Report from the CCQM Inorganic Analysis Working Group for the period (April 2024 – March 2025)

Michael Winchester, CCQM IAWG Chair

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Introduction

The IAWG has made excellent progress in its work over the past year. This year marks the first full year in which the IAWG operated from start to finish using the Decision Tree (DT, but often abbreviated NDT for NIST Decision Tree, because this methodology and software application were developed at NIST) for estimating KCRV values and uncertainties and degree of equivalence (DoE) values. The result is that five CCQM key comparisons have now been completed using the DT, including some that had been delayed while the DT was being developed by NIST and officially adopted by the IAWG. While not perfect (as is true for any approach to KCRV and DoE estimations), most of the IAWG members seem to regard the DT as a large improvement over past IAWG practice. It should serve the working group well until something better can be developed.

Global conflict remains. When necessary, the IAWG continues to operate according to the guidance from the CIPM that all work should continue to the greatest extent possible. Each situation is managed separately, but some general options delineated by the CIPM about 3 y ago are:

- Comparisons can be postponed or extended, or definite plans for a linked supplementary comparison (to be undertaken when world events have settled down) can be made, so that the original comparison may continue unhindered.
- Samples may be shipped through intermediaries.
- Likewise, communications may be performed through intermediaries.
- Where possible, and with the consent of the concerned parties, results of certain NMIs/DIs may be temporarily removed, so that an interim report can be published.
- When the review of CMCs is impacted, use of alternative technical reviewers can be considered.
- CMC claims can be supported using evidence other than performance on key comparisons – we sometimes forget about this in the CCQM.

Using these creative options where necessary, the IAWG has made significant advances in its work, and the deleterious effects of geopolitics are minimal. They are limited to some difficulties in shipping/receiving comparison samples, which has been solved using intermediaries; some prohibitions on direct communications, also solved through intermediaries; and smaller than normal participation in studies to be piloted by certain institutes, which can be addressed through a commitment to run additional comparisons later on. It is certainly hoped that the present global conflict will be a thing of the past by next year's report.

Meetings

The IAWG has held two sets of full meetings and one additional meeting since the 2024 IAWG annual report. The first set was the Spring 2024 meetings held at the BIPM on 23-24 April 2024. This was the usual two-day meeting that takes place as part of CCQM Week. It was fully hybrid, with a majority of the attendees online. Specifically, there were a total of 68 registered participants online and only 36 registered participants physically present, for a total registered attendance of 104. Joint working group meetings were held with the EAWG and the SAWG, due to activities of common interest. The total registered attendance for the joint IAWG/EAWG meeting was 138 (88 online and 50 onsite), and that for the joint IAWG/SAWG meeting was 140 (90 online and 50 onsite). There have been no reports of difficulty of participation from those who attended online, verifying that the BIPM has done an excellent job putting this format in place.

The Fall 2024 IAWG meeting was held virtually over three days (05-07 November 2024), with a total of 100 persons from 42 institutes registered to attend. While virtual meetings have some drawbacks – especially the inability to have side conversations while standing next to a colleague – this online meeting was successful, and much was accomplished. Virtual meetings continue to be a reasonable strategy to accommodate restrictive travel budgets and travel safety concerns, as well as to mitigate the cost and difficulty of hosting an IAWG meeting at one's home institution, especially with the new expectation of hybrid meeting capability. As a result, the IAWG plans to continue holding virtual meetings when it makes sense to do so, but particularly in the Fall of the year.

The IAWG and SAWG held a separate joint working group meeting virtually on 16 December 2024. The purpose was to discuss the key comparison reference value (KCRV) and degrees of equivalence (DoE values) for CCQM-K166/P210 (Nanoparticle number concentration in liquid suspension), which is jointly registered to both working groups. The meeting was well attended, and agreement on the KCRV and DoE values was attained. The next step for CCQM-K166 is for the Draft A report to be finalized.

