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Influence of AC field distribution on impedance of the conductivity cell

Abstract

The AC impedance model of a liquid conductivity has been developed to assess the influence of electromagnetic vector potential. It has been proved that the field in a liquid conductor is quasi-static. Approximation error, even taken for very concentrated solutions (e.g. sea water), does not exceed 0.01 ppm. The calculation of resistance of the four-electrode cell is given with the account of Ampere's circuit law. Two types of errors are defined: DC error due to finite thickness of electrodes, and AC error due to presence of displacement currents when using an impedance model.

Keywords: measurement, electrolytic conductivity, electrical field, error.

1. Introduction

In recent years the leading national metrology institutes (NMI) have established the standards for electrolytic conductivity (EC) k [S/m], which is based on usage of direct or "absolute" method for reproducing this physical value [1]. Its essence is reduced to measuring of resistance R of a liquid column with length L and cross-section area S. There are several ways to implement such method in the global practice. Their overview is given in [2]. However, in all variants of the method's implementation the standard cell can be represented as one physical model in the form of conductor section resembling right circular cylinder. The proposed operation principle contains two hypotheses. Firstly, the impact of electrochemical impedance on the results of measurement is eliminated by using Jones differential cell or four-electrode cell. Secondly, the field is uniform in the cell. Thus, the cell constant can be calculated using known parameters: length L and cross-section area S. However, for precision measurements both hypotheses need to be revised. There are several factors which cause the non-uniformity.

i) Virtually in all countries which participated in key comparisons K36, measurements of the cell's resistance were conducted at alternating current [3]. Therefore, it is necessary to investigate an impact of the surface effect and the proximity effect of return lead.

ii) The presence of displacement currents needs to be taken into account. In a multi-element electrical equivalent circuit such currents can cause systematic error.

iii) The reason of error for thin electrodes is their finite resistance. In such case the surface of electrodes is not equipotential one.

iv) Primary conductivity cells have finite dimensions and specific geometry of electrode system, as well as design for filling/ discharging experimental solution. As a result, the profile of liquid within the cell can differ from the profile of cylinder.

v) Most primary cells (e.g. Jones's cell) use removable (movable) part of the cylinder. Thus, we can observe a change in the profile of the external surface of the measured liquid column.

Above mentioned effects lead to occurrence of a methodical error in resistance measurement. Such error is systematic by type. It is convenient to consider it as a relative value

$$\delta = R_C / R_H - 1 \qquad (1)$$

where: R_H is resistance of cylindrical conductor for an ideal model with uniform field; R_C is resistance with non-uniformity.

The paper considers the impact of factors i) -iii). These are primarily effects due to alternating character of the cell's operating current.

2. Calculation of impedance components of cylindrical conductor

In contact conductometry the change of the magnetic vector potential **A** with time can be ignored upon calculating the cell's resistance [4].

$$\frac{\partial \mathbf{A}}{\partial t} = 0 \qquad (2)$$

For precision conductivity measurements the following question presents an interest: what is an error due to such simplification?

2.1. AC impedance model

Most designs of the primary conductivity cells [1, 2] can be represented as a column of liquid located inside a tube made of insulating material. Therefore, an idealized physical model for calculating cell's resistance can be represented as a system of direct conductor 1 (of circular cross-section with diameter D) and linear (infinitely thin) return conductor 2 through which sinusoidal current flows in opposite directions, Fig. 1. Return conductor is located in parallel with direct conductor at a distance h from isolation 3. To reduce differences in potentials, two points a and b are selected. These points are located at a distance l along the direction of current. One of the potential wires runs in parallel to the axis of the conductor with current to the connection with the second potential wire, and then plaits with the latter. Plaited wires are connected to the measuring terminals c and d. Such configuration of conductors in the potential circuit will largely allow minimizing area, i.e. to ensure bifiliarity and thereby to create conditions to form coaxial measuring circuits [5].
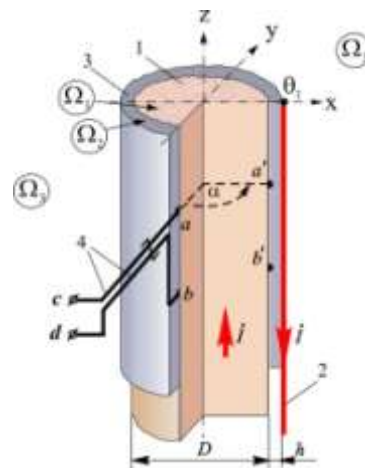

