CCQM WG on Electrochemical Analysis and Classical Chemical Methods

CCQM-K170 - Electrolytic Conductivity at 0.5 S m^{-1} and 20 S m^{-1}

Final Report

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Summary

The comparison CCQM-K170 is a subsequent key comparison of CCQM-K36.2016 and CCQM-K92. It aims to demonstrate the capabilities of the participating NMIs/DIs to measure the electrolytic conductivity of aqueous electrolyte solution in the electrolytic conductivity range around 0.5 S m^{-1} and 20 S m^{-1}. The coordinating institute (NIM) prepared two potassium chloride solutions with the nominal electrolytic conductivity of 0.5 S m^{-1} and 20 S m^{-1}, and verified their homogeneity and stability. Seventeen and twelve NMIs/DIs, respectively, reported their measurement results of 0.5 S m^{-1} and 20 S m^{-1} samples, respectively. The institutes used primary and secondary methods, and commercial instruments. Institutes using non-NMI CRMs as calibrants or CRMs from a participating NMI were excluded from KCRV calculation. The measurement results traceable to CRMs from the same non-participating NMI were combined into one result to be used for KCRV calculation. The results of institutes which have indicated technical problems were also excluded from KCRV calculation. The medians were agreed upon as the KCRVs for 0.5 S m^{-1} and 20 S m^{-1} solutions based on CCQM/2013-22 guidance document. Good agreement of the results was observed for the majority of participants. The results of this key comparison are considered representative for electrolytic conductivity measurement of aqueous electrolyte solution in the electrolytic conductivity range 0.15 S m^{-1} to 1.5 S m^{-1} and 5 S m^{-1} to 25 S m^{-1}, respectively. This KC is intended as an updated support for the corresponding calibration and measurement capabilities (CMCs) entries in the key comparison data base of the BIPM.

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2 List of participants

Participants are listed in Table 1. VNIIFTRI and VNIIM measured one sample each as their responsibilities in Russia are in different ranges in electrolytic conductivity. In this comparison, VNIIFTRI and VNIIM measured 0.5 S m^{-1} and 20 S m^{-1} samples, respectively.

Table 1 List of participants

Institute *i*	**Acronym**	**Country**	**Contact person**	**E-mail**
Government Office of the Capital City Budapest	BFKH	Hungary/HUN	Daniel Nagy	nagy.daniel2@bfkh.gov.hu
Centro Nacional de Metrología	CENAM	Mexico/MEX	Jorge Uribe Godínez José Luis Ortiz Aparicio	juribe@cenam.mx jortiz@cenam.mx
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National Institute of Quality	INACAL	Peru/PER	Javier Vásquez Arellán Christian Uribe Rosas	jvasquez@inacal.gob.pe curibe@inacal.gob.pe
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Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	Brazil/BRA	Fabiano Barbieri Gonzaga Kleiton da Cruz Cunha	fbgonzaga@inmetro.gov.br kccunha@inmetro.gov.br
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National Metrology Institute of Japan	NMIJ	Japan/JPN	Yuya Hibino	hibino.yuya@aist.go.jp

Institute *i*	Acronym	Country	Contact person	E-mail
National Institute of Metrology	NMIT	Thailand/THA	Nongluck Tangpaisarnkul	nongluck@nimt.or.th
Research Institutes of Sweden	RISE	Sweden/SWE	Emrah Yildirim Conny Haraldsson	emrah.yildirim@ri.se conny.haraldsson@ri.se
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3 Time schedule

Invitation	February 2023
Registration deadline	10 March 2023
Sample preparation	March / April 2023
Sample shipment	April / May 2023, delayed until early June 2023
Reporting deadline	31 August 2023, postponed to 30 September 2023
Preliminary result report	October 2023
KCRV estimation report	January and April 2024
Draft A report	October 2024
Draft B report	November 2024

4 Description of samples

4.1 Sample preparation, handling and shipment

Two potassium chloride (KCl) aqueous solutions with the nominal electrolytic conductivity of approximately 0.5 S m^{-1} and 20 S m^{-1}, which were produced by the coordinating institute (NIM) on March 30th and 27th 2023, respectively, were used for this international key comparison. The KCl aqueous solutions (15 L each sample) were prepared by dissolving primary chemical KCl (purchased from Tianjin Kemiou Chemical Reagent Co., Ltd) in pure water (produced from a Millipore Elix 3 water purification system) with a 20 L HDPE barrel. After fully homogenized with a mechanical stirrer, the KCl aqueous solutions were filled into 500 mL HDPE bottles (thirty bottles of each type of sample were obtained) which were subsequently closed with polypropylene screw caps. The bottle caps were then sealed with Parafilm. Bottles labels indicated: CCQM-K170, laboratory water, the value of electrolytic conductivity (0.5 S m^{-1} or 20 S m^{-1}), the filling date and the bottle number. The labelled bottles were then weighed. Afterwards, the bottles were sealed in an aluminium-laminated bag to prevent water evaporation.

The samples were dispatched to all participants in early June 2023. The bottles, together with the measurement technical protocol, were shipped, packed in Styrofoam, in a cardboard box by courier. The tracking numbers of the samples have been reported by e-mail to the contact persons of the participating institutes when the samples were dispatched. The participants received the number of requested bottles of the KCl aqueous solutions before June 30th 2023.

4.2 Sample bottle integrity

According to the technical protocol, the participants were requested to inspect visible bottle damage or leakage, and to weigh the received bottles to verify that they were unaffected from transport. The participants didn’t observe any visible bottle damage or leakage. They have reported the masses of the received bottles including the ambient conditions during weighing to the coordinating institute. The coordinating institute compared the reported masses with the initially weighed masses in order to verify bottle integrity. The masses were corrected for air buoyancy. Figure 1 and Figure 2 show the bottle mass differences of the 0.5 S m^{-1} and 20 S m^{-1} KCl solutions between masses measured at the participating institutes and those measured at the coordinating institute. For both types of aqueous KCl solutions, it was found that the differences did not exceed 0.03 g. Consequently, the sample shipment had negligible effect on the electrolytic conductivity of both types of aqueous KCl solutions.

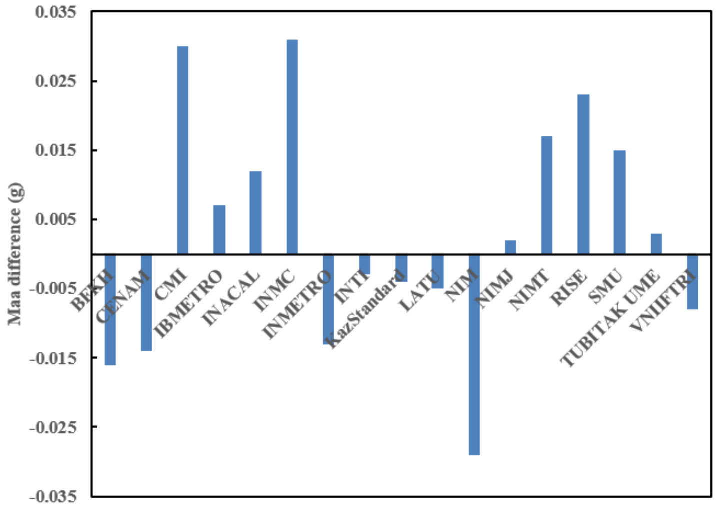

Figure 1 The bottle mass differences of 0.5 S m^{-1} KCl solution between masses measured at the participating institutes and those measured at the coordinating institute

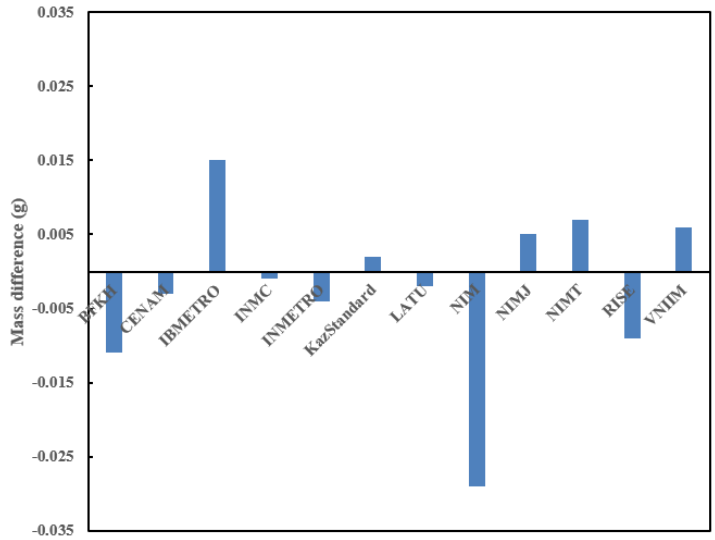

Figure 2 The bottle mass differences of 20 S m^{-1} KCl solution between masses measured at the participating institutes and those measured at the coordinating institute

