INFLUENCE OF GEOMETRIC UNCERTAINTIES ON THE ACCURACY OF CALCULATED CONSTANT OF THE PRIMARY CONDUCTIVITY CELL

MIKHAL A.[1], *WARSZA Z.*[2]

1 Institute of electrodynamics National Academy of Science, Kiev, Ukraine, a_mikhal@ukr.net
2 Industrial Research Institute of Automation and Measurements PIAP, Warszawa, Poland. zlw@op.pl

Abstract.

This report presents a functional diagram of the Ukrainian primary standard of electrolytic conductivity (EC) and construction of primary four electrode conductivity cell with the calculated coupling constant. The equations for calculating the cell constant and budget of errors for calculating uncertainty are presented. The components of budget are: error due to the non-uniformity of the force lines of the electric field; the error due to accuracy of measurement standards and measuring instruments when determining length and diameter of the tube; the error due to manufacturing techniques of tubes and their assemblage. The article considered in details the error due to non- ideal profile of the central part of the tube.

The process of precision machining and quality control of the inner surface of the tube are complex and expensive procedures. The report gives an algorithm for measuring of length and diameter of the tube. Experimental data show that distortion of profile may be two types. The first type is deviation of the tube profile from the rectangle along the longitudinal section. The reason is the precession of the grinding tool. The second type is deviation of the profile of the tube from circumference in the cross section. The reason is the presence of wedge-shaped cracks on the inner surfaces of the work piece. The presence of deterministic component in the distortion of the profile leads to a significant increase in the standard deviation of the mean (SDM).

The paper presents two methods to reduce the standard deviation: the method of linear interpolation for compensation of the concaveness which occurs along the axis of the tube and the method of equivalent triangles to compensate deviations from the circle that occurs across the axis of the tube.

Keywords: conductivity, primary cell, geometric errors, standard deviation.

1. INTRODUCTION

In the recent years, standards of the electrolytic conductivity (EC) have been established in the leading industrialized countries. These standards are a basis for the "absolute (direct)" method of the reproduction of conductivity of solution as physical quantity [1]. There are a lot of ways used to implement this method; however, the principle of operation is almost the same [2 - 4]. It is based on measurement of the resistance of the liquid column and calculation of the EC on the known length and cross sectional area of this column. The uncertainty of the standard by many factors will be affected. The most significant are errors of calculation of the constants of the primary cell. Components of the error caused geometric parameters of the liquid column have the greatest contribution. We consider these components of the error in primary four electrode conductivity cell, which is used in the national standard EC of Ukraine [4 - 6]. The basis of the primary cell is the sensor element. The sketch of it is shown in Fig. 1.

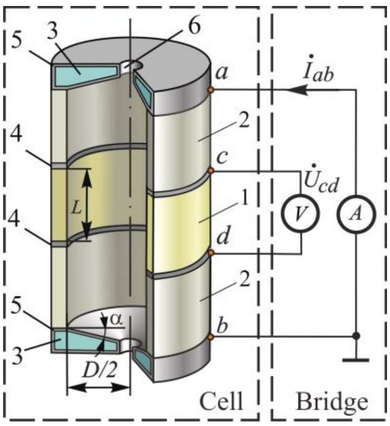

Fig. 1. Construction of the primary conductivity cell

The sensor element is a tube with an internal diameter *D*. The tube is filled with an electrolyte solution. As a rule, this is a solution of KCl (potassium chloride). This tube is used to fix the geometry of the liquid conductor. It consists of three parts. The central part of the tube 1 has a length *L*. Two side portions 2 have the same length *l*. At both ends of the central portion of the tube 1 the ring of potential electrodes 4 is plotted. Their width corresponds to the thickness of the tube wall. At the edges of the tube two discs 3 are fixed. The metallic film 5 is coated on the inner surface of the discs. It performs the function of current electrodes. Discs 3 have two central holes 6 of diameter *d*, which serve to pour the liquid. Inner disc surface has the form of a cone with an angle α. This configuration is intended to facilitate the removal of air bubbles when pouring the liquid into the cell. The tube and the discs are made of quartz glass. It has good insulating properties, the temporal stability and minimum coefficient of the thermal expansion. Electrodes are made from platinum, which is applied because of a minimum polarization effect for the most electrolytes Four points *a*, *b*, *c* and *d* of the cell are connected to the bridge, used for measurement of the conductivity or resistivity of the liquid column.

The cell constant as the ratio of the length of the tube 1 to the square cross-section is determined by calculation.

This definition is true for the idealized measured object with a uniform distribution of the current streamlines. Distortion of the streamlines will be exist due to: the presence of holes for grouting liquid, the form of the current electrodes, the presence of potential electrodes and not ideal profile of the inner quartz tube 1 (Figure 1). Therefore the calculated value of cell constant has error.

