CCQM Working Group on Electrochemical Analysis and Classical Chemical Methods

EAWG guideline for claims of Calibration and Measurement Capabilities

1. Scope

The requirements for Calibration and Measurement Capabilities (CMC) within the context of the CIPM-MRA are specified in detail in the document CIPM-MRA-G-13. Requirements for Key Comparisons (KC), which provide the main support for CMCs, are specified in the document CIPM-MRA-G-11. This document specifies requirements specifically applicable to measurement quantities that are lying in EAWG's area of responsibility, i.e. pH, electrolytic conductivity, the amount of substance measured with coulometry, and classical chemical methods.

2. General requirements

1. CMCs should be supported by participation in relevant KCs, organized by CCQM, by RMO or bilateral comparisons that are linked to KCs, or by Supplementary Comparisons (SC) organised by an RMO. Throughout this document these comparisons will be referred to as "CCQM-comparisons".
2. If no CCQM-comparison is available, other evidence might be used in compliance with the requirements specified by the CCQM-Key Comparison Working Group (see KCWG document KCWG/2020-01[1]). In particular, pilot studies may only be used to support a CMC if the respective report complies with the requirements stated in item 4 of this section.
   Note: A pilot study that has been performed in conjunction with a KC obviously complies with this requirement. However, such a pilot study is intended to help unexperienced institutes to assess their measurement capability. It must not be used as supporting evidence afterwards, even if the results suggest good performance. Institutes aiming at CMCs are obliged to participate in the corresponding KC.
3. CMC claims must be submitted via the KCDB 2.0 web-based platform, hosted by the BIPM. All documents supporting the claim must be submitted together with the CMC claim, except for final reports of CCQM-comparisons (they are available through the KCDB). The reports of CCQM-comparisons must be at least in the stage of Draft B to support CMCs.
   NOTE 1: Draft B versions should be submitted with the CMC claim, since they are not necessarily available to the reviewers.
   NOTE 2: CMC submissions for CRMs must include the CRM certificate. Furthermore, they must include evidence for the claimed uncertainty

[1] considering the latest revision, available at https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-kcwg

contributions for homogeneity and stability of the CRM. Accepted evidence is:

- A final report, proving participation in a "preparative comparison" that compares assigned CRM values and their uncertainties using a model 2 measurement pattern[2]. This may be a pilot study if it complies with the requirements given in item 4 of this section.
- A test reports of homogeneity and stability tests performed at the institute submitting the CMC.
- A report of an on-site peer review (see CIPM documents CIPM MRA G-12 and CIPM/2007-25). The report must explicitly assess the consistency of the values stated in the certificate with the QA documents available at the institute.

4. The comparison report must include the subsequent information in order to allow the assessment of the consistency of CMCs with the respective CCQM-comparison:
   - The best estimate x_i for each participating institute i and its expanded uncertainty $U(x_i)$ (95 % level).
   - The agreed comparison reference value (CRV)[3]
   - The degrees of equivalence $d_i = x_i - CRV$ and the corresponding expanded (95 % level) uncertainty $U(d_i)$ for each participating institute.
   - The minimum standard measurement uncertainty $u_{min}(\mathrm{CMC}_i)$ for each participating institute that is consistent with the CRV.
   - An "How Far The Light Shine" (HFLS) statement, indicating the validity of the CCQM-comparison with respect to measurement ranges and matrices.
   - An annex with the individual measurement reports of the participants.

   x_i, d_i, their expanded uncertainties and $u_{min}(\mathrm{CMC}_i)$ should be stated in a single table, if possible, to simplify the review process. The EAWG chair will copy the CRV, $U(x_i)$, d_i and the quotient $d_i/U(d_i)$ in an EAWG comparison record file, that includes a sheet for each institute (further information is given in the annex). In this way, the long-term performance of each EAWG member can be monitored. The file will be stored in the EAWG members area of the BIPM website.

5. Declared CMC ranges and matrices must comply with the HFLS statement of the report the supporting CCQM-comparison. CMC claims outside the HFLS statement would require strong additional supporting evidence and must be approved by EAWG.

