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

CCQM Working Group on Isotope Ratios (IRWG)

Strategy for Rolling Programme Development (2021-2030)

1. Executive summary

In April 2017, the Consultative Committee for Amount of Substance; Metrology in Chemistry and Biology (CCQM) established a task group to study the metrological state of isotope ratio measurements and to formulate recommendations to the Consultative Committee (CC) regarding potential engagement in this field. In April 2018 the Isotope Ratio Working Group (IRWG) was established by the CCQM based on the recommendation of the task group.

The main focus of the IRWG is on the stable isotope ratio measurement science activities needed to improve measurement comparability to advance the science of isotope ratio measurement among National Metrology Institutes (NMIs) and Designated Institutes (DIs) focused on serving stake holder isotope ratio measurement needs.

During the current five-year mandate, it is expected that the IRWG will make significant advances in:

i. delta scale definition,
ii. measurement comparability of relative isotope ratio measurements,
iii. comparable measurement capabilities for C and N isotope ratio measurement; and
iv. the understanding of calibration modalities used in metal isotope ratio characterization.

2. Scientific, economic and social challenges

Isotopes have long been recognized as markers for a wide variety of molecular processes. Indeed, applications where isotope ratios are used provide scientific, economic, and social value. Early applications of isotope measurements were recognized with the 1943 Nobel Prize for Chemistry which included the determination of the water content in the human body, determination of solubility of various low-solubility salts, and development of the isotope dilution method which has since become the cornerstone of analytical chemistry. While isotope ratio measurements have been conducted for many decades, recent efforts to revise the International System of Units (SI) have shown that this activity still remains at the forefront of science. In particular, measuring the isotopic composition of argon played a crucial role in setting the value of the Boltzmann constant whereas isotopic measurements of silicon were central in setting the values of the Avogadro and Planck constants. In fact, there is a rich history of examples where high-precision and high-accuracy isotope measurements have played a critical role in scientific discoveries.

Modern isotope ratio mass spectrometers are now capable of measuring isotope ratios with a precision reaching few parts in a million. This measurement capability has revealed isotopic variations in nearly every poly-isotopic element studied. High-precision isotope measurements are crucial to distinguish between the various sources of certain compounds or elements. Perhaps the most notable example of this is the long-term trend of the decreasing carbon-13 abundance in atmospheric carbon dioxide due to the burning of fossil fuels. The economic value of isotope ratio measurements lies largely in their ability to distinguish between similar materials of different origin. As an example, isotopic analysis has been used extensively in food origin and adulteration studies. Isotopic analysis of strontium is used in cheese provenance, isotopic analysis of carbon is used to distinguish between genuine and adulterated maple syrup, and isotopic analysis of hydrogen helps to determine whether water has been added to orange juice. Isotope ratio measurements have also been used to infer the authenticity of Renaissance paintings, determine body temperature of long extinct dinosaurs, enforce nuclear proliferation treaties, and to decide whether athletes have been doping.

One of the main challenges in utilizing isotope ratio measurements is to make sure the measurement results are comparable across the world and over time. In typical measurements, this is achieved by calibration standards. Calibration of isotopic standards is an expensive enterprise as it calls for separated isotope materials to be available both in high-purity and in weighable amounts. This request is prohibitively expensive for elements such as mercury or tin which have many stable isotopes. While the development of isotopic standards using gravimetric mixture methods originated in the 1950s, very few elements have isotopic standards based on this method. Still, most of the certified isotopic standards belong to the NIST 900 series [1]. The lack of high-precision isotopic standards traceable to the SI has resulted in a widespread practice of calibrating isotope measurements either relative to fixed assumed values of certain isotope ratios or relative to other materials arbitrarily set to 'zero points'.

For example, neodymium isotope measurements are typically calibrated by setting $x(^{146}Nd)/x(^{144}Nd) = 0.7219$ as a working constant. For other elements, such as hydrogen or carbon, one cannot assume that the isotope ratios are invariable across all materials. Instead, measurements are reported relative to common artefacts. Both approaches are a result of practical necessity and are tacit acknowledgments of the overall need for better standards in isotope ratio measurements. While isotope ratio artefacts will continue to serve valuable role in daily measurements worldwide, it is important that they are linked to the SI.

Many recent examples illustrate the fragile nature of isotopic standards where newer measurements boldly contradict the status quo. Thus, the initiatives by the NMIs/DIs to provide independent assessments of the isotopic composition of various elements should be welcomed as efforts to progress science and to enhance trust in these measurements rather than wasteful duplication of efforts. Indeed, the metrology of isotope ratio measurements remains a nascent field exemplified by the fact that the gravimetric calibration of isotopic standards was extended to three isotope systems for the first time only a decade ago and many NMIs/DIs are now employing this method to perform high-accuracy calibrated isotope ratio measurements in support of more reliable isotopic standards.

As pointed out above, isotope ratio data are utilized in nearly all scientific fields ranging from archaeometry, geochronology and geochemistry to even medicine, food safety and security, nuclear safeguards, nuclear forensics, and oceanography. Secondary data are calculated (e.g. age of a sample) and conclusions are drawn influencing the scientific landscape significantly. Reliability and comparability of these data, therefore, are mandatory. Consequently, suitable isotope reference materials (iRMs) and awareness of tools for realizing metrological principles such as uncertainty templates are urgently needed.

A short list of high-impact isotope applications from selected scientific and technological **sectors** may illustrate the importance of isotope ratio measurements and its **needs** for metrological support:

a) Climate – atmospheric monitoring of the environment: Isotope ratio measurements of atmospheric gases provide information on sources and atmospheric processes required to understand the impact of anthropogenic activities and mitigation initiatives. Long term trend analysis requires stable references for these measurements and the evolving instrumentation (e.g. cavity ringdown and other optical techniques) employed in monitoring networks. For background atmospheric measurements, the consistency of isotope ratios measurements for CO_2, for example, between differing monitoring sites worldwide is required at the 0.01‰ level for $\delta^{13}C$ measurements. Similar levels of measurement consistency are required for other isotopologue measurements of other greenhouse gases such as methane and nitrous oxide.

b) Climate – precipitation and hydrologic cycle: Hydrogen and oxygen isotopes (mainly ^{18}O and ^{2}H) in precipitation provide basic information for hydrological investigations, when temporal and spatial variations are monitored. This is realized in the Global Network of Isotope in Precipitation (GNIP, https://www.iaea.org/services/networks/gnip), which is run by the International Atomic Energy Agency (IAEA) and the World Meteorology Organization (WMO) These data allow a better simulation of hydrologic cycle in climate models and contribute to contribute to water resources inventory and its development.

c) Metrology and the SI: The development and use of calibrated isotope ratio measurements in the 1970s for assessing the Atomic Weights of the elements ushered in a whole new era for fundamental measurements.

