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Report of subsequent key comparison CCQM – K73.2018.2

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

Final report

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Abstract

The subsequent key comparison K73.2018.2 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.

There were two institutes and SMU as the coordinating laboratory participating in this subsequent comparison. UkrCSM obtained results in good agreement with the reference value; INMETRO results exhibited a large bias due to a calculation error found only after disclosure of the results.

CONTENTS

Introduction

The key comparison CCQM-K73.2018 on 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 subsequent key comparison was launched. A HCl solution of a slightly different composition to that in CCQM-K73.2018 was used.

All participants applied coulometric titration for the assay of HCl.

Metrology Area

Amount of Substance

Branch

Electrochemistry

Coordinating laboratory

Slovak Institute of Metrology, SMU

Subject

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

Time schedule

Dispatch of the samples:	May/June 2023
Deadline for receipt of the report:	31 August 2023
Discussion of results:	EAWG meeting, October 2023
Draft A:	October 2023

Participants

Table 1 Table of participants

Acronym	Participant	Country	Analyst
UkrCSM	State Enterprise "UKRMETRTESTSTANDART"	Ukraine	Anton Petrenko, Oleksandr Melnykov, Volodymyr Melnyk, Oleksandr Lameko
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brasil	Paulo Paschoal Borges, Sidney Pereira Sobral
SMU	Slovenský metrologický ústav	Slovakia	Michal Máriássy, Zuzana Hanková

Sample description

Sample preparation

2 L of 0.1 mol/kg HCl solution were prepared on 9 May 2023 by dilution of HCl Suprapur 30% solution (Merck) with deionized water in a 2 L PFA bottle. On the following day, the solution was homogenized and filled into precleaned numbered 250 mL HDPE bottles which were immediately closed with a lid. Afterwards, the bottle masses were measured, and the bottles were sealed in HDPE foil and aluminized plastic foil to minimize evaporation.
The homogeneity of the HCl solution was measured by the coordinating institute and the stability was measured two more times over the course of the comparison.

Solution homogeneity

As the solution of HCl can be expected to be homogeneous (there is no problem with homogenization of true solutions in small bottles), systematic sampling was used for homogeneity check (trend analysis). First, intermediate and last bottle were measured by coulometry. The results are given in Table 2.

Table 2 Results of homogeneity measurement

Bottle	**Amount content *v*/mol.kg^{-1}**	***U*(*v*) /mol.kg^{-1}** (*k*=2)
1	0.100455	0.000008
3	0.100455	0.000008
6	0.100454	0.000008

No observable difference between the bottles was seen, so it can be concluded that no systematic change occurred during the filling process and the solution can be considered homogeneous between bottles.

Solution stability

The amount content of acid was measured at intervals to cover the whole measurement period.

Table 3 Results of stability measurement

Date	**Bottle No.**	**Amount content *v*/mol.kg^{-1}**	***U*(*v*) /mol.kg^{-1}** (*k*=2)
May 16-17, 2023	1, 3, 6	0.100455	0.000008
July 6, 2023	6	0.100457	0.000008
September 6, 2023	1, 3	0.100459	0.000008

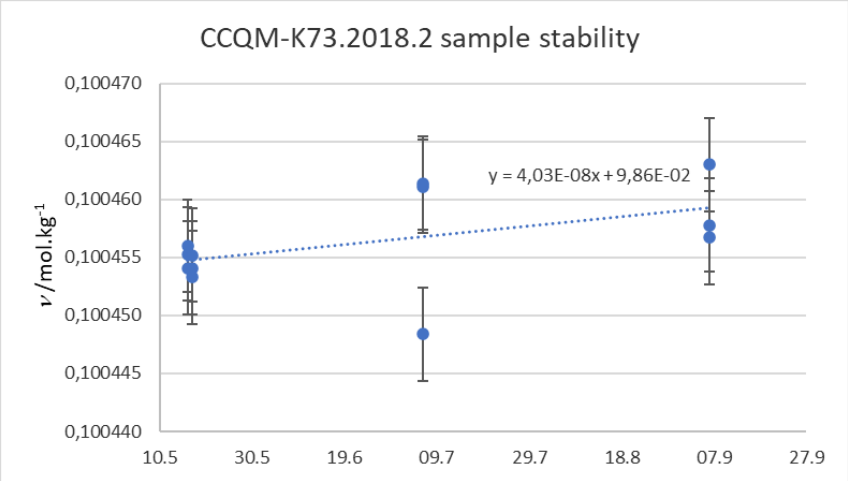

Figure 1 Stability of samples for CCQM-K73.2018.2. Standard uncertainties are given