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[2] participating institutes send their CRMs to the pilot institute that measures the equivalence of the stated quantity values and the consistency of the stated uncertainties

[3] If the supporting CCQM comparison is a KC, a supplementary KC (including linked bilateral comparisons) or a linked RMO comparison, the CRV is the stated $KCRV$ of the (linked) KC

6. Declared CMC uncertainties for CRMs must be consistent with the supporting documents (i.e. see Note 2 of item 3). They are expected to be larger than the uncertainty of the measurement capability due to the additional contributions for homogeneity and stability.
7. The uncertainty of a CMC claim must be consistent with the result of the supporting CCQM-comparison. The consistency criteria are
   - x_i is assumed to be consistent with the CRV, if $|d_i| \leq U(d_i)$. In this case, it is assumed that $U(x_i)$ is an adequate uncertainty estimate. Thus, the claimed expanded (95 % level) uncertainty of the CMC, $U(\mathrm{CMC}_i)$, must be equal to or larger than $U(x_i)$. Where $U(x_i)$ is significantly smaller than $U(CRV)$ the reliability of the uncertainty estimate of the NMI/DI may require further evidence.
   - x_i is assumed to be inconsistent with the CRV, if $|d_i| > U(d_i)$. In this case, the calculation of $u_{min}(\mathrm{CMC}_i)$ depends on the method used to calculate the CRV, which must be stated in the report of the CCQM-comparison.
8. Inconsistent results may arise from:
   a) A malfunction of the measurement system or other sources (e.g. use of an inappropriate measurement procedure) leading to an unexpectedly large d_i value. If there is evidence for such circumstances the result may be withdrawn from the CCQM-comparison. This must be noted in the report of the comparison. The comparison must not be used by the concerned institute to support a new CMC claim. However, an existing CMC might exceptionally remain valid if it is supported by the overall long-term performance of the institute, as monitored in the record file. Nevertheless, the concerned institute is asked to participate in a subsequent comparison.
   b) Underestimated or missing uncertainty contributions in the uncertainty budget. If 8.a) can be excluded a CMC claim can be supported by the respective CCQM-comparison despite the inconsistency. However, the claimed expanded uncertainty may not be smaller than the expanded minimum uncertainty $U_{min}(\mathrm{CMC}_i) = k\, u_{min}(\mathrm{CMC}_i)$[4] and the concerned institute must review its uncertainty budget adequately.
9. CCQM-comparisons are open for institutes using secondary methods. The measurement method and the source of traceability must be clearly stated in the CCQM-comparison report and in the CMC submission. The route of traceability has to be stated in the “Comments for publication” field of the CMC submission form. The quantity values of respective reference materials have to be within the declared CMC-ranges and they must be supported by respective CMCs.

[4] k is the coverage factor

10. The source of traceability has to be an NMI or an DI in accordance with the documents CIPM MRA G-12 and CIPM 2009-24. The source of traceability has to be stated only for the measurand the CMC is referring to[5].
11. Only CMCs based on the highest-level measurement method available at an institute for a given measurand/range should be listed.
12. If more than one comparison is relevant for a specific CMC claim, the average performance from the most recent two comparisons is used for evaluation[6].
13. CCQM-comparison data are not relevant longer than 10 years. If a new comparison on nominally the same measurand is available, the most recent performance is taken for evaluation, regardless of performance.
14. It is in the responsibility of each institute having CMCs to ensure knowledge transfer due to staff change. If adequate knowledge transfer cannot be assured the institute should initiate a reassessment of its measurement capabilities (e.g. by a bilateral comparison).
15. An uncertainty budget must be added to the CMC submission if the claimed uncertainty is not supported by a CCQM comparison.
    NOTE: It must be emphasized that the addition of an uncertainty budget must not be used to claim smaller uncertainties as stated in a CCQM comparison that is directly linked to the CMC. Item 15 rather relates to
    - CMCs not directly supported by a CCQM comparison (see item 2.2),
    - CMCs that can reasonably be supported by a CCQM comparison beyond its HFLS statement,
    - CMCs of CRMs stating smaller uncertainties as stated in the corresponding CCQM comparison: the repeatability contribution to the uncertainty might be smaller for CRMs compared to a CCQM comparison, since the number of measured samples could be larger.
16. The submission of CMCs of CRMs must include information on the form (solid, solution), packaging and validity period to facilitate the evaluation.

