中国计量科学研究院
National Institute of Metrology,China

Report of the bilateral Key Comparison CCQM-K73.2018.3

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

Final report

Bing Wu, Jianying Zhang, Tao Zhou, Lokman Liv and Serap Gençtürk Tosun

Beijing, 24 January 2025

Abstract

The subsequent key comparison K73.2018.3 was performed to demonstrate the capability of the participating institutes to measure the amount content of H^+ in hydrochloric acid as a follow-up of the previous key comparison CCQM-K73.2018. A HCl solution of a slightly different composition to that in CCQM-K73.2018 was used.

TUBITAK UME requeststhis bilateral comparison. Both participants used high accuracy constant current coulometry for measurement. The agreement of the results was good. National institute of metrology P.R.China (NIM) acted as the coordinating laboratory and served as a link to the reference value of CCQM-K73.2018.

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Introduction

The key comparison CCQM-K73.2018 on an assay of hydrochloric acid took place in summer 2019. Some institutes could not take part in the comparison at that time or did not consider their results representative for their capabilities. Therefore, a bilateral key comparison was launched on request of TUBITAK-UME. A HCl solution of a slightly different composition to that in CCQM-K73.2018 was used.

Both participants applied coulometric titration for the assay of HCl.

Metrology Area

Amount of Substance

Branch

Electrochemistry

Coordinating laboratory

National Institute of Metrology P.R.China, NIM

Subject

Assay of hydrochloric acid with nominal amount content of 0.1 mol/kg.

Time schedule

Dispatch of the samples: May/June 2024
Deadline for receipt of the report: 31 August 2024
Discussion of results: EAWG meeting, October 2024
Draft A: October 2024

Participants

Table 1. Table of participants

Acronym	Participant	Country	Analyst
TUBITAK UME	TÜBİTAK National Metrology Institute	Turkey	Lokman Liv, Serap Gençtürk Tosun
NIM	National Institute of Metrology P.R.China	China	Bing Wu, Jianying Zhang, Tao Zhou

Sample description

Sample preparation

Four liters of 0.1 mol/kg HCl solution were prepared in a HDPE carboy by dilution of hydrochloric acid 20% (TAMA Chemicals) with deionized water. The solution was filled into numbered 250 mL HDPE bottles which were closed with a lid immediately after filling. Afterwards, the bottle masses were measured, and the bottles were sealed in HDPE foil and aluminized plastic bag to minimize evaporation.

On the following day, the homogeneity of the HCl solution was measured by the coordinating institute. Stability was measured three times over the course of the comparison.

Solution homogeneity

Systematic sampling was used for homogeneity check (trend analysis). The first, intermediate and last bottles were measured by coulometry. The results are given in Table 2.

Table 2. Results of homogeneity measurement

Bottle	**Amount content v/mol.kg^{-1}**	**SD (v) /mol.kg^{-1}**
1	0.100342	4.1E-06
5	0.100341	5.4E-07
10	0.100340	2.5E-06
15	0.100341	1.1E-06

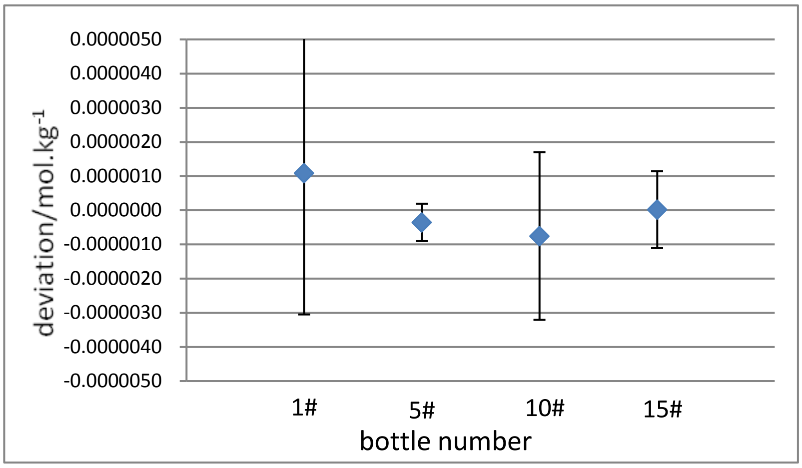

Figure 1. Homogeneity of samples for CCQM-K73.2018.3. The figure shows deviations of the mean, and the error bars indicate standard deviations of three measurements.