The spread in the values at the intermediate point in stability measurements is likely due to measurement itself, but the results were considered as fit for the purpose. The monthly drift of the value is 0.0012%, slightly lower than in the original comparison CCQM-K73.2018. The results obtained from the participants of this comparison were corrected using the linear regression line of the coulometric stability measurements.

Sample delivery

Each participant received one or two numbered bottles Shipment to all participants was performed by courier during May (UkrCSM) and June (INMETRO) 2023.

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

Table 4 Date of sample receipt and measurement period

Institute	Sample received	Measurement period	Date difference from SMU measurement date/d*	Date of report (revised report)
UkrCSM	15 May 2023	July 12 to 15	89	22 August (28 August)
INMETRO	26 June 2023	July 7 to 13 and July 19 to 26	55 and 66	8 August (22 August)
SMU	- - -	May 16 to 17	0	19 June

* 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 aluminium bag to measure the masses to check bottle integrity. No indication of leak or bottle damage has been observed; however, a small (0.003%) decrease of bottle masses was found, what is in agreementwith the predicted transpiration loss (see „Solution stability“ above).

Communication with participants

19 June 2023: SMU sent an encrypted report to EAWG chair, who has confirmed consistency (on 13.11.2023) between the values mentioned in the encrypted report and that reported in Draft A.

8 August 2023: INMETRO sent report

17 August 2023: INMETRO sent modified report
22 August 2023: UkrCSM sent report
22 August 2023: When both reports were received, the coordinating laboratory asked both participants to check their reports for numerical errors
22 August 2023: INMETRO sent a new report with one sensitivity coefficient corrected
28 August 2023: UkrCSM found a calculation error (a correction was made incorrectly) and sent a new report, as well as the Excel calculation sheets with original and corrected calculations.
5 September 2023: results were disclosed to participants
28 September 2023: INMETRO made a check of the coulometer and no problem was found; but an error was found in a spreadsheet that corrected the weighing of HCl added considering the correction of the certificate of the balance. This resulted in lower masses of HCl used in the calculation of the results.

Results and discussion

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

Measurement of HCl amount content

All participants used coulometry for measurement of acid. INMETRO has additionally diluted one of the samples and has 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 results are given in Table 5 and Figure 2.

Table 5 Measurement results of CCQM-K73.2018.2 with corresponding standard measurement uncertainties.

Institute	**Reported amount content v/(mol.kg^{-1})**	**Amount content corrected for drift v/(mol.kg^{-1})**	***k***	***RSD***
SMU	0.1004547 ± 0.0000039	0.1004547 ± 0.0000039	2	0.0010%
UkrCSM	0.100414 ± 0.000065	0.100410 ± 0.000065	2.32	0.21%
INMETRO	0.1057809 ± 0.0000052	0.1057785 ± 0.0000053	2.52	0.012%
INMETRO (diluted sample*)	0.102120 ± 0.000057	0.102117 ± 0.000057	2.43	0.14%

* recalculated to amount content of original solution

The result of UkrCSM agrees well with that of SMU; the high uncertainty is dominated by contribution of reproducibility.
In the case of INMETRO, the 3% difference between the two results obtained with and without dilution suggested a major problem. Subsequent check did not reveal any problem with the coulometer, but a calculation error was found in a spreadsheet (see above section ‘Communication with participants’). Corrected values of measurements of the undiluted samples would yield a value of 0.100491 mol/kg for amount content, and degree of equivalence D_i 0.00003 mol/kg with expanded uncertainty 0.000033 mol/kg, i.e. the result would agree with the reference value. For the diluted solution, the data for such a

recalculation are not available. In any case, the corrected result can unfortunately not be used as the official result in this comparison, as the error was not found before the disclosure of the results.

a) b)

