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Conveners: Mr. Vladimir I. Suvorov, Mr Alexey B. Diatlev

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Traceability of electrolytic conductivity measurements

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Foreword

The International Organisation of Legal Metrology (OIML) is a worldwide, intergovernmental organisation whose primary aim is to harmonise the regulations and metrological controls applied by the national metrological services, or related organisations, of its Member States.

The main categories of OIML publications are:

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Bureau International de Métrologie Légale
11, rue Turgot - 75009 Paris – France
Telephone: 33 (0)1 48 78 12 82
Fax: 33 (0)1 42 82 17 27
E-mail: biml@oiml.org
Internet: www.oiml.org

Traceability of electrolytic conductivity measurements

1 Scope

This Document deals with the procedure for disseminating the unit of electrolytic conductivity for fluids from national primary standards to working measuring instruments in the range from 1×10^{-5} to 0.5×10^2 ($\text{S} \cdot \text{m}^{-1}$) – Siemens per meter – and in the temperature range from 0 °C to 50 °C, in conformity with the recommendations for adequate uncertainty calculation.

This Document applies to laboratory and industrial conductivity measurement systems for fluids that are based on the conductance principle (conductivity meters) equipped with contact cells (sensors).

Measurement standards, reference materials, measuring instruments, their components, measurement procedures and provisions of this Document should be in conformity to metrological requirements for national standards and other regulatory documents establishing the corresponding metrological requirements.

2 Terminology

2.1 electrolytic conductivity (*EC*)

physical quantity that characterises the ability of an electrolyte to conduct electric charge

Note: In a linear isotropic electrolyte, *EC* is the coefficient of proportionality between the electric current density and electric field intensity.

2.2 standard solution reproducing conductivity

solution that is sufficiently homogeneous and stable in terms of electrolytic conductivity, whose value is used for calibration of conductivity meters

2.3 primary standard solutions

standard solution, whose conductivity is determined by the primary measurement procedure

Note: The constant of the cell is determined as a function of its geometrical characteristics, expressed in SI or that is prepared by an accepted recipe.

2.4 secondary standard solution

standard solution whose value is measured using a conductivity measurement system previously calibrated by means of a primary *EC* standard solution

2.5 working (*EC*) standard solution

standard solution that is used routinely to calibrate or verify conductivity measurement systems

Note: Usually, the *EC* value of working standards is measured with a calibrated conductivity measurement system. However, a primary *EC* standard solution or a secondary standard can also be used as a working standard.

2.6 conductance cell

vessel with electrodes at a defined distance from each other intended for *EC* measurements

Note: There are three types of conductance cells: filler cells, dip cells, and flow-through cells.

2.7 constant of the conductance cell (cell constant)

coefficient of proportionality between the *EC* of a solution and the resistance or conductance value respectively

Note: The constant of the conductance cell is determined either by the primary or the secondary method.

2.8 National Metrology Institute (NMI)

institution responsible for carrying out tasks prescribed by the national policy in the field of metrology

3 Units of measurement

In this Document the following units of measurement are used:

- for electrolytic conductivity – Siemens per meter, $S \cdot m^{-1}$;
- for resistance – Ohm, Ω ;
- temperature – Degree Celsius, $^{\circ}C$;
- cell constant – per meter, m^{-1} .

4 Principle of measurements

According to definition 2.1, the electrical conductivity (κ) of a solution is calculated by the formula:

$$\vec{j} = \kappa \times \vec{E} \quad (1)$$

where

\vec{j} – current density vector, A/m^2 ,

\vec{E} – vector of the electric field, V/m .

The definition of the unit of *EC* follows from equation (1): the unit of *EC* is numerically equal to the current (in amperes) passing through an electrolyte layer with a constant cross-section equal to $1 m^2$, under the influence of the electric field gradient of $1 V/m$. Hence, the unit of *EC* is $\kappa = A \times V^{-1} \times m^{-1}$ in SI units. It is abbreviated to $S \cdot m^{-1}$.

It is difficult to measure the current density, j , and the electrical intensity, E , with high accuracy. Therefore, in practice the *EC* of a solution is determined by comparison with a reference or working standard solution having a known *EC*.

When measuring $EC(\kappa)$ of a measurement standard solution and the resistance (R) between the conductance cell electrodes, the cell constant K , m^{-1} , is calculated by the formula:

$$K = \kappa \times R \quad (2)$$

The *EC* of an electrolyte solution is defined in homogenous media by the formula:

$$\kappa = K \times \frac{1}{R}. \quad (3)$$

where R is the resistance between the electrodes of the cell filled with the analysed electrolytic solution.

The process of determining the cell constant K is called “calibration of a conductance cell”.

