

Template for: Strategy 2021-2030

Consultative Committee for Amount of Substance; Metrology in Chemistry and Biology

CCQM Working Group on Surface Analysis

1. EXECUTIVE SUMMARY

Surface chemical analysis is required by a broad range of advanced industrial sectors. It influences decisions which affect product lines and economic activity across the globe. The metrological challenges are difficult to solve and the analytes and matrixes are manifold. Within this document we identify relevant technologies which have specific measurement needs within the scope of the Surface Analysis Working Group. There is a growing need for accurate surface chemical measurements and nanoparticle chemical measurements. We see this demand as a significant opportunity for NMIs to position themselves as the source of that accuracy. Key comparisons in this area are challenging to perform, largely because of the exacting requirements of reference materials, therefore the SAWG strategy will focus on specific activities that demonstrate a wider capability. In this regard, the important measurands that relate to our capabilities are: the measurement of relative elemental composition at a surface; the measurement of the amount of substance in a thin layer either at the surface or close to the surface; the measurement of the chemical properties of nanomaterials. In all these activities our aim is to establish traceability to the SI through fundamental physical understanding but note that in some areas this is not possible. In such areas there is still a pressing need to establish a common and unified approach at the highest metrological level and SAWG can act to co-ordinate international consensus in these areas.

In this document we set out a work plan which will address these measurands and, where relevant, the overlaps and interactions with other Working Groups. In recent years, we have initiated a strong collaboration with IAWG in the measurement of nanoparticle concentration. We have also noted that other Working Groups have interests and capabilities that overlap this measurement requirement. Within the core area of SAWG, one of the primary gaps that has been identified is the requirement for a KC to assess the measurement of relative elemental composition through which useful CMCs can be claimed and this will be addressed as a strategic priority.

2. SCIENTIFIC, ECONOMIC AND SOCIAL CHALLENGES

Metrology for surface chemical analysis at the nano and micro scales is a horizontal scientific-technical field which underpins almost all subject fields in natural sciences and engineering. It is a technically wide and multidisciplinary field under a common methodology – characterized by the scientific treatment of measurement uncertainties, mathematical methods and principles of metrological traceability. Metrology for surface chemical analysis at the nano and micro scales is a developing part of metrology in chemistry which is considered as one of the most rapidly growing fields of metrology, driven by the need for reliable chemical measurements in many fields of our daily life and requests from global trade and national as well as international legislation. Progress in such metrology needs to establish the degree of equivalence of national measurement standards maintained by NMI/DIs in all relevant disciplines of measurement, including surface chemical analysis at the nano and micro scales. Grand challenges identified so far comprise to meet key socioeconomic objectives in the fields of health, energy, environment, and new technologies. The priority setting for SAWG activities will be carried out in consultation with key stakeholders.

Amongst the new technologies, nanotechnology is a key enabling technology in which measurement infrastructure requires significant attention. The driving forces behind are the demand for ever increasing integration, e.g. in electronics and information technology, as well as the possibility of achieving new functionalities which are not possible otherwise such as through nano-structured surfaces, photonic crystals, optical meta-materials, quantum computing, energy materials, and nano-particles. In many cases in nanotechnology, quantum-mechanical effects prohibit a scaling-down of properties of larger systems and thus require new scientific approaches. For surface chemical analysis at the nano and micro scales, the key challenges have been identified in fields as the development of metrologically underpinned characterization tools and protocols for analysis of nano-structured surfaces, nano-particles, nano-electronics, nano-magnetic and nano-electro-mechanical systems and nano-materials. The increasing focus on graphene and other 2D materials as well as energy materials such as supercapacitors, batteries and fuel cell electrodes are of great relevance to SAWG.

Metrology which has to be developed for the field of health has to underpin the more reliable and efficient exploitation of diagnostic and therapeutic methods and the development of new techniques, which are needed to improve health care, limit costs and foster the competitiveness of the related industries and services. In addition, legislation requires new approaches to be covered by metrology and related measurement capabilities. The most competitive metrological activities within worldwide national research programmes are directly related to health applications. Key challenges which will be addressed also by surface chemical analysis at the nano and micro scales are the expansion of the range of “reference measurement procedures and reference materials of a higher order”, better quantitative diagnostics including imaging, modern microscopy and traceable multimodal measurement procedures and improved diagnostic devices (e.g. “lab-on-a-chip”), and therapeutic instrumentation. Additionally, the increasing use of nanomaterials will increase the discussion of the risks of such nanomaterials for health and the environment. In this field, the importance of surface properties is indisputable and reflects in activities of international organizations like the European Chemical Agency (ECHA) or the OECD.