Moreover, the accurate experimental determination of isotopic compositions was necessary for the quantification of the triple point temperatures of water. It also played a significant role in earlier determinations of the Faraday and Avogadro constants. More recently, the redefinition of the SI units the kilogram and the mole using the Si sphere-based X-Ray Crystal Density (XRCD) approach was materially improved by the development of new and exacting plasma multi-collector mass spectrometric methods for measuring absolute silicon isotopic abundances. Also, the absolute isotope ratio measurement of argon has contributed substantially to the determination of Boltzmann constant for the redefinition the kelvin. The improvement of existing and the development of new analytical procedures is essential for this filed.

d) Biological Sciences: The applications in the biological and health sciences are already quite diverse, with new innovative studies involving isotopes being proposed each year. Isotope ratio analyses have shed a unique light on plant metabolism and human diseases such as breast cancer, liver disease and most recently on Alzheimer's disease. Anti-doping activities are on the increase as the World Anti-Doping Agency strives to lead a collaborative worldwide movement for doping-free sport. The analysis of $^{13}C/^{12}C$ isotope ratios, reported as $\delta^{13}C$ values, is a well-proven and powerful method to detect abuse of endogenous steroids. Most of these applications are cutting edge research, which require the implementation of metrological principles to avoid overinterpretation even at this early stage.

e) Forensic Sciences: The international trade of illegally logged timber, protected wildlife, and counterfeit food products is growing rapidly with far reaching ecological and economic consequences for producer and consumer nations. Light stable isotopes have long been employed as forensic tools to help trace the geographic origin of a range of organic materials of economic importance by capitalizing on the predictable global distribution of hydrogen and oxygen isotopes of meteoric water, as reflected in the tissue of plants and animals. Isotope analyses of elements such as hydrogen, oxygen, carbon, nitrogen and strontium are critical in this role, as they can provide information on the provenance of the plants and animals and detect food adulteration. The scientific community has been actively creating Isoscapes (Isotope landscapes for individual important matrices) mapping the variations of the isotopic signatures of these elements around the world. Such an effort requires confidence in the comparability and compatibility of the data coming from the contributing labs, a property that is at times difficult to assess due to the paucity of isotopic PT programs. Fortunately, the light stable isotope forensic community is one of the few that has such a program making it almost unique in this regard. Metrological support is needed for realization of traceability and comparability of measurement results and for including measurement uncertainties in provenancing by means of databases and Isoscapes. An overarching need is the demand for suitable iRMs.

f) Nuclear forensics: Nuclear forensics also depends extensively on the isotopic signatures of pre- and post-detonation products to identify the (reactor) sources, fuel type, weapon design, and therefore the point-of-origin of nuclear materials. Nuclear and radiological consequence assessment measurements concern the assessment, decontamination and clearance of people, food, animals and inanimate objects like dirt and concrete involved in a nuclear incident. The accuracy and comparability of the various national and other specialist labs that do many of these measurements are also unclear. This is one arena that especially needs modern iRMs with an isotopic PT program in addition to and beyond those, which already have been provided by institutions such as NBL and JRC in the US and the EU. The goal, of course, is to make all such measurement comparable and tied back to the SI.

3. Vision and mission

Vision and mission of the IRWG are in line with those of the CCQM.

IRWG's Vision: A world in which all isotope ratio measurements are made at the required level of accuracy to meet the needs of science and society.

IRWG's Mission: To advance global comparability of isotope ratio measurement standards and capabilities, enabling member states and associates to make measurements with confidence.

4. Strategy

The strategic aims of the IRWG for the period 2021 to 2030 are the same as those for the CCQM itself, though focused on isotope ratio metrology and offering additional aspects:

To contribute to the resolution of global challenges such as climate change and environmental monitoring, energy supply, food safety, forensic sciences including nuclear forensics and 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 isotope ratio 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 the IRWG work program, with a special focus on the traceability exception for delta measurements.

To progress the state of the art of isotope ratio measurement science by investigating new and evolving technologies such as optical spectrometry, measurement methods, calibration approaches, and standards and coordinating programs to assess them.

To improve efficiency and efficacy of the global system of comparisons for isotope ratio measurement standards conducted by the IRWG by continuing the development of strategies for a manageable number of comparisons to cover core capabilities.

To continue the evolution of Calibration and Measurement Capabilities (CMCs) to meet stakeholders' needs, incorporating the use of broad CMC claims where applicable to cover a broader range of services and considering options to present these in a way that meets stakeholders' 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 Regional Metrology Organizations (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 International Bureau of Weights and Measures (BIPM).

To maintain organizational vitality, regularly review and, if required, update the IRWG 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.

5. Activities to support the strategy

5.1. Progressing metrology science

The major aim of metrology is to realize the comparability of measurement results over space and time. The largest obstacle in isotope ratio metrology nowadays are delta scale measurements and the corresponding SI traceability exception [2]. Although isotope delta scale measurements provide a means for consistency of measurements, they prove to be difficult to maintain over the long term due to inaccessibility of standards, the potential instabilities and eventual exhaustion of material supply. The way to improve the situation and to solve this issue is to link delta scales to absolute isotope ratios and to progress concepts for establishing measurements of absolute isotope ratios* instead of delta values and to realize absolute isotope ratios for isotope reference materials (iRMs) being used for calibration purposes. Of course, absolute isotope ratios should not only be provided for new iRMs, but even more

* 'Absolute isotope ratio' is still current terminology and corresponds to 'isotope amount ratio', which is a more recent term. Absolute isotope ratio often is preferred when authors want to differentiate from relative isotope ratios (also termed delta values).

important for already existing delta scale anchors such as VSMOW2, SLAP2 and others in order to link a major part of earlier performed delta scale measurements to the SI.