4.3 Sample homogeneity

4.3.1 0.5 S m^{-1} KCl aqueous solutions

Thirty bottles of samples were obtained by bottling 15 L aqueous KCl solution with the nominal electrolytic conductivity of approximately 0.5 S m^{-1}. Three bottles were chosen for the homogeneity testing with the bottle numbers distributed over the whole batch. NIM's secondary measurement standard of electrolytic conductivity (a two-electrode Jones-type cell with the cell constant of ca. 32 cm^{-1}) was used to measure the conductivity of three bottles of samples at 25 °C. The measurement results, which have been linearly corrected to 25 °C, are shown in Table 2. The relative standard deviation of three values of the conductivity was 0.004%. This value is significantly smaller than the typical relative measurement uncertainties of the reported measurement results of electrolytic conductivity. The within-bottle homogeneity has not been measured since KCl aqueous solutions can be assumed sufficiently homogenous within a bottle. The verification of the between-bottle homogeneity is sufficient for this key comparison. So, the 0.5 S m^{-1} KCl aqueous solutions can be assumed to be homogeneous.

Table 2 The homogeneity test results of 0.5 S m^{-1} KCl aqueous solutions

Bottle number	Temperature (°C)	Conductivity (S m^{-1})	Mean Conductivity (S m^{-1})	Standard deviation (S m^{-1})	Relative standard deviation (%)
02	24.999	0.50134	0.50136	0.00002	0.004
19	24.998	0.50138			
30	24.999	0.50136			

4.3.2 20 S m^{-1} KCl aqueous solutions

Thirty bottles of samples were obtained by bottling 15 L aqueous KCl solution with the nominal electrolytic conductivity of approximately 20 S m^{-1}. Three bottles were chosen for the homogeneity testing with the bottle numbers distributed over the whole batch. NIM's secondary measurement standard of electrolytic conductivity (a two-electrode Jones-type cell with the cell constant of ca. 141 cm^{-1}) was used to measure the conductivity of three bottles of samples at 25 °C. The measurement results, which have been linearly corrected to 25 °C, are shown in Table 3. The relative standard deviation of three values of the conductivity was 0.015%. This value is smaller than the typical relative measurement uncertainties of the reported measurement results of electrolytic conductivity. The within-bottle homogeneity has not been measured since KCl aqueous solutions can be assumed sufficiently homogenous within a bottle. The verification of the between-bottle homogeneity is sufficient for this key comparison. So, the 20 S m^{-1} KCl aqueous solutions can be assumed to be homogeneous.

Table 3 The homogeneity test results of 20 S m^{-1} KCl aqueous solutions

Bottle number	Temperature (°C)	Conductivity (S m^{-1})	Mean Conductivity (S m^{-1})	Standard deviation (S m^{-1})	Relative standard deviation (%)
02	24.999	20.138	20.136	0.003	0.015
15	24.999	20.135			
30	24.999	20.133			

4.4 Sample stability

4.4.1 0.5 S m^{-1} KCl aqueous solutions

Four bottles were chosen for the stability testing. NIM's secondary measurement standard of electrolytic conductivity (a two-electrode Jones-type cell with the cell constant of ca. 32 cm^{-1}) was used to measure the conductivity of four bottles of samples at 25 °C. Several measurements were conducted in approximately eight-week intervals over the whole comparison measurement period. The measurement results, which have been linearly corrected to 25 °C, are given in Table 4. The standard deviation of five values of the conductivity is of the same order of magnitude as the standard deviation of the homogeneity measurements. The relative standard deviation is smaller than the typical relative measurement uncertainties of the reported measurement results of electrolytic conductivity.

Table 4 The stability test results of 0.5 S m^{-1} KCl aqueous solutions

Bottle number	Measuring date	Temperature (°C)	Conductivity (S m^{-1})	Mean Conductivity (S m^{-1})	Standard deviation (S m^{-1})	Relative standard deviation (%)
02	Mar. 31, 2023	24.999	0.50148	0.50152	0.00005	0.011
19	May 30, 2023	24.999	0.50149			
30	Jul. 28, 2023	25.000	0.50158			
30	Sept. 27, 2023	25.001	0.50159			
23	Nov. 30, 2023	24.999	0.50146			

A linear regression line was fitted through the results shown in Figure 3 according to ISO Guide 35. The slope is b_1=1.0×10^{-7}, and its standard deviation is $s(b_1)$= 3.5×10^{-7} (the formulas are given in the annex). Since

$$|b_1|<t_{0.95,n-2}\times s(b_1) = 3.18\times s(b_1) = 1.1\times 10^{-6} \quad (1)$$

the slope is not significant, and no instability of the sample is observed. Consequently, the 0.5 S m^{-1} KCl aqueous solutions can be assumed sufficiently stable over the comparison measurement period.

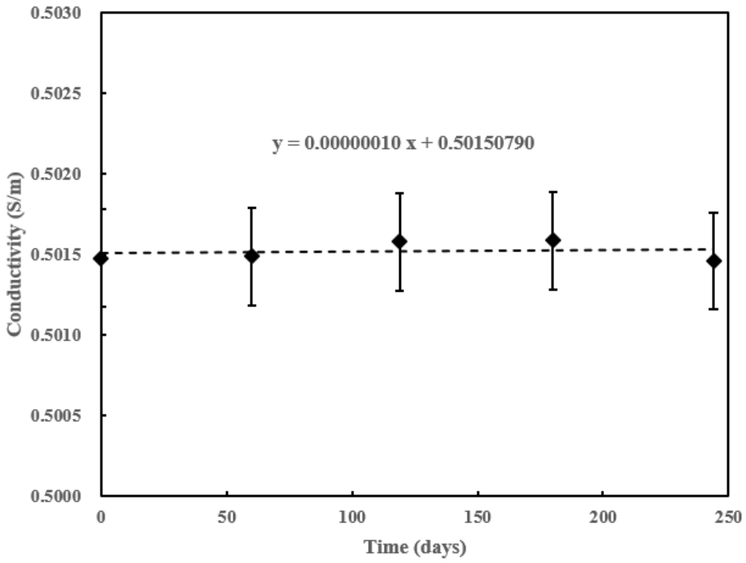

Figure 3 The stability test results of 0.5 S m^{-1} samples. The error bars indicate the combined uncertainties (ca. 0.00030 S m^{-1}) of measurements.

4.4.2 20 S m^{-1} KCl aqueous solutions

Four bottles were chosen for the stability testing. NIM's secondary measurement standard of electrolytic conductivity (a two-electrode Jones-type cell with the cell constant of ca. 141 cm^{-1}) was used to measure the conductivity of four bottles of samples at 25 °C. Several measurements were conducted in approximately eight-week intervals over the whole comparison measurement period. The measurement results, which have been linearly corrected to 25 °C, are given in Table 5. The standard deviation of five values of the conductivity is of the same order of magnitude as the standard deviation of the homogeneity measurements. The relative standard deviation is smaller than the typical relative measurement uncertainties of the reported measurement results of electrolytic conductivity.

Table 5 The stability test results of 20 S m^{-1} KCl aqueous solutions

Bottle number	Measuring date	Temperature (°C)	Conductivity (S m^{-1})	Mean Conductivity (S m^{-1})	Standard deviation (S m^{-1})	Relative standard deviation (%)
02	Mar. 31, 2023	24.999	20.138	20.140	0.0015	0.007
15	May 30, 2023	24.999	20.141			
30	Jul. 28, 2023	25.000	20.141			
30	Sept. 27, 2023	25.001	20.142			
25	Nov. 30, 2023	24.999	20.140			

A linear regression line was fitted through the results shown in Figure 4 according to ISO Guide 35. The slope is b_1=6.8×10^{-6}, and its standard deviation is $s(b_1)$= 6.9×10^{-6} (the formulas are given in the annex). Since

$$|b_1|<t_{0.95,n-2}\times s(b_1) = 3.18\times s(b_1) = 2.2\times10^{-5} \quad (2)$$

the slope is not significant, and no instability of the sample is observed. Consequently, the 20 S m^{-1} KCl aqueous solutions can be assumed sufficiently stable over the comparison measurement period.