No significant difference was found between the bottles. Thus, it can be concluded that no systematic alteration occurred during the filling process and the solution can be regarded as homogeneous.

Solution stability

To evaluate the stability of the sample solutions, the mean of the results of the homogeneity testing and additional coulometric measurements of the H^+ content from arbitrarily chosen samples were used. Table 3 shows the results from the stability measurements performed at the coordinating institute over the measurement period (21 May – 25 July 2024). Fig. 2 illustrates the results graphically. The coulometric results showed a slight instability over the measuring period of 65 days, indicated by a linear regression line (black).

Table 3. Results of stability measurement

Date	**Bottle No.**	**Amount content *v*/mol.kg^{-1}**	***SD*(*v*) /mol.kg^{-1}**
May 20-21,27, 2024	1, 5, 10	0.100341	2.5E-06
June 24-25, 2024	5	0.100340	2.9E-06
July 24, 2024	5	0.100352	1.7E-06
July 25, 2024	15	0.100342	2.6E-06

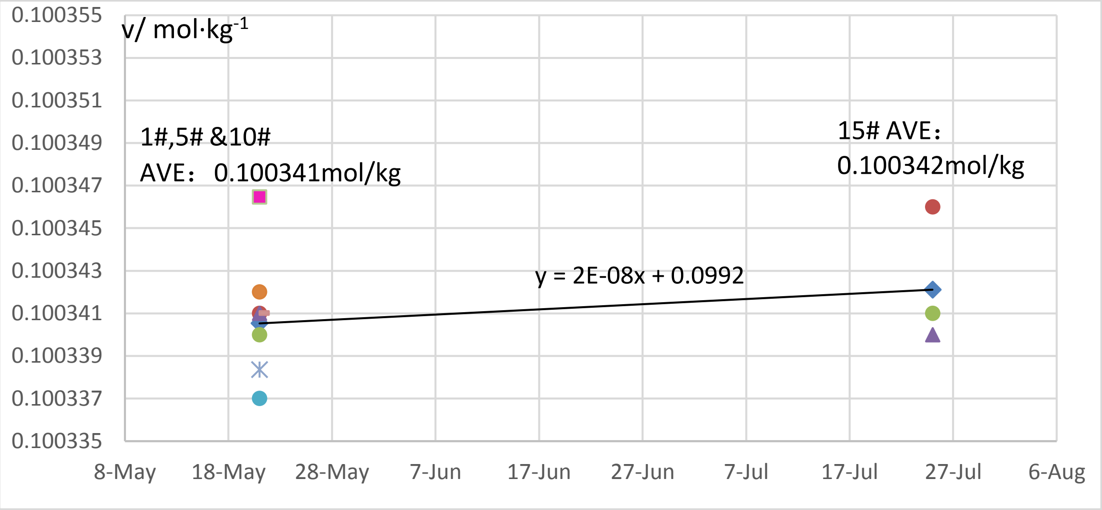

Figure 2. Stability of samples keeping in original package for CCQM-K73.2018.3.

