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ERROR OF MEASURING ELECTROLYTIC CONDUCTIVITY BY A CELL (JONES TYPE) DUE TO RADIAL DISPLACEMENT OF ITS PARTS AFTER ASSEMBLING

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The article describes the error in measuring the electrolytic conductivity of solutions using a differential electrolytic cell (with a removable central part), due to inaccurate assembling of its design. It appears when additional resistance of the test sample is formed after changing the current path in the solution in the presence of displacements between the parallel longitudinal axes of the connected parts of the cell. This resistance is similar to the constriction resistance defined in the theory of fixed electrical contacts. To take it into account when determining the required error, a parameter (the constriction coefficient) is introduced that characterizes the degree of constriction of the electric current lines at the joint of two parts of the cell. To evaluate the components of the error in the conductivity measurement, computer simulation of electrolytic cells and the finite element method were used. Expressions are obtained for determining the errors in measuring the electrolytic conductivity of solutions and cell resistance in the presence of radial displacement of parts of the cell after assembling. Using the finite element method, the dependences of the constriction coefficients on the radial displacement at the joints for cell models with different tube diameters are obtained. Also, the errors of measuring the resistance of cell models of different sizes are calculated. To evaluate the measurement error of electrolytic conductivity that can occur when using a specific measuring cell, the proposed expressions and the obtained dependences for the constriction coefficient can be used. Studies of cell models have shown that the error due to inaccurate assembling of differential cells can reach significant values (of the order of 0.01%) in the presence of radial displacements at the level of tens of µm. References 4, figures 4.
Key words: differential cell, radial displacement, solution, electrolytic conductivity, error, computer model, resistance.

Introduction. Electrolytic conductivity measurement is widely used to evaluate the degree of ionization of aqueous solutions. For accurate measurements of the electrolytic conductivity of solutions, a contact measurement method is used. According to this method, the electrical resistance of a solution sample is measured using a measuring cell. The cell provides a fixation of the shape of the test sample, a determination of its geometric dimensions, the supply and reception of measuring electrical signals. The measured resistance of the cell is theoretically strictly related to the geometric dimensions of the cell and the electrolytic conductivity of the sample solution. At the same time, various factors influence the accuracy of measuring the cell resistance. The main ones are associated with a number of parasitic phenomena that occur in the zone of contact of the solution with the measuring electrodes when an electrical signal is applied [1]. To eliminate the influence of these near-electrode processes on the accuracy of measuring the conductivity of solutions, two-electrode differential cells are widely used. The metrological centers of many countries use differential reference cells with a removable central part (Jones type) [1]. A differential cell of this type consists of three parts. Two identical half-cells contain fixed platinum electrodes and tubes for filling the cell with a solution. The third part of the cell (central) can be inserted and removed between two half-cells. It is a precision machined tube. The created differential cells in the leading world metrological centers are used to measure the electrolytic conductivity of solutions in the range of 0.001 S/m – 10 S/m. The extended measurement uncertainty lies in the range of 0.5% – 0.03% [1]. The main disadvantages of this type of differential cell are differences in the geometry of the solution column and possible contamination after each assembling of the cell.

The method for measuring the electrolytic conductivity of a solution using a differential cell of this type involves two measurements of the resistance between the electrodes of the cell. One measurement of resistance is carried out in the presence of the central part of the cell, and the second after its removal. The difference in the measured resistances depends on the geometric dimensions of the removable central part and is used to determine the electrolytic conductivity of the solution (k) according to the expression

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$$R_{\text{W}} - R_{\text{WO}} = \rho l / A = K_{\text{Cell}} / k \,, \tag{1}$$

where R_{W}, R_{WO} are cell resistances with and without the central part; l and A are the length and cross-sectional area of the central part of the cell; ρ is the resistivity of the solution; $K_{\text{Cell}}= l/A$ is the constant of the central part of the cell (called the cell constant).

When assembling parts of the cell (with and without the central part), there may be a radial displacement of its parts at their joint (i.e., the distance between the parallel longitudinal axes of the parts). Obviously, this will result in a decrease in the cross-sectional area of the conductive medium in the joint plane and a change in the path of the electric current inside the cell. These effects will lead to an increase in the resistance measured between the electrodes of the cell, compared with the resistance of the same cell at the most accurate assembling.