- Improving measurement capabilities for relative isotope ratio measurements: Relative isotope ratio measurements are a basic “skill” feeding into more complex measurement challenges. Although these measurements have been carried out for decades there are still significant issues around basic experimental design, uncertainty evaluation etc. IRWG is dedicated to systematically address these issues and establish current best practices and minimum requirements for evaluation.
- Metrological traceability to the SI: The only known approach to truly obtain absolute isotope ratios is the gravimetric mixture approach (FGIM = full gravimetric isotope mixture model [3]). This approach is based on blending isotopically enriched parent materials of the element of interest to obtain gravimetrically prepared (binary) mixtures. The uncorrected intensity ratios measured in the parent materials as well as in the mixtures eventually yield the mass bias correction factors necessary to calculate the SI traceable isotope ratios from the measured intensity ratios. Even though this approach has existed for some 70 years, it is not that common because of the sometimes extreme efforts needed to prepare the mixtures and calculating the results from the acquired data as well as the high costs for the pure end member materials. During the last fifteen years this approach has undergone a renaissance and optimization. Silicon [4], magnesium [5], molybdenum [6], and lead [7] were the latest examples where this approach was applied to its full extent. The working group decided to organize a Key Comparison covering the FGIM approach using enriched copper isotopes as parent materials which were chemically purified by a high-vacuum sublimation process in order to characterize at least two Cu materials to obtain SI-traceable Cu isotope amount ratios. This Key Comparison will be the follow-up of the current pilot study CCQM-P213 focusing still on delta values.
- Solid state measurement techniques: Techniques like laser ablation (LA), glow discharge (GD), secondary ionization (SI), and resonance ionization (RI) are fast, therefore cost-effective, and (because of the omission of one or more wet-chemistry sample preparation steps) exhibit fewer, or nearly no, blank issues. Another important advantage is the possibility to gather spatially resolved information about contents or isotope patterns. One of the biggest downsides of solid-state techniques is the calibration and therefore the SI traceability. Therefore, the working group plans to organize (jointly with the IAWG) at least a pilot study in the near future to survey the already existing abilities of NMIs and DIs to establish SI traceability of solid-state measurements and pave the way for further improvements.
- Isotope ratios of SHNOC elements (including gases): Long-term maintenance of the light element isotope delta scales is a significant challenge as these are based upon artefacts, some of which are virtual materials. Establishing a direct link to the SI for isotope delta scales of the light elements H, C, N, O and S, thereby removing the need for the current traceability exception for isotope delta values [2] is a vital long-term goal. For carbon there are additional challenges surrounding transfer of the Vienna Peedee Belemnite (VPDB) scale from the scale-defining carbonates to pure carbon dioxide, to methane and to these gases within mixtures (such as the atmosphere). Here, the CCQM Gas analysis Working Group, in close collaboration with CCQM-IRWG, will work on the establishment of a robust infrastructure for gas phase reference materials for the isotope ratio of carbon dioxide for source apportionment, both for delta scale measurements and absolute isotope ratio measurements for putting carbon dioxide isotope metrology on an SI basis for the first time. Developments in laser-based technology for gas and isotoplogue quantification has given rise to commercial instruments being deployed widely in monitoring networks for greenhouse gases and has led to demand for new calibration mixtures as well as the development of novel calibration methods [8]. The activity is being supported by the CCQM-P204 comparison, coordinated by the BIPM and International Atomic Energy Agency (IAEA), as a precursor to key comparisons that will be run in the future. For hydrogen, development of a reproducible means to determine the hydrogen isotope ratio of non-exchangeable hydrogen is also a pressing measurement challenge.

5.2. Improving stakeholder involvement

The stakeholders of the CCQM-IRWG include national and international scientific groups, professional organisations, standardisation and accreditation bodies, as well as isotope ratio reference material (iRM) producers and field laboratories and other users of services provided by the member institutes of the CCQM-IRWG. The services provided by CCQM-IRWG members include the production and certification of isotope ratio reference materials (pure single compounds and matrix-matched materials); organisation of PT schemes; provision of measurement service(s) and of measurement research; establishment of knowledge transfer activities to meet the needs of local field laboratories.

<u>CCQM-IRWG stakeholders:</u>

- National/international scientific groups and other professional organisations, including
  - Other CCQM Working Groups in particular CCQM-IAWG and CCQM-GAWG
  - Other Consultative Committees in the CIPM including CCM and CCT
  - International Union of Geological Sciences (IUGS)
  - World Meteorological Organization (WMO)-Global Atmospheric Watch (GAW) network
  - Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network
  - EURAMET European Metrology Programme for Innovation and Research (EMPIR) projects (e.g. Metrology for Stable Isotopes Reference Standards (SIRS) and the follow-up Stable isotope metrology to enable climate action and regulation (STELLAR) projects)
- National/international standardisation and accreditation bodies, including
  - International Union of Pure and Applied Chemistry (IUPAC) Commission on Isotopic Abundances and Atomic Weights (CIAAW)
  - International Organization for Standardization (ISO): Committee on Reference Materials (REMCO), to be replaced soon by TC344 in Reference Materials
  - World Anti-Doping Agency (WADA)
  - German Institute for Standardization (DIN)
- Isotope ratio RM producers, including
  - United States Geological Survey (USGS) Reston Stable Isotope Laboratory
  - University of Indiana, United States
  - International Atomic Energy Agency (IAEA)
  - New Brunswick Laboratory (NBL) Program Office, United States
  - National Institute for Standards and Technology (NIST), United States
  - Bundesanstalt für Materialforschung und -prüfung (BAM), Germany
  - National Institute of Metrology (NIM), China
  - National Institute of Metrology Japan (NMIJ)
- Field laboratories performing isotope ratio analyses and other users of services provided by CCQM-IRWG members.

<u>Interaction with stakeholders:</u>

The CCQM-IRWG and its members have some formal interaction with a number of these stakeholders. For example, the IAEA has a memorandum of understanding with the BIPM, is a liaison organization of the CCQM and a signatory of the Mutual Recognition Arrangement by the International Committee for Weights and Measures (CIPM MRA) and a custodian of the isotope delta scale reference materials for the elements H, C, N, O and S that are among the recognized measurement traceability exceptions by the CIPM. Similarly, there now exists a memorandum of understanding between the BIPM and IUPAC which specifically recognises the import role of the CIAAW for isotope ratio analysis and compilation of standard atomic weights. The establishment by NIST of an isotope reference material (iRM) User Group provides a specific arena for interaction between metrology institutes, iRM producers and the end-users and other stakeholders of these materials.

There are also some informal interactions between the CCQM-IRWG and the stakeholder groups through shared memberships. For example, two members of the CCQM-IRWG are also institutional members of the FIRMS network, while a number of institutes within the CCQM-IRWG also have representatives on the IUPAC CIAAW. In this way, there can be direct exchange of relevant information and influence between the CCQM-IRWG and its stakeholders even where no formal arrangement exists.

Collaborative research projects involving CCQM-IRWG members as well as stake holder laboratories are also a valuable means to disseminate activities and transfer knowledge. EURAMET projects concerning isotope ratio measurements of atmospheric gases (EMPIR SIRS and STELLAR projects) are one such example.

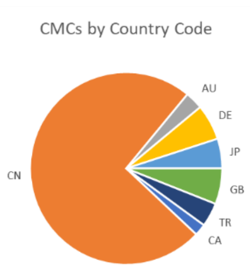
Activities aimed at improving stakeholder involvement:

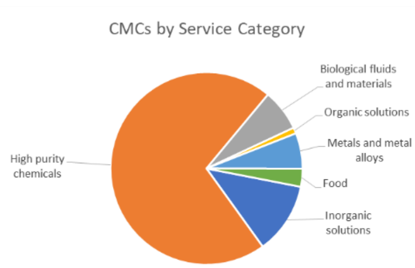
- Invite stakeholder laboratories to participate in parallel pilot studies.
    - During the first Key Comparison on light stable isotope ratio analysis performed under the CCQM-IRWG, three external expert laboratories were invited to participate in CCQM-P211, the parallel pilot study to CCQM-K167. These laboratories were the USGS Reston Stable Isotope Laboratory, the Centre for Isotope Research, Groningen, and the Max Plank Institute, Jena (which is also the WMO central calibration laboratory for CO_2 isotopes in air standards)
    - The CCQM-P204 comparison on pure CO_2 isotope ratios has expert laboratory participation from MPI-Jena, CSIRO (Australia), INSTAAR (US), LSCE (France), Environment Canada (Canada)
    - This is of particular value for isotope ratio analyses that are less common among participants of the CCQM-IRWG.
- Ensure active participation of IRWG member institutes within the various stakeholder networks continues and is encouraged. This enables CCQM-IRWG input into these bodies and into their outputs, e.g. future editions of the FIRMS Network's Good Practice Guide for Isotope Ratio Mass Spectrometry.
- Ensure that CCQM-IRWG members' iRMs are included in the revised IUPAC Technical report on iRMs that underpin the traceability exception for isotope delta being prepared by the CIAAW
- Encourage joint/collaborative research projects between CCQM-IRWG members and stakeholder laboratories to address specific measurement challenges
- Workshops/training activities/scientific conferences present the opportunity for knowledge transfer between CCQM-IRWG members and their stakeholders.

