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Possibilities of Employing a Calculable Four-electrode Conductance Cell to Substitute the Secondary Standards of Electrolytic Conductivity

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Abstract - It seems that a four-electrode conductance cell designed and used according to the van der Pauw method can be applied for an absolute determination of electrolytic conductivity of solutions with an accuracy comparable with that of the secondary standards of this quantity. Therefore a possibility of avoiding the use of those standards in some cases can be expected. The results of experimental investigations of a prototype model of the cell of that type, carried out by the authors, are consistent with the theoretical considerations and results of computer modelling. An absolute determining of electrolytic conductivity has been made for 0.01 and 0.1 M KCl solutions, with an overall uncertainty lower than 0.5 %.

I INTRODUCTION

An absolute determination of electrolytic conductivity (specific conductance) of the electrolyte solutions being used as the primary standards of this quantity is performed with application of conductance cells with well-defined, calculable geometry. At present the primary standards of the electrolytic conductivity are two aqueous KCl solutions of concentration 0.01 and 0.1 m (molal scale), measured with a two-electrode conductance cell having a removable cylindrical center section of accurately known length and cross-section area (electric field appearing there may be considered to be perfectly homogeneous) [1]. The overall uncertainty of those standards was estimated to be 0.03%. The secondary electrolytic conductivity standards, those are also electrolyte solutions, are used for calibration of conductance cells for most routine applications. The solutions prepared in molar scale (e.g. 0.01, 0.1 and 1 M KCl) are commonly used in practice for this purpose [2]. Their accuracy depends on purity of the components used and the accuracy of determining their mass and volume. There also commercially available calibration solutions of given conductivity values, e.g. 100 000 $\pm$ 25 µS/cm [3]. For many years numerous works, e.g. [4][5], have been devoted to an idea of realization of calculable four-electrode conductance cells enabling direct, absolute (i.e. without use of calibration solutions) and accurate measurements of electrolytic conductivity. Such an approach seems to be very attractive because it can give simultaneously two important advantages:

- the four-electrode measurement can minimize the errors resulting from polarization effects, also at relatively low measuring frequencies and without the use of platinum platinized electrodes (use of them can cause serious errors in some cases [4]),
- the absolute determination of electrolytic conductivity can eliminate the necessity of using calibration solutions and calibration procedures.

The above presented idea has been realized in two main ways:

- by applying a cell with homogeneous electric field [4] (a classic approach),
- by applying a cell with heterogeneous electric field, designed and used according to the van der Pauw method [5][6][7] (a novel approach).

The second one approach seems to have a number of virtues:

- it can give a good averaging of local resistivities of the solution sample measured [8],
- it may be easier for accurate manufacturing because its cell constant depends on a smaller number of factors (geometrical dimensions),
- its potential electrodes are located in the area of low strength of the electric field thus they will not disturb significantly the field distribution in the sample, etc.

Although a number of works have been devoted till now to investigations of the four-electrode conductance cells designed according to the van der Pauw method, no one, in the opinion of the authors, has solved the problem completely. It should be stressed there that the application of the van der Pauw method for the electrolytic conductivity measurements differs significantly from its original application for the measurements of solid state materials. In the first case an influence of an interfacial layer (electrode polarization impedance) must be additionally taken into account. An intention of the authors is to complete investigations of such a type cell with considering the unavoidable appearance of the interfacial layer. This paper is a preliminary report from an experimental work undertaken for an investigation of metrological properties of a prototype model of the four- electrode conductance cell designed and applied according to the van der Pauw method. The main task is to prove its ability to substitute the use of secondary standards of electrolytic conductivity.

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II PRINCIPLE of FOUR-ELECTRODE MEASUREMENT of ELECTROLYTIC CONDUCTIVITY USING the van der PAUW METHOD

The method of four-point probe measurement of electrical conductivity of conducting materials, elaborated by van der Pauw [7], in its original approach deals with the measurement of solid-state materials formed into flat samples of uniform thickness and arbitrary shape. The method can be applied without knowing the current pattern in the sample if the following conditions are fulfilled: the sample is homogeneous in thickness, the contacts (electrodes) are sufficiently small and they are at the circumference of the sample, the surface of sample is singly connected, i.e. the sample does not have isolated holes. The method, widely used for measuring the electrical conductivity of crystals and compressed powders, usually formed as circular disc samples, may be applied as well for an absolute determination of electrolytic conductivity of solutions [5]. The measured sample of a solution forms a cylinder of height h - Fig.1. Four metal electrodes 1, 2, 3, 4 of a very small width are located at the circumference of the cylinder, in parallel to its axis. Two neighboring electrodes, 1 and 4, are used to carry an electric current I_c to the sample. A potential difference V_p is measured between two remaining electrodes, i.e. 2 and 3. According to the van der Pauw theorem the following relationship is fulfilled then:

