Primary Measurements of Electrolytic Conductivity in Brazil

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ABSTRACT

National Institute of Metrology, Standardization and Industrial Quality, Inmetro from Brazil, established the primary system of electrolytic conductivity in 2007. The objective of this work is to present the traceability chain of electrolytic conductivity measurements and the use of primary system in the certification of reference materials, which are used for calibration of conductivity meter. The correct measurement of the electrolytic conductivity using certified reference materials to obtain reliability in the results is extremely relevant for the purity of water, health, environment and chemical processes. In 2007, Inmetro participated in a key-comparison, CCQM-K36.1, with this primary system in order to check its performance on different values of electrolytic conductivity.

1. INTRODUCTION

The measurement of electrolytic conductivity is a useful analytical tool often applied in many fields of science and technology. Electrolytic conductivity (EC) is a measure of the ionized substances in the solution and under certain conditions it can be used as an easily accessible quantitative measure of water quality, to a certain extent, replacing laboratories and expensive chemical analyses [1, 2].

EC measurements are very important in different fields. If the value is high (about 0.5 S/m) it is appropriate for application in areas such as water analysis (drinking water, sea water, waste water) and biological fluids (dialysis fluids, liquid fertilizers, etc.). If the value is low (about 5 mS/m) it will contribute to the purity of water and manufacture of vaccine and medicine. As such, it is the closest value, and thus the most appropriate for evaluation of measurement establishing traceability to measurements of conductivity of pure water; a main use of conductivity measurements [3].

The Chemical Metrology Division (Dquim) from National Institute of Metrology, Standardization and Industrial Quality – Inmetro, established the primary system of EC measurement in 2007. The main use of this system is to provide reliability and traceability to the EC measurements in Brazil, since its measurement is very important mainly for determining the purity of water. In order to show comparability and capability in primary EC measurement, Inmetro participated in the key-comparison organized by Consultative Committee for Amount of Substance (CCQM) [3] in 2007 called CCQM-K36.1 to measure the EC in two solutions: one with a nominal value of 0.5 S m^{-1} and the other, 5 mS m^{-1}.

The objective of this work is to present the traceability chain of EC measurements in Brazil in order to obtain results of this measurement with reliability and comparability.

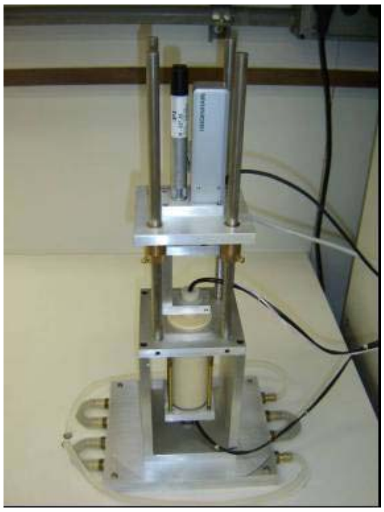

Fig. 1. Primary electrolytic conductivity cell.

2. EXPERIMENTAL

2.1. Equipments

The primary system of EC from Inmetro is based on one primary conductivity cell (Fig. 1) which consists of a piston type ceramic inserted in a tube, similar from the primary conductivity cell from PTB, whose diameter was calibrated at the Mechanical Metrology Division of Inmetro. The following equipments are used for the measurements of EC: a) Bath (Fluke/Hart Scientific 7011 with stability of 3 mK); b) Pt 100, calibrated at the Thermal Metrology Division of Inmetro; c) Super-thermometer (1590 Fluke/Hart Scientific), calibrated at the Thermal Metrology Division of Inmetro; d) Precision LCR meter (4284A Agilent), calibrated at Electrical Metrology Division of Inmetro; e) Micropositioner system (Heidenhain), calibrated at the Mechanical Metrology Division of Inmetro.

Fig. 2 Primary system of electrolytic conductivity.

2.2. Measurement Procedure

Approximately 170 mL of the sample solution was transferred into a closed recipient in the bath at the temperature of 25 °C. The cell and the electrodes were cleaned with deionized water (Milli-Q) and the cell was rinsed many times until the conductivity value of the water reached below 1.0 µS/cm. Then, the cell was air dried and rinsed with a little volume of the sample solution that was at the temperature of 25 °C and afterwards filled with approximately 160 mL of the same sample solution. The cell and the thermal isolation box were closed for temperature stabilization at 25 °C inside the cell.