2. BUDGET OF UNCERTAINTY CELLS

The constant K of the standard conductivity cell shown in Figure 1 is calculated from its dimensions. This constant can be determined from the mean values of diameter D_{av} and length L_{av} of the tube obtained from measurements.

$$K = \frac{4L_{av}}{\pi D_{av}^2} \qquad (1)$$

The calculated value of K has the uncertainty u_K dependent on some priori unknown relative systematic errors δk_i:

$$u_K = F[\delta_{St}, \delta_{Cal}, \delta_{Geom}(\delta_{Tec}, \delta_{PE})] \qquad (2)$$

where: δ_{St} – error due to the accuracy of measurement standards and measuring instruments used to determine the length and diameter of the tube; δ_{Cal} - error due to the deviation of the computational model of the cell constant in real terms from the idealized model; δ_{Geom} – the estimated error of geometric dimensions.

Estimation of the standard or expanded uncertainty u_k can be find if probability distributions of above errors from (2) are also estimated. Any attention on the method of processing the uncertainty u_K (function F) is not paid here. This subject is regulated by international normative documents as GUM.

Errors δ_i of the equation (1) can also have a number of their own components. Possibility of minimizing the error δ_{St} is limited by the level of metrological support of measurements of the tube length and diameter. It is defined by the accuracy of standards and length measurements.

The error δ_{Cal} has two causes, and accordingly that - two components: the error of the measurement of alternating current and the error due to violation of the homogeneity of the electric field in the cell, which becomes for finite size and design features. Both components have been analyzed in detail in [7, 8].

The geometric error δ_{Geom} has also two components:

δ_{Tec} – the error due to manufacturing techniques used for sections of tubes and assemblies thereof;

δ_{PE} – the error due to the presence of potential electrodes. This error depends on the final thickness of the potential electrode and on the displacement its axis during assembling. This component is related on the calculation of the electric field inside the cell and will be discussed in detail in other papers.

In this report the error δ_{Tec} is in detail only examined. It have two components: δ_L – the error of length and δ_D – the diameter measurement error. Both components are determined by the profile of the internal section 1 (Fig.1) of quartz tube, which depends on capabilities of the manufacturing technology. The problem arise as the cost of production of the reinforced quartz crystal tube becomes extremely high. As a rule, the cell tube is manufactured from a precision machining preform (finished tube). If thickness of the tube is maximized then geometric dimensions of the cell are not changed in time and in the wide range of temperature. For this purpose roughing and grinding of inner profile of the work piece for the minimum depth is made. On the other hand on the inner surface of the work piece can be wedge cracks parallel to the axis of the work piece. They are due to manufacturing techniques and depend on the quality of nozzles through which the work piece is pulled itself. Therefore, the processing of tubes is not deep a deviation from the circle along the entire profile may exits. The second reason for not an ideal profile is the precession of the grinding tool. During processing the control of the tube quality is not possible. After a final sanding the profile of tubes can differ from the ideal rectangle.

By modern technologies of processing quartz glass the tube with the stable length is much easier to manufacture than tube with the stable internal diameter. From the experimental data we observe distortions of the internal profile of the two types. The first - is a deviation from the profile of the tube along the longitudinal section of the rectangle. The reason is the precession of the grinding tool. The second – is roughness of the circumference of the tube cross section. The reason is cracks on the inner wedge-shaped surfaces of the quartz preform.

To determine the actual profile of the tube, its diameter and its length must be measured by the following special algorithm. Measurements of the tube length L have to be made in different directions in p points which are laying uniformly circumferentially. Conventionally, the tube along the length into m sections is uniformly divided. In the cross section of each such section n measurements of the diameter in different directions are made. As result of measurements, $n \times m$ values of the diameter pipe and of p values of the length is obtained.

Mean diameter of the tube is determined as

$$D_{av} = \frac{\sum_{i=1}^{m} D_{i,av}}{m} = \frac{\sum_{i=1}^{m} \sum_{j=1}^{n} D_{ij}}{m \cdot n} \qquad (3)$$

where: D_{ij} - j diameter in the i-th section of the tube and $D_{i,av}$ - mean diameter in the i-th section of the tube.