The development of new materials with functional surfaces is another field resulting in demands on future developments in surface chemical analysis at the nano and micro scales. Developments in materials science and engineering are pervasive as the building blocks for everything around us contributing enormously to improvements in health, the environment and wealth creation through, for example, modern medical implants, cheap renewable energy from photovoltaic or major changes in telecommunications. Material science is undergoing a revolution: new materials with surfaces “designed for function” offering the potential to generate products and provide services that would be impossible with conventional materials. However, such materials, in particular higher performance nano-materials, bio-materials, meta-materials, hybrid materials and materials for quantum devices, bring particular metrological challenges due to their very nature, scale and special properties and the combination of two or more functions at a single material’s surface. It is important to be able to quantify the complex interplay of the microscopic state and the resultant surface properties. Major challenges exist in validating and understanding the interrelationship of measurements in these areas: physical-chemical properties at surfaces and structural and compositional analysis. Establishing confidence in these measurements enables certification and other regulatory requirements to be met.

3. 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

The constituent elements, the chemical state of the elements, and the spatial arrangement of the elements are the dominant factors in the development of a material's function. Establishing a robust basis for the metrology necessary for their quantitative evaluation and quality control on the nanometer scale is the mission of the SAWG/CCQM. The vision is for the involved NMIs and DIs to provide accurate and comparable measurements of the quantity of chemical species on a length scale typically smaller than 100 nm.

SAWG will focus on the following four items:

- (1) 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 spatially resolved chemical surface analysis at the micro and nanoscale; 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 spatially resolved chemical surface analysis at the micro and nanoscale, 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 programmes and other technical activities of the WG members for spatially resolved chemical surface analysis at the micro and nanoscale and thereby creating new opportunities for collaboration.
- (4) To provide scientific validity to the measurement comparability that other WGs are seeking to establish.

5. ACTIVITIES TO SUPPORT THE STRATEGY

5.1. PROGRESSING METROLOGY SCIENCE

Following the strategic direction for SAWG, the primary aims of activities within SAWG are to address the following measurement challenges:

1. Accurate measurement of chemical composition and amount of substance in thin films, layers and coatings from atomic layers to 1 micrometre thickness to support the development of advanced technologies. For example, establishing traceability for compositional measurements of homogeneous thin films (ionic liquid pilot) and amount of material in thin layers (hafnium oxide KC and buried organic layer pilot)
2. Develop metrological understanding of methods used to map or image chemistry on the lateral scale length of less than 1 millimetre with high lateral resolution and to understand the uncertainties which arise from lateral inhomogeneity. For example, a pilot study on Raman microscopy.
3. The development of a metrology infrastructure for the chemical measurement of nanostructured and highly porous materials, maintaining and building upon gas sorption measurements.
4. Support the development of chemical metrology for nanoparticles in concert with other, relevant, working groups. For example, Gold nanoparticle concentration with IAWG.

SAWG will also act to underpin the measurement services of NMIs and DIs that provide surface chemical analysis and will conduct Pilot Studies and Key Comparisons to establish relevant CMCs which support those activities. The primary measurement services offered within the scope of SAWG include the measurement of surface elemental composition and the measurement of the amount of material in a thin film. These measurements are, in principle, traceable to fundamental atomic data, such as photoionization cross sections. The uncertainties of these and other parameters such as transport of photons, electrons or ions through matter and instrumental effects require attention. To address these SAWG will establish a series of studies with the primary aim of achieving traceable measurement of the surface elemental composition of pure materials using X-ray, electron and ion beam analysis. Here, support may be required from BIPM Laboratories and Services and other WGs to establish the bulk purity of the materials used in these studies.

5.2. IMPROVING STAKEHOLDER INVOLVEMENT

Relevant stakeholders of SAWG are listed below:

1. NMI/DIs: Delivery of measurement comparability of calibration and measurement capabilities used by CCQM NMI/DIs in delivering services to their customers in the area of surface chemical analysis at the nano and micro scales. Customers are testing laboratories in industry (for specific fields see 3.) and governmental and supranational institutions as well as regulation bodies,
2. Metrology organizations such as RMO Chemical technical committees,
3. Wide spread industry sectors¹,
4. OECD Sponsorship programme for the testing of manufactured nanomaterials,
5. National and international trade organizations,
6. National and international professional organizations.
7. Standard development organizations (SDOs) and VAMAS.