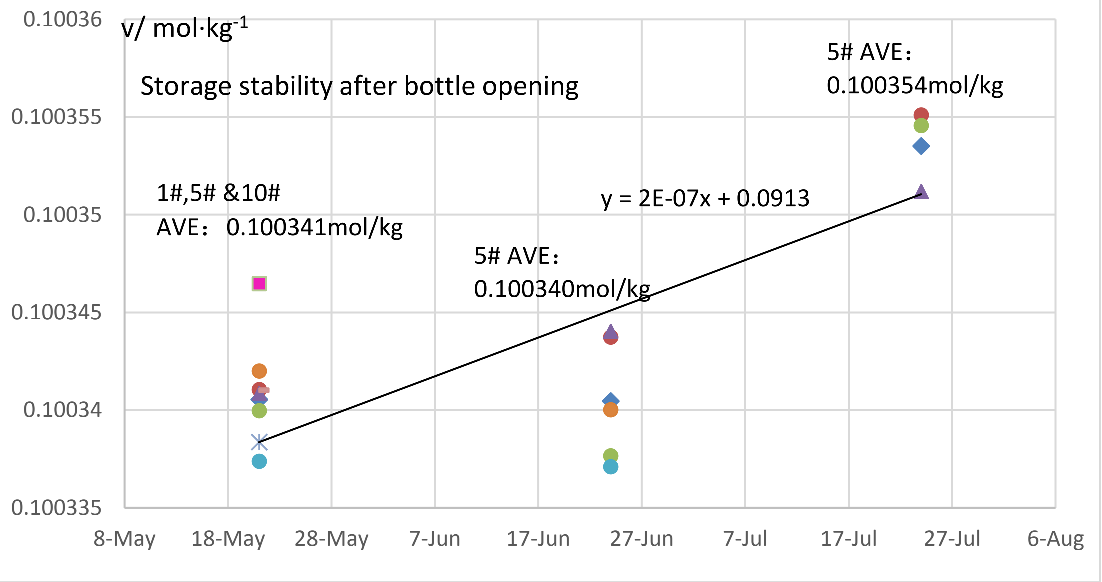

Figure 3. Storage stability of samples opened from the original package.

If kept in the original package or resealed, the monthly drift of the value is less than 0.002%. This was marginally lower than that in the original comparison CCQM-K73.2018. The coulometric measurement results and the calculated change in the amount content of H^+ due to mass loss exhibit a similar trend.

The experimental results verified the instability associated with long-term storage. The changes in the mass of the sample solution were ascertained by measuring the mass of the sample solution, which was computed based on variations in the mass of the bottle over time and the average mass of an empty bottle (32.16 ± 0.02 g). During the 100-

day measurement period, it was noted that the mass of the sample solution contained within the HDPE bottle decreased by 0.015%. In contrast, for samples stored in an HDPE bottle sealed within an aluminum foil plastic bag, a 0.013% decrease was recorded over a 105-day measurement period.

The feedback from the participants regarding the sample mass weighing results indicated that 22 days after the sample was mailed, the mass of the sample solution contained in the original package decreased by 0.004% to 0.008%, and the mass of the sample solution in the HDPE bottle decreased by 0.0033% on average after the aluminum foil bag was removed.

Consequently, the instability is a consequence of the evaporation of water. They must be regarded as significant over the measurement period. Therefore, the results obtained from the participants of this comparison were corrected using the linear regression line of the relative mass changes of the sample calculated from the weighing results of the coordinating institute. However, the correction did not change the reported values significantly.

Sample delivery

TUBITAK UME received three numbered bottles. Shipment was performed by courier in June 2024.

A spreadsheet for reporting was distributed by the time the samples were shipped.

Table 4. Date of sample receipt and measurement period

Institute	**Sample received**	**Measurement period**	**Date difference from NIM measurement date/d***	**Date of report (revised report)**
NIM	---	May21,27 and June24	0 and 34	30July
TUBITAK UME	12 June 2024	June 25 to July 5	40	2September

* The mean date of the measurement period was used

Check of the bottle integrity

The participants have inspected the bottles visually for damages after arrival. Afterwards, they have removed the aluminized plastic foil bag to measure the masses to check bottle integrity. No indication of leak or bottle damage has been observed; however, a small (0.0033%) decrease of bottle masses was found, what is in agreement with the predicted evaporation loss (see “Solution stability” above).

