# Strategy of the CCQM Working Group on Electrochemical Analysis and Classical Chemical methods (EAWG) from 2021-2030

## 1. EXECUTIVE SUMMARY

Electrochemical measurements, i.e., electrochemical sensors, are widely used since they are cost-effective, and they can easily be integrated in automated processes. They play an important role in meeting some of the present scientific, economic, and societal challenges. pH sensors are used to monitor ocean acidification due to climate change, electrolytic conductivity sensors are used in semiconductor, pharmaceutical, and power industries to monitor water purity, electrochemical biosensors are promising tools for non-invasive diagnostic of tumour biomarkers. Electrochemical sensors are part of multi-sensor-arrays, of miniaturized devices, of wearables in future life-style products, and they are part of the digitization process as they build a bridge between chemical measurements and electronic data processing. Their wide range of application challenges global metrology in the electrochemical area. New measurement methods and ranges, primary measurement standards, new measurands, even new ways of dissemination must be developed to address these developments.

EAWG's strategy aims at providing an international platform for its members, to present and discuss results of their national and regional metrology research programs addressing the above-mentioned challenges. EAWG will support its members interacting with their stakeholders, especially if international organizations are involved. Stakeholder needs will be brought to the attention of EAWG through its members. EAWG will conduct pilot studies and key comparisons if its members have expressed a respective need for international equivalence of a specific measurand, and it will address specific issues related to the equivalence of measurements by establishing dedicated task groups.

In this regard, EAWG has already started a few activities in the last decade that will be continued, others may be started within the next decade:

- support for international equivalence of measurands in ocean observation that are traceable to electrochemically characterised standards (i.e. salinity, pH, DIC and TA)
- support in establishing a unified pH scale
- extension of conductivity measurements to the pure water range
- impedance spectroscopy of conductivity and, possibly, battery cells
- electrochemical biosensors for application in laboratory medicine (e.g. measurement of antibodies)
- conductance of specialized key comparisons of new analytes by coulometry
- support of existing calibration and measurement capabilities (CMC) by repeated key comparisons
- better support of CMCs for certified reference materials (CRM) by adequate comparisons

Respective stakeholders include national and international organizations linked to metrology (calibration labs, standardization bodies, CRM manufacturers, etc.), companies from various areas (chemical, medical, food, power generation, automotive, and others) and international organization linked to oceanography.

At present, the number of key comparisons needed to constantly support the existing CMCs is relatively small in EAWG. However, the number is steadily increasing. It can be expected in the near future that CMCs can no longer be supported by key comparisons of the same measurand because of limited resources to conduct the comparisons. This holds especially for CMCs of CRMs, the selling of which is the

main metrological service for many NMIs in the electrochemical area. Thus, ways to support a larger number of CMC by fewer comparisons will be discussed within the next decade.

## 2. SCIENTIFIC, ECONOMIC AND SOCIAL CHALLENGES

Electrochemistry builds a bridge between physicochemical measurements and electronic data processing. Electrochemical sensors enable very effective and automated measurements at relatively low costs. Measurement results are readily available for further processing. As a consequence, some of the most prominent social challenges of our days are also involving measurements that are located in the electrochemical area.

In the past, metrology in electrochemistry has been determined by the provision of reference materials and the calibration of reference materials for industry, mainly for pH and electrolytic conductivity, with a few high-purity substances that are characterized by coulometry. The related metrological services are well implemented in the traceability structure of industrial measurements, usually within the framework of national accreditation or notification bodies. Nowadays, many new metrological challenges have evolved in the electrochemical area. These challenges often involve the application of or links to new measurement techniques, or the extension of classical electrochemical measurement methods into new, more extreme measurement ranges. For instance:

- Essential ocean variables in ocean observation, such as salinity, pH, dissolved inorganic carbon and total alkalinity are traceable to seawater standards the quantity values of which are characterised with electrochemical measurement techniques. Addressing unresolved traceability issues as well the implementation of adequate primary CRMs in the framework of the CIPM-MRA are requested by the oceanographic community (see for instance the recommendations of the 2022 BIPM/WMO workshop, i.e. 1B.3 ).
- Conductivity of feed water of steam turbines is measured in pure water at high temperatures.
- Conductivity is measured in non-aqueous matrices such as (bio)fuels.
- In the medical area and lifestyle area there is a significant tendency to downscale electrochemical sensors into the micro- and nanoscale region to implement them in mobile devices (lab-on-a-chip) or in cloths (wearables) to measure physiological parameters in blood such as electrolytes, glucose, lactate, or analyse sweat for potential health risks.
- Electrochemical measurement methods, such as stripping voltammetry, are applied in food industry to monitor food quality with respect to legal regulations.
- Likewise, the digital transformation of economy and society involves the application of miniaturized, multi sensor arrays, some of which also include electrochemical sensors. The quality assessment and quality assurance of data products that have been generated from electrochemical measurement results will require the application of adequate metrological concepts, i.e., with respect to interference, traceability and uncertainty propagation.
- The transition of the energy sector to a decarbonated energy and transport economy involves research into and application of electrochemical systems such as Li-ion batteries and fuel/electrolysis cells and related electrochemical measurement techniques to investigate and monitor electrochemical processes.

Significant step changes in any of the classical electrochemical services and classical chemical methods in metrology are unlikely in the foreseeable future. In the area of pH measurement, progress in solution theory and in the concept of single-ion activity are necessary to overcome the present limitations for the primary pH standards and to extend traceability to higher ionic strength for applications in clinical chemistry and in environmental samples (e.g. seawater) or to aqueous-organic solutions.

However, the application of electrochemical sensors in many areas of economic, societal, and environmental interest challenges global metrology in the electrochemical area. They require the development of new measurement methods, primary measurement standards and setups and even new measurands to address these demands technically, to establish traceability and international equivalence of electrochemical measurements.

Finally, there is also a non-technical, but nevertheless equally important challenge to be considered in future. The establishment of international equivalence of electrochemical measurements has strongly been driven by industrial stakeholders in the past, i.e., needing internationally accepted reference standards. The corresponding traceability structures and the verification of the equivalence of standards are manageable by EAWG and the linked institutions (RMOs, NMIs, calibration labs, accreditation bodies, etc.). However, response to global challenges such as climate change, digitization, food safety, or energy transformation is pushed by public institutions rather than by economic interests. The related stakeholder landscapes are extensive and diverse. Application of habitual traceability structures in these stakeholder communities might not be feasible, so that new concepts must be devised. Relevant actors are sometimes not even aware of metrology concepts. Consequently, the technical realization of adequate measurement methods is just one step to realise international equivalence in electrochemical (and probably other) measurements. Anchoring EAWG in communities that address the global challenges and establishing new ways to guarantee metrological comparability in these communities seems one of the most challenging future tasks.

## 3. CCQM-VISION AND MISSION

**The vision is:**

A world in which all chemical and biological measurements are made at the required level of accuracy to meet the needs of society.

**The mission is:**

To advance global comparability of chemical and biological measurement standards and capabilities, enabling member states and associates to make measurements with confidence.

**The responsibilities are:**

a. To demonstrate the global comparability of chemical and biological measurements, promoting traceability to the SI, and where traceability to the SI is not yet feasible, to other internationally agreed references.

b. To advise the CIPM on matters related to chemical and biological measurements including guiding international activities related to the definition and realization of the mole and advising on the BIPM scientific program.

c. To reach out to new and established stakeholders to promote the international measurement system and prioritize needs.

d. To progress the state of the art of chemical and biological measurement science and act as a forum for the exchange of information about measurement research, technical programs and service delivery.

e. To contribute to the implementation and maintenance of the CIPM MRA with respect to chemical and biological measurements.

**Strategic Aims:**

In line with the CCQM's vision and mission, the aims of the 2021 to 2030 strategy are

**To contribute to the resolution of global challenges** such as climate change and environmental monitoring, energy supply, food safety, healthcare including infectious disease pandemics, by identifying and prioritizing critical measurement issues and developing studies to compare relevant measurement methods and standards

**To promote the uptake of metrologically traceable chemical and biological measurements**, through workshops and roundtable discussions with key stakeholder organizations, to facilitate interaction, liaison and cooperative agreements, and receive stakeholder advice on priorities to feed into CCQM work programs.

**To progress the state of the art of chemical and biological measurement science,** by investigating new and evolving technologies, measurement methods and standards and coordinating programs to assess them.

**To improve efficiency and efficacy of the global system of comparisons for chemical and biological measurement standards conducted by the CCQM**, by continuing the development of strategies for a manageable number of comparisons to cover core capabilities.

**To continue the evolution of CMCs to meet stakeholders needs**, incorporating the use of broad claim CMCs where applicable to cover a broader range of services and considering options to present these in a way that meets stakeholder needs and encourages greater engagement with the CMC database.