4.1 Effect of temperature

Conductivity is heavily dependent on temperature. Consequently, *EC* values of standards are defined at specific temperature values t . The measurement temperature t_m usually deviates to some extent from the set temperature. If the deviation is not larger than $1^{\circ}C$, a conductivity value κ_{t_m} measured at t_m , can be compensated to its value α_{t_0} at the set temperature using:

$$\kappa_{t_0} = \frac{\kappa_{t_m}}{1 + \alpha_{t_0} \times (t_m - t_0)} \quad (4)$$

where α_{t_0} is the linear conductivity coefficient of the solution at t_0 . For KCl solutions $t_0 = 0.0195$ °C at 25 °C.

Note: For deviations larger than 1 °C, higher order polynomial functions must be used for temperature compensation.

5 Metrological traceability of results obtained in measurements of *EC*

5.1 Calibration hierarchy

The purpose of hierarchy schemes is to enable users to perform a practical realisation of metrological traceability of a measured value through calibration chains. An example of the practical implementation for conductivity of electrolytic solutions is given in Appendix A.

Such schemes must contain the necessary information to ensure the traceability in the national calibration chains, including the following information about accuracy levels and the measurement standards corresponding to each level:

- known principles used for the realisation of primary standards;
- evaluations of errors or uncertainty;
- methods of realisation of the reference value and comparison devices recommended for different accuracy levels;
- stability of metrological characteristics of the standards and reproducibility of the measurement results over time;
- periodicity of calibration.

At the hierarchy scheme levels, it is reasonable to indicate a number of sub-ranges of values, in which the applied standards differ in terms of their design and measurement method they use. Adjacent ranges should overlap to form a common area, in which the measurement results obtained by these standards in the common area can be compatible.

Characteristics of measurement errors or uncertainties should be established for all measurement results at all levels of the scheme.

5.2 General scheme of metrological traceability

The general scheme of metrological traceability has 3 levels (see Appendix A).

The primary standard of the *EC* unit is at level 1. The primary standard realises the unit with a best attainable accuracy. The primary standard is based on an experimental calculation method of the unit realisation and this method is the primary method of *EC* measurements, which means that the *EC* of the primary standard is “linked” to national primary standards of length [*L*], temperature [*T*] and electrical resistance [*R*] (electrolytic conductance [*G*]) by measuring those quantities and calculating the *EC* value from the measurement results. Periodic evaluation of the metrological characteristics of the primary standard is carried out through international key comparisons. The primary method (experimental calculation method) consists in determining the cell constant by results of the preliminary measurements of the geometrical dimensions that define the shape of the cell and thus, ultimately, the unit value is obtained from the standards of the meter and the ohm.

Note: Examples of such reference cells are the Jones-type cell or cells based on the realisation of van der Pauw and Lampard theorems.

Primary measurements have also been used to measure the *EC* values of defined KCl solutions having defined molalities [1, 3] (called recipe-based standard solutions). These solutions have been accepted as primary *EC* standards for practical reasons. The primary standards are usually maintained and used at NMIs.

Level 2 contains secondary standards. Usually, the *EC* unit is reproduced by secondary standards using a set of standard solutions. The *EC* values of such standards are obtained by calibration against primary standards. The use of secondary standards is determined by the geographical region, and/or economic or political organisation of the country. The secondary standards are mainly used at calibration laboratories.

Level 3 contains working standards, whose *EC* values are obtained from their calibrations against secondary or primary standards. Methods and instruments used for the calibration of secondary and working standards are especially important to ensure the accuracy. Third level working standards are used for:

- calibration of working instruments;
- calibration of working standards used by manufacturers of working measuring instruments. The accuracy characteristics of such standards are defined by the needs of the user.

5.3 Metrological requirements for standards

5.3.1 The measurement standards of the *EC* unit included in the hierarchical scheme should be traceable to internationally recognised primary standards.

5.3.2 The traceability of measurement standards should be provided through their certification according to the procedures established by the NMIs, under which, in particular, the evaluation of compliance with the following requirements is carried out:

- metrological requirements in accordance with the operating instructions for the measurement standard;
- requirements for the maintenance and use in accordance with the operating instructions for the measurement standard.

5.4 Uncertainty of values realised by the standards and of the results of measurements carried out at each level of the hierarchy scheme

According to the GUM [4], it is necessary to determine the type of type A or type B uncertainties and the order of their values. These values are determined by:

- uncertainties due to the definition of the unit or due to the value of its realisation;
- estimates for the uncertainty budget components at each level of the hierarchy scheme;
- requirements for the measurement uncertainty (the limits can be adjusted at regular intervals).

The transition from one level of the hierarchy scheme to another is characterised by the increase in the uncertainty of the standard.

6 Determination of the cell constant

6.1 Principles

6.1.1 The basic procedure for calibrating reference and working conductivity meters consists in determining the cell constant (*K*). Uncertainty of the value *K* tends to be a prevailing component of the general estimation of the uncertainty in conductivity measurements.