Communication with participants

18 October 2024: NIM sent a data report to EAWG chair, who has confirmed consistency (on 28.10.2024) between the values mentioned in the data report and that reported in Draft A.

22 July 2024: TUBITAK UMEhas sent an informal measurementreport to NIM and the chair of EAWG to clarify questions concerning correct reporting of measurement uncertainties before submitting the report officially.

1 August to 23 August 2024: Lokman LİV, Steffen Seitz, Michal Máriássy and Bing Wu have discussed issues regarding the uncertainty budget of TUBITAK UME’s result by e-mail, especially Dr. Michal Máriássy from the Slovakian Institute of Metrology has helped TUBITAK UME for checking their uncertainty calculations. It must be emphasized that neither had TUBITAK knowledge of the results of the coordinating laboratory by that time, nor did the discussion include a quantitative evaluation of the results of TUBITAK UME. The discussion was about general issues, such as which contributions to be considered and which measurement model to use because of the dilution of the samples (see below).

23 August 2024: TUBITAK UME requested to extend the reporting deadline for two weeks which was confirmed by the coordinating laboratory.

2 September 2024: TUBITAK UME submitted the measurement report officially to the coordinating laboratory.

25 October 2024: The result of NIM was disclosed to TUBITAK UME.

Results and discussion

The measurement protocol was almost identical to that in CCQM-K73.2018 [1] except for the calculation of the reference value. The participant received a template file for reporting the results.

Measurement of HCl amount content

Both participants used coulometry for the measurement. TUBITAK UME has diluted the samples and measured at nominal 0.01 mol/kg. The result of this measurement has been recalculated to the amount content of the original solution using the mass measurements of the dilution. The measured results submitted by the participants and the results corrected for drift are given in Table 5 and Figure 4.

Table 5. Measurement results of CCQM-K73.2018.3 with corresponding standard measurement uncertainties.

Institute	**Reported amount content v/(mol.kg^{-1})**	**Amount content corrected for drift v/(mol.kg^{-1})**	***k***	***RSD***
NIM	0.100341 ± 0.0000044	0.100341 ± 0.0000044	2.10	0.0022%
TUBITAK UME*	0.100365 ± 0.000028	0.100362 ± 0.000028	2.04	/
TUBITAK UME (diluted sample)	0.0100466± 0.0000028	0.0100463± 0.0000028	2.04	0.029%

* recalculated to amount content of original solution

The result of TUBITAK UME is consistent with that of NIM; However, TUBITAK UME has measured ten-fold-diluted (~0.01 mol/kg) samples and recalculated the results to 0.1 mol/kg, so, it didn't measure the 0.1mol/kg samples directly. As a consequence, the uncertainty at 0.1 mol/kg is larger compared to that of a direct measurement at 0.1 mol/kg, since it also includes the uncertainty of the dilution step.

