**CCQM Isotope Ratio Working Group 2025 Annual Report**

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**March 28, 2025**

**Background:**

In April 2017, the CCQM established a task group to study the metrological state of isotope ratio measurements and formulate recommendations to the Consultative Committee (CC) regarding potential engagement in this field. The task group has delivered its report identifying the metrology needs in the field. The report was tabled at the April 2018 meeting of the CCQM which has decided about the establishment of dedicated working group address the needs identified.

*Terms of reference*

i. To progress isotope ratio measurement science and support measurement applications in this field by providing a permanent forum for NM/DIs to exchange information, advance capabilities and demonstrate comparability;

ii. To carry out Key Comparisons, and where necessary pilot studies, to critically evaluate and benchmark NMI/DI claimed capabilities and competences for isotopic ratio measurements in pure materials and complex samples providing demonstrable evidence of the validity and international

equivalence of measurement services offered to customers.

iii. To provide isotope ratio characterization and data treatment support to other WGs of CCQM.

iv To act as a focal point for stakeholder engagement with the user community, expert laboratories and other stakeholders;

v. To develop and then operate a process which enable the CCQM to review and update the list of reference materials that meet requirements to define or realize isotope ratio delta scales and any other isotope ratio related MRA traceability exceptions. Carry this out in close cooperation with stakeholders.

**Activities (April 2024-April 2025):**

*Meetings*

Key message:

WG has successfully pivoted from full online work to hybrid operating mode finding some efficiencies in increased participation. The last two years all meetings were conduct as hybrid meeting models. Members still consider in person meetings key to in-depth discussions however there are recognized budget and international mobility challenges.

Past

In 2024 WG meeting was held at BIPM in April which included a joint session with GAWG on climate related isotope metrology. In October a four day WG meeting and symposium was held in KRISS Korea, enabling in-depth scientific discussion and special session dedicated to regional isotope ratio measurement capabilities. This regional event brought together, the first time, all NMI/DI laboratories in the APMP region with related capabilities who are not yet active at the CCQM level. Very successful community building event.

Full meeting reports/documentation could be accessed at the CCQM/IRWG site.

Overall meeting participation levels has increased significantly from about 20 participants at in person meetings to 40+ on the online meetings. The amount of time spent in real discussions and the quality of engagement has actually improved.

It is important to note however that easy of online engagement stems from close personal rapports already in place within the WG. If the remote meeting format persist and people change there is a risk of drop in efficiencies.

Future

The WG will continue with hybrid working arrangement as it is clear demand from membership for both face to face and online meeting modalities. The experience with both BIPM and KRISS hybrid meetings were excellent enabling productive access to NMIs who could not normally participate. The hospitality and efforts of BIPM and KRISS were greatly appreciated!

For 2025 face to face meeting is planned for April along with a joint IRWG & GAWG session. Format and location of 202g fall meeting will be decided at the April 2025 meeting. All meetings will be hybrid.

*Comparisons*

Key message:

As the working group has completed the first tranche of studies now planning for the next round of comparison program is underway. IRWG has completed the first key comparison CCQM- K167 on carbon delta measurement in vanillin in 2022, finishing a study on Li isotopes and launched 2 new studies on Cu an C and N isotope systems. Report which are posted on KCDB and available for CMC support. Overall as new working group an active study program with a reasonable level of work load on participants is being executed. It is expected that by the end of the decade all measurement areas relevant to NMIs/DIs will be addressed.

-CCQM-K182/P233, Li delta study, ONGOING

Li is high priority target analyte for climate / energy storage applications. For K182 the measurands are isotope deltas *δ*7/6Li of two sample solutions; for P233 the measurands are the absolute isotope ratios *n*(6Li)/*n*(7Li) of two sample solutions. The enriched isotopes and the blend will be provided by the pilot laboratory.. The possibility to use of non conventional IR methods is encouraged. Key comparison CCQM-K182 and a parallel pilot study CCQM-P233 was carried out in 2024-2025, and the first report on the outcome is expected in April 2025.

-CCQM-K183/P234, Cu absolute measurement study, ONGONG

This study will advance IRWG strategic objective of SI traceable measurements and standards for isotope characterization. This comparison planned for 2025-2026. Registration to the study is currently underway and completion is expected within a year. (annex I)

-CCQM-K193, Carbon and Nitrogen Stable Isotope δ-Values, ONGOING

A CCQM Key Comparison concerning the determination of the δ(13C) and δ(15N) values on pure organic (C and N) and inorganic (only N) compounds and on a real-world sample (C and N) is being carried out.