- 6.1.2** In this Document, the conductance cell is considered as a scaling factor by means of which the *EC* of the solution should be determined as a function of the resistance (or conductance) being measured.
- 6.1.3** The value of the cell constant *K* depends on the design of the cell, temperature and concentration of the solution, supply voltage frequency, cleanliness of the electrodes, etc., therefore, to obtain accurate results it is necessary to determine the contribution of these factors.
- 6.1.4** Standard solutions, resistance measuring devices and calibration conditions of the cells must be suitable to produce an uncertainty that does not exceed the level appropriate for the intended use.

6.2 Preparations for calibration

Before starting calibrations, the following procedures should be performed:

6.2.1 Electrodes

Check the setup stiffness of the electrodes and the state of their surface.

If there are any defects in their coating (whitish surface, spots, stripes, etc.), the coating should be removed and the platinised electrodes should be recoated with platinum black.

6.2.2 Degreasing and washing of the cell

Degreasing should be carried out using proper agents depending on the material of the cell and the electrodes.

The cell should be thoroughly washed with distilled water.

6.2.3 Standard solutions

The required amount of standard solutions must be prepared. For the calibration of the conductance cells, the following corresponding solutions can be used:

- standard solutions mentioned in this Document;
- working solutions whose *EC* is determined by measuring in the conductance cell calibrated with standard solutions mentioned in this Document.

6.3 Calibration

- 6.3.1** The cell should be washed with the standard solution at least five times. The least portion of the solution should be kept in the cell for at least 1 minute. After washing, the cell is filled with a new portion of the solution for subsequent measurements.
- 6.3.2** The cell with the solution is maintained at 25 °C to achieve the thermal balance. If the cell is intended to be used for solutions with a temperature other than 25 °C, the calibration should be carried out at the working temperature.
- 6.3.3** The thermostat fluids used for calibration and for *EC* measurements should be identical.
- 6.3.4** The frequency and waveform of the cell supply voltage for calibration and for *EC* measurements should be identical.
- 6.3.5** The cell constant *K* is determined by means of at least three solutions, the *EC* of which corresponds to the beginning, middle and the end of the measurement range.
- 6.3.6** If the change of the cell constant *K*, depending on the conductivity of the electrolyte solution, is lower than the maximum permissible error of the cell specified in the certificate or technical documentation, then the arithmetic mean value of *K1*, *K2*, *K3*, ... obtained for different standard solutions is used to be shown as the result of the calibration.

6.3.7 If the change of the cell constant K , depending on the conductivity of the electrolyte solution, exceeds the maximum permissible uncertainty of the cell, the calibration curves “cell constant vs. conductivity of the solution” are plotted to determine the cell constant as a function of the measured conductivity.

6.3.8 The influence “Cell constant vs. conductivity of a solution” should be plotted on the basis of at least three standard solutions in the required conductivity range.

6.4 Uncertainty in the constant K determination

When estimating uncertainty of the cell constant K the following factors should be taken into account:

- uncertainty of EC values of the standard solutions given in the Certificates of Analysis;
- uncertainty of preparation of the solutions (weighing errors, measuring glassware errors);
- uncertainty in maintaining the preset temperature (uncertainty of the thermostatic bath);
- uncertainty of determination of temperature coefficient of the conductivity;
- uncertainty of impurities of KCl ;
- uncertainty due to the effect of CO_2 on the EC of water.

Note: Additional uncertainty components can appear when using auxiliary instruments and linking cables for measurements and calibrations of cells.

6.5 Calibration certificate

Upon completion of the calibration procedure a calibration certificate including the following information is issued:

- identification of the cell;
- specification of the standard solutions used;
- calibration conditions, temperature of the electrolyte solution, thermostat fluid, voltage frequency, etc.;
- calibration results: the value of the constant K or the function $K = f(EC)$;
- uncertainty in the determination of the constant K .

7 Standard solutions reproducing EC

7.1 Metrological requirements

7.1.1 During the calibration of conductivity meters, it is recommended to use CRMs with EC values determined by measurements carried out at accredited laboratories or NMIs.

7.1.2 Alternatively, potassium chloride aqueous solutions with an assigned EC values and uncertainties (see Table 1) can be used to calibrate conductivity devices [2].

