

INTERNATIONAL
RECOMMENDATION

OIML R 68

Edition 1985 (E)

Calibration method for conductivity cells

Méthode d'étalonnage des cellules de conductivité



Foreword

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CALIBRATION METHOD for CONDUCTIVITY CELLS

1. Introduction

The conductivity of an electrolytic solution is defined using the formula :

$$x = \frac{j}{E} \quad (\text{S / m}) \quad (1)$$

where :

j is the current density (A/m^2) and

E is the electric field strength (V/m),

between the electrodes of the cell filled with the electrolytic solution.

Since an exact determination of the values of the quantities j and E is difficult, the measurement of conductivity of an electrolytic solution is carried out mainly by the method of comparison with a standard electrolytic solution having a known value of conductivity.

From the conductivity value x_0 (S/m) of the standard electrolytic solution and the measured resistance R_0 (Ω) between the electrodes of the conductivity cell, the constant K of the cell is determined using the formula :

$$K = x_0 \cdot R_0 \quad (\text{m}^{-1}) \quad (2)$$

Consequently, the conductivity of another electrolytic solution can be determined according to the formula :

$$x = K \cdot \frac{1}{R} \quad (\text{S / m}) \quad (3)$$

where R (Ω) is the measured resistance between the electrodes in the same cell, filled with the electrolytic solution under test.

The process of determination of the constant K is called calibration of the conductivity cell.

2. Scope

2.1. This Recommendation deals with the calibration of conductivity cells by direct or indirect reference to standard solutions covered by the International Recommendation No. 56 « Standard solutions reproducing the conductivity of electrolytes ».

The Recommendation determines the fundamental requirements for the calibration method based on the above formula (2).

Other calibration methods are accepted provided that they give similar results.

2.2. Conductivity cells calibrated according to this Recommendation may be used for measuring the conductivity of aqueous and non-aqueous solutions within the range $0.1 \text{ S/m} \leq x \leq 100 \text{ S/m}$.

3. General conditions

3.1. The conductivity of an electrolytic solution may be determined from the measured resistance of the cell, when it contains the solution, and the constant K of the cell.

3.2. The value of the cell constant K depends on the construction of the cell, on the temperature and concentration of the solution, on the measuring frequency, on the pollution of the coating of the electrodes, etc.

To obtain the highest possible accuracy of calibration, it is necessary to determine the influence of these factors.

3.3. The standard solutions, the instrument for measuring the resistance and the conditions of calibration shall be such that the inaccuracy in the determination of the constant K does not exceed the maximum permissible error as given in the certificate or in the technical documentation.

4. Preparation for calibration

Before starting the calibration, the following operations shall be carried out.

4.1. Electrodes

Check the rigidity of the fixing of the electrodes and the state of their surface. If the coating of the electrodes presents some defects (whitish surface, stains, spots, etc.), remove this coating and apply a new coating.

4.2. Degreasing and washing of the cell

The cell shall first be degreased with the appropriate solvent according to the materials of which the cell and electrodes are made, and then carefully washed with distilled water.

4.3. Standard solutions

The standard solutions shall be prepared in a quantity sufficient for the calibration.

The following may be used for calibrating the conductivity cells :

- either standard solutions as defined in the Recommendation No. 56, or
- working standard solutions, the conductivity of which has been determined by measurement in a conductivity cell calibrated with standard solutions as defined in the Recommendation No. 56.

5. Calibration

5.1. The cell shall be washed at least 5 times with the standard solution ; the solution of the last washing shall be left in the cell for 10 minutes.

After washing, the cell shall be filled with a new sample of the standard solution which will be used for the measurement.

5.2. The cell containing the solution shall be brought to 25 °C in a thermostatic bath and maintained at thermal equilibrium.

If the cell is designed to work with solutions at a temperature which differs from 25 °C, the calibration shall be carried out at the specified operating temperature.

- 5.3. The liquid in the thermostatic bath shall be the same during calibration and during conductivity measurements.
- 5.4. The measuring frequency on the cell shall be the same during calibration and during conductivity measurements and appropriate corrections shall be made for any differences in the frequency effect between standard and test solutions.
- 5.5. During calibration, the resistance of the electrolytic solution, measured between the electrodes of the cell, should preferably be between 100 Ω and 10 k Ω .
- 5.6. The cell constant K shall be determined using at least 3 standard solutions, the conductivity of which shall correspond approximately to the lowest, middle and highest values of the measuring range of the cell.
- 5.7. If the variation of the constant K , in relation to the conductivity of the electrolytic solution, is less than the maximum permissible error for the cell, as given in the certificate or in the technical documentation, the cell constant shall be calculated as the arithmetic mean of the values $K_1, K_2, K_3...$ obtained for the different standard solutions.
- 5.8. If the variation of the constant K , in relation to the conductivity of the electrolytic solution is greater than the maximum permissible error for the cell, curves of the relationship « cell constant — measured resistance (conductance) » shall be drawn and, according to this diagram, the cell constant shall be determined as a function of the measured resistance of the solution.

The diagram « cell constant — resistance (conductance) » shall be drawn using at least five standard solutions.

6. Uncertainty of determination of constant K

When estimating the uncertainty of determination of the constant, the following shall be taken into account :

- uncertainty on the value of conductivity of solutions used, with respect to conventional data obtained from tables (due to differences in purity, etc.),
- errors of preparing the solutions (error of weighing and, if applicable, of volumetric measurements),
- error of maintaining the prescribed temperature (error of thermostatic control of the cell containing the solution),

Note : the temperature dependence of the conductivity of a KCl solution can be estimated from data given in RI 56. It amounts to approximately 1.8 % for a variation of 1 °C.

- discrimination error (zone of indecision) of resistance measurements,

Note : systematic errors of resistance measurements can also occur if the resistance measuring equipment, or the connecting leads, are different between calibration and actual use of the cell.

7. Calibration certificate

At the end of calibration, a certificate is issued which shall include the following information :

- cell identification,
- specification for the standard solutions used for calibration,
- calibration conditions, electrolytic solution temperature, liquid for the thermostatic bath, measuring frequency, etc.,
- calibration result : value of the constant K , or calibrating curve $K = f(R)$,
- estimated uncertainty on the determination of the constant K .

References :

- [1] OIML International Recommendation No. 56 « Standard solutions reproducing the conductivity of electrolytes ».
- [2] KOHLRAUSCH F., HOLBORN J., DIESSELHORST H., Wiedemanns Annaleft, 64, 417 (1898).
- [3] IUPAC Recommended Calibration and Test Materials for Realization of Physico-chemical Properties. Section XIV ; Electric Conductivity of Aqueous Electrolytes, by E. Juhasz.

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