UNCERTAINTY BUDGET FOR PRIMARY ELECTROLYTIC CONDUCTIVITY MEASUREMENT COMPARING DIFFERENT METHODS

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Abstract: In 2007, the Chemical Metrology Division (Dquim) from National Institute of Metrology, Standardization and Industrial Quality – Inmetro, established the primary system of electrolytic conductivity (EC) measurement. 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 has participated in the key-comparison organized by Consultative Committee for Amount of Substance (CCQM) 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}. This work aims to present a comparison among the values of the uncertainty results from primary EC measurement in the solution of 0.5 S m^{-1} obtained by using the methods of ISO GUM, Kragten and Monte Carlo simulation. In addition, this work will also present an evaluation of the uncertainty related to all relevant sources in the uncertainty budget for EC measurement by using the primary EC system from Inmetro. Moreover, this study intends to show the main points which should be focused on in order to improve the process of primary EC measurement, when needed.

Keywords: uncertainty, electrolytic conductivity, primary measurements.

1. INTRODUCTION

EC measurement is an inexpensive electrochemical method and quite used by all the laboratories, mainly for determining the quality of water. It is an important parameter used as an input to the production or manufacturing of medicines and vaccines. Therefore, its precise measurement is very important in different fields such as health, food, environment, biotechnology among others. Inmetro guarantees the traceability and reliability of the measurement results through its primary EC measurement system. The aim of the primary EC system is to certify reference material [1] and provide the traceability in EC measurements for the country.

The ISO GUM 95 [2] aims at the international harmonisation of the uncertainty estimate calculation since the results of the measurements can be compared with others. The EURACHEM/CITAC Guide [3] based on ISO GUM 95 presents two alternatives for the uncertainty measurement calculation. The ISO GUM and its alternative methods [4-7] of calculation present some limitations, such as: model linearization, supposition of the measurand below the normal distribution and the Welch Sattethrwaite formula due to effective degrees of freedom calculation. Given that the objective is to advance the limitations of these methods, the Monte Carlo simulation method was introduced in order to evaluate the uncertainty measurement. Monte Carlo is a method for the propagation of distributions by performing random sampling from probability distributions. Recently, the Working Group 1 of the Joint Committee for Guides in Metrology (JCGM) chaired by the director of the International Bureau of Weights and Measures (BIPM) has prepared a Supplement 1 to the GUM for evaluation of measurement data using the Monte Carlo's method [8].

2. PURPOSE

The purpose of this work is to present the results of the uncertainty budget for EC primary measurement by comparing three different methods: ISO GUM, Kragten and Monte Carlo. Besides, this work will also present the main points which should be taken into account in order to improve the uncertainty measurement results.

3. METHODS

3.1 Primary System of Electrolytic Conductivity

The primary system of electrolytic conductivity measurement from Inmetro was described elsewhere [9]. The primary cell has cylindrical body and it is made of ceramic material. There are two platinum electrodes in each base of the cylinder. Figure 1 shows the cell at the Electrochemical Laboratory of Inmetro.

Figure 1 – Primary cell for electrolytic conductivity measurements.

3.2. Procedure for electrolytic conductivity measurement

Approximately 170 mL of the sample was put in a recipient, which was closed and inserted in a water bath at 25 ºC. The conductivity cell and the electrodes were washed with deionized water (Milli-Q® system), until the conductivity value from the rinsed water hit the value of 1.0 μS·cm⁻¹. After that, the cell was left to dry. Then, the dried cell was rinsed with a tiny volume of the sample solution, which was in the water bath and filled with 160 mL of the sample solution. The cell was closed and maintained at the temperature of 25 ºC. When the temperature was stabilized, impedance measurements were done in the range of frequencies from 100 to 5000 Hz. The measurements of the impedance were done in two different positions, related to the dislocation of one of the electrodes of the primary cell. The resistance of the sample was obtained graphically from the linear extrapolation to zero of the real part of the impedance measured versus inverse of frequency.

3.3 Procedure for estimation of the uncertainty

The ISO GUM´s method can be summarised in the following main steps: 1) measurand definition; 2) construction of the cause and effect diagram; 3) estimate of the standard uncertainties from the input quantity; 4) sensitivity coefficient calculation; 5) uncertainty components calculation; 6) components combination; 7) effective degrees of freedom calculation; 8) determination of coverage factor and 9) estimate of the expanded uncertainty.

The Kragten's method [10], based on ISO GUM, is an alternative calculation for the combination of the standard uncertainty of the sources of entry. These two methods follow all the steps of the traditional ISO GUM's method except that

in which calculates the sensibility coefficients of measurement related to each input quantity.

The Monte Carlo simulation's method to estimate the uncertainty of measurement, as in the ISO GUM, can be summarised in the following main steps: 1) measurand definition; 2) construction of the cause and effect diagram; 3) estimate of the standard uncertainties from the input quantity; 4) identification of the probability density functions related to each source of entry; 5) selection of the iteration numbers; 6) choice of the probability density function $p_{(xi)}$ and 7) estimate of the expanded uncertainty.

