Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

Key Comparison

CCQM – K36.2016 Electrolytic Conductivity at 0.5 S m^{-1} and 5 mS m^{-1}

Final Report

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Summary

Key Comparison CCQM-K36.2016 was a follow-up comparison for K36 and provided updated support for the corresponding calibration and measurement capability (CMC) entries in the BIPM CMC database. It aimed to demonstrate the capabilities of the participating NMIs to measure electrolytic conductivity of aqueous electrolyte solutions in the conductivity range 0.15 S m^{-1} to 1.5 S m^{-1} and in the conductivity range 1.5 mS m^{-1} to 15 mS m^{-1}. To this end electrolytic conductivity of a potassium chloride solution (nominal conductivity 0.5 S m^{-1}) and of a HCl solution (nominal conductivity 5 mS m^{-1}) had to be measured. 17 NMIs participated in the comparison. The key comparison reference value (KCRV) of the KCl solution was (0.50999 +/-0.00032) S m^{-1} and the KCRV of the HCl solution was (4.9877 +/-0.012) mS m^{-1}. Both values were estimated from the medians of the results considered eligible for KCRV calculation. They were given with their expanded uncertainties (95% coverage). The majority of the 0.5 S m^{-1} results were consistent with the KCRV. Two institutes showed a small inconsistency, one outlier was observed. The conductivity of the HCl solution showed a small, but steady linear drift of 0.00006843 mS m^{-1} per day during the measurement period that was corrected for KCRV calculation. Some institutes reported unstable measurement conditions for this solution. The results of seven participants have been inconsistent with the KCRV.

21.09.2017

Content

Coordinating laboratory and contact persons

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Metrology Area

Amount of Substance

Branch

Electrochemistry

Subject

Measurement of the electrolytic conductivity of two unknown samples with nominal values 0.5 S m^{-1} (aqueous KCl solution) and 5 mS m^{-1} (aqueous HCl solution.

Time schedule

Invitation	June 2016
Registration Deadline	31 July 2016
Sample preparation	August/September 2016
Sample shipment	Beginning of November 2016
Reporting Deadline	27 January 2017, extended 17.02.2017
Draft A	April 2017
Draft B report	April 2018

List of participants and contact persons

No	Akkr	Institute	Country	contact person email
1	DFM	Dansk Fundamental Metrologi	DEN	Alan Snedden asn@dfm.dk
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4	NIM	National Institute of Metrology (NIM)	CHN	Xiaoping Song songxp@nim.ac.cn
5	GUM	Central Office of Measures (GUM)	POL	Wladyslaw Kozlowski w.kozlowski@gum.gov.pl
6	BFKH	Government Office of the Capital City Budapest	HUN	Beáta Jakusovszky jakusovszky@mkeh.hu
7	UkrCSM	State Enterprise All-Ukrainian State Research and production Center of Standardization Metrology	UKR	Vladimir Gavrilkin vgavrilkin@ukrcsm.kiev.ua
8	VNIIFTRI	Federal Agency on technical regulation and metrology of Russia	RUS	Yuri Ovchinnikov jao@vniiftri.ru
9	LATU	Laboratorio Tecnológico del Uruguay	URY	Simone Fajardo Ferraz sfajardo@latu.org.uy

No	Akkr	Institute	Country	contact person email
10	INMETRO	Instituto Nacional de Metrologia Qualidade e Tecnologia	BRA	Fabiano Barbieri Gonzaga fbgonzaga@inmetro.gov.br
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14	PTB	Physikalisch-Technische Bundesanstalt	GER	Beatrice Sander beatrice.sander@ptb.de
15	LNE	Laboratoire National de Métrologie et d'Essais	FRA	Daniela Stoica daniela.stoica@lne.fr
16	VNIIM	D.I.Mendeleyev Institute for Metrology	RUS	V.I.Suvorov V.I.Suvorov@vniim.ru
17	INM	National Metrology Institute of Colombia	COL	Ronald Cristancho Amaya rcristancho@inm.gov.co

Description of samples

Preparation, shipment, handling

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

20 L KCl solution with a nominal conductivity value of 0.5 S m^{-1} have been prepared in a 25 L PE vessel using potassium chloride (Suprapur from Merck Millipore) and pure water. The water has been taken from a Millipore Elix purification system. The solution has been aerated for several hours after preparation to achieve equilibrium condition with ambient air. Afterwards the KCl solution has been homogenized, filled in 200 mL bore silicate glass bottles and closed with rubber stoppers. The stoppers have been fixed with aluminium crimps. Afterwards they have been weighed.

20 L HCl solution with a nominal conductivity of 5 mS m^{-1} has been prepared by dilution of hydrochloric acid (Titrisol 0.01 M from Merck Millipore) with pure water in a 25 L PE vessel. The solution has been aerated after preparation for a few days to achieve equilibrium condition with ambient air. In the meanwhile 500 mL HDPE bottles have been filled and stored with a similar HCl solution for a few days. Afterwards they have been spilled once with pure water and dried in an oven at 60°C. Then the HCl solution for the comparison has been homogenized and filled into the bottles. The bottles have been closed with lids immediately after filling. The lids have been sealed with tape and then the bottles have been weighed. Afterwards they have been sealed in aluminium laminated bags to prevent water evaporation.

The samples have been dispatched to all participants at the same time. They were shipped in a cardboard box by courier. After receipt the bottles have been visually inspected for damages. Bottle masses have been measured and corrected for air buoyancy. The results have been reported to the coordinating institute, where they have been compared with the initially weighed masses in order to verify bottle integrity. DFM and VNIIFTRI bottles have shown significantly deviating masses for the HCl solutions (also see section *communication with institutes*). One bottle of KCl solution sent to VNIIFTRI showed a deviation of about 0.1 g. Mass differences of all other bottles were smaller than 0.05 g (see figures 1 and 2). Apart from the conspicuous VNIIFTRI values all other masses of the HCl solution bottles have decreased. A plot of the deviation against the date of weighing (not shown) shows a tendency to decreasing masses and to increasing spread. Apparently, there has been a small residual loss of water. However, since the drop was 0.003 % on average its effect on conductivity could be neglected. After weighing the bottles had to be stored below 25 °C until the measurements started. The bottles containing HCl solution had to be put back into the aluminium bags for storage until the measurement, whereas the bags had to be closed with tape, but not to be re-sealed.

