Electrochemical processes on electrodes during electropuncture diagnostics. Message 1. Direct current

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SUMMARY

The analytical review considers the electrochemical processes occurring on the measuring electrodes during electropuncture diagnostics at the electrode-electrolyte interface and in the tissues of the body. A modern assessment of the influence and role of these processes in changes in the electrical properties of the skin on a constant electric current has been carried out. Contains critical remarks about some methods of electropuncture diagnostics.

Key words: electropunctural diagnostics, electrochemicalelectrode processes, electric double layer, electrode-skin contact, polarization.

RESUME

Analytical review covers electrochemical processes taking place at measurement electrodes during electrupunctural diagnostics at the electrode-electrolyte interface and in body tissues. Modern evaluation of influence and role of these processes in measurement of skin electrical properties utilizing direct current is given. Critical notes on certain methods of electropunctural diagnostics are presented.

Keywords: electropunctural diagnostics, electrochemical processes at electrodes, dual electrical layer, skin-electrode interface, polarization.

Introduction

Electropuncture diagnostics (EPD) is widely used both in clinical practice and in solving some practical problems associated with assessing the effect of adverse environmental factors on the human body [1–4]. This situation is due to the fact that EPD is one of the simplest and at the same time the fastest diagnostic methods, which can be used with acceptable accuracy and reproducibility in many cases.

The diagnostic application of electropuncture is based on the experimentally substantiated idea that individual zones and points of the skin indirectly reflect the level of functioning of various organs and systems of the human body by viscerocutaneous and cutanovisceral connections [5]. The assessment of the state of these zones and points of the skin during EPD is carried out indirectly by measuring their electrical properties - resistance when using

DC electric current and resistance and capacitance (impedance) at AC / pulse current.

Currently, a significant number of monographs, reviews and articles have been published devoted to the description of the EPD method with various modifications and its application in various fields of clinical medicine and in biomedical research. However, most of them focus on the issues of clinical diagnostics and, to a lesser extent, on the analysis of the mechanisms of the passage of diagnostic electric current (direct or alternating) from the measuring electrodes through the measurement points on the skin and the electrochemical processes occurring during this [6]. It is these processes that are the reason for the main difficulty in the implementation of almost all contact EPD methods, which consists in the instability of the electrical parameters of the contact zone of the measuring electrode with the skin surface, which leads to significant errors. Undoubtedly to reduce all metrological difficulties in EPD only to the electrochemical processes occurring on the electrodes would be wrong, since there are also hardware errors. However, in various publications much more attention is paid to the instrumentation of measurements during EPD than to electrode processes at the interface between the measuring electrode and the skin [7, 8].

In this report, we will analyze only some of those complex electrochemical processes occurring at the "metal electrode-skin surface" interface during the passage of a direct electric current, which are related to the EPD method and affect the diagnostic results. The subject of consideration will be the electrical properties of the contact "measuring electrode-skin" during the passage of a direct electric current, and the goal is to draw attention to the role and participation of these processes in the methods of contact EPD. Modern analysis of electrode processes and the nature of the phenomena occurring during contact and measurement of electrical parameters of the skin during EPD requires an understanding of the basic provisions of electrochemistry.

Electrochemical processes on electrodes and in tissues

The entire surface of the skin, including at the point of contact with the metal electrode, is covered as a result of perspiration (perceptible and imperceptible perspiration) with a thin layer of an aqueous solution of various substances, primarily ions, which is essentially an electrolyte. In this regard, the contact "electrode-skin" can be considered as the contact of two phases - a metal and an electrolyte solution, at the interface of which electrochemical electrode processes take place.

In accordance with the laws of electrochemistry, with such a contact, an excess electric charge in comparison with the volume arises at the phase boundary, which is accompanied by the appearance of an electric double layer. The formation of an electric double layer occurs when electrolyte ions, as a result of orientation under electrostatic attraction, cannot approach electrode at a distance closer to its solvation shell. The resulting space between the electrode surface and the plane passing through the centers of the electrolyte ions is a dense part of the electric double layer or the Helmholtz layer. By its structure, the electric double layer is similar to a flat capacitor, the distance between the plates of which is equal to the radius of the hydrated ion, due to which the average capacitance of such a molecular capacitor is large - about 0.01 F / m2. In an electrolyte solution, as a result of the thermal motion of ions, the orienting effect of the electric field is disturbed, which leads to the formation of a diffuse part of the electric double layer or Huey layer, which is diffuse in comparison with the dense part and has the properties of a space charge. In principle, an electrical double layer is formed at the interfaces of any two phases, including at the interface of biological tissues, plasma and intracellular membranes, differing in their electrical properties (conductivity and capacitance). [13].