Fig. 1. Physical model of the conductor's section for measuring impedance

Let us use the well-known equation from the alternative formulations of Maxwell's equation:

$$\mathbf{E} = -\text{grad } \varphi - \partial\mathbf{A}/\partial t \qquad (3)$$

Where: $\mathbf{E}$, is the density of electrical field φ and $\mathbf{A}$ is the electrical (scalar) and vector potential.

Let us modify the expression with regard to the parameter $\mathbf{A}$.

$$\text{rot}\left(\frac{1}{\mu_0\mu} \, rot\, \mathbf{A}\right) + j\omega k\mathbf{A} - \frac{j\omega k}{S} \int\limits_{(S)} \mathbf{A} ds = \frac{I}{S} \qquad (4)$$

where: $S = \pi D^2/4$. From the last equation it is possible to derive the expression for the impedance components:

$$R_C = \text{Re}(Z) = R_H + \text{Re}\left(\frac{j\omega l}{IS}\int\limits_{(S)}\mathbf{A}ds - j\omega\mathbf{A}l\right) \qquad (5a)$$

$$X = \text{Im}(Z) = \text{Im}\left(\frac{j\omega l}{IS}\int\limits_{(S)}\mathbf{A}ds - j\omega\mathbf{A}l\right) \qquad (5b)$$

where $R_H = l/kS$ is resistance of the cylindrical conductor with uniform field which covers (1).

To assess an impact of electromagnetic induction, we have considered two types of conductors. These are the metals with electronic conductivity ($k = 10^7$–10^8 S/m) and electrolyte solutions with ionic conductivity ($k = 10^{-4}$–10^2 S/m). The results of numerical calculation of an error (1) are shown in Fig. 2.
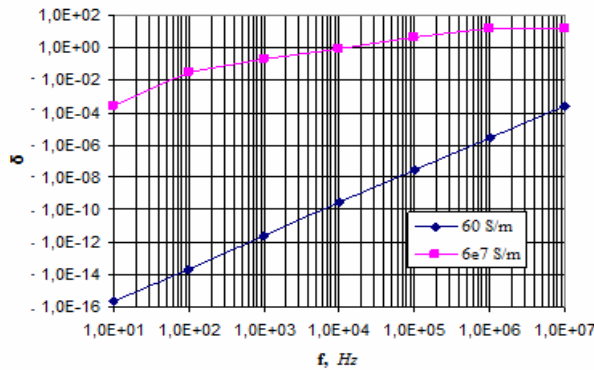

Fig. 2. Dependence of an error δ (eq. 1) of cylindrical conductor's resistance (Fig. 1) from frequency ($f = \omega/2\pi$) with geometrical dimensions D=10 mm, h=2.5 mm, for copper $k = 6 \cdot 10^7$ S/m and electrolyte solution $k = 60$ S/m

Fig. 2 shows that for concentrated aqueous solutions of electrolytes (of conductivity by 15 times higher than for sea water) we can ignore the occurrence of electromagnetic induction. Relative error in such case shall not exceed 0.1 ppm for frequencies less than 100 kHz. Such a small value can be disregarded in the budget of errors when assessing uncertainty even in the international comparisons.

At lower frequencies and in more diluted solutions an error will be even smaller. Thus, the field in conductivity cells can be considered as quasi-static [6] in primary conductivity measurements. Therefore, we can use the DC models in calculations of the components for electric and magnetic fields of conductivity cells.

