CCQM Working Group on Electrochemical Analysis and Classical Chemical Methods

# EAWG guidelines 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

- CMCs should be supported by participation in relevant KCs organized by CCQM, in RMO or bilateral comparisons that are linked to KCs, or in Supplementary Comparisons (SC) organised by an RMO. Throughout this document these comparisons will be referred to as "CCQM-comparisons".
- 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 KCWG01<sup>1</sup>). 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 'parallel' 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 at stage 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

<sup>&</sup>lt;sup>1</sup> 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<sup>2</sup>. This may be a pilot study if it complies with the requirements given in item 4 of this section.
- A test report 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 CCQM-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*)<sup>3</sup>
  - 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  $u_{min}(CMC_i)$  for each participating institute that is consistent with the *CRV*.
  - An "How Far the Light Shines" (HFTLS) statement, indicating the validity of the CCQM-comparison as CMC support with respect to measurands, analytes, matrices and measurement ranges.
  - An annex with the individual measurement reports of the participants.

 $x_i$ ,  $d_i$ , their expanded uncertainties and  $u_{min}(CMC_i)$  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 latest version of the file will be made available at the EAWG members area of the BIPM website. NOTE: A zipped file of the measurement reports of the participants of a CCQM-comparison must be uploaded to the EAWG area of the BIPMwebpage, so that they are available for the CMC review.

5. CMCs claims must comply with the HFTLS statement given in the report of the supporting CCQM-comparison. CMC claims outside the HFTLS statement

<sup>&</sup>lt;sup>2</sup> 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

<sup>&</sup>lt;sup>3</sup> If the supporting CCQM comparison is a KC, a subsequent KC (including linked bilateral comparisons) or a linked RMO comparison, the CRV is the stated KCRV of the (linked) KC

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would require additional evidence as stated in item 2 of this section. NOTE: If a CMC claim is outside the HFTLS statement of the corresponding CCQM-comparison, **it is strongly recommended to prepare a brief document** and add it to the submission. It should include a concise reasoning why an approval beyond the HFTLS is justified and it should summarize the supporting evidence. This will help to avoid queries by the reviewers and potential rejections of such CMCs due to insufficient information.

- 6. 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  $|d_i| \le U(d_i)$ . 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,  $U(CMC_i)$ , 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  $u_{min}(CMC_i)$  depends on the method used to calculate the *CRV*, which should be stated in the report of the CCQM-comparison.
- 7. 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. In this case, 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 7 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  $U_{min}(CMC_i) = k u_{min}(CMC_i)^4$  and the concerned institute must revise its uncertainty budget adequately.
- 8. Declared CMC uncertainties for CRMs must be consistent with the supporting documents (i.e. see Note 2 of item 3). They are usually expected to be larger than the uncertainty of the measurement capability due to the additional contributions for homogeneity and stability, unless those contributions can be reasonably neglected (a document should be added as described in the NOTE of item 5).
- 9. An uncertainty budget must be added to the CMC submission if the claimed uncertainty is not supported by a CCQM comparison (a document should be

<sup>&</sup>lt;sup>4</sup> k is the coverage factor

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added as described in the NOTE of item 5 of this section). NOTE: Item 9 applies to

- CMCs not directly supported by a CCQM comparison (see item 2),
- CMCs that can reasonably be supported by a CCQM comparison beyond its HFTLS statement,
- CMCs of CRMs stating smaller uncertainties as stated in the corresponding CCQM comparison: the repeatability contribution to the uncertainty of the assigned value might be smaller for CRMs compared to a CCQM comparison, since the number of measured samples could be larger.
- 10. 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 CMC claim must comply with the quantity values of respective reference materials, which must be supported by respective CMCs for their part.
- The source of traceability has to be an NMI or DI as stated in the CIPM regulations. The source of traceability has to be stated only for the measurand the CMC is referring to<sup>5</sup>.
- 12. Only CMCs based on the highest-level measurement method available at an institute for a given measurand/range shall be listed.
- 13. If a new comparison on nominally the same measurand is available, the most recent performance is taken for evaluation, regardless of performance. EAWG aims to repeat relevant CCQM comparisons as defined in the subsequent sections to keep up supporting evidence for CMCs.
- 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. The submission of CMCs of CRMs must include information on the form (solid, solution), packaging, and validity period with respect to the "Mechanism(s) for service delivery" stated in the submission form. The information should be added in the 'information to reviewer' section, in the 'Exact nature of service delivered' field.<sup>6</sup> The writer of the CMC might also refer to the CRM certificate, provided it is issued in English.