**To support the development of capabilities at NMIs and DIs with emerging activities,** by promoting a close working relationship with RMOs including mentoring and support for NMIs and DIs preparing to coordinate comparisons for the first time and promoting knowledge transfer activities including workshops, as well as secondments to other NMIs, DIs and the BIPM

**To maintain organizational vitality, regularly review and, if required, update the CCQM structure for it to be able to undertake its mission and best respond to the evolution of global measurement needs,** by prioritizing where new areas or issues should be addressed within the structure and evolving working group remits as required.

## 4. STRATEGY

As in the past, EAWG will continue supporting the international equivalence of electrochemical and classical chemical measurements. EAWG aims to provide a sound metrological foundation to various social and industrial areas such as food, environment, energy, health, research, chemical industry, and others. In this regard, EAWG will focus on the measurement quantities pH, electrolytic conductivity, amount of substance measurement using coulometry, gravimetry, and titrimetry.

EAWG aims to support its members in progressing state of the art electrochemical measurement science, and new and evolving technologies. This will especially consider optical pH measurements in seawater under high pressure, propagation of an SI traceable pH scale allowing measurement in matrixes beyond dilute aqueous solutions, measurement of components in medically relevant fluids (such as blood and dialysate solution), impedance spectroscopy of battery cells and fuel/electrolysis cells (use/generation of green hydrogen), extension of the conductivity measurement range with respect to conductivity, temperature, pressure and new matrices (including development of relevant reference materials), extension of coulometric measurements to new analytes, and electrochemical sensors. New electrochemical systems such as integrated, miniaturized, multi-sensor systems and their metrological challenges will be considered.

EAWG will support its members in their efforts to contribute to the resolution of global challenges. These efforts will focus on essential climate and ocean variables with respect to electrochemical and classical chemical measurement methods to support climate change research and ocean observation systems [1], and advances in the energy and transportation sector towards green energy.

EAWG will promote the uptake of adequate metrological references, preferably the SI, by concerned communities. It will particularly support its members in their engagement with stakeholders from industry, the oceanographic community, the energy sector, the medical sector, standardization, and accreditation bodies to establish adequate traceability structures within these areas.

EAWG will discuss new forms of communication and data exchange within the group considering the opportunities given by the internet.

## 5. ACTIVITIES TO SUPPORT THE STRATEGY

EAWG will advance the global measurement system with respect to electrochemical measurands through a number of activities addressing the strategic aims mentioned above. They will be tailored to the stakeholder needs, which are usually brought to the attention of EAWG through its members. EAWG will mainly conduct pilot studies and key comparisons to achieve these aims and it will provide an international platform for knowledge exchange on issues related to the equivalence of electrochemical measurements. Upon request by its members, EAWG will establish task groups to deal with issues related to the equivalence of specific measurements.

### 5.1. PROGRESSING METROLOGY SCIENCE

Challenges and activities to progress the state of the art of measurement science will be summarized in the following for the most relevant electrochemical quantities and methods.

**pH**

Progress in solution theory and in the concept of single-ion activity are necessary to overcome the present limitations for the primary pH standards and to extend traceability to higher ionic strength for applications in clinical chemistry and in environmental samples (e.g. seawater) or to aqueous-organic solutions. More work will be done also on official underpinning of relevant secondary measurement capabilities, including matrix effects. Contributions of the residual liquid junction potential, present in all non-primary pH measurements, including quantification of its contribution to uncertainty, are still required for the dissemination of pH, especially in more complex matrixes.

Even if theoretical problems will be solved, comparability of pH measurement results for more complex matrices, i.e. different solvents or solvent mixtures, is not yet achieved. Because each solvent has a different standard state, pH values within the same solvent can be compared to each other, but pH values between different solvents cannot. EAWG will follow the theoretical and practical progress towards the introduction of a universal pH (noted $pH_{abs}$) concept, currently made in a EURAMET project, spanning all solvents and phases. It will be linked to the so called $pH_{abs}^{H_2O}$-scale, considered as the "intersolvental" continuation of the classical aqueous pH-scale. The concept of a unified pH scale, so called $pH_{abs}$, will be considered to overcome the fundamental limitation of pH as a basically water-based quantity that cannot easily be applied to other solvents [2]. A pilot study to investigate its applicability might be considered. "$pH_e$" (the pH scale relevant to high ethanol content water-ethanol mixtures) has been proposed as a quality metric for the international trading of bioethanol. However, due to limitations of this pH scale, and identified issues with the proposed method-defined measurand, provision of measurement services (with international comparability) of the $pH_{abs}^{H_2O}$-scale for water-ethanol mixtures (i.e., bioethanol) may ease any barriers in trade of "green fuels."

