly over the entire volume of the sample. In practice, a homogeneous sample has enough time to melt even before the electron gas can acquire an excess energy comparable with the energy of lattice vibrations.

The Yanson point contact is able to ensure the needed separation of the thermal and quantum non-equilibrium processes in a small nano-sized area thanks to the heterogeneity of its structure, provided that the mean free path of electrons allows the ballistic mode of electric current flow. Ideally, the greater the mean free path of charge carriers in the contact, the easier it is to separate the thermal phenomena and the current ones caused by the non-equilibrium of the electron gas. At room temperature, the mean free path of electrons is significantly smaller than it is at low temperatures, and it becomes much more difficult to realize a ballistic mode of current flow. However, the special technology proposed in Ref. [13] allows creation of dendritic Yanson point contacts with a perfect crystalline structure, in which a maximum value of mean free path of electrons can be reached. More details about the quantum sensor effects implemented using dendritic Yanson point contacts are provided in the next section.

According to the estimates made in Ref. [72], the mean free path of electrons in pure copper can reach 300 Å at room temperature. This means that in dendritic Yanson point contacts with a perfect crystalline structure, we can obtain a ballistic mode of current in the resistance range of 10 Ω - 12.9 kΩ. The electrochemical synthesis of the material used to produce dendritic Yanson point contacts provides the necessary conditions for obtaining perfect crystals and fulfils the specified requirements. This makes it possible to separate the nonlinear current phenomena in the contact and the thermal effects, thus taking the manifestation of the latter far beyond the contact area. This allows using Yanson point contacts as sensing elements in quantum sensors that can effectively operate at room temperature [17, 18, 21].

Human breath is a good example of effective implementation of the quantum detection mechanisms with point-contact sensors. The gas exhaled by a person is a complex environment that contains more than 2000 components [73]. A large number of these substances are volatile organic compounds, which are metabolic products of the human body. This allows using breath components as markers of certain states of the human body which indicate either healthy metabolism or some problems in the functioning of human organs and systems. This idea served

as the starting point for a wide range of studies focused on human breath and aimed at obtaining information about markers that can be associated with the various diseases and used to develop non-invasive methods of medical diagnostics [74].

A wide arsenal of analytical methods can be used to solve the problems related to analysis of human breath. The main ones are mass spectrometry and gas chromatography, which are mostly employed for high-tech scientific research. Even though these traditional techniques yield adequate results, they are hampered by a number of restrictive disadvantages, being costly, sophisticated, and bulky. The necessity of sample collection and their pre-processing in some of the techniques, as well as the need for highly skilled personnel to provide technical maintenance, prevent them from being actively used in everyday medical practice. The active development of nanostructured sensors and relevant technologies provide inexpensive, easy-to-use, and reliable alternatives for breath analysis.

Conventional sensors for analysis of human breath are mostly developed within the marker approach [75]. The task of selective detection of single gases can be solved with conventional nanosensors based on different operation principles. A leading position among them is occupied by chemical sensors using change in their electrical conductance as their detection principle. These samples demonstrate good results in detection of separate gases. However, when it comes to human breath, many problems arise which significantly lower the reliability of the operation of conventional sensors. The reason is that human breath, like any multicomponent environment, is characterized by a pronounced dynamic behaviour [76]. Human breath contains oxidizers (for example, nitrogen oxides, carbon monoxide, sulphur oxide), reducing agents (for example, hydrogen sulphide, ammonia, mercaptans, organic molecules), and other reactive and active elements. The 2000 components of this complex environment include substances with a high reactivity that can quickly interact with each other, leading to the formation of new compounds. The newly formed substances can, in turn, be catalysts for new chemical reactions, which means that progressive autocatalysis cannot be ruled out. This entails significant changes in the qualitative and quantitative composition of the original system in a short period of time, which can significantly affect the reproducibility of results when a complex gas mixture is analysed by means of identification of its individual components [77].

Registration of a sensor profile of the analysed medium can be an alternative solution. Among the conventional sensors, this approach is typical of the so-called *electronic noses*. *Electronic-nose* sensors are usually an array of 20-30 traditional sensors, each focused on finding a certain component of the gas mixture [78]. The sensor profile of the gas mixture is obtained by summarizing the data coming from each sensor, that is, by getting some 20-30 points that can provide an approximate presentation of the complex profile curve formed by the components of the gas mixture. This approach requires complex mathematical processing of the measured data and large machine-time resources to obtain acceptable information. In the case of human breath, the reliability of results obtained by *electronic noses* remains low because of the complex composition of the analysed environment and its dynamic behaviour. It is clear that, having data on 20-30 components, it is difficult to expect high accuracy in getting a complete portrait of an object consisting of 2000 components actively interacting with each other. This problem can be solved by recording a spectral sensor profile of breath [18, 20]. However, obtaining it is only possible with the help of quantum sensor tools, such as Yanson point contacts. Registration of the spectral sensor profile of breath using point-contact sensors occurs in real time and allows one to get comprehensive energy information about the analysed environment, which would be sufficient for its successful analysis [18, 20, 21].

The spectral nature of the response of quantum point-contact sensors to the action of a complex gas mixture makes it possible to apply the quantum spectral mechanism of selective detection to complex gas mixtures [18]. Currently, several concepts of detection based on this mechanism are already proposed and tested. Their use opens up great prospects for the development of various methods of medical diagnostics in real time. The diagnostic methods based on the principles of analysis of human breath with quantum point-contact sensors can offer a

comprehensive one-technology solution to a number of diagnostic problems. In the next section of this review, we briefly describe the methods based on the quantum detection mechanisms which have already been tested in medical practice.

6. Conductance quantization: innovative mechanism of selective detection and new principles of analysis

6.1. Cyclic switchover effect. Gapless electrode system

The electrochemical cyclic switchover effect is one of the striking effects discovered in the study of transport properties of dendritic Yanson point contacts [13]. It is a cooperative effect arising from conductance quantization in the Yanson point contact and the unique electrochemical nature of its conduction channel. The effect is based on the original property of Yanson point contacts of being able to undergo a fundamental transformation in electrochemical solutions. The cyclic switchover effect makes it easy to demonstrate the quantum properties of these nanoobjects in their electrical conductance and can be an efficient tool to register a variety of quantum states of this point-contact system in dynamic mode.

The cyclic switchover effect is a classical self-oscillating process. Here, the energy which is necessary to maintain self-oscillations is supplied by a constant source, and the characteristic oscillation frequencies are determined by the system itself, not by the frequency characteristics of the source of energy. The cyclic switchover effect consists of consecutive cycles of growth and dissolution of the dendritic nanochannel of a Yanson point contact during the process of electric current flow through the “needle electrode-electrolyte-anvil electrode” system. When current is fed into this system, a dendrite starts to grow in the area with the highest concentration of the electric field. In the configuration of the “needle-anvil” technique applied to the dendritic Yanson point contact preparation (Fig. 3), the maximum concentration of the electric field is localized between the needle tip and the nearest part of the counterelectrode surface. When the needle is the cathode and the anvil is the anode, any inhomogeneity on the surface of the needle tip can create favourable conditions for the start of dendrite growth. Dendrites may have different linear growth rates. After a certain period of time, a dendrite grows as big as to reach the counterelectrode surface and create a dendritic Yanson point contact.

The cyclic switchover effect is possible thanks to another unique property of Yanson point contacts, which manifests itself in the current mode in a liquid medium. At the moment the dendritic Yanson point contact is created, a new electrochemical electrode system is formed on the surface of its conduction channel. This electrode system was named *gapless electrode system* [13, 17]. The very name suggests that during a half-cycle corresponding to the dissolution of the dendritic conduction channel of the Yanson point contact, there is an electrode system with no electrolyte layer separating the electrodes. The existence of the gapless electrode system is due to the specific potential distribution in the Yanson point contact that causes all the electric field to be concentrated in the area of the conduction channel of this nanoobject [5, 13]. This system differs fundamentally from the existing electrochemical systems. The gapless electrode system in the dendritic Yanson point contact configuration can be presented as a continuous electrode “metal-electrolyte” interface along the generatrix of the conduction channel. The junction of the conduction channel with the anvil connected to the positive pole of the current source is maximally positively polarized. As a result, the dissolution rate under these conditions is maximum too. The opposite end of the channel on the side of the needle has the maximum negative polarization and, respectively, the maximum rate of recovery processes. Between these two poles, there is a polarization inversion boundary characterized by the absence of directed electrochemical processes. If the conduction channel of the Yanson point contact has the shape of a uniform cylinder, then the polarization inversion boundary is located in the middle of the channel. In contrast to the concept of electrode surface equipotentiality, which is used by default in classical electrochemical kinetics, in the gapless electrode system, the concept of potential continuum along the interface is applied, and the presence of a continuous number of electrodes can be considered.

The gapless electrode system makes it possible to combine the ability of the Yanson point contact to concentrate electric field and preserve its properties under ultrahigh current densities with an oppositely directed electrochemical activity at the ends of the point-contact conduction channel. The electric field concentration and the monotonic change of the potential along the point-contact channel create the conditions needed for the reductive processes to occur on the side of the negative pole of the electric energy source and the oxidative ones on the side of the positive pole. It should be noted that in the case of Yanson point contact it is possible to attain a situation when the oppositely directed electrochemical processes can occur at an extremely close distance to each other. As a result, the gapless electrode system forms anode and cathode areas at the ends of the point contact conduction channel and launches the cyclic switchover effect.

The cyclic switchover effect can be thought of as follows. When an electric current flows through the needle-electrolyte-anvil system, we have a conventional electrochemical situation. A dendrite grows on the tip of the needle and produces a Yanson point contact after reaching the anvil. At this moment, a gapless electrode system appears on the point-contact conduction channel and stimulates the process of dissolution of the Yanson point contact in the anode area. After the dissolution of the point-contact conduction channel, the needle-electrolyte-anvil system returns to its initial state, and the cycle of dendrite growth-dissolution repeats. It should be noted that the cyclic changes are automatic with no external influence involved.

The existence of a gapless electrode system and the principle of its operation were confirmed in the model experiments [31, 79]. The functioning of the gapless electrode system was simulated on a long silver wire in a specially designed electrochemical cell. The dimensions of the conductor corresponded to the ratio $(d_{\text{eff}}/l_{\text{el}}) \rightarrow 0$, where d_{eff} was an effective dimension of the cross section and l_{el} was the length of the silver conductor in contact with the electrolyte. In the studies using a non-contact magnetic method, the distribution of electrochemical currents along the main axis of a long conductor placed in a liquid electrically conductive medium was determined. This made it possible to find out that the local minimum of the magnetic field created by the current corresponds to the envelope on the conductor, which separates the coupled electrochemical processes. This envelope, called the polarization inversion boundary, divides the conductor into two subspaces – the cathode and the anode – formed by the gapless electrode system. Long exposure of this sample to an electric field results in a significant transformation of its shape. As a result, the surface of the anodic polarized area dissolves. The dissolution occurs in the form of a cone till the electrode breaks and a tip is formed with a small radius of curvature at the waterline of the conductor in the electrolyte. In this case, the cathodically polarized section of the conductor thickens because of the deposited metal and, in the waterline region, the cross-sectional diameter becomes maximum. In the localization area of the potential inversion boundary, the diameter does not change because of the absence of polarization. The performed model experiments yielded a general picture of the transformations of the conduction channel of Yanson point contact occurring during the cyclic switchover effect.