<sup>&</sup>lt;sup>5</sup> 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 molality used to measure the standard potential of the AgAgCl-electrode, even if it is provided by another institute.

<sup>&</sup>lt;sup>6</sup> It is noted that this field is not optimal, but it is the only available field that is suitable to some degree.



### 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.
- 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<sup>7</sup>, should be 'aqueous pH buffer solution', not just 'aqueous solution'. Likewise, other matrixes should be specified appropriately.
- 3. Table 1 indicates the pH ranges for a number of most relevant buffers which should be used for HFTLS statements irrespective of the actual pH values of the buffers used in the corresponding CCQM-comparisons.
- 4. The measurement ranges for measurements based on a differential (Baucke) cell must be commensurate with the values of primary buffers available.
- 5. 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. The metrological service the CMC is referring to must be conducted with CRMs provided by NMI/DIs holding CMCs for these CRMs. The source of traceability of each CRM must be stated in the CMC submission.
- 6. CMC claims of difficult to measure buffers ('extended capability', see table 1) should be underpinned by participation in the CCQM-comparison testing that particular buffer. The exception to this would be if the increase of the claimed uncertainty compared to the performance demonstrated in comparisons of core capability buffers is 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).
- 7. Good performance in either the last two comparisons (extended or core capability), or the last two easy to measure buffers (core capability) may be used as supporting evidence for any CMC claim related to core capability buffers.
- 8. The difficulty of a few buffers mentioned in table 1 has not been assessed yet. These are indicated as "tbd". They must be considered as "extended capability" for CMC submissions until further notice.
- 9. 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 two extended capability buffers, may justifiably claim a complete pH

<sup>&</sup>lt;sup>7</sup> according to IUPAC recommendations 2002



measurement range from approximately 1.2 to 10.5 (covering the tetroxalate through carbonate buffers), provided the claimed uncertainty is justified.

рН	buffer	KC-ID	difficulty	HFTLS range	
1.7	tetroxalate	К20.уууу	core	1.2 to 2.2	
3.6	tartrate	n/a	tbd	3.1 to 4.1	
3.8	citrate	n/a	tbd	3.3 to 4.3	
4	phthalate	К91.уууу	extended	3.6 to 4.6 (3.8 to 4.2)	
4.7	acetate	n/a	tbd	4.3 to 5.3	
6.9	phosphate	К9.уууу	core	6.4 to 7.6	
7.7	tris	n/a	tbd	7.2 to 8.2	
9.2	borate	К19.уууу	core	8.5 to 9.6	
10	carbonate	К18.уууу	extended	9.5 to 10.5	
12.5	calcium hydroxide	n/a	extended	12.3 to 12.7	

### Table 1 Difficulty of various buffers.

- 11. The performance in a CCQM-comparison of a specific buffer prevails any other support of a CMC that refers to this buffer<sup>8</sup>.
- 12. The type of the buffer must 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 consider the stated temperature range in compliance with the supporting CCQM-comparison.

NOTE1: It is possible to add tables to the CMC submission assigning individual uncertainties to pH values at different temperatures.

<sup>&</sup>lt;sup>8</sup> e.g. good performance in a tetroxalate and a borate comparison cannot be used to compensate bad performance in a phosphate comparison with respect to a phosphate CMC.



- 14. CMC claims outside the typical 15 °C to 37 °C range that are not directly supported by CCQM-comparisons must provide sufficient additional evidence.
- 15. The "Comments for publication" field of the CMC submission form must include the information whether the uncertainty does or 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)."
- 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, and existing CMCs of NMIs will not be affected.
- 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, and these guidelines for traceability and uncertainty statements must be considered.
- 18. Uncertainty contributions due to stability issues can usually be neglected in CMC claims for solid CRMs (also see item 8 in section 2), except for borax.
- 19. CMC claims for pH are recommended to refer to uncertainty convention 1.

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### 4. Specific requirements for electrolytic conductivity

- 1. CMCs related to electrolytic conductivity must be expressed in the SI unit S m<sup>-1</sup>. Commonly used prefixes may be used to account for the measurement range, i.e.  $\mu$ S cm<sup>-1</sup> or mS cm<sup>-1</sup>.
- 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 require additional evidence (also see note 5 of the general section).
- 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  $\mu$ S cm<sup>-1</sup> to 50 S m<sup>-1</sup>. If this timescale is not met, NMIs will not be punished as a result and existing CMCs of NMIs will not be affected.
- 6. The HFTLS 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).