$$\exp(-\pi\, h\, R_{14,23}\, \kappa) + \exp(-\pi\, h\, R_{12,34}\, \kappa) = 1 \qquad (1)$$

where κ is the conductivity of the solution,
$R_{14,23} = V_{p23}/I_{c14}$ is the resistance of the sample ("four-electrode resistance") defined for the potential electrodes 2 and 3, and the current electrodes 1 and 4 (as in Fig.1), $R_{12,34} = V_{p34}/I_{c12}$ is the resistance of the sample when 3 and 4 are the potential electrodes and 1 and 2 are the current-carrying ones. For a symmetrical electrode configuration, when $R_{14,23} = R_{12,34} = R$, the electrolytic conductivity κ of the sample can be expressed as:

$$\kappa = \ln 2/(\pi\, h\, R) \qquad (2)$$

In this case a single measurement suffices to determine κ. The cell constant of such a conductance cell is:

$$K_n = \kappa\, R = \ln 2/(\pi\, h) \qquad (3)$$

Thus the cell of a unity height h = 1 cm has $K_n = 0.22064$ 1/cm. Applying the above described geometry one can obtain then a four-electrode conductance cell with a heterogeneous current paths distribution but with well-defined, calculable cell constant K_n. The K_n value depends on one characteristic parameter only - the height h. For comparison, the cell with homogeneous electric field [1][4] has its cell constant $K_u = 4L/(\pi\, d^2)$ where L is the length and d is the diameter of the cylinder. Thus its K_u value depends on two characteristic dimensions, in this one in the second power. Assuming that the only factors influencing the cell constants are those characteristic dimensions and that all the dimensions are determined with the same inaccuracy, the cell constant K_n can be determined with a three times lower inaccuracy than K_u. Deviations from the assumption of the van der Pauw method, e.g. finite dimensions of electrodes and their non-ideal location at the circumference of the sample have been theoretically considered in [6][5]. Using (2) and (3) one assumes symmetry of the resistances, i.e. $R_{14,23} = R_{12,34}$. If their values are not equal, an equivalent mean value R_m has to be calculated as [6]:

$$R_m = f\,(R_{14,23} + R_{12,34})/2 \qquad (4)$$

where f is a coefficient depending only on the ratio $R_{14,23}/R_{12,34}$ (when this ratio approximates 1, also f coefficient approximates 1). However, the assumptions of the method formulated by van der Pauw for solid-state materials seem to be unsufficient when the electrolyte solutions are measured.. This problem has not been discussed till now in any known publication. An interfacial layer always appears at the boundary metal electrodes - solution. The layer has features of an electrical impedance with a capacitive reactance component. The value of this impedance (electrode polarization impedance) depends on many factors, most of all on the electrode material and its surface state, type and concentration of the solution, as well as on the measuring frequency applied. The electrode impedance can have its value comparable with, or even considerably greater than the resistance of the solution filling the cell , particularly that the cell has a rather small value of its cell constant K_n. There is a number of questions to be answered, e.g.: (i) does the appearance of electrode impedance influence the electric field distribution in the solution sample filling the cell, and thus the four-electrode resistances measured according to the van der Pauw method? (ii) what additional conditions should be fulfilled when applying the van der Pauw method for measurements of the electrolytic conductivity of solutions? (iii) what feasibility of absolute determination of the electrolytic conductivity using the van der Pauw method can be expected ? Some answers can be found by theoretical considerations and computer modelling [9]. In this way it has been found, for instance, that current-carrying

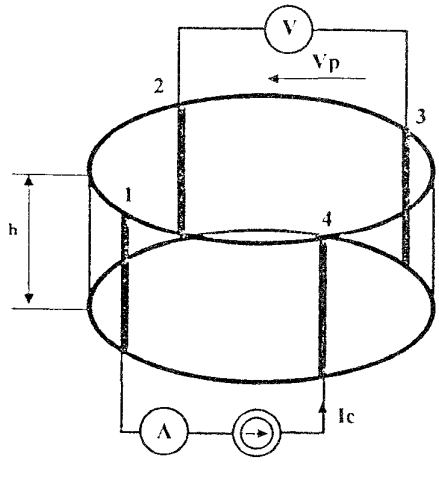

Fig.1 Principle of the four-electrode measurement of electrolytic

electrodes of the cell should be driven from a constant-current source. In this case current paths distribution and resulting from that potential distribution in the solution sample are not affected by the electrode impedance even that of a considerable big value. However, full answering all the questions requires carrying out experiments with a real cell.