6.2. New method of quantum detection in dynamic mode

The transformation of dendritic Yanson point contacts during the cyclic switchover effect is registered by measuring the dependence of the resistance R of the dendritic point-contact structure on time t . Since the electrical resistance of a Yanson point contact is inversely proportional to the contact diameter [4], a decrease or an increase in the resistance is caused by the corresponding increase or decrease in the point contact diameter (Fig. 9). The maxima in the $R(t)$ dependence in Fig. 9 correspond to the contacts with small cross sections, while the minima in the curve correspond to the contacts with large diameters. The point contact resistance varies with time, going through the phases of growth, reduction, and stabilization. The phases are repeated many times, accounting for the cyclic changes in the physical and chemical properties of the object.

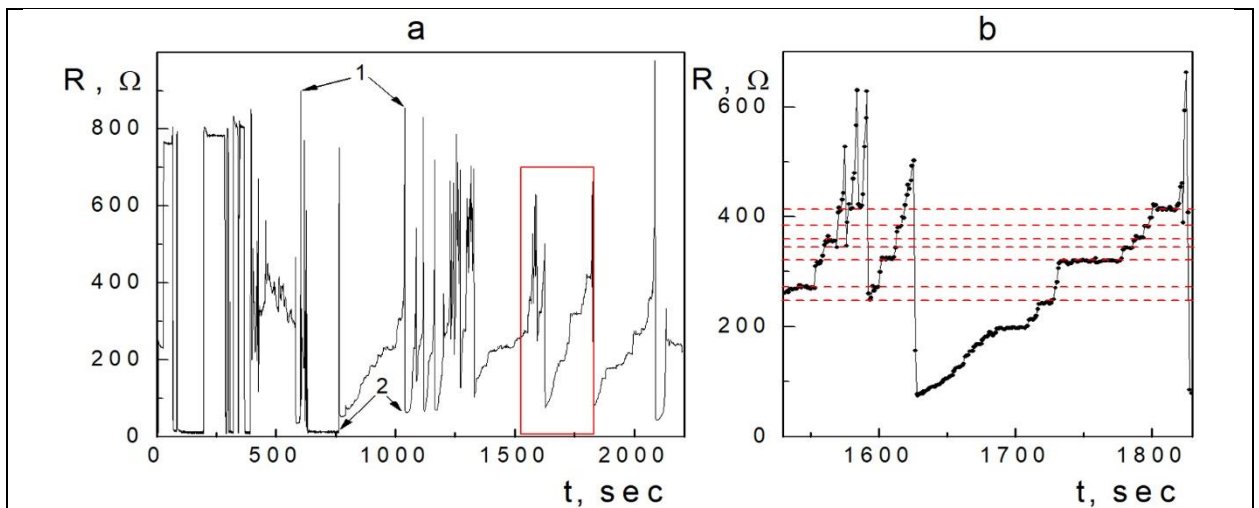
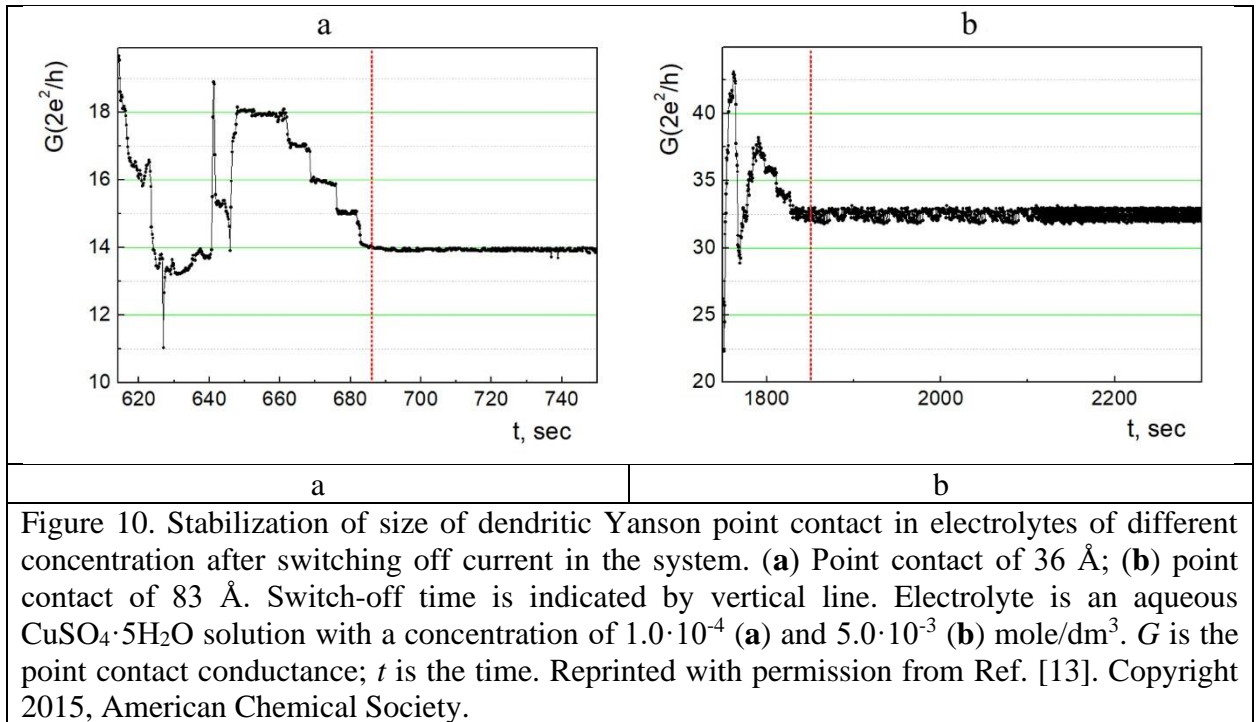


Figure 9. Point-contact resistance R versus time t . (a) General view of the dependence $R(t)$; 1 – examples of peaks in the $R(t)$ dependence corresponding to point contacts with small diameters; 2 – examples of local minima in the $R(t)$ dependence corresponding to point contacts with large diameters; (b) a magnified portion of the dependence within a red rectangle in “a”. Dashed lines show conductance steps and metastable states of the contact. The concentration of the aqueous $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution is $5.0 \cdot 10^{-1}$ mole/ dm^3 . $I = 20 \mu\text{A}$. Reprinted with permission from Ref. [13]. Copyright 2015, American Chemical Society.

The uniqueness of the cyclic switchover effect is related to the fact that all transformation processes in dendritic Yanson point contact are shaped by the quantum shell effect [13]. As a consequence, the crystalline structure of the contact is formed within the transition from one metastable quantum crystal state to another. One of the original peculiarities of the electric conduction of Yanson point contacts is the conductance quantization. Cross-sectional diameters of metallic channels of point contacts have direct correlation with their electrical transport properties. Each metastable state of Yanson point contact is characterized by a certain value of quantized electrical conductance [14, 16, 80]. This means that during the lifetime of a metastable state, the electrical conductance of the nanostructure remains unchanged. Upon a transition from one metastable crystalline state to another, the electrical conductance changes drastically by a certain amount of conduction quanta. After that, a rest period sets in again with a constant level of electrical conductance, which corresponds to the new metastable crystalline state of the dendritic Yanson point contact. These fluctuations of electrical conductance lead to the appearance of steps in the dependence of electrical resistance of the system R on time t (Fig. 9b) [13].

The step-like shape of the curve and the cyclic character of the process make it easy to find the point contact dimension by measuring conductance. This allowed us to propose and implement a new method for synthesis of nanostructures with predetermined sizes with atomic resolution [13]. The speed of the synthesis process during the cyclic switchover effect can easily be adjusted by varying the electrolyte concentration and magnitude of the electric current. The size of the Yanson point contact is controlled by measuring the dependence $R(t)$ and registration of the steps of constant electrical conductance in a metastable state. Each conductance step arises in a metastable quantum state with a certain number of atomic-sized conduction channels measured in the units of conductance quantum G_0 . Since the conductance quantum G_0 is formed by one atom, it is possible to determine the number of atoms in the cross section of the nanostructure having a certain conductance. By switching off the current once the required metastable state is reached, we can obtain dendritic Yanson point contacts with a predetermined atomic size and a perfect crystal lattice. Figure 10 demonstrates the formation of point contacts with a diameter of approximately 14 (curve (a)) and 32 Cu atoms (curve (b)) corresponding to a size of 36 and 83 Å for a Cu atomic size of 2.6 Å, respectively. Such contacts, as shown in Ref. [13], are characterized by a ballistic mode of current flow at room temperature.



As we have already mentioned, a quantum physical system is characterized by a set of energy eigenstates, which corresponds to the local minimum of the total system energy. A specific set of such states is characteristic only of a certain system, being its individual energy *fingerpr*int (profile) at an atomic level. Knowledge of the energy parameters of this profile is a key factor for determining and predicting the properties of a physical object. Such quantum tool as the Yanson point contact, which is able to determine the metastable states of a system, can become the basis for the development of quantum sensor technologies. The mechanism for identification of substances by analysing their energy parameters provides brand new possibilities of differential analysis of various states of physical objects and makes it possible to obtain all data needed for analysis of complex systems without determining their individual components.

An electrical conductance step in the dependence $R(t)$ characterizes a certain quantum state of the dendritic Yanson point contact. A set of all steps shows all metastable quantum states of the system of dendritic point contacts formed under certain conditions and can be interpreted as an integrated profile of the entire system [17]. The cyclic switchover effect serves as a tool that allows us to register the entire set of metastable quantum states of the system in dynamic mode. At the same time, it should be emphasized that the cyclic switchover effect is an automatic repetition of the cycles of dendrite growth and dissolution leading to creation and destruction of dendritic Yanson point contacts. That is, all transformations occur in a quantum system without any external interference, which guarantees that the information is obtained in its original, undistorted form. The quantum nature of the transformations of a dendritic point-contact nanostructured system and the multiple repetition of the cycles make it possible to observe the entire set of metastable quantum states that manifest themselves in a given system with some probability. The probability of appearance of certain metastable quantum states in the process of dynamic transformation of the system can be determined using a conductance histogram [17, 81]. A conductance histogram is based on the temporal dependencies of the conductance $G(t)$ of dendritic Yanson point contacts obtained by inverse transformation of the experimental curves $R(t)$.