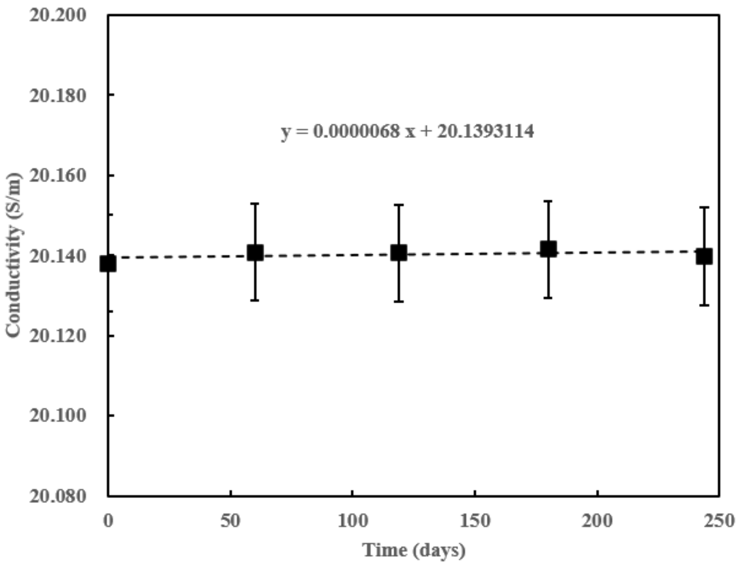

Figure 4 The stability test results of 20 S m^{-1} samples. The error bars indicate the combined uncertainties (ca. 0.012 S m^{-1}) of measurements.

4.5 Sample temperature coefficient

The temperature coefficient is an important parameter in the measurement of the conductivity of electrolyte solutions. Measuring the conductivity of 0.5 S m^{-1} and 20 S m^{-1} KCl aqueous solutions at 24 °C and 26 °C was additionally encouraged in the technical protocol for the calculation of the temperature coefficient of each type of solution. Several institutes reported these values which are listed in Table 6 and Table 7. The 4th and last columns show the deduced temperature coefficients of two samples. The average temperature coefficients from several institutes are 0.0192 K^{-1} and 0.0164 K^{-1} for 0.5 S m^{-1} and 20 S m^{-1} KCl aqueous solutions, respectively.

Table 6 Reported conductivity and deduced temperature coefficient of 0.5 S m^{-1} KCl solutions

Institute *i*	Temperature (°C)	Conductivity (S m^{-1})	Temperature coefficient (K^{-1})	Average temperature Coefficient (K^{-1})
INACAL	24	0.49238	0.0186	0.0192
	26	0.51165	0.0198	
NIM	24	0.49168	0.0195	0.0192
	26	0.51093	0.0189	
NIMT	24	0.491	0.0200	0.0190
	26	0.510	0.0180	
NMIJ	24	0.49136	0.0197	0.0196
	26	0.51096	0.0194	
VNIIFTRI	24	0.490679	0.0190	0.0191
	26	0.509790	0.0192	

Table 7 Reported conductivity and deduced temperature coefficient of 20 S m^{-1} KCl solutions

Institute *i*	Temperature (°C)	Conductivity (S m^{-1})	Temperature coefficient (K^{-1})	Average temperature Coefficient (K^{-1})
NIM	24	19.810	0.0163	0.0165
	26	20.473	0.0166	
NIMT	24	19.78	0.0164	0.0164
	26	20.44	0.0164	
NMIJ	24	19.825	0.0165	0.0162
	26	20.479	0.0160	
VNIIM	24	19.2856	0.0164	0.0164
	26	19.9285	0.0164	

5 Correspondence with institutes

Some participating institutes, BFKH, CENAM, INTI, KazStandard, LATU, TUBITAK UME, VNIIFTRI and VNIIM, have been asked to check, confirm or add information (probable typing errors, reported values, traceability route, calibrants, uncertainty evaluation, etc.) in their measurement reports. Partly, intensive communication between the coordinating institute and several of these institutes was necessary. During these communications, no information on sign or magnitude of the apparent anomaly has been given to the participating institutes. The following feedback has been given:

BFKH: The BFKH results of 20 S m^{-1} KCl solutions showed anomalous deviations. BFKH has realised an erroneous calculation of the cell constant of the secondary cell used in the measurement of 20 S m^{-1} KCl solutions only after the results of the key comparison have been disclosed on Oct. 11th 2023. The updated conductivity value was 20.2113 S m^{-1} associated with the expanded uncertainty of 0.0178 S m^{-1}. However, since the results had already been disclosed by that time, the originally reported results of BFKH could not be replaced. It should however be mentioned that the corrected results are calculated only from data presented in the original measurement report.

CENAM: The results of CENAM of the 20 S m^{-1} KCl solutions showed anomalous deviations. CENAM has realised technical problems when the cell constant of the commercial sensor has been calibrated with SMU CRMs. CENAM reported these problems only after the preliminary results of the key comparison had been disclosed on Oct. 11th 2023. Consequently, the original results stand.

INTI: The results of INTI showed anomalous deviations. INTI has realised technical problems when the cell constant of the commercial sensor has been calibrated with CRMs from the Supelco company. INTI reported these problems only after the preliminary results of the key comparison had been disclosed on Oct. 11th 2023. Consequently, the original results stand.

KazStandard: KazStandard requested to postpone the reporting deadline to Sept. 30th 2023 for internal reasons, which was accepted by the coordinating institute. Its results of the 20 S m^{-1} KCl solutions showed anomalous deviations. KazStandard confirmed the reported values. However, it made significant modifications to the description of the traceability route in the revised measurement report. The calibration solutions (OIML R56 recipe solutions) for secondary cell were replaced with non-NMI CRMs from ZMK company in the measurement of 0.5 S m^{-1} KCl solutions. For the measurement of 20 S m^{-1} KCl solutions, the cell constant of the secondary cell used was described as being traceable to reference solutions the conductivities of which were determined by another secondary cell which had a long and complicated traceability chain. However, the lab could not provide the reference values of reference solutions and their uncertainties.

LATU: LATU requested to postpone the reporting deadline to Sept. 30th 2023 for internal reasons. This was accepted by the coordinating institute.

TUBITAK UME: TUBITAK UME confirmed the reported values. In addition, the lab changed the description of measurement method from primary method into secondary method using DFM CRMs. This was accepted by the coordinating institute.

VNIIFTRI: The results of VNIIFTRI showed anomalous deviations. VNIIFTRI confirmed the reported values and gave a more detailed description of their traceability. Afterwards, the lab has asked to modify the measurement uncertainty after the preliminary results of the key comparison were disclosed on Oct. 11th 2023. This modification was not accepted because it is not supported by the data in the original measurement report.

VNIIM: The results of VNIIM showed anomalous deviations. VNIIM confirmed the reported values and gave a more detailed description of their traceability. VNIIM found some technical problems when the cell constant of the used secondary cell was calibrated with OIML R56 recipe solutions after the preliminary results of the key comparison were disclosed on Oct. 11th 2023. However, the originally reported values have not been changed.

6 Instructions for measurement

The received bottles had to be stored at temperatures between 20 °C and 25 °C. They had not to be stored above 25 °C. The bottle cap and its parafilm must only be opened immediately before the measurements. If possible, the bottle cap should have been re-sealed with Parafilm following each opening.

Each participant had to measure the electrolytic conductivity of the solutions with respect to 25 °C using the method its existing or planned CMC claims are referring to. Additional data at 24 °C and 26 °C were welcome, allowing for the calculation of temperature coefficient of each solution.

7 Results and analyses

7.1 Reported results of 0.5 S m^{-1} KCl aqueous solutions and related analyses

Table 8 lists the reported results of the 0.5 S m^{-1} KCl solutions. The sixth and the last columns list the type of cell used and the stated source of traceability, respectively. Figure 5 shows the reported results graphically.