The measurements of the impedance were made in different values of frequency (100, 400, 1000, 1500, 2 000, 2 500, 3 000, 3 472, 4 000 and 5 000) Hz and in high and low position of the electrode. The stabilization time of the temperature into the cell was about 5 h. The distance of the electrode displacement (ΔL) used was 0.002 m. After the measurements, the cell was emptied and all its parts were cleaned with deionized water.

2.3. Calculation

The calculation of the EC was based on the cross section area of the cell ($\pi \cdot D^2/4$). The electrode displacement (ΔL) and the difference in impedance which were measured in high and low positions of the displaceable electrode (R_h – R_l), are shown in Eq. (1).

$$\kappa = \left[\frac{4 \cdot \Delta L}{(R_h - R_l) \cdot \pi \cdot D^2} - \kappa_{CO_2} \right] \left[1 + \alpha (T - T_o) \right] \quad (1)$$

where κ_{CO2} is the CO_2 contribution for the EC of the solvent; α is the temperature coefficient (0.5 S/m, α = 2.017 %/°C); T is the measurement temperature; and T_o is the reference temperature (25 °C).

3. RESULTS

3.1. Establishment of the primary system of EC

The primary system of EC, which can be observed in Fig. 2, followed different steps, from the acquisition and calibration of the equipment and its installation to the preliminary studies of the best conditions and performance which had influence on the results of the EC measurements, in order to establish the primary EC measurements at Inmetro.

3.2. Results of the Measurements

Since 2007, Inmetro has been doing its primary measurements in order to improve the performance of the primary system and uncertainty calculation [4]. The measurements were done using different values of electrolytic conductivity solutions and also in Table 1 are shown the results of Inmetro's participation in a key comparison, CCQM-K36.1.

Table 1. Results of nominal value 0.5 S m^{-1} solution.

n^*	Electrolytic Conductivity (S/m)
1	0.51606
2	0.51654
3	0.51450
4	0.51590
5	0.51526
Mean (S/m)	0.51565
u A (S/m)	0.00027
u B (S/m)	0.00014
U (*k*=2) (S/m)	0.00030

n = measurement*

3.3. The Traceability Chain in Brazil

The establishment of the traceability chain of electrolytic conductivity measurements in Brazil has started with the primary system established by Inmetro. It is important to highlight that accredited laboratories in calibration of conductometer have been asking for production and certification of reference material to this quantity.

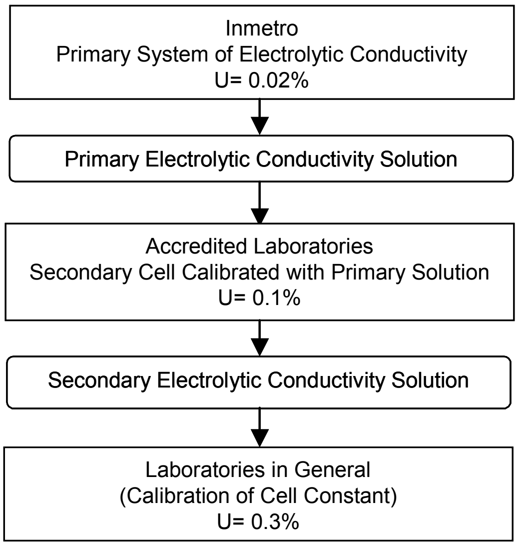

Fig. 3 Diagram of the traceability chain.

The primary reference solutions are used by accredited laboratories to calibrate secondary cells. These cells are used to derive secondary reference solutions. The traceability chain in Brazil is in its initial stages and, in a near future, the establishment of this chain will be done according to the diagram in Fig. 3

4. DISCUSSION

After the establishment of the primary system at Inmetro, the best conditions of measurements, such as the time of stabilization of the measurement temperature and the distance of the electrodes, as well as the automation of the data, are being studied. The establishment of the traceability chain will be very helpful for the improvements of the results of this important parameter to Brazil and many other countries from South America.

5. CONCLUSIONS

It is important to emphasize that the traceability chain in electrolytic conductivity measurements in Brazil is beginning with the establishment of the primary system of this quantity at Inmetro, which has the certification of primary reference materials as its main objective. Consequently, these certified reference materials will guarantee the quality of the measurement results of this quantity, establishing the traceability chain in Brazil and contributing to the increase of the exportation of these reference materials.

ACKNOWLEDGMENTS

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