As shown in Ref. [13], the conductance histogram of copper dendritic Yanson point contacts obtained during the cyclic switchover effect agrees well with the results of the study of conductance in mechanically controllable break junctions [82]. In the latter case, the process of creating and destroying contacts was carried out by periodic external action on the substrate with an electrode attached to it. A general view of the main element of such a design is shown in Figure

4. A periodic change in the bending of the substrate led to an alternate rupture and connection of the electrode at the notch site. The process was accompanied by a change in the diameter and, accordingly, electrical conductance of point contacts, which made it possible to observe the quantum nature of the transformations. With this technology, the lifetimes of contacts in metastable states are quite short and do not exceed one second. As a result, the stabilization of electrical conductance in a metastable state is observed, as a rule, in the form of inflections in the temporal dependence of electrical conductance [81]. This behaviour is due to manual control of the process of changing the size of the point contact. In contrast, the process of synthesis of dendritic Yanson point contacts during the cyclic switchover effect occurs without external intervention, and the nature of the processes of transformation of the crystalline structure can be seen in its pure form [13]. In states of increased stability, dendritic Yanson point contacts live for several seconds, which makes it possible to observe well-defined horizontal sections in the dependencies $R(t)$ (Fig. 9, 10). The conductance behaviour of dendritic Yanson point contacts synthesized in the process of the cyclic switchover effect also agrees well with the results obtained for nanowires formed using the traditional technique of electrochemical dissolution or deposition of electrodes [83, 84].

Thus, by launching the cyclic switchover effect and measuring the electrical conductance of dendritic Yanson point contacts in dynamic mode, one can get a complete set of data needed for obtaining an energy portrait of the object under study and identifying it. This idea was first proposed and successfully implemented in Ref. [17]. Moreover, this study showed that a change in environmental conditions, for example, addition of a gaseous agent, leads to the appearance of a new set of quantum states of the dendritic point-contact system, which manifest themselves under new specific conditions. Addition of a gas to the reaction volume changes the quantum profile of the entire system in a reproducible manner. Thus, conductance quantization of dendritic Yanson point contacts can serve as a new quantum mechanism for selective detection in gases and liquids.

6.3. Selective detection in gaseous and liquid media

Experiments on the implementation of the idea of scanning the energy states of a quantum point-contact system in dynamic mode using the cyclic switchover effect were carried out on dendritic Yanson point contacts placed in a drop of pure (distilled) water [17]. This choice was determined by the desire to ensure the purity of the experiment, to avoid the possible presence of background substances and influence of side effects on the results. As a result of the hydration process, some of the surface copper ions in contact with water migrate from their lattice sites into the solution. This process weakens with time since the double electric layer formed at the phase boundary increasingly impedes the outflow of ions from the crystal. As a result, the studied environment that comes into contact with the surface of the point-contact conduction channel is not the de-ionized water, but an electrolyte solution containing copper ions. Despite the extremely low conductivity of such water, electrochemical processes are observed to occur at the cathode and anode sections of the gapless electrode system formed in the point-contact conduction channel [44].

The studies of Ref. [17] carried out in different gaseous media revealed that the conductance histograms of dendritic Yanson point contacts have a certain form for each specific case. A comparison of the conductance histograms obtained for different gaseous media showed that they were completely different from each other. Moreover, the quantum states and the conductance histograms of dendritic Yanson contacts synthesized in a medium consisting of one gaseous substance of different concentrations also differ significantly. To increase the complexity of the task, experiments were carried out with noble gases and gases that are difficult to detect using conventional sensor devices. As a result, it was found that point-contact sensors can easily solve the detection problems. In fact, for a quantum point-contact sensing element, it does not matter which object it has to work with. The quantum detection mechanism based on conductance

quantization ensures the versatility of operation of point-contact sensing elements and their absolute selectivity.

Figure 11 shows some examples of the conductance histograms obtained in Ref. [17] for dendritic Yanson point contacts which underwent transformations under various conditions during the cyclic switchover effect. They explicitly demonstrate a significant dependence of the quantum structural transformations of the conduction channel and associated changes in the conductance on the environmental factor. Gas molecules diffusing into the liquid medium that surrounds the dendritic point-contact system penetrate into the transformation region of the nanostructured conduction channel of the dendritic Yanson point contact in the process of the cyclic switchover effect and affect the electrochemical synthesis of the dendrite point-contact structure. This leads to the appearance of new metastable states in the growing dendritic point-contact structure. Histograms obtained for dendritic point contacts synthesized in different gaseous media are fundamentally different. A change of the external gas agent leads to a change in the step structure of the dependencies $R(t)$ associated with certain metastable quantum states in the conductance of dendritic Yanson point contact. Thus, the conductance histograms show a pronounced effect of external agents on the formation of electrical transport properties of the conduction channel of dendritic Yanson point contacts.

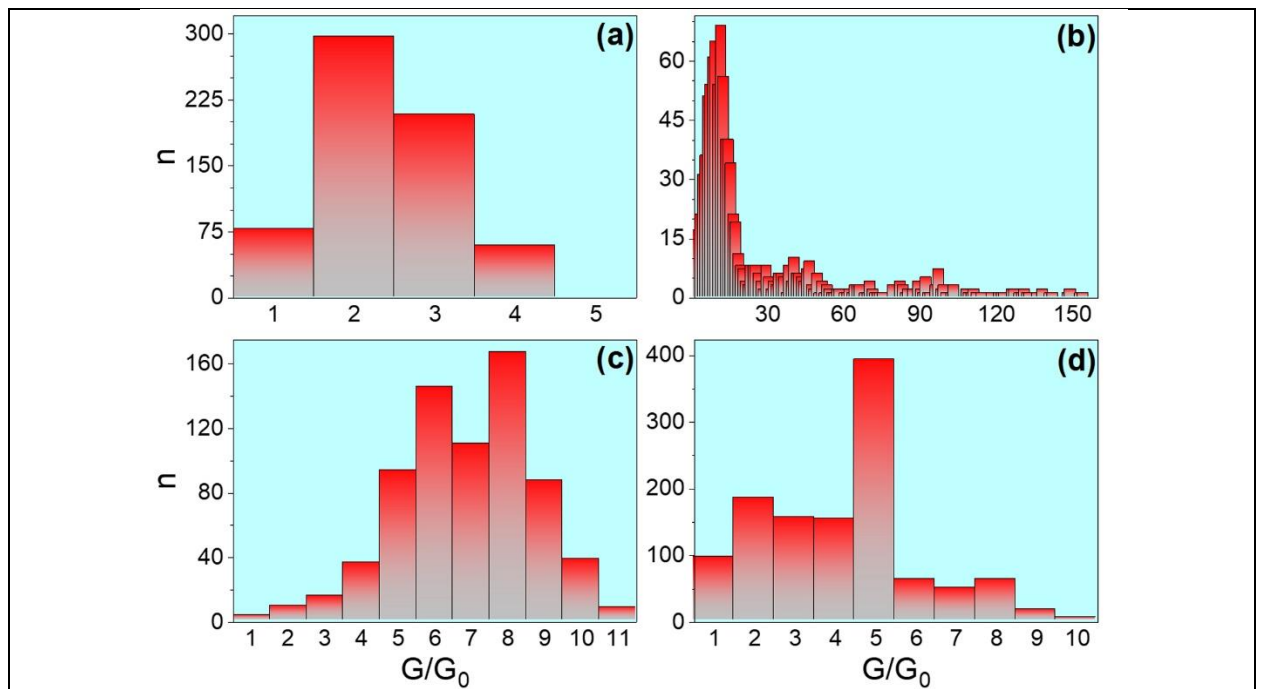


Figure 11. Conductance histograms of copper dendritic Yanson point contacts grown in a nanolayer of a drop of pure water near the copper surface under the action of a gas. (a) Dendritic Yanson point contacts in a 100% Ar medium; (b) dendritic Yanson point contacts in an Ar (80%) + CO₂ (20%) medium; (c) dendritic Yanson point contacts in an Ar (99.99%) + CO₂ (0.01%) medium; (d) dendritic Yanson point contacts in an Ar (99.99%) + CH₄ (0.01%) medium. G – conductance, G_0 – conductance quantum, n – number of counts. Reprinted with permission from Ref. [17].

When considering the conductance histograms, attention is drawn to the fact that the process of conductance quantization in dendritic Yanson point contacts in inert media is accompanied by the exclusive formation of atomic-sized structures containing only a few atoms. Here, the synthesis of ultra-small contact formations takes place in the process of the cyclic switchover effect. In an argon medium, this effect leads to the formation of dendritic Yanson point contacts with a conduction channel cross section made up by 1 to 4 atoms with a pronounced maximum in the region of two-atomic structures. At the same time, the sizes of contacts formed

in other gaseous media, including the cases of weakly interacting gases or gases containing small amounts of the active substance, lie in much larger ranges. This makes it possible to use rare gases as a background medium for the detection of a wide range of objects. In the general case, as the gas concentration decreases, the length of the conductance histogram along the x-axis and, accordingly, the size range of the formed conduction channels of Yanson point contacts also decreases.

The positions of conductance maxima in the histograms, which correspond to the most probable metastable states, are related to the specific cross sections of dendritic point contacts produced in the self-oscillatory process. A histogram maximum corresponds to the most probable point contact formed under the experimental conditions. As can be seen from Fig. 11 and from other results of the study of the quantum mechanism of detection based on conductance quantization (see, for example, Refs. [8, 19, 41], a conductance histogram maximum provides ample opportunities for selective detection of various gaseous agents. Its position and intensity contain the information needed for the detection. At the same time, the quantum mechanism for detection in gaseous and liquid media offers a variety of approaches to solving the sensor-related problems. The reliability of the analysis based on these capabilities almost doubles if the parametric approach, which consists in using the position and intensity of the maxima, is supplemented with the complete energy information about the metastable states of the object. Such information is provided by the energy profile of the detected substance, which can be called the *fingerprint* of the medium under study. It is exactly the conductance histogram that is such a *fingerprint*. It uniquely characterizes each individual substance. In the case of different gaseous media, and even of the same gaseous medium but with different concentrations of the active substance, the conductance histogram changes so significantly that it becomes possible to easily identify the sample to be detected. For this approach to be used in practice in automatic mode, it is necessary to create a data library for as many gaseous media as possible. Then it will be possible to intellectualize point-contact quantum sensors with the help of machine learning systems, such as artificial neural networks, and raise them into the category of autonomous systems that can operate without human intervention.