As a result of the processes occurring at the metal-electrolyte interface, the electrode acquires a potential that, in the absence of an external electric current, is equilibrium or reversible. Such a potential has an electrode that is in a solution of its own salt, for example, Ag / AgCl, Zn / ZnCl, and when an exchange of charge carriers occurs at the interface, and an equilibrium exchange current flows. However, when an external electric current flows through the electrode-electrolyte interface, its potential deviates from the equilibrium one, which leads to electrode polarization and a change in the exchange current. In the general case, the polarization process consists of successive stages, associated with a change in the concentration of ions in the diffuse part of the electric double layer (concentration polarization) and the transition of charges across the interface (overvoltage polarization). In the first case, the rate of diffusion from the depth of the solution to its surface plays a role in the formation of polarization; in the second, the processes of oxidation-reduction. The main difference between concentration polarization and overvoltage polarization determines the magnitude of the potential that was formed at the electrode when an external electric current flows. This, for example, is the potential at the electrode of the order of 1 V, above which electrolysis occurs, accompanied by the evolution of hydrogen at the platinum electrode in a 0.85% NaCl solution in equilibrium with respect to oxygen [14]. As a result, electrons cross the "electrode-electrolyte" interface, which leads to the occurrence of an oxidation or reduction reaction, depending on the polarity of the external electric current. The passage of a direct electric current leads to the emergence of an electromotive force on the electrodes, which opposes the passage of current. The reverse electromotive force is due to the concentration of positive charges (cations) and negative charges (anions) at the respective electrodes. All these processes, when measured with contact metal electrodes, lead to the fact that the electrode, when an external electric current is switched on, behaves like a capacitor with a parallel resistance, which is quickly charged and then relatively slowly discharged. Capacitive properties of the boundary The passage of a direct electric current leads to the emergence of an electromotive force on the electrodes, which opposes the passage of current. The reverse electromotive force is due to the concentration of positive charges (cations) and negative charges (anions) at the respective electrodes. All these processes, when measured with contact metal electrodes, lead to the fact that the electrode, when an external electric current is switched on, behaves like a capacitor with a parallel resistance, which is quickly charged and then relatively slowly discharged. Capacitive properties of the boundary The passage of a direct electric current leads to the emergence of an electromotive force on the electrodes, which opposes the passage of current. The reverse electromotive force is due to the concentration of positive charges (cations) and negative charges (anions) at the respective electrodes. All these processes, when measured with contact metal electrodes, lead to the fact that the electrode, when an external electric current is switched on, behaves like a capacitor with a parallel resistance, which is quickly charged and then relatively slowly discharged. Capacitive properties of the boundary The reverse electromotive force is due to the concentration of positive charges (cations) and negative charges (anions) at the respective electrodes. All these processes, when measured with contact metal electrodes, lead to the fact that the electrode, when an external electric current is switched on, behaves like a capacitor with a parallel resistance, which is quickly charged and then relatively slowly discharged. Capacitive properties of the boundary The reverse electromotive force is due to the concentration of positive charges (cations) and negative charges (anions) at the respective electrodes. All these processes, when measured with contact metal electrodes, lead to the fact that the electrode, when an external electric current is switched on, behaves like a capacitor with a parallel resistance, which is quickly charged and then relatively slowly discharged. Capacitive properties of the boundary

"Electrode-electrolyte" due to polarizing capacity, which is represented by a double electric layer (dense and diffuse parts), and the shunt resistance is represented by the exchange current. The processes of concentration of cations and anions on the corresponding electrodes also participate in the formation of the polarization capacitance. Thus, in the electrode-electrolyte system at the initial moment of the passage of a direct electric current, its value increases sharply, which in polarography is called inrush current [15]. After some time, which depends on the magnitude of the current, the nature of the electrolyte and the material of the electrodes, the magnitude of the current decreases and then settles at a certain level. Similar processes take place not only on the contact surface of the measuring electrode with the skin, but also in all tissues through which current flows to one degree or another.