3. Specific requirements for pH

1. pH is a dimensionless quantity, therefore the unit “1” should be assigned in the respective field of the CMC submission form.
2. The matrix or material specified to support a primary measurement claim for low ionic strength (I<0.1 mol/kg) aqueous buffers, i.e. standard pH reference materials[7], should be ‘aqueous pH buffer solution’, not just ‘aqueous solution’. Likewise, other matrixes should be specified appropriately.

[5] For instance, a pH-CMC based on a secondary measurement must state the NMI/DI providing the primary pH standard. However, a pH-CMC based on primary measurement needs not to state the source of traceability of the HCl solution used to measure the standard potential of the AgAgCl-electrode, even if it is provided by another institute.
[6] e.g. a pH claim at pH 7 that is not supported by a CCQM-comparison of a phosphate buffer, might be supported by participation in two or more CCQM-comparisons of other buffers (see item 9 of sec. 3).
[7] according to IUPAC recommendations 2002

3. The pH range quoted in the CMC should encompass the pH value of the buffer measured during the supporting CCQM-comparison
4. For CMC claims based on a particular buffer, a range up to about ± 0.5 from the CRV of the supporting KC can be justifiably claimed without additional evidence to account for the pH range of different compositions of the same type of buffer solution. Buffers with smaller buffer capacities may require a smaller range of validity of the corresponding CMC.
5. The measurement ranges for measurements based on a differential (Baucke) cell must be commensurate with the values of primary buffers available.
6. Larger measurement ranges may be claimed for glass electrode measurements. The range must be supported by an appropriate number of calibration points and adequate uncertainties.
7. Where the ranges and/or expanded uncertainties of the “dissemination range of measurement capability” and “range of certified values in reference materials” are significantly different, the reasons for these differences should be explained in the comments added to the CMC submission.
8. For difficult to measure (‘extended capability’) buffers such as phthalate and carbonate CMC claims should be underpinned by participation in the CCQM-comparison testing that particular buffer. The exception to this would be if the claimed uncertainty is higher than the performance demonstrated in comparisons of core capability buffers by a quantity large enough to recognise the increased difficultly of these measurements, and if the institution in question had demonstrable experience in handling ‘extended capability type’ measurements (e.g. with reference to the EAWG record file).
9. For easier to measure (‘core capability’) buffers such as phosphate, borate and tetroxalate, good performance in a comparison involving these buffers, or in a comparison of extended capability buffers, indicates the ability to measure all core buffers with a similar uncertainty. Participation in two or more CCQM-comparisons of any primary pH buffers is sufficient to support CMC claims of all core capability buffers. If there are not special problems with measurements, the measurements of the acidity function in buffers of different composition should be covered (for the primary measurement). The uncertainty claimed for pH (as opposed to that claimed for the acidity function) will generally include an enlarged contribution associated with the conversion to pH.
10. NMIs successfully participating in at least three CCQM-comparisons at a primary level within 10 years before the CMC submission, including both extended capability buffers, may justifiably claim a complete pH measurement range from approximately 1.2 to 10.5 (covering the tetroxalate through carbonate buffers), provided the claimed uncertainty is justified.

Table 1 Difficulty of various buffers.

pH	buffer	KC-ID	difficulty
1.7	tetroxalate	K20.yyyy	core
3.6	tartrate	n/a	core
4	phtalate	K91.yyyy	extended
4.7	acetate	n/a	core
6.9	phosphate	K9.yyyy	core
7.4	phosphate (physiol.)	K99.yyyy	core
7.7	tris	tbd	core
9.2	borate	K19.yyyy	core
10	carbonate	K18.yyyy	extended
12.5	calcium hydroxide	n/a	extended

11. The performance in a CCQM-comparison of a specific buffer prevails any other support of a CMC that refers to this buffer, i.e. supports based on items 9 and 10 not including this buffer[8]. Likewise, bad performance in a core capability comparison cannot be compensated by good performance in an extended capability comparison[9].
12. The type of the buffer should be mentioned (e.g. “phosphate buffer”) in the CMC submission form (e.g. in the comments added to the submission) as it simplifies the review process.
13. pH values and the corresponding uncertainties of CMC submissions must be assigned to temperatures in compliance with the supporting CCQM-comparison.

