CIPM MRA
Comparison reports

CCQM-K73.2018.4

Amount content of H^+ in an HCl solution

KEY COMPARISON

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CCQM WG on Electrochemical Analysis and Classical Chemical Methods

Final report on Key Comparison CCQM-K73.2018.4
Amount Content of H^+ in Hydrochloric Acid (0.1 mol·kg^{-1})
October 2025

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Abstract

The CCQM key comparison K73.2018.4 is a follow-up comparison of CCQM K73.2018. It was performed to demonstrate the capability of the participating institutes to measure the amount content of H^+ in hydrochloric acid of 0.1 mol·kg^{-1} molality. 3 NMIs participated in this comparison with PTB being the linking lab. The comparison was coordinated by PTB.

The sample showed a slight but significant instability by loss of water of around 0.13 µmol kg^{-1}d^{-1} corresponding to 0.006 % over the measurement period. The results were corrected for this instability.

The results of this subsequent key comparison showed significant deviations from the KCRV.

Subject field

Amount of substance

Subject

Determination of the Amount Content of H^+ in Hydrochloric Acid (0.1 mol·kg^{-1})

Table of Content

Purpose of the comparison

The CCQM key comparison CCQM-K73.2018.4 is a follow-up comparison of CCQM-K73.2018. It was performed to demonstrate the capability of the participating institutes to measure the amount content of H^+ in a HCl solution with a nominal value of 0.1 mol/kg by use of a measurement method of their choice. The results of the key comparison may serve as evidence to support CMC claims complying with the “how far the light shine” statement.

Time schedule

Registration	October 2024
Dispatch of the samples	January 2025
Deadline for receipt of the report	28 February 2024
Draft A report distributed	04 April 2025
Discussion of Draft A report:	via e-mail April-July 2025
Draft B report	16 July 2025
EAWG approval of Draft B report	EAWG autumn meeting 2025

Coordinating laboratory

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Participants

Table 1: List of participants in the key comparison CCQM-K73.2018.4

Acronym	Institute	Country	Contact
BFKH	Government Office of the Capital City Budapest	Hungary	Dániel Nagy
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges, Sidney Pereira Sobral
PTB	Physikalisch-Technische Bundesanstalt	Germany	Frank Bastkowski

Sample preparation, distribution and handling

5 L of 0.1 mol/kg HCl solution were prepared on 26 November 2024 by mixing five bottles of 0.1 mol/kg HCl solution in a 5 L PFA bottle. Each bottle was individually prepared by dilution of Titrisol ampules (Merck, product number 1.09973.0001) with deionized water. 11.5 g of deionized water was added as to decrease the amount content slightly. The solution was homogenized on 4 December 2024 and filled into numbered 250 mL HDPE bottles which were immediately closed with a lid and sealed with parafilm. Afterwards, the bottle masses were measured, and the bottles were sealed in aluminized plastic bags to minimize evaporation. The homogeneity of the HCl solution was measured by the coordinating institute before shipment and the stability was measured four times over the course of the comparison between 9 December 2024 and 11 March 2025.

Each participant received two numbered bottles. Shipment to all participants was performed at the same time by courier during January 2025. A spreadsheet for reporting was distributed to the participants by the time the samples were shipped.

The participants have inspected the bottles visually for damages after arrival. Afterwards, they have removed the aluminium bag to measure the bottle masses as to check their integrity. Table 2 shows the weighing results. A significant deviation was found for bottle 15 sent to INMETRO. The coordinating institute therefore proposed INMETRO not to use this bottle for analysis. No further bottle damage has been observed.

The bottles had to be put into the aluminium bags afterwards and stored at room temperature until the measurement.

Table 2: Relative mass change of the sample bottles determined for the sample integrity check after shipping

Institute	Bottle No.	Date received	Weighing date	Date difference from preparation at weighing date/d	rel. mass deviation of bottle
BFKH	6	09.01.2025	10.01.2025	45	-0.005%
	16				-0.002%
INMETRO	3	30.01.2025	31.01.2025	66	-0.006%
	15				-0.013%

* prepared and bottled at PTB

Sample homogeneity and stability

Before shipment the homogeneity between the bottles was checked by coulometric measurements of the H^+ content of five bottles. The selected bottles were distributed over the whole batch. The results are summarized in table 3 and shown in figure 1. The samples can be considered homogeneous.

Table 3: Coulometric homogeneity check at the coordinating laboratory before shipment

Bottle no.	**Date**	**Molar Amount content of H^+/ (mol·kg^{-1}) ν (related to the mass of solution) with expanded uncertainties***
2	09.12.2024	0.099825 ± 0.000016
7	10.12.2024	0.099824 ± 0.000011
12	12.12.2024	0.099819 ± 0.000015
17	12.12.2024	0.099813 ± 0.000022

* Level of confidence: 95.45%. The stated expanded uncertainties include only repeatability contributions, since systematic uncertainties are irrelevant for the assessment of homogeneity.

