

## Final report on CCQM-K36

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### *Abstract:*

Results of CCQM Key Comparison K36, ‘Electrolytic conductivity at 0,5 S/m and 5 mS/m’ are reported. Good agreement is found between the majority of participants.

### Subject field

Amount of substance.

### Subject

Electrolytic conductivity: 0,5 S/m (KCl in water) (K36.a) and 5 mS/m (HCl in water) (K36.b).

### Participants and acronyms

Acronym	Participant	Country
CENAM	Centro Nacional de Metrologia	Mexico
CMI	Czech Metrology Institute	Czech Republic
DFM	Danish Fundamental Metrology	Denmark
GUM	Główny Urząd Miar/Central Office of Measures	Poland
IEN	Istituto Elettrotecnico Nazionale “Galileo Ferraris”	Italy
INMETRO	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brazil
INPL	The National Physical Laboratory of Israel	Israel
NIST	National Institute of Standards and Technology	USA
OMH	Országos Mérésügyi Hivatal/National Office of Measures	Hungary
PTB	Physikalisch-Technische Bundesanstalt	Germany
SMU	Slovenský Metrologický Ústav/Slovak Institute of Metrology	Slovakia
SP	Swedish National Testing and Research Institute	Sweden
Ukrmetrteststandart	All-Ukrainian State Research and Production Centre for Standardization, Metrology, Certification and Consumers’ Rights Protection	Ukraine
VNIIFTRI	National scientific and Research Institute for Physical-Technical and Radiotechnical Measurements	Russia

**Table of content**

<b>Subject field .....</b>	<b>1</b>
<b>Subject.....</b>	<b>1</b>
<b>Participants and acronyms .....</b>	<b>1</b>
<b>1 Comparison background .....</b>	<b>3</b>
<b>2 Schedule.....</b>	<b>3</b>
<b>3 Sample preparation.....</b>	<b>3</b>
3.1 <i>The 0,5 S/m solution, CCQM-K36.a.....</i>	<i>4</i>
3.2 <i>The 5 mS/m solution, CCQM-K36.b.....</i>	<i>4</i>
3.3 <i>Shipment and travel events.....</i>	<i>4</i>
<b>4 Characterisation .....</b>	<b>5</b>
4.1 <i>CCQM-K36.a, 0,5 S/m .....</i>	<i>5</i>
4.2 <i>CCQM-K36.b, 5 mS/m.....</i>	<i>5</i>
<b>5 Participants results.....</b>	<b>6</b>
5.1 <i>Communication with the participants .....</i>	<i>6</i>
5.2 <i>Communication after circulation of Draft A .....</i>	<i>7</i>
<b>6 Reported results and analysis.....</b>	<b>7</b>
6.1 <i>Reference value, 0,5 S/m (K36.a).....</i>	<i>8</i>
6.2 <i>Plots for 0,5 S/m (K36.a).....</i>	<i>9</i>
6.3 <i>Degrees of Equivalence, 0,5 S/m (K36.a).....</i>	<i>10</i>
6.4 <i>Reference value, 5 mS/m (K36.b) .....</i>	<i>11</i>
6.5 <i>Plots for 5 mS/m (K36.b).....</i>	<i>12</i>
6.6 <i>Degrees of Equivalence, 5 mS/m (K36.b).....</i>	<i>13</i>
<b>7 Further results .....</b>	<b>14</b>
7.1 <i>Dispersion versus bottle number / filling sequence.....</i>	<i>14</i>
7.2 <i>Comparison on measurement methods and traceability .....</i>	<i>14</i>
7.3 <i>Uncertainty evaluation details .....</i>	<i>16</i>
<b>8 Conclusions .....</b>	<b>16</b>

## 1 Comparison background

Two pilot comparisons have been organised by the Consultative Committee on the Quantity of Matter Working Group on Electrochemical Analysis (CCQM-WGEA) in the field of electrolytic conductivity: In 2001 the pilot study CCQM-P22 at the values 1,28 S/m and 0,1 S/m and in 2003 the study CCQM-P47 at the values 50 mS/m and 5 mS/m.

At the 9th meeting of the CCQM in 2003 it was decided to initiate a Key Comparison in the field, designated K36. The key comparison was to encompass 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.

At the April meeting 2004 of CCQM-WGEA Danish Fundamental Metrology (DFM) agreed to act as organising laboratory, and NIST and PTB was appointed as supporting laboratories.

## 2 Schedule

Details on the comparison procedure and the preliminary schedule were discussed at the meeting of the CCQM-WGEA at BIPM in Paris, 11 April 2005.

The draft protocol was circulated together with the invitation on 28 April 2005, and replies received soon thereafter. CMI was not on the initial distribution list, but received, and accepted, the invitation at the end of June.

Samples were prepared during the latter half of May and the first half of June 2005, initial characterisation was performed by the end of June 2005, and the samples distributed in mid-July 2005.

Measurements were performed in the participating laboratories during July–September 2005.

All measurement reports were sent to the organising laboratory by the deadline 15 September 2005, except for GUM who reported values by email and with the agreement of the organising laboratory submitted a full report by the end of September.

The Draft A report was distributed in the beginning of October 2005 and discussed at the CCQM WGEA meeting hosted by BAM in Berlin, 19 October 2005. Among the points of discussion was the establishment of the Key Comparison Reference Value (KCRV). The Draft A report presented three models for the KCRV, and it was the consensus of the participants to use a KCRV derived from the measurement results which formed a consistent set on a 95 % confidence level combined with an uncertainty contribution for the inherent dispersion of property values in the samples distributed. It was noted, that the three different models for the KCRV did not change the qualitative result of the comparison and only slightly shifted the derived Degrees of Equivalence.

Comments from the participants, including clarifications on calculation mistakes were received during November and December 2005.