The accurate measurement of surface chemistry is of major importance to a wide range of innovative industries and, due to the increasing concern over irreproducible results there is an increasing need to develop, demonstrate and disseminate accurate methods. We see this as a major opportunity for the Surface Analysis Working Group and will direct significant effort in the coming years to ensure that NMIs and DIs are positioned to be the source of traceability to their customers for these measurements.

The involvement of those stakeholders into decisions about measurement needs works through the many collaborative links of the NMI/DIs participating in SAWG. All of them are in direct contact to the stakeholders or even actively participating in their working programmes.

The increasing amount of out-sourcing of surface and microanalysis is driving the need for laboratory accreditation such as ISO 17025 and demonstration of competence for accurate measurement is of increasing importance with emerging regulation activities. The outcome of SAWG comparisons is beneficial to those stakeholders listed above. A major route to engagement and consultation will be through SDO activities led by members of SAWG, of specific importance are ISO TC229 (nanotechnologies) and ISO TC201 (surface chemical analysis).

1. ¹ Nanotechnology, microelectronics, photonics, photovoltaic devices, coatings for optical, wear, etc., bonding and corrosion for aerospace and transport, protein adhesion and toxicity for body implants, polymer surface changes for construction work, drug delivery and biosensing etc.; microanalysis has also a very broad suite of applications with particular emphasis on microelectronics, metallurgical products and materials for the body.

5.3. PROMOTING GLOBAL COMPARABILITY

In order to promote global comparability in the scope of the SAWG, the following activities are planned. Target measurands and measurement methods may change rapidly in the field covered by SAWG, we continually monitor the needs of society and industry.

2021 Key comparison on traceable measurement of the amount of substance in hafnium oxide thin film

2021 Key comparison and pilot study on measurement of nanoparticle number concentration in liquid suspension in conjunction with IAWG

2021 Key comparison on measurement of Specific Adsorption (mol/kg) of Ar on zeolite at 87 K to enable a traceability specific surface area

2022 Pilot study on Comparability of quantitative data for the amount of matter in a buried organic layer

2022 Pilot study on Traceable Quantitative Measurements with Raman Microscopy

2022 Pilot study on Surface Elemental Composition of Ionic Liquids

2023 Comparison to underpin a key enabling technology in the field of *nanotechnology* (to be defined following stakeholder demands).

2024 Key Comparison on Surface Elemental Composition of Ionic Liquids

2025 Comparison to underpin better *quantitative diagnostics* including imaging, modern microscopy and traceable multimodal measurement procedures and improved diagnostical devices and therapeutical instrumentation (to be defined following stakeholder consultation).

2026 Comparison to underpin the chemical measurement of graphene in functional devices (to be defined following stakeholder consultation).

2027 Comparison to underpin the amount of drug in nanomedicine delivery vehicles (to be defined following stakeholder consultation).

2028 Comparison in the field of New Materials with functional surfaces (to be defined following stakeholder consultation).

Broad Claims: It is not possible to support a large number of comparisons for every possible analyte within SAWG due to the demanding nature and expense of reference materials and analysis. Therefore, the activities outlined above are designed to demonstrate a broad capability, for example elemental composition or amount of material in a layer, using specific and relevant analytes. Currently CMC claims in SAWGs are specific but are designed to be extensible to other analytes. A general scheme has not yet been made on how to extend specific claims to have a broader reach and a position for SAWG will be decided after discussion and consultation with members and with CCQM in the next few years.

5.4. INTERACTION WITH RMO ACTIVITIES

Based on the environmental health and safety demands, several EMPIR projects and other EU projects, such as npSize, ISOGScope and ACEnano are underway in Europe. In TCMM/APMP pilot studies for thickness evaluation and scale correction for electron microscopy are ongoing. Although particle size and thickness are measurands with length dimension, measurement of the amount of substance could be key

to estimate reliable value when the target is extremely small. SAWG will provide essential information to establish the traceability of the amount of substance in nanoparticles, concentration of nanoparticles and both the amount of substance and composition nanoscopic layers. SAWG members are encouraged to contribute the RMO activities and VAMAS workshop related to the technical fields SAWG cover.