The high sensitivity and selectivity of dendritic Yanson point contacts in dynamic detection mode was demonstrated in the studies in which gaseous methane was used as an example (Fig. 11d). Methane is a hard-to-detect substance, and the clearly observable response to the action of its low concentrations is a reliable confirmation of the high effectiveness of the proposed approach based on the conductance quantization. Conventional electrically conductive sensors use the operation principle of changing electrical conductance of their sensing element when the analysed agent is adsorbed on it. In this case, to obtain a reliable and well-registered response signal, it is necessary that the adsorption energy is sufficient to form a stable adsorbate layer [85] which is not affected by external factors that are not related to the analyte concentration. Such factors include, for example, the Joule heat from external or internal sources. If the analyte molecules have donor or acceptor properties, the useful signal of a conventional electrically conductive sensor is formed by a change in the concentration of charge carriers in the bulk of the conductor. On the other hand, if the adsorbate is electrochemically inactive, the electrical resistance differential necessary for the measurement is obtained by shifting the electron density in the near-surface layer of the conductor. Gases that are not electrochemically active, usually are more difficult to study using resistometric analysis because of the low adsorption energy (about 50 kJ/mol) for the main conductive materials. Methane is one of such gases. That is why it is traditionally analysed using special optical methods, including IR and Raman spectroscopy, for which rather sophisticated equipment is needed. But the problem can easily be solved using a quantum point-contact sensor, since it can provide a reliable response to the appearance of trace amounts of methane thanks to the nature of the Yanson point contact. As was shown in the studies of Yanson PCS, electron-phonon relaxation processes leading to nonlinear effects in the electrical conduction of Yanson point contacts occur with a frequency of at least 10^{10} - 10^{11} s⁻¹ [86, 87]. This yields an almost instantaneous change in the electrical conductance of the Yanson point contact as a response to any act of adsorption on its

conduction channel. In addition, as we have already noted, Yanson point contacts are not affected by thermal effects which could prevent the process of adsorption of gas molecules on the surface of the conduction channel. Gases with minimal adsorption energies can be freely adsorbed onto the conduction channel of the Yanson point contact. The mere fact of their appearance on the surface of the conduction channel is sufficient for this event to be displayed in the temporal dependence of the electrical conductance of the point-contact sensing element. In addition to the fundamental properties of the Yanson point contact, geometric factors also play an important role in the operation of the point contact sensor. The comparability of the size of gas molecules and that of the conduction channel of the Yanson point contact, on the surface of which the molecules are adsorbed, significantly enhances the effects caused by the electron density shift. Moreover, in the process of the cyclic switchover effect, the act of creation of a freshly formed surface of the conduction channel is repeatedly reproduced, which significantly increases the reliability of the data obtained. For the same reasons, a quantum sensor makes it possible to reliably record and quantify the presence of any gaseous agent in the atmosphere, regardless of their nature and concentration.

The behaviour of the conductance histograms obtained for dendritic Yanson point contacts undergoing transformation in electrolytes is in many ways similar to that in standard experiments with a gaseous medium, when the cyclic switchover effect takes place in a drop of pure (distilled) water. But it also has some peculiarities. In the case of experiments with electrolytes, the cyclic switchover effect is launched almost instantaneously, while in distilled water there may be a delay in the start of the cyclic process. It may be caused by the state of the surface of the metal involved in the creation of the point contact. The state of the surface, in turn, is largely determined by the composition of the liquid medium in which the cyclic switchover effect occurs. One of the main factors affecting the nature of the metal surface is the concentration of protons in the solution (hydrogen index, pH). Along with acidity, the thermodynamic stability of compounds is determined by the potential of the metal surface. For all basic metals, Pourbaix diagrams are obtained, which reflect the nature of stable metal compounds as a function of acidity and potential [88]. From the Pourbaix diagram for copper it follows that in order to preserve the active surface of the metal, it is necessary to maintain the pH of the medium no higher than 4. At the same time, it is necessary to control the potential of the metal, which must be at least 0.37 V according to the normal hydrogen reference electrode. Even if the necessary acidity is maintained, the stationary potential of the copper surface may drop, which indicates the formation of surface oxides in the process of self-oscillations. To activate the surface, it is necessary to expose the metal to solution until the formed oxide is completely dissolved, which can be evidenced by the initial value of the potential.

Synthesis of dendritic Yanson point contacts during the cyclic switchover effect in an electrolyte is characterized by the same physical and chemical transformations as those taking place in the case of a gaseous medium diffusing into distilled water. Structural changes are observed in the dendritic conduction channel of the Yanson point contact with well-pronounced quantum metastable states, the lifetime of which under experimental conditions can reach several seconds. This can clearly be seen when registering the steps in the dependency $R(t)$ of Yanson point contacts, which characterize quantum states with a higher stability and a certain level of quantized electrical conductance [13]. When dilute electrolyte solutions are used, the cyclic growth-dissolution process of dendritic Yanson point contacts shifts to the region of nanostructures with a minimum cross section, as evidenced by the conductance histograms of the synthesized point contacts. In this case, the width of the conductance histogram decreases, which indicates that the synthesis of dendritic Yanson point contacts proceeds in a narrower resistance range. There is a similarity in the behaviour of the conductance histograms of dendritic point contacts synthesized in gaseous media and electrolytes with a low concentration of the active substance. An increase in the concentration of the electrolyte solution shifts the cyclic process to the area of formation of large-diameter point contacts. At the same time, the width of the conductance histogram increases

[13]. Thus, by selecting the electrolyte concentration, it is possible to influence the electrically conductive parameters of the synthesized dendritic point-contact structures.

The probability distribution of dendrite nanostructures within a specific range of resistance and cross sections during the point contact synthesis depends essentially on the electrolyte concentration. Figure 12 shows a strong nonlinear dependence of the conductance G of dendritic Yanson point contacts on electrolyte concentration found during a series of special experiments performed in Ref. [13]. A variation in the electrolyte composition leads to a change of the synthesis process. Such a nonlinear dependence of the electrical conductance of dendritic point-contact sensing elements on the concentration of the agent to be detected correlates with the results obtained earlier for Au/SWNT heterocontacts [6]. That study showed that heterocontact sensors exhibit a strongly nonlinear dependence on NH_3 concentration. A dilution of gas by two orders of magnitude resulted in only halving the signal amplitude. This is evidence that the heterocontact sensor properties are fundamentally different from those of conventional chemical gas sensors.

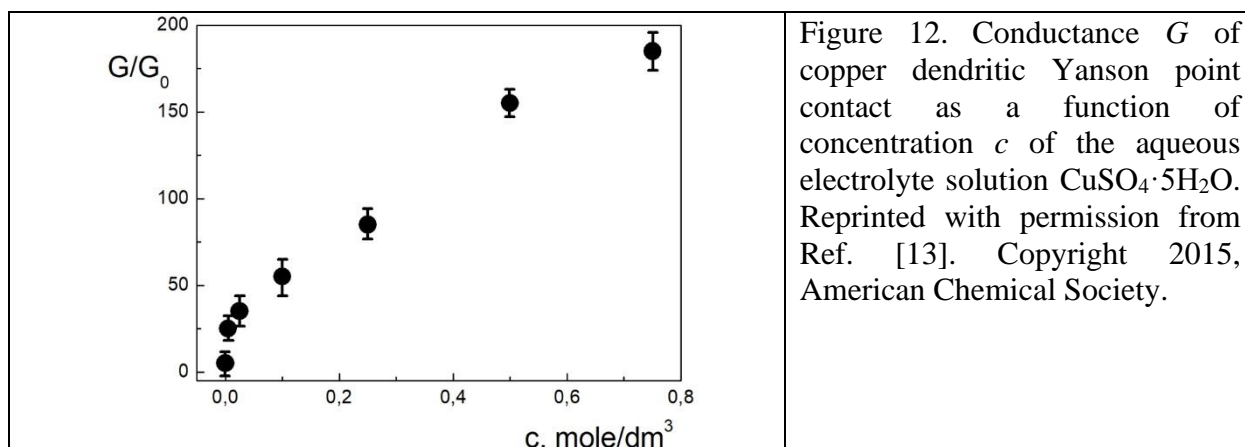


Figure 12. Conductance G of copper dendritic Yanson point contact as a function of concentration c of the aqueous electrolyte solution $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Reprinted with permission from Ref. [13]. Copyright 2015, American Chemical Society.

The correlation in the behaviour of quantum point-contact sensing elements of different types is another evidence of the non-traditional nature of the quantum detection mechanisms on which the operation of point-contact sensing elements is based. The non-linear behaviour of the response signal of Yanson point contacts in the region of low concentrations of substances to be detected ensures an ultrahigh sensitivity of quantum sensors based on them, since a slight change in the ultralow concentration of the agent under study leads to a well-pronounced change in the response signal of the quantum sensor, which, of course, does not go unnoticed and makes it possible to register even slightest changes in the state of the detected medium. This condition opens up wide prospects for designing high-performance nanostructured quantum point-contact sensing elements for detection in liquid media.

7. Application of point-contact sensors in medicine

7.1. Detection of carcinogenic strains of *Helicobacter pylori*

The implementation of the spectral mechanism of detection in complex gas mixtures using quantum point-contact sensors provided some top-priority results that were successfully used to develop new methods of non-invasive medical diagnostics [7]. At present, several concepts based on the spectral detection mechanism have already been proposed. The first to be tested was the concept based on direct use of the characteristic parameters of the response curve of quantum point-contact sensors [38, 89]. The characteristic parameters of the response curve reflect certain physical and chemical processes of the interaction of a quantum point-contact sensing element with the components of the analysed medium. By virtue of this, they provide unique information about the energy component of the interactions in the quantum system "point-contact sensor - human breath" and make it possible to analyse this multicomponent medium without determining its individual components.

Sensor studies based on the use of innovative methods that implement the spectral mechanism of quantum detection in complex gas mixtures (see Section 5) were carried out using point-contact mesoscopic multistuctures [7, 32]. Such a multistucture is an original version of the sensor matrix. This matrix is based on quantum Yanson point contacts, in which the electrode material is a TCNQ compound (Fig.6). The difference between a point-contact sensor matrix and the sensor arrays used in "electronic nose" systems is not only their operation principles, but also the number of sensing elements. The density of Yanson point contacts in the point-contact sensor multistucture is over 5×10^5 contacts per mm^2 . At the same time, sensing elements of the point-contact sensor matrix are characterized by absolute selectivity thanks to their ability to record the energy component of the spectral interactions of conduction electrons with the molecules adsorbed on the surface of the conduction channel of the Yanson point contact (see Fig. 8). The large number of sensing elements in the point-contact multistucture provides a high level of the sensor output signal even for an interaction with single atoms and gas molecules. At the same time, modern "electronic nose" systems, which are also a sensor matrix, contain only a few dozen traditional low-selectivity sensors. In "electronic nose" devices, extracting a useful signal from monotonic response signals requires involvement of a complex mathematical apparatus and large computer resources. The operation of the point-contact sensor matrix is based on the use of a quantum spectral mechanism for detection in complex gas mixtures, which allows one to directly receive the complete energy information about the object under study in real time. The nature of the response signal of the point-contact sensing element allows a comprehensive analysis of the detected medium without resorting to complex mathematical procedures.