III THE DESIGN of THE CONDUCTANCE CELL, EXPERIMENTS

The construction of the cell

A conductance cell has been design according to Fig.1. The cell body is made up of polymetacrylan. It has shape of a regular cylinder, with an inner diameter of 50 mm and height of 22 mm. The cylinder is permanently closed from both its sides (first experiments, performed with an open cell, showed a noticeable influence of stray field effect or meniscus effect) and has a small filling tubing mounted along the cylinder diameter. The four stainless steel electrodes, each of width of 1 mm, are symmetrically located at the inner circumference of the cylinder. Their length is equal to the height of the cylinder. The cell constant value calculated from (3) is 0.10029 $^{+}_{-}$ 0.00023 1/cm, assuming the mean value of h to be determined with the uncertainty $^{+}_{-}$ 0.05 mm.

Experiments

Three major experiments are necessary to answer the questions asked in part II: (j) measurement of the cell resistances (defined according to the van der Pauw method) at various frequencies and for at least two different solutions, (jj) the same as in (j), repeated in all possible configurations of the cell connections, (jjj) determination of the electrolytic conductivity of at least two different calibration solutions. These experiments have the following aims: (j) is a commonly used test for determining polarization impedance influence on the conductance cell impedance, (jj) has to prove symmetry of the resistances measured in the cell. (jjj) has to prove whether the conductance cell being considered is really calculable.

The computer driven measuring system applied for measurements of the cell resistances consists of a Hewlett-Packard HP 34401A multimeter and a reed-relay multiplexer. The cell is put into a constant temperature chamber and the temperature of the solution filling the cell is measured using a Pt100 resistance thermometer. Current-carrying electrodes of the cell are supplied from an audio frequency sinewave generator output connected in series with a resistance box (to ensure constant-current supply) and a polystyrene capacitor of 100 μF capacitance (to eliminate any dc offset). The current is measured as a voltage drop across a known resistance. A Metex M 4650 multimeter, driven from the same computer system, is applied for measuring the generator frequency. Two KCl solutions, 0.01 and 0.1 M, were measured at temperature 18 °C, in the frequency band 20 - 6000 Hz. The current applied was 0.6 and 3 mA, respectively. The cell electrodes connection was changed in the clockwise direction using the multiplexer, starting from the configuration shown in Fig.1.

IV RESULTS and DISCUSSION

The measurements performed in all possible cell connection configurations showed that four-electrode resistances of the cell were constant over a relatively wide band of measuring frequency. The ratio of these resistances measured at a given frequency to their values measured at 200 Hz is presented in Fig.2. Letters a,b,c,d denote particular configurations, "a" letter denotes the configuration shown in Fig.1.

