Summary Report on the activities of

**CCQM WG on Electrochemical Analysis and Classical Chemical Methods (EAWG)**

in the period 04/2024 to 03/2025

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# EAWG terms of reference

To carry out Key Comparisons, and where necessary pilot studies, to critically evaluate and benchmark NMI/DI claimed competences for measurement standards and capabilities for pH, electrolytic conductivity, coulometry and classical chemical methods.

To assist in identifying and establishing inter‐laboratory work to improve the SI traceability of electrochemical measurement results.

# Meetings

## Meetings

EAWG has held a hybrid meeting at the BIPM 22 April 2024 and a two-day online meeting 29/30 October 2023. 46 people from 27 countries have registered to the April meeting and 42 people from 27 countries have registered to the October meeting. Table 1 shows the number of participating countries with respect to RMOs.

|  |  |  |
| --- | --- | --- |
|  | Apr 24 | Oct 24 |
| EURAMET | 12 | 11 |
| APMP | 5 | 5 |
| SIM | 7 | 7 |
| GULF | 1 | 1 |
| AFRIMET | 1 | 1 |
| COOMET | 1 | 1 |

**Table 1** Number of participating countries by region

# Comparison summary

Completed in reporting period K91.2022 (pH of phthalate buffer)

 K170 (conductivity at 0.5 and 20 S/m)

 K96.2023 (assay of potassium dichromate)

 K73.2018.2 (amount content of HCl)

 K173.1 (assay of sodium carbonate)

In progress P221 (pH of seawater)

 K169 (assay of sodium oxalate)

 P228 Impedance Spectroscopy

 K96.2023.1 (assay of potassium dichromate)

 EURAMET.QM-K170 (conductivity at 0.5 and 20 S/m)

 EURAMET.QM-K19.2018 (pH of borate buffer)

 EURAMET.QM-K91.2022 (pH of phthalate buffer)

 K20.2025 pH of Tetroxalate buffer

 K173.2 (assay of sodium carbonate)

 Kxxx assay of EDTA

Aborted none

Request for CCQM approval Pilot study on the pH of Ca(OH)2 buffers

 KC on the conductivity of KCl solutions at 0.05 and 5 S m-1

Up to now, 68 comparisons have been conducted by EAWG. 13 subsequent or supplementary comparisons have been conducted by RMOs. Figure 1 summarizes the comparisons by technical areas.

**Figure 1** Comparisons by technical areas. KC&SC: Key Comparisons (including subsequent and linked regional comparisons), Supplementary Comparisons; PS: Pilot Studies.

# Status of comparisons in progress

## CCQM-K170 – Conductivity at 0.5 and 20 S m-1

The comparison is a subsequent KC of CCQM-K36.2016 and CCQM-K92. It is intended to provide updated support for respective CMCs. It has been coordinated by NIM China. The results have been intensively discussed by the participants in an online meeting, and in previous EAWG meetings. KCRV estimators have been decided upon. See minutes of the April meeting for more details. In the meanwhile, Draft B has been released and approved. The Final report is available at the KCDB and can be used as evidence for CMC approval.

## CCQM-P221 – pH of Tris/(artificial) seawater

The comparison is coordinated by NIST with LNE being the co-piloting institute. Two measurands have been measured. Measurand A was p(*a*H*a*Cl) of a TRIS-TRIS.HCl buffer in artificial seawater (ASW). Measurand B is the pHT value of an ASW sample. More detailed information is given in the summary report of April/2024.

The report has been completed according to the coordinator and is under internal review at NIST. However, the report is overdue since 2023. The EAWG has therefore informed the CCQM secretary, who has contacted NIST. NIST cannot provide the report in the near future due to heavy workload. It has however agreed to provide the report by September.

## CCQM-K169 – Assay of sodium oxalate

K169 is a joint comparison with IAWG. Participants that will successfully take part in the KC will demonstrate their capability to measure the amount content of reductants in high-purity sodium oxalate. VNIIM-UNIIM is coordinating the comparison. Measurements have been completed. A. Sobina has presented anonymised results. Five NMIs participated in the KC.