General Issues

Decision Tree (DT; i.e., NIST Decision Tree, NDT)

As stated above, the IAWG has been using the DT for the entire year. No additional changes to the DT or the ways in which it is being used by the IAWG have been necessary. Because the main issues that surrounded the DT and its implementation during its development have been mostly solved, a number of comparisons using it have been finished this year (see top five rows in Table 1), at least to the point of the final report being approved to support CMC claims. The DT is freely available for use at https://decisiontree.nist.gov/. IAWG instructions on how to implement its outputs into comparison reports are given in the document "IAWG Guidance on Using NIST Decision Tree for Comparison Reporting" found at https://www.bipm.org/documents/20126/189731284/IAWG+Guidance+on+Using+NIST+Decision+Tree+for+Comparison+Reporting/ad9e39d8-c20a-4591-60bc-651d28abad34.
Guidance on making and judging CMC claims based on comparisons that employed the DT is provided in "IAWG Guidance on Making and Judging CMC Claims with Supporting Evidence from Key Comparisons for which the Decision Tree is Employed" found at

https://www.bipm.org/documents/20126/270516260/IAWG+Guidance+on+Making+and+Judging+CMC+Claims+with+Supporting+Evidence+from+Key+Comparisons+for+which+the+Decision+Tree+is+Employed/01d446dc-1e3d-661c-aada-c2f2227d85b9.

As a reminder, the DT is based on combining reasonable judgment with a minimum of statistical tests. As depicted in Fig. 1, it comprises four branching nodes (orange) and five leaves (blue) that suggest different mathematical models for the measurement results and corresponding procedures for data reduction. A question needs to be answered at each node: if the answer is YES, then one follows the green branch; if the answer is NO, then one follows the red branch, until one reaches a leaf. The DT requires only two or three statistical tests once the candidate dataset, which enters the tree at the top, has been selected. The DT only recommends, but does not require, the pathway to be taken, preserving the freedom to use scientific judgment. One situation in which judgement is required is when the candidate dataset is small (e.g., < 5 values). In such a case, the power of the statistical tests that make up the DT can be poor. So far, this has not caused the IAWG any large problem, but it is an issue to which more attention might be needed in the future.

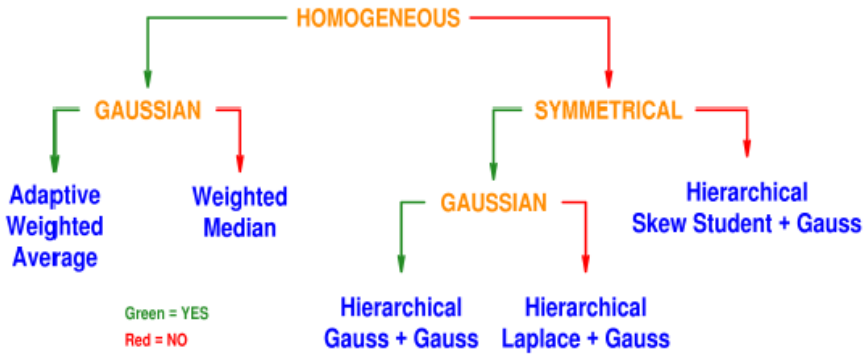

Figure 1. Diagram of Decision Tree (DT).

Core Capability Approach and CMC Claims

In the past year, there has been one significant change to the IAWG's core capability (CC) matrix (Fig. 2). The need for the change became apparent during the April 2024 IAWG meeting, when it was pointed out that the IAWG has quite old CMC claims in the KCDB for analysis of metals and alloys that have no possible support from recent comparisons. When discussing this problem, the IAWG realized that the CC matrix had no place for metals and alloys, except those that are difficult to dissolve. To solve this problem without adding another matrix challenge across the top of the matrix, the title of the fifth matrix challenge was simply expanded to "Metals, alloys, and difficult to dissolve metals (Autocatalysts, …)."

Concerning the lack of recent comparison support for CMC claims on analysing metals and alloys, the IAWG is now considering a new key comparison (with parallel pilot study) on this topic. The study is expected to be undertaken and will provide new support to validate and update the old CMC claims in the KCDB.

Broad scope CMC claims based on using the CC approach continue to be made and approved. However, it has become clear over the past CMC claim cycle that there is some confusion regarding what a broad scope CMC claim really is and how to support it. To assist the IAWG with such questions about broad scope claims, as well as more general questions about both broad and specific CMC claims, a new IAWG task group is being formed to clarify the issues. We expect to ratify the following Terms of Reference during the upcoming April 2025 IAWG meeting:

- To update the IAWG guidance and processes for making and judging CMC claims, the TG will:
  - Review all relevant documentation and guidance on the IAWG website regarding CMC claims
  - Consider recent experiences of IAWG member institutes regarding making and judging CMC claims, especially broad-scope claims
  - Recommend changes to the IAWG documentation and guidance (and the processes described therein) to accommodate lessons learned, while maintaining adherence to the rules established by the CIPM and the CCQM
- The findings and recommendations of this TG shall be presented at the Fall 2025 meeting of the IAWG in November 2025. If the recommendations are ratified by the IAWG during this meeting, they will be put in place in time for the next CMC cycle.

