Report of Key Comparison SIM.QM-K92

“Electrolytic conductivity at 0.05 S m\(^{-1}\)”

Final Report

F.B. Gonzaga, I.C.S. Fraga, J.C. Lopes, A.O. Costa, L.R. Cordeiro, L.H. Leal, W.F.C. Rocha,
A. Reyes, A. Rodríguez, G.T. Canaza, J. Rodríguez, L.A. Chavarro, R. Cristancho

February 2015
Abstract

At the SIM meeting in Buenos Aires, from 05/30/2012 to 06/01/2012, it was decided to perform a RMO Key Comparison and a Pilot Study to evaluate the performance of SIM national metrology institutes for measuring electrolytic conductivity. The Brazilian Institute of Metrology, INMETRO, agreed to act as coordinating laboratory.

The proposed RMO Key Comparison aims to investigate the equivalence of electrolytic conductivity measurement results around 0.05 S m\(^{-1}\) at 25 °C.

Four institutes took part of the comparison. There was a good agreement of the reported results with the average value, considering the measurement uncertainties.
Contents

ABSTRACT .............................................................................................................................. 2
INTRODUCTION ................................................................................................................... 4
  METROLOGY AREA ........................................................................................................... 4
  BRANCH ............................................................................................................................ 4
  SUBJECT ............................................................................................................................ 4
  TIME SCHEDULE ............................................................................................................. 4
  PARTICIPANTS ................................................................................................................ 4
SAMPLE DESCRIPTION ...................................................................................................... 5
  SAMPLE PREPARATION AND DISTRIBUTION ................................................................. 5
  CHECK OF BOTTLES INTEGRITY ....................................................................................... 5
  CHECK OF HOMOGENEITY ............................................................................................... 5
  CHECK OF STABILITY ....................................................................................................... 6
RESULTS AND DISCUSSION ............................................................................................... 7
  REPORTED RESULTS ......................................................................................................... 7
  DEGREES OF EQUIVALENCE AND LINK TO CCQM-K92 .................................................. 8
  HOW FAR THE LIGHT SHINES .......................................................................................... 9
ACKNOWLEDGMENTS ....................................................................................................... 9
REFERENCES .................................................................................................................... 10
ADRESSES ....................................................................................................................... 10
Introduction

Metrology area

Amount of Substance

Branch

Electrochemistry

Subject

Determination of the electrolytic conductivity for a sample with 0.05 \( \text{S m}^{-1} \) nominal value.

Time schedule

Dispatch of the samples 31 May 2013
Deadline for receipt of the measurement report 19 August 2013
Draft A Report 18 November 2013
Draft B Report 20 December 2013

Participants

Five institutes, including INMETRO, made the registration in the SIM.QM-K92 comparison. Information about these institutes are shown in Table 1. As INEN did not send its measurement report due to problems in its measurement system, only four institutes took part in the comparison.

Table 1. Participants registered in the SIM.QM-K92 comparison.

<table>
<thead>
<tr>
<th>No</th>
<th>Acronym</th>
<th>Institute</th>
<th>Country</th>
<th>Contact Person</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CENAM</td>
<td>Centro Nacional de Metrología</td>
<td>Mexico (MEX)</td>
<td>Aarón Rodríguez López, Adrián Reyes del Valle</td>
</tr>
<tr>
<td>2</td>
<td>INDECOPI</td>
<td>Instituto Nacional de Defensa de la Competencia y de la Proteccion de la Propiedad Intelectual</td>
<td>Peru (PER)</td>
<td>Galia Ticona Canaza</td>
</tr>
<tr>
<td>3</td>
<td>INEN</td>
<td>Instituto Ecuatoriano de Normalización</td>
<td>Ecuador (ECU)</td>
<td>Juana Rodrígues</td>
</tr>
<tr>
<td>4</td>
<td>INM</td>
<td>Instituto Nacional de Metrología de Colombia</td>
<td>Colombia (COL)</td>
<td>Luiz Alfredo Chavarro</td>
</tr>
<tr>
<td>5</td>
<td>INMETRO</td>
<td>Instituto Nacional de Metrología, Qualidade e Tecnologia</td>
<td>Brazil (BRA)</td>
<td>Fabiano Barbieri Gonzaga</td>
</tr>
</tbody>
</table>
Sample description

Sample preparation and distribution

On 04/12/2013 one batch of solution having 0.05 S m\(^{-1}\) nominal electrolytic conductivity was prepared using high-purity potassium chloride and deionised water. The solution was filled into 250 mL borosilicate glass bottles, which were sealed using Parafilm® and put into plastic bags in order to prevent composition change of the solution. Two bottles of the sample were sent to each participant in 05/28/2013 by courier company FedEx.