pH standard solutions for seawater such as Tris buffers, the pH of which is similar to that of seawater, are demanded over a wide temperature and salinity range (0°C – 30 °C, and salinities 5 to 40 g/kg) to provide traceability for optical pH measurements, which are most common in oceanography [3] to investigate ocean acidification due to climate change. A pH reference electrode that is insensitive to salinity variations is developed within a metrological research project for alkalinity in deep-sea. EAWG will support respective activities of some NMIs in this area. EAWG plans to extend its scope into the area of electrochemical measurements in oceanography. A task group on the pH and the salinity (see below) of seawater is under discussion. A pilot study and a key comparison on seawater pH are planned.

pH measurements in fluids of biological interest are of critical importance in the medical industry. Continued implementations of reference methods, recognized by the IFCC and ideally traceable to the SI, are critical. Further, development of miniaturized, and implantable sensors for real-time monitoring of pH in real-time are likely to require a clear means of traceable calibration.

First ideas have been discussed to address pH measurements under high pressure which are frequently performed in oceanography, i.e., next generation Argo floats will be equipped with such sensors. However, the metrological support for this kind of measurement must be established yet. EAWG will support regional research projects in this area by providing a platform for discussion and pilot studies in case of need.

**Conductivity/impedance spectroscopy**

Many applications tend to push the limits of conductivity measurements into more extreme ranges with respect to conductivity, temperature, pressure, sensor size, sensor integration, and matrixes. As a consequence, some institutes have started metrological research projects to address these demands, such as measurements in ultra-pure water, extended temperature ranges, conductivity based measurements of seawater salinity up to 2000 MPa, measurement in volatile matrices (e.g., biofuels), or in situ measurements of small amounts of battery electrolytes.

Furthermore, efforts are undertaken to establish new measurement methods to quantify the state of health and state of charge of Li-ion batteries, used in electromobility applications and in the energy sector, by electrochemical impedance spectroscopy. As part of the green energy transition, the increased use of both fuel and electrolysis cells is anticipated. Impedance spectroscopy is already used in the research & development phase of these devices. New, standardized measurement methods will be required for these devices as their use increases for renewable fuel consumption (fuel cell) and generation (electrolysis cell).

EAWG will provide a platform to present the results of such projects. It will support knowledge transfer to other institutes aiming at a broader bases to establish international equivalence in new measurement ranges and applications. These will include supporting the development of industry relevant reference materials, and conductivity sensor calibration services (round-robin type comparisons).

Primary and secondary conductivity measurement systems can fundamentally be used to measure the conductivity of any kind of electrolyte solution traceable to the SI, independently from the matrix. One of the main challenges is understanding the impedance spectrum that is usually measured to derive the solution bulk resistance [4].

**Coulometry**

Coulometry is one of the primary direct methods in chemistry and is invaluable for assay determination - a key first step to providing SI traceability for chemical measurement. Coulometry also supports primary pH measurements. The skill of EAWG participants in undertaking this measurement adds significant value to the joint IAWG/EAWG pure materials comparisons.

Specialized key comparisons are needed to benchmark the capability of the participating institutes to handle the involved chemistry. Determinations of acids, oxidants, and chlorides were tested; determination of bases (sodium carbonate), reductants (sodium oxalate) and complexing agents (EDTA) will complete the range. Other analytes to be discussed in future will be sulfuric acid and sodium fluoride. Another application of coulometric titration and potentiometry would be the measurement of antioxidant capacity in human blood, pharmaceuticals, food, drinks etc. [5]

Instruments to measure essential ocean variables of the seawater $CO_2$ system, or related products, i.e. 'dissolved inorganic carbon (DIC)' and 'total alkalinity (TA)', are calibrated in practice with seawater standards. The quantity values of these seawater standards are derived from measurement procedures that involve coulometric measurements, the traceability and uncertainty of which has not been specified on solid metrological grounds. EAWG members are asked by the oceanographic community to support respective investigations and establish measurement capabilities to characterize respective seawater standards, and to support their equivalence in the context of the CIPM-MRA.