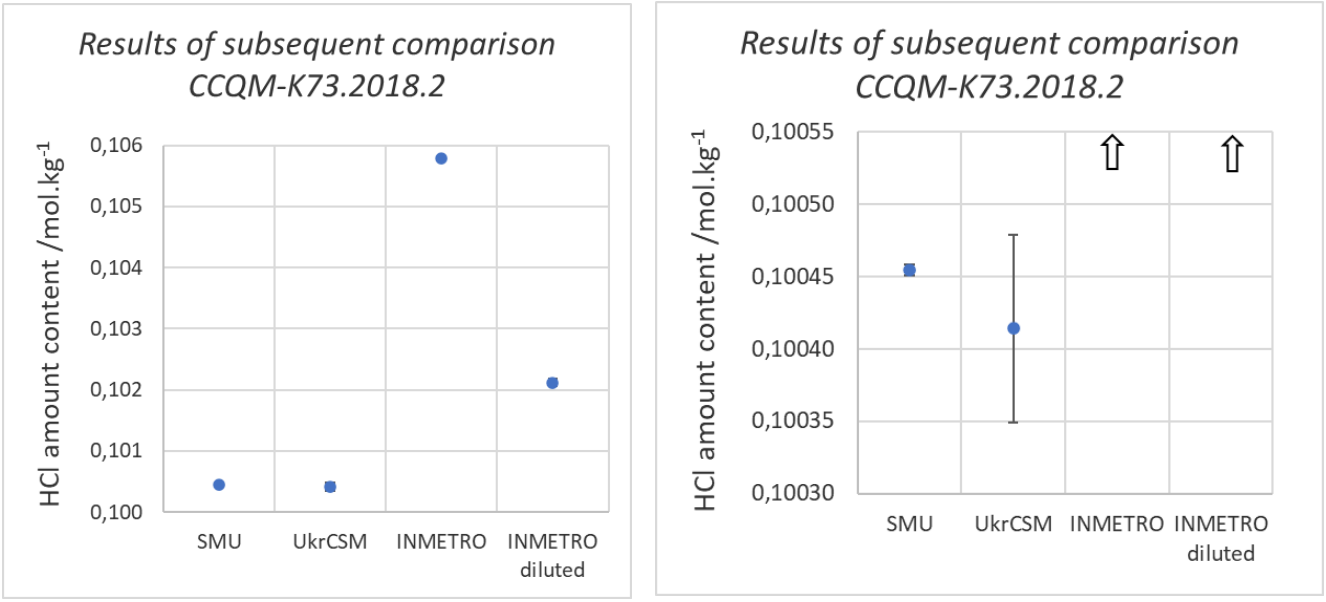

Figure 2 Results of subsequent comparison CCQM-K73.2018.2. Standard uncertainties are given. a) full scale; b) enlarged scale

Degrees of equivalence

The degree of equivalence of the participants 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.

$$D_{\text{NMI, K73.2018.2}} = v_{\text{NMI, K73.2018.2}} - v_{\text{SMU, K73.2018.2}} + D_{\text{SMU, K73.2018}} \quad (1)$$

$D_{\text{NMI, K73.2018.2}}$ degree of equivalence of the participant of the subsequent comparison
$D_{\text{SMU, K73.2018}}$ degree of equivalence of SMU in CCQM-K73.2018
$v_{\text{NMI, K73.2018.2}}$ time corrected result of NMI in CCQM-K73.2018.2
$v_{\text{SMU, K73.2018.2}}$ result of SMU in CCQM-K73.2018.2

For the calculation of uncertainty of the degrees of equivalence equation (2) was used, assuming no significant correlation between both SMU results. The meaning of the symbols is analogous to those above.

$$u^2(D_{\text{NMI, K73.2018.2}}) = u^2(D_{\text{SMU, K73.2018}}) + u^2(v_{\text{NMI, K73.2018.2}}) + u^2(v_{\text{SMU, K73.2018.2}}) \quad (2)$$

The degrees of equivalence are given in Table 6. In figure 3 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 ($E_n=D_i/U(D_i)$). The last column on the right side lists the minimal standard uncertainties $u_{CMC,min}(v_i)$ that are consistent with the KCRV.

