CHARACTERISTICS OF IMPEDANCE PROPERTIES OF METALLIC BIOELECTRODES

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UDC 578.087.87:612.014.422

The dependence of interelectrode impedance on the type of metal, the area of the electrode, the method of finishing of its working surface, and the frequency of the current was studied. A series of 15 materials was obtained in order of impedance properties and definite correlation was established with the order of preparations of heavy metals based on the density of albuminates formed by them. The electrode difference between impedances of extreme members of the series was shown to be very substantial in the region of low frequencies but to become very small at frequencies higher than 10-50 kHz.

KEY WORDS: biolectrodes; electrode impedance; mechanical purity of finishing.

During measurement of electrical conductance of tissues, the bioelectrical activity of organs, and their electrical stimulation electrodes made from various metals are widely used. Their polarization (electrode) impedance is an important parameter characterizing the suitability of the chosen type of electrode for electrophysiological purposes. However, few comparative studies have been made in this field, allowing for the material from which the electrodes are made [1, 3, 6-12].

The object of this investigation was to study electrode impedance allowing for the type of metal, the area of the electrode, the method of finishing of its working surface, and the frequency of the current.

EXPERIMENTAL METHOD

Interelectrode impedance was measured in man (10 persons) and animals (15 rabbits) by the "two voltmeters" method [4], using percutaneous electrodes and frequencies within the range 0.1-100,000 Hz. Circular electrodes with an area of 3 cm^2, made from various metals, and with the usual mechanical purity of surface (within the range ∇5-∇6) were applied to shaved areas of the skin of both forearms. Besides metallic, liquid and graphite electrodes also were studied. Before each application the electrodes were lightly moistened with physiological saline. Since such incidental factors as incomplete identity of the electrodes for effective area, drift of skin impedance, and so on, have some effect on the variability of the experimental results, the difference between impedances of pairs of metals compared was judged on the basis of averaged results of three measurements made during alternation of the materials. To distinguish pairs of metals with different impedances reliably during comparison, the main experiments were carried out at a frequency of 1 Hz. The current used was below the threshold of stimulation and did not extend outside the linear region of the voltage—current characteristic curve of the interelectrode medium [5].

To estimate the effect of quality of mechanical finish of the electrode surface on impedance, besides ordinary electrodes (∇5-∇6), coarsely finished (∇3-∇4) and polished (∇9-∇10) electrodes also were used. Chloriding and platinizing of the electrodes were carried out by the usual methods, and chemical finishing with a mixture of nitric and hydrochloric acid lasted 5-10 min. The total number of measurements was 650.

EXPERIMENTAL RESULTS AND DISCUSSION

The materials could be arranged in the following order of decreasing electrode impedance: Ta, Ti, Ni, Al, Fe, W, Pb, C, Zn, Cu, Au, Pt, Cd, Hg. Whereas the difference in impedance between neighboring metals in the series was between 5 and 25%, between the extreme members

Department of Biophysics, N. E. Bauman Kazan' Veterinary Institute. (Presented by Academician of the Academy of Medical Sciences of the USSR P. N. Veselkin.) Translated from Byulleten' Eksperimental'noi Biologii i Meditsiny, Vol. 87, No. 5, pp. 494-496, May, 1979. Original article submitted April 19, 1976.

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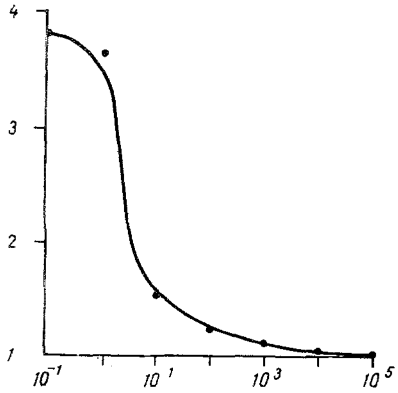

Fig. 1. Ratio of interelectrode impedance with tantalum and silver electrodes as a function of current frequency. Abscissa, frequency of measuring current (in Hz); ordinate, ratio between impedances obtained with tantalum and silver electrodes (in relative units).

it reached several hundred percent. When impedance was measured in an electrolytic cell using 1% sodium chloride solution the order of arrangement of the metals in the series was the same (Ni, Al, Fe, Cu, Au, Pt, Ag). Consequently, the order of the materials given above was valid for both percutaneous and conductometric electrodes. The results not only reveal the precise arrangement of individual metals in the series described previously [3] (Au, Ni, Al, Cu, Ag, Pt), but they also add to it substantially. The order of the metals revealed by the present experiment evidently applies also at higher strengths of current, for the series of materials (Fe, W, Au, Pt) obtained under the appropriate conditions [11, 12] also fits into the series given above.