In the first experimental studies, it was noticed that when a direct electric current is turned on, the tissue resistance is small, but over time it rapidly increases and the recorded current decreases [16]. This process is accompanied by the appearance of an oppositely directed electromotive force associated with polarization, and initially its appearance was explained by an increase in tissue resistance. However, it later became clear that the electromotive force is associated with the formation of additional charges inside the tissues as a result of the accumulation of ions of the opposite sign at the interfaces of tissues with different electrical characteristics. Thus, the polarization capacitance is added to the static electrical capacitance in any tissue of the body and due to its structure. The oppositely directed electromotive force is recorded in the form of polarization or residual potentials, slowly decreasing after switching off the current. In the experiments that were performed when measuring on the skin, it was found that after 1 min. after switching off the current, the value of the residual potentials reached 0.2–0.4 V, which slowly (within tens of minutes) decreased according to the hyperbolic law [17]. It should be noted that the complex complex of electrochemical polarization processes occurring on the electrodes and in body tissues during EPD and affecting the reproducibility and accuracy of diagnostics is practically impossible to separate or eliminate. However, in order to increase the reproducibility and objectivity of the EPD, it is necessary to achieve the stability of electrode processes, take them into account in measurements and minimize them.

As an example, let us consider how these provisions were solved to limit the instability of the electrical parameters of the electrode-skin contact in the two main EPD methods according to R. Voll and I. Nakatani, each in its own way. In both methods, the residence time of the active electrode on the skin (measurements), as well as the material and design of the electrode, are unambiguously determined, which made it possible to minimize the errors in the contact “electrode-skin” and, in essence, the inrush current was measured, which is characterized by greater stability and information content. In addition to this, in the method of R. Voll, as a result of the dosed pressure of the electrode on the skin surface, the cells of the epidermis and, in particular, the stratum corneum, which introduces the greatest distortions due to changing hydration, are mechanically flattened, which makes it possible to obtain comparable diagnostic results. I. Nakatani's method uses liquid contact of the skin with a measuring electrode, through a cup with a tampon, moistened with an electrolyte solution - 0.9% sodium chloride. All this allowed R. Voll and I. Nakatani to create reproducible and objective EPD methods, as evidenced, for example, by the coincidence of the measuring scales of these seemingly different methods [7].

Analysis of some controversial provisions of electropuncture diagnostics

In conclusion, one cannot but touch upon one of the directions that existed in the EPD in the mid-1970s in our country. The whole absurdity of this direction, which consists in assessing the functional state of the acupuncture point, was that the acupuncture point at that time was considered as an independent and, for some unknown reason, not related to the human body structure. The foundations of this misunderstanding, which lasted for several years, were set forth by V.G. Nikiforov, who believed that “... the active points of the skin of a healthy person should have the same conductivity index under the action of negative and positive currents. These are normal points or conductors that do not require medical intervention. Points with asymmetric conductivity (lower on a positive current than on a negative one) are called semiconductor points by the author. The task of electrotherapy is to align the conductivity of the semiconductor points "and further" The treatment continues until at all points the magnitude of the negative and positive charge becomes the same, i.e. until the points become electrically neutral ”[18, p.26]. In passing, we note that the quote fully retains the terminology of the author.