The motivation for this comparison is to conduct the first Key Comparison on δ(15N) of pure compounds, one organic and two inorganic, and on δ(13C) and δ(15N) in a real-world sample. A Key Comparison on bulk δ(13C) and δ(15N) in a high purity chemical, one organic and one inorganic compound, has been planned in the CCQM-IRWG Strategy 2021-2030. Moreover during the CCQM-IRWG meeting of April 2024 it was recommended to organise a Key Comparison study on a real-world sample for both δ(13C) and δ(15N). The study is currently in the registration stage and it is expected that measurement portion of the study will be completed by December 2025 and the first discussions will take place at the April 2026 meetings. (Annex II)

-Sr isotope ratio measurement in flour material, PLANNED

This comparison was planned for late 2021 then suspended in 2022 because of operation constraints at the pilot institution.

In October 2023, the WG decided to explore re-launching the study with a new pilot organization. Likely timeline is 2025-2026. Update expected at the April 2024 meeting

-Zr isotope ratios, PLANNED

Zr isotope ratios in environmental samples are great interest. Pilot laboratory has been presenting a comparison concept for analysing Zr isotope ratios in matrix samples. The study would advance IRWG strategic agenda on heavy isotopes moving from pure materials to matrix samples. Decision regarding this study was made in April 2024 and the preparation for the study was suspended to be reconsidered in later year, likely after 2026.

*Task groups*

**CCQM IRWG Quantities, Units and Symbols Task Group**

TOR:

Development of a guidance document on names and symbols of quantities and units used in stable isotope ratio measurement in support of CMC formulation and uniform service description for NMIs/DIs.

Expected task duration: 1 year

Chair: Dr. Philip Dunn, LGC

Membership: from regular IRWG members or experts nominated from NMIs/DIs

Update:

TG has met regularly during the reporting period and the document was finalized and approved at the 2023 fall meeting of the WG. The project now is transferred to IUPAC, lead by the current CCQM task group members where a much wider consensus building exercise is underway to harmonize basic nomenclature for the stable isotope ratio measurement field.

Detail on the IUPAC project @ <https://iupac.org/project/2023-014-2-200/>

**CCQM-IRWG/GAWG Task Group on Stable Isotope Ratio Metrology for Atmospheric Source Apportionment of Greenhouse Gases**

TOR:

The task group is to undertake specific actions to facilitate the development of a robust measurement infrastructure for the accurate, real-time measurement of stable isotope ratios for atmospheric greenhouse gases. The group will require collaboration between NMIs and expert laboratories, the GGMT community and measurement networks as well as engagement with instrument manufacturers.

The focus of the task group will be on measurements of: δ13C-CO2, δ13C-CH4, δ18O-CO2, δ2H-CH4, δ15Nα-N2O, δ15Nβ-N2O and δ18O-N2O

Expected task duration: TBD

Chair: Dr. Abneesh Srivastava, NIST

Membership: from regular GAWG&IRWG members or experts nominated from NMIs/DIs

Update:

TG was approved at the IRWG and GAWG joint meeting in April 2023. Formal launch with an associated science event was carried out at the IRWG&GAWG joint meeting in October 2023. CCQM-GAWG Workshop on Carbon Dioxide and Methane Stable Isotope Ratio Measurements took place at LATU with hybrid arrangement and was extremely productive connecting experts from the two WGs and academia industry. Detailed report on the event could found @ <https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg/2023-10-09>

The Task has been active developing guidance

**CCQM IRWG Task Group on the Isotope Delta Traceability Exception in the CIPM MRA**

Chair: Dr. Juris Meija, NRC

-concept presented at October 2023 meeting

-TOR drafted and presented at the April 2024 meeting.

-devise a process for the selection and upkeep of information on key/primary CRMs

-first outcome of the Task Group is the updated definition of Carbon and Nitrogen isotope delta scales and an associated recommendation on preferential use

See annex III

**CCQM IRWG Task Group on Isotope CMCs**

Chair: Dr. Kyoung Seok Li, KRISS

-concept presented at October 2023 meeting

–TOR drafted and presented at the April 2024 meeting.

-develop guidance for the uniform / comparable presentation of CMS for isotope ratio community

**IRWG goals for 2025**

-Launching the next tranche of studies to support comparability and advance fundamental metrology issues

-Continue refining measurement space and comparison planning process

-Explore novel isotope measurement modalities not currently practiced by NMIs to better understand emerging metrological challenges (clumped isotopes, site specific isotope measurements etc)

-Advance international discussion of nomenclature and delta scale definition and realization. Develop plans for advancing the nomenclature recommendations developed by IRWG in the wider science community, specifically, work toward inclusion to IUPAC green book /gold books.