2.2. Impedance quasi-DC model

It is known [5] that the best elimination of resistance in supply leads is achieved upon four-pair inclusion of an object. These requirements have been implemented when creating four-electrode AC conductivity cells. Their specific feature is the fact that current and potential electrodes are spaced over a distance, Fig. 3 [2].

Liquid is located inside the tube with inner diameter D and total length $L+2l$. The tube serves for the fixation of the liquid conductor geometry. It consists three sections: central section 1 and two side sections 2. Metal circular potential electrodes 3 are located at the ends of the central section 1, these electrodes 3 have thickness h_P and width which corresponds with the thickness of the tube wall. Two discs 4 are fixed at the edges of the tube. Inner surface of the discs is coated with metal films 5 with thickness h_T performing the function of current electrodes. The material for tubes and discs 4 is quartz glass which has good insulating properties, temporal stability and minimal coefficient of thermal expansion. Platinum is used as a metal for electrodes since such material has minimal polarizing effect for most electrolytes.
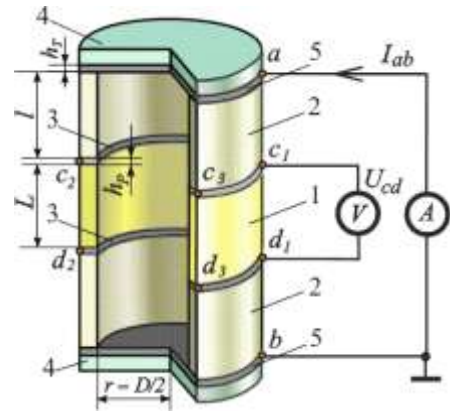

Fig. 3. Physical model of the four-electrode cell [2]

In the audio frequency range upon isotropic nature of solution one should consider electrolytic conductivity as a complex value. It follows from Ampere's circuital law.

$$\mathbf{J}_{total} = k\mathbf{E} + \frac{\partial\mathbf{D}}{\partial t} \qquad (6a)$$

Then, upon harmonic action we have:

$$\mathbf{D} = \varepsilon\varepsilon_0\mathbf{E} = \varepsilon\varepsilon_0 E(\mathbf{r})e^{j\omega t} \qquad (6b)$$

where: ε - relative permittivity, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m permittivity of free space.

Substituting the last equation, we receive:

$$\mathbf{J}_{total} = (k + j\omega\varepsilon\varepsilon_0)\mathbf{E} = \sigma\mathbf{E} \qquad (6c)$$

On this basis the full 3D task of calculating electromagnetic field can be reduced to 3D task of so-called approximation of small currents which significantly simplifies the calculation. In this case the task is reduced to solving calculation subareas (electrolyte column and quartz tube) of Laplace equation

$$\nabla\sigma_i\nabla\varphi = 0 \qquad (7)$$

where $\sigma_i = k_i + j\omega\varepsilon_0\varepsilon_i$ is a complex electrolytic conductivity, ε_i is a relative permittivity of electrolyte or quartz.

Upon conducting calculations the following requirements were set: the outer and inner diameters of the quartz tube (15 and 10 mm correspondingly); the length of the central tube section (30 mm); electric conductivity of platinum (10^7 S/m) and of quartz (10^{-14} S/m); relative dielectric permittivity of electrolyte (81) and of quartz (3); operating frequency (1000 Hz). Variations undertook lengths of the side tube sections, thicknesses of current and polarizing electrodes, values of liquid's EC.

According to the results of calculation the values were determined for electric potentials in points c and d. Total current was calculated by integrating the normal component of the current density by an arbitrary cross section of the tube with electrolyte. Further on, according to (1) we determined the relative error. The results of numerical analysis are shown in Fig. 4.