5.3. PROMOTING GLOBAL COMPARABILITY

Key Comparisons

Key Comparisons are the primary way through which NMIs and DIs can demonstrate their degree of equivalence with other metrology institutes, and support CMCs under the CIPM MRA. As of December 2020, only three Key Comparisons (CCQM-K98, CCQM-K122, CCQM-K140) and four Pilot studies (CCQM-P48, CCQM-P75, CCQM-P105, CCQM-P160) have been completed relating to isotope ratio measurements, all under the IAWG and conducted prior to the formation of the IRWG. In addition, the CCQM-K120 comparison, organized through the GAWG and coordinated by the BIPM, on CO_2 in air mole fraction standards required measurements of carbon and oxygen isotopes in all 46 standards submitted to the BIPM, to correct for optical comparator response for isotope ratio [9]. Since the formation of the IRWG, one Key Comparison and three Pilot studies have been initiated. The Key Comparisons conducted to date are inadequate at providing even modest coverage for the isotope ratio measurement space, for which definitions were discussed during October 2019 (see Annex).





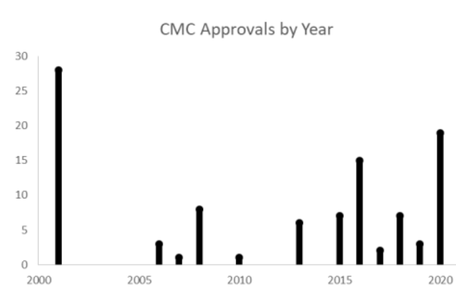


Fig. 1: Key Comparison Data Base (KCDB) CMC listings by Country Code, by Measurement Service Category and by Approval Date (from the left to the right)

There currently exist 100 CMCs related to isotope ratio measurements in the Key Comparison Data Base (KCDB). The existing CMCs originate from seven NMIs/DIs, predominantly listed under the high purity chemicals measurement service category. Of these CMCs, almost 50% were approved after 2015 (Fig. 1). It is vital to ensure that future Key Comparisons provide adequate and ongoing coverage of the measurement space, directed not only by the capacity of NMIs/DIs to act as coordinators, but also with consideration to the priorities of IRWG member institutes with respect to current and future CMCs. To this effect, the IRWG should conduct periodic surveys of its members to determine priorities for Key Comparisons. Results of these surveys should assist in aligning conduct of Key Comparisons with the needs of IRWG members. A list of potential Key Comparisons and stand-alone Pilot Studies is provided in the attached Annex.

Nomenclature Harmonisation

Ensuring global comparability in isotope ratio analysis requires agreement on and consistent application of clearly defined terminology. Within the scope of CCQM activities, IRWG members should identify areas within the measurement space where inconsistencies have occurred, find consensus on nomenclature, and promote its use in studies and CMCs. Especially in the latter case, harmonization is urgently needed, because CMCs often use different terminology although referring to the same claim or even the same measurand. This requires the IRWG to work with other international bodies such as IUPAC to harmonise these nomenclatures used globally to define the isotope delta scales. Although general guidelines published by T.B. Coplen in 2011 [10] and the IUPAC Technical report [11] released in 2014 has addressed some of these issues, some of the information has been outdated. One such example relates to the artefact materials defining the carbon isotope scale VPDB. The artefact material NBS-19 which defined the zero point of the scale is now exhausted and replaced by IAEA-603, whilst the secondary anchor LSVEC was found to be isotopically unstable and was no longer able to be used from 2017 [12]. The IUPAC commission on Isotopic Abundances and Atomic Weights (www.ciaaw.org) recommends all carbon isotopic measurements to be normalised to the VPDB scale using at least two suitable international iRMs deemed appropriate by the users. Although LSVEC can no longer be employed directly for carbon measurements, many measurements are made using iRMs traceable to LSVEC. Currently, a new realization of the VPDB scale, namely VPDB2020, is proposed [13]. Clarity on nomenclature regarding the VPDB scale will also be a first step to elucidating methods for realizing the scale with agreed levels of measurement uncertainty. Within the CCQM, this will aid harmonisation of CMC claims in the KCDB, which is currently lacking.

Besides this specific case, there is a pressing need for harmonized terminology and nomenclature in all fields of isotope ratio analysis, worldwide. Unclear definitions of the measurand, mixing up delta values, isotope ratios and isotopic compositions are only a few examples here. CCQM-IRWG will contribute to solving these issues on a global scale. Through parallel memberships in IUPAC, CIAAW, and standardization bodies such as ISO/REMCO IRWG members work on a global harmonization concerning isotope metrology.

Guidance Documents for IRWG Activities

Since the IRWG is still in its infancy, general guidance on working group activities and decision-making pathways has not yet been established. The related CCQM-IAWG, CCQM-OAWG, and CCQM-GAWG working groups are more mature and collaboration with these groups would be valuable in establishing guidance documents covering conduct of Key Comparison and Pilot studies including activities as:

- Proposal of Key Comparisons consistent with CCQM-IRWG strategies
- Acceptance criteria for Key Comparison study material (e.g. homogeneity, minimum sample size)
- Calculation and treatment of data
- Statistical approaches to calculating KCRV

Where the need exists, guidance may also be provided for specific technical challenges where minimum criteria are required to obtain comparable data quality between CCQM-IRWG members, for example with respect to calibration approaches.

Provision of 'best practice' advice to CCQM-IRWG members and stakeholders

Through the CIPM MRA, confidence in scientific measurement traceable to SI has been well demonstrated globally which is critical for international trade and industrialisation. However, in the area of isotopic measurements, many are currently not traceable to the SI, resulting in the CIPM issuing a traceability exception for these measurements and recognising and supporting traceability of such measurements to internationally recognised iRMs [2]. IAEA acts as custodian of the δ-scales in the area of SHNOC isotopic measurements, for all other elements no such role is attributed, though CIAAW took up the duty to list and compile all applied delta scales and their scale defining materials [11]. Given that these iRMs were assigned δ-values by consensus and zero uncertainty was applied to the respective scale, uncertainties relating to heterogeneity in these materials are often not considered or accounted for by end-users. And, when a primary artefact defining the δ-scale becomes short in supply, another material is introduced as a replacement, accompanied by stated uncertainties of the assigned values. Some guidance on how these uncertainties can be incorporated by the iRMs' users and propagated in their final measurement would improve global comparability of measurement results.