The Draft B report was presented at the CCQM WGEA meeting in Paris, 4 April 2006. Among the point of discussion was the handling of revised uncertainties in respect to the calculation of the KCRV and the Degrees of Equivalence. At the CCQM meeting immediately following the WGEA meeting it was pointed out, that Degrees of Equivalence must be reported based on the originally reported results from the participating laboratories, but that the reference value may be calculated using the best available data.

An error in the value for the standard uncertainty for GUM, Poland, in K36.b was uncovered during CMC claims review in 2010. The present report contains corrected data.

## 3 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.

### 3.1 The 0,5 S/m solution, CCQM-K36.a

The solution preparation was initiated at the end of May. The solution was mixed in a 25 litre plastic container from about 25 kg water tapped from a Millipore Milli Q Gradient A10 water purifier and approximately 70,9 g potassium chloride. The water had initial conductivity less than 40  $\mu\text{S/m}$ . The potassium chloride was Merck Suprapur<sup>®</sup> with a nominal purity of 99,999 %. The potassium chloride was dried in an oven for 4 hours at 500 °C and stored in a desiccator before being used for the solution.

The solution was mixed using a motorised propeller for about one week. During the mixing some litres was tapped off and reinserted into the container.

A sufficient number of 500 ml Schott DURAN glass bottles from the same manufacturing batch was rinsed thoroughly several times in deionised water, soaked in deionised water for 48 hours and dried at room temperature in a laboratory ventilation hood for 24 hours.

The dry bottles were filled in sequence, closed with the cap, labelled, tightened and sealed with a strip of parafilm. A total of 44 samples were prepared. The bottles were weighed initially and left to settle for two weeks. During this time, the initial characterisation measurements were performed. The bottles were then weighed again and packed for shipment together with samples from solution CCQM-K36.b.

### 3.2 The 5 mS/m solution, CCQM-K36.b

The solution preparation was initiated at the end of May. The solution was prepared in 25 L HDPE container. Hydrochloric acid (3.0361 g, 0.999017 mol/kg solution) was added into the container and deionised water was added until the balance reading was 25 kg. The solution was homogenized manually by rocking the bottle for about 15 minutes.

A sufficient number of 500 ml Nalgene HDPE bottles was rinsed several times by deionised water and dried at 60°C in a drying oven. The dry bottles were quickly filled in sequence, closed with the cap, labelled, and tightened. The samples for homogeneity check were taken at the start of filling and at its end.

A total of 45 samples were prepared. The bottles were weighed and each bottle was sealed in a bag of Mylar type TEN AL/111S foil produced by Chemosvit in Slovakia. 40 bottles were shipped from Slovakia on 20 June and received at DFM on 22 June. The remaining 5 bottles were used for stability measurements. Initial characterisation measurements were performed at DFM 24–27 June, and the stability of the samples was monitored by SMU over the course of the comparison.

### 3.3 Shipment and travel events

All samples were shipped on July 8<sup>th</sup>. Most laboratories reported receipt of samples by July 20<sup>th</sup>. However, samples had seemed to disappear en route to CENAM, and replacement samples were shipped 3 August 2005.

Ukrmetrteststandart reported a significant mass loss, about 1 g, in one sample, and a replacement sample was sent 29 August 2005. Shipment was late to SP who did not receive samples until 19 August.

INPL reported a mass loss in one bottle of 0,33 g and did not perform measurements on that sample. Other reports of mass loss were below 0,15 g.

When several laboratories did not confirm receipt of samples by 27 July a complaint was filed with the parcel service and attempts to track the parcels initiated. However, after direct contact to the laboratories it was found that parcels had in fact been received, but without a note given to the organising laboratory.

NCM reported in mid September, that technical difficulties prevented that results could be submitted.

#### 4 Characterisation

From each batch, three bottles were taken, one from each end and one from the middle of the filling sequence. Further samples from the batch were measured during the comparison to assess the stability. The bottles were measured in the DFM setup with the results reported below. During measurements, the variation in CO<sub>2</sub> partial pressure in the laboratory during measurement was within  $\pm 10$  ppm-vol, and the pressure variation was  $(1010 \pm 10)$  hPa.

##### 4.1 CCQM-K36.a, 0,5 S/m

The 0,5 S/m solution was measured using the procedure specified in the DFM measurement report, and the following values found:

Measurements by the coordinating laboratory, 0,5 S/m				
Date	Sample	$\kappa$ (S/m)	$s(\kappa)$ (S/m)	$n$
2005-06-21	bottle #1	0,506885	$1,0 \times 10^{-5}$	30
2005-06-22	bottle #22	0,506882	$1,4 \times 10^{-5}$	103
2005-06-22	bottle #44	0,506916	$1,2 \times 10^{-5}$	39
2005-08-16	bottle #29	0,507089	$1,3 \times 10^{-5}$	132
2005-08-17	bottle #19	0,507080	$1,2 \times 10^{-5}$	163
2005-09-30	bottle #39	0,507147	$1,5 \times 10^{-5}$	114

The experimental standard deviation of the three initial measurements is  $1,87 \times 10^{-5}$  S/m. From this 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, i.e. 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:

$$\sigma_{SS} = 4,9 \times 10^{-5} \text{ S/m}$$

The single sample standard deviation was found low enough (less than one half of the expected lowest measurement uncertainty) that further initial measurements was not performed.

##### 4.2 CCQM-K36.b, 5 mS/m

The 5 mS/m solution by DFM and by SMU. The drift of the conductivity value over the measurement time was compensated by extrapolating the results back to the time of the final filling of the measurement cell.

