Report of Key Comparison SIM.QM-K92

"Electrolytic conductivity at 0.05 S m^{-1}"

Final Report

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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

Introduction

Metrology area

Amount of Substance

Branch

Electrochemistry

Subject

Determination of the electrolytic conductivity for a sample with 0.05 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.

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

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).

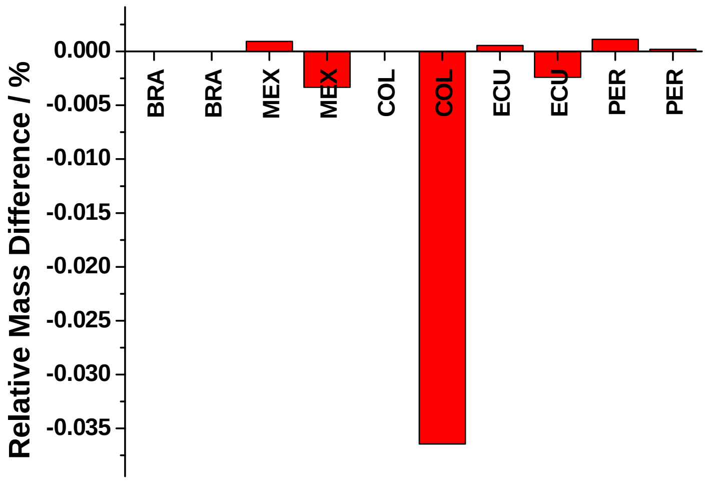

Figure 1. Relative mass difference between origin (INMETRO) and destination.

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.

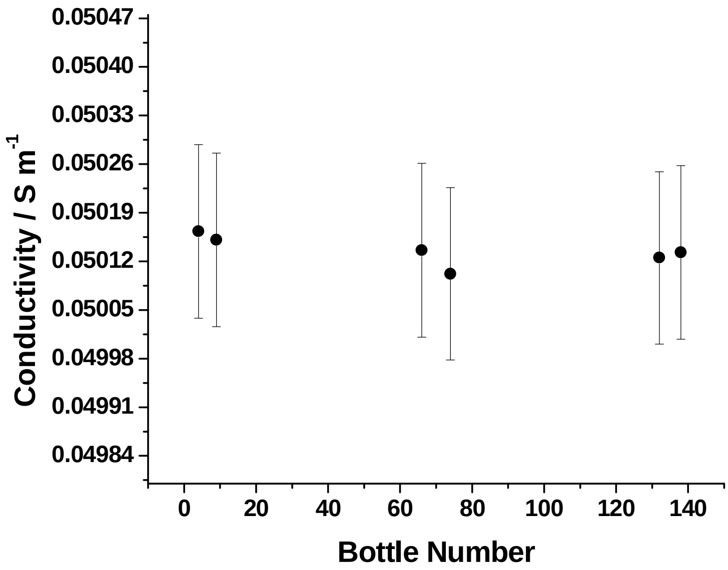

Figure 2. Measurement results for checking the homogeneity of the sample, with expanded uncertainties (k=2).

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).

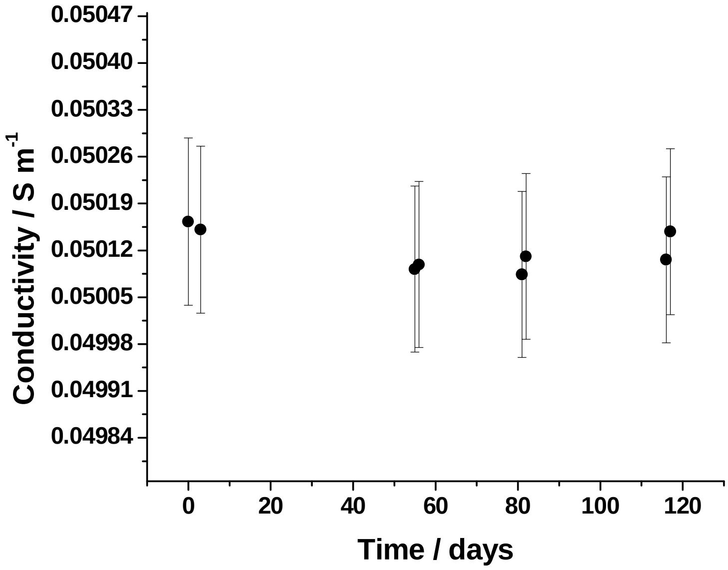

Figure 3. Measurement results for checking the stability of the sample, with expanded uncertainties (k=2).