Check of bottles integrity

The participants were requested to inspect the received bottles for visible damage (bottle broken or with leakage) and to weigh them in order to verify if they keep unchanged during the transport. In three cases (CENAM, INDECOPI and INEN) one bottle was received with visible damage. In these cases, a replacement bottle was sent immediately and the participants received the new bottles with no damage.

Figure 1 shows the relative mass difference for the bottles received with no visible damage, taken into account the mass at origin (measured at INMETRO) and the mass at destination (measured by the participants), with all data corrected for buoyancy. The mass difference was smaller than 0.03 g in all cases, except to one bottle of INM (variation of 0.197 g).

Check of homogeneity

The homogeneity of the sample was checked after filling the bottles. To identify possible trends, primary measurements of electrolytic conductivity were taken for bottles from the beginning, middle and end of the batch, considering the order of filling. The data are shown in Figure 2. As can be seen, the results can be considered statistically similar to each other within the measurement uncertainties.
Figure 2. Measurement results for checking the homogeneity of the sample, with expanded uncertainties ($k=2$).

Check of stability

In order to check the stability of the sample, primary measurements of electrolytic conductivity were taken for some bottles in irregular intervals along 117 days (from 04/26/2013 to 08/21/2013). The measurement results are given in Figure 3. For these results, the linear regression statistical test (using the least-squares method), for 95% probability, gave a $p$-value (for the time) of 0.267, showing that the conductivity variation along time is statistically not significant ($p$-value > 0.05).

Figure 3. Measurement results for checking the stability of the sample, with expanded uncertainties ($k=2$).
Results and discussion

Reported results

The measurement conditions used by the participants are given in Table 2. The electrolytic conductivity results reported by the participants are shown in Table 3 and Figure 4. As can be seen, there was a good agreement of the reported results with the average value, considering the measurement uncertainties.

Table 2. Measurement conditions used by the participants.

<table>
<thead>
<tr>
<th>Institute</th>
<th>Country</th>
<th>Date of report</th>
<th>Traceability</th>
<th>Measurement system</th>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CENAM</td>
<td>MEX</td>
<td>08/19/2013</td>
<td>IUPAC [1]</td>
<td>Jones type cell</td>
<td>500 - 2000</td>
</tr>
<tr>
<td>INDECOPI</td>
<td>PER</td>
<td>08/05/2013</td>
<td>SMU CRM</td>
<td>Jones type cell</td>
<td>200 - 2000</td>
</tr>
<tr>
<td>INM</td>
<td>COL</td>
<td>07/08/2013</td>
<td>SMU CRM</td>
<td>Jones type cell</td>
<td>25 - 200</td>
</tr>
<tr>
<td>INMETRO</td>
<td>BRA</td>
<td>08/19/2013</td>
<td>Primary measurement</td>
<td>Piston type cell</td>
<td>6000 - 8000</td>
</tr>
</tbody>
</table>

Table 3. Electrolytic conductivity (EC) results reported by the participants, with standard uncertainties (u).

<table>
<thead>
<tr>
<th>Institute</th>
<th>Country</th>
<th>EC (S m⁻¹)</th>
<th>u (S m⁻¹, k=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CENAM</td>
<td>MEX</td>
<td>0.049965</td>
<td>0.000081</td>
</tr>
<tr>
<td>INDECOPI</td>
<td>PER</td>
<td>0.050036</td>
<td>0.000060</td>
</tr>
<tr>
<td>INM</td>
<td>COL</td>
<td>0.050016</td>
<td>0.000051</td>
</tr>
<tr>
<td>INMETRO</td>
<td>BRA</td>
<td>0.050095</td>
<td>0.000062</td>
</tr>
<tr>
<td>Average</td>
<td>—</td>
<td>0.050028</td>
<td>0.000027</td>
</tr>
</tbody>
</table>
Degrees of equivalence and link to CCQM-K92