The response signal of a quantum point-contact sensor based on a TCNQ compound to the action of a complex gas mixture is the dependence of electrical conductance of the sensor on time. It consists of two parts, one of which is recorded during the exposure of the sensor to the gaseous medium and the other during its relaxation after the exposure (Fig. 13). A detailed description of the methodology for measuring the response signal of point-contact sensors based on TCNQ compounds is given in Refs. [20, 33, 89] and on the website at http://qs.net.ua/results_eng.html. The dependence of electrical conductance of a quantum sensor on time is a complex spectrum-like curve that includes a series of maxima and minima, as well as areas of nonmonotonic and nonlinear signal changes. This behaviour correlates with the structure of the point-contact electron-phonon interaction spectra measured in the Yanson PCS [2, 18, 21, 48]. The point-contact spectrum makes it possible to determine the energy of the phonons involved in the interaction with the electrons in a non-equilibrium state. This allows one to reveal groups of phonons with energies characterizing the various types of atomic vibrations in a solid and find the concentration of phonons in a certain region of the spectrum. The quantum properties of point-contact sensors allow registration of spectral profiles of human breath in the form of response curves, which contain comprehensive information about this complex gaseous environment. Point-contact sensors are thus an effective tool for visualizing the features of the energy interactions in the "point-contact sensor - human breath" system.

A set of characteristic parameters was proposed in Refs. [38, 89] which made it possible to estimate the main energy processes in the system "point-contact sensor matrix - human breath". For the sake of general understanding of the possibilities provided by this approach, let us consider examples of the parameters characterizing the slope of the initial section of the maximum exposure period $d_1 = \text{tg}\alpha$ and the slope of the initial part of the most intense peak in the relaxation period $d_{21} = \text{tg}\beta$ (Fig. 13). The d_1 value characterizes the dynamics of the processes at the initial stage of the interaction between the point-contact sensor and breath components and depends on the concentration of the components adsorbed on the surface of the conduction channel of the Yanson point contact and their adsorption energy. The d_{21} value characterizes the rate of desorption at the initial stage of the sensor transition to the stationary state and reflects the efficiency of the interaction of a non-equilibrium electron flow in the Yanson point contact with the gas molecules on its surface. The gas molecules adsorbed on the surface of the conduction channel of the Yanson point contact create regions with defects in the crystalline structure of the material. In these places,

the mean free path of charge carriers decreases, as a result of which the probability of electron scattering at the sites of the adsorbed atoms and molecules increases. During the interaction, the excess energy of the non-equilibrium electrons is transferred to the adsorbed molecules. As a result of the desorption of molecules, the energy they acquired is removed from the contact. In this case, variations in the time and energy of the interaction of electrons with atoms or molecules of various adsorbed substances lead to a change in the rate of rise of the response signal in a given section of the relaxation curve.

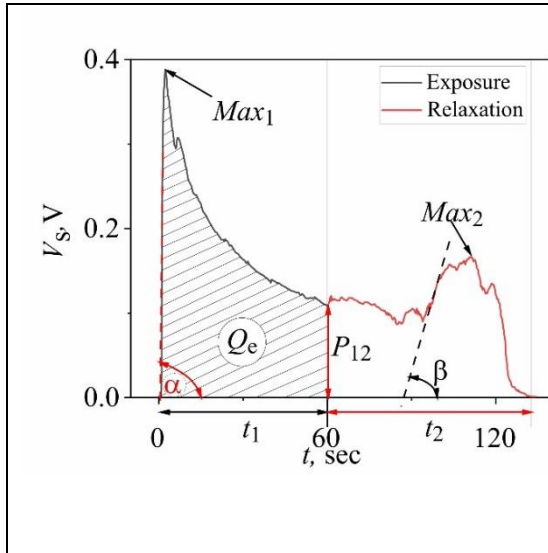


Figure 13. Examples of characteristic parameters of the response curve of a point contact sensor based on a TCNQ compound: t_1 – exposure time; t_2 – relaxation time; Max_1 – maximum of the exposure period; Max_2 – maximum of the relaxation period; p_{12} – ordinate of the final segment of the exposure phase; $d_1 = tg\alpha$ – slope of the initial part of the exposure peak; $d_{21} = tg\beta$ – slope of the initial part of the most intense peak in the relaxation period; Q_e – area under the exposure curve. V_s – voltage drop in the sensor; t – time. Reprinted with permission from Ref. [21].

A very important and highly informative characteristic parameter of the point-contact sensor response curve is the relaxation time t_2 . It is an integrated indicator of the adsorption energy that the breath components have. This characteristic parameter determines the length of the point-contact sensor profile of breath during the relaxation period. In the Yanson PCS, the energy extension of the point-contact spectrum makes it possible to determine a number of important parameters, such as the Debye temperature [46]. Thanks to its energy nature, the sensor relaxation time is one of the most important components of the breath profile which makes it possible to distinguish the metabolism of one patient from that of another [7] similarly to how the energy parameters of the point-contact spectrum in the Yanson PCS make it possible to uniquely characterize the material under study [2, 3]. It should be noted though that in conventional electrically conductive sensors, the “time” parameter does not play such an important role. For example, the response time of this kind of sensors only reflects the period of waiting for the sensor to respond to an external impact, and the relaxation time is the period during which the gas molecules desorb from the surface of the sensing element, leaving no characteristic energy traces in the response signal.

Quantum point-contact sensors based on TCNQ compounds armed with a spectral mechanism for detection in complex gas mixtures and a set of characteristic parameters of the response signal were used to detect the states of human body associated with its infection with the bacterium *Helicobacter pylori* [89, 90]. World Health Organization recognizes the *Helicobacter pylori* infection as a primary causing factor in the development of peptic ulcer disease, gastric cancer, and gastric mucosa-associated lymphoid tissue (MALT) lymphoma [91-95]. It is the toxigenic strains of *Helicobacter pylori* which are responsible for the appearance of the above diseases; while non-toxigenic strains cause a disease in a minimal percentage of cases [96]. This means that real-time detection of the virulent strains of *Helicobacter pylori* can become a basis for designing a screening technology that could significantly decrease the prevalence of *Helicobacter pylori* and associated diseases all over the world. This prospect has predetermined the use of quantum point-contact sensors for solving the problem.

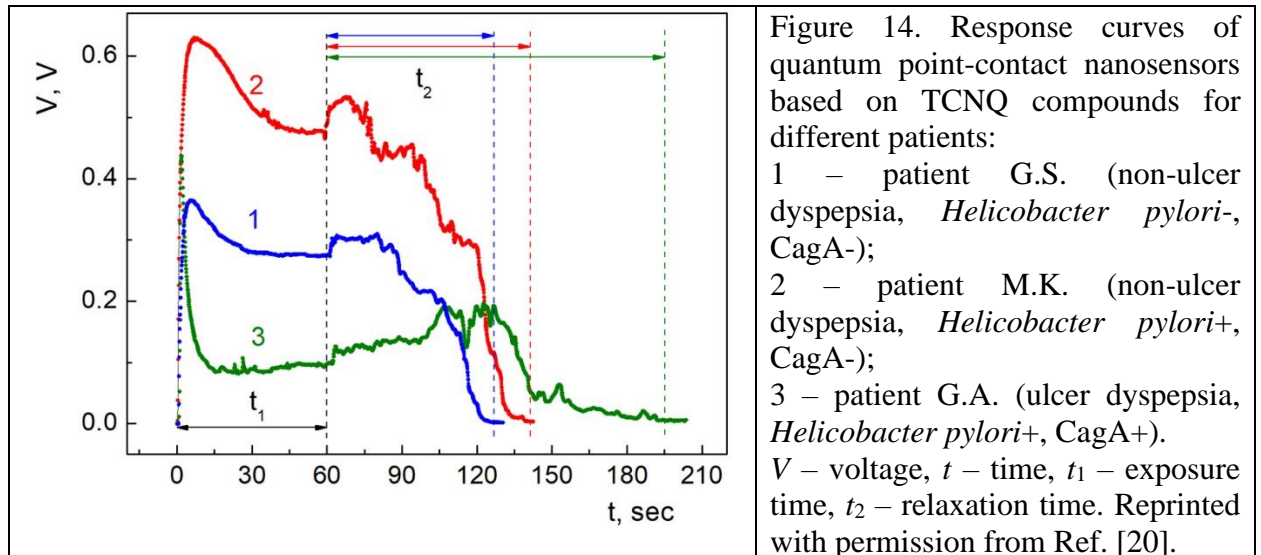
Taking into account the fundamental properties of point-contact sensing elements, in Ref. [89] attention was drawn to the relationship between the response signal of a quantum point-contact sensor and the nature of the pathology of the gastrointestinal tract. As a result, a clear dependence of the duration of the response signal of point-contact sensors on the degree and nature of the infection with *Helicobacter pylori* was found. Analysis of the data obtained allowed us to conclude that it was the presence of *Helicobacter pylori* that determined the behaviour of the point-contact sensor relaxation time, which characterizes the integrated value of the adsorption energy of the components of breath of patients with various forms of gastroduodenal pathology. Breath of patients with diseases associated with the *Helicobacter pylori* infection contains metabolic products of this microorganism which slowly desorb from the sensor surface. Since the products of the *Helicobacter pylori* metabolism have higher adsorption energies and form more stable bonds with the gas-sensitive sensor material, a longer relaxation time of the point-contact sensor was observed when its sensing element was exposed to the breath of such patients compared to the results obtained for healthy people. In this case, the sensor reacts not only to individual substances, but also to the entire spectrum of metabolic products of this bacterium. This ability of quantum point-contact sensors opens up the possibility of selective detection of the various conditions of the human body associated with this infection, as well as selective detection of the various strains of *Helicobacter pylori*.

Modern methods of medical diagnostics allow detection of the presence of *Helicobacter pylori* by using a marker approach to the breath analysis. All existing breath tests for diagnostics of *Helicobacter pylori* use the ability of this bacterium to disintegrate carbamide (urea) to ammonia and carbon dioxide by urease enzyme (carbamide urease $\rightarrow \text{NH}_3 + \text{CO}_2\uparrow$) which are then detected in breath by means of various techniques [92]. Despite a number of advantages, such as, for example, the non-invasiveness of the analysis, the diagnostic methods based on the analysis of breath also have a number of disadvantages. In particular, the complex composition of breath and its dynamic behaviour can cause false-positive or false-negative results in medical diagnosis [77]. Also, it is not possible to distinguish between different strains of *Helicobacter pylori* using the existing breath tests.