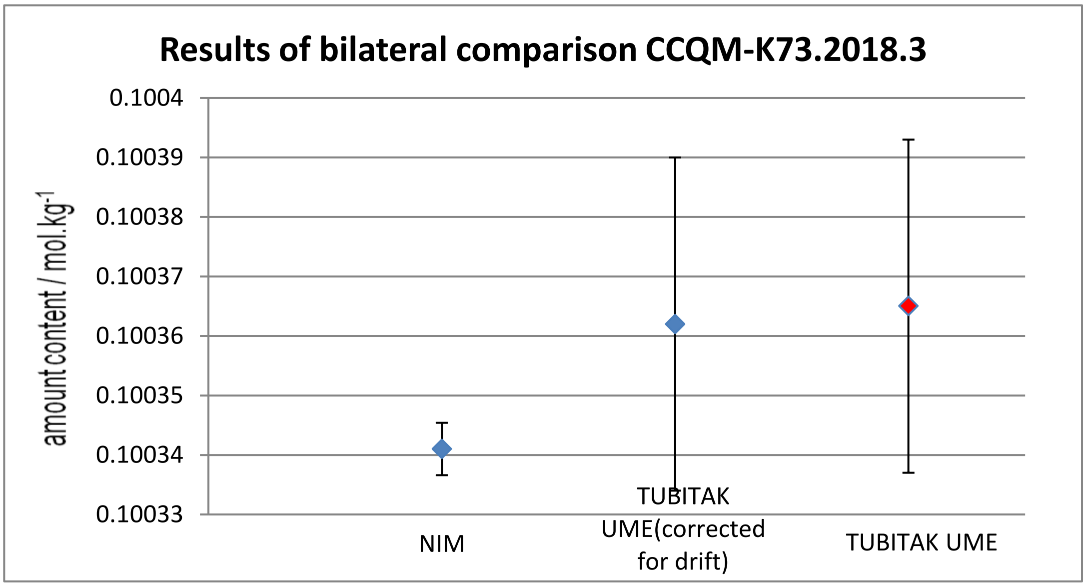

Figure 4. Results of bilateral comparison CCQM-K73.2018.3. Standard uncertainties are given.

The results were linked to the key comparison reference value of CCQM-K73.2018 through the results of NIM as the linking laboratory.

Degrees of equivalence

The degree of equivalence of the participant of the subsequent comparison relative to the original CCQM-K73.2018 comparison was calculated using the results of the coordinating laboratory according to the equation (1), based on assumption that the deviation of the coordinating laboratory’s result from the reference value is constant.

$$DoE\,(_{\text{NMI, K73.2018.3}}) = x\,(_{\text{NMI, K73.2018.3}}) - x\,(_{\text{NIM, K73.2018.3}}) + DoE\,(_{\text{NIM,K73.2018}}) \qquad (1)$$

$DoE\,(_{\text{NMI, K73.2018.3}})$: degree of equivalence of the participant of the bilateral comparison
$DoE\,(_{\text{NIM, K73.2018}})$: degree of equivalence of NIM in CCQM-K73.2018
$x\,(_{\text{NMI, K73.2018.3}})$: time corrected result of NMI in CCQM-K73.2018.3
$x\,(_{\text{NIM, K73.2018.3}})$: result of NIM in CCQM-K73.2018.3

For the calculation of the uncertainty of the degrees of equivalence, equation (2) was employed, which took correlations into account. The meaning of the symbols is similar to those mentioned above.

$$U^2(DoE_{\text{NMI,K73.2018.3}}) = U^2(x_{\text{NMI,K73.2018.3}}) + U^2(x_{\text{linklab,K73.2018.3}}) + U^2(x_{\text{linklab,K73.2018}}) + U^2(KCRV_{\text{,K73.2018}}) - 2 \times \mathrm{r} \times U\,(x_{\text{linklab,K73.2018.3}}) \times U\,(x_{\text{linklab,K73.2018}}) \qquad (2)$$

Since no significant correlation is assumed between the two NIM results, the correlation coefficient r = 0, and equation (3) has been employed

$$U^2\,(DoE_{\text{NMI, K73.2018.3}}) = U^2(x_{\text{NMI,K73.2018.3}}) + U^2(x_{\text{linklab,K73.2018.3}}) + U^2(\mathrm{DoE}(x_{\text{linklab,K73.2018}})) \qquad (3)$$

The degrees of equivalence are given in Table 6. In Figure 5, the degrees of equivalence are shown together with the original CCQM-K73.2018 results.

Table 6. Degrees of equivalence for the measurement of the amount content of H^+ in a 0.1 mol kg^{-1} HCl solution with corresponding expanded uncertainties and E_n numbers ($E_n = DoE(x_i)/U[DoE(x_i)]$). The last column on the right-hand side shows the minimalexpanded uncertainty $U_{CMC,min}(\nu_i)$ consistent with the KCRV. U_{minCMC} is equivalent with the expanded uncertainty reported by TUBITAK UME, since the E_n value is smaller than 1.