For historical reasons, the scale defining iRMs for SHNOC elements are inorganic compounds and are not directly comparable to stable isotope analysis of organic compounds and materials by continuous flow IRMS. Secondary iRMs have been produced to bridge this gap, however they are often value assigned through the efforts of expert laboratories in their fields. Such materials serve the user as calibration and quality control materials due to their better supply, while they are carrying the major disadvantage of consensus value based materials, which is the variation of the assigned value with time based on regular peer reviews and changes in the state-of-the-art in measurement technology. For Non-SHNOC elements pure compounds or elemental solutions are used as calibration materials (primary iRMs), which mainly differ from the sample matrix. For verification of a bias-free sample preparation matrix materials are applied and reference δ-values are taken from literature compilations such as GeoRem [14]. In the light that these secondary iRMs and matrix materials are used for calibration and validation purposes and that in most cases the materials are provided without a documented assigned value, a central location or database for the currently accepted isotope delta values would reduce ambiguity and confusion and promote global comparability of measurement data.

Recently, another inconsistency for SHNOC elements was discovered relating to the published values for the absolute ratios of the δ-scale anchors. A large number of the absolute ratios defining these iRMs have been published in literature over the past decades [15]. The variation in these ratios have been propagated into proprietary software supplied by instrument producers and has led to inconsistency in normalisation of data particularly when normalisation against a working reference gas was employed. A central location of best estimate of these absolute isotope ratios for δ-scale defining iRMs would ensure global consistency in isotope ratio expression.

Promotion of reference material use

Global comparability of isotope measurements is best achieved when appropriate iRMs are employed in routine measurement for calibration and/or as quality control [16]. Although there are more iRMs available in the market now with traceability to the δ-scale, the appropriate choice of iRMs to act as anchor points is crucial for measurement comparability between laboratories world-wide [17]. Having a forum where iRM producers and iRM users can meet would promote the exchange of information between the two groups and minimise any disconnect between parties. Such a forum has great potential to facilitate the development of ideas for new iRMs in emerging analytical spaces. The involvement of various representatives from IRWG with the external stakeholders in these forums will allow knowledge and expertise to be transferred to the measurement community. The CCQM-K140 key comparison is such an example where the study sample was extended in parallel to a number of forensic laboratories (FIRMS) in an inter-laboratory comparison (ILC) for bulk isotope ratio of carbon. This exercise has provided a direct impact of the CCQM's activity on the validity of the routine measurements carried out by routine forensic laboratories [18]. Another example is CCQM-K98 where the measurement capability of NMIs/DIs for obtaining absolute Pb isotope ratios in a water and bronze sample was tested. The outcome of this key comparison directly resulted in the first matrix reference material being certified for absolute isotope ratios [19]. Transfer of knowledge on calibration techniques and proper selection of appropriate material are key to achieving global comparability in these types of measurements.

Improving δ-scale definitions

Contributing to the global discussion on improving the definition and realization of delta scales working with international stake holders. As at this point there is no coherent internationally underwood and agreed upon approach for the definition and realization of delta scales CCQM IRWG is in unique position to bring expertise from other measurement fields to develop best practices and nomenclature for the stable isotope ratio community.

Linking δ-scale to SI

While efforts are being undertaken within the isotope community to maintain the continuity of the primary isotope δ-scales, active collaboration between the stakeholders and NMIs/DIs is required to pilot and potentially produce a new generation of iRMs to build new infra-structure based on absolute isotope ratio measurements. New iRMs featuring SI traceable isotope ratios will ensure the continuity of δ-scales and the validity of all previous iRMs. An example of such an endeavour has already been undertaken by LGC in the production and characterisation of glycine certified reference materials for $n(^{13}C)/n(^{12}C)$ isotope amount ratio measurements [20]. The work has highlighted the challenges associated with the characterisation of matrix reference materials for $n(^{13}C)/n(^{12}C)$ values traceable to the SI. In the field of metal isotopes, a set of new iRMs for Mg isotope amount ratios have been developed, which for the first time offers SI traceable isotope amount ratios with measurement uncertainties at the precision level of routine δ-scale measurements [5]. Additionally, all existing Mg δ-scale standards have been cross-calibrated such, that for any sample being measured against one of these cross-calibrated Mg isotope standards SI traceable isotope amount ratios can be calculated [21]. These are first examples, however, there is a growing need for development of such iRMs in the following analytical spaces - environmental, biological, forensics and nuclear sciences. This task can only be approached with in-depth consideration and collaboration between various academic institutions and NMIs/DIs to consider the current capability of analytical instrumentation and the elements required to improve accuracy in isotope ratio measurements. This would be the key towards minimising the uncertainty defining the relative isotope delta scales and metrology traceable to SI.

CO_2 isotope ratio measurements in support to climate research

The future comparison strategy of IRWG and GAWG for CO_2 isotope ratios relies on using specialist comparison facilities of the BIPM Laboratories. Data quality objectives set by the WMO-GAW for long term analysis of $\delta^{13}C$ in CO_2 in air require consistency of measurements at the 0.01‰ level at monitoring sites. This is at a level where inconsistencies in scale definitions or realizations would make the objectives unobtainable, and thus ensuring the robustness and consistency of the current reference measurement for $\delta^{13}C$ measurements is crucial. In addition, the demand for CO_2 gas and CO_2 in air isotope ratio standards is increasing, with the availability laser -based systems for direct field measurements of isotope ratios of CO_2 in air. The pilot study, CCQM-P204, utilizing on-demand pure CO_2 isotopic gas mixture comparison samples produced at the BIPM and calibrated by IAEA [22], for comparing both optical and mass spectrometric capabilities, will be followed up by an on-going comparison coordinated by the BIPM, BIPM.QM-K3, allowing on-demand comparisons on pure CO_2 at any value across the range -1 ‰ to -45 ‰ vs VPDB, with metrological traceability provided by an IRMS carbonate reference system maintained at the BIPM. The range of the BIPM's comparison sample preparation facility is extendable and will also be available to support advancing measurement science and developing SI traceable calibration hierarchies for CO_2 isotope ratio measurements. Comparisons on isotope ratios of CO_2 in air will be supported by the on-going comparison BIPM.QM-K4 using an IRMS reference system with cryogenic extraction of CO_2 from air, and with metrological traceability provided by the carbonate reference system maintained at the BIPM. The BIPM activities provide the possibility of on-demand comparisons, providing flexibility for NMI needs in this rapidly developing field.