If such classical averaging of results of measuring the diameter (eq. 3) is used then the standard deviation of D_{av} significantly rises. Hereinafter, this is the standard deviation of the mean diameter (SDM). For each i-th section it is evaluated by the formula:

$$\sigma_{iD} = \sqrt{\frac{1}{n(n-1)} \sum_{j=1}^{n} (D_{ij} - D_{iav})^2} \ . \qquad (4)$$

Then the related measurement uncertainty of the diameter D_{av} can be expressed as:

$$\delta_D = \frac{1}{D_{av}} \sqrt{\frac{1}{m(m-1)} \sum_{i=1}^{m} \sigma_{iD}^2} \ . \qquad (5)$$

2.1 Error in the longitudinal section

Geometric dimensions of the individual fabricated tube much more accurately can be measured than the standard uncertainty of its production process. As the example on Fig. 2. results of measuring the mean diameter of section of some tube unit with n = 8 and m = 10 are shown

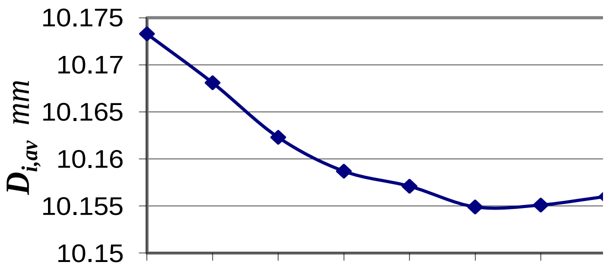

Fig. 2. Profiles along the axis of the tube.

These data indicate that average diameters of the section 1 and 6 differ by 20 μm. In general, the profile of the internal section of the tube can be an arbitrary function $D(x)$. Results of measurements the average diameter along the length of the tube (Figure 2) indicate that this dependence is fully determined. On basis of obtained discrete data the linear interpolation of the function $D(x)$ may be applied and then the result of K is following

$$K = \frac{4}{\pi}\int_0^L \frac{dx}{D(x)^2} = \frac{4}{\pi}\sum_{i=0}^{m}\int_0^{\Delta X_i} \frac{dx}{(ax+b)^2}, \tag{6}$$

where: a and b - linear interpolation coefficients of $D(x)$; ΔX_i - the length of the region between i-th and i +1 section.

Coefficients of the polynomial $D(x)$ can be expressed as:

$$a = \frac{D_{i+1} - D_i}{\Delta X_i} \tag{6a}$$

$$b = D_i \tag{6b}$$

After simple transformations, the expression for calculating the constant K takes now the form:

$$K = \frac{4}{\pi}\sum_{i=1}^{m}\frac{\Delta X_i}{D_{i,av}D_{i+1,av}}, \tag{7}$$

Let us now on Figure 3 to show graphs of the SDM of measurement results of the diameter without deterministic component and using linear interpolation of the deterministic component. If the deterministic component of the diameter D_{iav} is taking into account, it can be seen that SDM of measurement results are laying around almost near one value. The range of dispersion of these results is much smaller if compared to the case where the deterministic component is ignored and average value of the diameter by equation (3) is calculated. As the result of such correction the SDM changes along the cross-section are reduced 10 to 15 times.

It should be noted that such a correction method shifts the average value of the diameter. Therefore, the constant K of the tube 1 (Figure 1) calculated by the equation (2) or (7)

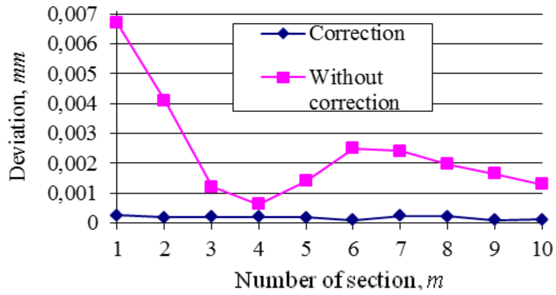

Fig. 3. Influence of the linear interpolation of the diameter D on the level of SDM (σ_{iD}).

differs on 0.027%. This value was used for correction to reduce the bias error of the calculated value of constant K of the primary cell.

2.2 Error of the cross-section

Let us consider such tube, for which the values of the mean diameter of the each section along the virtually horizontal line are grouped. However, the profile of each individual cross-sectional surface differs from the circle. In Fig.4. function of deviations from the mean D_{iav} (D_{iav}=2×4,569 mm is represented by te circle) of one of the sectors with m=3 are shown

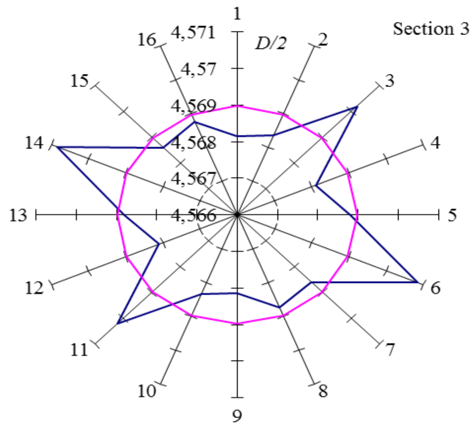

Fig. 4. Profile across the axis of the tube, section m=3.