The purpose of the article is to evaluate the component of the error in measuring the electrolytic conductivity of solutions using a cell (Jones type), which will appear in the presence of radial displacements of parts of the cell after assembling.

Cell resistance measurement error. In the presence of radial displacements, the measured cell resistances with and without a central part (R_{mW} and R_{mWO}) will differ from the desired values (R_{W} and R_{WO} – resistance in the absence of displacements) by a certain amount (ΔR). Obviously, the value of ΔR in each case will depend on the values of the displacements (b) of the parts of the assembled cell. The measured cell resistances will be determined by the expressions

$$R_{\text{mW}}(b_1,b_2) = R_{\text{W}} + \Delta R_{W1}(b_1) + \Delta R_{W2}(b_2) = R_{\text{W}}(1+\delta_{W1}+\delta_{W2}) = R_{\text{W}}(1+\delta_{W}) \,, \tag{2}$$

$$R_{\text{mWO}}(b_3) = R_{\text{WO}} + \Delta R_{WO}(b_3) = R_{\text{WO}}(1+\delta_{WO}) \,, \tag{3}$$

where ΔR_{W1}, ΔR_{W2}, ΔR_{WO} are the additional cell resistances due to the presence of radial displacements at the joints (between half-cells and the middle part, half-cells without the middle part); b_1, b_2, b_3 are the values of the corresponding radial displacements; $\delta_{\text{W}}=\delta_{\text{W1}}+\delta_{\text{W2}}$, δ_{WO} are the corresponding errors in the measurement of cell resistances (with and without removable part).

The additional resistance of the cell in the presence of radial displacements of its parts can be compared with the "constriction resistance", which is defined in the results of the study of the resistance of a stationary electrical contact [2]. It says that the electric current lines should be constricted together, passing through the limited areas of the apparent contact surface, that causes an increase in resistance compared with the case of full conductivity. This increase in resistance is constriction resistance. An accurate calculation of the constriction resistance is very difficult even for idealized, symmetrical contacts.

In [2], "constriction areas" are called contact areas where, due to the smallness of the contact spots, the current lines are significantly curved. These areas in cylindrical conductors depend on the ratio of the radii of the contacts and the contact spot between them. As a rule, the actual area of electrical contact is much smaller than the area of the apparent contact surface. In the case of an electrolytic cell, the difference in similar areas is extremely small. It is determined by the very small radial displacement of the parts of the cell, which can occur during the next assembling. Given the geometric dimensions of real electrolytic cells with a removable central part [3, 4], it is obvious that the possible displacement is much smaller than the radius of the cell tubes. It can be assumed that the constriction areas in the connected parts of the cell will be small. They depend on the magnitude of the displacement and the radius of the cell tubes.

In the studies performed by the author, computer simulation was used to evaluate the magnitude of the constriction resistance in the areas of the joint of the cell parts (in the presence of radial displacement) and the corresponding error in measuring the cell resistance. The constriction area near one joint in the cell with the solution was investigated using a model to connecting two parts of the cell (two tubes with a solution) of different lengths and diameters. The value of the constriction resistance (ΔR_{S}) was calculated as the difference between the model's resistances in the presence of displacement (R_{b}) and without it (R_0), which were determined by the finite element method. The calculation results showed that the length of the constriction area in each of the connected cell parts can be considered (as applied to these studies) less than cell tube radius (r) at $b \ll r$.

As for electrical contacts, the constriction resistance in the electrolytic cell is proportional to the specific resistance of the solution. For further calculations, a parameter K_{S} (called the constriction coefficient) is used, which characterizes the degree of constriction of electric current lines in the area of one joint of the cell parts

$$K_S = (R_{\text{b}} - R_{\text{O}})\rho^{-1} = \Delta R_S k \,. \tag{4}$$

Further, it can be assumed (based on an evaluation of ΔR_S, actual cell sizes and possible radial displacements of cell parts) that the constriction coefficient of each cell joint depends only on the geometric dimensions of the joint and does not depend on the distance to the other joint and electrodes (this assumption will be verified).