4. RESULTS

Figure 1 shows the cause and effect diagram related to the primary EC measurement of a solution of nominal value of 0.5 S m⁻¹. On the other hand, Figure 2 presents the contributions of the components to the uncertainty budget which is shown in Table1, afterwards.
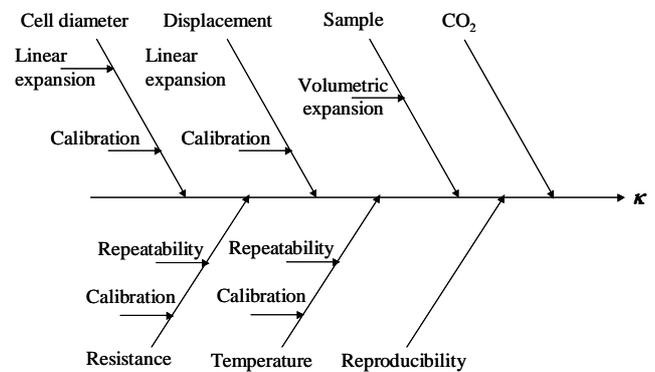

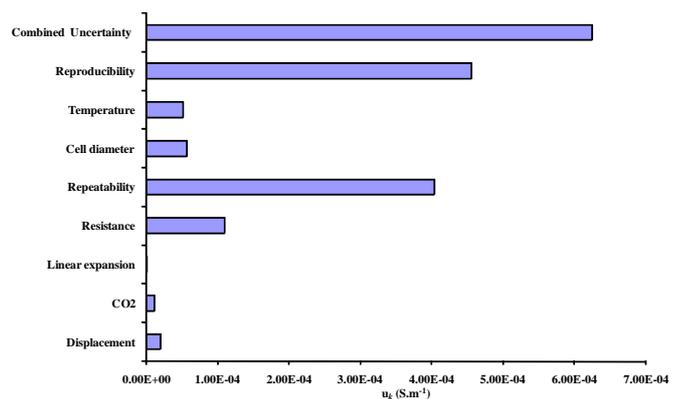**Figure 1 – Cause and effect diagram for primary EC measurement.**

Figure 2 – Contribution of components to the uncertainty budget.

The uncertainty budget for primary EC measurement for 0.5 S m⁻¹ nominal solution is shown in Table 1. The measurement result at 25 ºC was 0.515654 ± 0.001250 S m⁻¹ (k=2; 95% confidence).

Table 1. Uncertainty budget for 0.5 S m^{-1} solution.

Uncertainty source X_i	Value x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $/c_i/$	Contribution to standard uncertainty $U(y)$ $(S \cdot m^{-1})$
Impedance measurement $(R_i\text{-}R_j)$	$10.15\,\Omega$	normal	$0.00212\,\Omega$	$0.049\,\Omega^{-2}m^{-1}$	1.1×10^{-4}
Cell diameter	$0.0500003\,m$	normal	$2.86 \times 10^{-6}\,m$	$20.1\,\Omega^{-1}m^{-2}$	5.7×10^{-5}
Electrode displacement (ΔL)	$0.01\,m$	rectangular	$4.00 \times 10^{-7}\,m$	$50.2\,\Omega^{-1}m^{-2}$	2.0×10^{-5}
Temperature measurement plus temperature correction (ΔT)	$25.00\,°C$	normal	$5.22 \times 10^{-3}\,°C$	$1.01 \times 10^{-2}\,\Omega^{-1}m^{-1}°C^{-1}$	5.2×10^{-5}
Temperature coefficient	$0.02017\,°C^{-1}$	rectangular	$5.77 \times 10^{-5}\,°C^{-1}$	$7.1 \times 10^{-3}\,\Omega^{-1}m^{-1}°C$	4.1×10^{-7}
CO_2	$0.0001\,\Omega^{-1}m^{-1}$	rectangular	$1.15 \times 10^{-5}\,\Omega^{-1}m^{-1}$	1	1.2×10^{-5}
Repeatability	$0\,\Omega^{-1}m^{-1}$	normal	$4.0 \times 10^{-4}\,\Omega^{-1}m^{-1}$	1	4.0×10^{-4}
Reproducibility	$0\,\Omega^{-1}m^{-1}$	normal	$4.6 \times 10^{-4}\,\Omega^{-1}m^{-1}$	1	4.6×10^{-4}

Combined standard uncertainty: 6.2×10^{-4} S·m^{-1}
Expanded uncertainty: 12.4×10^{-4} S·m^{-1}

The standard uncertainty (u_κ) for primary EC measurement obtained by three different methods using a solution of nominal value of 0.5 S m^{-1} is shown in Table 2.

Table 2. Standard uncertainty (u_κ) for primary EC measurement obtained by different methods from 0.5 S m^{-1} solution.

Method	u_κ (S m^{-1})
ISO GUM	6.2×10^{-4}
Kragten	6.2×10^{-4}
Monte Carlo	6.1×10^{-4}

5. DISCUSSION

The standard uncertainties obtained by ISO GUM's, Kragten's and Monte Carlo's methods showed excellent comparability since no significant difference was found among them (Table 2). Additionally, as it can be seen on Figures 1, 2 and Table 1 that there is a necessity for improvement in the uncertainty measurement of the primary system of EC from Inmetro for nominal value of 0.5 S m^{-1}, therefore the studies must be initially focused on the methodology of the measurement since repeatability and reproducibility are the main components of the uncertainty budget as clearly shown in Figure 2.

6. CONCLUSIONS

The studies presented in this work are very relevant in order to identify the influence of uncertainty contributions and the application of the three powerful tools to estimate the uncertainty measurement of electrolytic conductivity in primary level, according to ISO GUM's (the classical method), Kragten's and Monte Carlo's method. The Monte Carlo's method contributes to solve the problems which the other two methods could not deal with in the identification of the contribution of the uncertainties. It is important to point out that these results will definitely contribute with the guarantee of traceability and reliability of the electrolytic conductivity measurement for solutions of nominal value of 0.5 S m^{-1} in Brazil.

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