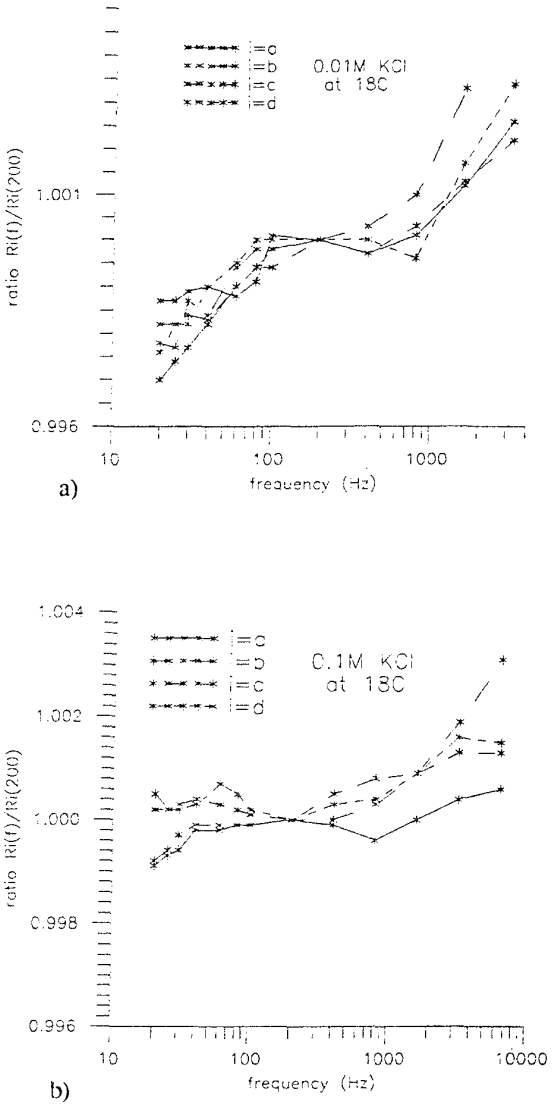

Fig.2 Four-electrode resistances of the conductance cell measured in particular connection configurations at a given frequency, related to their values at 200 Hz, as a function of applied frequency.

The variation of this ratio is below ± 0.1% in the frequency range 60 - 800 Hz for 0.01M solution (Fig. 2a)and 20 -1600 Hz for 0.1M one (Fig. 2b). That means a weak influence of the polarization impedance on the four-electrode resistances of the cell at those frequencies. For comparison, there is shown in Fig.3 a plot of two-electrode resistance of the cell (measured between current-carrying electrodes) as a function of the measuring frequency. The variations observed are hundreds times greater. That confirms a high effectiveness of the four-electrode method of measurement. It was found that the four-electrode resistances $R_{14,23}$ and $R_{12,34}$, i.e. measured for adjacent configurations, were considerably different although the cell was intended to be made symmetrically. The difference was about 0.7% in the case of 0.01M solution and about 1% for 0.1M one. It cannot be absolutely said whether that resulted from an irregularity in the electrode arrangement (it was impossible to check again the geometry because the cell was permanently pasted). However, the four-electrode resistances measured for opposite configurations, e.g. $R_{14,23}$ and $R_{23,14}$, were equal. This is an important test because it proves the interchangeability of current and potential electrodes, according to the reciprocity theorem for passive fourpoles. Because of the considerable asymmetry of the resistances obtained in two adjacent configurations it was necessary to apply (1) or (4) to calculate an equivalent mean value of those resistances. When assuming f = 1, the discrepancy between the results found from (1) and (4) was below 0.06%. The mean resistances determined from (4) for particular pairs of adjacent configurations are presented in Fig.4 as the ratios of these resistances determined at a given frequency related to the mean value from the results obtained at 200 Hz. The mean resistance calculated for all the configurations applied is also shown there (abcd curve), for comparison. All these results show variations smaller than ± 0.1% in the measuring frequency range 60 - 800 Hz for 0.01M solution (Fig. 4a) and 20 - 1600 Hz for 0.1M one (Fig. 4b). Therefore there is a freedom in choosing measuring frequency.

The results of an absolute determination of the electrolytic conductivity of 0.01M and 0.1M KCl solutions using the conductance cell investigated are presented in Table 1. There are also given the cell four-electrode resistances measured in particular connection configurations, the mean resistances calculated for adjacent configuration and for all the configurations as well. The difference between the measured conductivity and that reported in literature [2] is - 0.25% in the case of 0.01M solution and + 0.18% for 0.1M one. These results may be considered to be very good ones as the overall instrumentation error (root-sum-square error) is estimated to be about ± 0.5 %. A coefficient $S_{\kappa 0.01/0.1M}$ defined as the ratio of the conductivities of 0.01 and 0.1 M solutions, commonly used as a quality factor in testing conductance cells, is also presented in Table 1. Its observed value, not differing from the reported value by more than 0.5 %, additionaly confirms correctness of the results obtained. The uncertainty of measuring the temperature of the solution filling the cell seems to be the most critical part of that error. Moreover, there was found that measuring a strongly conducting solution a great attention should be paid to avoid excessive heat dissipation in the cell, appearing as a drift of measured

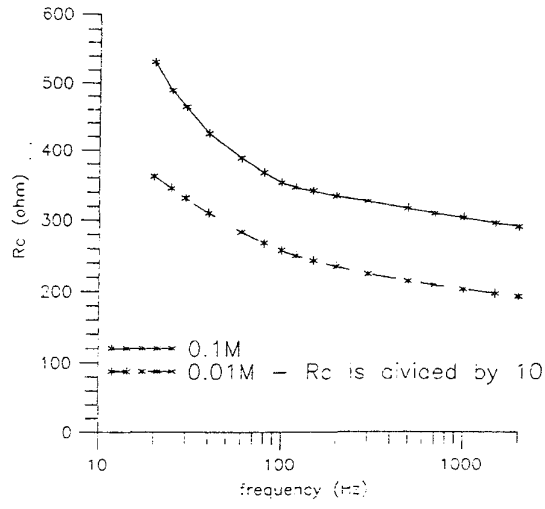

Fig.3 Two-electrode resistances measured between current-carrying electrodes of the conductance cell, as a function of frequency.