7. 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. Additional evidence, e.g. in terms of a test measurement report, might be necessary.



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

**Table 2** Difficulty of electrolytic conductivity measurements

### 5. Specific requirements for coulometry

- Coulometry depends on correct realisation of the underlying chemical reaction. Therefore, the performance of the instrumentation alone is not a sufficient condition to prove that measurement results are correct. Claims must be supported by CCQM-comparisons reflecting the capability of the participating institute to handle the involved chemistry. Table 3 lists the main measurands of CCQM-comparisons of substances typically assayed by coulometric titration and provided by NMIs as CRMs. They are grouped in reaction types to indicate similar chemistries with respect to coulometric analysis.
- 2. EAWG aims to conduct CCQM-comparisons in the coulometry area once every two years. It is therefore expected that six CCQM-comparisons can be conducted in a re-review cycle of CMCs (assuming a period of 12 years). If this timescale is not met, NMIs will not be punished as a result and existing CMCs of NMIs will not be affected.

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- 3. It is recommended to select those analytes for CCQM-comparisons that are marked in the 'Analyte or component' column of table 3. The colour code is explained in the caption of table 3. On the one hand, the marked analytes are recommended because of their importance as reference materials. On the other hand, the selection aims to provide CCQM comparisons as support for CMC of each measurand listed in table 3.
- 4. The measured quantity should be reported as amount content in respective CCQM-comparisons. The final reports should additionally provide the results of the participants in terms of mass fractions, since those are often the preferred quantity in CMC submissions. The kind of mass fraction must however be unambiguously specified in the final report, and the calculation must be stated. Any differences between the representation of the quantities in the CMC submission and that of the supporting CCQM-comparison must be explicitly mentioned in the CMC submission form.

NOTE1: The specification of the measurand of a CMC must consider that coulometric titration is not selective. If CMC claims are made with respect to a specific analyte, they must be supported by use of other techniques for impurity measurements. For instance, a CMC claim for "amount content of total acid" requires no assessment of acidic impurities. In contrast, a CMC for "amount content of HCI" requires a correction for the presence of other acids.

NOTE2: If possible, it is recommended that the measurand of a CMC claim should follow the specification in table 3 (columns 2-4).

- 5. The Technical Protocols of CCQM-comparisons must state mandatory uncertainty contributions to be considered and explicitly reported by the participants. The coordinator must ask the participant for a revised measurement report if the requested uncertainty contributions have not been addressed. The final report of the CCQM-comparison must include a statement that all participants have provided an uncertainty budget according to the requirements of the Technical Protocol. Table A2 in the annex states the uncertainty contributions which must be considered for each analyte of table 3.
- 6. An institute may use a CCQM-comparison to support any CMC of the same type of reaction, provided the following requirements are met:
  - A full uncertainty budget must be added to the CMC submission if the measurands of the supporting CCQM-comparison and the CMC are different. The uncertainty budget must quantify the uncertainty contribution stated in table A2. In this case, the relative uncertainty stated in (or derived from) the CCQM-comparison may not be the basis for the uncertainty claim. The validity of the uncertainty claim must rather be evaluated by the CMC reviewers.
  - If the degree of difficulty of the measurand of the submitted CMC is larger compared to that of the supporting CCQM-comparison, additional evidence must be provided in accordance with section 2 item 5. Moreover, the record card of the institute must indicate that



the institute is basically capable to measure analytes of at least the same degree of difficulty. CCQM comparisons of any type of reaction can be used for this assessment.

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**Table 3** Measurands to be supported by CCQM comparisons of coulometric titration. CCQM comparisons of analytes in red letters should be regularly repeated (every 12 years) since they are important, widely used CRMs. Analytes marked with (+) can be alternatively used within the group of the same color. It should be noted that some materials are poisons, oxidants or corrosives and would be difficult for shipping.