In all ten sections of m = (1-10), observed is the triangular deviation along the lines 3 - 11 and 6 - 14. For such profile distortions the method the equivalent triangles can be used. The effective area S_{ief} of the tube section can be find and and subsequent adjustments of diameter is made. Algorithm for computing is following: diameters of the section 3 and 6 replaced are by the value of the average diameter D_{av}. Using the standard formula the base values of the mean diameter D_{bias} and the sectional area S_{bias} of the tube are calculated, ie.:

$$S_{bias} = \pi(D_{bias})^2/4 \tag{8}$$

Next, the offset value in each section separately is calculated. It represents the areas of triangles:

$$S_i = c_i h_i/2 \tag{9}$$

where: c_i - base of the triangle in the direction of lines 3 and 11 or 6 and 14 (Fig. 4);

h_i - height of the triangle in the direction of standard 3 and 11 or 6 and 14 (Fig. 4).

The influence of the deterministic component is taken into account by forming the effective area of each section as follows:

$$S_{ief} = S_{bias} + 2\sum_{i=3,6} S_i = S_{bias} + \sum_{i=3,6} c_i h_i \qquad (10)$$

The corrected value D_{icor} is calculates by formula

$$D_{icor} = \sqrt{4S_{ief}/\pi} \qquad (11)$$

This value substitutes D_{iav} in equation (2), (3).

Differences between the values of the SDM (with and without correction) are shown on Fig. 5.

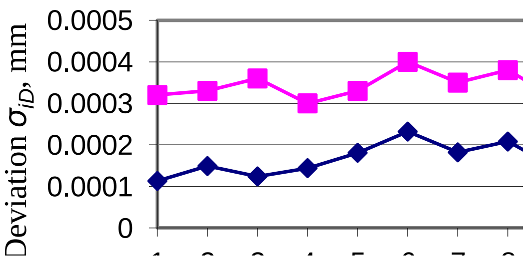

Fig. 5. Standard deviation SDM (σ_{iD}) without correction D_{iav} and with correction D_{icor}.

As from Fig. 5 can be seen, the SDM with correction of the deterministic-centered component is 2.5 - 3 times smaller than without correction. The mean diameter is shifted when the algorithm of the effective areas is used. The constant K calculated by equations (2), (3) or by (2), (11) differs each other on 0.015%. Just as in the previous case, for the correction of the bias error in computation of the constant K of the primary cell the value D_{icor} is used.

3. CONCLUCIONS

Diameters D_{ij} of the primary standard tube are measured by the instrument with LSB 0.1 μm. From Figures 3 and 5 follows, that methods of the correction of the deterministic component of the profile allow for reduction the SDM of geometric dimensions to the level of the sensitivity of measuring instrument. For example, if cells are produced with deviation of up to 20 μm (Fig. 2) and the error of the diameter and length measurements is less than 0.4μm, then the expanded uncertainty of the determination of constants K does not exceed 0.004%.

Thus the use of the proposed methods minimizes the uncertainty of the primary conductivity standard. Correctness, sufficiency and adequacy of the selected models of correction the influence of no ideal profile of the cells is confirmed by international comparisons. In these measurements the primary standard of Ukraine (laboratory UkrCSM) was involved [6]. Results are shown on Fig. 6.

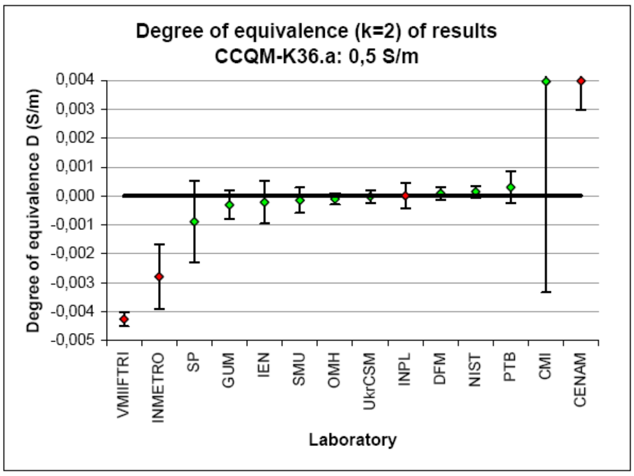

Fig. 6. Results of international comparisons CCQM-K36.a of the primary conductivity standard of Ukraine [6].

ACKNOWLEDGEMENTS

Authors would like to express their best gratitude to Gavrilkin V. G., Head of department of metrological provision of physical and chemical quantitative measurements (lab. UkrCSM), for agreement to publish data on Figure 6 and for his very valuable advice.

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