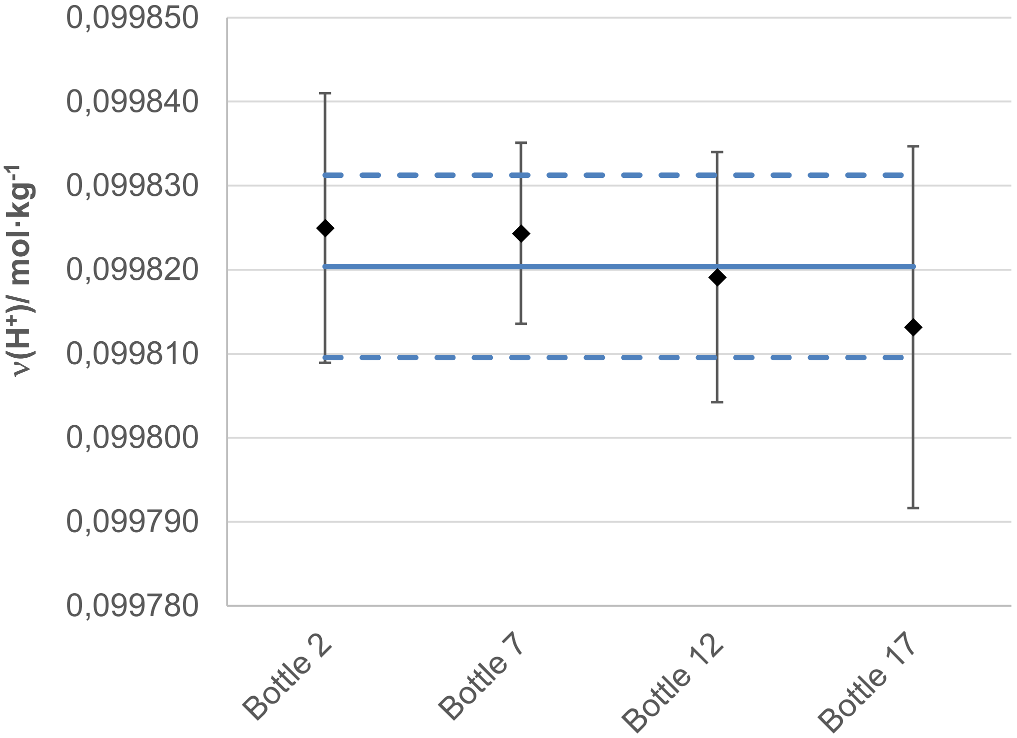

Figure 1: Measurement results of homogeneity together with the mean (solid blue line) and the corresponding expanded (level of confidence: 95.45%) measurement uncertainty (dashed blue lines)

To evaluate the stability of the sample solution, the mean of the results of the homogeneity testing and of 3 additional coulometric measurements of the H^+ content from arbitrarily chosen samples were used. Table 4 shows the results from the stability measurements performed at the coordinating institute over the period 09.12.2024 – 11.03.2025. Figure 2 illustrates the results graphically. The coulometric results showed a slight instability over the period of 13 weeks, indicated by a linear regression line (black). The instability was confirmed by the change of the mass of the sample solution (calculated from the measured bottle mass over time and the mass of the corresponding empty bottle). The mass of the samples decreased during the period of 13 weeks by 0.01 % (dashed green line). Figure 3 shows the relative mass changes of the sample calculated from the weighing results. The change of mass measured by weighing basically confirms the drift measured at the coordinating institute by coulometry.

Table 4: Sample stability of the H^+ content over the period 09.12.2024 – 11.03.2025 measured by coulometry.

Bottle no.	**Date measured**	**Amount content of H^+/ (mol·kg^{-1}) ν (related to the mass of solution) with expanded uncertainties***	**Number of measurements**
2, 7, 12, 17	09./12.12.2024	0.099820 ± 0.000006	24
13	07.01.2025	0.099822 ± 0.000007	5
5	10.02.2025	0.099826 ± 0.000006	6
9	11.03.2025	0.099832 ± 0.000008	7

* Level of confidence: 95.45%, The stated expanded uncertainties include only repeatability contributions, since uncertainties due to systematic effects are irrelevant for the assessment of stability, assuming that the measurement system has been stable over the measurement period.

