Final report on CCQM-K36.1 with erratum

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Summary

A follow-up comparison to CCQM-K36 has been carried out November 2007 to February 2008, designated CCQM K36.1. Four laboratories are repeat participants, one laboratory is new. Three laboratories provided linking to CCQM-K36.

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Content

1 Summary information

Subject field:

Amount of substance.

Subject:

Electrolytic conductivity at 0,5 S/m (KCl(aq)) and 5 mS/m (HCl(aq)).

Participants and acronyms

Acronym	Participant	Country
CENAM	Centro Nacional de Metrologia	Mexico
CMI	Czech Metrology Institute	Czech Republic
DFM*	Danish Fundamental Metrology	Denmark
INMETRO	Intituto Nacional de Metrologia, Normalição e Qualidade Industrial	Brazil
MKEH	Hungarian Trade Licensing Office (formerly National Office of Measures)	Hungary
NIM	National Institute of Metrology	P.R. China
PTB*	Physikalisch-Technische Bundesanstalt	Germany
SMU*	Slovak Institute of Metrology	Slovakia
VNIIFTRI	National scientific and Research Institute for Physical-Technical and Radiotechnical Measurements	Russia

* Laboratories providing linking to CCQM-K36

2 Comparison background

In 2005 a key comparison, K36, was carried out on the subject of electrolytic conductivity. The key comparison encompassed the quantity in the two ranges of interest: A high value appropriate for standard reference solutions, clinical and process control use, and a low value appropriate for, or at least as near as practically possible, the use for pure water characterisation. The values 0,5 S/m and 5 mS/m were chosen as representative values for the two ranges.

The comparison was organised by Danish Fundamental Metrology (DFM) with NIST and PTB as supporting laboratories. 14 laboratories participated and the results showed generally good agreement among laboratories. A few laboratories obtained unsatisfactory results and it was decided to organise a follow-up comparison, K36.1, using the same types of solutions and the same values.

3 Schedule

The comparison was initiated after the autumn meeting of the CCQM-WGEA, October 2007. The protocol was essentially identical to that of K36. Invitation and protocol was sent to CCQM members on 11 October 2007. Positive replies was received from six institutes.

Samples were prepared during the latter half of October 2007, with initial characterisation in the same period, and the samples were distributed in the beginning of November 2007.

Measurements were performed in the participating laboratories during November 2007 to February 2008. CMI had to withdraw due to technical problems.

Due to late delivery of samples at some laboratories, the reporting deadline was extended by one month to 15 February 2008. Measurement reports were received in time.

The Draft A report distributed in March 2008 and discussed at the CCQM WGEA meeting in Paris, 31 March 2008

The Draft B report was distributed January 2009 with deadline for comments 20 February 2009.

The Final report was distributed among CCQM WG conveners by the end of February 2009, and their comments incorporated in this final version.

A transcript error of the measurement uncertainty of GUM for measurements of the 5 mS/m solutions in the original CCQM-K36 comparison, caused a small shift in the Key Comparison Reference Value. This affect also the result of CCQM-K36.1 when linked to K36. In this version, these changes has been taken into account in the table values and graphs in section 7.2.

4 Sample preparation

The two solutions were prepared, one by SMU, 5 mS/m – HCl in water, and one by DFM, 0,5 S/m – KCl in water. The preparation followed that of K36 and the details may be found in the final report.

4.1 Shipment and travel events

All samples were shipped on 9 November 2007. Most laboratories reported receipt of samples by 13 November 2007. However, samples were significantly delayed to INMETRO and CENAM.

Samples to CENAM were received by the end of November 2007, but one sample had apparently been inspected by customs. The seal had been compromised and a weight loss was determined. A replacement sample was shipped 4 December 2007 and received 21 December 2007. Samples to INMETRO were released by customs only by 8 January 2008 and received by the laboratory shortly thereafter; no weight loss or damage was reported.

5 Characterisation

Initial characterisation of the batches were performed by the laboratory that manufactured the batch. Further samples were measured by the organising laboratory during the time of the comparison.