17 NMIs measured this solution. Primary cells the cell constants of which are traceable to length standards were used by three NMIs: CMI (Jones type cell with a removable middle part), INMETRO (piston type cell) and NIM (Jones type cell with a removable middle part). A number of institutes used secondary cells, and three institutes (INTI, CENAM and RISE) used commercial sensors which can essentially be considered as secondary cells here. INTI and KazStandard used non-NMI CRMs from the companies Supelco and ZMK to calibrate the cell constants of their secondary cells. Three institutes (CENAM, INMC and INACAL) used SMU CRMs as calibrants. Their results were therefore not independent results, all the more SMU also participated to measured 0.5 S m^{-1} KCl solution. Similarly, the results from TUBITAK UME, NIMT, RISE, LATU and IBMETRO were also not independent results since they used DFM CRMs as reference solutions.

Most measurement results show good consistency for 0.5 S m^{-1} KCl aqueous solutions. The result of INTI is far below the other results.

Table 8 Reported conductivities of 0.5 S m^{-1} KCl solutions at 25 °C and their uncertainties

Institute *i*	Quantity value x_i	Standard uncertainty $u(x_i)$	Coverage factor k_i	Expanded uncertainty $U(x_i)$	Cell type	Source of traceability
acronym	(S m^{-1})	(S m^{-1})		(S m^{-1})		
INTI	0.4802	0.0052	2.65	0.01378	Commercial sensor (Secondary cell)	Supelco CRMs
VNIIFTRI	0.500184	0.00020	2.00	0.00040	Secondary cell	CRMs certified by own primary cell
CENAM	0.5003	0.0051	2.00	0.0102	Commercial sensor (Secondary cell)	SMU CRMs
TUBITAK UME	0.5004	0.0010	2.00	0.0020	Secondary cell	DFM CRMs
NIMT	0.5010	0.00086	2.00	0.00172	Secondary cell	DFM CRMs
BFKH	0.50116 *	0.000345	2.00	0.00069	Secondary cell	OIML R56 recipe
NMIJ	0.50125	0.00048	2.00	0.00096	Secondary cell	CRMs certified by own primary cell
NIM	0.50146	0.000125	2.00	0.00025	Primary cell	Length standard
RISE	0.5015	0.0006	2.00	0.0012	Commercial sensor (Secondary cell)	DFM CRMs
INMC	0.50151	0.00045	2.00	0.00090	Secondary cell	SMU CRMs
SMU	0.50153	0.00013	2.00	0.00026	Secondary cell	Bradshaw's recipe
INACAL	0.50172	0.00045	2.00	0.00090	Secondary cell	SMU CRMs
CMI	0.5018	0.00055	2.00	0.0011	Primary cell	Length standard
LATU	0.50182	0.00038	2.00	0.00076	Secondary cell	DFM CRMs
KazStandard	0.501901279	0.000436	2.00	0.000872068	Secondary cell	ZMK CRMs
IBMETRO	0.5020	0.0008	1.97	0.001576	Secondary cell	DFM CRMs
INMETRO	0.50225	0.00025	2.00	0.00050	Primary cell	Length standard

* The results from BFKH were corrected to exact 25 °C with the temperature coefficient of 0.0192 K^{-1} since the submitted results (0.50126 S m^{-1}) were at 25.01 °C.

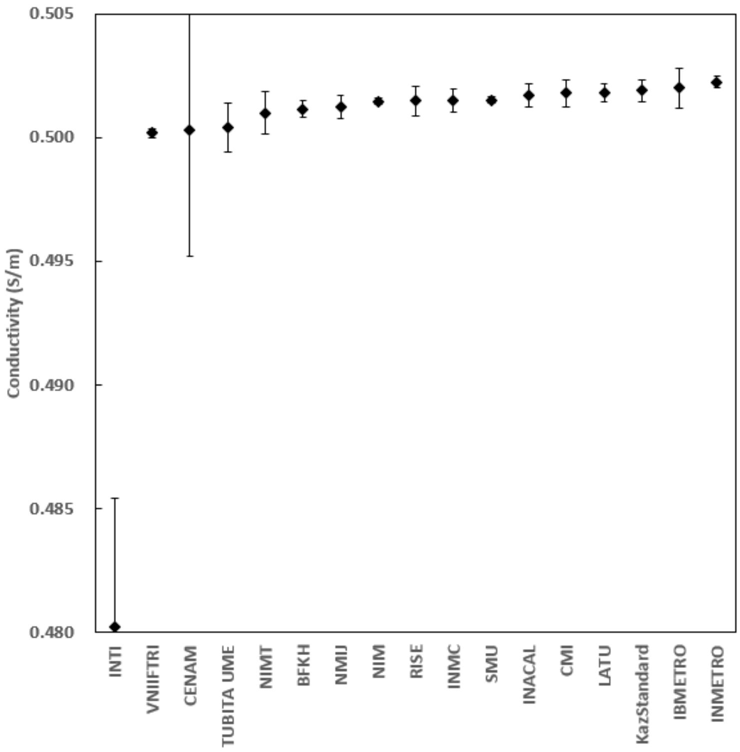

Figure 5 The reported conductivities of 0.5 S m^{-1} KCl solutions at 25 °C. The error bars indicate the standard uncertainties.

7.2 Reported results of 20 S m^{-1} KCl aqueous solutions and related analyses

Table 9 lists the reported results of the 20 S m^{-1} KCl solutions from 12 institutes. The sixth and the last columns list the type of cell used and the stated source of traceability, respectively. Figure 6 shows the reported results graphically.

12 NMIs measured this solution. Three NMIs (INACAL, INTI and SMU) requested and received this solution, but they did not report their measurement results. Primary cells the cell constants of which are traceable to length standards were used by two NMIs to measure the solutions: INMETRO (piston type cell) and NIM (Jones type cell with a removable middle part). A number of institutes used secondary cells, and two institutes (CENAM and RISE) used commercial sensors which can essentially be considered as secondary cells here. IBMETRO used non-NMI CRMs from ZMK company to calibrate the cell constant of its secondary cell. Two institutes (CENAM and INMC) used SMU CRMs as calibrants, so that their results were not independent. Likewise, the results from NIMT, RISE and LATU were also not independent since they used DFM CRMs as reference solutions.

The measurement results show acceptable consistency for 20 S m^{-1} KCl aqueous solutions. The results of VNIIM and CENAM are far below the other results, and the results of BFKH and KazStandard are higher than the other results. Secondary measurements of the 20 S m^{-1} solutions are more challenging, since CRMs with such a high conductivity are not commonly available for calibration. Calibration is therefore often done at somewhat smaller conductivities (i.e. around 10 S m^{-1}). These measurements can thus be classified as "extrapolation measurements".

Table 9 Reported conductivities of 20 S m^{-1} KCl solutions at 25 °C and their uncertainties

Institute *i*	Quantity value x_i	Standard uncertainty $u(x_i)$	Coverage factor k_i	Expanded uncertainty $U(x_i)$	Cell type	Source of traceability
acronym	(S m^{-1})	(S m^{-1})		(S m^{-1})		
VNIIM	19.6049	0.0016	2.00	0.0032	Secondary cell	OIML R56 recipe
CENAM	19.8159	0.0293	2.00	0.0586	Commercial sensor (Secondary cell)	SMU CRMs
INMC	20.110	0.024	2.00	0.048	Secondary cell	SMU CRMs
NIMT	20.110	0.021	2.00	0.042	Secondary cell	DFM CRMs
LATU	20.131	0.013	2.00	0.026	Secondary cell	DFM CRMs
NIM	20.138	0.005	2.00	0.010	Primary cell	Length standard
RISE	20.156	0.025	2.00	0.050	Commercial sensor (Secondary cell)	DFM CRMs
NMIJ	20.157	0.024	2.00	0.048	Secondary cell	CRMs certified by own primary cell
INMETRO	20.166	0.021	2.00	0.042	Primary cell	Length standard
IBMETRO	20.1935	0.3717	2.05	0.761985	Secondary cell	ZMK CRMs
BFKH	20.2636 *	0.00627	2.00	0.01254	Secondary cell	OIML R56 recipe
KazStandard	20.28405	0.00912	2.00	0.01824945	Secondary cell	Reference solutions certified by another secondary cell

* The results from BFKH were corrected to exact 25 °C with the temperature coefficient of 0.0164 K^{-1} since the submitted results (20.2669 S m^{-1}) were at 25.01 °C.