The results obtained at DFM are:

Measurements by DFM, 5 mS/m				
Date	Sample	$\kappa$ (mS/m)	$s(\kappa)$ (mS/m)	$n$
2005-06-24	bottle #1	5,12333	$2,1 \times 10^{-4}$	57
2005-06-24	bottle #22	5,12282	$2,2 \times 10^{-4}$	61
2005-06-27	bottle #40	5,12376	$1,9 \times 10^{-4}$	50
2005-09-20	bottle #13	5,12468	$2,1 \times 10^{-4}$	61
2005-09-21	bottle #29	5,12498	$2,0 \times 10^{-4}$	40

The results obtained at SMU are:

Measurements by SMU, 5 mS/m				
Date	Sample	$\kappa$ (mS/m)	$s(\kappa)$ (mS/m)	$n$
2005-07-04	bottle #41	5,1243	$4 \times 10^{-4}$	3
2005-07-19	bottle #42	5,1248	$6 \times 10^{-4}$	3
2005-09-20	bottle #43	5,1256	$4 \times 10^{-4}$	3
2005-09-26	bottle #44	5,1258	$4 \times 10^{-4}$	3
2005-10-03	bottle #45	5,1261	$3 \times 10^{-4}$	3

The experimental standard deviation of the three initial measurements is  $4,74 \times 10^{-4}$  mS/m. The standard deviation of the single sample conductivity value is then estimated as:

$$\sigma_{SS} = 1,2 \times 10^{-3} \text{ mS/m}$$

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

After the completion of the comparison, the dispersion was estimated from the standard deviation of the residuals of a linear regression from the DFM and SMU results, found as  $5,19 \times 10^{-4}$  mS/m, with 11 measurements. The estimate of the standard deviation of the single-sample deviation then becomes  $6,1 \times 10^{-4}$  mS/m. This value is used as the uncertainty contribution to the reference value due to stability and dispersion of the property value.

## 5 Participants results

Participants reported their results in the period from end of July to end of September.

Acknowledgement of receipt of the report was sent to the laboratories soon after receipt. Results were collected and analysed as they were reported, to monitor the progress and stability of the distributed samples.

### 5.1 Communication with the participants

When reported results were found anomalous or “suspicious”, e.g reported uncertainties much higher than expected, probable typing errors or reported values in significant disagreement with other results, a message was 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:

**CMI:** Some reported values and uncertainties seemed to be off by a factor of 10, i.e. probable typing errors for exponents. A revised report was submitted.

**NIST:** The reported uncertainty for the 5 mS/m seemed large. The laboratory subsequently reported a miscalculation of the uncertainty due to CO<sub>2</sub>. A revised report was submitted.

**VNIIFTRI:** Reported values for both solutions differed significantly from other reported results, and a request to recheck measurements was sent.

**CENAM:** Reported values for both solutions differed significantly from other reported results, and a request to recheck measurements was sent.

**OMH:** Reported values for 5 mS/m differed significantly from other reported results, and a request to recheck measurements was sent. The laboratory reported no problems found.

## 5.2 Communication after circulation of Draft A

In response to the discussion of the Draft A report at the CCQM-WGEA meeting in Berlin, October 2005, on issues concerning uncertainty evaluation and quantification of certain influence factors, especially temperature, three laboratories, CMI, INPL and INMETRO submitted revised uncertainty budgets. Because the new uncertainty values had been calculated more in line with the approach of the majority of laboratories, the revised uncertainties were used in the calculation of the KCRV, as specified below.

## 6 Reported results and analysis

The rules of Key Comparison specify, that a Key Comparison Reference Value must be derived against which the participants' results are compared, and a Degree of Equivalence of each laboratory must be inferred. On the basis of previous results obtained in the pilot studies, P22 and P47, it is found that the reported results and uncertainties are sufficiently well-founded, that a reference value derived from the reported results is possible.

To derive a reference value from the reported results, it is necessary to set up a model. The JCRB working group has suggested several possible models, e.g. a constant value, a value subject to a linear drift over time, a constant value with an inherent stability, and others. When an appropriate model has been selected, it is possible to derive the parameters of the model from a least squares fit against the input data; the reported results. When the fitted values are obtained, it is then possible to calculate the reference value, its uncertainty, and the absolute and relative deviations of the participants' results to the reference value and the associated uncertainty, and perform statistical tests on whether the model is consistent with the data.

The appropriate model was discussed during the CCQM WGEA meeting in Berlin, October 2005. In the Draft A report an analysis was presented, in which three possible models were explored:

1. The reference value is constant and stable.
2. The reference value is constant, but there is a dispersion of property values of the samples distributed or there is an inherent instability. This quantity is characterised by a standard uncertainty assigned to the property value being measured.
3. The reference value is subject to linear drift over time, as well as an inherent dispersion/instability.

Analysis showed, that no statistically significant drift could be assigned to the property values of the samples over the time of the comparison. Hence, it was decided to base the KCRV on model 2:

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

The reference value was thus based on a set of results reported by the participants that forms a consistent set, i.e. where the model for the reference value based on the set of data cannot be rejected from a Chi-square test at 5% confidence. For the analysis, the normalised deviation defined as

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

was used to identify values not consistent with the model. The Degree of Equivalence and its associated uncertainty is given as

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

To form the consistent set, all reported results were initially included in the analysis, and then the value with the highest normalised deviation was removed from the set, until consistency (Chi-square test with probability larger than 5%) was reached.

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.

### 6.1 Reference value, 0,5 S/m (K36.a)

The reference value was found from a consistent set of reported results as described above. Basically, the reference value is calculated as the weighted average of the set of results with a normalised deviation less than approximately 2,0. The weight factor is the inverse of the square of the reported standard uncertainty combined with the variance of the dispersion assigned to the property values.