5.1 CCQM-K36.1.a, 0,5 S/m

The following values found:

Measurements by DFM, 0,5 S/m			
Date	**Sample**	**κ (S/m)**	**u(κ) (S/m)**
2007-10-18	21	0,514294	0,000148
2007-10-18	3	0,514274	0,000148
2007-10-19	14	0,514280	0,000148
2007-12-14	19	0,514344	0,000149
2007-12-15	16	0,514241	0,000148
2008-02-19	18	0,514190	0,000155
2008-02-20	15	0,514233	0,000155

The experimental standard deviation of the three initial measurements is $1{,}14 \times 10^{-5}$ S/m. From the observed experimental standard deviation it is possible to derive an estimate of the standard deviation of the conductivity values of the samples of the batch, ie. an estimate for the spread of the conductivity values of all the individual samples in the batch. In the case of three measured samples, a multiplier of 2,61 on the experimental standard deviation gives the desired estimate under the assumption, that the conductivity values are normally distributed. This "Single Sample" standard deviation of the conductivity value is thus estimated as

$$\sigma_{SS} = 3{,}0 \times 10^{-5} \text{ S/m}$$

The single sample standard deviation was found low enough that further initial measurements was not performed.

The relative temperature coefficient at 25 °C was found as 1,93 %/°C.

5.2 CCQM-K36.1.b, 5 mS/m

The 5 mS/m solution was measured at SMU after production.

The results obtained are:

Measurements by SMU, 5 mS/m			
Date	**Sample**	**κ**	**u(κ)**
2007-11-28	25	5,3980	0,0023
2007-11-28	25	5,3980	0,0023
2007-11-29	26	5,4000	0,0023
2007-11-29	26	5,3982	0,0023
2007-11-30	27	5,3980	0,0023
2007-11-30	27	5,3980	0,0023

The experimental standard deviation of the three initial measurements (average per sample) is $6{,}3 \times 10^{-4}$ mS/m. The standard deviation of the single sample conductivity value is then estimated as:

$$\sigma_{SS} = 1{,}7 \times 10^{-3} \text{ mS/m}$$

The single sample standard deviation was found low enough that no further initial measurements were performed.

The relative temperature coefficient at 25 °C was found as 1,47 %/°C.

Due to the composition of the solution, HCl(aq), there is a suppression by a factor of 50 of the dissociation of dissolved atmospheric CO_2 in comparison with pure water, as reported by NIST[a] in connection with CCQM-K36.

[a] Kenneth Pratt, "Report of CCQM-K36: Measurement of Electrolytic Conductivity of Two Solutions: Nominal Values 0.5 S m^{-1} and 5 mS m^{-1}", National Institute of Standards and Technology Report of Analysis 839.03-05-163, 12 September 2005.
Kenneth Pratt: "H is for Hydrogen, K is for Potassium: On the Contribution of CO_2 to the Uncertainty of CCQM-K36", document EAWG/05-17

6 Participants results

Participants reported their results in the period from end of November to mid February. Acknowledgement of receipt of the report was sent to the laboratories soon after receipt. Results were collected and analysed as their were reported, to monitor the progress and stability of the distributed samples.

6.1 Communication with the participants

The CIPM rules allows contact to participants when reported results seems anomalous or "suspicious", here interpreted to cases where e.g reported uncertainties are much higher than expected, probable typing errors or reported values in significant disagreement with other results. In such cases a message is sent to the laboratory with a request to recheck reported values. No information on sign or magnitude, other than specified below, was given to the participants.

The following feedback was given:

INMETRO: The laboratory was asked to check the values reported and confirm the measurement report. The laboratory confirmed reported values.

Further communication received from the participants:

VNIIFTRI: The VNIIFTRI uncertainty in the summary sheet appeared too high for the 0.5 S/m solution compared to the value submitted in K36. VNIIFTRI contacted the coordinator with a corrected value after the results were distributed in the Draft A report. In fact, in the original report sheet the value in the uncertainty budget was ten times less the uncertainty value in the summary, so this can be regarded as a transcription error. The issue was discussed at the CCQM EAWG meeting in Paris, april 2008, and the change was accepted.

7 Reported results and analysis

In CCQM-K36 a Key Comparison Reference Value (KCRV) was derived similar to a variance weighted mean and a contribution from the estimated dispersion among sample values, based on the largest consistent set of participants values. Consistency was based on the criteria, that the set could not be rejected from a Chi-square test at 5% confidence. The model of the KCRV is thus a constant plus a normally distributed term estimated from the observed dispersion

$$\kappa_{ref} = \kappa_0 + \delta\kappa; \quad \delta\kappa \in N\left(0, \sigma_{ss}^2\right)$$

The values of the model are determined by least-squares estimation.