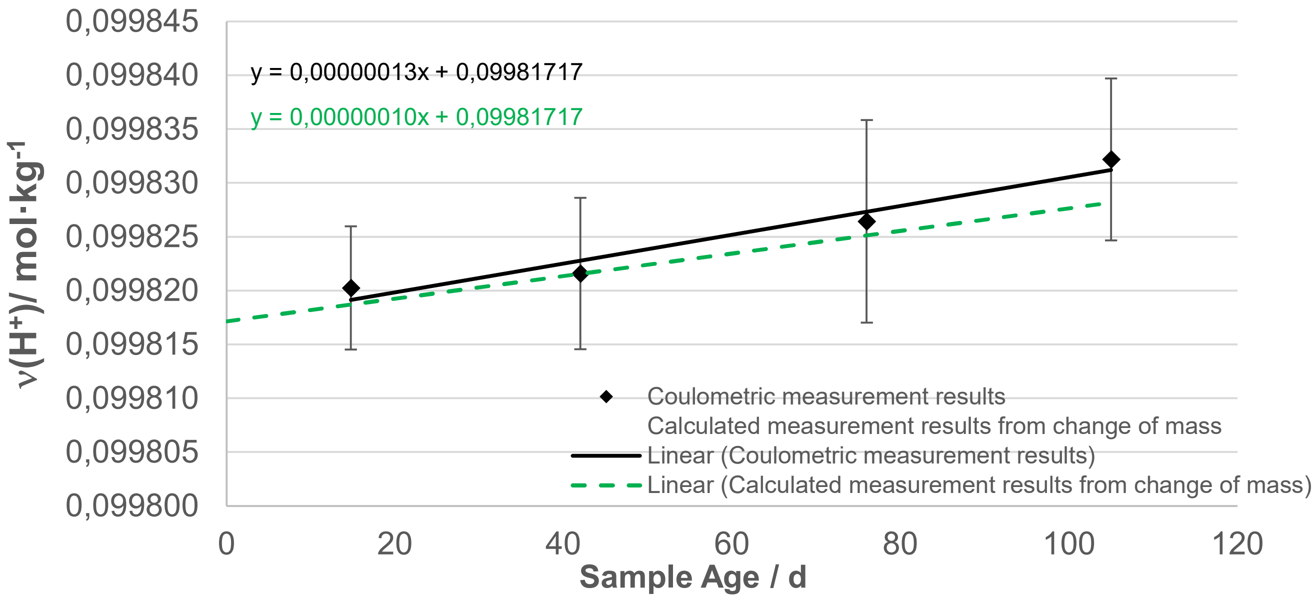

Figure 2: Stability of the amount content of H^+, measured by coulometry (diamonds). The error bars indicate the repeatability of the measurements (expanded uncertainty, level of confidence: 95.45%). The black line indicates a linear regression. The dashed green line indicates the change of the amount content of H^+ as it can be expected from the change of the sample mass (see below).