Institute	Result*ν_i/ ($mol \cdot kg^{-1}$)	Exp.unc. $U(\nu_i)$/ ($mol \cdot kg^{-1}$)	Coverage factor	D/ ($mol \cdot kg^{-1}$)	$U(D)$/ ($mol \cdot kg^{-1}$)	E_n	$U_{CMC,min}(\nu_i)$/ ($mol \cdot kg^{-1}$)
TUBITAK UME (calculated) calibration drift	0.100362	0.000057	2.04	0.000028	0.000062	0.45	0.000057
Diluted HCl							
TUBITAKUME diluted	0.0100463	0.0000057	2.04	0.0000028	0.0000062	0.45	0.0000057

* Corrected for drift

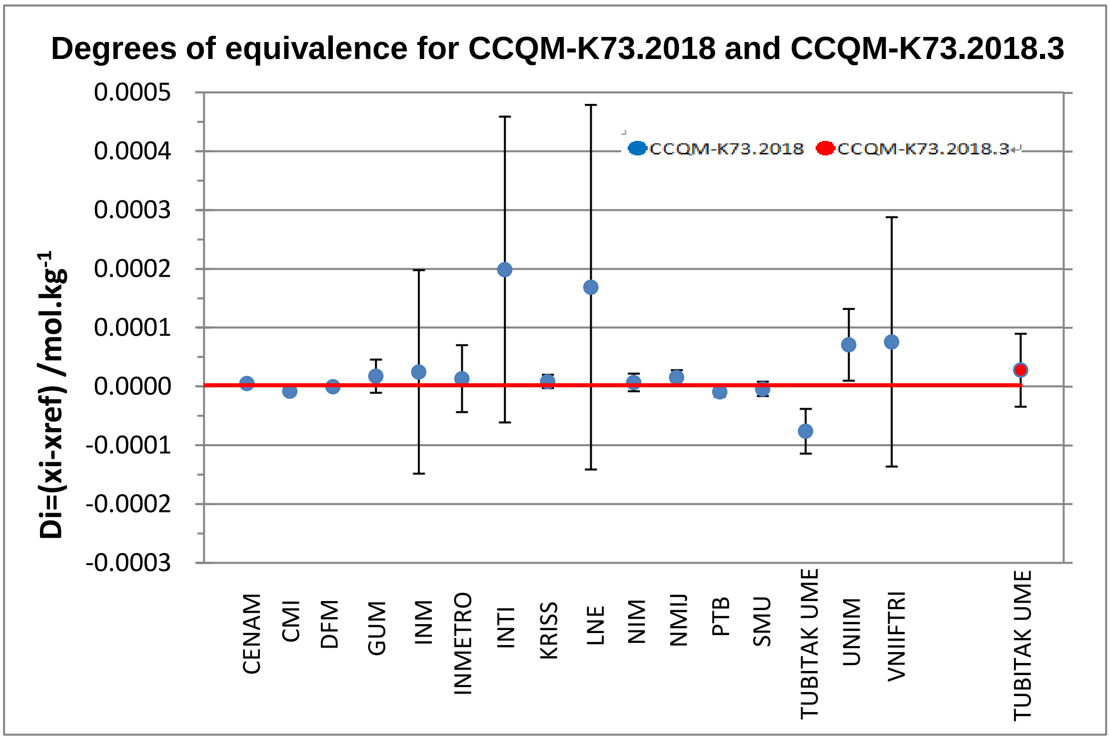

Figure5.Degrees of equivalence with expanded (k=2) uncertainties given

How far the light shines

The original HFTLS statement of CCQM-K73.2018 applies:
The participants of CCQM-K73.2018 have demonstrated their capability to measure the amount content of H^+ in 0.1 mol/kg hydrochloric acid. The comparison is suitable to support CMC claims for the measurement of hydrochloric acid of amount content 0.09 mol/kg and above. However, the relative measurement uncertainty at higher 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 furnished additional information regarding the measurement of a diluted sample at 0.01 mol/kg hydrochloric acid might utilize this comparison to uphold CMC claims for the amount content within the range of 0.01 mol/kg ± 10%, which is particularly pertinent in the context of primary pH measurements. The relative uncertainty stipulated for CMC claims at 0.01 mol/kg must be consistent with the relative uncertainty stated in Table 6.