Since different forms of the gastroduodenal pathology are characterized by infection with different strains of *Helicobacter pylori* and their metabolic products differ not only quantitatively, but also qualitatively [96, 97], the breath of patients with such conditions will differ significantly. It is known that the development of duodenal ulcers is primarily related to the colonization of the mucosa by toxigenic strains of *Helicobacter pylori*, while non-destructive chronic inflammatory processes are associated with less virulent but more antibiotic-resistant strains. Patients with peptic ulcer disease are mostly infected with VacA (vacuolating cytotoxin A) and CagA (cytotoxin-associated gene A) strains of *Helicobacter pylori*. People infected with such strains have a greater probability of developing a peptic ulcer disease than the carriers of *Helicobacter pylori* without the CagA gene [98, 99]. The strains differ in their biochemical properties; therefore, their metabolic products, including those of a non-urea nature, also differ. The spectral nature of the response of quantum point-contact sensors makes breath tests of patients infected with this bacterium a valuable source of information for quantitative determination of the degree of microbial population of the gastric mucosa by finding the concentration of metabolic products of the bacterium of urease and non-urease origin. But what is even more important is the possibility of qualitative recognition of pathogenic and conditionally pathogenic strains of *Helicobacter pylori*.

This was successfully demonstrated by the first evidence for detection of virulent strains of *Helicobacter pylori* in the real time using quantum point-contact sensors and the spectral mechanism of selective detection in the complex breath medium [20]. It was found that such a characteristic parameter of the metabolic profile of patients with gastroduodenal pathology as the relaxation time t_2 of point-contact sensors provides the diagnostic capabilities of detecting the *Helicobacter pylori*-associated destructive processes of gastric and duodenal mucosa (Fig. 14). In the case of CagA seropositive patients, the parameter t_2 is longer than that for those patients with

Helicobacter pylori-associated pathology for whom there was no definition of bacterium toxigenicity in the study. The recovery time of the sensors to the baseline value after the end of their exposure to breath becomes even longer in the case of infection with cytotoxic CagA strains. Comparison with the obtained results indicates that the CagA strains of *Helicobacter pylori* preferentially contribute to the breath sensor characteristics of the patients with *Helicobacter pylori*-associated gastroduodenal pathology and give rise to some of the features in the sensor response curves, in particular, influence the duration of sensor recovery time.



The studies carried out in Ref. [20] demonstrated for the first time the innovative capabilities of the quantum spectral detection mechanism and concept of using spectral characteristic parameters of the sensor profile for breath analysis. The obtained results showed that relaxation time of quantum point-contact nanosensors can be a diagnostic criterion for non-invasive determination of *Helicobacter pylori*-associated destructive lesions of gastroduodenal area by using the point-contact spectroscopic concept of breath analysis. This allowed the characteristic parameters of the quantum point-contact sensor profile of a complex gas mixture to serve as a prerequisite for the development of new methods for analysing complex gas mixtures. One of the already developed and tested methods is presented in the next section.

7.2. Diagnosis of hormonal state of the human body

7.2.1. Concept of spectral analysis

It is well-known that any spectrum contains energy information about the components of a system and their interactions. Based on this, in Ref. [18], a new concept for analysis of human breath was proposed and implemented, which uses the quantum spectral mechanism for detection in a complex gas mixture. The idea of the concept is that the spectral profile of a complex gas mixture recorded with point-contact sensors, which reflects the whole variety of energy interactions in the system "quantum Yanson point contact - human breath", can be used to directly determine any substance that is contained in this complex biological environment. The validity of this approach is based on the common nature of point-contact sensing elements used in quantum point-contact sensors and point contacts in the framework of the Yanson PCS. The operation principle of the Yanson PCS is based on recording the interaction of electrons with other quasiparticle excitations using point contacts and their ability to obtain information about these interactions in explicit form. In Yanson point contacts with current flowing through them, unique conditions for the manifestation of the quantum properties of these objects arise. These properties determine the unique possibilities offered by both Yanson PCS and quantum point-contact sensors. In the process of research carried out within the framework of the Yanson PCS, a technology was

developed for extracting useful information about various types of quasiparticles from point-contact spectra [2, 3, 100]. Using the techniques of the Yanson PCS and involving a new mathematical apparatus, it became possible to successfully solve the problem of developing an innovative method for direct extraction of useful information from the point-contact spectral profile of human breath [18].

The molecules of a gas mixture adsorbed on the surface of the conduction channel of a Yanson point contact leave their imprints in certain sections of the dependence of electrical conductance of the quantum point-contact sensor on time, by analogy with phonons, which leave information about themselves in the point-contact electron-phonon interaction spectra [2, 8]. Positions of these imprints are determined by the energy of interaction of the gas molecules with conduction electrons in the point contact. Since each type of molecule is characterized by its own adsorption energy, it is this energy that determines the position of the section of the point-contact profile of breath that is associated with this molecule. This allowed the authors of Ref. [18] to propose a method for detecting individual components of a complex gaseous medium by determining the section of the curve of the spectral sensor profile that corresponds to the energy of interaction of conduction electrons with these components.

It is known from the general principles of spectrum analysis in the Yanson PCS that it is easy to obtain information about the contribution of any process or quasiparticles involved in the interactions affecting the nature of changes in spectral dependencies provided you know the interaction energies [2, 3]. For example, if the energy of phonons is known from the results of similar studies carried out by other methods, then the section of the point-contact spectrum corresponding to the processes in which they participate can be easily determined using the relation $eV = \hbar\omega$, where ω is the frequency of phonons. This makes it possible, for example, to obtain information on various types of atomic vibrations in a solid. If the phonon energy is not known, then the inverse problem of its determination using a point-contact spectrum can be solved by comparing the data obtained from different sources. Following this approach, the section of the spectral profile of human breath, which corresponds to the contribution of the interaction of conduction electrons in the point contact with the gas molecules adsorbed on the surface of the conduction channel can be determined. To do that, it is necessary to measure the spectral profiles of breath using point-contact sensors and simultaneously determine the concentration of the analysed metabolic product in the body of a certain number of patients. After that, one should compare the obtained results and, using the tools of statistical physics, analyse the level of correlation of the sensor output parameter (voltage) with the target detection parameter (marker concentration in the breath) during the analytical act, that is, during the measurement of the spectral point-contact profile of breath. Implementation of this approach in Ref. [18] resulted in a new method for finding the region of the spectral profile with the maximum correlation between the response signal of the quantum point-contact sensor and the concentration of the analysed substance in the human body.

Implementation of this new method of selective detection in a complex gas mixture based on the spectral detection mechanism and its testing were carried out by studying the hormonal state of the human body in regard to several important hormones that are part of the main hormonal processes. These hormones include serotonin, cortisol, and melatonin.

Serotonin (5-hydroxytryptamine, chemical formula $C_{10}H_{12}N_2O$) performs a wide range of biological functions [101, 102]. It is one of the main neuromediators of the central nervous system [103] and plays an important role in the formation of human psycho-emotional states [104, 105]. Its concentration increases in the state of euphoria and decreases during depression, that is why it is also known as the “hormone of happiness”. Serotonin participates in the physiological regulation of various functions of digestive organs, including those of gastric secretion and motility [106, 107]. As much as 60% to 90% of serotonin is produced in the digestive tract [108], which is where this amine becomes part of the exhaled gas.

Cortisol (11 β ,17 α ,21-trihydroxypregn-4-ene-3,20-dione, chemical formula $C_{21}H_{30}O_5$) is a glucocorticoid hormone produced by adrenal cortex [109]. Its functions are quite diverse and

include carbohydrate, lipid, and protein metabolism, conservation of energy, synthesis of cellular enzymes, etc. [110]. Cortisol participates in the defence reactions of the human body to external threats and stressful situations [111], hence its popular name of “stress hormone”. It can stir up the activity of muscles by decreasing their consumption of glucose and stimulating its arrival from other organs, it can also prevent secretion of the substances which cause inflammation [112]. At the same time, a high level of cortisol inhibits the immune system and worsens the ability of the organism to resist infections and other harmful factors [113].

Melatonin (N-acetyl-5-methoxy tryptamine, chemical formula $C_{13}H_{16}N_2O_2$) is another key hormone in the human body [114]. It is secreted by pineal gland and affects various physiological functions of the body. Melatonin acts as a photoregulator of circadian biorhythms, all endogenous rhythms of the body being subordinated to its effect, so it is sometimes referred to as the “sleep hormone”. Melatonin also has some unique anti- and prooxidant properties that determine its protective capabilities against free radical damage to DNA, proteins, and lipids. The small size of the melatonin molecule allows it to penetrate the plasma membrane, and the fact that the antioxidant effect of melatonin is not mediated by membrane receptors makes it efficient in affecting free radical processes in virtually any cell of the human body.

The starting point of the strategy for analysing patients' metabolic profiles proposed in Ref. [18] was finding the dependency of the correlation between the analysed component of breath and the level of the sensor output signal on time. The higher the correlation in a certain period, the more likely it is during this period that the analysed hormone or derivatives of its interaction with certain components of breath can leave their “imprint” in the response curve of the quantum point-contact sensing element. The linear correlation coefficient (Pearson correlation coefficient) r between the response signal voltage V and the hormone concentration C in the human body is calculated using the following equation:

$$r = \frac{\text{cov}_{VC}}{\sigma_V \sigma_C} = \frac{\sum_{j=1}^n (V_j - \bar{V})(C_j - \bar{C})}{\sqrt{\sum_{j=1}^n (V_j - \bar{V})^2 \sum_{j=1}^n (C_j - \bar{C})^2}}. \quad (1)$$

Here cov_{VC} is the covariance of the values V and C , σ_V is the root-mean-square deviation of the value V , σ_C is the root-mean-square deviation of the value C , V_j is the response voltage at a given time for the j -th patient (out of n patients), C_j is the hormone concentration of the j -th patient, \bar{V} and \bar{C} are the mean values of the respective samplings:

$$\bar{V} = \frac{1}{n} \sum_{j=1}^n V_j, \bar{C} = \frac{1}{n} \sum_{j=1}^n C_j.$$

The obtained dependences of correlation coefficient of the response signal of quantum point-contact sensor and the concentration of the studied hormones allowed finding the periods of maximum correlation in the spectral profile of breath for each of the target substances. It was shown that the characteristic time interval of breath test was 70 to 85 s for assessing the level of serotonin in the patient's blood, 89 to 92 s for assessing the level of cortisol in the patient's blood, and 63.5 to 67.5 s for assessing the melatonin concentration in the patient's urine [16, 46]. This means that these intervals corresponded to the energies in the sensor response curve of the spectral type shown in Figs. 13 and 14, which characterize with a maximum probability the contribution

of the respective hormone and products of its interaction to the breath profile. The values of the average voltage of the breath profile of a patient for this period of time and the concentration of hormone, for example, serotonin, in the patient's body determine the position of points in the coordinates "response voltage – hormone (serotonin) concentration".