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.

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

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

Institute	Country	EC (S m^{-1})	u (S m^{-1}, k=1)
CENAM	MEX	0.049965	0.000081
INDECOPI	PER	0.050036	0.000060
INM	COL	0.050016	0.000051
INMETRO	BRA	0.050095	0.000062
Average	—	0.050028	0.000027

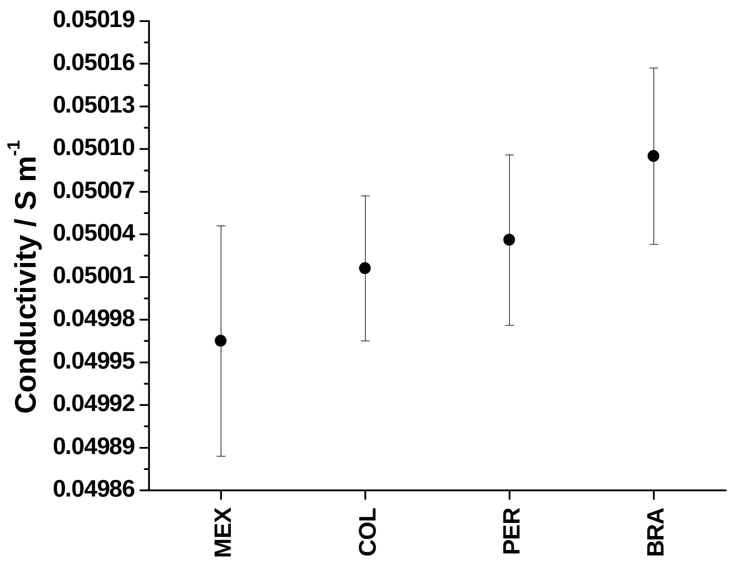

Figure 4. Electrolytic conductivity results with standard uncertainties.

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.

$$D_{\text{avg-CCQM}} = EC_{\text{avg-CCQM}} - KCRV_{\text{CCQM}} \qquad (1)$$

Where $EC_{\text{avg-CCQM}}$ 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.

$$D_i = EC_i - EC_{\text{avg-SIM}} + D_{\text{avg-CCQM}} \qquad (2)$$

Where EC_i is the result of INDECOPI or INM in the present comparison and $EC_{\text{avg-SIM}}$ 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.

$$U_{D_i} = 2\sqrt{u^2_{EC_i} + u^2_{EC_{\text{avg-SIM}}} + u^2_{KCRV_{\text{CCQM}}}} \qquad (3)$$

Where u_{EC_i} is the standard uncertainty of INDECOPI or INM in the present comparison and $u_{EC_{avg\text{-}SIM}}$ is the standard uncertainty of the average result between INMETRO and CENAM also in the present comparison. The $u_{EC_{avg\text{-}SIM}}$ was calculated according to Equation 4.

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

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.

Institute	Country	D_i (S m^{-1})	U_{D_i} (S m^{-1}, k=2)
INDECOPI	PER	0.000011	0.000177
INM	COL	-0.000009	0.000166

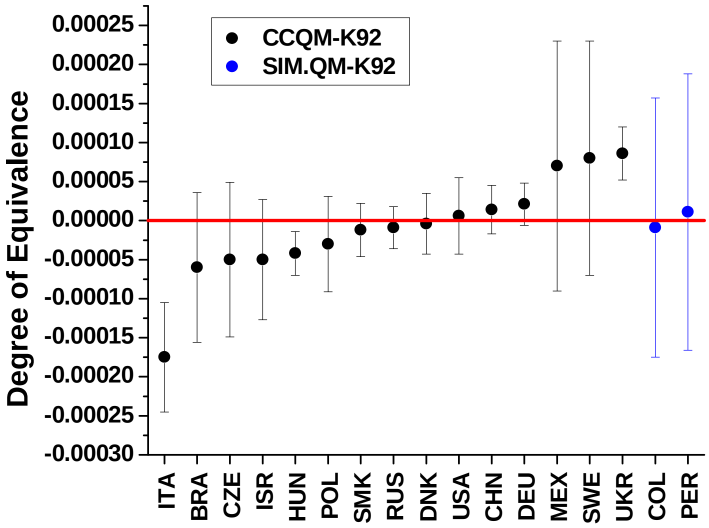

Figure 5. Degrees of equivalence linked to CCQM-K92.

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

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