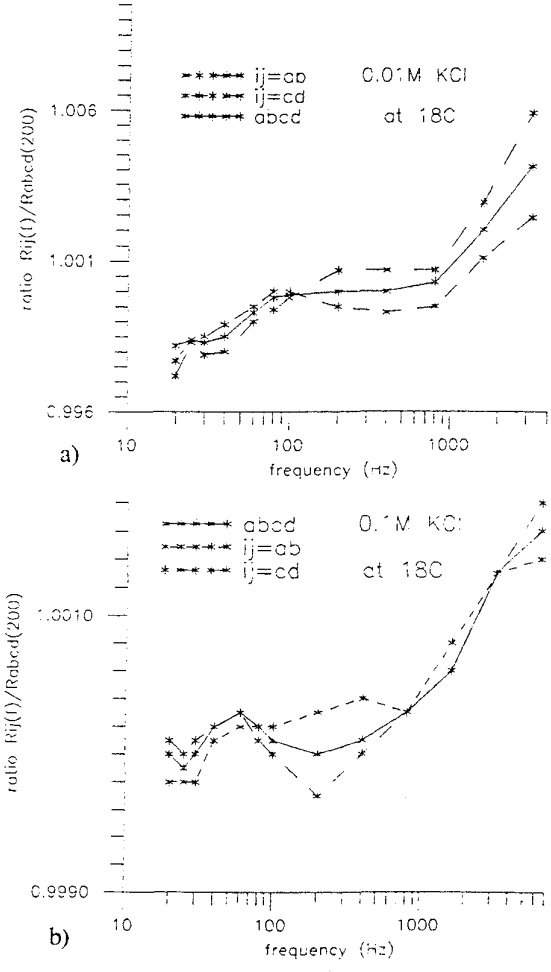

Fig.4 Equivalent mean four-electrode resistances of the conductance cell determined for particular connection configurations at a given frequency, related to the mean resistance value for all the configurations applied at 200 Hz, as a function of frequency.

Table 1

Results of an absolute determining the electrolytic conductivity of 0.01 and 0.1 M Kcl solutions at 18 ^{0}C, at 80 Hz measuring frequency

	Four-electrode resistances of the cell measured in particular conection conigurations (ohm)									Conductivity κ (mScm^{-1})	
					mean values R_m						
Solution	a	b	c	d	ab	cd	ad	bc	abcd	observed	reported [2]
0.01 M	81.73	82.31	81.83	82.41	82.02	82.12	82.07	82.07	82.07	1.222	1.225
0.1 M	8.900	9.002	8.903	8.992	8.951	8.948	8.946	8.953	8.949	11.21	11.19
$S_{\kappa\ 0.01/0.1\ M}$					0.1091	0.1090	0.1090	0.1091	0.1090	0.1090	0.1095

$S_{\kappa\ 0.01/0.1\ M} = \kappa\ (0.01\ M) / \kappa\ (0.1\ M) = R_m\ (0.1\ M) / R_m\ (0.01\ M)$

resistance value. For that reason it is advisable to reduce to minimum measuring current. This is a disadvantage typical for such type conductance cell. It has, from principle, small electrode surface area and thus large resistances and large voltage drops in the regions surrounding current-carrying electrodes [9].

CONCLUSIONS

The following conclusions can be formulated considering the results obtained in the experiments performed with the conductance cell presented there:

1) An application of the van der Pauw method for measuring the electrolytic conductivity of solutions is feasible when supplying current-carrying electrodes of the cell from a constant-current source.
2) The mean value of the four-electrode resistances measured in two adjacent configurations of the cell connection may be considered as a measure of the electrolytic conductivity of a solution filling the cell.
3) Some precautions have to be undertaken to avoid an excessive heat dissipation in the regions of current-carrying electrodes.

The authors are going to redesign the cell to give it the features of a device useful for routine measurements. Some improvements are necessary to introduce, e.g.:

- designing the cell with an available access to its electrodes (to clean them when necessary) but still with a closed electric field,
- improving heat sinking from the cell (measuring current cannot be decreased too much) or increasing the electrode surface area to a value being accepted from the point of view of fulfilling the assumptions of the method, etc.

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