Linear regression equations were constructed on the basis of the obtained data, which allow determining the concentration of each of the studied hormones. In particular, for serotonin, the equation is [18]:

$$C_{\text{ser}}[\mu\text{mol/l}] = 1.17 - 2.41 \times \bar{V},$$

where \bar{V} is the value of the average voltage of the metabolic profile of a particular patient for the period of the greatest correlation with the hormone concentration in the patient's blood. As we can see, this equation has a simple form, which permits quick calculation and real-time detection. Similar expressions were obtained for cortisol and melatonin. Such equations are calibration characteristics for estimation of hormone concentration using breath tests based on quantum point-contact sensors.

Verification of the linear mathematical models used for the studied hormones showed that all results of the sensor analysis fall into the corresponding confidence intervals. The research performed in Refs. [18, 48] demonstrated that the problem of non-invasive determination of hormone concentration in the human body can be successfully solved by using breath tests based on the spectroscopic quantum mechanism of selective detection in complex gaseous media and quantum point-contact sensors.

7.2.2. Concept of characteristic parameters

Another method for determining the concentration of hormones in the human body using a non-invasive respiratory test was developed as part of the concept of characteristic parameters of the spectral sensor profile of breath [21]. This method has become an example of successful mathematical modelling of the processes in the quantum system "point-contact sensor - human breath" and characterization of its behaviour using a set of characteristic parameters of the spectral profile of breath. In Section 7.1, we have already presented the results of effective use of the quantum point-contact sensor relaxation time, which characterizes the energy length of the desorption processes, for detection of carcinogenic strains of the bacterium *Helicobacter pylori* [20]. In Ref. [21], a wide range of characteristic parameters was involved and significant capabilities of this approach were demonstrated for selective detection of components of complex gas mixtures with serotonin and melatonin used as examples.

Characteristic parameters are an effective tool for describing physical-chemical processes in the quantum system "point-contact sensor - human breath" [38, 89]. Some of these parameters are presented in Fig. 13. Taking into consideration the physical meaning of the characteristic parameters, it is possible to find a certain combination of them, which will allow modelling of the system behaviour and identification of those components of the complex gaseous environment which make the main contribution to the energy processes recorded in the spectral response of the point-contact sensor. The spectral nature of the response curve of point-contact sensors with numerous characteristic parameters makes it possible to apply a statistical approach to the analysis of the sensor profile of breath. To this end, a regression analysis of the experimental data was performed in Ref. [21].

Identification of the exact regression dependence of the parameters of the point-contact sensor breath profile on the hormonal level in the human body is a complex task. To solve it, in Ref. [21], patients were divided into groups with certain ranges of concentrations of serotonin and melatonin. After that, the indicators of serotonin and melatonin were averaged for each group of patients. Similarly, the normalized characteristic parameters of the response curves were averaged for each group. A regression analysis was carried out with the averaged data and expressions were

obtained which allow determination of the concentrations of serotonin in the blood and melatonin in the urine using the characteristic parameters of the spectral profile of breath presented in Fig. 13:

$$C_{\text{ser}} [\mu\text{mol/l}] = 5.2369 - 0.9040 \times t_2 - 4.1749 \times p_{12} - 4.4346 \times Q_e.$$

$$C_{\text{mel}} [\text{nmol/l}] = -183.685 + 2.3764 \times t_2 + 2.0288 \times d_1 + 5.1425 \times d_{21}.$$

Besides the parameters $d_1 = \text{tg}\alpha$, $d_{21} = \text{tg}\beta$, and t_2 , already discussed in Section 7.1, the obtained relations contain the parameters p_{12} and Q_e [38, 89]. The p_{12} parameter is the ordinate of the final segment in the exposure phase. It is the magnitude of the sensor response signal formed at the final stage, which includes adsorption of the breath components on the surface of the point-contact sensor array and formation of a metastable structure of the adsorbed molecules on the surface of the Yanson point-contact conduction channels. The Q_e parameter is the area under the exposure curve. It reflects, in an integrated way, the interaction between electrons in the point contact and all components of the analysed gaseous medium. It is very sensitive to changes in the composition and state of breath, as well as to the concentration of certain breath components that significantly affect the conductance of the contact as they are adsorbed on its surface.

We can see that different characteristic parameters play different roles in the hormone identification: t_2 contributes to both serotonin and melatonin dependences, p_{12} and Q_e are correlated mostly with the serotonin concentration, while d_1 and d_{21} are especially informative when it comes to melatonin. The studies conducted in Ref. [21] showed that to solve a rather difficult task of determining serotonin and melatonin concentration in the human body, it is enough to have only five parameters of the spectral sensor profile of breath. These parameters make it possible to determine with high accuracy the hormonal state of a person in real time, without resorting to invasive diagnostic methods.

The obtained results demonstrate the rich opportunities provided by the concept of characteristic parameters implemented within the framework of the spectral mechanism of detection in complex gas mixtures. Only five characteristic parameters of the spectral point-contact profile of a complex gas mixture, taken as an example, provide a possibility of reliably controlling the hormonal background of the human body in real time using quantum point-contact sensors. In fact, the spectral nature of the sensor response to human breath implies that all parts of the response curve contain information about the energy transfer processes occurring between the material of the sensor conduction channel and the breath components. This means that reducing the whole variety of interactions “encrypted” in the breath profile to just five parameters which demonstrate a maximum correlation (effectively, to only three of them, as we can see from the obtained relations for the serotonin and melatonin concentrations) is a simplification of the extremely rich pattern provided by the quantum point-contact sensors. Yet, even this simplified approach has proven to be very successful in analysing such a complex gaseous medium as human breath and accurately finding quantitative parameters of such complex biological substances as human hormones. An increase in the number of characteristic parameters provides unlimited opportunities for the development of new express methods of detection based on quantum sensors and successful solution to the most difficult tasks of analysis of complex gas mixtures.

8. Conclusion. New tasks and prospects for development of quantum point-contact sensors

In this review, we presented generalized information on the new type of universal quantum detectors operating on the basis of Yanson point contacts. Right from their invention, these nanoobjects demonstrated their ability to be used as a multifunctional innovative instrument to get a deep insight into the quantum nature of a solid body on the basis of the research performed in the field of Yanson point-contact spectroscopy. The development of the Yanson point-contact spectroscopy [1] laid the foundation for a series of revolutionary fundamental studies of the subtle

structure of solid bodies carried out at low temperatures [2, 3]. The discovery of the point-contact gas-sensitive effect [5, 6] was a turning point in the context of the prospects for practical use of Yanson point contacts. It marked the beginning of the active use of the unique properties of these nanoobjects to develop sensing elements of quantum sensor devices. This work acquired an interdisciplinary character. Along with physicists chemists, biologists, physicians, and mathematicians began to explore the properties of quantum point-contact sensing elements. The joint activity has resulted in an effective strategy for a gradual achievement of the final result via a series of consistent interdependent steps, the key aspects of which are represented by the logical chain: theory - criteria - properties - methods of creation - control of conformity - purposeful modification and adaptation - testing - proposals and recommendations. In this review, each of these aspects was paid significant attention.

It is the original fundamental properties of Yanson point contacts that are responsible for the behaviour of quantum point-contact sensing elements. This makes the behaviour and capabilities of quantum point-contact detectors totally different from those of the conventional sensors based on the principle of changing electric conductance. To give an idea of the nature of these differences, we examined some spectral properties of point contacts thoroughly studied in the Yanson point-contact spectroscopy, which are of fundamental importance for understanding the operation mechanisms of quantum point-contact sensors. In this regard, special attention was paid to compliance with the criteria of the Yanson point-contact spectroscopy [2], the implementation of which together with the implementation of the original technology provides the possibility of creating nanoobjects with predetermined or predictable properties. Consideration of the theoretical models of point contacts proposed in the framework of the theory of Yanson point-contact spectroscopy [4] was focused on creating macroscopic patterns that contribute to a deep understanding of the processes taking place in the point-contact sensing elements.

The technology for creating point contacts is an important part of the Yanson point-contact spectroscopy and point-contact sensor research. Its distinctive feature is its high science intensity combined with the simplicity of the technical solutions [8]. The numerous “know-how” technologies of the Yanson point-contact spectroscopy allow creation of a wide range of nanostructured tools based on point contacts by using bulk materials, simple and reliable equipment. Along with the classical methods for creating point contacts proposed in the Yanson point-contact spectroscopy, a description of the original developments made in the process of sensor research were given. Among them is the dendritic Yanson point contact, creation of which led to the discovery of the cyclic switchover effect [13]. A deep study of the quantum spectral mechanism and the development of new concepts of detection in complex gas mixtures contributed to the creation of original point-contact sensor matrices with an ultra-high density of quantum sensing elements.

The prerequisites that contributed to the discovery of the point-contact gas-sensitive effect were discussed. The originality of the point-contact gas-sensitive effect and the fundamental differences of the sensory properties of Yanson point contacts from those of the conventional sensing elements served as evidence for the powerful capabilities of the quantum nanosensors, the operation principle of which is based on a change in their electrical conductance. To understand the prospects of research in this area, the results of comparison of the laboratory samples of point-contact sensors with the known analogues were given. The reliability of the analysis was ensured by the use of data obtained at approximately the same stage of sensor development without the use of specific solutions which can artificially improve the parameters of the sensing elements. It was shown that the laboratory samples of quantum point-contact sensors significantly surpass their modern counterparts in all metrological characteristics. This was achieved, in the first place, thanks to the fact that the sensory properties of point-contact sensing elements are due to the quantum nature of Yanson point contacts.

One of the most important features that determine the functioning of point-contact sensing elements is the quantum detection mechanisms discovered during the study of the point-contact gas-sensitive effect. In this review, we considered some of the requirements for a conductive object

to be a candidate for becoming a quantum sensing element capable of operating at room temperature. Using the example of Yanson point contact, we demonstrated how we can avoid the influence of thermal effects that may completely destroy the manifestation of quantum processes in the conductor at room temperature. Among the non-traditional detection mechanisms, the implementation of which is currently unknown for classical nanosensors with the operation principle based on changing electrical conductance, are mechanisms based on the energy approach proposed in the study of point-contact sensing elements. The quantum detection mechanisms based on the energy principles of analysis are a universal approach that results in the absolute selectivity of quantum sensors [17, 20].