The dispersion of the property value among the samples measured was determined from the observed experimental standard deviation of the results of the coordinating laboratory DFM, see section 4.1. The value is  $\sigma_{ss} = 4,9 \times 10^{-5}$  mS/m.

The following table shows the reported results, and the resulting reference value, uncertainty of the reference value and the normalised deviation of the reported result to the reference value.

Reported values (S/m)				KCRV (S/m)		
<i>lab</i>	<i>t</i>	<i>y</i>	<i>u(y)</i>	<i>y<sub>ref</sub></i>	<i>u(y<sub>ref</sub>)</i>	<i>d</i>
VMIFTRI	2005-08-12	0,50273	0,00010	0,506992	0,000072	-34,6
INMETRO	2005-08-08	0,50420	0,00055			-5,0
SP	2005-08-24	0,50610	0,00070			-1,3
GUM	2005-08-01	0,50668	0,00025			-1,3
IEN	2005-07-19	0,50677	0,00037			-0,6
SMU	2005-07-19	0,50684	0,00022			-0,7
OMH	2005-07-21	0,50689	0,00010			-1,0
UkrCSM	2005-09-06	0,50697	0,00011			-0,2
INPL	2005-08-31	0,50700	0,00021			0,0
DFM	2005-08-17	0,50708	0,00011			0,9
NIST	2005-08-17	0,50714	0,00011			1,4
PTB	2005-08-10	0,50729	0,00028			1,1
CMI	2005-07-26	0,51095	0,00365			1,1
CENAM	2005-09-04	0,51097	0,00050			7,9

\*

The statistics of the analysis are:

Chi-square value found,  $\chi^2 = 10,5$

Degrees of freedom,  $\nu = 11$

Ratio,  $\chi^2/\nu = 0,957$

Consistency accepted, as  $\Pr\{\chi^2/\nu > 0,957\} = 48,3 \% > 5 \%$

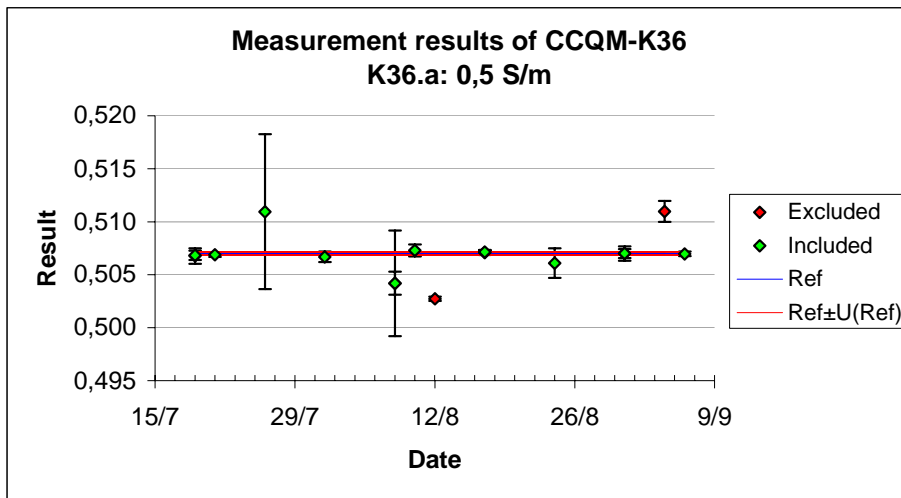
From the analysis three results, with *d*-values marked in red, were found not to form part of a consistent set at a 95% confidence level, and are thus considered discrepant.

After discussions, INPL and INMETRO submitted revised uncertainty calculations. The revised standard uncertainties were  $u_{\text{INPL}} = 0,00034$  mS/m and  $u_{\text{INMETRO}} = 0,0025$  mS/m. The revised uncertainties were used in the calculation of the KCRV

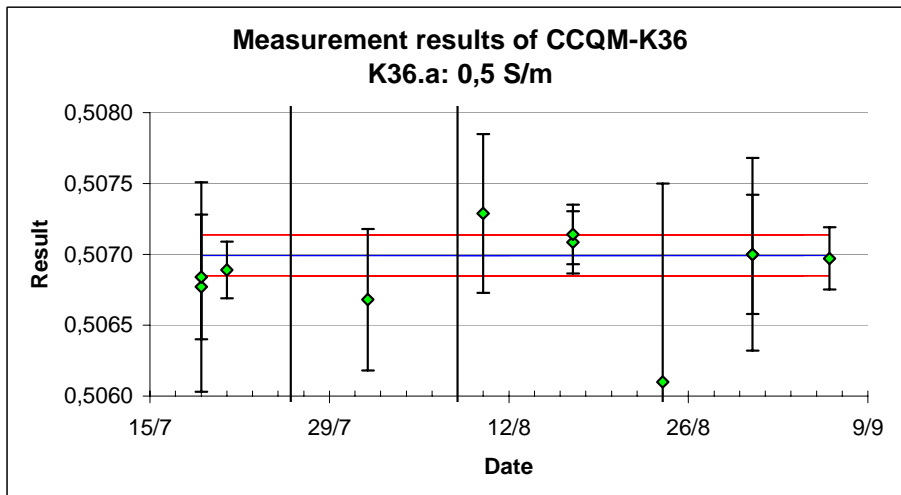
\* In this and the following tables Ukrmetrteststandart is identified as UkrCSM.