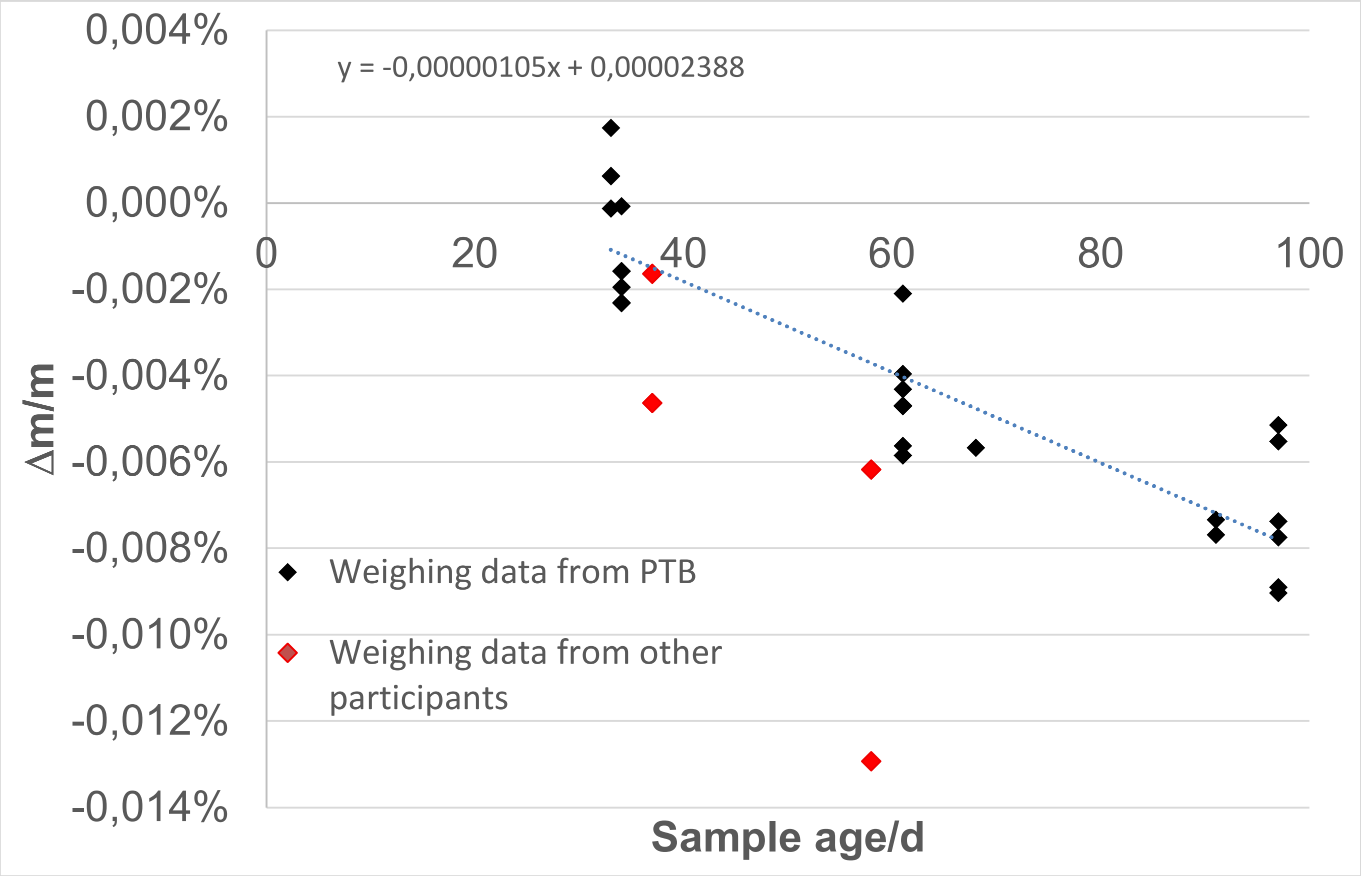

Figure 3: Relative change of mass of the solutions measured by the participants. Black diamonds represent the weighing results obtained at the coordinating institute, red diamonds represent the weighing results obtained at the participating institutes.

Both, the coulometric measurement results and the calculated change in amount content of H^+ due to mass loss, show a very similar trend. Hence, the instability is a result of the evaporation of water. As the slopes of the two lines are larger than their uncertainties, they must be considered significant over the measurement period. Therefore, the results obtained from the participants of this comparison were corrected using the linear regression line of the coulometric stability measurements.

Timetable of measurements

Table 5: Dates of samples received and dates of the measurement reports

Institute	Bottle No.	Measurement period	Date difference from preparation at measurement date/d*	Date of report (revised report)
BFKH	6,16	10.01.2025	45	28.02.2025
INMETRO	3,15	13.-24.02.2025	84	28.02.2025
PTB	5	10.02.2025	76	04.04.2025**

* the sample age at the measurement time was calculated as the mean of the measurement period

** together with draft A

Communication with participants

22 Nov 2024: The technical protocol was shipped to the participating institutes.
17 Dec 2024: The coordinating institute informed the participating institutes that the sample is homogeneous.
6 Jan 2025: The coordinating institute informed the participating institutes that the samples have been shipped.
9 Jan 2025: BFKH confirmed that the sample has arrived at their institute.
10 Jan 2025: BFKH provided sample integrity data.
10 Jan 2025: The coordinating institute confirmed the integrity of the samples send to BFKH.
30 Jan 2025: INMETRO confirmed that the sample has arrived at their institute.
31 Jan 2025: INMETRO provided sample integrity data.
03 Feb 2025: The coordinating institute informed INMETRO that the integrity weighing result of bottle 15 was anomalous and proposed INMETRO to use only bottle 3 for their analysis.
03 Feb 2025: INMETRO confirmed to use only bottle 3 for their analysis.
28 Feb 2025: BFKH sent their measurement report.
28 Feb 2025: INMETRO sent their measurement report.
20 Mar 2025: The coordinating institute informed both BFKH and INMETRO that their results are inconsistent with the result of the coordinating institute and asked to check their results for transcription or calculation errors. No numerical information was given on the nature of the deviation.
24 Mar 2025: INMETRO declared that they have checked their results errors, but did not find any.
27 Mar 2025: BFKH declared that they have checked their results forerrors, but did not find any. However, they found that their pH electrode was malfunctioning at the time of the coulometric measurements.

Results and discussion

All participating institutes conducted coulometric measurements (see table 6a). This comparison offered the possibility to measure the sample at a molar amount content of 0.01 mol/kg HCl after dilution to support corresponding calibration and measurement capabilities of the participating institute., The amount content of H^+ of 0.01 mol/kg HCl solutions is often used as a part of the primary pH measurement procedure. In this comparison, it was also possible to measure only the diluted sample. However, institutes were nevertheless obliged to provide a measurement result for the amount content of H^+ of the original sample solution (0.1 mol/kg hydrochloric acid) and to add the uncertainty of the dilution step to the measurement uncertainty budget. INMETRO has measured the H^+ content of the sample directly and has additionally measured the sample diluted to 0.01 mol/kg. BFKH has measured the H^+ content of the sample only after dilution to 0.01 mol/kg. Tables 6 a) and b) lists the reported results and those corrected for the drift. It should be mentioned that the correction had only an insignificant effect on the results with respect to their uncertainties and their deviation from the KCRV.