Due to the problems with using permanganate as an oxidant all participants have decided to use cerium to assay sodium oxalate. A. Sobina has shown that various gravimetric and coulometric titration procedures have been used for the measurements. Moreover, it was demanded that the uncertainty budgets must include the contributions specified in the CMC guidelines of EAWG. NIM identified 72 impurities by semi-ICP-MS, with Si, K and NO3 having the largest contribution (≈10-20 mg/kg). VNIIM-UNIM identified 48 impurities with ICP-MS, with Ca being the largest one (14 mg/kg). The results have been presented as the amount content of reductants expressed as sodium oxalate. It seems that there is a significant overdispersion, since the spread of the results is not covered by the assigned uncertainties for the most part. A. Sobina presented a number of potential KCRV estimators, also including calculations with the NIST decision tree and dark uncertainty. The results and the selection of the best estimator for the KCRV must be discussed in more detailed. Therefore, S. Seitz asked A. Sobina to prepare a Draft A, distribute it among the participants and invite them to an online meeting afterwards. M. Marissy and T. Asakai are asked to join the meeting.

## CCQM-K91.2022 – pH of a phthalate buffer

The comparison is a follow-up comparison of K91, which is intended to provide updated support of respective CMCs. Phthalate is one of the buffers to prove ‘extended capabilities’ (according to the EAWG CMC guidelines). PTB was supposed to coordinate the comparison with CMI being the co-piloting institute. However, both institutes had to withdraw from coordination after registration had been completed as a consequence of their national politics in the face the current international situation. INMETRO has agreed to take on the coordination. 13 Institutes have participated. First results have been shown at the autumn meeting. The participants have connected online 5 December 2023 to discuss the results in more detail and decide upon the KCRV. The weighted mean was chosen for all temperatures. Draft A has been approved by the participants and presented in the EAWG meeting April. Afterwards Draft B has been released and approved. The Final report is available at the KCDB and can be used as evidence for CMC approval.

## CCQM-K96.2023

The comparison is a follow-up comparison of K96, which is intended to provide updated support for respective CMCs. It demonstrates the capability to measure the amount content of oxidants as potassium dichromate. KRISS is coordinating the comparison. After feedback from the IAWG meeting, proposing to consider dark uncertainties for KCRV calculation to deal with the two outliers, the participants have held another online meeting 20 September 2024. It was decided to follow CCQM/2013-22 guidelines for KCRV calculation. The median was chosen as most appropriate KCRV estimator. Dark uncertainties have not been included. Afterwards Draft B has been released and approved. The Final report is available at the KCDB and can be used as evidence for CMC approval. The result of the subsequent CCQM-K96.2023.1 comparison has been linked to CCQM-K96.2023. It is consistent with the KCRV. Draft B has been sent to CCQM for approval. Approval is expected before the April meeting 2025. Draft B can already be used to support CMC submission.

## CCQM-P228 pilot study on impedance spectroscopy

The pilot study investigates practices to measure the impedance spectra of typical conductivity reference solutions with the aim to establish a best practice guide for the determination of the solution resistance in a conductivity measurement cell. It is coordinated by PTB. To this end, impedance spectra of a 0.1 and a 10 S/m KCl solution are measured by the participants which must also complete a survey to collect information on their measurement practice. 13 institutes have registered. Measurements have been completed. 11 institutes have sent measurements reports. Two institutes have withdrawn. A first evaluation of the results will be shown at the CCQM meetings in April 2025. The coordinator has however mentioned that the evaluation is not expected before the October meeting in 2025 since the evaluation of the questionnaire is time consuming.

## Bilateral Comparisons

CCQM-K96.2023.1: see 4.5.

CCQM-K73.2018.2 (assay of HCl) has been completed. Participants: SMU (linking lab), INMETRO, Ukrmetrteststandard. The final report is published in the KCDB and can be used for CMC support.

CCQM-K73.2018.3 (assay of HCl) has been completed. Participants: TUBITAK-UME and NIM (linking lab). The final report is published in the KCDB and can used for CMC support.

CCQM-K73.2018.4 is in progress. Participants: PTB (linking lab), BFKH, INMETRO. The measurements have been completed. Draft A is expected soon.

CCQM-K173.1 (assay of sodium carbonate) has been completed; Participants: KRISS and SMU(linking lab). The final report is published in the KCDB and can used for CMC support.

CCQM-K173.2 (assay of sodium carbonate) is in progress. Participants: SMU (linking lab) and INMETRO, BFKH and KEBS. At present, samples are prepared.