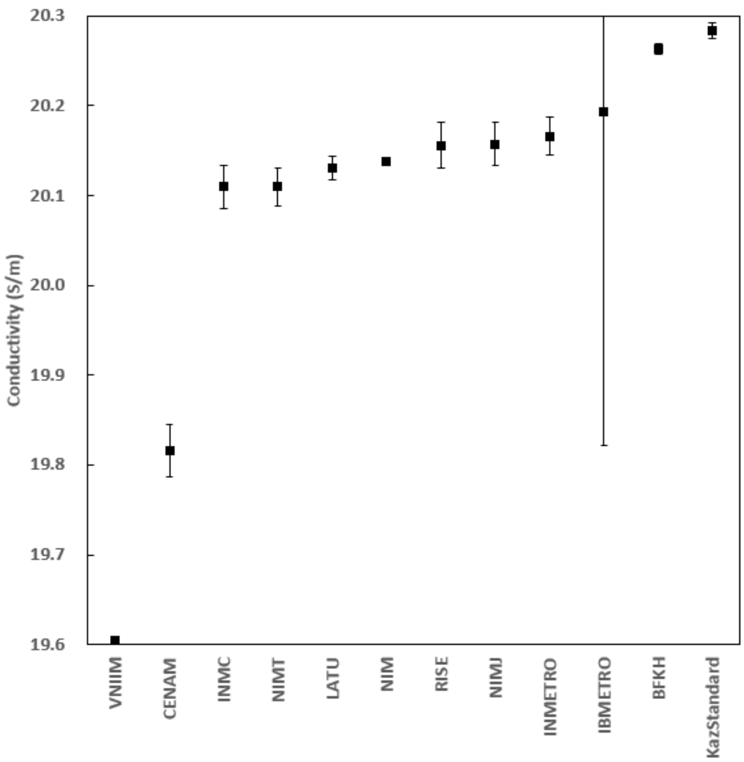

Figure 6 The reported conductivities of 20 S m^{-1} KCl solutions at 25 °C. The error bars indicate the standard uncertainties.

8 Estimators for the Key Comparison Reference Value (KCRV)

The description of the above-mentioned results and their routes of traceability make it obvious that the selection of an appropriate subset of results to calculate the KCRV is challenging, in particular with respect to the 20 S m^{-1} KCl solution. Following the relevant guides (CIPM MRA-G-11 and CCQM/2013-22), and after consulting the chair of the CCQM Key Comparison Working Group (CCQM KCWG), and after discussions at the meetings of the participants and EAWG, held on Jan. 18th and Apr. 22th 2024, respectively, rules to select a subset of results for KCRV calculation were agreed upon as follows:

a) The secondary measurement results using non-NMI CRMs (e.g. from a company) as calibrants must be excluded from KCRV calculation.
b) Results are excluded from KCRV calculation if technical problems have been reported in measurement reports or other sources (e.g. communications).
c) The secondary measurement results traceable to CRMs from the same NMI are not independent and may be classified into two categories. Firstly, secondary measurement results must be excluded from KCRV calculation if the NMI providing metrological traceability has participated in the measurement. Secondly, secondary measurement results can be combined into one result by an appropriate averaging method to be used for KCRV calculation if the NMI providing metrological traceability has not participated in the measurement.

The chair of EAWG, Dr. Steffen Seitz, has received approval for these decisions from CCQM KCWG. These decisions can also be found in the minutes of CCQM EAWG meeting held on Apr. 22th 2024.

8.1 KCRV estimators of the 0.5 S m^{-1} KCl aqueous solution

Table 10 shows a summary on whether the reported results from NMIs are used for KCRV calculation. The third column gives the justification according to the above-mentioned rules.

Table 10 A summary on whether the reported results from NMIs are used for KCRV calculation

Institute *i*	Reported results included or excluded for KCRV calculation	Justification	Other information
CENAM	excluded	Technical problems, see b) SMU CRMs as calibrants, see c)	
INACAL	excluded	SMU CRMs as calibrants, see c)	
INMC	excluded	SMU CRMs as calibrants, see c)	
INTI	excluded	Technical problems, see b) non-NMI CRM as calibrants, see a)	
KazStandard	excluded	non-NMI CRM as calibrants, see a)	
BFKH	included		
CMI	included		
INMETRO	included		
NIM	included		
NMIJ	included		
SMU	included		
VNIIFTRI	included		
IBMETRO	excluded	DFM CRMs as calibrants, see c)	These five results were combined into one result to be used for KCRV calculation
LATU	excluded	DFM CRMs as calibrants, see c)	
NIMT	excluded	DFM CRMs as calibrants, see c)	
RISE	excluded	DFM CRMs as calibrants, see c)	
TUBITAK UME	excluded	DFM CRMs as calibrants, see c)	

The results from IBMETRO, LATU, NIMT, RISE and TUBITAK UME were not independent since they used DFM CRMs as calibrants, so these five results were combined into one result to be used for KCRV calculation. These results are mutually consistent by Chi-squared test and their distribution fits best to figure 1A of CCQM/2013-22. Thus, the uncertainty weighted mean without correction for dispersion (abbreviated as weighted mean (w/o disp.)) of this subset data was obtained and then used for subsequent KCRV calculation. The conductivity value of the weighted mean (w/o disp.) for this subset data was 0.50159 S m^{-1} associated with the standard uncertainty of 0.00027 S m^{-1}.

Consequently, eight results have been used to calculate KCRV estimators for the 0.5 S m^{-1} KCl solution. The arithmetic mean, the weighted mean (w/o disp.), the uncertainty weighted mean with correction for dispersion (abbreviated as weighted mean (w disp.)), the median and the DerSimonian-Laird were calculated as KCRV estimators (the formulas are given in the annex). The KCRV estimators are shown in Table 11 together with their standard uncertainties. The KCRV estimators are almost the same although the median is slightly higher than the other four KCRV estimators.

Table 11 KCRV estimators and their standard uncertainties, calculated according to CCQM/2013-22

KCRV estimator	Value of conductivity (S m^{-1})	Standard uncertainty (S m^{-1})
Weighted mean (w/o disp.)	0.50138	0.00007
Weighted mean (w disp.)	0.50138	0.00019
Median	0.50150	0.00018
DerSimonian-Laird	0.50138	0.00023
Arithmetic mean	0.50140	0.00021

The conductivity labelled with the symbol of wm_5 NMIs is the weighted mean (w/o disp.) of the reported results from IBMETRO, LATU, NIMT, RISE and TUBITAK UME. The distribution of eight results used to calculate KCRV estimators (see Figure **3**7) fits best to figure 1C of CCQM/2013-22. Therefore, the median was agreed upon as the KCRV of the 0.5 S m^{-1} KCl solution. The reported results from all 17 NMIs (see Figure **3**8) also fit best to figure 1C of CCQM/2013-22.

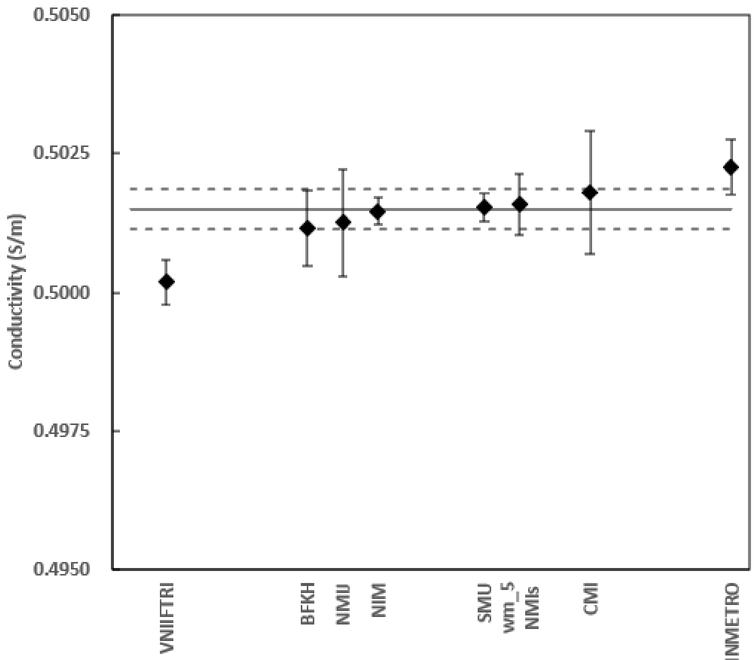

Figure 7 The results used to calculate KCRV estimators of the 0.5 S m^{-1} KCl solution at 25 °C. The error bars indicate their expanded uncertainties. The solid and dashed lines indicate the median and its expanded uncertainty.