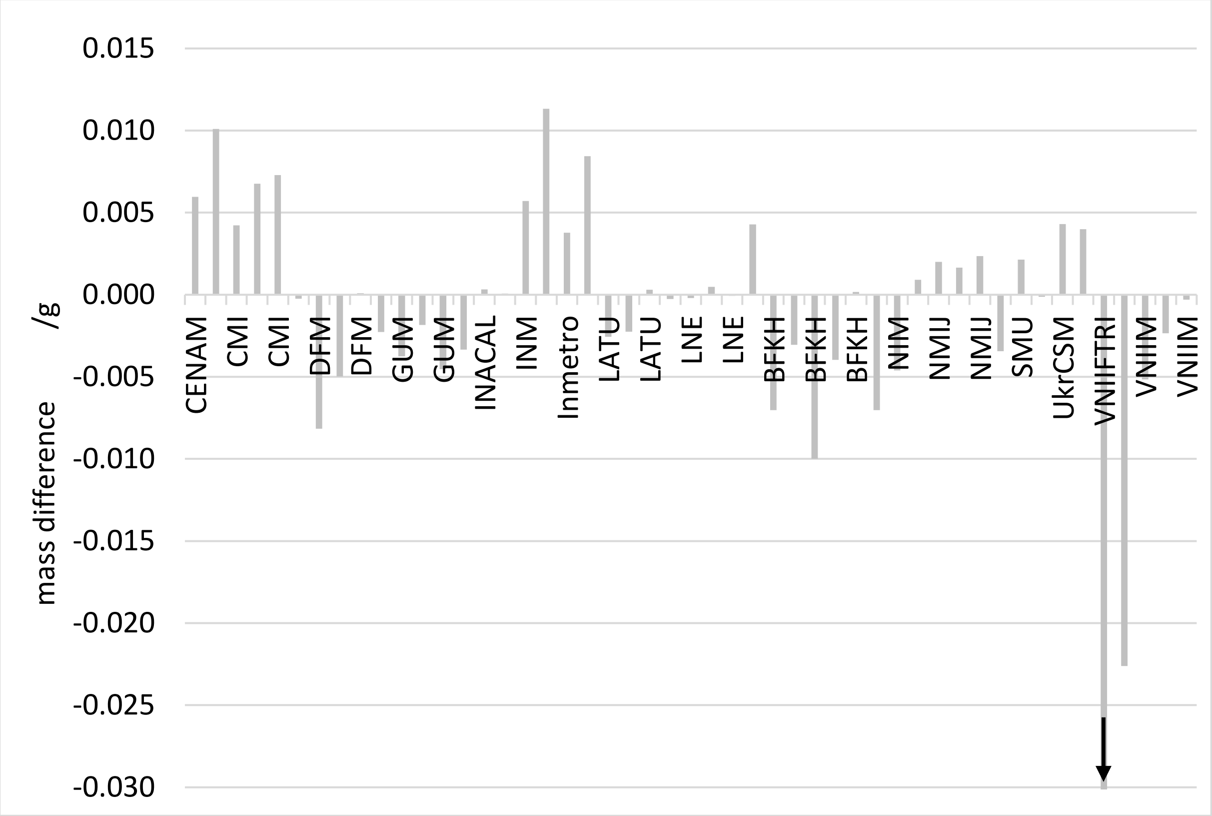

Figure 1 Measured mass differences of 0.5 S/m KCl solution with respect to the initial weighing at the coordinating institute. One value from VNIIFTRI has been cut off.

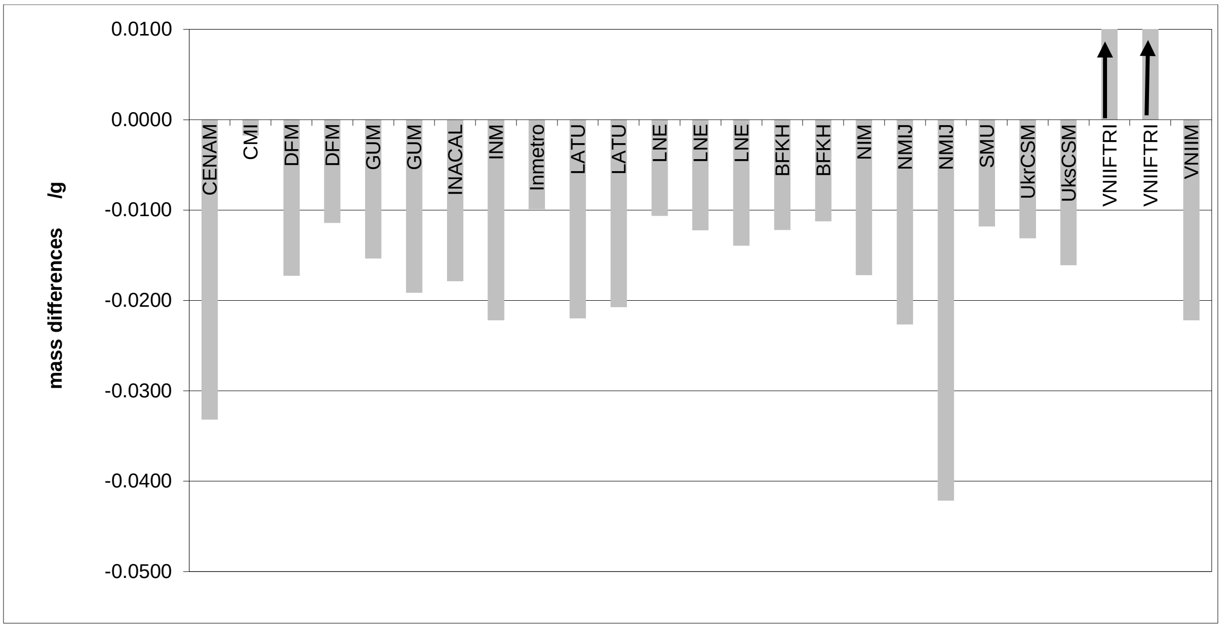

Figure 2 Measured mass differences of 5 mS/m HCl solution with respect to the initial weighing at the coordinating institute. The values from VNIIFTRI have been cut off.

Homogeneity

0.5 S m^{-1} KCl solution

5 bottles have been chosen for homogeneity testing with bottle numbers distributed over the whole batch. A Guildline Autosal B salinometer has been used to measure conductances of the samples. The relative standard deviation of the conductances was 0.0024 %. This is significantly smaller than the measurement uncertainties of conductivity measurements, so that the samples can be assumed sufficiently homogeneous for the comparison. The results of the individual measurements are shown in table 1.

Table 1 Results of homogeneity test of the KCl solution samples

bottle #	bath temperature	conductance
	°C	arbit. units
3	23.993	0.19244
20	23.993	0.19244
56	23.993	0.19243
77	23.993	0.19244
93	23.993	0.19244

Mean conductance (arbit. units): 0.19244
Standard deviation < 0.00001
Relative standard deviation 0.0024 %

5 mS m^{-1} HCl solution

5 bottles have been chosen for homogeneity testing with bottle numbers distributed over the whole batch. A two electrode Jones-type cell has been used to measure conductivity of the samples. The relative standard deviation was 0.003 %. This is significantly smaller than the expected measurement uncertainties of the comparison conductivity measurements, so that the samples can be assumed sufficiently homogeneous for the comparison measurement. The results of the individual measurements are shown in table 2. Note that conductivities have been linearly corrected to 24.980 °C.

Table 2 Results of the homogeneity test of the HCl solution samples

bottle #	bath temperature	conductivity @ 24.980°C
	°C	mS/m
10	24.981	4.98954
14	24.978	4.98986
26	24.984	4.98954
35	24.993	4.98966
47	24.982	4.98990

Mean conductivity: 4.9897 mS/m
Standard deviation: 0.0017 mS/m
Relative standard deviation 0.0034 %

Stability

0.5 S m^{-1} KCl solution

5 bottles have been arbitrarily chosen for stability testing. A Guildline Autosal B salinometer has been used to measure conductances of the samples. Measurements have been conducted in approximately 4 week intervals over the whole measurement period. No significant drift has been observed. The relative standard deviation is 0.0076%, which is small enough for the requirements of this comparison, albeit a factor 3 larger than the measured homogeneity. Therefore another homogeneity test has been performed at the end of the measurement period. The relative standard deviation of that measurement was 0.00024%, which was even an order of magnitude smaller than the first homogeneity test. The relative deviation of the means of both homogeneity tests is 0.0016%. Thus the spread of the stability results is more likely due to (small) instabilities of the measurement device during the measurement period than due to sample instabilities. Consequently the KCl solution samples can be assumed sufficiently stable for the comparison measurement. The results of the individual measurements are shown in table 3 and figure 3.