[8] e.g. good performance in a tetroxalate and borate comparison cannot be used to compensate bad performance in a phosphate comparison with respect to a phosphate CMC (unless 8a of sec. 2 applies, meaning the phosphate result has been withdrawn for good reasons)

[9] e.g. if an institute has performed badly in a borate (core), but well in a carbonate (extended) comparison, it must base a phosphate (core) CMC on the borate comparison (given no phosphate comparison is available for the institute)

NOTE: This requirement applies only to submissions using the web-based platform KCDB 2.0, i.e. submissions after the review cycle XXI. CMCs submitted before that must indicate the temperature range in which the service is provided in the “Comments for publication” field of the submission form (e.g. “Temperature range for service: xx °C to xx °C, values given for 25°C.”).

14. The “Comments for publication” field of the CMC submission form must include the information that the uncertainty does not include the contribution of the Bates-Guggenheim convention (e.g. “Declared uncertainties do not include the uncertainty contribution due to the Bates-Guggenheim convention (approximately 0.010, k=2).”
15. CMC claims outside the typical 15-37 ^{o}C range that are not directly supported by CCQM-comparisons must provide sufficient additional evidence.
16. It is expected that at least once every five years relevant comparisons in core and in extended capability buffers will take place. If this timescale is not met, NMIs will not be punished as a result.
17. CCQM-comparisons for two different buffers can be used to support all buffers for secondary (differential cell) measurement capabilities. In these cases, the secondary measurement range may not be greater than the associated primary buffer range.

4. Specific requirements for electrolytic conductivity

1. Preferred units used to express electrolytic conductivity are S m^{-1} for the upper conductivity range (0.05 to 50 S m^{-1}) and µS cm^{-1} in the lower conductivity range (0.05 to 500 µS cm^{-1}).
2. The matrix the CMC is referring to must be specified in the "Matrix" field of the CMC submission form.
3. It is recommended to express the uncertainty of electrolytic conductivity in relative units to simplify the review process.
4. The temperature range in which the service is supplied should be given in the "Comments for publication" field of the CMC submission form. CMCs of electrolytic conductivity should usually be referred to 25 °C. For pure aqueous electrolyte solutions (i.e. KCl & NaCl solutions), a temperature range of 15-35°C can be stated, given the CMC is supported by a CCQM-comparison conducted at 25 °C. The corresponding relative measurement uncertainty may be assumed to be constant in this temperature range. CMCs claims beyond this temperature range must be formally approved by EAWG, if they are not directly supported by a CCQM-comparison.
5. It is expected that at least once every three years a CCQM-comparison will take place, covering at least two conductivity ranges (see table 2). The CCQM-comparisons should cover subsequently the conductivity range from 0.055 µS cm^{-1} to 50 S m^{-1}. If this timescale is not met NMIs will not be punished as a result.
6. The HFLS statement of a CCQM-comparison should usually cover a conductivity range of one order of magnitude, with the CRV being nominally in the (logarithmic) centre of this range. A respective CMC claim should be within this range.
   NOTE: A comment should be added to the CMC submission if uncertainties of two adjacent ranges are inconsistent at the transition range (e.g. use of different measurement set-ups or improved performance in a newer CCQM comparison).

Conductivity CMCs can hardly be divided into core and extended capability measurements, since the measurement difficulty is also determined by cell properties and the specific measurement set-up used by an institute. Therefore, table 2 indicates the difficulty of measuring the conductivity of aqueous solutions just qualitatively. However, a CMC claim in a different sample matrix, but at a similar conductivity value to that supported by a CCQM-comparison may be acceptable, provided the effect of cell properties, sample handling, gas absorption, etc. on measurement uncertainty is similar compared to the matrix used in the supporting CCQM-comparison. Such CMC claims must be formally approved by EAWG. Additional supporting evidence, e.g. in terms of a test measurement report, might be necessary.

