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Mark M. Goldin

G. J. Blanchard

A. K. Evseev

V. A. Kolesnikov

Yu S. Goldfarb

See next page for additional authors

Author(s)
Mark M. Goldin, G. J. Blanchard, A. K. Evseev, V. A. Kolesnikov, Yu S. Goldfarb, A. G. Volkov, and Mikhail M. Goldin

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REDOX POTENTIAL MEASUREMENT IN AQUEOUS SOLUTIONS AND BIOLOGICAL MEDIA

Mark M. Goldin[a], G.J. Blanchard[b], A. K. Evseev[a], V.A. Kolesnikov[a], Yu.S. Goldfarb[c], A.G. Volkov[d], Mikhail M. Goldin[b]

[a]Department of Electrochemistry Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, Moscow, 125047, Russia; [b]Department of Chemistry, Michigan State University,East Lansing, MI 48824-1322, USA; N.V. Sklifosovsky Research Institute for Emergency Medicine, 3 Sukharevskaya Pl., Moscow, 129010, Russia; [d]Department of Chemistry, Oakwood College, 7000 Adventist Blvd., Huntsville, Al 35896, USA

At the present time, measurements of oxidation-reduction potentials (ORP) in potable water are used extensively because the ORP is a simple and quite reliable parameter for quality control of drinking water. Since Vincent's work in the late 1940's, ORP measurements in blood and other biological media have also been applied to tissue evaluations [1]. The above methods are based on measuring the potential of a platinum electrode against the silver/silver-chloride reference electrode immersed in the medium under investigation. In other words, the phenomenon used here is that of a shift in the potential of the platinum electrode placed in an aqueous solution due to adsorption of oxygen on surface of platinum, first obtained by Frumkin [2].

Modern devices and methods designed to measure oxidation-reduction potentials (ORP) in water or biological media enable to obtain discrete value of ORP only. Because the working electrode is typically made of platinum, the platinum surface continually undergoes changes in the composition of surface oxides on the phase boundary. Therefore, each subsequent measurement occurs on newly oxidized or reduced surface of platinum (depending on oxidation-reduction properties of the medium tested). Indeed, if two or more measurements of potential are made sequentially, the disagreement in the measured ORP is considerable. For example, the difference between ORP of the same solution of Na_2SO_4 is ca. 100 mV (Figure 1, curves 1 and 2).

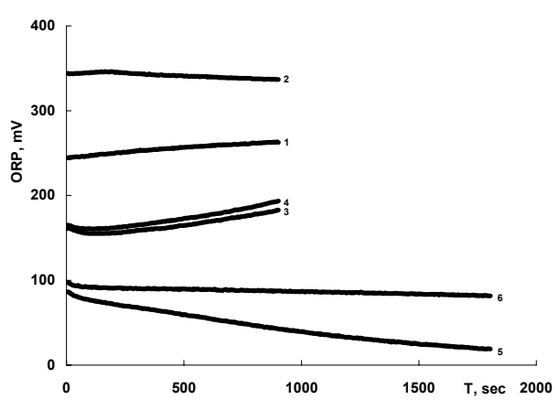

Figure 1. Measurements of ORP vs. time:
1, 2 - Na_2SO_4 0.14 M by the standard method; 3, 4 - Na_2SO_4 0.14 M by the proposed method (pretreatment of Pt electrode); 5 – blood plasma by the proposed method
6 – blood by the proposed method.

To freeze the composition of platinum surface oxides and, special pretreatment of the platinum working electrode (prior to each successive measurement) was developed. The platinum electrode was placed into a deoxygenated solution of inorganic salt prior to measurement, where it was treated by cyclic voltammetry with a rate of scanning of 500 mV/sec for 50 cycles in the potential range of -400 mV to +800 mV and then for 10 cycles in the range of +300 mV to +400 mV. This treatment led to a stable value of the working electrode potential (15—20 mV) in deoxygenated solution. The reproducibility of ORP measurements after such pretreatment is illustrated by curves 3, 4 (Figure 1). The maximal divergence of the results is less than 10 mV.

It is very important that, until now, ORP was generally considered a "stationary" value for a given solution; thus, discrete values of ORP were measured and discussed in literature (3). The data for blood and plasma (Fig. 1, curves 5, 6), as well as concentrated aqueous solutions of certain electrolytes show that ORP values change with time for various media. Therefore it is obvious that kinetic ORP measurements can uncover new information about the object tested. Further investigation of the kinetics involved in the above oxidation-reduction processes is necessary to develop a more reliable measure of ORP and apply such measurements for diagnostic or prognostic testing in medicine.

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