Electrochemical processes on electrodes during electropuncture diagnostics. Message 2. Alternating current

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SUMMARY

The analytical review considers the electrochemical processes occurring on the electrodes during electropunctural diagnostics at the "measuring electrode-electrolyte" interface under conditions of the passage of alternating current. A modern assessment of the influence and role of these processes in measuring the electrical properties of the skin with alternating electric current has been carried out.

Key words: electropunctural diagnostics, electrochemical electrode processes, variable current, electrode-skin contact, electrode polarization, methods for excluding electrode polarization.

RESUME

The analytical review examines electrochemical processes occurring at the electrodes during electropunctural diagnostics on the interface “measuring electrode-electrolyte” while alternating current flows. Modern assessment of the influence and the role of these processes in the measurement of electrical properties of the skin on alternating electric current is carried out.

Keywords: electropunctural diagnostics, electrochemical processes at electrodes, alternating current, skin-electrode interface, electrode polarization, methods for exclusion of electrode polarization.

Introduction

The most important trend in the development of electropunctural diagnostics (EPD) is its gradual transformation from a semi-quantitative method to a more accurate quantitative one. Due to this, the diagnostic efficiency of EPD increases, since new measurement principles aimed at the quantitative study of the electrical properties of the skin at certain points of it, allow revealing the mechanisms that underlie this method [1]. All this makes it possible to approach their quantitative description and reveal the general physiological laws and physicochemical mechanisms underlying EPD. The generally accepted approach to measuring the electrical properties of the skin, with rare exceptions, does not take into account the electrochemical processes that occur on the electrodes in the "measuring electrode-skin" system. In the overwhelming number of publications, as a rule, the processes occurring mainly on the measuring electrodes during the registration of biopotentials [2]. Meanwhile, ignoring these processes introduces significant errors in the measured values, which can significantly distort the results obtained and affect the quality of the EPD.

There are very few systematic studies of the electrochemical processes that occur on the measuring electrodes in the area of contact with the skin during EPD. It can be assumed that this article, which is a continuation of the previously published [3], in which electrochemical processes at the interface - "measuring electrode-electrolyte" on alternating current with EPD are considered, will to some extent contribute to the development of these studies.

Electrochemical processes on electrodes with alternating current

The use of alternating electric current in EPD is based on the study of the response, or response, of the skin at its specific point to the applied impact. The quantitative characteristic in this case is the complex electrical resistance, which is the sum of resistance and capacitance at the frequency of an alternating electric current. It should be noted that measurements of the electrical properties of the skin on alternating current are more informative than on direct current, since alternating current propagates through the skin and deep tissues of the body, and constant current - mainly along the surface [4].

In this regard, many measurements of the electrical properties of the skin on alternating current were carried out, however, it was found that the measured value varies significantly and depends in a complex way on the potential difference, current magnitude, frequency, size of electrodes, distance between them, measurement time and others. hard-to-measure indicators. Therefore, in order to obtain reproducible and informative indicators, various methodological techniques began to be used that could only be used with alternating current, for example, measuring the magnitude of electrical losses in the skin (phase angle) [5], its dependence on frequency [6], as well as mathematical methods - Bode analysis [7], Laplace transform [8], etc. The results of measurements by M. Reichmanis, AA Marino and RO Becker, who applied the Laplace transform to the analysis of the correlation of the electrical properties of the acupuncture points of the colon meridian He-gu (Li 4) and Zhou-liao (Li 12) [9] and the heart meridian Shao-hai (H 3) and Ling-dao (H 7) [10, 11]. To this end

measurements of electrical properties (values of resistance and capacity) of the skin were carried out at acupuncture points and at its control points at frequencies up to 1 MHz and the correlation between them was assessed. In all the measurements performed, the resistance values at the acupuncture points were statistically significantly lower than at the control points of the skin, which confirmed one of the fundamental points of view of EPD.