The Degree of Equivalence and its associated uncertainty is given as

$$D_{lab} = \kappa_{lab} - \kappa_{ref}, \quad U(D) = 2u\left(\kappa_{lab} - \kappa_{ref}\right)$$

A normalised deviation is also calculated:

$$d = \frac{\kappa_{lab} - \kappa_{ref}}{u\left(\kappa_{lab} - \kappa_{ref}\right)}.$$

In the follow-up comparison a Key Comparison Reference Value is not derived, but a linking to the original comparison is constructed.

The model used to link K36 and K36.1 is a combination of that above plus a linking parameter, $\Delta\kappa$, equivalent to the difference between the property value of K36.1 and K36.

$$\kappa_{ref-combined} = \kappa_0 + \Delta\kappa \cdot \left\{ \begin{matrix} 1, \text{ if K36.1} \\ 0, \text{ if K36} \end{matrix} \right\} + \delta\kappa; \quad \delta\kappa \in N\left(0, \sigma_{ss}^2\right)$$

The linking parameter is determined by extending the least-squares-fit used in K36, to determine the parameter $\Delta\kappa$ by including the results of the linking laboratories, DFM, PTB and SMU, obtained in K36.1, in the model. An estimate of the correlation coefficient, r(K36, K36.1) = 0.5, is used between the individual results in K36 and K36.1 of the linking laboratories.

In the case where a participant reported more than one measurement value and did not submit a final summary result, the average of the reported results was used for the main comparison result.

From the combined reference value, the Degree of Equivalence and normalised deviation can be calculated as given above.

7.1 Results CCQM K36.1.a, 0,5 S/m

Reported values, (S/m):

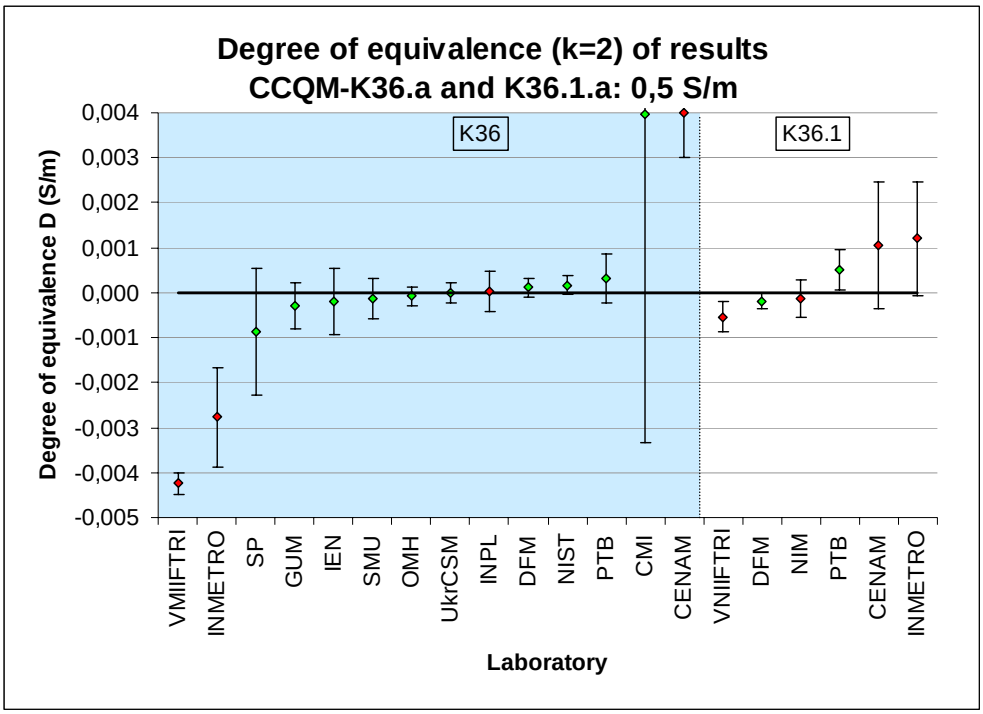
Lab	Date	κ	u(κ)	D	U(D)	d
VNIIFTRI	2007-11-20	0,513910	0,000098	-0,00046	0,00032	-2,9
DFM	2007-12-09	0,51426	0,00015	-0,00011	0,00018	-1,2
NIM	2007-11-27	0,51432	0,00016	-0,00005	0,00040	-0,3
PTB	2007-12-12	0,51496	0,00026	0,00059	0,00047	2,5
CENAM	2008-01-06	0,51550	0,00069	0,0011	0,0014	1,6
INMETRO	2008-01-29	0,51565	0,00062	0,0013	0,0013	2,0

The table gives the laboratory acronym, the date of measurement, the conductivity value reported, the standard uncertainty of the conductivity, the Degree of Equivalence, the expanded uncertainty of the DoE and the normalised deviation (dimensionless).