Thus, the relative errors of measuring the resistance of the cell with and without the central part, due to the presence of radial displacements of the cell parts, according to (2–4), will be determined by the expressions

$$\delta_W = \delta_{W1} + \delta_{W2} = \frac{\Delta R_{W1} + \Delta R_{W2}}{R_W} = \frac{\rho (K_{SW1} + K_{SW2})}{\rho K_W} = \frac{K_{SW1}}{K_W} + \frac{K_{SW2}}{K_W}, \quad (5)$$

$$\delta_{WO} = \frac{\Delta R_{WO}}{R_{WO}} = \frac{\rho K_{SWO}}{\rho K_{WO}} = \frac{K_{SWO}}{K_{WO}}, \quad (6)$$

where K_{SW1}, K_{SW2}, K_{SWO} are the constriction coefficients for two joints in the cell with the central part and one joint in the cell without the central part; $K_W = kR_W$, $K_{WO} = kR_{WO}$ are the cell constants with and without the central part.

Calculation results. To evaluate the constriction coefficient of one joint in a cell, the finite element method was used. The dependences $K_S(b)$ were obtained for cell joint models with different internal radii of the tubes (5 mm, 7.5 mm, and 10 mm). The results were shown in Fig. 1 and Fig. 2 (the lengths of the connected tubes are equal to their inner radius).

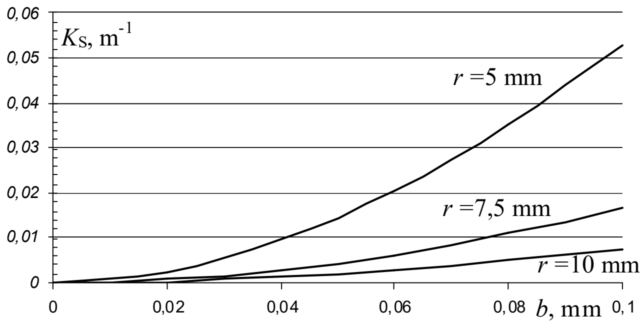

Fig. 1

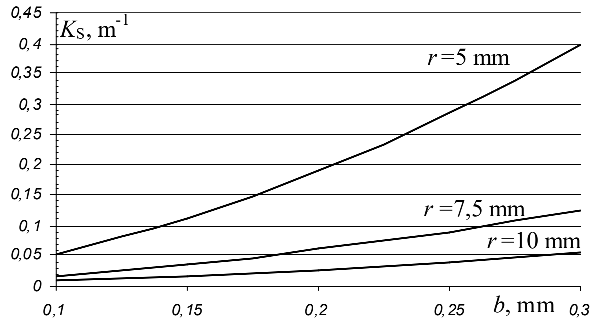

Fig. 2

The dependences $K_S(b)$ were calculated for various lengths of the cell parts forming the joint. The relative difference in the K_S values obtained with the length of the cell parts equal to the tube radius (r) and equal to $10r$ did not exceed several percent. Therefore, it can be assumed that each joint in the cell is characterized by its constriction coefficient, which depends on the radius of the tube (r) and the magnitude of the displacement (b).

To confirm the possibility of using formulas (5), (6) for evaluating the investigated error in measuring the cell resistance, the dependences $\delta_W(b) = \delta_{W1}(b_1) + \delta_{W2}(b_2)$ for cell models with different sizes were calculated by the finite element method. The case of identical displacements ($b_1 = b_2$) of the central part of the cell relative to the side parts was considered. In Fig. 3 and Fig. 4 show graphs of such dependences for two cell models with an inner radius of 5 mm (l = 80 mm, $K_{Cell} \approx 1000$ m^{-1}) and 7,5 mm (l = 10 mm, $K_{Cell} \approx$ 55 m^{-1}) for different values of the cell constant with central part (K_W).