Table 1 – *EC* values of primary standard solutions (recipe-based standard solutions).

t , °C	Electrolytic conductivity, S/m					
	$m(\text{KCl}) = 0.01 \text{ mol/kg}$		$m(\text{KCl}) = 0.1 \text{ mol/kg}$		$m(\text{KCl}) = 1.0 \text{ mol/kg}$	
	0.74552 g of KCl in 1 kg of water		7.4552 g of KCl in 1 kg of water		74.552 g of KCl in 1 kg of water	
	Value	u_c	Value	u_c	Value	u_c
0	0.077292	0.000012	0.711685	0.000143	6.3488	0.0013
5	0.089096	0.000013	0.818370	0.000163	7.2030	0.0014
10	0.101395	0.000015	0.929172	0.000186	8.0844	0.0016
15	0.114145	0.000017	1.04371	0.00021	8.9900	0.0018
18	0.121993	0.000019	1.11406	0.00022	-	-
20	0.127303	0.000019	1.16159	0.00023	9.9170	0.0020
25	0.140823	0.000021	1.28246	0.00025	10.8620	0.0021
30	0.154663	0.000023	1.40592	0.00028	11.8240	0.0023
35	0.168779	0.000026	1.53160	0.00031	12.7970	0.0025
40	0.183127	0.000028	1.65910	0.00033	13.7810	0.0027
45	0.197662	0.000030	1.78806	0.00036	14.7720	0.0029
50	0.212343	0.000032	1.91809	0.00038	15.7670	0.0031

7.1.3 The *EC* values of secondary and working standard solutions given in Table 1 are obtained by means of the following instruments:

- water or oil thermostat that maintains the solution temperature with an instability not exceeding $\pm 0.01 \text{ }^\circ\text{C}$;
- thermometer that provides measurement uncertainty of within $\pm 0.005 \text{ }^\circ\text{C}$ in the range 5°C to $50 \text{ }^\circ\text{C}$.

7.2 Preparation conditions of recipe-based standard solutions

The *EC* of the purified water used for the preparation of the standard solutions should not exceed $1 \times 10^{-1} \text{ S/m}$. The water must be kept for at least 12 hours in an open polyethylene or fluoroplastic vessel before use to ensure the equilibrium with atmospheric CO_2 . The *EC* value of the purified water should be taken into account when preparing solutions with *EC* values less than $1 \times 10^{-1} \text{ S m}^{-1}$. If it cannot be measured, it is reasonable to assume a value of $1 \text{ } \mu\text{S/cm}$.

The purity of KCl used for the standard solution preparation shall be at least 99.95 %.

The KCl shall be dried at 400–500 °C for 4 h in an oven. Afterwards it shall be stored in a desiccator over anhydrous $\text{Mg}(\text{ClO}_4)_2$ before use.

The balance readings shall be corrected for the air pressure.

The conductivity set values given in Table 1 should be corrected for deviations of the actually weighed KCl molalities from the set values given in Table 1, i.e.

$$EC_{actual} = \frac{M_{actual}}{M_{set}} \times EC_{set} \quad (5)$$

where:

EC_{actual} = actual electrolytic conductivity values,

EC_{set} = electrolytic conductivity set value according to Table 1,

M_{actual} = actually weighed molalities of KCl,

M_{set} = set value of KCl molality according to Table 1.

7.3 Calibration method for secondary standard solutions and working devices

7.3.1 The relative standard uncertainty of the conductance cell value (G) is determined by means of at least five solution samples as follows (uncertainty type A):

- the conductance cell value is measured for each of the five solution samples;
- the relative standard uncertainty of the conductance cell value (u_A) due to random factors is calculated by the following formula:

$$u_A = \sqrt{\left[\frac{\sum (G_i - G_0)^2}{n(n-1)} \right]} \times 1/G_0 \quad (6)$$

Where:

G_i = the conductance cell value of the i th sample,

G_0 = the conductance cell value,

n = the number of samples ($n = 5$).

1. The combined standard uncertainty (u_c) of the conductance cell constant (uncertainty type B) is calculated by considering the following components as given in Table 1 [4]:
 - uncertainty in maintaining the preset temperature (error in temperature stability in the cell containing the solution);
 - uncertainty of measurement of the temperature;
 - uncertainty in the determination of the water EC value.

7.3.2 The form of the calibration certificate for secondary standards or working devices shall contain the following information:

- serial number of the Certificate;
- name and address of the calibration laboratory;
- date of calibration;
- item calibrated;
- client's name

- calibration method with instructions to ensure traceability;
- calibration conditions.

The calibration results shall be accompanied by the following information:

- range of EC;
- values of the conductivity constants of the cells incorporated in the device (if necessary);
- actual and reference values of conductivity of solutions at the temperatures: 15 °C, 20 °C, 25 °C, 30 °C;
- issue date of the Certificate;
- name of the person who carried out the calibration.

8 References

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- [3] Paul De Bièvre, René Dybkaer, Aleš Fajgelj, and D. Brynn Hibbert, *Metrological traceability of measurement results in chemistry: Concepts and implementation (IUPAC Technical Report)*, 2011vol.83, Issue 10, pp. 1873-1935.
- [4] OIML G-100:2008, *Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM - JCGM 100:2008)*.

Appendix A

Example of the national metrological traceability scheme