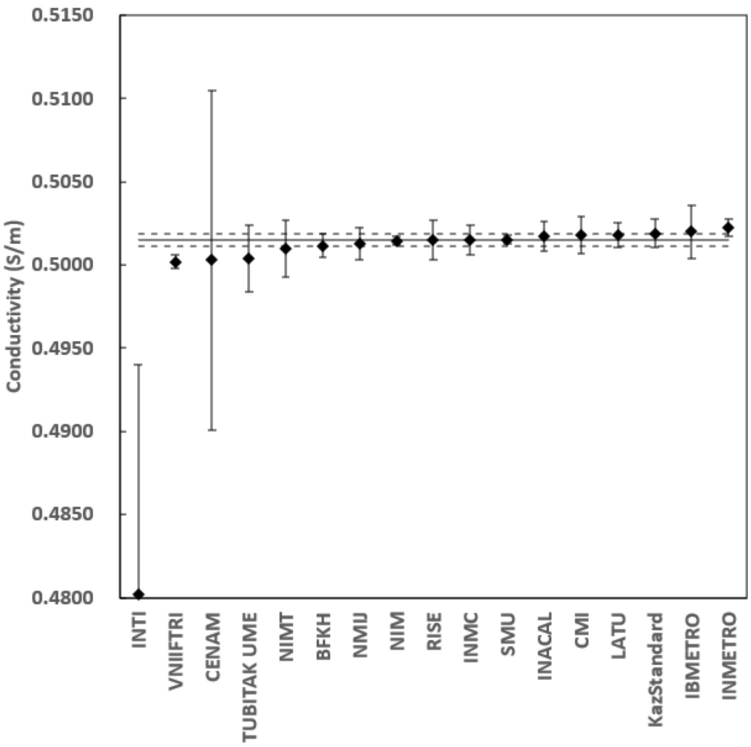

Figure 8 The reported results of the 0.5 S m^{-1} KCl solution at 25 °C. The error bars indicate their expanded uncertainties. The solid and dashed lines indicate the median and its expanded uncertainty.

8.2 KCRV estimators of 20 S m^{-1} KCl aqueous solution

Table 12 shows a summary on whether the reported results from NMIs are used for KCRV calculation. The third column gives the justification according to the above-mentioned rules.

Table 12 A summary on whether the reported results from NMIs being used for KCRV calculation

Institute *i*	Reported results included or excluded for KCRV calculation	Justification	Other information
CENAM	excluded	Technical problems, see b) SMU CRMs as calibrants, see c)	
IBMETRO	excluded	non-NMI CRM as calibrants, see a)	
KazStandard	excluded	Technical problems, see b)	
VNIIM	excluded	Technical problems, see b)	
BFKH	included		
INMC	included		The only NMI using SMU CRMs as calibrants except CENAM
INMETRO	included		
NIM	included		
NMIJ	included		
LATU	excluded	DFM CRMs as calibrants, see c)	These three results were combined into one result to be used for KCRV calculation
NIMT	excluded	DFM CRMs as calibrants, see c)	
RISE	excluded	DFM CRMs as calibrants, see c)	

The results from LATU, NIMT and RISE were not independent since they used DFM CRMs as calibrants, so these three results were combined into one result to be used for KCRV calculation. These results are mutually consistent by Chi-squared test, and their distribution fits best to figure 1A of CCQM/2013-22. Thus, the weighted mean (w/o disp.) of this subset data was obtained and then used for subsequent KCRV calculation. The conductivity value of the weighted mean (w/o disp.) for this subset data was 20.130 S m^{-1} associated with the standard uncertainty of 0.010 S m^{-1}.

Consequently, six results have been used to calculate KCRV estimators for the 20 S m^{-1} KCl solution. The arithmetic mean, the weighted mean (w/o disp.), the weighted mean (w disp.), the median and the DerSimonian-Laird were calculated as KCRV estimators (the formulas are given in the annex). The KCRV estimators are shown in Table 13 together with their standard uncertainties. The median is slightly smaller than the other four KCRV estimators, which values are similar. The standard uncertainty of the median is between that of the weighted mean (w/o disp.) and those of the other three KCRV estimators.

Table 13 KCRV estimators and their uncertainties, calculated according to CCQM/2013-22

KCRV estimator	Value of conductivity (S m^{-1})	Standard uncertainty (S m^{-1})
Weighted mean (w/o disp.)	20.177	0.004
Weighted mean (w disp.)	20.177	0.026
Median	20.148	0.014
DerSimonian-Laird	20.162	0.023
Arithmetic mean	20.161	0.022

The conductivity labelled with the symbol of wm_3 NMIs is the weighted mean (w/o disp.) of the reported results from LATU, NIMT and RISE. The distribution of six results used to calculate KCRV estimators (see Figure **3**9) fits best to figure 1C of CCQM/2013-22. Therefore, the median was agreed upon as the KCRV of the 20 S m^{-1} KCl solution. The reported results from all 12 NMIs (see Figure **3**10) also fit best to figure 1C of CCQM/2013-22.

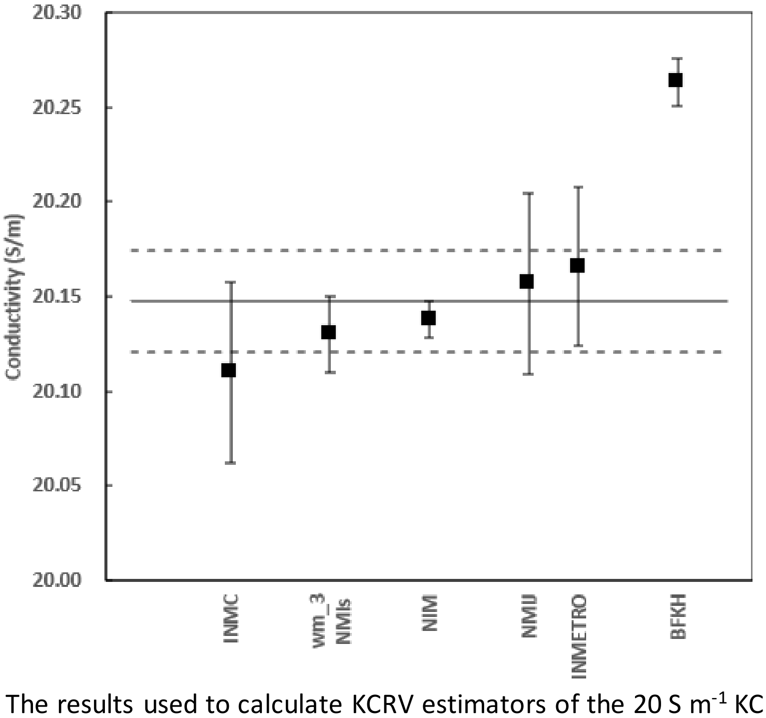

Figure 9 The results used to calculate KCRV estimators of the 20 S m^{-1} KCl solution at 25 °C. The error bars indicate their expanded uncertainties. The solid and dashed lines indicate the median and its expanded uncertainty.

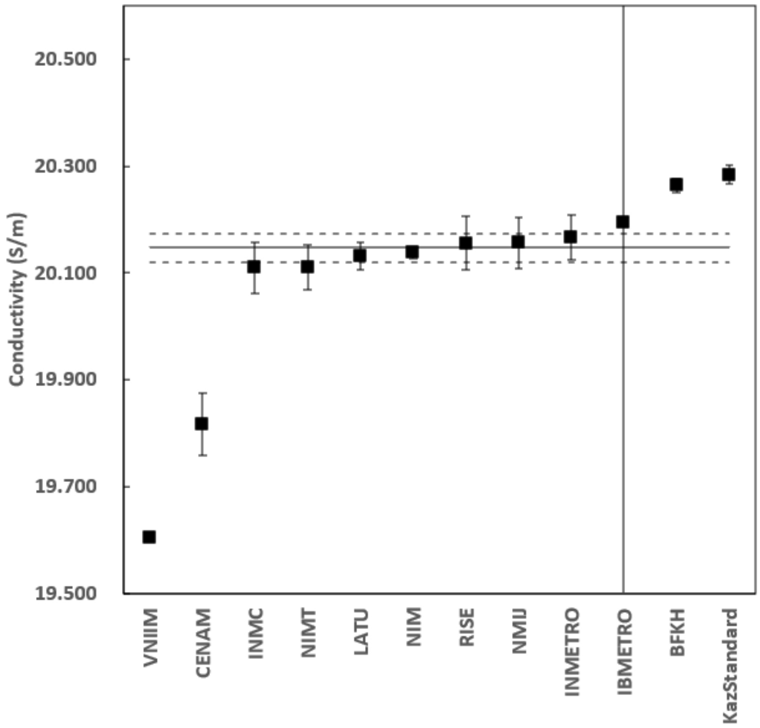

Figure 10 The reported results of the 20 S m^{-1} KCl solution at 25°C. The error bars indicate their expanded uncertainties. The solid and dashed lines indicate the median and its expanded uncertainty.