Table 6a: Measurement results of CCQM-K73.2018.4 with corresponding standard measurement uncertainties.

NMI	Method	Reported amount content of H^+/ ($mol \cdot kg^{-1}$) ν (related to the mass of solution)	Amount content of H^+/ ($mol \cdot kg^{-1}$) ν (related to the mass of solution), corrected for drift
BFKH	Coulometry	0.1000338 ± 0.0000476	0.1000278 ± 0.0000476
INMETRO	Coulometry	0.0999420 ± 0.0000347	0.0999309 ± 0.0000347
PTB	Coulometry	0.0998264 ± 0.0000046	0.0998163 ± 0.0000049

Table 6b: Additional results and standard uncertainties calculated from measurements of samples diluted to an H^+ amount of substance content of 0.01 mol/kg. The uncertainties include the additional uncertainty introduced by the dilution step.

NMI	Method	Reported amount content of H^+/ ($mol \cdot kg^{-1}$) ν (related to the mass of solution)	Amount content of H^+/ ($mol \cdot kg^{-1}$) ν (related to the mass of solution), corrected for drift
INMETRO	Coulometry	0.0999632 ± 0.0000187	0.0999519 ± 0.0000188

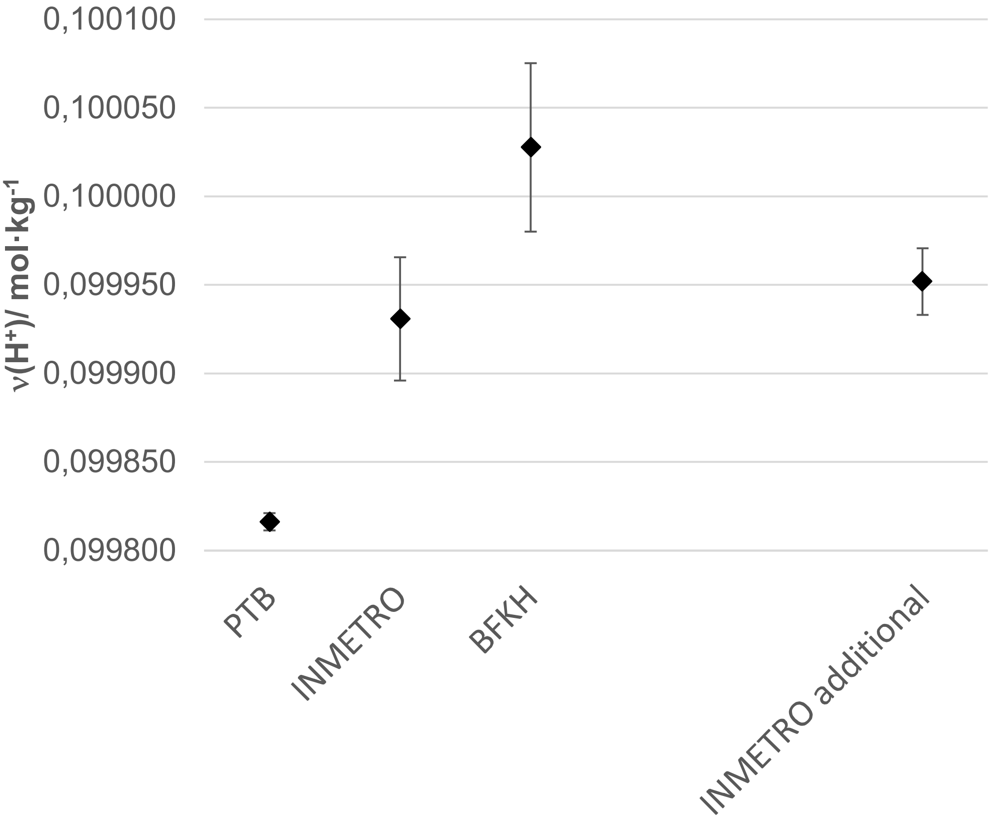

Figure 4: Measurement results with corresponding standard uncertainties corrected for drift due to evaporation of water (recalculated). The result from INMETRO from the measurement of the diluted sample is given on the right side.

The results of this subsequent comparison revealed significant deviations of the results of BFKH and INMETRO with respect to the result of PTB which serves as link to the KCRV., To verify the validity of the PTB result, the coordinating institute asked the Slovak Institute of Metrology (SMU) to perform coulometric measurements of the sample. SMU found the H^+ molar amount of substance content of the sample to be consistent with that of the coordinating institute.

The participants were asked to provide detailed information about their measurement setup and procedure. The following information was provided by the participants:

- the cell geometry (horizontal or vertical) and the number of intermediate chambers
- the shape and type of electrodes used
- the electrolyte
- the type of inert gas
- the maximum applied current
- their method of endpoint detection
- if the sample was degassed
- how much and which kind of acid they added as to perform the initial titration
- the duration of each titration
- the slopes at the endpoints at the pre- and main titration.