ANNEX

1. GENERAL INFORMATION

CC Name	CCQM	
CC Working Group	Surface Analysis Working Group (SAWG)	
Date Established	2004	
Number of Members	17 (16 NMI, 1 DI)	
Number of Participants at last meeting	25	
Periodicity between Meetings	1 Year in normal years	
Date of last meeting	Friday 5 June 2020, Virtual Meeting	
CC WG Chair	Dr. T. Fujimoto, AIST, 1 Year in post	
Number of KCs organized (from 2004 up to and including 2020)		8
Number of Pilot studies organized (from 2004 up to and including 2020)		13
Number of CMCs published in KCDB supported by CC body activities (up to and including 2020):		32

Terms of Reference

The responsibilities of the SAWG are:

- (1) 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 spatially resolved chemical surface analysis at the micro and nanoscale; 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 spatially resolved chemical surface analysis at the micro and nanoscale, 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 programmes and other technical activities of the WG members for spatially resolved chemical surface analysis at the micro and nanoscale and thereby creating new opportunities for collaboration.

2. LIST OF PLANNED KEY AND SUPPLEMENTARY COMPARISONS AND PILOT STUDIES

available at https://www.bipm.org/utis/common/xls/CCQM_KCs_PSS.xls

3. SUMMARY OF WORK ACCOMPLISHED AND IMPACT ACHIEVED (2017-2020)

CCQM-K153 Measurement of BET specific surface area of nonporous SiO₂, report published.

Because of its importance in the chemical and construction industry a study of the comparability of the measurement of Specific Surface Area was strongly requested by stakeholders of the participating

NMIs/DIs. The key comparison on the determination of specific adsorption of N₂ or Kr on nonporous silicon dioxide at liquid nitrogen temperature has been organized to enable a traceable determination of the Specific Surface Area (BET) of non-porous particulate substances. Five NMIs/DIs participated in this key comparison. All participants used the gas adsorption method. In general, very good agreement of the results has been observed. Validity of the procedure NMIs/DIs employed for the measurement of specific nitrogen and krypton adsorption at liquid nitrogen temperature to enable a determination of the BET specific surface area of non-porous particulate materials was confirmed.

CCQM-P190 Thickness (nm) of HfO₂ film

CCQM-K157 Thickness measurement of HfO₂ Films, Launched

The measurement of the amount of material in a thin film at the surface of a substrate is a core competence for members of SAWG. The first key comparison of SAWG, K-32, used the amount of silicon oxide on silicon as the measurand. In P190, and the recently launched K-157 this core competence is revisited to establish traceability and uncertainty in the measurement of the amount of material in oxide films at semiconductor surfaces. A critical feature of these studies is that there are no common elements between the substrate and the thin film, and this provides some additional complexity which has stimulated useful discussions within SAWG. The outcome of these discussions will enable NMIs and DIs to strengthen the metrological basis of their measurements and claim CMCs relevant to their stakeholders.

CCQM-P194 Measurement of nanoparticle number concentration in liquid suspension, significant SAWG contribution to IAWG study, report in preparation

CCQM-K166/P210 Measurement of nanoparticle number concentration in liquid suspension, with IAWG, will be launched

Particle number concentration is a measurement for which there is significant demand. The first steps toward realizing this measurand in a metrological manner were taken in the EMPIR Innanopart project, led by NPL and with significant involvement from LGC, PTB, BAM and INRIM. P194, led by LGC within IAWG was conducted concurrently with a VAMAS study (TWA34, project 10) led by NPL and using the same materials. There was a strong and useful contribution from SAWG in P194 and this has led to a joint IAWG / SAWG key comparison which will start in 2021. We have numerous reports from

NMIs and DIs within SAWG and IAWG that the reference materials and measurement methods are in strong demand from instrument manufacturers and industries, especially the pharmaceutical industry where nanoparticle drug delivery vehicles are being developed. This is an area where CCQM activity can have a strong and positive effect and we note that there are synergies with the recently proposed activity in CAWG “*Number concentration measurement of particles for cellular analysis*”.

4. REFERENCES

5. DOCUMENT REVISION SCHEDULE

SAWG – Strategy 2021-2030; type of revisions; 31/12/2020