9 Degrees of equivalence (DoE) based on the proposed KCRV

The DoE_i of the result x_i of institute *i* and its uncertainty is calculated according to CCQM/2013-22 with respect to the selected KCRV (the formulas are given in the annex). The results of 0.5 S m^{-1} and 20 S m^{-1} KCl aqueous solutions are listed in Table **1**14 and Table 15, respectively. The tables also state the uncertainty weighed *DoE* (E_n value).

$$E_\mathrm{n}(x_i) = \frac{DoE_i}{U(DoE_i)} \quad (3)$$

A result is considered consistent with the KCRV if $|E_\mathrm{n}(x_i)| \leq 1$. Table **1**14 and Table 15 also show the minimal relative expanded uncertainties (U_{minCMC}) consistent with the proposed KCRV, which makes the submission and review of claims of calibration and measurement capabilities (CMCs) easier. The U_{minCMC} is equivalent with the expanded uncertainty reported by the institute if a result is consistent with the KCRV. If it is not consistent with the KCRV, the $u_{\mathrm{minCMC}}(x_i)$ is calculated based on Eq. (4) being taken from the unpublished paper of M.G. Cox, et al..

$$u_{minCMC}(x_i) = \sqrt{\left(\frac{DoE_i}{k_i}\right)^2 \pm \left(\frac{2}{k_i}\right)^2 u^2(\mathrm{KCRV})} \quad (4)$$

k_i is the reported coverage factor. The minus sign applies for results that contributed to the KCRV calculation and the plus sign applies to those that didn't contribute. Figure 11 and Figure 12 show the DoEs and their uncertainties graphically.

9.1 Degrees of equivalence (DoE) based on the proposed KCRV estimators of the 0.5 S m^{-1} KCl solution

Table 14 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission for the 0.5 S m^{-1} KCl solution

Institute i	DoE_i (S m^{-1})	$U(DoE_i)$ (S m^{-1})	$E_n(x_i)$	$U_{minCMC}(i)$ (S m^{-1})
INTI	-0.021	0.014	-1.54	0.021
VNIIFTRI	-0.00131	0.00050	-2.62	0.0013
CENAM	-0.001	0.010	-0.12	0.010
TUBITAK UME	-0.0011	0.0020	-0.54	0.0020
NIMT	-0.0005	0.0018	-0.28	0.0017
BFKH	-0.00033	0.00070	-0.48	0.00069
NMIJ	-0.00025	0.00091	-0.27	0.00096
NIM	-0.00004	0.00042	-0.08	0.00025
RISE	0.0000	0.0013	0.00	0.0012
INMC	0.00001	0.00097	0.02	0.00090
SMU	0.00004	0.00043	0.08	0.00026
INACAL	0.00023	0.00097	0.23	0.00090
CMI	0.0003	0.0010	0.30	0.0011
LATU	0.00033	0.00084	0.39	0.00076
KazStandard	0.00041	0.00094	0.43	0.00087
IBMETRO	0.0005	0.0016	0.31	0.0016
INMETRO	0.00075	0.00056	1.34	0.00066

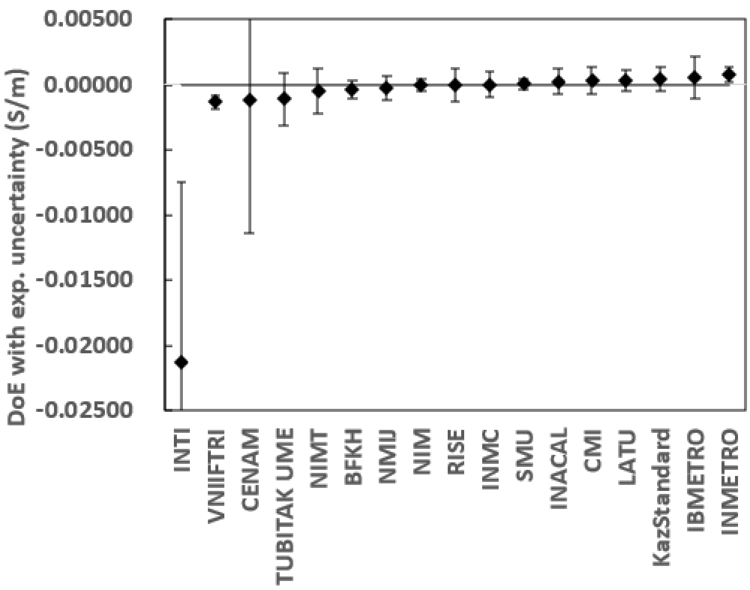

Figure 11 DoEs and their expanded uncertainties from 17 NMIs for the 0.5 S m^{-1} KCl solution

9.2 Degrees of equivalence (DoE) based on the proposed KCRV estimators of the 20 S m^{-1} KCl solution

Table 15 Degrees of equivalence, their expanded uncertainties, E_n values and minimal expanded uncertainties admissible for CMC submission for the 20 S m^{-1} KCl solution

Institute i	DoE_i (S m^{-1})	$U(DoE_i)$ (S m^{-1})	$E_n(x_i)$	$U_{minCMC}(i)$ (S m^{-1})
VNIIM	-0.543	0.027	-19.85	0.54
CENAM	-0.332	0.065	-5.13	0.33
INMC	-0.038	0.048	-0.79	0.048
NIMT	-0.038	0.050	-0.75	0.042
LATU	-0.017	0.038	-0.44	0.026
NIM	-0.009	0.028	-0.34	0.010
RISE	0.008	0.057	0.15	0.050
NMIJ	0.009	0.048	0.20	0.048
INMETRO	0.018	0.044	0.42	0.042
IBMETRO	0.05	0.76	0.06	0.76
BFKH	0.116	0.029	4.00	0.11
KazStandard	0.137	0.033	4.17	0.14

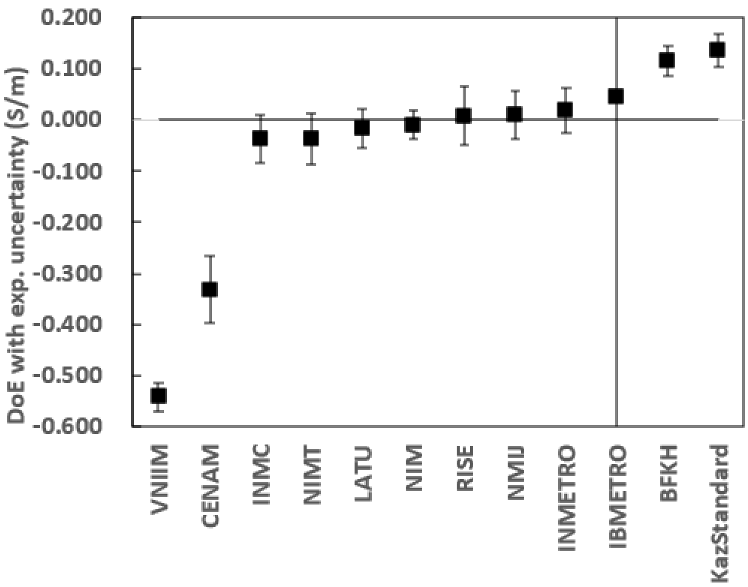

Figure 12 DoEs and their expanded uncertainties from 12 NMIs for the 20 S m^{-1} KCl solution

10 How Far Does The Light Shines statement

The results of this key comparison are considered representative for electrolytic conductivity measurements of aqueous electrolyte solutions in the electrolytic conductivity range 0.15 S m^{-1} to 1.5 S m^{-1} and 5 S m^{-1} to 25 S m^{-1}, respectively. The uncertainties claimed in CMCs must not be smaller than the U_{minCMC} values stated in Table 14 and Table 15, unless exceptions stated in EAWG-CMC guidelines can be applied.

It must be emphasized that the HFTLS range of CCQM-K105 (1 to 15 S m^{-1}) overlaps with that of the 20 S m^{-1} solution used in this KC. In case an institute has participated in both KCs, CCQM-K105 prevails in the overlapping range, unless the institute has demonstrated a lower uncertainty in this KC.

