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

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 acid 20% (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 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 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.

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

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

Contact person and coordinating laboratory

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