-further develop inter WG, inter CC relations with a special focus on climate change and nuclear safety

**Appendix I**

**CCQM-K183 & CCQM-P234**

**“Copper isotope ratios” Technical Protocol**

The determination of absolute isotope ratios is of particular interest in analytical sciences as analytical chemistry, geosciences, archaeology, life sciences, forensics, atmospheric sciences and others. [1,2] From a metrological point of view, isotope ratios must be traceable to the International System of Units (SI). However, the determination of isotope ratios is performed using mass spectrometry which suffers from an effect called *mass bias* or *isotope fractionation*: The measured intensity ratios are different from the “true” ratios and have to be corrected. For this purpose, certified isotope reference materials (CRMs) are usually needed. The traceability of CRMs is best obtained by applying the primary method for determining isotope ratios, known as *Full Gravimetric Isotope Mixtures* (FGIM). [3]

This topic is emphasized also in the “Strategy for Rolling Programme Development (20212030)” released by the CCQM-IRWG. The current key comparison and pilot study are intended as a follow-up of the CCQM-P213 pilot study focusing on copper delta values. [4,5] The absolute determination of isotope ratios traceable to the SI via this method can be tested and verified using copper with the two isotopes 63Cu and 65Cu. This two-isotope system can be used as a prototype measurand by the members of the CCQM-IRWG demonstrating their capability to determine the isotope ratios *R*(63Cu/65Cu) on the highest metrological level. [6,7] Copper is a proper candidate element for this purpose, since it consists of only two isotopes (FGIM approach is simplified) and the results of the comparison can be cross-validated using the standard reference material NIST SRM 976. [8]

Both a key comparison (K183) aimed at the absolute determination of the isotope ratios *R*(63Cu/65Cu) applying the FGIM approach as well as a pilot study (P234) intended for the determination of the isotope ratios of the same samples using alternative approaches (e.g. TETIMS or the mass bias regression model) are jointly organized by BAM and PTB.

**Appendix II**

**Key Comparison CCQM-K193**

**“Carbon and Nitrogen Stable Isotope δ-Values”**

Background

IAEA is organising in collaboration with NIST a CCQM Key Comparison concerning the determination of the δ(13C) and δ(15N) values on pure organic (C and N) and inorganic (only N) compounds and on a real-world sample (C and N).

The motivation for this comparison is to conduct the first Key Comparison on δ(15N) of pure compounds, one organic and two inorganic, and on δ(13C) and δ(15N) in a real-world sample. A Key Comparison on bulk δ(13C) and δ(15N) in a high purity chemical, one organic and one inorganic compound, has been planned in the CCQM-IRWG Strategy 2021-2030. Moreover during the CCQM-IRWG meeting of April 2024 it was recommended to organise a Key Comparison study on a real-world sample for both δ(13C) and δ(15N).

**Appendix III**

**Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology submitted to the International Committee for Weights and Measures**

**Recommendation X (2025):**

**Recommendation of the measurement scales for carbon and oxygen isotope delta measurements**

The Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology (CCQM), **considering**

* the importance of comparable and accurate isotope ratio measurements of carbon and oxygen,
* that these measurements are made traceable to materials recognised as international standards, in accordance with the CIPM decision CIPM/104-26,
* that a number of measurement scales are used to report carbon and oxygen isotope ratio measurements;

**recognizing**

* that isotope delta measurements require unambiguous accepted measurement scales,
* the agreement by the international community of experts regarding the definition of measurement scales for carbon and oxygen isotope measurements has been reached [1];

**recommends** that

* carbon and oxygen isotope delta measurements be reported on one of the scales defined below,
* the VPDB scale for the carbon-13 isotope delta value, expressed as *δ*(13C), is defined by taking the fixed numerical value of +0.00195 for the *δ*(13C) of the NBS 19 Reference Material, when expressed relative to VPDB,
* the VPDB-LSVEC scale for the carbon-13 isotope delta value, expressed as *δ*(13C), is defined by taking the fixed numerical value of +0.00195 for *δ*(13C) of the NBS 19 Reference Material and −0.0466 for the *δ*(13C) of the LSVEC Reference Material, when expressed relative to VPDB.
* the VSMOW-SLAP scale for oxygen-18 isotope delta value, expressed as *δ*(18O), is defined by taking the fixed numerical value of 0 for *δ*(18O) value of the VSMOW Reference Material and −0.0555 for the *δ*(18O) value of the SLAP Reference Material, when expressed relative to VSMOW.
* the VPDB scale for oxygen-18 isotope delta value, expressed as *δ*(18O), is defined by taking the fixed numerical value of −0.0022 for *δ*(18O) of the NBS 19 Reference Material, when expressed relative to VPDB.
* the VPDB-CO2 scale for oxygen-18 isotope delta value, expressed as *δ*(18O), is defined by taking the fixed numerical value of −0.0022 for *δ*(18O) of the CO2 gas liberated from the NBS 19 Reference Material in reactions with oversaturated phosphoric acid at 25 oC, when expressed relative to VPDB-CO2.

**Reference**

[1] Camin F et al (2025) Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting. *Rapid Comm. Mass Spectrom.* **39**, e10018. doi: 10.1002/rcm.10018