**Other (electrochemical) methods**

A variety of further measurement methods and electrochemical sensors fall into the responsibility of EAWG that require metrological research or, at least, metrological support. Stakeholders have for example expressed needs to address the following measurement techniques:

- stripping voltammetry to measure cadmium in cacoa beans,
- ion-selective electrodes to measure electrolytes in laboratory medicine
- electrochemical sensors to measure dissolved oxygen and $CO_2$ in the environmental area and in the clinical area,
- electrochemical biosensors for non-invasive diagnostic [6],
- gravimetry performed by conversion to sulfate salt to assay the contents of sodium ions in sodium fluoride and of potassium ions in potassium hydrogen phthalate

Often, such needs are addressed by individual NMIs through local collaborations.

### 5.2. Improving stakeholder involvement

The scope of EAWG covers electrochemical measurements in various sectors. Stakeholders within these sectors are public institutions as well as companies. EAWG mainly interacts with them in a bottom-up approach. Thus, the work program of EAWG is mainly driven by its members and their national/regional programs in metrology and the interaction with their stakeholders, which in turn express their needs for world-wide comparability of specific electrochemical measurements through the NMIs.

In this way the following links have been established and will be maintained:

- Collaboration with calibration and testing laboratories
- Collaboration with national accreditation and standardization bodies, such as ISO, ILAC, CEN, REMCO, DIN, AFNOR, etc.
- Collaboration with producers of certified reference materials, i.e., with respect to pH, electrolytic conductivity standards and CRMs of high-purity substances and calibration solutions as well as some matrix CRMs characterized by titrimetry.
- Collaboration with chemical industry
- Collaboration with medical institutions
- Collaboration with other international bodies related to metrology in chemistry such as IUPAC and OIML
- Collaboration with manufacturers of electrochemical sensors
- Collaboration with universities

These stakeholders coming from many nations have demanded continual dissemination of fundamental pH standards: oxalate, phthalate, phosphate, borate, and carbonate buffers, conductivity standards and different types of CRMs of substances.

Further links have been established by individual NMIs or a group of NMIs and will be continued as appropriate:

- Links to the oceanographic community have been recently established to support the development of traceability concepts for salinity and pH measurements in seawater. In this regard, members of EAWG also actively participate in the work of related international organizations and bodies such as IAPSO (International Association for the Physical Sciences of the Oceans), IAPWS (International Association for the properties of water and steam), JCS (IAWPS/IAPSO-Joint Committee on Seawater) and JPI-Ocean.
- Collaboration with fuel industry to characterize pH standards of ethanol/water mixture.
- Collaboration with automotive industry (with respect to electrochemical storage systems) and producers of batteries and fuel/electrolysis cells.
- Collaboration with the nuclear power plant industry for industrial control of the plutonium content in the MOX fuel (Mixed-Oxide fuel).
- Collaboration in European Metrology Networks.
- Participation in metrology research programs such as the European Metrology Programme for Innovation and Research (EMPIR).
- Collaboration with medical/pharmaceutical industry, especially in the dissemination of electrolytic conductivity over a wide conductivity and temperature range.
- Collaboration with food industry

### 5.3. PROMOTING GLOBAL COMPARABILITY

EAWG will continue to coordinate repetitions of key comparisons for the fundamental calibration and measurement capabilities (CMC) of electrochemical measurands, methods and CRMs to promote the international equivalence in measurement within the framework of the CIPM-MRA. For the most part, CMCs of EAWG are supported by directly related key comparisons.

Regarding fundamental aqueous pH reference solutions, the working group aims at regularly conducting key comparisons for all primary standard buffer solutions mentioned in the IUPAC Recommendations 2002 [7]. EAWG has classified pH key comparisons as 'core capability' (i.e. easier to measure) or 'extended capability' (i.e. more difficult) and has defined criteria to base pH CMCs on the participation in key comparisons of these categories. EAWG will make sure, that key comparisons of both categories are conducted within a five-year period, so that NMIs can maintain their CMCs without the need to conduct comparisons of all buffers within the CMC validity period of 10 years.

All other CMCs, i.e. those related to conductivity and coulometry, are directly supported by respective key comparisons within the range of the "How far the light shines" statements.

Conduction of comparisons to cover the conductivity range in the ultra-pure and pure water region is currently pushed by EURAMET but will be established at EAWG in future, since more and more institutes outside Europe have started to provide respective calibration services.