Institute	Result* v_i/ (mol·kg^{-1})	Exp.unc. U(v_i)/ (mol·kg^{-1})	Coverage factor	D/ (mol·kg^{-1})	$U(D)$/ (mol·kg^{-1})	E_n	$u_{CMC,min}(v_i)$/ (mol·kg^{-1})
UkrCSM	0.100410	0.00015	2.32	-0.00005	0.00013	-0.36	0.00007
INMETRO	0.105779	0.000013	2.52	0.00532	0.000033	164	0.0026
Diluted HCl							
INMETRO	0.010246	0.000014	2.43	0.000166	0.000012	14	0.00009

* corrected for drift

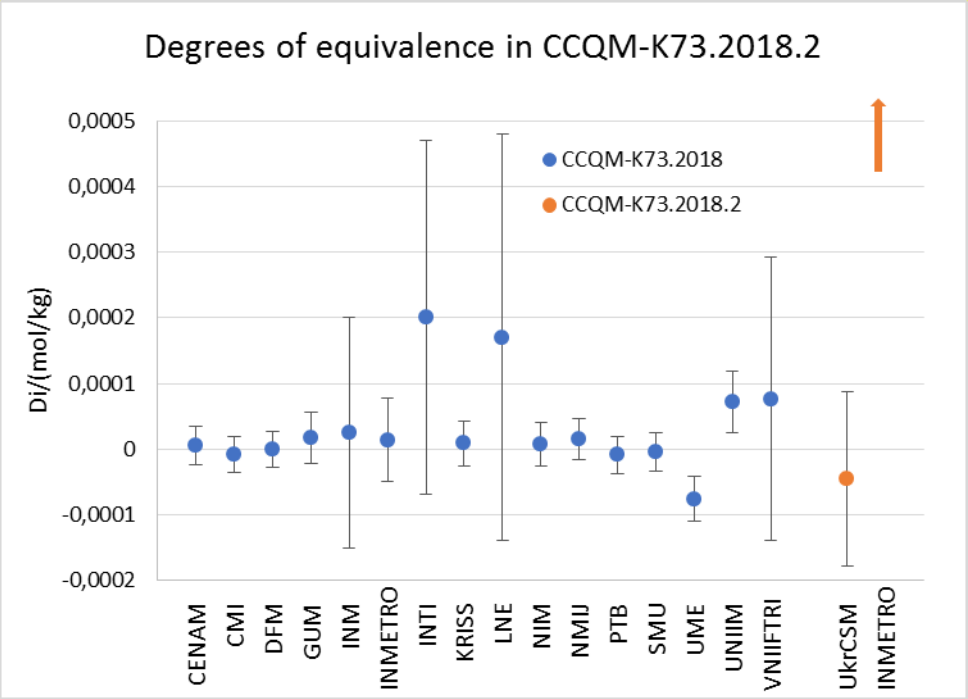

Figure 3 Degrees of equivalence with expanded (k=2) uncertainties given

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 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 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 6.

References

1. F Bastkowski et al: Final report of key comparison CCQM-K73.2018. Amount Content of H^+ in Hydrochloric Acid (0.1 mol·kg^{-1}), Metrologia 58 08002 (2021); DOI 10.1088/0026-1394/58/1A/08002

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Appendix 1 Technical protocol

CCQM WG on Electrochemical Analysis and Classical Chemical Methods

Key Comparison CCQM-K73.2018.2

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

Technical protocol

Purpose of the comparison

The CCQM key comparison K73.2018.2 is a subsequent comparison to CCQM K73.2018. It will be performed to demonstrate the capability of Ukrmetrteststandart 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 2023
Reporting deadline:	31 August 2023
Draft A report:	autumn 2023
Discussion:	EAWG meeting, autumn 2023
Draft B report:	November 2023

Description of the sample

Two liters of 0.1 mol/kg HCl solution will be prepared in a HDPE carboy from Suprapur HCl (Merck) and 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.

Each 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 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.
    - 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 kg·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 kg·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.
- 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 2023 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 SMU 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 of 0.01 mol/kg +/- 10%, which is in particular relevant in the context of primary pH measurements.

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

Contact person and coordinating laboratory

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