One of the significant factors influencing the results of measurements on alternating current is the polarization of the electrodes at the interface "electrode-skin surface", more precisely, "metal-electrolyte". When an alternating current passes between current and voltage, a phase shift occurs, which allows us to consider the total resistance of this interface as the sum of active and reactive components [12]. The magnitude of these components, as well as the ratio between them, is determined by the properties of the electrode and the electrolyte in contact with it and by the processes occurring at the interface during the passage of current. The electrical equivalent in this case can be parallel or series connection of resistance and capacitance. The capacity is a double electric layer, which results in a phase shift between current and voltage for sinusoidal alternating voltage. A quantitative characteristic of the electrochemical processes occurring on the electrodes is the complex resistance (impedance), which is connected in series with the electrodes during the measurement. As a result, during EPD, the measurement results undefinedly include the polarization impedance of the electrodes, the value of which, at a certain ratio of parameters, can be comparable or even exceed the measured results of the electrical parameters of the skin.

Alternating current through the "electrode-electrolyte" interface can pass in two different ways, which depend on the type of electrode - polarizable or non-polarizable. The overwhelming majority of electrodes used in EPD are metal immersed in an electrolyte solution, i.e. are polarizable. Unlike a non-polarizable electrode, there are irreversible reactions on it - there is no dynamic equilibrium between the metal and the charge (ion) common to it and the electrolyte. As a result, the potential at the polarizable electrode can take on any values and, thus, is not equilibrium, and in the linear region its value is limited by the decomposition voltage of water. The potential of a non-polarizable electrode, in contrast to a polarizable one, does not deviate from the equilibrium value during the passage of current and is less prone to polarization, since the electrode reactions are reversible here. At an equilibrium potential, the charges (ions) do not cross the phase interface, and the current flows due to the charging or discharging of the electric double layer. In this case, changes in concentration at the electrode surface occur due to alternating current, and then the polarization of the electrode is concentration. When the potential deviates from the equilibrium one during the passage of an alternating current, not only the double layer is charged, but also an electrochemical reaction, for example, oxidation or reduction, occurs. In this case, the impedance of such an electrode is the sum of the capacitance of the double layer and the impedance (Faraday impedance) of the electrochemical reaction.

Thus, there is a complex nature of the polarization processes occurring on the electrodes, the dependence of the polarization impedance on the material of the electrodes, as well as the magnitude of the current passing through them (Table 1).

As a more detailed example, we can focus on the results of studies carried out by P. Mirtaheri et al., In which the values of the polarization impedance components (resistance and capacitance) were obtained for silver, aluminum, gold, platinum electrodes and medical stainless steel in the frequency range from 10^{-2} Hz to 1.0 kHz in an aqueous solution of NaCl with concentrations from 2.4 to 77.0 mmol / l [15]. Maximum resistance at frequency 10^{-2} Hz was for stainless steel electrodes and was about 2000 kOhm, for aluminum electrodes the resistance was in the range of 150–300 kOhm, and for silver, gold and platinum electrodes it was 200–100 kOhm, 400–1500 kOhm and 300–1000 kOhm, respectively ... At a higher frequency (1 kHz), the resistance of aluminum electrodes ranged from 200 Ohm to 40 kOhm, platinum - from 200 Ohm to 20 kOhm, silver and stainless steel - 100–500 Ohm, and, finally, the lowest value was for gold electrodes. - between 20 and 70 ohms. Largest capacity at 10^{-2} Hz was observed for aluminum electrodes
- 900–10000 μF, while for silver, gold and platinum electrodes these values were in the range of 20–50 μF, 8–30 μF and 20–80 μF, respectively. The capacitance for stainless steel electrodes at the same frequency was about 2.0 μF and did not depend on the concentration of the NaCl solution. At a frequency of 1 kHz, the capacitance value for aluminum electrodes was in the range of 0.04–0.06 μF, silver - 0.1–0.9 μF, and gold - from 0.8 to 2 μF. Smaller capacitance values were noted for stainless steel electrodes, which ranged from 0.2 to 0.7 μF.