Furthermore, EAWG will be a forum allowing for bilateral comparisons, e.g., to confirm measurement capability and permit verification of new CRMs, strongly suggested under international guidelines (e.g., ISO) and by national accreditation bodies (supporting national CMCs).

In general, only a limited number of comparisons can be performed in view of manpower restrictions. It must be noted that electrochemistry groups at institutes usually consist of 1-6 persons. Necessary resources can vary widely depending on the institute, comparison type, sample and difficulty. Piloting a comparison usually requires between 2 to 6 person-months. Moreover, just a small number of institutes are currently carrying the workload to pilot comparisons, since many labs either lack the resources or the experience.

At present, the number of key comparisons needed to constantly support the existing CMCs is relatively small in EAWG compared to other working groups. However, the number of measurands and corresponding CMCs is increasing. Therefore, extending the validity range (how far the light shines) of specific key comparisons will be discussed in the next decade. More efforts should be undertaken to promote the international equivalence of CRMs by model 2 type of comparisons. They have hardly been considered in the past, even though the majority of NMIs provide their metrological services in the electrochemical area mostly by selling CRMs. However, there are by no means enough resources available to also support CRM-CMCs in the same manner as measurement CMCs. Two pilot studies have been conducted in the last decade. Thus, there is at least some support for CRMs available at EAWG. Ways to nevertheless support CRM-CMCs adequately will be established within the next decade. Furthermore, efforts will be undertaken to gain new pilot laboratories.

Further comparisons planed within the strategic planning period are:

A new pilot study and subsequent key comparison on solutions with pH values > 11 (e.g. calcium hydroxide) is planned.

A pilot study and a key comparison on the pH of seawater/Tris and/or artificial seawater/Tris solutions will be conducted to characterize the equivalence of standards for optical pH measurements and pave the way for respective CMCs.

A pilot study will be conducted investigating the equivalence of impedance measurements using a variety of conductivity measurement cells.

Salinity of seawater is an essential ocean and climate variable, monitored by ocean observation systems to assess the implications of climate change. It is based on conductance ratio measurements. These are traceable to a stand-alone metrological reference defined in the oceanographic community, the so-called PSS-78. EAWG aims to include this measurand in its scope. A pilot study has already been performed. A key comparison or a regional, supplementary comparison is planned.

A number of coulometric comparisons (pilot and key) will be performed to provide support for international equivalence for new analytes and new types of coulometric measurements, i.e. the measurement of bases (sodium carbonate) using back-titration, reductants (sodium oxalate) and complexing agents (EDTA).

The table below gives an updated overview on regular and new comparisons.

| year | pH | | conductivity | | coulometry | | pilot study |
|---|---|---|---|---|---|---|---|
| | **KC-ID** | **buffer** | **KC-ID** | **value (solution)** | **KC-ID** | **assay** | |
| 2021 | | | | | K173 | sodium carbonate | P221 Tris/seawater pH |
| 2022 | K91.2022 | phtalate (extended) | | | | | |
| 2023 | | | K170 | 0.5 S/m (KCl)<br>20 S/m (KCl) | K96.2023 | potassium dichromate | |
| 2024 | Kxxx | Tris/seawater | | | K169 | sodium oxalate | P228 Impedance / conduct. |
| 2025 | K20.2025 | tetroxalate (core) | Kxxx | | Kxxx | EDTA | pH >11 (e.g. calcium hydroxide) |
| 2026 | | | Kxxx | 0.05 S/m (KCl)<br>5 S/m (KCl) | K48.yyyy | KCl | |
| 2027 | Kxxx | Extended buffer, e.g. (calcium hydroxide or carbonate) | | | | | |
| 2028 | | | | | K73.yyyy | HCl | |
| | | | | | K34.yyyy | KHP | |
| 2029 | Kxxx | Core buffer: e.g. tartrate or phosephate) | Kxxx | 0.055-50 µS/cm (pure water) | | | |
| 2030 | | | | | K152.yyyy | potassium iodate | |

## 5.4. INTERACTION WITH RMO ACTIVITIES

The RMOs feature an important role to establish worldwide comparability of electrochemical measurement results. RMOs have already coordinated comparisons linked to EAWG-key comparison in the past. RMO members which are not represented in EAWG have been integrated in the mechanisms of the CIPM-MRA in this way and they have been enabled to benchmark their measurement and calibration capabilities with respect to sound key comparison reference values. It is expected that these regional activities will be continued in future, after the respective key comparisons have been concluded.