In the next experiments the effects of different states of the working surface of the electrodes on the level of interelectrode impedance (Z) were evaluated. These experiments showed that annealing certain metals (Ti, Fe, and Ag) for 10 min at a temperature of 300-400°C with the aim of reducing their internal voltage, followed by removal of scale, caused no significant changes in impedance. The use of electrodes made from Ti, Al, Fe, Cu, and Ag, kept for over 3 h beforehand in physiological saline, led to a significant decrease in Z by 4-5% ($P < 0.05$). When polished electrodes of this group of metals were replaced by coarsely finished electrodes their impedance decreased by 15-25% ($P < 0.05$). Finishing the electrodes with a mixture of acids also led to a reduction in impedance by 15-25% ($P < 0.05$). Mechanical treatment of the electrodes with emery paper followed by keeping them in a mixture of acids caused no significant further decrease in the value of Z.

During coating of silver electrodes with silver chloride impedance is reduced by 5-25% ($P < 0.05$), and during blackening with platinum it is reduced by 10-20% ($P < 0.01$). On preliminary etching of silver electrodes with a mixture of acids, followed by chloriding, a further but very small decrease in Z takes place.

One possibility is that the decrease in impedance obtained by different methods of finishing the materials is based on an increase in the effective area of the electrodes. It must also be pointed out that processes of chemical and electrochemical finishing of electrodes are laborious, and the inadequate strength of the surface layer leads to an increase in impedance with time of 10-15%. Mechanical finishing of electrodes is to some extent free from these disadvantages, but as regards effectiveness of reducing impedance, it is only slightly inferior to the other methods.

Comparison of impedance of liquid and graphite electrodes showed that for electrodes of the first type the level of impedance is 26% less than silver plates with ordinary purity of surface (∇5-∇6). When comparison electrodes with a broken surface were used this difference disappeared. The complexity of construction of liquid electrodes and the absence of any appreciable difference in impedance makes their use undesirable in practice. Graphite electrodes, despite their broken working surface, have comparatively high impedance relative to silver and platinum electrodes.

With an increase in the quality of treatment of the epidermis an increase in the difference between impedances of the extreme members of the series by 1.5-2 times is observed. With a tenfold increase in the area of the electrodes (Ta and Ag; from 0.3 to 3 cm^2), however, the ratio between their impedances also increased by approximately 20% (data obtained at 100 Hz). The results of these investigations are evidence that with a decrease in the relative contribution of skin resistance, the difference between the impedances of the electrode pairs increases. Comparison of the frequency characteristics of impedances of two extreme metals

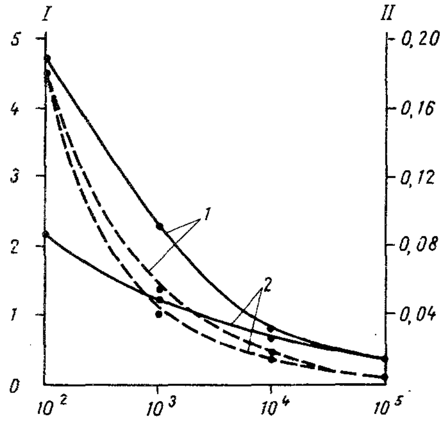

Fig. 2. Character of change in structure of impedance with tantalum (1) and silver (2) electrodes on increasing current frequency. Abscissa, frequency of current (in Hz); ordinate: I) active resistance R (in k); II) capacitance C (in F). Continuous line represents active component of impedance (R); broken line capacitance (C).

of the series (Ta and Ag) showed that the greatest difference between them is found in the region of the frequency spectrum of bioelectrical activity of the living organism (Fig. 1). As the working frequency of the current increases, this difference falls exponentially and, starting from 50 kHz, lies below the 5% level. When impedances of neighboring metals in the series are compared their difference can be disregarded at frequencies higher than 10 kHz. Consequently, whereas during electrography and low-frequency conductometry of biological objects, allowance must be made for the material from which the electrodes are made and the method of finishing their working surface, this is not necessary in rheographic investigations. During electrical stimulation of tissues the role of the material of the electrode is likewise very important.

The decrease in impedance due to the replacement of a tantalum electrode by silver is accompanied by a change in its structure. The greatest difference in the values of R and C is observed when low frequencies are used, and in particular between their active components (Fig. 2), and it is this which causes the shift in the position of the maximum of the phase angle of impedance. This factor must be taken into account during electrospectroscopic investigations of biological objects and the interpretation of their results.

The materials used in these investigations can be classed as heavy metals, and they are known not only to participate in the formation of polarization impedance, but also to have an astringent, irritative, and caustic action on biological tissue. Heavy metals in the order of decreasing density of albumins formed by them can be arranged in a certain sequence [2]: Al, Pb, Fe, Cu, Zn, Ag, Hg. Comparison of the metals of this series with the order of distribution of the metals by their impedance properties indicates that the two are to some extent identical. Consequently, the results and the method of impedance studies can evidently be used for preliminary forecasting of the pharmacological action of metals so far inadequately studied from this standpoint.

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