NOTE: CMCs referring to the same matrix, but to a conductivity range outside the HFLS statement are not acceptable.

Table 2 Difficulty electrolytic conductivity measurement

conductivity	comparison ID	comparison method	difficulty
0.05 µS/cm	EURAMET SC-QM.12	Round Robin calibration of flow through cell	increasing with decreasing conductivity
0.5 µS/cm			
5 µS/cm			
50 µS/cm			
50 µS/cm	K36	HCl solution	
0.05 S/m	K92 (new Kxxx.yyyy)	KCl_{aq} solution	less difficult
0.5 S/m	K36 (new: K170.yyyy)	KCl_{aq} solution	
5 S/m	K105 (new Kxxx.yyyy)	KCl_{aq} solution	increasing with increasing conductivity
20 S/m	K92 (new K170.yyyy)	KCl_{aq} solution	

5. Specific requirements for assay measurements by coulometry

1. The measurand of the CMC claim should correspond to the measured quantity of the supporting CCQM-comparison. If specific claims are made, they must be supported by use of other techniques for impurity detection[10].
2. Coulometry depends on correct realisation of the desired chemistry (chemical reaction) in performing the measurements. Thus, respective CMCs must not only be supported by CCQM-comparisons of the instruments used to perform a coulometric measurement (e.g. of current meters). They must be supported by CCQM-comparisons reflecting the capability of the participating institute to handle the involved chemistry.

[10] This means for instance that for “concentration of total acid” impurity check is not necessary, but for “concentration of HCl” a correction has to be made for presence of other acids.

3. For two acids measured with the same procedure, good performance in a CCQM-comparison involving one of these acids indicates the ability to measure the other. To this end, the other acid must be easier to measure and a weak acid with a similar dissociation constant (pK_a not more than by 1 larger than the pK_a of the acid in the CCQM-comparison). Furthermore, there must not be special problems with stability, solubility, etc. Analogous reasoning holds for other analytes determined using identical electrolyte/method combination as in the CCQM-comparison.
4. The capability to measure an assay of weak acids is expected to be inferior to that for strong acids, unless there are valid reasons for the contrary. Thus, CMC claims for weak acids may usually not be supported by CCQM-comparisons of strong acids.
5. If claims are made on solutions, the uncertainty should reflect the dependence on the amount of analyte measured.
6. NMIs successfully participating in all available comparisons (after completion of CCQM-comparisons covering the different types of supporting systems for acid-base, redox, precipitation, and complexometric titrations) may justifiably claim measurement capabilities for other compounds as well, providing the uncertainty is justified.
7. It is expected that at least once every three years relevant comparisons will take place. If this timescale is not met, existing CMCs of NMIs will not be affected.

6. Specific requirements for measurands using classical methods

Currently, no requirements have been specified.

Annex 1

Basic information to be compiled in the record-card of an institute

Institute

Compa-rison ID	Year	type of sample	Method	KCRV	Unit	x_i	$U(x_i)$	$U_r(x_i)$	d_i	$U(d_i)$	$d_i/U(d_i)$	Analyst

$U(x_i)$ is the expanded (95% level) uncertainty of the reported result x_i, $U_r(x_i)$ is the relative expanded uncertainty, d_i is the degree of equivalence; $U(d_i)$ is the expanded (k=2) uncertainty of d_i.
A graph with plotted $d_i/U(d_i)$ and $U(x_i)$ values is recommended to illustrate the overall performance of an institute with respect to consistency and achievable measurement uncertanties

Remarks
Inclusion of pilot studies is limited to studies which include degrees of equivalence in the final report.
$U(x_i)$, d_i and $U(d_i)$ and KCRV will be copied from the final report. The other values will be calculated in the record-card. Therefore, there might be small deviations of calculated values from the reported values due to rounding errors. Moreover, results from linked comparisons will show larger deviations from the reported values due to the adjustment to the KCRV.
$-1 \leq d_i/U(d_i) \leq 1$ indicates consistency of the reported results with the CRV. Values outside this range indicate underestimated or missing uncertainty contributions of a measurement result.