EURAMET has established significant metrology research programs in the past and it seems that these efforts will continue in the next decade. The outcomes of some of these research projects are having direct effect on the activities of EAWG. Activities related to pure water conductivity, seawater salinity and pH and impedance spectroscopy are examples of these efforts. Currently, EURAMET is establishing European Metrology Networks (EMN). EAWG members have close links to the ocean section of the EMN for Climate and Ocean observation, basically focusing on seawater salinity and pH. Further networks are expected. It is possible that EAWG will establish links to networks dealing with energy, pollution, and food quality monitoring.

# ANNEX

## 1. General information

| | |
|---|---|
| **CC Name** | CCQM; Consultative Committee for Amount of Substance – Metrology in Chemistry |
| **CC Working Group** | WG on Electrochemical Analysis and Classical chemical Methods |
| **Date Established** | 1998 |
| **Number of Members** | 31 institutes |
| **Number of Participants** | at last meeting: 42 |
| **Periodicity between Meetings** | 1-2 per year |
| **Date of last meeting** | 29 October 2024 |
| **CC WG Chair** | Steffen Seitz, Physikalisch-Technische Bundesanstalt, 5 years in post |
| **Number of KCs organized** (1999 up to and including 2024) | 45 (including 16 jointly with IAWG) |
| **Number of Pilot studies organized** (1999 up to and including 2024) | 23 (including 9 jointly with IAWG) |

**Number of CMCs** published in KCDB supported by CC body activities
(up to and including 2024)

| | |
|---|---|
| Electrolytic conductivity | 66 |
| pH | 122 |

plus a number of inorganic CMCs supported by joint comparisons with IAWG (based on coulometry)

**Terms of Reference**

The responsibilities of EAWG are:

(1) To carry out Key Comparisons, and where necessary pilot studies, to critically evaluate and benchmark NMI/DI claimed capabilities and competences for electrochemical measurement quantities and classical chemical methods, in particular: pH, ionic activities, electrolytic conductivity, coulometry, titrimetry and gravimetry; providing demonstrable evidence of the validity and international equivalence of NMI measurement services offered to customers.

(2) To identify and carry out inter-laboratory work and pilot studies required to underpin the development of reference measurement systems in the field of electrochemical metrology, of the highest possible metrological order with traceability to the SI, where feasible, or to other internationally agreed units, to support NMI/DI measurement services being developed in response to customer needs.

(3) To act as a forum for the exchange of information about the research and measurement service delivery programs and other technical activities of the WG members in electrochemical metrology and thereby creating new opportunities for collaboration.

## 2. List of planned key and supplementary comparisons and pilot studies

*available at https://www.bipm.org/utils/common/xls/CCQM_KCs_PSs.xls*

## 3. Summary of work accomplished and impact achieved (2017-2020)

In the period from 2017 to 2020, EAWG has conducted or completed 7 key comparisons from the three electrochemical areas the group is occupied with, i.e. pH, conductivity and coulometry. 6 of them have been repeat comparisons to maintain support for respective CMC claims. One key comparison, also including a pilot study, was conducted to provide support for a new analyte (potassium iodate).

An important pilot study was conducted to provide support for equivalence of pH CRMs (see case study 1). Institutes from 3 RMOs are involved in seawater pH measurements in the meanwhile. Even though no comparisons have been conducted at EAWG level yet, EAWG has provided a platform in the last years to discuss related metrological issues, finally resulting in the upcoming pilot and key comparisons, which will pave the way for equivalence in ocean pH measurements (case study 2). Finally, there is an increasing demand in industry for calibration services and CRMs in the low conductivity range. EAWG supported a respective EURAMET study in terms of a supplementary comparison, thereby opening the comparison to participants from other RMOs to ensure international equivalence in this difficult conductivity range (case study 3).

**Case studies to demonstrate recent activities to maintain and improve the equivalence of electrochemical measurements**