## 6.2 Plots for 0,5 S/m (K36.a)



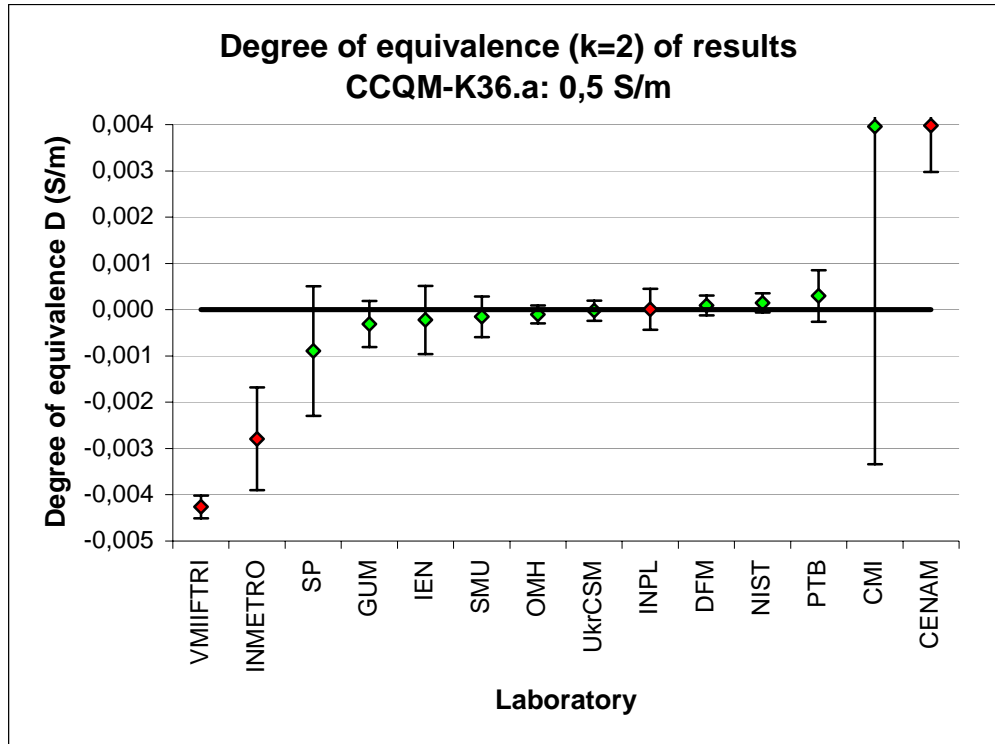
The measurement results reported by the participants (expanded uncertainties,  $k = 2$ ).



A zoom of the central region around the reference value (expanded uncertainties,  $k = 2$ ).

### 6.3 Degrees of Equivalence, 0,5 S/m (K36.a)

	<i>D</i>	<i>U(D)</i>
<i>Lab ID</i>	S/m	S/m
VMIIFTRI	-0,00426	0,00025
INMETRO	-0,0028	0,0011
SP	-0,0009	0,0014
GUM	-0,00031	0,00050
IEN	-0,00022	0,00074
SMU	-0,00015	0,00044
OMH	-0,00010	0,00020
UkrCSM	-0,00002	0,00022
INPL	0,00001	0,00044
DFM	0,00009	0,00022
NIST	0,00015	0,00021
PTB	0,00030	0,00056
CMI	0,0040	0,0073
CENAM	0,0040	0,0010



#### 6.4 Reference value, 5 mS/m (K36.b)

The reference value was found from a consistent set of reported results as described above. Basically, the reference value is calculated as the weighted average of the set of results which all give a normalised deviation less than approximately 2,0. The weight used is the inverse of the square of the reported standard uncertainty combined with the variance of the dispersion assigned to the property values.

The dispersion of the property value among the samples measured was determined from the observed experimental standard deviation of the results of the coordinating laboratories DFM and SMU, see section 4.1. The value is  $\sigma_{ss} = 6,1 \times 10^{-4}$  mS/m.

The following table shows the reported results, and the resulting reference value, uncertainty of the reference value and the normalised deviation of the reported result to the reference value.

Reported values (mS/m)				KCRV (mS/m)		
<i>lab</i>	<i>t</i>	<i>y</i>	<i>u(y)</i>	<i>y<sub>ref</sub></i>	<i>u(y<sub>ref</sub>)</i>	<i>d</i>
VNIFTRI	2005-08-15	4,9810	0,0019	5,1235	0,0011	-64,3
CMI	2005-07-26	5,019	0,075			-1,4
CENAM	2005-09-07	5,040	0,021			-4,0
OMH	2005-07-18	5,0401	0,0017			-40,7
INMETRO	2005-08-09	5,100	0,060			-0,4
GUM	2005-07-30	5,1075	0,0075			-2,1
PTB	2005-08-04	5,1136	0,0063			-1,6
UkrCSM	2005-08-02	5,1166	0,0031			-2,1
INPL	2005-08-30	5,1170	0,0033			-1,9
DFM	2005-07-27	5,1239	0,0012			0,5
SMU	2005-07-19	5,1245	0,0022			0,5
NIST	2005-08-15	5,1250	0,0020			0,8
IEN	2005-07-15	5,130	0,019			0,3
SP	2005-08-26	5,155	0,018			1,8

The statistics of the analysis are:

Chi-square value found,  $\chi^2 = 15,3$

Degrees of freedom,  $\nu = 9$

Ratio,  $\chi^2/\nu = 1,70$

Consistency accepted, as  $\Pr\{\chi^2/\nu > 1,70\} = 8,3\% > 5\%$

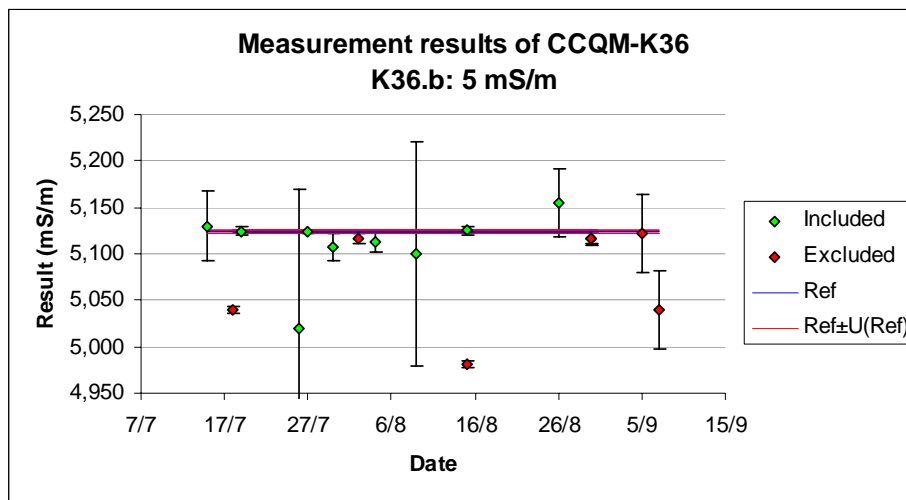
From the analysis four results, with *d*-values marked in red, were found not to form part of the consistent set at a 95% confidence level, and are thus considered discrepant.

After discussions with INPL, a revised uncertainty calculation was submitted. The revised standard uncertainty was  $u_{INPL} = 0,0043$  mS/m, this value was used in the calculation of the KCRV

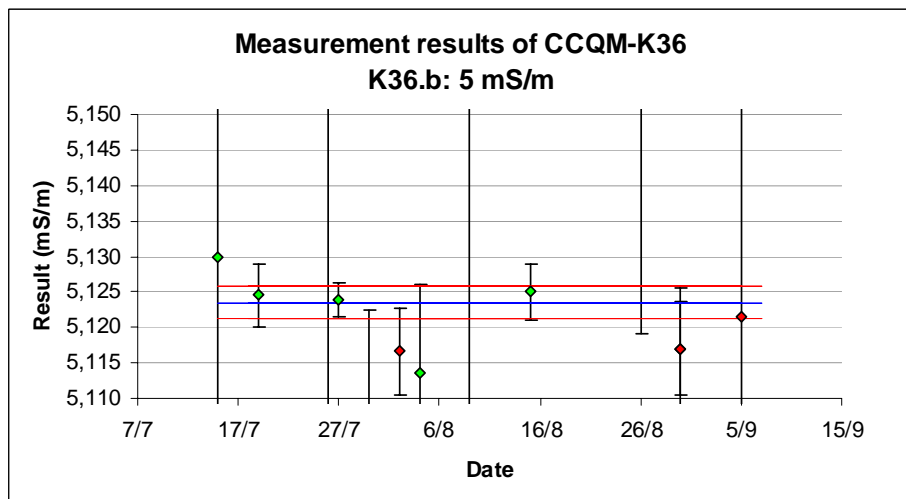
After the distribution of Draft A OMH reported measurements on a second sample in a different measurement cell and reported a value ( $5,1216 \pm 0,042$ ) mS/m. This value, however, was not used in the evaluation of the KCRV.

In 2010, a typing mistake was found in the value for the uncertainty of GUM, Poland. In the table above the corrected value is used. The correction causes the value of UkrCMS to fall outside the consistent set, and has thus been excluded from the calculation of the KCRV. There are no other qualitative effects.

### 6.5 Plots for 5 mS/m (K36.b)



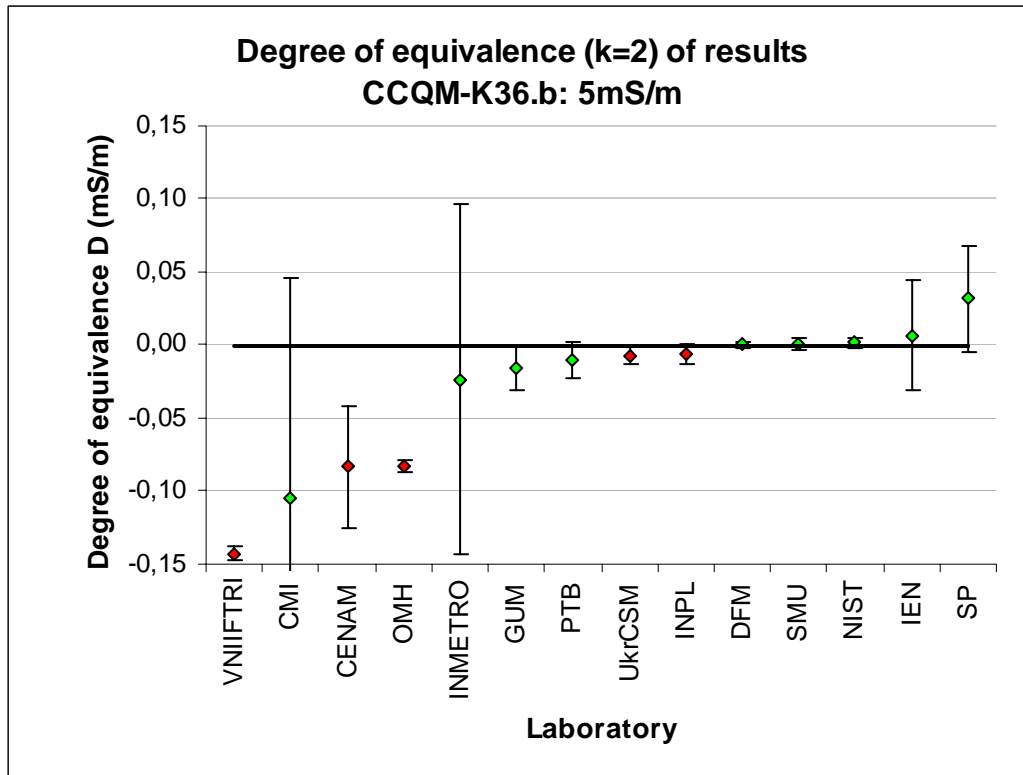
The measurement results reported by the participants (expanded uncertainties,  $k = 2$ ).