Table 3 Results of the stability test of the KCl solution samples

bottle #	date measured	bath temperature	conductance @ 24.000 °C
		°C	arbit. units
from homgeinty tests	09.09.2016	23.993	0.19244
50	04.11.16	24.001	0.19245
96	13.12.16	24.001	0.19243
41, 59	06.01.2017	24.000	0.19241
68	02.02.2017	24.001	0.19243
13, 35, 57, 78, 101	17.02.2017	24.000	0.19244

Mean conductance (arbit. units): 0.19243
Standard deviation: 0.000015
Relative standard deviation 0.0079 %

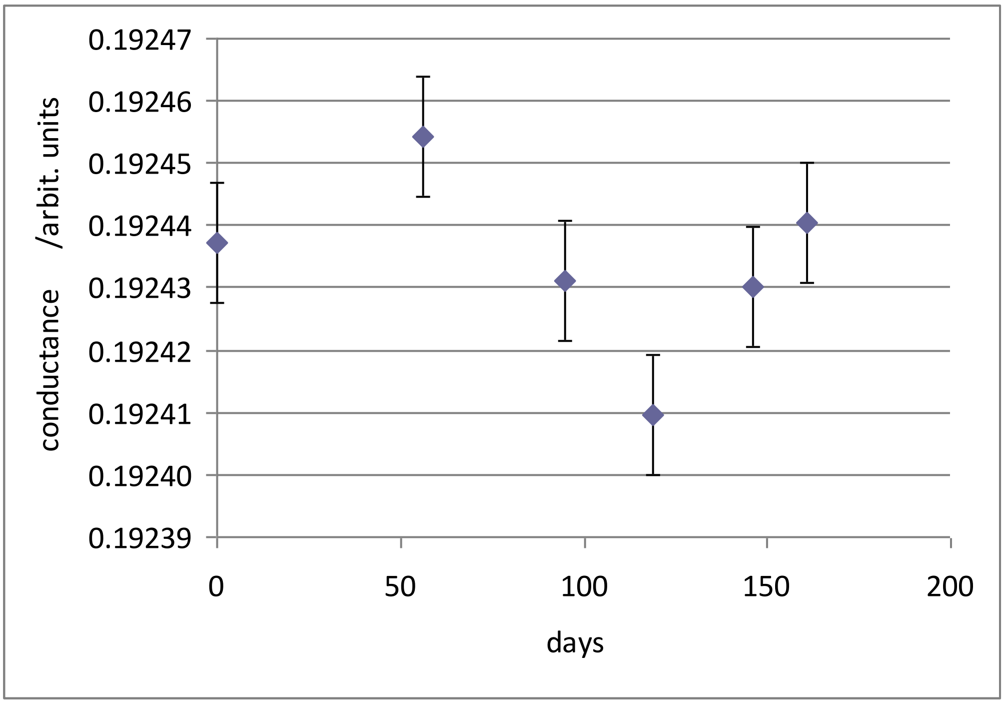

Figure 3 Stability tests of KCl solution samples. The error bars indicate the double standard deviation of the (first) homogeneity test. Note that the smallest, expanded standard uncertainties of the comparison are about a factor 10 larger.

5 mS m^{-1}HCl solution

4 bottles have been arbitrarily chosen for stability testing. The samples have been stored in the laboratory at room temperature and kept in the aluminium bags until the measurement. A two electrode Jones-type cell has been used to measure conductivity of the samples. Measurements have been conducted in approximately 4 week intervals over the whole measurement period. A linear increase of the measured conductivity values of 0.00006843 mS m^{-1} per day has been observed. The results of the individual measurements are shown in table 4 and figure 4. Note that conductivities have been linearly corrected to 24.980 °C.

After drift had been realised stability of the Jones-type cell has been verified with a stable 100 mS m^{-1} KCl solution to check if the measured drift results from a change of solution conductivity, but not from a change of cell properties. The samples have been prepared and characterised for homogeneity in the same way as the 0.5 S m^{-1} KCl solution of this comparison. Starting 22.12.2016, KCl solution samples have been measured once a month during the remaining measurement period. Since the spread of the resistance values over time (<0.004%) was compatible with the results of the homogeneity measurement, it is concluded that the cell and the 100 mS m^{-1} KCl test solution were stable during the measurement period.

At the end of the measurement period the homogeneity test has been repeated with another 4 bottles of HCl solution. The relative standard deviation of those measurements has been 0.01 %, which is somewhat larger than the spread of the first homogeneity test, however, it is still acceptable. Thus it can be reasonably assumed that all HCl solution samples underwent a similar drift within acceptable limits. All reported measurement results have been corrected for the observed drift to a date in the middle of the measurement period (18.12.2016) in order to calculate the KCRV and the DoEs. It must be noted that the drift correction had only a small effect on the results.

Table 4 Results of the stability test of the HCl solution samples

bottle #	date measured	bath temperature	conductivity @ 24.980°C
		°C	arbit. units
from homogeneity tests	31.10.16	24.980 (mean)	4.9897
17,38	05.12.16	24.971 (mean)	4.9919
12	23.12.16	24.971	4.9935
7	02.02.2017	24.995	4.9960
4,8,31,36,43	09.03.2017	24.997 (mean)	4.9985

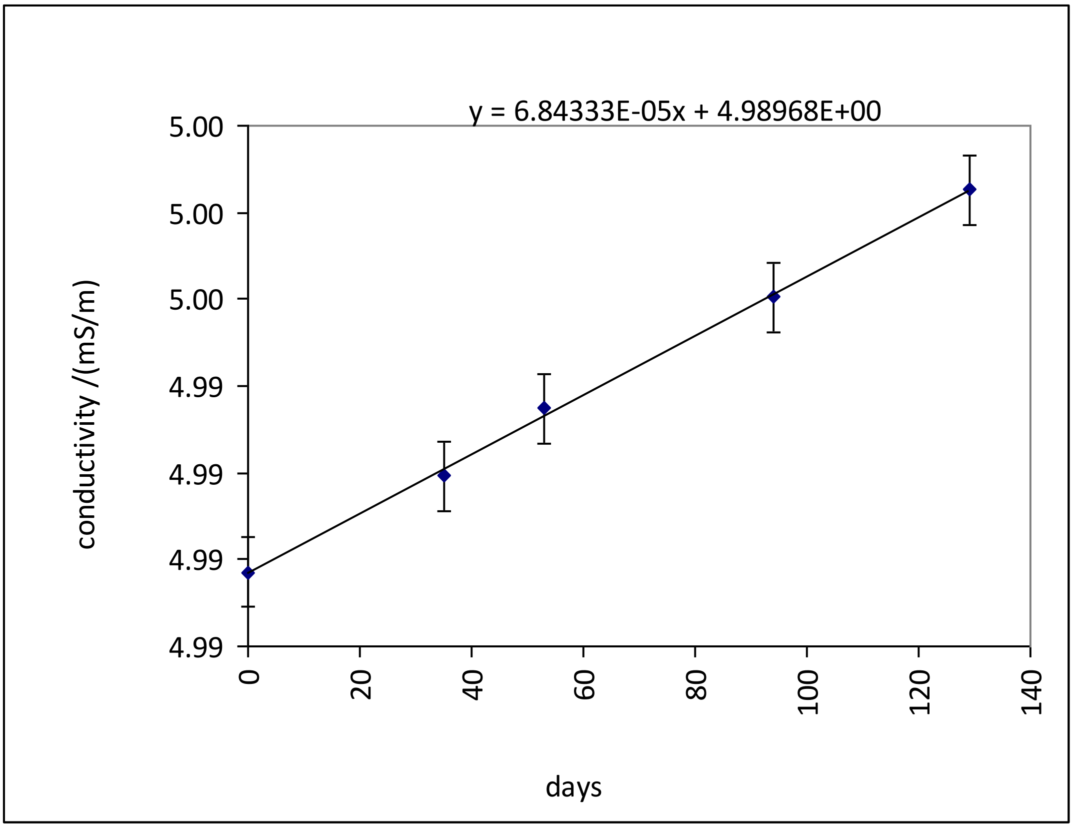

Figure 4 Stability tests of the HCl solution samples. The error bars indicate the double standard deviation of the (first) homogeneity test. Note that measurement uncertainties of most institutes are significantly larger.

Correspondence with institutes

DFM has been informed that the reported bottle masses of the HCl solution deviated significantly from the masses measured at the coordinating laboratory. It turned out that DFM had reported masses including the aluminium bag and has sent results without the bags later on, which then showed a deviation within the accepted limits.