Type of	Meas	Titrant	Titration type	Degree of	Important CRM	Latest KC		
reaction	Analyte or component	Quantity	Intraint	intration type	difficulty ***		Lucest Ne	
	Potassium hydrogen phthalate (KHP)	Amount content of acids		direct	3	very	K34.2016	
	Benzoic acid	Amount content of aclus	ОН⁻	direct	3	less	-	
Acid-base	Sulfamic acid			direct	1	less	-	
	Strong acid solution			direct	1	very	K73.2018	
	Sodium carbonate <mark>(+)</mark>	Amount content of bases		back**	3	very	K173	
	Tris <mark>(+)</mark>			back**	1	very	-	
	Sodium oxalate <mark>(+)</mark>	Amount content of	*	*	5	less	K169	
Redox	Arsenic (III) oxide <mark>(+)</mark>	Teduciants	l <sub>2</sub>	direct	1	less	-	
	Potassium iodate <mark>(+)</mark>	Amount content of	$I_2$	back	4	less	K152	
	Potassium dichromate (+)	oxidants	Fe <sup>2+</sup>	direct	2	very	K96.2023	
Complexing	Disodium EDTA <mark>(+)</mark>	Amount content of	M <sup>2+</sup>	direct	4	very	-	
	EDTA <mark>(+)</mark>	complexing agents		direct	4	very	-	
Precipitation -	Sodium chloride <mark>(+)</mark>	Amount content of	Ag⁺	direct	3	very	-	
	Potassium chloride <mark>(+)</mark>	precipitated ions		direct	3	very	K48.2014	

\* for sodium oxalate the classification depends on which procedure is used to measure its content (direct/back titration; oxidant used – Mn(III) or Ce(IV))

\*\* also, a direct titration with electrogenerated H<sup>+</sup> is possible

\*\*\* 1=least difficult, 5=most difficult

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### 6. Specific requirements for measurands using classical methods

- 1. Classical chemical methods include titrimetry and gravimetry, both of which have the potential to be considered as primary methods. Gravimetry is a direct primary method. Titrimetry is a ratio based primary method.
- 2. Since titrimetry is a ratio based primary method, it is necessary to use a titrant with known amount content or a CRM of an analyte. That is, CMCs based on titrimetry require specifying the source of traceability, which can be an in-house coulometry facility or a CRM, provided by another NMI. Note that item 11 of the general section applies.
- The characteristic properties of titrimetry with respect to CMC submissions are similar to that of coulometry. For instance, it is a non-selective method (see item 4 of section 5). Thus, CMCs based on titrimetry must follow the requirements specified in section 5 accordingly.



#### Annex

#### A1 Basic information to be compiled in the record-card of an institute

#### **Table A1** Information to be compiled in the record card.

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

#### <u>Remarks</u>

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.

 $-1 \le d_i/U(d_i) \le 1$  indicates consistency of the reported results with the CRV. Values outside this range indicate underestimated or missing uncertainty contributions of a measurement result.



#### A2 Additional specification of coulometric analytes

The following uncertainty contribution must be considered in general:

- All quantities of the measurement equation, i.e. sample mass, electric charge (coulombs, or current and time, or voltage, resistance and time). Faraday constant is used as an accurate value without uncertainty.
- Current efficiency.
- End point determination, including mathematical model used to fit titration curves.
- Migration of analyte or titrant into intermediate chamber /counter compartment.
- Impurities in electrolyte and purging gas.

Analyte or component	Special difficulty	Specific Uncertainty sources to be considered	HFTLS
Potassium hydrogen phthalate (KHP)	Reduction, CO <sub>2</sub> elimination	Reduction, CO <sub>2</sub> influence, impurities in KHP, titration curve slope	The comparison provides support for the capabilities to measure the amount content of acids in an assay of high purity KHP. Results provide evidence for the capabilities to assay the purity of strong and weak acids in the range 0.999 to 1 kg/kg. It may also provide indirect support for respective bases.
Benzoic acid	CO <sub>2</sub> elimination, dissolution	CO <sub>2</sub> influence	To be considered: Strong solid acids; bases indirectly; range: 0.999 to 1 kg/kg.
Sulfamic acid	-	CO2 influence, hydrolysis	The comparison provides support for the capabilities to measure the amount content of acids in an assay of high purity NH2SO3H. Results provide evidence for the capabilities to assay the purity of strong acids in the range 0.999 to 1 kg/kg with low uncertainty. It may also provide indirect support for respective bases.
Strong acid solution	-	CO <sub>2</sub> influence	The comparison provides support for the capabilities to measure the amount content of strong acid in the range 0.09 mol/kg and above. The relative measurement uncertainty at higher amount contents must not be smaller than the relative uncertainties consistent with the results of the comparison unless further evidence is given. It may also provide indirect support for assay of bases.