A zoom of the central region around the reference value (expanded uncertainties,  $k = 2$ ).

### 6.6 Degrees of Equivalence, 5 mS/m (K36.b)

	<i>D</i>	<i>U(D)</i>
<i>Lab ID</i>	mS/m	mS/m
VNIIFTRI	-0,1425	0,0044
CMI	-0,10	0,15
CENAM	-0,083	0,042
OMH	-0,0834	0,0041
INMETRO	-0,02	0,12
GUM	-0,016	0,015
PTB	-0,010	0,013
UkrCSM	-0,0069	0,0066
INPL	-0,0065	0,0070
DFM	0,0004	0,0019
SMU	0,0010	0,0041
NIST	0,0015	0,0037
IEN	0,007	0,038
SP	0,032	0,036

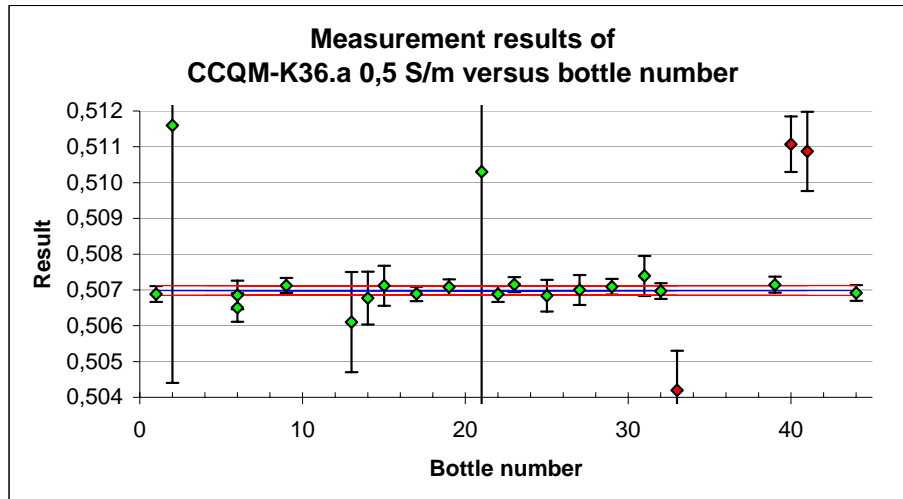


## 7 Further results

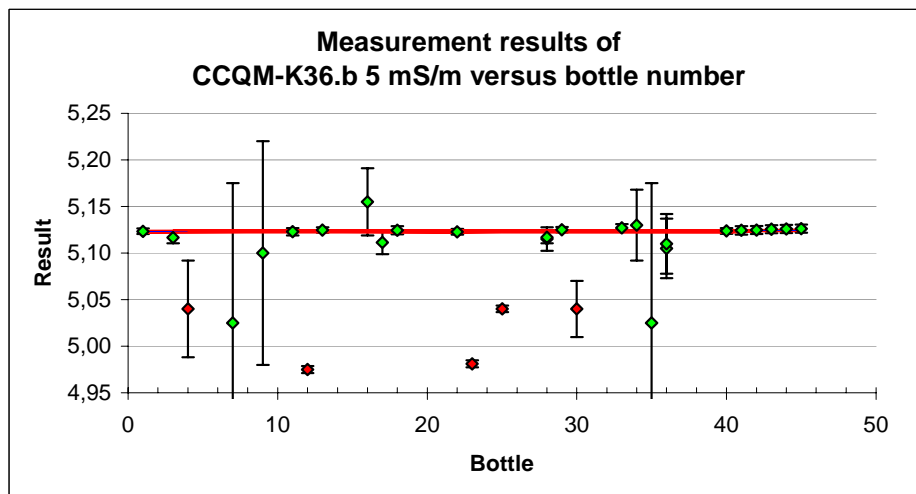
### 7.1 Dispersion versus bottle number / filling sequence

From the individual measurement results reported per bottle versus the bottle number showed no significant correlation.

For the 0,5 S/m solution in glass bottles: (uncertainties are  $k = 2$ )



For the 5 mS/m solution in HDPE bottles: (uncertainties are  $k = 2$ )



### 7.2 Comparison on measurement methods and traceability

An attempt was made by the coordinating laboratory to compare the magnitude of the same basic uncertainty contributions to the reported results of the participating laboratories. In the table given below is shown the relative contribution of each of the main uncertainty components to the combined uncertainty from

1. Cell constant
2. Impedance measurement
3. Temperature measurement and compensation
4. Repeatability/reproducibility/stability
5. CO<sub>2</sub> contribution

### 7.2.1 Comparison table for 0,5 S/m

CCQM-K36.a 0,5 S/m		Relative uncertainty contribution					
Lab	Traceability	Cell	Imp/res	Temp	Reprod	CO2	Combined
CENAM	Piston cell	0,031%	0,030%	0,021%	0,090%		0,102%
CMI	Differential cell	0,005%	0,000%	0,000%	0,760%	0,000%	0,760%
DFM	Differential cell	0,018%	0,009%	0,010%	0,001%	0,001%	0,023%
GUM	CRM; NIST	0,041%	0,015%	0,010%	0,004%	0,000%	0,045%
IEN	Differential cell	0,001%	0,045%	0,012%	0,057%	0,001%	0,073%
INMETRO	CRM; NIST	0,071%	0,006%	0,458%	0,072%		0,469%
INPL	CRM; Radiometer	0,040%	0,004%	0,054%	0,013%	0,002%	0,069%
NIST	IUPAC calibrant	0,017%	0,006%	0,009%	0,004%	0,006%	0,021%
OMH	OIML calibrant	0,017%	0,011%	0,003%			0,020%
PTB	Piston cell	0,007%	0,048%	0,010%	0,024%	0,000%	0,055%
SMU	OIML calibrant	0,036%	0,020%	0,012%	0,004%		0,043%
SP	IUPAC calibrant	0,107%	0,077%	0,050%	0,007%	0,040%	0,146%
UkrCSM	Absolute 4T cell	0,014%	0,013%	0,010%		0,004%	0,022%
VNIIFTRI	primary cell	0,004%	0,010%	0,006%			0,012%