Also, similar dependencies of errors are calculated by the formula (5), taking into account the

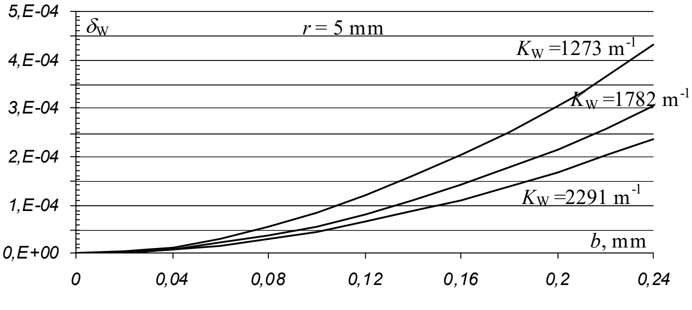

Fig. 3

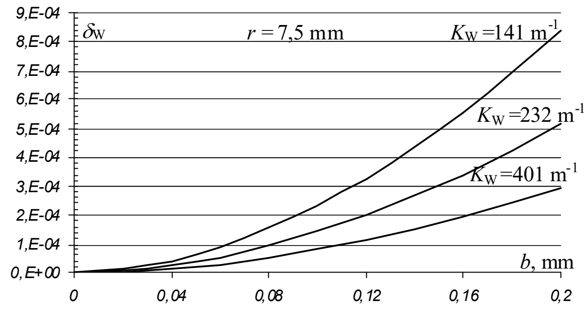

Fig. 4

previously determined values for (K_S). The relative difference in the values of the errors obtained in both cases does not exceed two percent. Therefore, in the presence of various displacements at the joints during the assembling of a cell of three or two parts, the calculation of the desired error can be carried out using formulas (5), (6) and the obtained dependences $K_S(b)$ for a certain radius of the cell tubes.

Studies show that the error in measuring the cell resistance (due to radial displacement of cell parts) is approximately proportional to the square of the displacement at the joint. Also, it is inversely proportional to the constant of the assembled cell. For a cell of three parts, the value of the error in the measurement of resistance can reach a significant value (of the order of 10^{-4}) in the presence of sufficiently large displacements (more than 0.05 mm) at both joints.

Measurement error of electrolytic conductivity. The considered errors in measuring the cell resistances will lead to the appearance of a corresponding additional error (δ_k) in determining the electrolytic conductivity of the solution. From (1), taking into account the expressions for the measured resistances of the cell (2), (3), the expression for electrolytic conductivity is

$$k = \frac{K_{Cell}}{R_{mW} - R_{mWO}} = \frac{K_{Cell}}{R_W - R_{WO}}(1-\delta_k) = \frac{K_{Cell}}{R_W - R_{WO}}\left(1 - \frac{R_W\delta_W - R_{WO}\delta_{WO}}{R_W(1+\delta_W) - R_{WO}(1+\delta_{WO})}\right). \quad (7)$$

Considering that the errors δ_W, δ_{WO} are much less than unity, an approximate expression for the errors δ_k is

$$\delta_k \approx \frac{\delta_W - \delta_{WO}K_{WO}/K_W}{1 - K_{WO}/K_W} = (\delta_W - \delta_{WO}K_{WO}/K_W) \times \frac{K_W}{K_{Cell}}. \quad (8)$$

Since $K_W / K_{Cell} > 1$, the investigated error in determining the electrolytic conductivity of the solution (8) using the differential cell can reach a value that will be greater than the error in measuring the resistance of the cell with the central part δ_W (at $\delta_{WO} = 0$).

Conclusions. The presence of radial displacements of the parts of the differential electrolytic cell (Jones type) after assembling leads to the appearance of an additional component of the error in measuring the cell resistance, which depends on the geometric dimensions of the cell and the magnitude of the displacements. It must be taken into account when determining the electrolytic conductivity of a sample of a solution.

For each joint in the cell, a "constriction coefficient" can be determined, that characterizes the constriction of the lines of electric current in the area of the cell joint. It depends on the radius of the cell tube and the magnitude of the radial displacement of the parts of the cell at the joint. Using computer simulation by the finite element method, the dependences of this coefficient on the displacement value for the joints of real cells are obtained.

To evaluate the investigated error in measuring the electrolytic conductivity of a particular cell, the expressions obtained in this work can be used. In this case, information on the cell constants (assembled from two and three parts) and the obtained dependences of the constriction coefficient on the magnitude of the radial displacement are needed.

The calculations show that the considered error in measuring the cell resistance can reach significant values (of the order of 0.01%) with radial displacements at the level of tens of μm. At the same time, the error in determining the electrolytic conductivity of the solution can be several times larger.