VNIIFTRI has reported a significantly delayed delivery of the samples (24.01.2017) due to problems with customs clearance. As a consequence, VNIIFTRI could not meet the reporting deadline. When the report finally arrived end of February a few days after the extended deadline, there was no time for further actions. However, the deviation regarding the HCl solution bottle masses matched the mass of the aluminium bag, so VNIIFTRI most probably didn’t remove the bag either. Moreover, the reported conductivity results of the two KCl solution samples measured by VNIIFTRI didn’t correspond to the observed mass differences. In contrast, the conductivities of both samples were equivalent within measurement uncertainty. Consequently, integrity of all samples sent to VNIIFTRI can be assumed.

BFKH and CMI have reported problems to meet the deadline due to illness of staff. INMETRO has reported technical problems. The coordinating institute has agreed to postpone the deadline until 17.02.2017. Eventually all reports have arrived, even though with an acceptably small delay.

Conducting a preliminarily evaluation the coordinating laboratory identified results showing unusual deviation of some measurement results from the median or unusual measurement uncertainties. Moreover, some of the reports did not contain requested information. The institutes concerned were asked to provide the lacking information and to check their results for calculation or typing errors respectively. No information was given about the magnitude or the sign of the deviation. Subsequently the following institutes have sent revised values: CENAM, GUM, INM, INMETRO, VNIIFTRI, UkrCSM, LATU and CMI. LNE and NMIJ have confirmed the original results. UkrCSM, VNIIFTRI, VNIIM and CMI have sent additional information.

Results of 0.5 S m^{-1} KCl solution

Reported results

Table 5 lists the reported results. The last column lists the stated source of traceability. Figure 5 shows the results graphically.

Table 5 Reported conductivity results of the 0.5 S m^{-1} KCl solution

Laboratory i	quantity value κ_i	standard uncertainty $u(\kappa_i)$	coverage factor k_i	expanded (95%) uncertainty $U(\kappa_i)$	cell type	source of traceability
akkr.	S/m	S/m		S/m		
VNIIM	0.4970	0.0005	2	0.001	secondary	VNIIM RM / recipe OIML
NMIJ	0.50898	0.00065	2	0.00129	primary/ Jones	SI
GUM	0.50939	0.00014	2	0.00027	primary/ Piston	SI
INMETRO	0.50955	0.00035	2	0.0007	primary/ Piston	SI
INACAL	0.50963	0.00044	2	0.00089	secondary	SMU CRM
LATU	0.50966	0.00042	2	0.00084	secondary	DFM CRM
VNIIFTRI	0.50995	0.00013	2	0.00026	secondary	VNIIFTRI RM/SI
BFKH	0.50996	0.00017	2	0.00034	secondary	BFKM RM / recipe/ OIML
PTB	0.50999	0.00010	2	0.00020	primary/ Piston	SI
SMU	0.51008	0.00012	2	0.00024	secondary	SMU RM/recipe Bradshaw values
DFM	0.51017	0.00022	2	0.00044	secondary	DFM CRM / SI
NIM	0.51026	0.00015	2	0.0003	secondary	NIM RM / recipe IUPAC
CMI	0.51029	0.00025	2	0.00050	secondary	CMI CRM / SI
LNE	0.510291	0.001026	2	0.002052	primary/ Jones	SI
UkrCSM	0.510459	0.00009	2	0.00018	secondary	Ukraine RM / SI
CENAM	0.5105	0.0021	2	0.0041	secondary	SMU CRM
INM	0.510569	0.000395	2	0.00079	secondary	SMU CRM

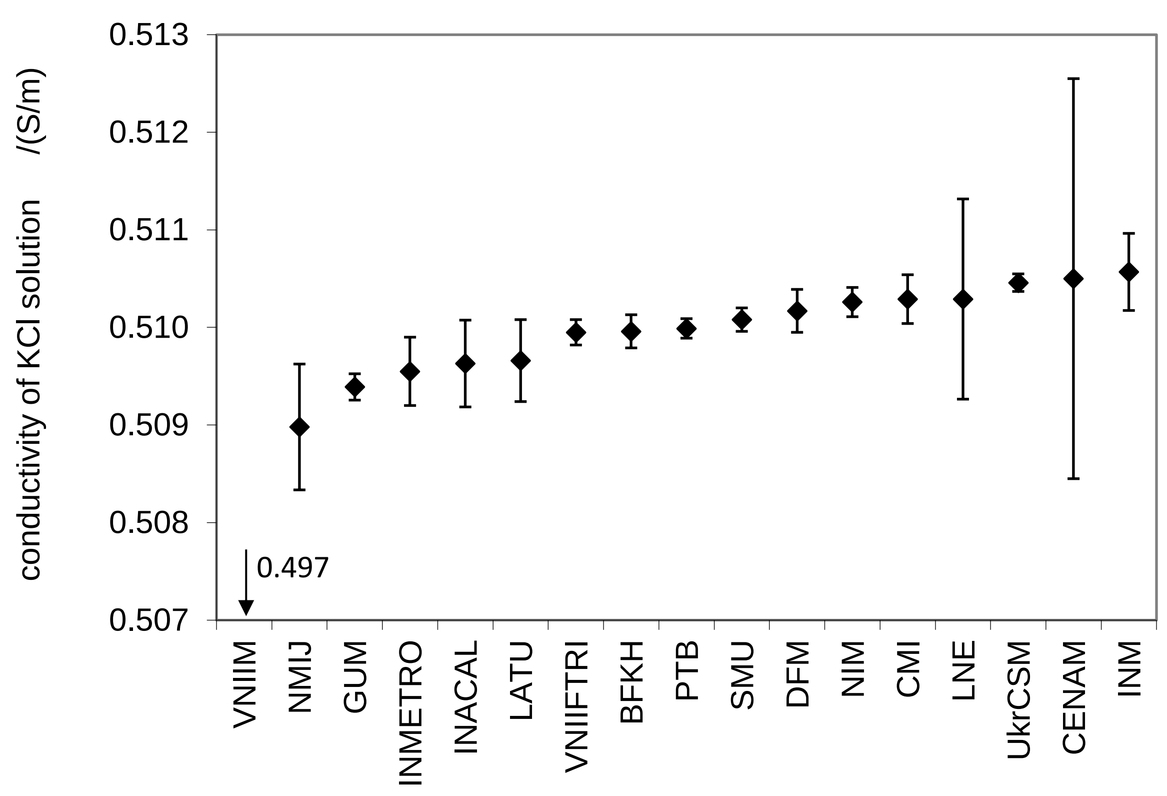

Figure 5 Reported results of the 0.5 S/m KCl solution. The error bars indicate standard uncertainties.

KCRV calculation

Only independent results have been used for calculation of the key comparison reference value (KCRV) [1]. Hence, values of institutes that have used standards from other participating institutes for cell calibration have been excluded from KCRV calculation. Three candidate KCRV estimates and the corresponding standard uncertainties have been calculated (see appendix A for the formula used): the arithmetic mean, the (external) weighted mean and the median. The candidate KCRVs and their standard uncertainties are shown in table 6. A Chi-square consistency check of the input data for the weighted mean calculation has been performed according to [2]. Since the F_{13} value is larger than the $X_{12,0.95}$ value the results must be considered inconsistent with the weighted mean. Because of the deviating VNIIM value, the arithmetic mean does not reflect the bulk of the results and it has an unacceptably large uncertainty. EAWG has decided in the CCQM spring meeting 17. April 2017 in Paris to use the median as KCRV. Even though the result of VNIIM is probably an outlier (for unknown reasons) it has not been excluded, since its effect on the median is negligible.