### 7.2.2 Comparison table for 5 mS/m

CCQM-K36.b 5 mS/m		Relative uncertainty contribution					
Lab	Traceability	Cell	Imp/res	Temp	Reprod	CO2	Combined
CENAM	Piston cell	0,030%	0,074%	0,010%	0,400%		0,408%
CMI	Differential cell	0,007%	0,008%	0,013%	1,634%	0,008%	1,634%
DFM	Differential cell	0,020%	0,009%	0,007%	0,001%	0,003%	0,024%
GUM	CRM; DFM	0,140%	0,011%	0,015%	0,035%	0,000%	0,146%
IEN	Differential cell	0,001%	0,260%	0,012%	0,247%	0,115%	0,377%
INMETRO	CRM; NIST	1,176%	0,060%	0,320%	0,221%		1,240%
INPL	CRM; Radiometer	0,040%	0,007%	0,054%	0,024%	0,046%	0,085%
NIST	IUPAC calibrant	0,024%	0,008%	0,006%	0,030%	0,002%	0,040%
OMH	OIML calibrant	0,017%	0,029%	0,003%			0,034%
PTB	Piston cell	0,006%	0,060%	0,100%	0,040%	0,020%	0,125%
SMU	OIML calibrant	0,036%	0,020%	0,012%	0,006%		0,043%
SP	Kohlrausch-curve	0,132%	0,194%	0,049%	0,101%	0,233%	0,349%
UkrCSM	Absolute 4T cell	0,022%	0,038%	0,020%		0,040%	0,063%
VNIIFTRI	primary cell	0,026%	0,007%	0,005%			0,027%

Please note, that the tables above represents the attempt of the coordinating laboratory to “condense” the reported uncertainty budgets into a common form, by combining uncertainty contributions into the five categories.

### 7.3 Uncertainty evaluation details

Two issues concerning uncertainty calculation in conductivity measurements can be addressed on the background of the experiences gained in this and the previous pilot comparisons:

1. Uncertainty due to temperature should be handled by using a multiplicative model, i.e.  $\kappa(T) = \kappa(T_0) \cdot [1 + \alpha_{T_0} \cdot (T - T_0)]$ , where the linear temperature coefficient,  $\alpha_{T_0}$ , in general is approximately 2 %/°C for water based solutions at 25 °C; the exact value varies with conductivity and reference temperature – for the solutions used in the present comparison, a value of  $\alpha_{25} = 1,93$  %/°C was found for the 0,5 S/m solution, and  $\alpha_{25} = 1,47$  %/°C for the HCl based 5 mS/m solution.
2. Uncertainty due to dissolution of CO<sub>2</sub> in the solution should be handled using an additive model, where this additional conductivity scales with the partial pressure of CO<sub>2</sub>, in the form

$$\kappa = \kappa_0 + \kappa_{CO_2} \left( \frac{\sqrt{p_{atm} \cdot x_{CO_2}}}{\sqrt{p_{atm}^0 \cdot x_{CO_2}^0}} - 1 \right) \approx \kappa_0 + \frac{1}{2} \kappa_{CO_2} \frac{\Delta p_{atm}}{p_{atm}^0} \cdot \frac{\Delta x_{CO_2}}{x_{CO_2}^0},$$

where  $\kappa_{CO_2}$ ,  $p_{atm}^0$  and  $x_{CO_2}^0$  are the equilibrium values for conductivity due to CO<sub>2</sub>, the atmospheric pressure (typical value is 1013 hPa) and the mole fraction of CO<sub>2</sub> in air (typical value 380 μmol/mol); and  $\Delta p_{atm}$ ,  $\Delta x_{CO_2}$  are the changes or variations from the equilibrium values during the measurement. A detailed calculation by NIST<sup>1</sup> derives the equilibrium value at 25 °C as  $\kappa_{CO_2} = 0,11$  mS/m for pure water based solutions, while  $\kappa_{CO_2} = 0,00192$  mS/m for the HCl based solution<sup>2</sup> in the K36 comparison, i.e. a suppression of about a factor of 50.

## 8 Conclusions

It was found that the majority of participants reported values and uncertainties consistent with the reference value, and supports the Calibration and Measurement claims of the institutes.

The KCRV is found from a least squares minimisation of a constant property value with a dispersion term (normally distributed with mean zero and variance derived from the observed dispersion), and a set of the reported results that form a consistent set on a 95 % confidence level.

Three values reported for the 0,5 S/m samples and three values reported for the 5 mS/m samples were found to be discrepant.

Two further models for the KCRV was explored, as well as the simple median, in all cases the qualitative result remains the same.

At the request of several laboratories, a follow-up comparison, CCQM-K36.1, will be arranged.

<sup>1</sup> K. W. Pratt, W. F. Koch, Y. C. Wu, and P. A. Berezansky, Pure Appl. Chem., 73, 1783, 2001.

<sup>2</sup> K. W. Pratt, "Report of CCQM-K36: Measurement of Electrolytic Conductivity of Two Solutions: Nominal Values 0.5 S m<sup>-1</sup> and 5 mS m<sup>-1</sup>", National Institute of Standards and Technology Report of Analysis 839.03-05-163, 12 September 2005.