11 Remarks regarding CMC submissions of specific participants

The results of 0.5 S m^{-1} and 20 S m^{-1} KCl solutions from KazStandard have no acceptable traceability (non-NMI CRMs as calibrants or an unclear route of traceability) and must not be used to support CMC submissions. Likewise, INTI must not submit CMC based on its results at 0.5 S m^{-1} KCl solution since INTI used non-NMI CRMs as calibrants. IBMETRO must not submit CMCs based on its results at 20 S m^{-1} KCl solution since IBMETRO used non-NMI CRMs as calibrants.

12 Acknowledgements

This work was supported by a grant from State Administration for Market Regulation of China (No. ANL2301). The coordinating laboratory gratefully acknowledges the contributions of all participants and the members of the CCQM Working Group on Electrochemical Analysis for their valuable suggestions concerning the measurement protocol and the evaluation process.

13 References

ISO Guide 35: 2017, Reference materials — Guidance for characterization and assessment of homogeneity and stability

CIPM MRA-P-11 Overview and implementation of the CIPM MRA, available at https://www.bipm.org/en/cipm-mra/cipm-mra-documents

CCQM/2013-22 CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, available at https://www.bipm.org/documents/20126/28430045/working-document-ID-5794/49d366bc-295f-18ca-c4d3-d68aa54077b5

Draft minutes of CCQM WG on Electrochemical Analysis and Classical Chemical Methods (CCQM EAWG) meeting held on April 22th 2024

M.G. Cox, P. Harris, M. Milton, Method for determining acceptable CMCs to ensure consistency with KC results, 2009, unpublished

GUM: Guide to the Expression of Uncertainty in Measurement, available at https://www.bipm.org/en/committees/jc/jcgm/publications

CCQM-K170

Annex (Formula)

Formula

Verification of stability

$$b_1 = \frac{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)\left(Y_i - \overline{Y}\right)}{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}$$

$$s\left(b_1\right) = \frac{s}{\sqrt{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}}$$ with $$s^2 = \frac{\sum_{i=1}^{n}\left(Y_i - b_0 - b_1 X_i\right)^2}{n-2}$$ and $$b_0 = \overline{Y} - b_1\overline{X}$$

b_0 (intercept) and b_1(slope) are the parameters of a linear regression through the stability measurement results X_i (date of measurement) and Y_i (measurement parameter, usually the conductivity or conductance of the samples). $\overline{X}$ and $\overline{Y}$ are the means of n stability measurements i = 1...n. The sample can be considered stable if $|b_1| < t_{0.95,\, n\text{-}2}\, s(b_1)$, with $t_{0.95,\, n\text{-}2}$ being the 95% student-t factor at n-2 degrees of freedom.

KCRVs and DoEs

See CCQM/2013-22
Arithmetic mean: page 23
Uncertainty weighted mean: page 24
Median: page 25
DerSimonian-Laird: page 28

Annex (Technical Protocol)

Key Comparison

CCQM-K170: Electrolytic Conductivity at 0.5 S m^{-1} and 20 S m^{-1}

Technical Protocol

Introduction

Key Comparison CCQM-K170 aims to demonstrate the capabilities of the participating NMIs and DIs to measure the electrolytic conductivity of aqueous electrolyte solutions in the electrolytic conductivity range around 0.5 S m^{-1} and 20 S m^{-1}. To this end the electrolytic conductivity of two potassium chloride solutions (nominal electrolytic conductivity 0.5 S m^{-1} and 20 S m^{-1}) must be measured. CCQM-K170 is associated with CCQM-K36.2016, which included 0.5 S m^{-1} and CCQM-K92, which included 20 S m^{-1}. It is intended as an updated support for the corresponding calibration and measurement capabilities (CMCs) entries in the BIPM CMCs database.

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CCQM-K170

Time Schedule

Invitation	February 2023
Registration Deadline	March 10 2023
Sample Preparation	March / April 2023
Sample Shipment	April / May 2023
Reporting Deadline	August 31 2023
Draft A	November 2023
Draft B report	April / May 2024

Description of Samples

The solutions used for the comparison have been produced by the coordinating laboratory.

Two KCl solutions with the nominal electrolytic conductivity values of approximately 0.5 S m^{-1} and 20 S m^{-1} have been prepared from potassium chloride and pure water, respectively. The solution has been homogenized, then filled in 500 mL HDPE bottles and closed with polypropylene screw caps. The bottle caps have been sealed with Parafilm and the bottles have been sealed in an aluminium laminated bag to prevent water evaporation.

Bottles labels are indicating “CCQM-K170”, “laboratory water”, the electrolytic conductivity value, the filling date and the bottle number. The participants have for the most part received the number of requested bottles of the KCl solutions. Shipment to all participants has been started at the same time. The bottles have been shipped, packed in Styrofoam, in a cardboard box by courier. The tracking number has been reported by email to the contact person of the laboratory. The contents are labelled “aqueous solution for electrolytic conductivity measurements” with a value of 1 dollar per bottle. Specific customs requirements stated by the laboratories have been considered.

Homogeneity of each solution has been measured from 3 arbitrarily chosen bottles before shipment. Stability will be measured after preparation in 4 to 6 weeks intervals throughout the whole measurement period.

Actions after receipt of samples

a) The packaging material must be removed after arrival of the samples and the bottles must be inspected for visible damage or leakage. The Styrofoam consists of two halves, which can be opened from the side seams.

b) The bottles shall be equilibrated in the weighing room overnight. The Parafilm sealing of the cap of the KCl samples and the labels must not be removed for weighing. Each bottle (0.5 S m^{-1} and 20 S m^{-1}) shall be weighed with a balance having 0.01 g resolution to verify its integrity during shipment. The weighing results, the pressure, the temperature and the relative humidity at the time of weighing need to be recorded.

c) The sample receipt and the measured masses (balance reading and bottle mass corrected for air buoyancy), pressure, temperature and relative humidity of the bottles must be reported to the coordinating laboratory by e-mail within two weeks after arrival. Any mishaps should be reported immediately. If a bottle is damaged, a replacement bottle will be sent. Templates for buoyancy correction and sample mass report are provided.

Instructions for Participants

a) The bottles should be stored at temperatures between 20°C and 25°C, however, they must not be stored above 25°C. The caps of the bottles may only be opened immediately before the measurements. If possible, the caps should be re-sealed with Parafilm following each opening.
b) Each participant has to measure electrolytic conductivity of the samples with respect to 25°C using the method its existing or planned CMC claims are referring to. Additional data at 24°C and 26°C are also welcome, allowing for the calculation of temperature coefficient of each solution.

Reporting

A measurement report must be written, containing the following information:

a) Name and address of the laboratory performing the measurements.
b) Name(s) of the operator(s).
c) Date of receipt of samples.
d) Identification of the samples (bottle numbers) measured.
e) Date(s) of measurement.
f) Mass of each bottle (corrected and uncorrected for air buoyancy), pressure, temperature, and relative humidity at the time of weighing.
g) Description of the method used, including a photo of the experimental setup, if available.
h) Complete uncertainty budget according to the Guide to the Uncertainty in Measurement. All significant uncertainty sources must be accounted for.
i) The measurement results with the associated standard uncertainties, expanded uncertainties and the corresponding coverage factors *k*, referring to a 95,45% probability interval. Note that *k* is 2 if an infinitive number of degrees of freedom can be reasonably assumed.
j) The route of traceability.

<u>The report must be sent to the coordinating laboratory before 31 August 2023 by e-mail.</u> It should preferably be sent as a pdf file in order to ensure data integrity. The coordinating laboratory will confirm the receipt of each report. If the confirmation does not arrive within one week, please contact the coordinating laboratory to identify the problem.

Additionally, a word template will be provided to summarise the results. Please be aware that only a single result may be provided for each kind of solution. The summary report can be sent individually, or it can be integrated into the measurement report.

Key comparison reference value

The determination of the key comparison reference value will be agreed upon during the EAWG meeting at the BIPM, Sèvres (or online) in spring 2024.

How Far Does The Light Shines statement

The results are considered the representative for electrolytic conductivity measurements of aqueous electrolyte solutions in the electrolytic conductivity range 0.15 S m^{-1} to 1.5 S m^{-1} and 5 S m^{-1} to 25 S m^{-1}, respectively.