| Case study 1: Support for equivalence of pH CRMs |
| --- |
| Up to now, the vast majority of CCQM comparisons in general, and of EAWG in particular, is clearly related to the equivalence in measurement (model 1 type of comparisons). In fact, many NMIs sell CRMs to disseminate electrochemical units rather than performing calibration services. While model 1 comparisons are important to support the international equivalence of the quantity value assigned to CRMs, they give no information on the stability and homogeneity uncertainty of them. The assessment of uncertainty claims of respective CRM-CMCs is therefore not based on sound comparison data. In best case, the submitting laboratory provides a test report when submitting an CMC. Usually, the CMC reviewer can only assess the uncertainty claim of an CRM for plausibility. To overcome this unsatisfying situation, EAWG has conducted two model 2 type of comparisons: P143 for conductivity (concluded in 2016) and P93 for pH (concluded in 2020). The pilot studies aimed to give information on the equivalence of the CRMs provided as services by the NMIs/DIs, as given in the Appendix C of the CIPM-MRA. For this reason, the samples to be measured should have been preferably taken from an existing batch of CRM. However, the participants could produce a fresh batch in the same way as when producing a batch of CRM for sale. Each CRM was measured within 4 weeks after the samples were arrived at the coordinating laboratory, and were also measured 3 months later, in order to assess the stability of the materials, and thus, indirectly, the suitability of the packaging. From the certified values and the results of measurement, a reference function was established, and respective degrees of equivalence have been derived. These studies can be used to give further evidence for claimed CRM uncertainties in pH and conductivity CMC claims. Strictly spoken, they can only be used for the specific types of CRMs measured in the comparison. However, they give, for the first time, some general evidence of the relation between measurement CMCs and CRM-CMCs. |
| **Case study 2: pH of seawater** |

Mitigating the effects of climate change has increasingly become the prime driver in politics at an international level. The on-going uptake by the ocean of anthropogenic atmospheric $CO_2$ is resulting in a decrease in pH, a process termed ocean acidification. Reliable monitoring of ocean pH has therefore become an important international task, that has also been reflected in the Sustainable Development Goals issued by the United Nations (target 14.3 specifically addresses the need to "minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels"). The reliability of results, i.e. their metrological comparability, provided by databases of global ocean observation systems is crucial. The traceability, even the definition, of seawater pH measurements are ambiguous. Furthermore, the requirements to measurement uncertainty are challenging since ocean acidification is a slow process. In the last decade, European NMIs have addressed these metrological issues within the European metrology research programs. The results and related problems have been regularly presented and discussed within EAWG. In the meanwhile, NMIs from SIM and AMPM are also addressing seawater pH. Through the discussion at EAWG, the issue has been lifted from the regional to the international metrological level. As a consequence, a pilot study on the characterization of the pHT values of artificial seawater/Tris buffers has been conducted to assess the international equivalence of seawater pH measurement results at NMI level. A respective KC is planned. Furthermore, an CCQM EAWG Task Group on the Metrological traceability for seawater pH and $pH_T$ values has been established. The TG aims to define the metrological traceability for pH and $pH_T$ measurement results, to implement pH and $pH_T$ measurements in the CIPM-MRA framework and to prepare a liaison between international stakeholder organisations relevant to ocean pH and $pH_T$ measurements with CCQM.

## Case study 3: Conductivity in the pure water range

Electrolytic conductivity in aqueous solutions is one of the most common electrochemical measurement techniques in industry. Since it is sensitive to the amount content of dissolved ions in a solution, a limiting value for conductivity is a clear and simple quality criterium for the ionic purity of pure water (~ 0.055 $\mu S\ cm^{-1}$ to 150 $\mu S\ cm^{-1}$ at 25 °C). For instance, the European, Japanese and United States (USP) Pharmacopoeia have specified the requirements for purified water, highly purified water and water for injection for pharmaceutical use based on conductivity. Sectors that also use conductivity limits for water purity are electrical power production, food industry, electronic industry and analytical laboratories. International regulations are becoming stricter with regards to metrological traceability to guarantee compliance of measurement results with relevant standards. Consequently, the NMIs active in this area have been facing an increasing request for the calibration of respective conductivity sensors and for adequate CRMs over the past years. First activities to address these demands have mainly been started by EUARAMET. A first, regional comparison has been conducted in 2013/14 (EURAMET 1271). Since an increasing number of NMIs, also from other regions, seek providing respective services and establishing CMCs, EURAMET, i.e. the Sub-Committee on Electro Analysis of TC-MC, opened a follow-up comparison to EAWG in terms of a supplementary comparison (EURAMET.QM-S12, 2018-2020). The comparison has proven good equivalence between the results, which is now enabling NMIs (6 from Europe and 4 from other regions) to support their services by respective CMCs. Furthermore, the usefulness of supplementary comparisons has been demonstrated, so that NMIs from other regions can benefit from activities that are mainly conducted at an individual RMO.

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## 5. DOCUMENT REVISION SCHEDULE

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