DFM and PTB results used in establishing the link between K36.a and K36.1.a.

The linking parameter to the KCRV value of K36 is determined as Δκ = 0,00739 S/m, u(Δκ) = 0,00012 S/m.

Figure 1. Linking result at 0,5 S/m.



Results at right are CCQM-K36.1. Green points are linking laboratories.

Results at left are CCQM-K36. Green points contribute to KCRV.

7.2 Results CCQM-K36.1.b, 5 mS/m

Reported values (mS/m):

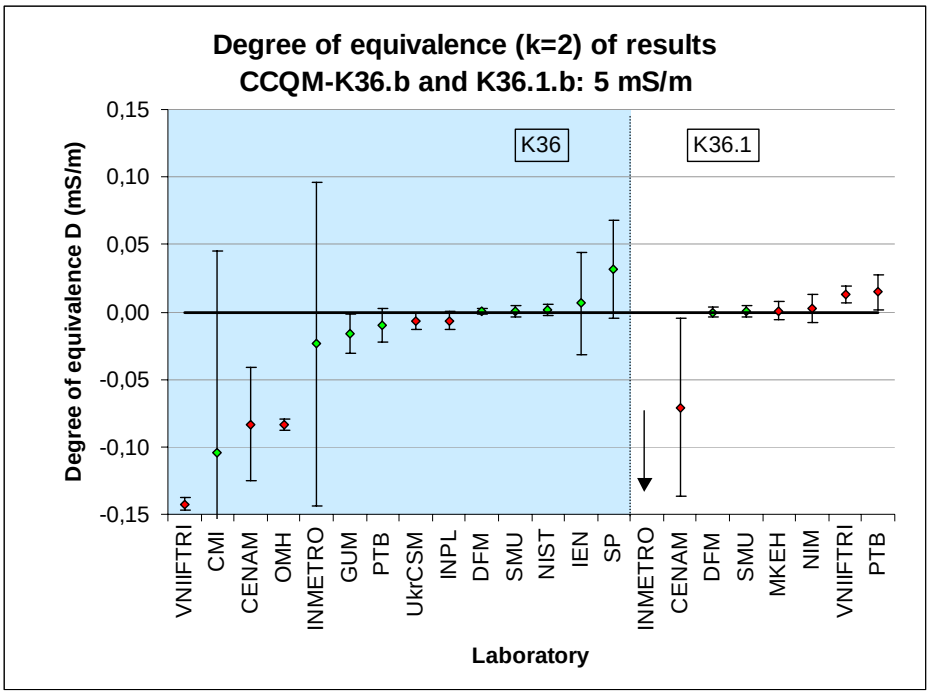
Lab	Date	κ	u(κ)	D	U(D)	d
INMETRO	2008-02-12	5,004	0,018	-0,394	0,036	-21,7
CENAM	2008-02-04	5,327	0,033	-0,071	0,066	-2,1
DFM	2008-01-29	5,3977	0,0022	0,0000	0,0040	0,0
SMU	2007-11-29	5,3984	0,0023	0,0007	0,0041	0,3
MKEH	2008-01-06	5,3984	0,0021	0,0007	0,0066	0,2
NIM	2007-11-27	5,4006	0,0046	0,003	0,011	0,6
VNIIFTRI	2007-11-28	5,411	0,0018	0,0133	0,0063	4,2
PTB	2007-12-14	5,4124	0,0060	0,015	0,013	2,3

As above the table gives laboratory acronym, date, conductivity value, standard uncertainty, DoE, expanded uncertainty of the DoE and the normalised deviation.

DFM, SMU and PTB results used in establishing the link between K36.b and K36.1.b.

The linking parameter to the KCRV value of K36 is determined as
Δκ = 0,2742 mS/m, u(Δκ) = 0,0020 mS/m.

Figure 2. Linking result at 5 mS/m.



Results at right are CCQM-K36.1. Green points are linking laboratories.

Results at left are CCQM-K36. Green points contribute to KCRV.