## EURAMET comparisons

Three regional comparisons have been initiated at EURAMET that are linked to preceding CCQM comparisons. The comparison are initiated for institutes that had to withdraw from the corresponding CCQM-comparisons because of the international situation. EURAMET.QM-K19.2018 (pH of borate buffer) is coordinated by GUM. The samples had to be prepared again due to homogeneity issues with the first batch. Measurements have been completed. Draft A is expected soon. EURAMET.QM-K170 (conductivity at 0.5 and 20 S/m) is coordinated by PTB. Measurements had been completed by 21 March. Draft A is expected by the autumn meeting of EAWG. Finally, EURAMET.QM-K91.2022 (pH of phthalate) was supposed to be coordinated by CMI. Unfortunately, CMI was unable to continue coordination the KC due to health issues of involved staff. LNE kindly took over the coordination The KC will start in the second half of 2025.

# New Comparisons

## K20.2025 pH of a Tetroxalate buffer

A new key comparison on the pH of a tetroxalate buffer has been approved by CCQM in spring 2024. The KC will be coordinated by INMETRO. This buffer has a nominal pH value around 1.7. The KC is supposed to prove core competence in pH measurements and to support respective CMCs according to the EAWG guidelines. It is a follow-up comparison of K20. The comparison is open to NMIs or DIs of member or associate states of the CIPM MRA. Measurements will be conducted at 15 °C, 25 °C, 37 °C and, optionally, at 5°C and 50 °C. Invitations have been sent in January 2025. Registration has been completed. 16 NMI/DIs have registered. Measurement period will be in autumn.

## KC of an assay of EDTA

The has been approved by CCQM in spring 2025. It aims to provide evidence for the capabilities of participating NMIs to measure the amount content of an assay of EDTA or EDTA salts. NMIs using complexometric coulometry or titration with EDTA may use this comparison for supporting CMC of complexometric value of liquid and pure solid (EDTA, ZnO, MgO, CaCO3, etc). KRISS will presumably coordinate the KC. Details will be discussed at the next meeting.

## Pilot study on the pH of a Ca(OH)2 buffer

A saturated Ca(OH)2 buffer (pH 12.45) is a standard solution for the pH range above 11. Currently, there is no key comparison available to provide evidence for the calibration and measurement of NMIs in this difficult pH range. Therefore, a pilot study is planned to get first insight in the equivalence of measurement results and pave the way for a subsequent KC. The pilot study will be coordinated by PTB. Registration will start in autumn 2025. Measurements are expected in 2026.

# Upcoming comparisons

## KC on the pHT of a ASW/TRIS buffer

The participants of the pilot study P221 had agreed to start the KC in 2024. However, there have been changes of personnel at LNE. Moreover, due to the pending release of the Report of P221, it is difficult to write a Technical Protocol that considers lessons learnt from the pilot study. Coordination and schedule will be discussed again at the spring meeting 2025.

## K48.xxxx on an assay of KCl or NaCl

A follow-up of K48 on an assay of KCl or NaCl will presumably be conducted after the KC on EDTA has been completed in 2027. The salts are representatives to demonstrate the capability to measure the amount content of precipitating ions by direct coulometry. Corresponding CRMs are very important. The KC is needed to keep up supporting evidence for respective CMCs.

# Overview on work programme 2024-2026

Table 2 Workplan

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|   | **pH** | **conductivity** | **coulometry** | **pilot study** |
| **year** | **KC-ID** | **buffer** | **KC-ID** | **value(solution)** | **KC-ID** | **assay** |   |
| 2024 |   |   |   |   | K173.1 | sodium carbonate (SMU) |   |
|   | EURAMET.QM-K19.2018 | borate(GUM/SMU) | K170 | 0.5 S/m (KCl)20 S/m (KCl)(PTB) | K96.2023.1 | potassium dichromate (KRISS) |   |
|   |   |   |  |   | K73.2018.3 | HCl(NIM) |   |
|   |   |   |   |   | K73.2018.4 | HCl(PTB) |   |
| 2025 | EURAMET.QM-K91.2022 | phtalate(LNE/PTB) |   |   | Kxxx | EDTA(KRISS) | pH >11(PTB) |
|   | K20.2025 | Tetroxalate(INMETRO/PTB) |   |   |   |   |   |
| 2026 | K.xxx | Tris/seawater(tbd) | EURAMET.QM-Kxxx | 0.05 S/m (KCl)5 S/m (KCl) (tbd) |   |   |   |

# CMC and KC topics

## Feedback from KCDB

T. Asakai, who is the representative of EAWG at the KCWG, reported from the KCWG meeting held 20-21 April 2024. 20 CMCs have been submitted in the area of EAWG. Common reviewer comments have been:

* Missing evidence for CRM uncertainty, i.e. stability and homogeneity contribution, certificates, peer review reports or accreditation certificates etc.
* Temperature range not adequate, especially for pH.
* Missing declaration of Bates-Guggenheim convention in the uncertainty of pH.
* Effect of atmospheric CO2 in low EC areas not conisdered.
* Minimum uncertainty of KC results inconsistent the KCRV not considered.
* Use of outdated KC as the evidence.