The character of dependence $\delta(AC)$ is explained by the presence of two components (sources) for such error $\delta(AC)=\delta_h+\delta_\varepsilon$. The first component δ_h causes almost linearly increasing character of the error's dependence starting from $\sigma \approx 1$ S/m. It shows that for such EC range the resistance of the liquid column between the current and potential electrode is low and becomes comparable with the resistance of the current electrode 5, Fig. 3. As a result, the share of the drop in potential (voltage) on the current electrode increases in the overall distribution of the potential of the cell.
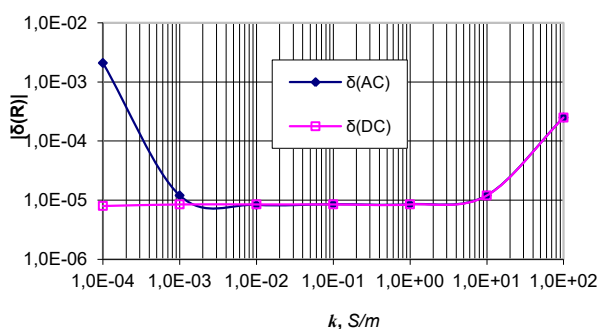

Fig. 4. Dependence of the module of error $\delta(R)$ from conductivity EC for the thickness of electrodes $h_T= h_P=0.3\mu m$

The surface of thin films 5, Fig. 3, is not the surface of equal (uniform) potential. To reduce this component of the error δ_h we can suggest the following:
- Calculate the value of the error and consider it as a correction to the measurement results. However, in this case it is necessary to measure the thickness of electrodes.
- Increase the thickness of electrodes. But electrode can becomes loose and its operational reliability can get worse.
- Change manufacturing technology. For such purpose the discs 4, Fig. 3, shall be made of metal.

The second component δ_ε in area $\sigma < 1$ mS/m indicates the contribution of the displacement currents in high-resistivity area of the EC range. The character of such error component is close to the quadratic dependence. For example such value for distilled water can reach 0.3%.

From matching of errors $\delta(AC)$ and $\delta(DC)$ in low-resistivity area of EC range it follows that $\delta(DC) = \delta_h$. Thus, the calculation of error on the direct and alternating currents allows us to consider errors δ_h and δ_ε separately.

3. Analysis of results

In this paper we do not consider the phenomena that describe the near-electrode processes at the border of metal /solution. They are modeled by the electrochemical impedance. Typically, this is the Randles equivalent circuit [7], for which is necessary to devote a separate study. The models discussed in sections 2.1, 2.2, and our subsequent arguments relate exclusively to the bulk impedance [8]. Upon quasi-static character of the electrical field is

$$I_{ab} = \int\limits_{(S)} \mathbf{J}_{total}ds = -\left(k + j\omega\varepsilon\varepsilon_0\right) \int\limits_{(S)} \mathrm{grad}\,\varphi\, ds \qquad (8a)$$

$$U_{cd} = -\int\limits_{c}^{d} \mathrm{grad}\varphi\, dl \qquad (8b)$$

Two circuit models: impedance and admittance, are used

$$Z_C = U_{cd}/I_{ab} \; , \qquad (8c)$$

$$Y_C = I_{ab}/U_{cd} \qquad (8d)$$

Then for the impedance model we receive:

$$R_C = \mathrm{Re}\left(\frac{U_{cd}}{I_{ab}}\right) = \frac{K}{k}\mathrm{Re}\left(\frac{1}{1 + j\omega\varepsilon\varepsilon_0/k}\right) \qquad (9)$$

where: K - is the cell's constant, $K/k = R_H$ is the resistance of some liquid volume with uniform field.