One of the unique properties of Yanson point contacts is the conductance quantization, which can be easily observed at room temperature during the cyclic switchover effect [13]. The essence of the effect is that in an electric field the conduction channel of a dendritic Yanson point contact immersed in an electrolyte undergoes quantum structural transformations shaped by the quantum shell effect. Each metastable crystalline state of the dendritic Yanson point contact is characterized by a certain value of quantum electrical conductance. The cyclic character of the processes accompanied by the synthesis and destruction of the conduction channel material results in dendritic point contacts repeatedly going through the metastable quantum states of the system, that can be realized with a certain probability in the experiments. The values of quantum electrical conductance corresponding to the metastable states of dendritic point contacts are a source of data for plotting a conductance histogram, which reflects the unique energy profile of the analysed environment and can be viewed as the output characteristic of a quantum sensor with an absolute selectivity. The quantum point-contact sensor implements a new concept of selective detection in gaseous and liquid media developed as part of the mechanism functioning on the basis of conductance quantization [17].

The unique fundamental properties of quantum point-contact sensing elements are supported by the original results obtained in the process of developing new methods of non-invasive medical diagnostics. Human breath was used as a source of information in these studies. This complex gaseous environment became not only a good model object to verify the effectiveness of the quantum mechanisms of selective detection, but also the main source of information for innovative diagnostic methods developed using quantum point-contact sensors. These methods made it possible for the first time to detect in real time carcinogenic strains of the bacterium *Helicobacter pylori* and hormonal background of the human body.

While developing point-contact sensory devices focused on detection in human breath, a unique mesoscopic multistructure was created – a point-contact sensory matrix with a surface contact density of more than $5 \times 10^5 \text{ mm}^{-2}$. Given the fact that each Yanson point contact is a sensing element of quantum nature, this development leaves far behind all modern *electronic noses* containing, at best, several dozen elementary sensory units. In addition, the spectral nature of the quantum point-contact sensor response guarantees simplicity and high reliability of the analysis of any complex gaseous environment in real time. Using a point-contact sensor matrix, it was possible to carry out a comprehensive analysis of the complex gas mixture – the human breath, which contains more than 2000 components. The quantum devices for non-invasive medical diagnostics using *in situ* express tests of breath were successfully tested in clinical conditions (see, for example, http://qs.net.ua/results_eng.html). The metabolic profile of breath, obtained with ultradense matrices of quantum Yanson point contacts, contains rich information about patients' health, which can be successfully used for a wide range of medical diagnosis. The future work in this area will be focused on universalizing the technology of quantum point-contact sensors and expanding the list of diagnosed conditions of the human body.

The methods of medical diagnosis, already developed on the basis of quantum point-contact sensors, have become a significant scientific and technological breakthrough. The method of diagnosing carcinogenic strains of the bacterium *Helicobacter pylori* is a bright example of that. *Helicobacter pylori* is the most widespread infection in the world. The World Health Organization recognizes the *Helicobacter pylori* infection as the primary causing factor in the development of

peptic ulcer disease, gastric cancer, and gastric mucosa-associated lymphoid tissue (MALT) lymphoma [94, 95]. It should be noted that these and other severe diseases are the result of infection with carcinogenic strains of the bacterium. The currently existing methods for their diagnosis are very laborious and expensive. In addition, they do not allow the identification of virulent strains of the bacterium in real time. Therefore, the development of a breakthrough screening technology to identify the carcinogenic strains of *Helicobacter pylori* using quantum point-contact sensors is an urgent task, successful fulfilment of which would be able to significantly decrease the prevalence of *Helicobacter pylori* and the associated diseases all over the world.

Studies aimed at the development of new methods of non-invasive diagnosis of the hormonal state of human body using quantum point-contact sensors are a vivid example of innovative solutions that can be obtained on the basis of the quantum mechanisms of detection in complex gas mixtures [18, 21, 48]. The quantum detection mechanisms discovered during the studies on point-contact sensors make it possible to put forward numerous detection concepts that can become the basis for the development of various sensor-related methods of analysis. As a result, the same task can be simultaneously solved in several ways in real time. This ensures a high reliability of the results of detection in gaseous and liquid media using quantum point-contact sensors, and, accordingly, the results of the medical diagnosis based on them. Combination of the different methods of analysis of point-contact spectral data can further increase the efficacy and reliability of the new sensor technique. The new quantum technique will be able to extend the list of detectable hormones to evaluate the state of the human endocrine system and help prevent or cure both widely spread and rare endocrine diseases, which include obesity, hormone-related cancers, as well as various conditions associated with metabolic disorders [115].

Another promising area of application of the quantum point-contact sensor technique is evaluation of the general state of the human body. Here too, an easy and fast non-invasive determination of the level of such basic human hormones as serotonin (“hormone of happiness”) or cortisol (“hormone of stress”) will be able to help solve some of the medical and social problems of the modern society. It is well known that, for example, serotonin deficiency has various symptoms including low mood and low sleep quality [116]. It can also affect fear responses in the human brain which can trigger various anxiety-, stress-, and trauma-related disorders [117], as well as aggression [118]. An imbalance in serotonin may cause simultaneous sleep disorder symptoms and even depression. The latter is an extremely important problem since, according to the recent studies [119], 7.2% of people in the EU suffer from chronic depression.

The ability of sensors based on Yanson point-contacts to register at the molecular level complex interactions in multicomponent gaseous and liquid media makes it possible to successfully use them for solving the global ecological problems that threaten the survival of mankind. One of them is the problem of climate change which can lead to global or local food shortage, armed conflicts, and mass migration. To avert these imminent negative consequences of the global warming, an efficient control of the earth’s climate needs to be organized. A successful control and prediction of climate change implies continuous monitoring of greenhouse gases in the atmosphere and a quick and efficient control over their sources. The quantum point-contact approach to selective detection in gaseous and liquid media has already resulted in the creation of a portable devices which can become the basic element of a simple and inexpensive technology for global monitoring of climate-unfriendly gases and liquids [17, 42].

One of the important greenhouse gases is methane, which is emitted during the production and transportation of coal, natural gas, and oil. Methane emissions also result from livestock and various agricultural practices, land use, and decay of organic waste in municipal solid waste landfills. Even though methane is a short-living climate pollutant (compared to the long-living pollutant CO₂), while it’s in the atmosphere it has a more detrimental effect than CO₂, up to 85 times worse than CO₂ over a 20-year time span and 34 times worse over 100 years [120]. There are large deposits of methane in the form of methane clathrates on the oceanic floor and in the continental permafrost areas. Global warming may cause release of methane from these huge

reservoirs and thereby extremely aggravate the problem of climate change. Quantum point-contact sensors can reliably detect methane in a wide range of concentrations [17] and be an effective tool for developing the technology for monitoring this pollutant.

The list of the natural characteristics of potential analytes does not have any restrictions on their detection and analysis using quantum point-contact sensors, since each analysed substance is characterized by its specific energy of interaction with the material of the point-contact conduction channel. It is noteworthy that the quantum point-contact sensor is able to detect and quantitatively estimate trace concentrations (ppb units) of both electrode-active substances and those which are not affected by electrode reactions. This is far from the detection limit, since, theoretically, Yanson point-contacts can easily detect the presence of even one atom or molecule adsorbed on the surface of its conduction channel. Research in this area requires special equipment to accurately prepare analytes with extremely small concentrations of the active substance.

Another important aspect of the problem of detecting dangerous substances, especially gases, is that of providing industrial safety by controlling the air in potentially hazardous industrial areas, such as factories, mines, pipelines, etc. In addition to being an important greenhouse, methane is a gas that poses significant threats in industry – coal mining, in the first place. The simplicity of construction of the point-contact sensor device and its low cost will allow a global multi-position impact monitoring of the environment to quickly detect areas of chemical pollution in potentially dangerous regions of intense anthropogenic influence. Development of cheap, efficient, and easy-to-use quantum gas detectors based on Yanson point contacts that would be able to monitor the composition of air in real-time mode in potentially hazardous areas will significantly contribute to the safety of the personnel involved in the activities potentially related to emission of methane, nitrogen oxides, and other toxic gases, as well as to making both extractive and processing industry more ecology-friendly by preventing leakage of substances which can harm the environment.

The quantum approach provides a wide choice of options for the development of an unlimited spectrum of novel methods and devices. The energy parameters of the point-contact sensor response allow distinguishing materials one from another. To get an advanced analytical tool for detection of a wide range of gases and liquids, it is necessary to create a library (database) of conductance histograms of dendritic point-contact structures synthesized in different gaseous and liquid media. The first steps in creating such a database have already been made. Further studies will be aimed at obtaining comprehensive information about a wide range of gaseous and liquid media, which will be accumulated in the database and used to develop innovative technologies of quantum point-contact detectors.

The presented analysis of the performed work marks the initial stage of the research aimed at practical use of Yanson point contacts as quantum sensing elements. It did not include the unexpected original results of the many already conducted experiments. The new area in the sensor studies initiated by the unique capabilities of Yanson point contacts is at the initial stage of its development. Given the large number of nontrivial fundamental results that arise in every new study, the prospects for these activities are quite promising.

Studies are continued in order to improve the already developed structures and technologies, as well as to create fundamentally new devices. New experiments are planned with various materials to be used to create point-contact sensing elements. This approach was already successfully tested during the studies performed as part of the Yanson point-contact spectroscopy that led to a few top-priority results. A number of original data obtained in the studies of the point-contact gas-sensitive effect and cyclic switchover effect stimulate new experiments. For example, preliminary studies showed the high specificity of the nature of the self-oscillation during the cyclic switchover effect for each metal, which is an obvious prerequisite for finding new fundamental correlations and quantum effects. The effects accompanying the process of quantum transformations of the dendritic point-contact structure during the cyclic switchover effect are a source of information for the development of fundamentally new principles of analysis and devices based on them. There is also a large series of works aimed at studying the sensory properties of

heterocontacts, for which it is necessary to further develop the theoretical and experimental base. The results obtained using the Au/SWNT heterocontacts, as well as copper and its compounds with organic conductors, give reason to believe that the sensorics of heterocontacts is another alternative way to create modern quantum analytical devices. Naturally, applied and fundamental research will lay the foundation for mutual stimulation and enrichment. Many ideas are waiting to be implemented technologically. But even more ideas and technical solutions will appear in the future, which is guaranteed by the unique quantum nanostructure – the Yanson point contact.

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CRedit authorship contribution statement

Conceptualization, G.K., O.P., V.V. and E.F.; Writing – original draft preparation, G.K., O.P., V.V.; Writing – review & editing, G.K., V.V., E.F.; Visualisation, G.K., O.P., V.V.; Supervision, G.K., E.F.; Project administration, G.K., E.F.; Funding acquisition, G.K., O.P., E.F. All authors provided critical feedback and helped shape the research and manuscript. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare no conflicts of interest. The funders had no role in the writing or in the decision to publish the manuscript.

Data Availability

The data are available from the corresponding author upon reasonable request.

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