KCWG has discussed to update the categories and especially the subcategories. EAWG has decided that there is no need for a change with respect to EAWG.

There has been a discussion on understanding and assigning the correct uncertainty convention to CMCs. It is recommended to apply uncertainty convention 1 to pH CMCs, and uncertainty convention 2 to conductivity CMCs.

The chair has encouraged EAWG members to thoroughly read and consider the EAWG CMC guidelines before CMC submission to accelerate their approval.

## Revision of EAWG CMC guidelines

A draft of a revised version (v16) of the CMC guidelines of EAWG has been sent to EAWG members before the April and the October meeting in 2024. S. Seitz has explained the revised items during the meetings. They have coThey were related to the pH section and were mainly intended to improve clarity and to consider a few comments from former CMC reviews. The draft has been approved. Version 16 has been published in the EAWG area of the BIPM website. It must be used for the review of CMCs of EAWG members in the next review cycle.

## General KC issues

1. Calculation of the uncertainties of the degrees of equivalence in subsequent KCs. Current calculation results in larger uncertainties compared to the original KC, which means that it is easier for participants of the subsequent KCs to be consistent with the KCRV. The correlation between the results of the linking lab should rather be considered. This would result in DoE uncertainties that are similarly to those of the original KC. However, the quantification of the correlation coefficient could be challenging. It was decided to that should have a look at former subsequent KCs and recalculate U(DoE) to assess the effect.

The number of participants in KCs has significantly increased in recent KCs, i.e. in pH and conductivity KCs. If unexperienced participants contribute to the KCRV calculation, this might put the soundness of the KCRV at risk. S. Seitz suggested to establish some eligibility criteria in this regard. This proposal has been discussed. There have been concerns that institutes would be excluded from participation It has been proposed to specify the institutes that would be included in KCRV calculation at the beginning of a KC on the bases of the EAWG record file.

EAWG-KC guidelines: At the autumn meeting it was decided that the chairs will prepare KC guidelines for EAWG addressing issues that are not covered by the CIPM and CCQM KC guidelines, such as the method for KCRV & U(DoE) calculation, implementation of dark uncertainty and eligibility criteria for participants to be included in KCRV calculation. A Draft has been written and distributed among EAWG before the meeting in April 2025.

# Technical presentations

## Biosensors

A. Wain from NPL has given a presentation on the metrology of electrochemical biosensors. NPL aims to establish capability to support the development and manufacturing of electrochemical and electrical biosensors. Many stakeholders of NPL consider the quantification of surface biofunctionalisation as the most important metrological challenge. To this end, NPL has investigated different kinds of sensors and measurement conditions, using electrochemical measurement techniques such as cycling voltammetry and impedance spectroscopy. A. Wain has shown results of these preliminary characterisation measurements which demonstrate a strong sensitivity of measurement stability and repeatability on various preparation and measurement conditions. Details are given in the presentation available at the EAWG area of the BIPM website. Since NPL is, besides TUBITAK-UME, the second NMI that has started activities in this area, S. Seitz has proposed that EAWG should include the topic in the scope of EAWG and reach out for respective activities in other CCQM-WGs.

## EMPIR project “SapHTies”

G. Capitaine from LNE as summarized the outcomes of the European metrology research project “SapHTies” which has reached the end of its runtime at the end of April 2024. The project has paved the way to establish a traceability chain for spectrophotometric measurements of the pHT of seawater, to calculate reliable measurement uncertainties, and has verified the equivalence of pHT measurements by an ILC. More details are given in the presentation available at the EAWG area of the BIPM website.

## Seawater CO2 system

S. Seitz has presented a project proposal submitted to the Green Deal call of the European Partnership for Metrology program of EURAMET. Four quantities are measured in oceanographic research and in ocean observation with respect to the seawater CO2 system. The provision of reliable seawater reference materials for these quantities is not guaranteed. Furthermore, the measurement results obtained in past cruised have turned out to be inconsistent. The project will address these issues. More details are given in the presentation available at the EAWG area of the BIPM website.