5.4. INTERACTION WITH RMO ACTIVITIES

CCQM IRWG provides a platform for the NMIs and DIs to exchange information, advance capabilities and demonstrate comparability for the isotopic measurement and metrology. The RMOs play an important role within the CIPM MRA. Like other working groups within CCQM, IRWG interacts with the RMOs primarily through its members who are active both in the IRWG and in their respective RMOs. IRWG works with the RMOs to plan, execute and monitor KCs and support the process of CMC review.

At present, there are very few comparisons on isotope ratio analysis within the RMOs. However, based on regional measurement requirements, a large number of comparison activities related to IDMS applications have been carried out by the various RMOs. IDMS actually is a highly appreciated application of the isotope technology in the accurate measurement of chemical components. In this case, IRWG can provide technical guidance, such as how to calibrate isotope ratio measurements and how to achieve traceability in all occurring IDMS applications, and recommend the use of isotope reference materials if needed. In addition, some NMIs/DIs have claimed CMCs on isotope ratio measurements, which should be reviewed in their respective RMOs in the early stage. IRWG also can provide guidelines for reviewing isotope ratio CMCs within the RMOs. It is expected that in the future isotope ratio key comparisons, supplementary comparisons and other actions will be organized by the IRWG, the RMOs or jointly by both in strategic sectors where analytical challenges have been raised, such as ecological environment and food safety.

The present definition of the mole, which is based on a fixed numerical value for the Avogadro constant, N_A, was adopted in Resolution 1 of the 26th CGPM (2018). Highly accurate isotope ratio measurements along with the determination of the chemical purity of elements play a key role in the realization of at least four SI units (kelvin and ITS90, kg, mol) and in the determination of fundamental constants (Avogadro, Boltzmann, Planck) within the CIPM framework. Especially, the isotope ratio measurements resulting in the isotopic composition and the molar mass of ^{28}Si enriched silicon represent a performance of isotope technology at the highest metrological level. The new definition of the mole and the kilogram require new traceability capabilities for dissemination, which is the intrinsic mission of a typical NMI. Consequently, new research objectives will be added to the NMIs/DIs' scope. RMOs and CCQM-IRWG can jointly support this development by carrying out relevant comparisons under the framework of the CCQM-IRWG plan in the near future.

CCQM-IRWG will strengthen directly and via the RMOs the cooperation with relevant international organizations, including IUPAC, CIAAW, ISO/REMCO, and IAEA to promote the international standardization process of isotope ratio measurement methods and related iRMs. The stakeholder needs in each RMO will be implemented as well into the CCQM-IRWG work program and the dialogue between the NMIs/DIs and global stakeholders will be facilitated in order to define new possibilities for metrology impact.

ANNEX

1. General Information

A snapshot of the IRWG:

CC Name: CCQM
CC Working Group: Isotope Ratio Working Group (IRWG); Date Established: 2018
Number of Members: 17 institutes representing a total of 15 countries have designated contact persons to the IRWG as of November 2020
Number of participants at last meeting: 41 persons from 20 institutes
Periodicity between meetings: Approximately every six months, although web meetings may be held more frequently as needed
Date of last meeting: 22 October 2020 (web meeting)
CC WG Chair (Name, Institute, and years in post): Dr Zoltan Mester, NRC Canada, ≈ 1.5 a
Number of KCs organized (up to and including 2020): 1
Number of Pilot Studies organized (up to and including 2020): 2
Number of CMCs published in KCDB supported by CC body activities (up to and including 2020): 100 (thought to be accurate to the hundred)

IRWG Terms of Reference

The responsibilities of the IRWG are:

To carry out Key Comparisons, and where necessary Pilot Studies, to critically evaluate and benchmark NMI/DI claimed competencies for isotope (amount) ratios, delta values or conventional isotope ratios of elements, isotopologues and isotopomers in pure substances, calibration solutions or complex matrices; providing demonstrable evidence of the validity and international equivalence of NMI measurement services offered to customers.

To identify and carry out inter-laboratory work and Pilot Studies required to underpin the development of reference measurement systems and to advance standards and calibration materials in the field of isotope ratio metrology of the highest possible metrological order with traceability to the SI, where feasible, or to other internationally agreed measurement standards, to support NMI/DI measurement services being developed in response to customer needs.

To act as a forum for the exchange of information about the research and measurement service delivery programs and other technical activities within the CCQM-IRWG members and also worldwide between stakeholder organizations with a special focus on the traceability exception for delta measurements.

2. List of Planned Key and Supplementary Comparisons and Pilot Studies

The CCQM-IRWG was established less than 2 years ago. In 2019 two task groups were formed for elaborating on strategic issues such as measurement space, future comparisons and CMC format, one group for the ‘classical stable isotopes’ (SHNOC elements) and one group for all other elements (Non-SHNOC elements). The outcome was discussed in the 2019 fall meeting. It was obvious that the strategies for both groups differ significantly, because the SHNOC elements are more susceptible to isotope fractionation during sample preparation due to the high relative mass difference than most Non-SHNOC elements and because the delta values are measured in bulk elements, in molecules (e.g. hormones) and even in isotopomers. Therefore, the different applications and the required instrumental techniques for sample preparation play a major role. Consequently, the measurement space for the SHNOC elements consists of many individual fields, which is visualized in Fig. 2.