The presented results of measurements of the components of the polarization impedance (resistance and capacitance) showed significant variability depending on the electrode materials and on the frequency in the range from 10^{-2} up to 1.0 kHz, while the effect of changes in the concentration of NaCl solution on these values was less pronounced. Probably, one should be inclined to the opinion of LA Geddes and R. Roeder about the individual selection of electrode material in relation to specific measurement tasks and, in addition, to extend this provision not only to implantable, but to cutaneous measuring electrodes [16]. It all makes elimination or minimization

polarization of electrodes with EPD is a rather difficult task.

Table 1

The value of the polarization impedance of some metals in saline at a frequency of 220 Hz.

According to [14] as amended

Материал	Плотность тока	
	3 мкА/мм²	70 мкА/мм²
	Поляризационный импеданс, кОм/мм²	
Нихром	14,7	7,3
Платина	8,0	4,6
Золото	5,5	–
Серебро (блестящее)	2,02	1,72
Серебро (свежехлорированное)	0,52	0,72

Methods for Eliminating or Minimizing Electrode Impedance

There are several methodological techniques that allow, if not completely, then at least partially, to reduce the value of the electrode impedance so that it does not have a significant effect on the EPD results. H. Kalvøy et al. in their publication selected the most optimal methods for reducing electrode polarization during measurements, which are summarized in table. 2 [17].

At the same time, not all methods of elimination or reduction to an acceptable level of the value of the electrode impedance, which are listed in table. 2 can be used for EPD.

table 2

Methods for changing or correcting the parasitic properties of electrodes. According to [17] as amended

No. p. p.	Methods	Description	Literature
one.	Mathematical an exception	Estimation of electrode polarization impedance by simulation and subtraction from measurement results	[15, 18, 19, 20, 21, 22]
2.	Distance change between electrodes	Eliminate the contribution of a homogeneous sample by measuring with different electrode spacing	[19, 23]
3.	Substitution method	Replacing the sample with a calibrated solution with known parameters to estimate the electrode polarization impedance	[19, 22, 24, 25]
4.	4-electrode method	Separation of a pair of electrodes and selection of current for pairs of electrodes so that the electrode polarization impedance does not participate in measurements	[26, 27]
5.	Increasing current density	The current density in the linear region can significantly change the electrode polarization impedance	[19, 23]
6.	Modification of electrodes	Modification of electrode properties by improving the quality and reducing the electrode polarization impedance	[18, 19, 21, 22]
7.	Change in conductivity sample	Electrode polarization impedance is less pronounced in less conductive media	[nineteen]
eight.	Contact liquid	The electrodes can be withdrawn from the current area or released by using a conductive couplant to establish contact with the sample.	[28]

The most optimal should be considered the mathematical elimination of electrode polarization, an increase in the current density and, with certain restrictions, modification of the surface of the electrodes, as well as the use of a contact liquid. Mathematical modeling of electrochemical processes has shown its applicability using various software tools [29].

An increase in the density of the measuring current can also be used to reduce the value of the electrode impedance, however, its value should not exceed physiologically acceptable and safe values.

Modification of the surface of metal electrodes has long been used in electrochemistry, which makes it possible to reduce the effects associated with double layer charging and Faraday processes. For this purpose, the electrodes are coated with spongy platinum black, which increases the surface area and leads to an increase in the capacity of the double layer and a corresponding decrease in the value of parasitic resistance. Unfortunately, this methodical technique cannot always be applied, since it is necessary to use only platinum electrodes, and the spongy layer of platinum is very fragile and capable of adsorbing proteins. More promising is the use of sandblasting the surface of electrodes, for example, from

stainless steel, although the increase in surface area is significantly less than with platinum black coating.

The use of a contact liquid (gel) to some extent solves the problem of eliminating the polarization of the electrodes, although in full it can be achieved only in the case of a non-polarizable electrode (Ag / AgCl, Zn / ZnCl).

The rest of the methods should be recognized as practically unacceptable, since changing the distance between the electrodes, as well as the 4-electrode method with EPD, is definitely not suitable. The replacement method is only possible when measuring in vitro, as well as changing the conductivity of the sample.