In fairness, it should be said that this provision was not directly advertised, but was a subtext in many articles, methods and developed diagnostic and therapeutic equipment. So, for example, in the "Instructions for the use of the device PEP-1" (device for electropuncture), the content of the order of the Ministry of Health of the USSR No. 303/40 dated March 25, 1976 "On the introduction of electropuncture and microelectrophoresis in BAP into medical practice" is set out, where the method assessment of the functional state of acupuncture points is carried out as follows. A point was considered "normal" when the value of the current of positive polarity was either equal to the current of negative polarity, or slightly differed from it. In cases where the current with positive polarity was greater or less than negative, then the current was considered a "semiconductor point" and was subject to the so-called "treatment", i.e. influence until the currents are restored to equality. However, this is not all - there were also so-called "insulator points" in which the current value was determined only at one polarity, and which were also subject to treatment. In general, the dependence of the current value on the voltage at the electrode or the polarization curve is nonlinear, but at a low potential value of the order of tens of mV, an initial linear segment can be distinguished on it. An increase in the potential at the electrode and the occurrence of overvoltage shifts the operating point on the polarization curve to the nonlinearity region, which leads to the appearance of rectifying properties at the interface. In other words, volt-ampere However, this is not all - there were also so-called "insulator points" in which the current value was determined only at one polarity, and which were also subject to treatment. In general, the dependence of the current value on the voltage at the electrode or the polarization curve is nonlinear, but at a low potential value of the order of tens of mV, an initial linear segment can be distinguished on it. An increase in the potential at the electrode and the occurrence of overvoltage shifts the operating point on the polarization curve to the nonlinearity region, which leads to the appearance of rectifying properties at the interface. In other words, volt-ampere However, this is not all - there were also so-called "insulator points" in which the current value was determined only at one polarity, and which were also subject to treatment. In general, the dependence of the current value on the voltage at the electrode or the polarization curve is nonlinear, but at a low potential value of the order of tens of mV, an initial linear segment can be distinguished on it. An increase in the potential at the electrode and the occurrence of overvoltage shifts the operating point on the polarization curve to the nonlinearity region, which leads to the appearance of rectifying properties at the interface. In other words, volt-ampere but at a low potential of the order of tens of mV, an initial linear segment can be distinguished on it. An increase in the potential at the electrode and the occurrence of overvoltage shifts the operating point on the polarization curve to the nonlinearity region, which leads to the appearance of rectifying properties at the interface. In other words, volt-ampere but at a low potential of the order of tens of mV, an initial linear segment can be distinguished on it. An increase in the potential at the electrode and the occurrence of overvoltage shifts the operating point on the polarization curve to the nonlinearity region, which leads to the appearance of rectifying properties at the interface. In other words, volt-ampere the characteristic of the "metal-electrolyte" interface coincides with the curve, which is characteristic of the rectifying properties of the diode [19]. As a result of different mobility of ions (anions and cations) in a solution of a completely or partially dissociated electrolyte, the character of the development in time of the rectifying properties of the metal-electrolyte interface, and, consequently, of the direct current at the anode and cathode will be different. In a living organism, similar processes occur, and when measuring the resistance of tissues at direct current, their rectifying ability (rectification coefficient) is determined as the ratio of those passed through the tissue in the forward and backward direction [15].

It is likely that these phenomena were not taken into account in the development of the method of volt-ampere characteristics of acupuncture points, the metrological aspects of which were presented in an article published in a collection devoted to the biomedical and physical-technical foundations of reflexotherapy [20]. Modern analysis shows that during such measurements, the rectifying properties of the "electrode-electrolyte" interface were mainly recorded, and the contribution of the intrinsic properties of skin points was extremely uncertain. The nonlinearity and hysteresis of the obtained voltammetric curves are explained by the memristor effect, which was later confirmed [21]. However, by coincidence, another article was published in the same collection, in which, as a model for studying the conduction mechanisms of acupuncture points, “... a saturated electrolyte solution was chosen, obtained on the basis of NaCl salt, where the contact between the electrode and the electrolyte was carried out through a paper filter ”[22, p.228]. The character of volt-ampere characteristics in such a model of acupuncture points, i.e. of the electrode-electrolyte-electrode system, in these measurements was similar to the previous ones and the memristor effect was also manifested in them, although the skin itself (its point) was not present in these measurements. Here one cannot but pay attention to the fact that, according to the method of V.G. Nikiforov, it would be possible to completely "cure" such a point by passing a current "... until at all points the magnitude of the negative and positive charge becomes the same ..." [18, p.26] or in other words, until the cations, and anions, as a result of different mobility and concentration, after a certain time of "treatment" will not collect at the positive and negative electrodes,

Conclusion

V the result analysis performed shown role and participation electrochemical processes occurring at the interface "metal electrode-skin surface" during the passage of direct electric current with contact methods of EPD. A modern assessment of the influence of these electrochemical processes on the objectivity and reproducibility of diagnostic results when measuring the electrical properties of skin points at direct current has been carried out. The erroneousness of some previously developed EPD methods was shown, the reason for which was insufficient attention to the influence of electrochemical processes on the measuring electrodes, as well as to the polarization processes occurring both in the area of the electrode-skin contact and in the underlying tissues. Probably, an interdisciplinary approach to the EPD problem will increase its diagnostic value as one of the promising diagnostic methods of traditional medicine.

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