As further assistance with making and judging CMC claims, especially broad scope claims, the IAWG is also making an effort to improve the HFTLS statements in comparison reports, so that they explicitly state the breadth of applicability better than in the past.

Analyte groups	**Matrix challenges**						**Calibration materials and solutions**
	Water/aqueous	**High Silica content (e.g. Soils, sediments, plants, …)**	**High salts content (e.g. Seawater, urine, …)**	**High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, …)**	**Metals, alloys, and difficult to dissolve metals (Autocatalysts, …)**	**High volatile matrices (e.g. solvents, fuels, …)**	
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)							
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Sn, Tl, Pb, Po)							
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)							
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)							
Non-metals (P, S, C, N, O, H)							
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							
Small organo-metallics							
Proteins							
Nanoparticles							

Low level (e.g. below 50 µg/kg)
High level (e.g. above 50 µg/kg)

Fig. 2. The core capability matrix currently used by the IAWG.

IAWG Policy

For the first time, the IAWG now has a policy document (CCQM-IAWG/GD-09, found at https://www.bipm.org/documents/20126/260329910/IAWG-GD-09-IAWG+Policy+02+August+2024/3f5498b4-b62c-68bf-9ef5-88249439bf72. Having such a collection of written policies and procedures has become necessary as a way to track decisions made from time to time. This policy document is not intended to repeat rules and guidelines that already exist in CIPM and CCQM documents. Rather, it is to be a living document that will be expanded and revised as needed in the years to come to record the idiosyncratic practices and policies of the IAWG that complement, but do not contradict, overarching CIPM and CCQM rules and guidelines.

IAWG Key Comparisons and Pilot Studies

The key comparisons and pilot studies in which the IAWG is currently involved are delineated in Table 1. Several points to note:

- As stated earlier, excellent progress has been made in finishing key comparisons. Specifically, CCQM-K160 and CCQM-K161 have been completed, including publishing the Final Reports and populating the information tabs (Graphs of Equivalence, Degrees of Equivalence, Equivalence Statements, and Laboratory Measurements) in the KCDB. Also, the Final Reports for CCQM-K155 and CCQM-K158 have been published, with only the KCDB information tabs remaining to be completed. Finally, CCQM-K144 is almost done, with the Final Report having been approved and sent to the KCDB office for publication, after which the KCDB information tabs will be populated.
- Three pilot study reports (CCQM-P200, CCQM-P207, and CCQM-P215) have been published on the IAWG website.
- CCQM-K178/P223 (Rare earth elements, uranium, and thorium in soil) was originally open to participation by CCRI(II). However, there are no participants from that group.
- CCQM-K187/P240 (Elements in pork) is the 7th IAWG benchmarking comparison. In the IAWG, benchmarking comparisons, which are undertaken every few years, are intended to serve as a way to assess the overall inorganic chemical metrology performance of as many IAWG member institutes as possible. Therefore, participation is strongly encouraged. Each benchmarking study is designed for a common and important matrix, with a small number of measurands that are mandatory if an institute decides to participate in the key comparison; other measurands are optional. For CCQM-K187, the matrix is pork, representing the important food sector, and the mandatory measurands are the mass fractions of Mg and Pb. Participation is very strong, with 29 institutes having registered for CCQM-K187.
- CCQM-K191/P245 (Nonmetallic and metallic impurities in copper) is the latest effort in the IAWG to evaluate and demonstrate SI-traceability for elemental analysis at a most basic level. This comparison will assess the capabilities of the participants to measure metals – and especially the important nonmetals – in relatively high-purity copper. This exercise will help to develop and demonstrate further the IAWG's capabilities to assay the purity of high-purity metals that serve as the foundation of metrology traceability to the SI for so much of inorganic chemical metrology.

Table 1. Key comparisons and pilot studies registered by the IAWG for the period (April 2024 – March 2025), including progress made.