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ПОГРЕШНОСТЬ ИЗМЕРЕНИЯ ЭЛЕКТРОЛИТИЧЕСКОЙ ПРОВОДИМОСТИ ЯЧЕЙКОЙ (JONES TYPE), ОБУСЛОВЛЕННАЯ РАДИАЛЬНЫМ СМЕЩЕНИЕМ ЕЕ ЧАСТЕЙ ПОСЛЕ СБОРКИ

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В статье описана погрешность измерения электролитической проводимости растворов с помощью дифференциальной кондуктометрической ячейки (со съемной центральной частью), обусловленная неточностью сборки ее конструкции. Она появляется при образовании дополнительного сопротивления исследуемого образца после изменения пути протекания тока в растворе при наличии смещений между параллельными продольными осями соединяемых частей ячейки. Это сопротивление аналогично сопротивлению стягивания, определенному в теории неподвижных электрических контактов. Для его учета при определении искомой погрешности введен параметр (коэффициент стягивания), который характеризует степень стягивания линий электрического тока в области стыка двух частей ячейки. Для количественной оценки составляющих погрешности измерения электропроводности использовалось компьютерное моделирование электролитических ячеек и метод конечных элементов. Получены выражения для определения погрешностей измерения электролитической проводимости растворов и сопротивления ячейки при наличии радиального смещения частей ячейки после сборки. Методом конечных элементов получены зависимости коэффициентов стягивания от величины радиального смещения на стыках для моделей ячеек с различным диаметром трубок. Проведены расчеты погрешностей измерения сопротивления моделей ячеек разных размеров. Для оценки погрешности измерения электролитической проводимости, которая может возникнуть при использовании конкретной измерительной ячейки, можно воспользоваться предложенными выражениями и полученными зависимостями для коэффициента стягивания. Исследования моделей ячеек показали, что погрешность, обусловленная неточностью сборки дифференциальных ячеек, может достигать существенных значений (порядка 0,01%) при наличии радиальных смещений на уровне десятков µm. Библ. 4, рис. 4.

***Ключевые слова*:** дифференциальная ячейка, радиальное смещение, раствор, электролитическая проводимость, погрешность, компьютерная модель, сопротивление.

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ПОХИБКА ВИМІРЮВАННЯ ЕЛЕКТРОЛІТИЧНОЇ ПРОВІДНОСТІ КОМІРКОЮ (JONES TYPE), ОБУМОВЛЕНА РАДІАЛЬНИМ ЗСУВОМ МІЖ ЇЇ ЧАСТИНАМИ ПІСЛЯ ЗБІРКИ

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Описано похибку вимірювання електролітичної провідності розчинів за допомогою диференціальної кондуктометричної комірки (із з'ємною центральною частиною), обумовлену неточністю збірки її конструкції. Вона з'являється за утворення додаткового опору досліджуваного зразка після зміни шляху протікання струму в розчині у разі наявності зсувів між паралельними поздовжніми осями з'єднувальних частин комірки. Цей опір аналогічний опору стягування, визначеному в теорії нерухомих електричних контактів. Для його врахування під час визначення шуканої похибки введений параметр (коефіцієнт стягування), який характеризує ступінь стягування ліній електричного струму в області стику двох частин комірки. Задля оцінки складових похибки вимірювання електропровідності використовувалося комп'ютерне моделювання електролітичних комірок і метод кінцевих елементів. Отримано вирази для визначення похибок вимірювання електролітичної провідності розчинів і опору комірки у разі наявності радіального зміщення частин комірки після складання. Методом кінцевих елементів отримано залежності коефіцієнтів стягування від величини радіального зміщення на стиках для моделей комірок з різним діаметром трубок. Проведено розрахунки похибок вимірювання опору моделей комірок різних розмірів. Задля оцінки похибки вимірювання електролітичної провідності, яка може виникнути у разі використання конкретної вимірювальної комірки, можна скористатися запропонованими виразами і отриманими залежностями для коефіцієнта стягування. Дослідження моделей комірок показали, що похибка, обумовлена неточністю збірки диференціальних комірок, може досягати істотних значень (близько 0,01%) за наявності радіальних зсувів на рівні десятків µm.
Бібл .4, рис. 4.

Ключові слова: диференціальна комірка, радіальний зсув, розчин, електролітична провідність, похибка, комп'ютерна модель, опір.

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