From equations (8) and (9) follow few interesting properties.
• Firstly, the cell constant in general is defined by the expression:

$$K = \frac{\int\limits_{c}^{d} \mathrm{grad}\,\varphi\, dl}{\int\limits_{(S)} \mathrm{grad}\,\varphi\, ds} \qquad (10a)$$

For a uniform field, when grad φ = const, we obtain the well-known formula

$$K = \frac{L}{S} = \frac{4L}{\pi D^2} \qquad (10b)$$

where S, L, D - are the cross-sectional area, length and diameter, respectively, of the tube 1 in Fig. 3.
• Secondly, the ratio $j\omega\varepsilon\varepsilon_0/k$ characterizes the phase shift between density $\mathbf{J}$ of current and strength $\mathbf{E}$ of electric field. Lets denote this ratio as the tangent of the phase angle φ

$$\omega\varepsilon\varepsilon_0/k = \mathrm{tg}\phi \qquad (11a)$$

The phase shift occurs due to the presence of the bias current. In the equivalent circuit diagram, this phenomenon appears as the admittance of C_B in Fig. 5.
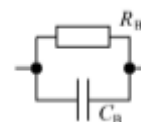

Fig. 5. Equivalent circuit of the liquid conductivity in AC field

In this scheme $G_B = 1/R_B$ and C_B - are, respectively, the electrical conductivity and the capacity of the liquid column inside the tube 1 in Fig. 3. They are the parameters of the bulk conductance. In the circuit theory, a phase shift of the parallel circuit is defined as:

$$\mathrm{tg}\phi = \omega C/G \qquad (11b)$$

To use this equation, a calculations similar to (8) and (9) must be performed firstly. But numerical methods are here inconvenient for further analysis. There are methods for calculating linear (per unit of length) parameters. They are based on conformal transformations and on Schwarz-Christoffel integral [9, 10]. In modern research, for the calculation of the planar electrodes of biosensor transducers these methods are successfully used [11]. For electrodes of different geometry solution is the ratio of elliptic integrals as tabular data. However, the model of volume impedance is a parallel RC circuit.

Third, for the harmonic excitation of the electrical field the parameter $\omega\varepsilon\varepsilon_0$ is orthogonal to the parameter k (8a). In the theory of electrical circuits (equivalent circuits) this is reflected as orthogonal admittance components of conductance G and

capacitance C. Both parameters can be calculated independently of each other [11] . Therefore we can write as useful the relation:

$$\frac{k}{G} = \frac{\varepsilon\varepsilon_0}{C} = K \qquad (12)$$

This means that the cell constant can be calculated theoretically or experimentally for determine separately the both, active and reactive, components of the admittance. In the experimental assessment, G and C are obtain as the measurement results. It is important to note that a calculated constant of capacitance is independent on the electrode processes. This property can be used to analyze the frequency corrections to the constant of secondary two-electrode conductometry cells.

From the signal conversion point of view the equation (12) is the ratio of input and output physical quantities. Hence, the cell constant and the conversion factor of the cell as sensor are reciprocal quantities.

Impedance model and properties (8-12) are the cause of several contradictions. Some of them, we propose to discuss.

4. Discussion

1. Quadratic character of dependence for the error δ_ε (Fig. 4) calls for more detailed studies of the impact of displacement current on the result of calculation. From (1) and (9) the following expression for the impedance model is easy obtained:

$$\delta_\varepsilon = \mathrm{Re}\left(\frac{1}{1+\mathrm{jtg}\,\phi}\right) - 1 = \frac{\mathrm{tg}^2\phi}{1+\mathrm{tg}^2\phi} \approx \mathrm{tg}^2\phi \qquad (13)$$

Approximate expression is true for small tangents. The last two equations are analytic expressions justifying quadratic character of the frequency dependence of the error component $\delta(AC)$ from liquid's EC obtained by numerical methods and from the range $k < 1$ mS/m shown in Fig. 4.