The information provided has been analyzed by the coordinating institute to reveal correlations with the measurement results. However, no significant correlation between the measurement results and the above-mentioned measurement conditions could be observed.

Calculation of the degrees of equivalence

As to link the results of the participants from this subsequent comparison to the original comparison CCQM-K73.2018, degrees of equivalence *DoE*(NMI, K73.2018.4) were calculated according to equation (1):

$$DoE_{NMI,K73.2018.4} = x_{NMI,K73.2018.4} - x_{LinkingLab,K73.2018.4} + DoE_{LinkingLab,K73.2018} \qquad (1)$$

with:

$x_{NMI,K73.2018.4}$: Measurement result of participating institute in the subsequent comparison CCQM-K73.2018.4

$x_{LinkingLab,K73.2018.4}$: Measurement result of linking lab (PTB) in the subsequent comparison CCQM-K73.2018.4

$DoE_{LinkingLab,K7\ .2018}$: Degree of equivalence of linking lab (PTB) in the original comparison CCQM-K73.2018

The uncertainty of the *DoE*s was calculated according to equation (2):

$$\begin{aligned} u^2\left(DoE_{NMI,K7\ .2018.4}\right) = {} & u^2\left(x_{NMI,K73.2018.4}\right) + u^2\left(x_{\mathrm{LinkingLab},K73.2018.4}\right) + u^2\left(x_{\mathrm{LinkingLab},K73.2018}\right) + \\ & u^2(KCRV) \end{aligned} \qquad (2)$$

Table 7 shows the results recalculated according to the drift of the sample due to evaporation and *DoE*s, and their corresponding expanded uncertainties, U(*DoE*), of the subsequent comparison CCQM-K73.2018.4. Moreover, the last column of the table lists the minimal, relative expanded uncertainties $U_{\text{CMC-min}}(x_i)$ that are consistent with the KCRV. Figure 5 shows the *DoE*s for all participants of both, the original comparison CCQM-K73.2018 and the subsequent comparison CCQM-K73.2018.4.

Table 7a: Measurement results of the amount content of H$^+$ in a 0.1 mol kg^{-1} HCl solution with corresponding expanded uncertainties recalculated according to the drift of the sample due to evaporation. The last column on the right-hand side lists the minimal, relative uncertainties $U_{\text{CMC-min}}(x_i)$ that are consistent with the KCRV.

NMI*i*	**Result x_i/ (mol·kg^{-1})**	**U(x_i)/ (mol·kg^{-1})**	**Coverage factor k**	***DoE*$_i$/ (mol·kg^{-1})**	**U(*DoE*$_i$)/ (mol·kg^{-1})**	**E_n**	**Relative $U_{\text{CMC-min}}(x_i)$**
BFKH	0.1000278	0.0000952	2.00	0.0002030	0.0000975	2.08	0.199%
INMETRO	0.0999309	0.0000876	2.52	0.0001061	0.0000725	1.46	0.126%

Table 7b: Additional information values of the amount content of H$^+$ in a diluted 0.01 mol·kg^{-1} HCl solution, recalculated according to the drift of the sample due to evaporation. The last column on the right-hand side lists the minimal relative uncertainties $U_{\text{CMC-min}}(x_{i0.01})$ that are consistent with the KCRV.

NMI*i*	**Result x_i/ (mol·kg^{-1})**	**U(x_i)/ (mol·kg^{-1})**	**Coverage factor k**	***DoE*$_i$/ (mol·kg^{-1})**	**U(*DoE*$_i$)/ (mol·kg^{-1})**	**E_n**	**Relative $U_{\text{CMC-min}}(x_{i0.01})$***
INMETRO	0.0999519	0.0000473	2.52	0.0001272	0.0000429	2.97	0.153%

* the relative uncertainty of CMC claims around 0.01 mol/kg must be equal or larger to $U_{\text{CMC-min}}(x_{i0.01})$, see HFDTLS statement.