Probably, the most appropriate graphical-analytical method for assessing the nature of electrode processes, which was proposed by JH Sluyters, as well as JH Sluyters and JJC Oomen [30, 31], is most suitable for the electrochemical processes occurring on the electrodes during EPD. In this case, three cases are considered that are associated with electrode polarization: a) completely reversible electrode reaction, b) completely irreversible electrode reaction, c) partially reversible reaction. Assessment of the degree of reversibility consists in representing the frequency dependence of the impedance components (resistance and capacitance) in the complex plane. In the case of a completely reversible reaction, the graph of such a dependence has the form of a straight line intersecting the abscissa axis at an angle of 45 °. With a completely irreversible reaction, the dependence has the form of a semicircle centered on the abscissa axis, while in a partially reversible reaction, the relationship is represented by a combination of a circle with a straight line. An analysis of such dependences will make it possible to determine the proportion of polarization processes occurring at the electrodes and to estimate their contribution to the measured values.

Conclusion

A modern analysis is presented, which shows the role of electrochemical polarization processes occurring at the "metal electrode-skin surface" interface during the passage of an alternating electric current during EPD. The level of influence of electrode electrochemical processes on alternating current on the measured values of the electrical properties of the skin has been determined. Modern methods of minimizing or eliminating the electrode polarization of the electrode-skin contact area are analyzed and the applicability of the methods used is shown. It is shown that in practical conditions, from the existing methods of excluding or minimizing electrode processes in EPD, it is possible to use mathematical modeling and modification (processing) of the surface of measuring electrodes without applying adsorbent coatings. Apart from these methods, The most promising is the graphical analytical method, which makes it possible to assess the degree of reversibility of an electrochemical reaction and to determine the level of electrode polarization. It can be assumed that the individual selection of the electrode material in relation to specific tasks of the EPD will increase its objectivity, diagnostic quality and reduce the dependence on measuring instruments.

Literature

1. Ahn AC, Colbert AP, Anderson BJ, Martinsen Ø.G., Hammerschlag R., Cina S., Wayne PM, Langevin HM Electrical properties of acupuncture points and meridians: a systematic review // Bioelectromagnetics. - 2008. - Vol.29, N.4. - P.245-256.

2. Drozdov D.V. Influence of electrodes on the quality of registration of biopotentials // Medical technology and equipment. - 2010. - No. 1. - P.43–47.

3. Gotovsky M.Yu., Perov Yu.F. Electrochemical processes on electrodes during electropuncture diagnostics. Message 1. Direct current // Traditional medicine. - 2013. - No. 4 - P.4-9.

4. Martinsen Ø.G., Grimnes S., Haug G. Measuring depth depends on frequency in electrical skin impedance measurements // Skin. Res. Technol. 1999. - Vol.5, N. - P. 179-181.

5. Barnett A. The phase angle of normal human skin // J. Physiol. - 1938. - Vol. 93, No. 4. - P.349–366.

6. Plutchik R., Hirsch HR Skin impedance and phase angle as a function of frequency and current // Science. - 1963. - Vol.141, N.3584. - P.927-928.

7. Burton CE, David RM, Portnoy WM, Akers LA The application of Bode analysis to skin impedance // Psychophysiology. - 1974. - Vol.11, N.4. - P.517-525.

8. Reichmanis M., Marino AA, Becker RO Laplace plane analysis of skin impedance: a preliminary investigation // J. Electrochem. Soc. - 1978. - Vol. 125, N.11. - P.1765-1768.

9. Reichmanis M., Marino AA, Becker RO Laplace plane analysis of impedance between acupuncture points H-3 and H-4 // Comp. Med. East. West. - 1977. - Vol.5, N.3-4. - P.289-295.

10. Reichmanis M., Marino AA, Becker RO Laplace plane analysis of transient impedance between acupuncture points Li-4 and Li-12 // IEEE Trans. Biomed. Eng. - 1977. - Vol.24, N.4. - P.402-405.

11. Reichmanis M, Marino AA, Becker RO. Laplace plane analysis of impedance on the H meridian // Am. J. Chin. Med. - 1979. - Vol.7, N.2. - P.188–193.