CCQM Designation	Title	Track [a]	Model [b]	Status	
				April 2024	March 2025
K144/P182	Trace elements in alumina powder	A	1	Draft A	K144 Final Report approved but not yet published [c]; P182 report not yet written
K155/P196	Elements and tributyl tin in seawater	A	1	Draft A	K155 Final Report published [d]; P196 report not yet written
K158/P200	Elements and inorganic As in rice	A	1	Draft A for Part A; Draft B for Part B; a single report containing both parts will be published	K158 Final Report published [d]; P200 report published
K160	Platinum group elements in automotive catalyst	A	1	Final report approved but not yet published [c]	Completed
K161/P207	Anions in seawater	A	1	Draft B	Completed
K166/P210 [e]	Nanoparticle number concentration in liquid suspension	C	1	Draft A	Draft A
P215	Arsenic speciation in seafood (aquatic animals)	D	1	Awaiting publication	Completed
K169/P220 [f]	Amount content of sodium oxalate	A	1	Measurement	Draft A
K178/P223 [g]	Rare earth elements, uranium, and thorium in soil	A	1	Measurement	Draft A
K187/P240 [h]	Elements in pork	A	1	Planning	Measurement
K188/P241	Elements in particulate matter	A	1	Planning	Planning
K191/P245	Nonmetallic and metallic impurities in copper	A	1	Planning	Planning

[a] "Track A" refers to measurements that constitute core functions performed routinely by the member institutes; "Track C" refers to more specialized measurements that are not yet commonly used to provide measurement services; "Track D" refers to standalone pilot studies.

[b] "Model 1" means the pilot institute sends samples to the participants to be measured; "Model 2" means the participants send samples to the pilot institute for measurement.

[c] Final Report approved and sent to KCDB office, but not yet uploaded to the KCDB.

[d] Final Report available on the KCDB, but other information tabs (e.g., degrees of equivalence) unavailable.

[e] Registered jointly under both the IAWG and the SAWG.

[f] Registered jointly under both the IAWG and the EAWG.

[g] Participation in P223 is open to the CCRI(II).

[h] 7th IAWG benchmarking comparison.

Advancing Measurement Science in the IAWG

Particle Metrology

The IAWG continues to have a strong interest in particle metrology, arising primarily from the development and use of single particle (sp)ICP-MS for measuring metal-containing (and in some cases, carbon-containing) nanoparticles in liquid suspension. Because such nanoparticles are often measured using techniques in which the SAWG has extensive expertise, this is a natural area for cross-WG cooperation. This is more recently also the case with respect to the CAWG and the NAWG, due to their interest in biological particles and surrogates for such particles.

The reader might recall that the CCQM held a virtual workshop on particle metrology 25-27 October 2022. One of the action items arising from the workshop was to form a task group jointly between the IAWG and the SAWG to chart courses of action for particle metrology. The joint IAWG/SAWG task group has been operating for longer than the past year, but outputs are still in the future. Information about the task group can be found at https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-iawg-sawg-tg-particle/. For the interested reader, information about the past workshop can be found at https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-ws/2022-10-25. The workshop findings and recommendations are presented in more detail in document CCQM-WS/2022-22 found at https://www.bipm.org/documents/20126/83406431/Microparticles-2022-22-Recommended+Action+Items.pdf/9643bca6-4d12-cbf0-cc0f-c1b6bdd297cb.

As part of the IAWG/SAWG collaboration, CCQM-K166/P210 (Nanoparticle number concentration in liquid suspension), which is jointly registered in the two working groups, is well underway (see Table 1). It should be completed by the time of the next IAWG annual report. The results showed good agreement among several measurement techniques, with no clear method dependencies.

In a separate collaboration, the CAWG invited members of the IAWG and the SAWG to participate in CCQM-P222 [Number concentration measurement of particles for cellular analysis – Aqueous suspension of polystyrene latex (PSL) microspheres]. Several IAWG institutes are participating, and participation from the SAWG members is also strong. Measurements have been done, and the coordinators are in the first stages of evaluating the set of reported measurement results. This comparison is not listed in Table 1, because it is registered only under the CAWG.

Finally, the NAWG invited member institutes of the IAWG and the SAWG to participate in CCQM-P244 (Lipid nanoparticles with encapsulated RNA). There are a number of measurands for this complicated pilot study, some of which are inaccessible using the methods commonly applied by IAWG institutes. However, lipid nanoparticle size, size distribution, and number concentration might be measurable using spICP-MS or another technique with which IAWG member institutes have expertise. Therefore, some IAWG institutes are expected to register. This study will help chart the boundaries of the types of particle measurement problems that can be approached by the IAWG using spICP-MS.