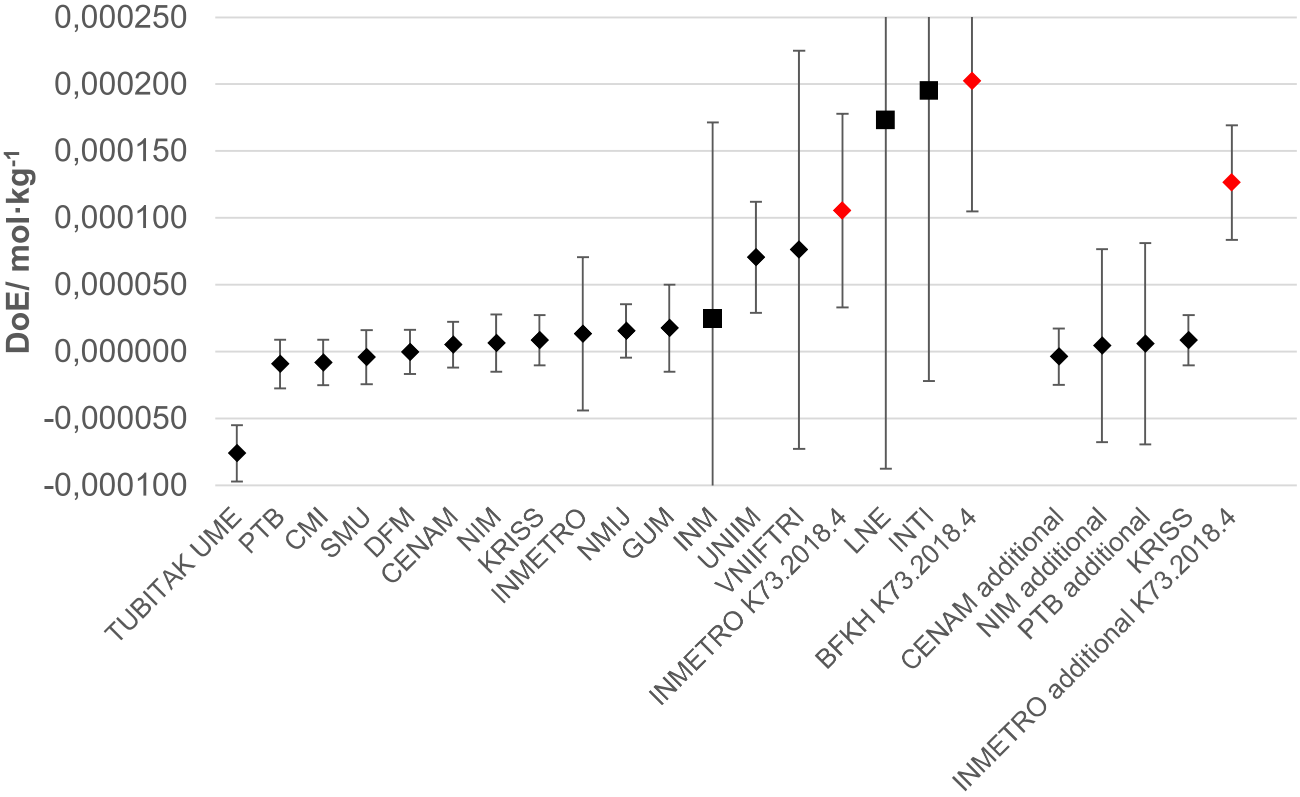

Figure 5: *DoE*s with corresponding expanded measurement uncertainties of CCQM-K73.2018 (black) and CCQM-K73.2018.4 (red). Solid squares represent measurement values obtained with titrimetry.

How far the light shines

The original HFTLS statement of CCQM-K73.2018 applies: The participants of CCQM-K73.2018.4 have demonstrated their capability to measure the molar amount content of H^+ in 0.1 mol/kg hydrochloric acid.

The comparison has provided largely inconsistent results. Nevertheless, it is suitable to support CMC claims for the measurement of hydrochloric acid of molar amount content 0.1 mol/kg - 10% and above with uncertainties stated in the last column of table 7a, which takes the inconsistencies of the results into account. However, the relative measurement uncertainty at higher molar amount contents must not be smaller than the relative uncertainties consistent with the results of this comparison unless further evidence is given. Institutes that have performed measurements of a diluted sample at 0.01 mol/kg hydrochloric acid may use this comparison to support CMC claims for molar amount content in the range of 0.01 mol/kg +/- 10%, which is in particular relevant in the context of primary pH measurements. The relative uncertainty stated for CMC claims at 0.01 mol/kg has to be consistent with the relative uncertainty stated in table 7b.

References

[1] CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version 10, 2013.
[2] Measurement comparisons in the CIPM MRA, CIPM MRA-D-05, Version 1.6, 2016.
[3] M. G. Cox, "The evaluation of key comparison data: determining the largest consistent subset," Metrologia, vol. 44, pp. 187-200 (2007).
[4] CCQM document CCQM-13/22, CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, v10

Appendix 1 Technical protocol

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

Trilateral Key Comparison CCQM-K73.2018.4
Amount Content of H^+ in Hydrochloric Acid (0.1 $mol \cdot kg^{-1}$)

Technical protocol

Purpose of the comparison

The CCQM key comparison K73.2018.4 is a trilateral follow-up comparison of CCQM-K73.2018. It will be performed to demonstrate the capability of the participating institutes to measure the amount content of H^+ in a HCl solution with a nominal molality of 0.1 mol/kg. The institutes can use a method of their choice, although the use of coulometry or titrimetry with potentiometric determination of the endpoint is expected.
Samples of 0.1 mol/kg HCl solutions will be sent to the participants. Participants can either measure the 0.1 mol/kg solution directly or after dilution. In any case, the results must be referred to the 0.1 mol/kg solution.
The results of the key comparison may serve as evidence to support respective CMC claims.