Hence, the value of the chosen KCRV and its standard uncertainty is

KCRV(0.5 S m^{-1} KCl) = (0.50999 ± 0.00016) S m^{-1}

Table 6 Candidate KCRVs of the 0.5 S/m KCl solution and their standard uncertainties.

weighted mean κ_{WM} S/m	u_{WM} S/m	$F_{13}(\kappa_{WM})$	$X_{12,0.95}$
0.50998	0.00034	730.51	21,03
		results are inconsistent with the weighted mean	

median κ_M S/m	u_M S/m
0.50999	0.00016

mean μ_κ S/m	Std.-Dev σ_κ S/m
0.50895	0.0010

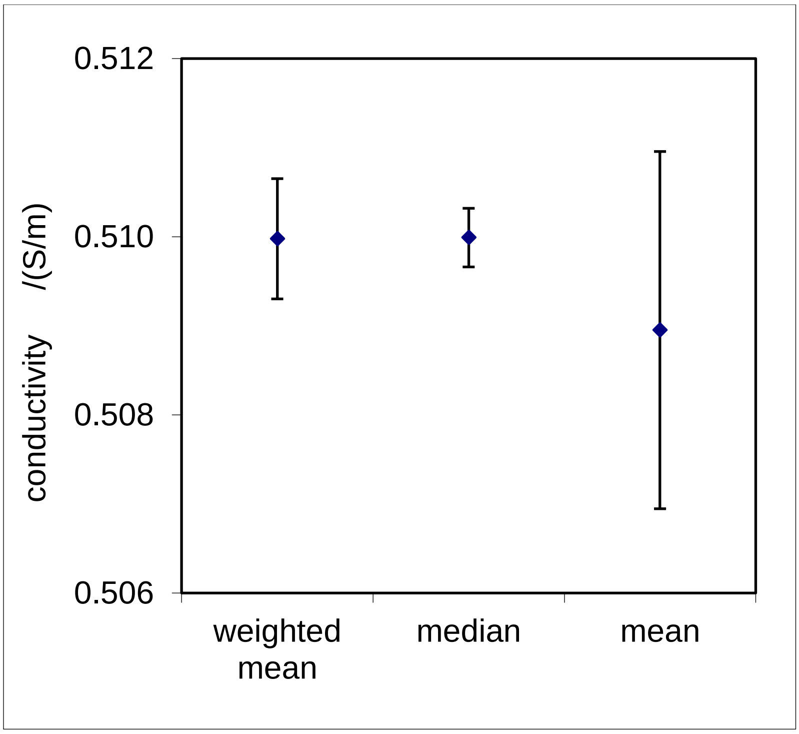

Figure 6 Candidate KCRVs for the 0.5 S/m KCl solution. The error bars indicate their expanded uncertainties.

Degrees of Equivalence

Table 7 shows the degrees of equivalence (DoE) with the KCRV. Their expanded uncertainties, shown in column 4, have been calculated from the combined expanded uncertainties of the reported values and the KCRV (95% coverage). The last column indicates the minimal standard uncertainties $u_m(\kappa_i)$ for laboratory i that are consistent with the KCRV. They can be stated for CMC entries. In case of consistency of a result with the KCRV, that is $|DoE_i| \leq U(DoE_i)$, $u_\mathrm{m}(\kappa_i)$ is the reported standard uncertainty. If it is not consistent with the KCRV $u_\mathrm{m}(\kappa_i)$ is calculated with [3]

$$u_m(\kappa_i) = \sqrt{\left(\frac{DoE_i}{k_i}\right)^2 \pm \left(\frac{2}{k_i}\right)^2 u^2(KCRV)} \quad . \qquad (1)$$

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 7 shows the DoEs and their uncertainties graphically.

Table 8 Degrees of Equivalence for the 0.5 S/m KCl solution

lab i	DoE_i	lab contributed to KCRV	$U(DoE_i)$	consistency $\lvert DoE_i\rvert \leq U(DoE_i)$	E_n	$u_\mathrm{m}(\kappa_i)$
akkr..	S/m	yes/no	S/m	yes/no	$DoE_i/U(DoE_i)$	minimal (CMC) uncertainty consistent with KCRV
VNIIM	-0.0130	yes	0.0011	no	-12.37	0.0065
NMIJ	-0.00101	yes	0.0013	yes	-0.76	0.00065
GUM	-0.00060	yes	0.00042	no	-1.43	0.00025
INMETRO	-0.00044	yes	0.00077	yes	-0.57	0.00035
INACAL	-0.00036	no	0.00095	yes	-0.38	0.00044
LATU	-0.00033	no	0.00090	yes	-0.37	0.00042
VNIIFTRI	-0.00004	yes	0.00041	yes	-0.10	0.00013
BFKH	-0.00003	yes	0.00047	yes	-0.06	0.00017
PTB	0.00000	yes	0.00038	yes	0.00	0.00010
SMU	0.00009	yes	0.00040	yes	0.22	0.00012
DFM	0.00018	yes	0.00054	yes	0.33	0.00022
NIM	0.00027	yes	0.00044	yes	0.62	0.00015
CMI	0.00030	yes	0.00059	yes	0.51	0.00025
LNE	0.00030	yes	0.0021	yes	0.14	0.0010
UkrCSM	0.00047	yes	0.00037	no	1.28	0.00017
CENAM	0.00051	no	0.0041	yes	0.12	0.0021
INM	0.00058	no	0.00085	yes	0.68	0.00040

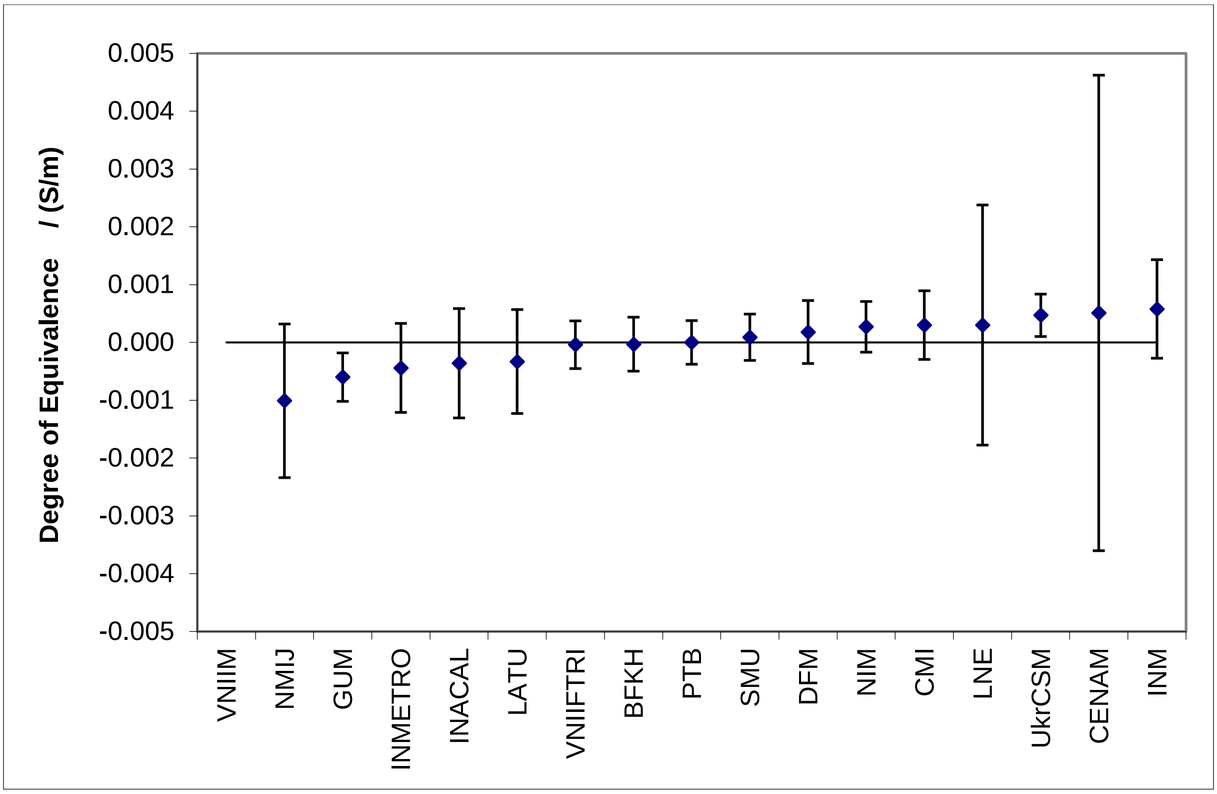

Figure 7 Degrees of equivalence and the corresponding expanded uncertainties.