## EPM project GrainMET

F. Durbiano from INRiMN has given a presentation on the project GrainMET “Metrology for standardised moisture content measurement in plant-origin bulk materials in support of International and European food safety and trade”. Moisture determination is necessary to support quality and fair trade in the grain market. The project aims to ensure consistent moisture measurements by a number of activities such as the establishment of coulometric Karl Fischer (KF) titration as a primary method, conducting comparisons and developing guidelines and procedures. She also presented the principles of coulometric KF and compared it volumetric KF titration.

# Task groups

## CCQM/EAWG TG on the establishment of metrological traceability for seawater pH and pHT values

The TG has met in five online meetings this year. Basically, it aims to achieve three goals. I) Improve primary measurements of pHT ii) Establish proper metrological traceability within the CIPM MRA and iii) engage with relevant stakeholders. The improvement of pHT measurements is delayed since the report of P221 is still not available yet (see 4.2). As a consequence, the TG has decided to evaluate the measurement data of P221 again, independently form the report. T. Asakai has volunteered to evaluate the results. Unfortunately, he was unable to take on the task due to a prolonged illness. It will be decided in the next meeting, how to continue. A few members of the TG meet with oceanographers prior to the 1st Stakeholder meeting of the CIPM Sectorial Task Group on Climate and Environment in September to discuss the draft of traceability document. They partly disagreed with the proposed route of traceability, mainly for practical reasons. In particular, they prefer to use artificial seawater just for instrument check, but not as calibrant with batch-to-batch characterization. This approach is questionable from a metrological perspective, which has led to some discussion. Afterwards, the TG has revised the document, considering the mentioned concerns. In January, the revised document has been discussed again and accepted. Next a “Quick Guide to Establish metrological Traceability for pHT measurements” will be prepared and presented to the broader oceanographic community.

## CCQM/EAWG TG on Metrology for Li-ion batteries

The TG has meet four times in this reporting period. A list of potential measurands to be considered in the context of the CIPM-MRA has been established and intensively discussed. Specifying and grouping measurands to be considered in the stakeholder workshop has turned out to be quite difficult due to the variety of technical areas, technical readiness levels, stakeholder interests and allocation in the value chain of Li-ion batteries. Finally, it has been decided that each NMI partner will briefly present its activity, likewise participating stakeholders are to present their needs with respect to measurement comparability. It has been agreed to prepare in interactive workshop in first place. The TG has decided that the workshop will take place online on September 23 and 24. Currently, the TG is preparing the agenda. In May the members will start to invite selected stakeholders, but will also advertise for the workshop within their networks. Furthermore, the workshop will be organised in conjunction with a VAMAS project on LiBs which perfectly complements the scope of the TG. The VAMAS project (VAMAS is the Versailles Project on Advanced Materials and Standards, www.vamas.org), aims to define key metrological parameters for Li-ion cell standardisation and currently organises a comparison measurement for those parameters. The TG did not manage to conclude the objectives yet. Therefore, it is asking CCQM for approval to extent the runtime of the TG for another year.

## Potential Task Group on electrochemical biosensors

Two institutes of EAWG are currently active in the characterisation of electrochemical biosensors (TUBITAK, NPL). It has turned out that NMI/DIs from other WGs are also active in this area. Therefore, the EAWG chair has invited colleagues from the institutes in question (TUBITAK, NPL, LGC and NIM) in December 2024 to discuss potential objectives of a TG on bio sensors. The group has met again in February to continue the discussion. Even though the measurements are different at the involved institutes, it seems that a general metrological framework for the characterisation of bio-sensors to achieve equivalence in measurement could be a common object of a potential task group. A number of related activities would be addressed, such as:

* Identification of sensor types + measurement quantities
* Specification of characterisation methods for the sensors
* Specification of metrological reference + (C)RMs
* Specification of quantitative criteria for the characterisation, such as, sensitivity, specificity, reproducibility, effect on scalability, etc.
* specification of uncertainty sources
* specification of QC criteria
* establishing a show case: e.g. characterisation of Au-electrodes for various bio-sensor applications (already envisioning a comparison with other WG)

Unfortunately, none of the participating institutes has the capacity to coordinate such a TG. One possible approach could be to extend the scope to include bio-sensing techniques in general. However, if no one can be found to take the lead, the idea of a CCQM-TG on bio-sensors or bio-sensing technologies will have to be discarded.