Time schedule

Dispatch of the samples:	December/January 2025
Deadline for receipt of the report:	28 February 2025
Draft A report distributed	30 April 2025
Discussion of Draft A report:	via e-mail April/May 2025
Draft B report	May 2025
EAWG approval of Draft B report	EAWG autumn meeting 2025

Description of the sample

Depending on the number of institutes applying for this comparison a specified amount of 0.1 mol/kg HCl solution will be prepared by mixing several 0.1 mol/kg HCl solutions in a 5 L PFA bottle. Each of those solutions will be individually prepared by dilution of Titrisol (Merck) ampules with deionized water. After thorough homogenization, the solution will behttps://en.pons.com/translate/english-german/is filled into numbered 250 mL HDPE bottles which are immediately closed and sealed with parafilm.
The coordinating laboratory will measure the homogeneity of the HCl solution before shipment and the stability in the course of the comparison.

Each participant will receive two numbered bottles, each sealed in an aluminized plastic bag. Shipment to all participants will be performed at the same time by courier. The tracking number will be reported by E-Mail.
A spreadsheet for reporting will be distributed by the time the samples will be shipped.

Actions after receipt of the samples

1. Inspect the aluminized bags thoroughly for visible damage or leakage. If damage or leakage are noticed, please contact the coordinating laboratory immediately.
2. Confirm receipt of the samples and any mishaps by e-mail to the coordinating laboratory.
3. Weigh the bottles immediately after receipt
    - Allow the bagged bottles to equilibrate in the weighing laboratory at least overnight before performing the weighing.
    - Remove the aluminized plastic bag. Weigh the bottle with a balance having 0.01 g resolution. You **must not** remove the label or the parafilm seal. Enter balance reading, ambient atmospheric pressure, relative humidity and temperature into the spreadsheet. The bottle mass will be automatically corrected for air buoyancy (assuming 1000 $kg\cdot m^3$ density).
4. Report the masses of the bottles (corrected for air buoyancy) to the coordinating laboratory **by e-mail** and report any mishaps. If a bottle leak is observed a replacement bottle will be sent.
5. Reseal the bottles into the aluminumized bags (adhesive tape can be used) if you will start measurements later.

Measurements

Participants are requested to measure the amount content ν_{H^+} of the provided HCl solution. They should apply the measurement procedures they usually use.
Some institutes measure the amount of H^+ of 0.01 mol/kg HCl solutions as part of primary pH measurements. In order to support respective CMC claims, the participants may dilute the sample to 0.01 mol/kg and conduct the amount of substance measurement with the diluted HCl solution.
According to the limited stability of the sample solution detected in K73.2018 the **measurements** of all participants **must be conducted within the same time period comprising not more than two weeks**. Accordingly, the measurement capacities of the participating institutes will be coordinated beforehand.

Reporting

The participants are requested to use the spreadsheet for reporting, which will be distributed by the time the samples will be sent. The report must contain the following information:

- Name and address of the laboratory performing the measurements
- Name of the analyst(s)

- Date of receipt of samples
- Identification of the samples (bottle numbers) measured
- Date(s) of measurement
- Mass of each measured bottle (with buoyancy correction, assuming bottle density 1000 kg/m^3)
- Description of the method used
- Complete uncertainty budget according to the *Guide to the Uncertainty in Measurement*[1]. All significant uncertainty sources must be accounted for.
- The measurement result, including standard uncertainty, coverage factor and the expanded uncertainty. **All measurement results must be reported with respect to the H$^+$ content of the original sample to enable the assessment of the equivalence of the results.** Consequently, if the provided sample has been diluted to measure at around 0.01 mol/kg, the measurement result must be recalculated for the dilution step afterwards. The report must include the data for the dilution (masses/balance readings). The uncertainty budget must include the uncertainty of the dilution.

  It is also possible to report the result of a measurement of the original, undiluted solution (at 0.1 mol/kg nominal value) and to provide the measurement result of the diluted solution as additional information.
- Raw data for one measurement and the measurement equation
- The route of traceability
- Participants are encouraged to provide further information, e.g. on impurities like bromide.

Participants performing titrimetric measurements are requested to provide additional information of their measurement setup in the “Additional information” data sheet of the reporting file.

The report must be sent by e-mail to the coordinating laboratory by 28 February 2025 at the latest. The coordinating laboratory will confirm the receipt of each report. If the confirmation *DoE*s not arrive within two weeks, please contact the coordinating laboratory to identify the problem.

Key comparison reference value

The results will be compared to the key comparison reference value of CCQM-K73.2018 through the results of PTB as the linking laboratory.

How Far the Light Shines statement

HFTLS statement of this subsequent comparison will be equal to the HFTLS statement of CCQM-K73.2018.

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[1] http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

Contact person and coordinating laboratory

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