12. Stoynov Z.B., Grafov B.M., Savova-Stoynova B., Elkin V.V. Electrochemical impedance. - M .: Science, 1991.

13. McAdams ET, Lackermeier A., McLaughlin JA, Macken D., Jossinet J. The linear and non-linear electrical properties of the electrode-electrolyte interface // Biosens. Bioelectron. - 1995. - Vol.10, N.1–2. - P.67–74.

14. Egorov Yu.V., Kuznetsova G.D. The brain as a volumetric conductor. - M .: Nauka, 1978.

15. Mirtaheri P., Grimnes S., Martinsen Ø.G. Electrode polarization impedance in weak NaCl aqueous solutions // IEEE Trans. Biomed. Eng. - 2005. - Vol.52, N.12. - P.2093 - 2099.

16. Geddes LA, Roeder R. Criteria for the selection of materials for implanted electrodes // Ann. Biomed. Eng. - 2003. - Vol.31, N.7. - P.879-890.

17. Kalvøy H., Johnsen GK, Martinsen Ø.G., Grimnes S. New method for separation of electrode polarization impedance from measured tissue impedance // Open Biomed. Eng. J. - 2011. - Vol. 5. - P.8-13.

18. Grimnes S., Martinsen Ø.G. Bioimpedance & Bioelectricity Basics. Second Ed. - San Diego, Academic Press, 2008.

19. Schwan HP Linear and nonlinear electrode polarization and biological materials // Ann. Biomed. Eng. - 1992. - Vol.20, N.3. - P.269–288.

20. Bordi F., Cametti C., Gili T. Reduction of the contribution of electrode polarization effects in the radiowave dielectric measurements of highly conductive biological cell suspensions // Bioelectrochemistry. - 2001. - Vol.54, N.1. - P.53–61.

21. Raicu V., Saibara T., Irimajiri A. Dielectric properties of rat liver in vivo: a noninvasive approach using an open-ended coaxial probe at audio / radio frequencies // Bioelectrochem. Bioener. - 1998. - Vol.47, N2. - P.325–32.

22. Marx J., Mikkelson W., Tjoe J., Raicu V. Correction of electrode polarization contributions to the dielectric properties of normal and cancerous breast tissues at audio / radiofrequencies // Phys. Med. Boil. - 2007. - Vol.52, N.22. - P.6589-6604.

23. Geddes LA, Da Costa CP, Wise G. The impedance of stainless steel electrodes // Med. Biol. Eng. - 1971. - Vol. 9, No. 5. - P.511-521.

24. Gabriel S., Lau RW, Gabriel C. The dielectric properties of biological tissues: II. Measurement in the frequency range 10 Hz to 20 GHz // Phys. Med. Biol. - 1996. - Vol.41, N.11. - P.2251–2269.

25. Davey CL, Markx GH, Kell DB Substitution and spreadsheet methods for analysing dielectric spectra of biological systems // Eur. Biophys. J. - 1990. - Vol. 18, No. 5. - P.255-265.

26. Schwan HP, Ferris CD Four electrode null techniques // Rev. Sci. Instrum. - 1968. - Vol.39, No. 4. - P.481–485.

27. Grimnes S., Martinsen Ø.G. Sources of error in tetrapolar impedance measurements on biomaterials and other ionic conductors // J. Phys. D. App. Phys. - 2007. - Vol.40, N.1. - P.9-14.

28. Schwan HP Alternating current electrode polarization // Biophysik. - 1966. - Vol.3, N.2. - P.181–201.

29. Scaramuzza M., Ferrario A., Pasqualotto E., De Toni A. Development of an electrode / electrolyte interface model based on pseudo-distributed elements combining COMSOL, MATLAB and HSPICE // Procedia Chemistry. - 2012. - Vol. 6. - P.69–78

30. Sluyters JH On the impedance of galvanic cell. I. Theory // Rec. trav. chim. –1960. - Vol.79, N.10. - P.1092-1100.

31. Sluyters JH Oomen JJC On the impedance of galvanic cell. II. Experimental verification // Rec. trav. chim. - 1960. - Vol. 79, N. 10. - P. 1101-1110.

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