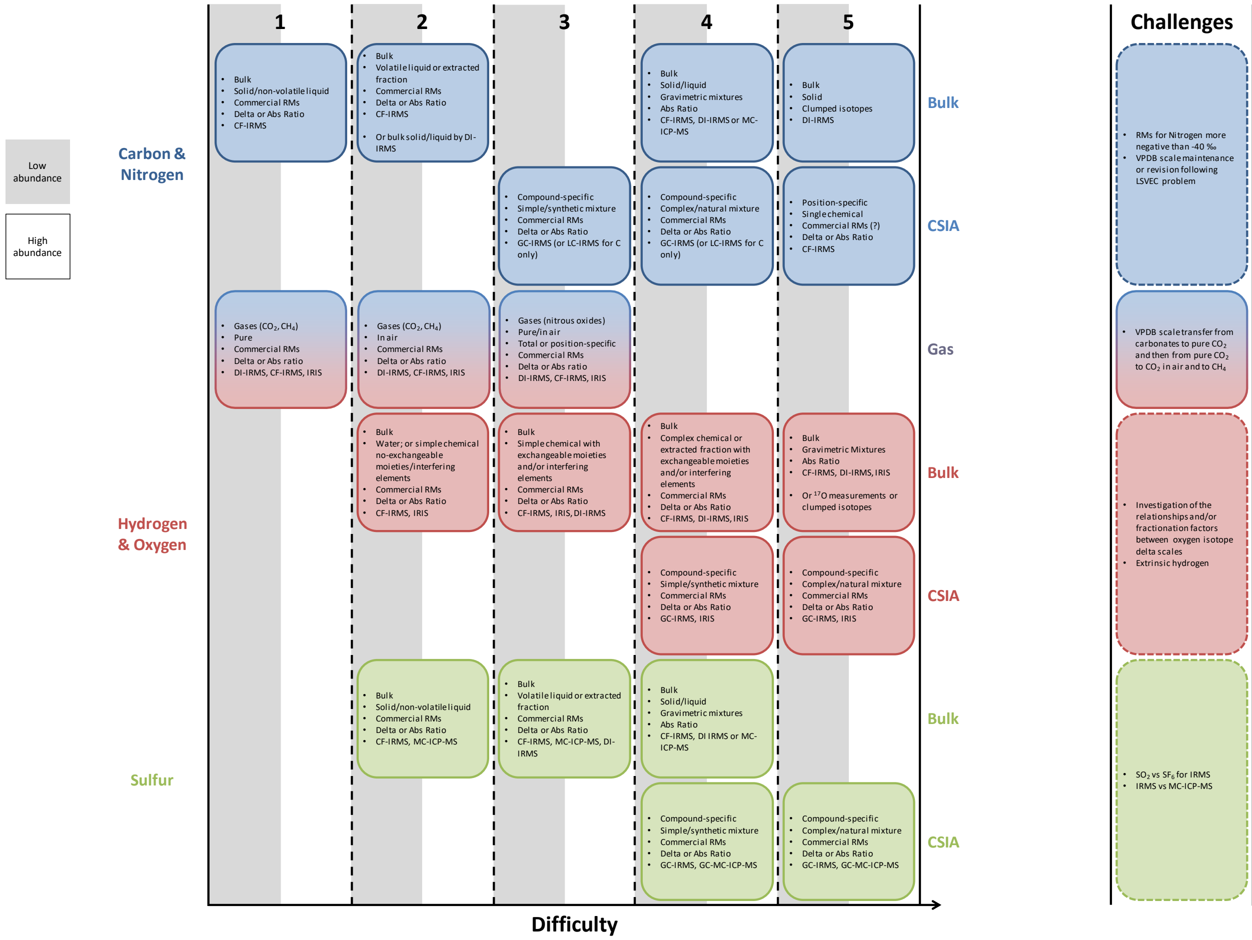


Fig. 2. Measurement space of the SHNOC elements

In case of the Non-SHNOC group more than 50 elements might be investigated from ultra-trace components (e.g. sub ng amounts of Pb in ice-cores) to major components (e.g. Mg in dolomite) by applying different mass spectrometric techniques such as ICP-MS, TIMS, and SIMS. Additionally, the measurands for Non-SHNOC elements range from isotope amount ratios to delta values and conventional isotope ratios, while for the SHNOC elements the measurand predominantly is a delta value. This huge variety, which will be increased by species-specific isotope ratio measurements in the near future, cannot be visualized in a one-to-one schematic. Here, the complexity must be reduced, preferably to a two- or three-dimensional diagram. The measurement space of the Non-SHNOC elements, therefore, is spanned by the isotope ratio vs. the matrix complexity and is subdivided in 9 rectangular fields (Fig. 3), which should depict the subspaces for the coverage by Key Comparisons. The third dimension is being added by a colour code depicting moderate, good and extremely good uncertainties.

The identified measurement spaces for SHNOC and Non-SHNOC elements are not finalized yet and are subject to an ongoing discussion. Regular updates will be provided within this document. Due to its provisional character it is obvious that a complete coverage of the measurement space(s) by Key Comparisons for the coming ten years is not possible. However, an outlook of up to seven Key Comparisons and five Pilot Studies can be given in Tables 1 and 2. With the decision of the IRWG to organize one Key Comparison per year and with considering the already running comparisons and studies a coverage for the next five years can be ensured. Furthermore, benchmark comparisons will be identified, which will be repeated on a regular basis (e.g. every five years) and will serve to support existing and upcoming CMC claims.

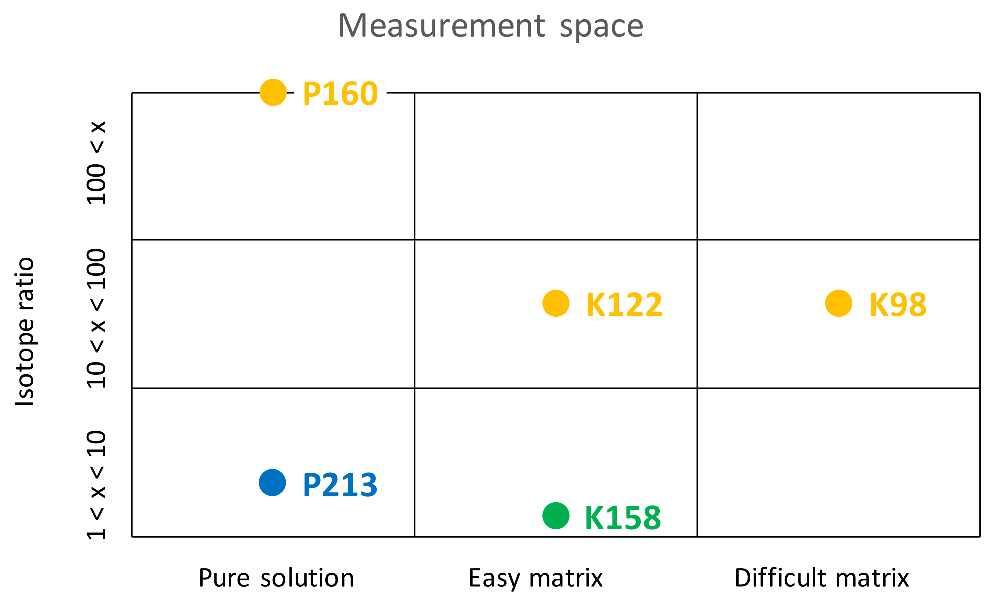


Fig. 3. Measurement space for Non-SHNOC elements with current examples: a) K98 Pb isotope ratios in bronze, K122 anionic impurities and lead in salt solutions and P160 isotope ratios of silicon highly enriched in ^{28}Si (all completed), b) P213 Cu delta measurements in high-purity materials (currently running), and c) K158 Sr isotope ratios in rice (scheduled for 2021/2022); the colour reflects the uncertainty level of the isotope ratio: ● moderate, ● good, ● extremely good

Table 1: Currently planned Key Comparisons for the period 2021-2030

#	Topic	Target elements	Key Comparison	
			Benchmark	**Code**
1	Bulk $\delta^{13}C_{VPDB}$ and bulk $\delta^{15}N_{Air}$ in a high purity single chemical, one organic and one inorganic compound.	C, N		
2	Delta measurements of metal elements in pure mono-elemental solutions	Li, B, Mg, Cu, Fe, Zn, Ag, Cd, Pb	X	
3	Bulk $\delta^{13}C_{VPDB}$ in a high-purity compound	C	X	
4	Calibration of isotope amount ratios by applying the FGIM approach	Cu		
5	$\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB\text{-}CO2}$ of pure CO_2	C, O		
6	Conventional isotope ratios in a pure solution and in a matrix sample	Sr, Nd, Hf		K158*
7	Bulk $\delta^{13}C_{VPDB}$ of an extracted fraction of a real-world sample requiring substantial sample preparation, e.g. collagen isolated from bone, “proteins” within honey.	C		