#### **Table A2** Points to be considered in the Technical Protocol and the Final Report of CCQM-comparisons.

CCQM-EAWG			
Analyte or component	Special difficulty	Specific Uncertainty sources to be considered	HFTLS
Sodium carbonate	Drying, CO <sub>2</sub> elimination	Drying, CO2 influence	The comparison provides support for the capabilities to measure the amount content of bases in an assay of high purity sodium carbonate. Results provide evidence for the capabilities to assay the purity of solid bases like tris (tris(hydroxymethyl)aminomethane) and hydroxides and carbonates of alkali metals and alkaline earth metals with mass fraction not less than 99,8 % as well as their water solutions for sample sizes similar to those used in the comparison (equivalent to 3 to 40 mmol base). NMIs that used back titration implementation of coulometry or titrimetry may use this comparison for supporting CMCs of assays of strong acids and their solutions in the same ranges as well.
Tris	-	CO2 influence	The comparison provides support for the capabilities to measure the amount content of bases in an assay of high purity Tris. Results provide evidence for the capabilities to assay the purity of weak bases in the range 0.998 to 1 kg/kg. NMIs that used back titration implementation of coulometry or titrimetry may use this comparison for supporting CMCs of assays of strong acids and their solutions in the same ranges as used as well.
Sodium oxalate	Reaction with KMnO4 empirical	O <sub>2</sub> sensitivity, reaction kinetics, current efficiency, stoichiometry	The comparison provides support for the capabilities to measure the amount content of reductants in high-purity sodium oxalate. Results achieved using coulometry or titrimetry (direct approach), or a combination of both methods, provide evidence for the capabilities to determine the amount content of reductants in pure salts in the range 0.999 to 1 kg/kg, as well as in their aqueous solutions. For indirect methods, it may also provide indirect support for assay of oxidants.
Arsenic (III) oxide	As₂O₃ dissolution	O2 sensitivity, Oxidation of As(III) during dissolution	The comparison provides support for the capabilities to measure the amount content of reductants in an assay of high purity arsenic (III) oxide. Results achieved using coulometry or titrimetry (direct approach), or a combination of both methods, provide evidence for the capabilities to assay the amount content of reductants in pure oxides or salts in the range 0.999 to 1 kg/kg with low uncertainty, as well as their aqueous solutions.
Potassium iodate	Thiosulfate stability	Thiosulfate and tetrathionate stability, I <sub>2</sub> volatility	The comparison provides support for the capabilities to measure the amount content of oxidants in an assay of high purity potassium iodate. Results provide evidence for the capabilities to assay the purity salts in the range 0.999 to 1 kg/kg and to determine non-metallic elements from their content. Results achieved from coulometry or titrimetry (direct approach), provide evidence for the capabilities to assay the purity of pure salts such as iodate, chlorate and bromate as well as to measure the mass fraction of iodate, chlorate and bromate anions in solution (1 mmol/L and higher) and to determine other oxidizing agents by iodometry. Furthermore, results achieved from an indirect approach based on a sufficient number of impurities assessments provide evidence for the capabilities to assay the purity of pure inorganic salts (mass fraction not less than 99.0 %) and to determine constituent elements of these salts.

# <u>|||CCQ</u>M

Analyte or component	Special difficulty	Specific Uncertainty sources to be considered	HFTLS
Potassium dichromate	O <sub>2</sub> sensitivity, electrolyte impurities	O <sub>2</sub> sensitivity, current efficiency	The comparison provides support for the capabilities to measure the amount content of oxidants in an assay of high purity potassium dichromate. Results achieved from coulometry (direct approach) provide evidence for the capabilities to assay the purity of pure salts in the range 0.995 to 1 kg/kg.
Disodium EDTA	O <sub>2</sub> sensitivity	O2 sensitivity, endpoint	To be considered: Complexing agents and their salts; range 0.995 to 1 kg/kg
EDTA	O <sub>2</sub> sensitivity	O2 sensitivity, endpoint	
Sodium chloride	Adsorption	Adsorption, light sensitivity, current efficiency	The comparison provides support for the capabilities to measure the amount content of precipitated ions in an assay of sodium chloride. Results achieved from coulometry (direct approach) provide evidence for the capabilities to assay chloride content in concentrated solutions and in solid pure chlorides in the range 0.999 to 1 kg/kg.
Potassium chloride	Adsorption	Adsorption, light sensitivity, current efficiency	The comparison provides support for the capabilities to measure the amount content of precipitated ions in an assay of sodium chloride. Results achieved from coulometry (direct approach) provide evidence for the capabilities to assay chloride content in concentrated solutions and in solid pure chlorides in the range 0.999 to 1 kg/kg.