Results of 5 mS m^{-1} HCl solution

Reported results

Table 9 lists the reported results for the 5 mS m^{-1} HCl solution. The third column shows the results corrected for drift as described above. Figure 8 shows the reported results and the drift corrected results graphically. Obviously, the conductivity drift during storage was small and the effect on the KCRV and the DoEs is insignificant compared to the uncertainty of the KCRV (≈0.03% vs 0.12%). Some institutes have measured more than one bottle at different dates. In this case a mean date has been used for drift correction (7th column). The 8th column lists times that have passed between filling of the cells and the actual measurements. The 9th column lists if the corresponding institute has corrected for a short-term drift during the measurement.

Table 9 Reported conductivity results of the 5 mS m^{-1} HCl solution

lab i	quantity value κ_i	quantity value κ_i (drift corrected)	standard uncertainty $u(\kappa_i)$	coverage factor k_i	expanded (95%) uncertainty $U(\kappa_i)$	date measured (mean)	time between filling and measurement	drift during measure-ment corrected	cell (*)	source of traceability
abbr.	mS/m	mS/m	mS/m		mS/m		min			
NMIJ	4.8437	4.8444	0.0126	2	0.0253	9.12.16	720	n/m	primary	SI
INM	4.948	4.9484	0.006	2	0.012	13.12.16	20	no	secondary	SMU CRM
GUM	4.9723	4.9723	0.0037	2	0.0074	18.12.16	50	yes	primary	SI
CMI	4.9792	4.9766	0.0042	2	0.0084	25.1.17	120	n/m	secondary	CMI RM/SI
SMU	4.9778	4.9796	0.0015	2	0.003	22.11.16	30	no	secondary	SMU CRM / recipe Bradshaw values
INACAL	4.9808	4.9819	0.0205	2	0.041	2.12.16	n/m	n/m	secondary	SMU CRM
BFKH	4.9843	4.9835	0.00191	2.52	0.00483	30.12.16	30	n/m	secondary	BKEH RM/recipe OIML
NIM	4.9895	4.9875	0.0020	2	0.0040	17.1.17	120	no	secondary	NIM RM/recipe IUPAC
LNE	4.9868	4.9877	0.00632	2	0.01264	6.12.16	130	n/m	primary	SI
DFM	4.9957	4.9936	0.0027	2	0.0055	18.1.17	15	yes	secondary	DFM RM/SI
PTB	4.9926	4.9959	0.0015	2	0.003	31.10.16	130	yes	secondary	PTB RM / SI
UkrCSM	5.007	5.0046	0.0015	2	0.003	23.1.17	40	yes	secondary	UkrCSM RM/SI
LATU	5.011	5.0084	0.013	2	0.026	26.1.17	40	n/m	secondary	DFM CRM
INMETRO	5.0245	5.0219	0.0054	2	0.0108	26.1.17	432	yes	primary	SI
VNIIM	5.035	5.0330	0.010	2	0.020	16.1.217	200	n/m	secondary	VNIIM RM/recipe OIML
CENAM	5.039	5.0375	0.043	2	0.086	10.1.17	120	n/m	secondary	SMU CRM
VNIIFTRI	5.099	5.0957	0.005	2	0.010	5.2.17	4	n/m	secondary	VNIIFTRI RM/SI

n/m = “not mentioned”

(*) for the kind of primary cell type see table 5

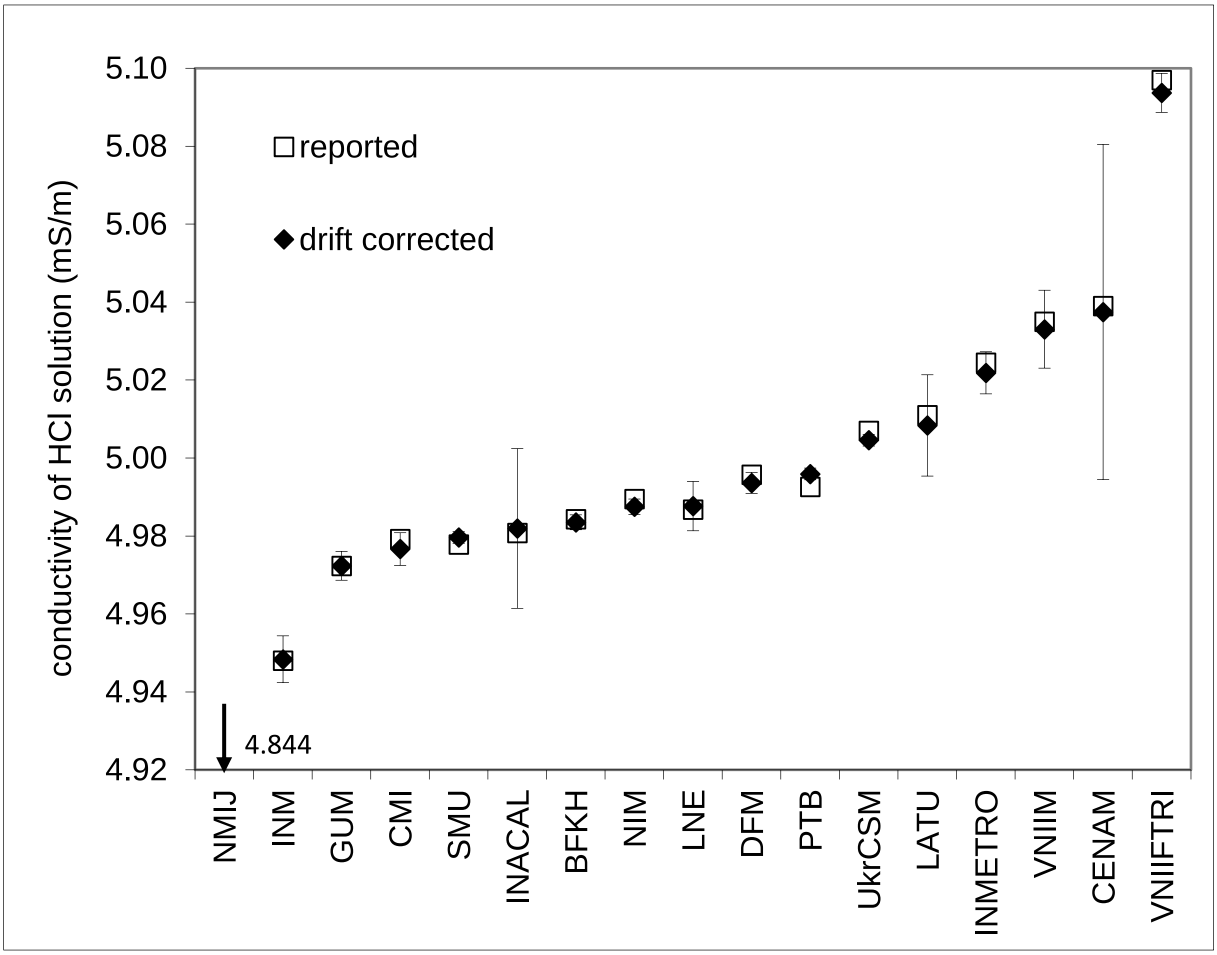

Figure 8 Results of the 5 mS/m HCl solution. The solid diamonds indicate the results corrected for (storage) drift, while the void squares show the originally reported values. The error bars indicate standard uncertainties.