In order to link the results of the present key comparison to those of the original comparison CCQM-K92 [2], the results of CENAM and INMETRO (linking laboratories) in both comparisons were taken into account in the calculation of the degrees of equivalence for INDECOPI and INM in the present comparison, as shown previously [3,4]. For that, the average degree of equivalence of INMETRO and CENAM in the original comparison \( D_{\text{avg-CCQM}} \) was calculated according to Equation 1.

\[
D_{\text{avg-CCQM}} = E_{\text{avg-CCQM}} - KCRV_{\text{CCQM}} \quad (1)
\]

Where \( E_{\text{avg-CCQM}} \) is the average result from INMETRO and CENAM in the original comparison and \( KCRV_{\text{CCQM}} \) is the reference value of the original comparison. Therefore, the \( D_{\text{avg-CCQM}} \) value was used in the calculation of the degrees of equivalence for INDECOPI and INM in the present comparison \( D_i \), as shown in Equation 2.

\[
D_i = E_i - E_{\text{avg-SIM}} + D_{\text{avg-CCQM}} \quad (2)
\]

Where \( E_i \) is the result of INDECOPI or INM in the present comparison and \( E_{\text{avg-SIM}} \) is the average result from INMETRO and CENAM also in the present comparison. For the calculation of the degree of equivalence uncertainties for INDECOPI and INM in the present comparison \( U_{D_i} \), the standard uncertainty of the KCRV value of the original comparison \( u_{KCRV_{\text{CCQM}}} \) was also taken into account, as shown in Equation 3.

\[
U_{D_i} = 2 \sqrt{u_{E_i}^2 + u_{E_{\text{avg-SIM}}}^2 + u_{KCRV_{\text{CCQM}}}^2} \quad (3)
\]
Where $u_{EC}$ is the standard uncertainty of INDECOPI or INM in the present comparison and $u_{EC_{avg-SIM}}$ is the standard uncertainty of the average result between INMETRO and CENAM also in the present comparison. The $u_{EC_{avg-SIM}}$ was calculated according to Equation 4.

$$u_{EC_{avg-SIM}} = \sqrt{\frac{s^2}{N}}$$ (4)

Where $s$ is the standard deviation between the results of INMETRO and CENAM in the present comparison and $N$ is the number of results (equals to 2 in this case). The $D_i$ and $U_{D_i}$ results are given in Table 4. Figure 5 shows a plot of these results in comparison to those of the original comparison.

Table 4. Degrees of equivalence linked to CCQM-K92.

<table>
<thead>
<tr>
<th>Institute</th>
<th>Country</th>
<th>$D_i$ (S m$^{-1}$)</th>
<th>$U_{D_i}$ (S m$^{-1}$, $k=2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>INDECOPI</td>
<td>PER</td>
<td>0.0000011</td>
<td>0.000177</td>
</tr>
<tr>
<td>INM</td>
<td>COL</td>
<td>-0.000009</td>
<td>0.000166</td>
</tr>
</tbody>
</table>

![Figure 5. Degrees of equivalence linked to CCQM-K92.](image)

**How far the light shines**

The results of this comparison can be considered to be representative for measurement capabilities in the range from 0.016 to 0.15 S m$^{-1}$.

**Acknowledgments**

INMETRO gratefully acknowledges the contributions of all participants and of the members of the CCQM Working Group on Electrochemical Analysis for their valuable suggestions concerning the measurement protocol and the evaluation process.
References


Addresses

Adrian Reyes, Aaron Rodríguez
Centro Nacional de Metrología (CENAM)
Km 4.5 Carretera a Los Cués C.P. 76246. El Marqués, Querétaro
Mexico

Galia Ticona Canaza
Instituto Nacional de Defensa de la Competencia y de la Protección de La Propiedad Intelectual (INDECOPI)
Calle De la Prosa 104 San Borja, LIMA 41, Lima
Peru

Juana Rodríguez
Instituto Ecuatoriano de Normalización (INEN)
Autopista General Rumiñahui, Puente 5, Conocoto, Quito
Ecuador

Luis Alfredo Chavarro Medina
Instituto Nacional de Metrología de Colombia (INM)
Avenida Carrera 50 No 26 – 55 Interior 2, Bogotá, D.C.
Colombia

Fabiano Barbieri Gonzaga
Instituto Nacional de Metrología, Qualidade e Tecnologia (INMETRO)
Av. Nossa Senhora das Graças, 50, Duque de Caxias, RJ, 25250-020
Brazil