Other, analytical methods calculation gave similar results [9-11]. It should be noted that error δ_ε is the methodical error. If the result of measurement is presented not in the form of resistance (5a, 9) but in the form of conductivity (14), then the error δ_ε will be absent. It is fair that by definition we receive the following expression

$$G_C = \mathrm{Re}\left(I_{ab}/U_{cd}\right) = k/K \qquad (14)$$

The result does not depend on frequency, and the error δ_ε is absent. However, the requirement to present the result of measurement in the form of conductivity contradicts with the requirements for primary measurements. It is known that in a contact conductometry electrochemical processes appear on the line metal/solution. Such processes are interfering factors. Therefore, in the precision conductometry a differential measurement method and impedance cell model [1, 2, 12] practically in the most cases are used to eliminate the influence of electrochemical impedance. But in this case, in accordance with (9, 13), the error will occur. We can't abandon the impedance model because electrochemical impedance will not be compensated in an efficient way. The solution is seen in what can be used, but the result of measurement shall be corrected by value $\delta_\varepsilon R_H$, which follows from (1, 9). If it will not be applied, then we will get significant methodical error for solutions with low concentration according to (1, 13). For example, for super pure water ($k \approx 200$ µS/m) at frequency 10 kHz such error will reach 4%. It should be noted that this effect shall be considered both for primary cells and for secondary precision cells [13].

2. The method given in [1, 12] laid on the extrapolation procedure. When $\omega \to \infty$ assumed that $R_C \to R_B$. But from the Bode diagram (9) at $\omega \to \infty$ we get $R_C \to 0$. This coincides with the experimental results [11]. As a contradiction, it is pointed out in [8]. The reason lies in the bias currents of the solution, which in the high-frequency shunt conductivity currents. Therefore, extrapolation procedure provided for $\omega \to \infty$ should be reconsidered. Full electric model of two contact electrode conductivity cell should be verified.

3. In [14] a definition of EC for DC current is given. It is the first component of (15). At the same time, in most NMI the primary EC standard is implemented with using AC measurement procedures. For AC field of frequency ω the following chain of relations is obvious

$$k_{def} \equiv \frac{\mathbf{J}}{\mathbf{E}} \equiv \frac{k\mathbf{E}+\partial\mathbf{D}/\partial t}{\mathbf{E}}^{(\sin)} \equiv k + \mathrm{j}\omega\varepsilon\varepsilon_0 \qquad (15)$$

The equality $k_{def}=k$ is possible only if $\omega = 0$. Hence, for the AC in the definition of [14] there is a contradiction and the new definition valid for the AC is needed

$$k_{def} = \mathrm{Re}\left(\frac{\mathbf{J}}{\mathbf{E}}\right) \qquad (16)$$

Otherwise, for the harmonic AC current a new physical quantity is need to introduce. This vector quantity can be called "complex electrolytic conductivity of the liquid." It is related to the known characteristics of the measured liquid (k, and ε) by the following expression:

$$\sigma = k + \mathrm{j}\omega\varepsilon\varepsilon_0 \qquad (17)$$

5. Conclusions

1. The relative error caused by the phenomenon of induction is linearly dependent on EC. Even for fairly concentrated solutions of electrolytes (sea water) such error does not exceeds 0.1 ppm at frequencies less than 100 kHz. It means that interaction is not observed between electric and magnetic components of the field. The field in solutions of electrolytes is the quasi static field. Therefore, for the calculation of the electric fields in environments with ionic type of conductivity models of direct current are used.

2. For diluted aqueous solutions of electrolytes or for organic solvents it is necessary to consider bias currents. Upon harmonic nature of the field within the cell electrolytic conductivity will be a complex value. The electrical model of volume impedance should be represented in the form of two-element parallel capacitive equivalent circuit. It is convenient to assess the phase shift in such circuit using such parameter as tangent of the phase angle. For its determination there is no need in calculating conductivity and capacity in a separate way. It is possible to use the parameters of complex EC.

3. For primary methods of reproducing the small values of EC (diluted solutions), for which differential measurement method of resistance is applied, it is necessary to make a correction. It is connected with the parameters recalculation from the parallel to series equivalent circuit. Without such approach for $k < 100$ µS/m at frequencies (10-100) kHz the error can reach units in percents.

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