References

1. F Bastkowskiet al: Final report of key comparison CCQM-K73.2018. Amount Content of H^+ in Hydrochloric Acid (0.1 $mol{\cdot}kg^{-1}$), Metrologia58 08002 (2021); DOI 10.1088/0026-1394/58/1A/08002
2. Michal Máriássy et al: Report of subsequent key comparison CCQM - K73.2018.2amount content of H+ in hydrochloric acid (0.1 mol/kg-1), Metrologia 61 08009 (2024) DOI 10.1088/0026-1394/61/1A/08009
3. JCGM 100:2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM) JCGM (available at https://www.bipm.org/en/committees/jc/jcgm/publications).

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Appendix 1 Technical protocol

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

The Bilateral Key Comparison CCQM-K73.2018.3

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

Technical protocol

Purpose of the comparison

The CCQM key comparison K73.2018.3 is a bilateral comparison to CCQM K73.2018. It will be performed to demonstrate the capability of TUBITAK UME 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.

Proposed time schedule

Dispatch of samples:	May 2024
Reporting deadline:	31 August 2024
Draft A report:	autumn 2024

Discussion: EAWG meeting, autumn 2024
Draft B report: November 2024

Description of the sample

Two liters of 0.1 mol/kg HCl solution will be prepared in a HDPE carboy by dilution of hydrochloric acid20% (TAMA Chemicals) with deionized water. Afterwards, the solution will be filled into numbered 250 mL HDPE bottles which will be closed immediately.

The coordinating laboratory will measure the homogeneity of the HCl solution and the stability in the course of the comparison.

The participant will receive two numbered bottles, each sealed in an aluminized plastic bag. Shipment will be performed by courier.

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 is 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.
    - Weigh the bagged bottle with a balance having 0.01 g resolution or better. Do **not** remove the label and bag. Enter balance reading, ambient atmospheric pressure, relative humidity, temperature and bottle mass (assuming density 1000 $\mathrm{kg{\cdot}m^3}$) into the spreadsheet.
    - Remove the aluminized plastic bag. Weigh the bottle with a balance having 0.01 g resolution or better. Do **not** remove the label. Enter balance reading, ambient atmospheric pressure, relative humidity, temperature and bottle mass (assuming density 1000 $\mathrm{kg{\cdot}m^3}$) into the spreadsheet.
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 for both bottles, replacement bottles will be sent; otherwise use the non-leaking bottle.
5. Reseal the bottles into the aluminized bags (adhesive tape can be used) if you will start measurements later.

Measurements

Participants are requested to measure the amount content 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 also the amount of substance measurement with the diluted HCl solution.

The measurement should be conducted within six weeks after receipt of the solution.

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.

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

- 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 31 August 2024 at the latest. The coordinating laboratory will confirm the receipt of each report. If the confirmation does 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 NIM as the linking laboratory.

How Far the Light Shines statement

The HFTLS statement is effectively the same as in the original comparison:

Good results provide support CMC claims for the measurement of hydrochloric acid with amount content 0.09 mol/kg and above. 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 provided additional information on the measurement of a diluted sample at 0.01 mol/kg hydrochloric acid may use this comparison to support CMC claims for amount content in the range of0.01 mol/kg +/- 10%, which is in particular relevant in the context of primary pH measurements.

Contact person and coordinating laboratory

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