* Planned as CCQM-K158 part C “Conventional Sr isotope ratios in rice”, shifted to 2021/2022, new Key Comparison number will be applied for

Table 2: Planned stand-alone Pilot Studies for the period 2021-2030

#	Topic	Target elements
1	$\delta^{34}S_{VCDT}$ in pure compounds or solutions by IRMS and MC-ICP-MS	S
2	Direct (solid-state) measurements by e.g. LA-(MC)-ICP-MS, SIMS…	Pb, Sr, B, Nd, Hf
3	Isotope ratios or delta values of non-metals by IRMS and MC-ICP-MS	Cl, Br, S, Se
4	Compound specific carbon delta value of a single component within a mixture, e.g. a single steroid in an artificial mixture of steroids	C
5	Bulk $\delta^{2}H$ and/or $\delta^{18}O$ in a simple single chemical with no exchangeable moieties perhaps with a follow-up Key Comparison	H, O

3. Summary of work accomplished (2017-2020)

In April 2017 the CCQM formed a task group to investigate on the current state of isotope ratio metrology and to draw conclusions concerning a potential engagement in this field. In April 2018, this task group presented its report the CCQM. The report and its conclusions convinced the CCQM to establish a new working group on isotope ratios (IRWG). The IRWG took up work immediately and organized regular meetings since then, one in April and one in October of each year. In parallel to the meetings work started on strategic issues such as identifying the measurement spaces, required comparisons to cover those spaces and on harmonizing CMC formats in isotope ratio measurements. Practical work focused on the planning and initiating of the first Key Comparison and Pilot Studies of the IRWG.

CCQM-P204 (Start 02/2020)

The Pilot Study CCQM-204 is aimed at evaluating the level of compatibility of laboratories' measurement capabilities to value assign isotope ratios in samples of pure CO2 gas, ($\delta^{13}C$ vs. VPDB and $\delta^{18}O$ vs. VPDB-CO_2). It will also provide insight into the traceability chains and reference standards being employed to currently achieve these measurement results. The comparison is organised by the BIPM and the IAEA. It will consist of pure CO_2 samples being prepared by the BIPM. The BIPM will fill and send to each participating laboratory four 50 mL cylinders containing pure CO_2, each one filled with a gas with a different nominal $\delta^{13}C$ value vs VPDB: -1 ‰; -9 ‰; -35 ‰; and -42 ‰. Laboratories wishing to participate in the comparison will be required to purchase and send the 4 small cylinders and valves (mandatory models recommended by the BIPM) for filling. Transport costs to and from the BIPM are to be covered by the participating laboratory.

Results of the comparison will be compiled by the BIPM and evaluated jointly by the BIPM and the IAEA. All calculations will be performed based on the comparison results and the values and uncertainties submitted by the participants and the study coordinators. Nominal values for each gas sample distributed to participants will be based on measurements performed at the BIPM and the IAEA with traceability to standards maintained at the IAEA. Proposals for reference values for the samples will be calculated from the results from the participants. The results of the comparison are expected to provide a description of the current level of performance of laboratories and the state of the art to be achieved, as well as information for planning a future Key Comparison.

CCQM-K167/P211/P212 (Start 11/2019)

Verification of the authenticity of food items is essential to ensure the quality and safety of food products. Carbon isotope delta, $\delta^{13}C_{VPDB}$, measurements are routinely used to determine the authenticity of food products by determining the source of the food product and detecting adulteration of the food products via addition of unreported additives.

The first Key Comparison for $\delta^{13}C_{VPDB}$ measurements (CCQM-K140) was conducted in 2015-2016, and honey samples were measured. The October 2018 meeting of the IRWG in Ottawa, Canada, included a need for more Key Comparisons for SHNOC measurements. This proposed Key Comparison will support Calibration and Measurement Capability (CMC) claims for $\delta^{13}C_{VPDB}$ measurements, allowing for institutions to demonstrate and improve core capabilities in this area. The goal of this Key Comparison is to establish current best achievable uncertainties for $\delta^{13}C_{VPDB}$ measurements.

The Key Comparison is coordinated by NRC Canada and is focusing on $\delta^{13}C_{VPDB}$ measurements in pure vanillin. In parallel to K167 the Pilot Study P211 is organized, which gives less experienced institutes the chance to participate. In addition, P212 is conducted, which evaluates the coherence of $\delta^{13}C_{VPDB}$ values assigned to the various international reference materials in a multi-laboratory intercomparison.

CCQM-P213 (Start 02/2020)

Accurate and precise isotope ratio measurements are playing an increasingly important role in modern analytical sciences. Significant and often unique applications include terrestrial and extra-terrestrial investigations involving geochronology, archaeology, provenance studies (chemical "finger-printing"), life/medical sciences, forensic sciences, environmental and atmospheric sciences, as well as traditional analytical chemistry and physics. Most studies are reporting isotope ratios in a delta notation, which allows small isotopic differences to be expressed unambiguously without the need for the exact knowledge of absolute isotope ratios of the standard, and which is fit for purpose for many studies. After numerous discussions at Isotope Ratio Working Group (IRWG) meetings (October 2018, April 2019 and October 2019), it was decided to conduct a Pilot Study on delta Cu isotope ratio measurements relative to NIST SRM976 Cu isotopic standard in high purity materials first, to demonstrate measurement capabilities of NMIs/DIs.

4. Examples of impact of CCQM activities (2017-2020)

No complete impact case studies are available yet, because practical work of IRWG has been taken up in 2018 with first studies/comparisons starting in 2019/2020. Due to the strong involvement of CCQM-IRWG member in stakeholder associations/committees, however, a impact has already been created.

Triggered by CCQM-P213 "Delta values of copper isotope ratio measurements in high purity materials" the certification of a Cu isotopic reference material certified for Cu delta values has been started at BAM.

The recently published "FIRMS Guidance for the forensic interpretation of isotope ratio data" [23] emphasises that methods used to obtain isotope ratio data should be traceable and measurement uncertainty must be evaluated. This inclusion of important metrological principles is a direct result of the participation of IRWG members in drafting the content of this guidance.

An IUPAC project [24] has been initiated seeking to review and assess all published absolute isotope ratios for the international measurement standards realizing isotope delta scales. The aim is to update the current recommended values and linking the isotope delta scales to the SI.

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6. Document revision schedule

Draft CCQM-IRWG Strategy V1.docx	1st draft without executive summary	2020-12-11
Draft CCQM-IRWG Strategy V2.docx	revised draft without executive summary	2020-12-16
Draft CCQM-IRWG Strategy V3.docx	revised draft with executive summary	2021-01-16
Draft CCQM-IRWG Strategy V4.docx	revised version incl. comments by IRWG members	2021-01-29
Draft CCQM-IRWG Strategy V5.docx	revised version incl. comments by IRWG members	2021-02-17