KCRV calculation

Three candidate KCRV estimates and the corresponding standard uncertainties have been calculated (see appendix A for the formula used): the arithmetic mean, the (external) weighted mean and the median. The results are shown in table 6. A Chi-square consistency check of the input data for the weighted mean calculation has been performed [2]. Since the F_{13} value is larger than the $X_{12,0.95}$ value the results must be considered inconsistent with the weighted mean. Basically, all candidates provide compatible KCRV estimates, whereas the median is more robust with respect to outliers. Therefore, CCQM-EAWG has decided in the meeting held 17. April 2017 in Paris to use the median as KCRV.

Hence, the value of the chosen KCRV and its standard uncertainty is

KCRV(5 mS m^{-1} HCl) = (4.9877 ± 0.0060) mS m^{-1}

Table 10 Estimates for the KCRV of the 5 mS/m HCl solution

weighted mean κ_{WM} mS/m	u_{WM} mS/m	$F_{13}(\kappa_{WM})$	$X_{12,0.95}$
4.9924	0.0055	827.00	21.03
		results are inconsistent with the weighted mean	

median κ_M mS/m	u_M mS/m
4.9877	0.0060

mean μ_κ mS/m	Std.-Dev σ_κ mS/m
4.990	0.015

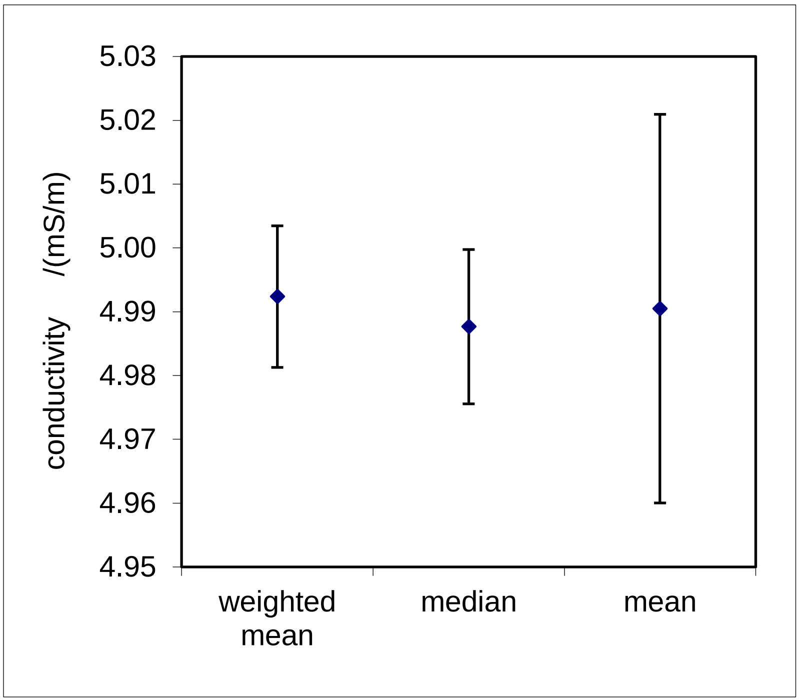

Figure 9 Various candidate KCRV estimates for the 5 mS/m HCl solution. The error bars indicate their expanded uncertainties (*k*=2).

Degrees of Equivalence

Table 11 shows the degrees of equivalence based on the median. Their expanded uncertainties, shown in column 4, have been calculated from the combined expanded uncertainties of the reported values and the KCRV (95% coverage). The last column indicates the minimal uncertainties $u_m(\kappa_i)$ that are consistent with the KCRV. They can be stated for CMC entries. In case of consistency with the KCRV $u_m(\kappa_i)$ is the reported standard uncertainty. In case it is not consistent with the KCRV it is calculated with eq (1). Figure 10 shows the DoEs and their uncertainties graphically.

Table 11 Degrees of equivalence for the 5 mS/m HCl solution

lab i	DoE_i	lab contributed to KCRV	$U(DoE_i)$	consistency $\lvert DoE_i\rvert \le U(DoE_i)$	E_n	$u_m(\kappa_i)$
akkr.	S/m	yes/no	S/m	yes/no	$DoE_i/U(DoE_i)$	minimal (CMC) uncertainty consistent with KCRV
NMIJ	-0.143	yes	0.028	no	-5.12	0.071
INM	-0.039	no	0.017	no	-2.32	0.021
GUM	-0.015	yes	0.014	no	-1.09	0.0048
CMI	-0.011	yes	0.015	yes	-0.76	0.0042
SMU	-0.0081	yes	0.012	yes	-0.65	0.0015
INACAL	-0.0058	no	0.043	yes	-0.14	0.0205
BFKH	-0.0042	yes	0.013	yes	-0.32	0.0019
NIM	-0.0002	yes	0.013	yes	-0.02	0.0020
LNE	0.0000	yes	0.017	yes	0.00	0.0063
DFM	0.0059	yes	0.013	yes	0.45	0.0027
PTB	0.0082	yes	0.012	yes	0.66	0.0015
UkrCSM	0.0169	yes	0.012	no	1.36	0.0059
LATU	0.0207	no	0.029	yes	0.72	0.013
INMETRO	0.0342	yes	0.016	no	2.12	0.016
VNIIM	0.0453	yes	0.023	no	1.94	0.022
CENAM	0.0498	no	0.087	yes	0.57	0.043
VNIIFTRI	0.108	yes	0.016	no	6.91	0.054

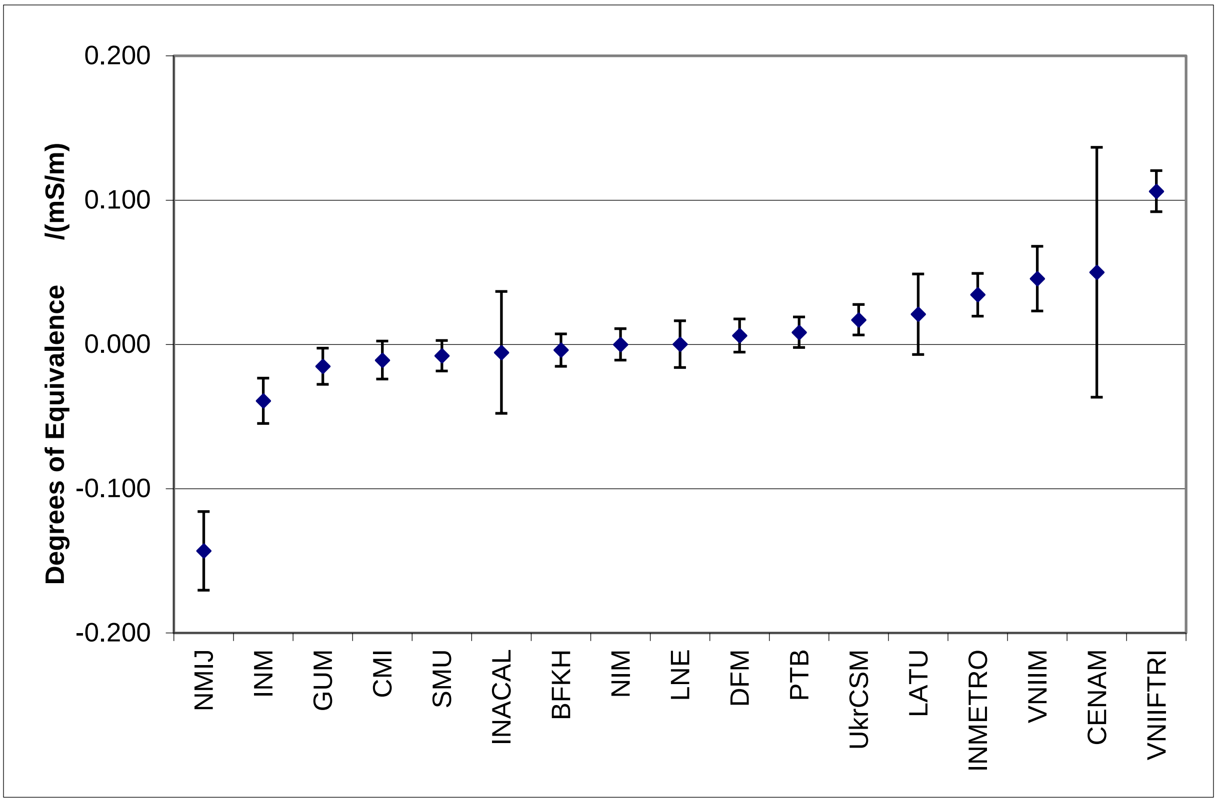

Figure 10 Degrees of equivalence and the corresponding expanded uncertainties of the 5 mS/m HCl solution.