Improving SI-traceability for Elemental Analysis

The IAWG continues to work to improve and demonstrate SI-traceability for inorganic chemical analysis and will probably continue doing so for years to come. It is important to note that for all practical purposes, SI-traceability has already been attained, but the evolving needs of the modern world place more stringent demands for its demonstration and enhancement.

The working group is now in the final stages of planning a comparison on the determination of nonmetallic and metallic impurities in high-purity copper. This is important, because high-purity metals often are the foundational materials used to establish SI-traceability for determinations of metallic elements. For such high-purity metals, the dominant impurity elements are often nonmetals. This makes accurate measurements of the nonmetals of paramount significance. The planning of this comparison has now progressed to the point of requiring study numbers, which have been assigned as CCQM-K191/P245 (see Table 1).

The IAWG and EAWG are planning to begin a key comparison and parallel pilot study, jointly registered in the two working groups, on measuring water (not moisture) in high-purity hydrated crystals. This is a somewhat unusual study for the IAWG and can be categorized as Track C. However, it is quite relevant to our interests, because it is pertinent to purity analysis of chemical compounds that might underpin SI-traceability in inorganic analysis. Because this type of measurement pertains also to the OAWG, it is likely that this third working group will also be invited to participate. Request for approval of this comparison is expected soon, after which study numbers will be requested. Because those study numbers do not yet exist, this comparison does not appear in Table 1.

As another endeavour in this area, the IAWG is in the beginning stages of planning a Mode 2 comparison on the preparation of elemental calibration solutions. If undertaken, this comparison will be a successor to CCQM-K143/P181 (Copper calibration solutions), in which nearly 20 participating institutes demonstrated their ability to prepare single-element copper calibration solutions. For the new proposal, one of the goals is to increase the difficulty by moving to one or more elements that present greater challenges than copper. Because the planning for this comparison is not very far along, approval by the CCQM and study numbers have not yet been requested.

Elemental Speciation

The IAWG also continues to work in elemental speciation metrology, which is not a new field, but still is not very well developed. For inorganic species, the issue of establishing and demonstrating SI-traceability in a way that satisfies the requirements of the CIPM MRA continues to be a topic of discussion. For many inorganic species, pure calibration standards that can serve as calibrants can be lacking and/or not substantiated yet through approved CMC claims. The IAWG is working to alleviate this problem, so that key comparisons can be conducted appropriately in the future.

Given the still somewhat underdeveloped nature of speciation analysis, an important aspect of the IAWG's activities in this area is building capacity among its member institutes. To this end, we are now beginning to plan a successor comparison to the recent pilot study, CCQM-

P215 [Arsenic speciation in seafood (aquatic animals)]. The focus of the subsequent key comparison and parallel pilot study is like to be on measuring arsenic species in seafood and botanical samples. The planning is not yet far enough along for this potential comparison to appear in Table 1.

Metalloproteins

Metalloproteins is an important measurement problem to which IAWG methods can be applied. However, at the time of last year's annual report, it was unclear how much interest there was from IAWG member institutes. To help answer this question, the topic was explored in the April 2024 IAWG meeting during a mini workshop. It included two expert presenters from the IAWG discussing application of atomic spectrometric methods and one expert presenter from the PAWG discussing applications of other techniques. It is important to note that the techniques that can be applied by the two working groups are complementary and independent for this type of measurement. Even so, the conclusion of the workshop and discussion was that the level of interest in the IAWG is too small to pursue further.

Laser Ablation Analysis Small Sample and Chemical Imaging Metrology

Expanding support for small sample and chemical imaging metrology is part of the IAWG strategy for 2021-2030 (https://www.bipm.org/documents/20126/57465575/CCQM-IAWG+Strategy+document+2021-2030.pdf/56c8a480-f539-0ea2-b486-7c0fee0e0c1c). The most relevant measurement approach that is in the IAWG purview is laser ablation (LA) sampling, usually with ICP-MS detection. The IAWG is pleased that coordinating laboratories for a potential pilot study focused on LA-ICP-MS have recently come forward, and initial planning is now underway. Two samples are being discussed – a glass sample containing about 50 potential elements at measurable levels and a gelatin sample, pertinent for biological measurement problems, with five or more elements at measurable levels. Given the anticipated complexity of such a pilot study, planning will likely require longer than usual.