Effect of Carbon Dioxide

HCl has been chosen for this comparison to supress the effect of CO_2 on the conductivity measurement result. Aqueous solutions not preventing the dissociation of dissolved CO_2, such as commonly used aqueous KCl and NaCl conductivity standards, can be subject to significant conductivity variation in the conductivity range below 15 mS m^{-1} if exposed to ambient air. Common measurement practice does not avoid such air contact, since this would require immense efforts. The contribution of dissolved and subsequently dissociated CO_2 to the conductivity of such solutions is around 0.1 mS m^{-1} under equilibrium conditions [4]. Hence, the uncertainty budget must account for this kind of solution instability. In fact, it is only the change of the amount of hydrogen carbonate and carbonate ions during the measurement process that contributes to the uncertainty. This uncertainty contribution is difficult to be estimated in general since the change depends on the partial CO_2 pressure present at the site of measurement, the usually unknown carbonate ion concentrations in the solution and the time the solution is exposed to air during filling and measurement. Consequently, it might be negligible in one measurement and substantial in another. However, under typical operation procedures it is reasonable to assume that the conductivity change due to CO_2 is not larger than ±0.02 mS m^{-1} with respect to the initial value before opening the bottle. Thus, a standard uncertainty contribution of 0.012 mS m^{-1} should be generally considered in the combined standard uncertainty of conductivity measurements of pure aqueous electrolyte solutions.

“How Far Does The Light Shine” statement

The results of this KC are considered representative for conductivity measurement capabilities of stable aqueous electrolyte solutions in the conductivity range 0.15 S m^{-1} to 1.5 S m^{-1} and 1.5 mS m^{-1} to 15 mS m^{-1}, respectively. For the reasons described in the previous section an uncertainty contribution of 0.012 mS m^{-1} must be considered in the minimal uncertainty $u_{\mathrm{mCO2}}(\kappa_i)$ permissible for CMCs of aqueous solutions, having conductivities $\leq$ 15 mS m^{-1}, in order to account for the effect of CO_2 on conductivity:

$$u_{mCO2}(\kappa_i) = \sqrt{u_m^2(\kappa_i) + \left(0.012\,\frac{mS}{m}\right)^2} \qquad (2)$$

$u_{\mathrm{m}}(\kappa_i)$ corresponds to the value of laboratory *i* given in table 11.

This statement particularly holds for aqueous, low conductivity KCl and NaCl conductivity standard solutions.

Traceability statement

During the spring meeting in 2016 EAWG has decided to accept IUPAC Technical Report 2001 [4] as metrological reference for the traceability of conductivity measurement results for practical reasons. Therein conductivity values and their uncertainties are assigned to KCl solutions, prepared according to a defined recipe. An evaluation of previous key comparisons and pilot studies has shown no evidence for a significant deviation in the DoEs of such results compared to those traceable to the SI. It was also decided that this statement has to be verified based on the results of every future conductivity key comparison in order to retain the link of such measurements to the SI. Figure 9 shows the normalised DoEs of all results contributing to the KCRV. No significant deviations of recipe based values are observed. Hence, the statement is still considered valid.

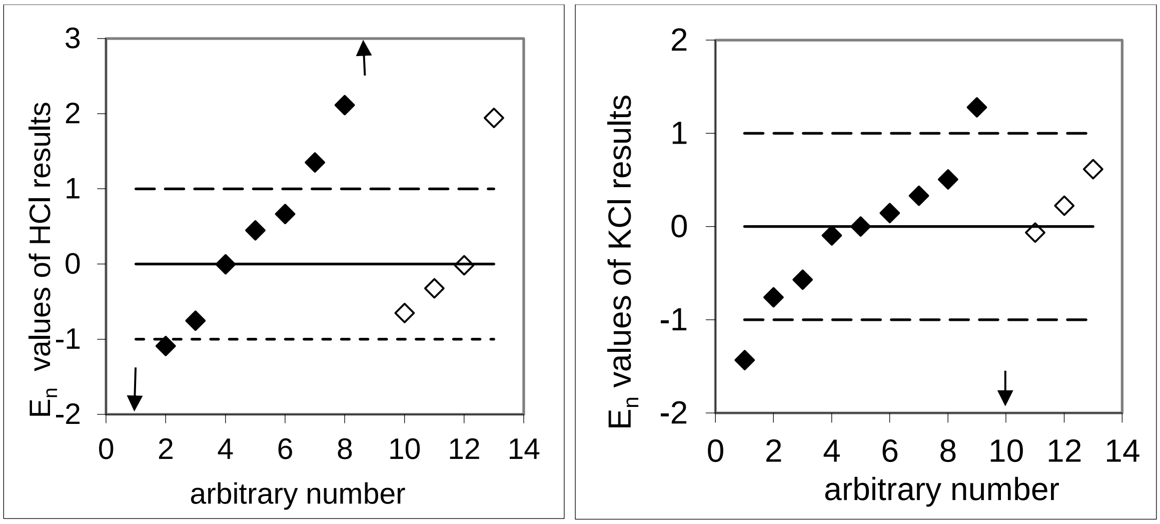

Figure 11 E_n values (DoEs normalized with the corresponding U(DoE)). Solid diamonds indicate results traceable to the SI, void diamonds those traceable to [4]. $|E_n| \leq 1$ indicates consistency with the KCRV.

References

[1] M. G. Cox, "The evaluation of key comparison data," Metrologia, vol. 39, pp. 589-595 (2002).

[2] M. G. Cox, "The evaluation of key comparison data: determining the largest consistent subset," Metrologia, vol. 44, pp. 187-200 (2007).

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

[4] K. W. Pratt, W. F. Koch, Y. C. Wu, and P. A. Berezansky, "Molality-based primary standards of electrolytic conductivity," Pure Appl. Chem., vol. 73, pp. 1783-1793 (2001).

Appendix A: Equations used to calculate KCRV estimates

n	number of labs contributing to the estimate
i	= 1 .. n, index for lab contributing to the estimate
κ_i	conductivity value of lab i
u_i	standard uncertainty of κ_i

Arithmetic mean $\bar{\kappa} = \frac{\sum \kappa_i}{n}$

Standard deviation of arithmetic mean $\sigma_\kappa = \sqrt{\frac{\sum (\kappa_i - \bar{\kappa})^2}{n(n-1)}}$

Weighted mean $\kappa_{WM} = \sum w_i \kappa_i$

with $w_i = \frac{\left(\frac{1}{u_i}\right)^2}{\sum \left(\frac{1}{u_i}\right)^2}$

Uncertainty of weighted mean $u_{WM} = \sqrt{\frac{w_i (\kappa_i - \kappa_{WM})^2}{(n-1)\sum w_i}}$

Uncertainty of median $u_M = \frac{1.9}{\sqrt{n-1}} Median(|\kappa_i - \kappa_{Median}|)$