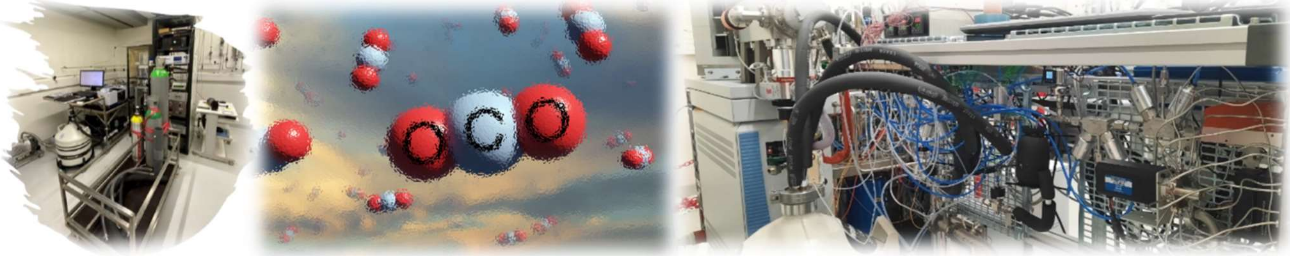
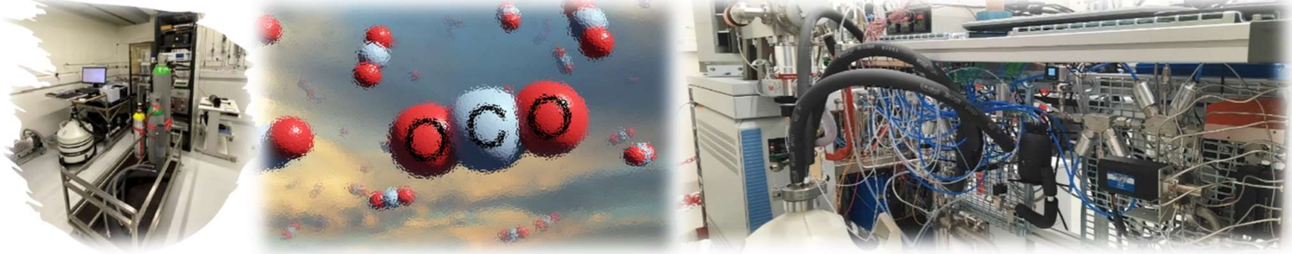


CCQM GAWG-IRWG Workshop on Carbon Dioxide and Methane Stable Isotope Ratio Measurements

Laboratorio Tecnológico del Uruguay (LATU), Montevideo, Uruguay, 9-10 October 2023



Report

The workshop on "Carbon Dioxide and Methane Stable Isotope Ratio Measurements" was held at LATU (Laboratorio Tecnológico del Uruguay), Montevideo, Uruguay on the 9th and 10th of October 2023. The workshop marked the formal launch of the isotope ratio task group, an initiative under the aegis of the CCQM (consultative committee for amount of substance in chemical and biological measurements) gas analysis and isotope ratio working groups (GAWG and IRWG) to support the development of a global metrology infrastructure for isotope ratio measurements in atmospheric greenhouse gases and related applications. As its first activity the task group conducted a workshop, aided by organizational support from LATU, assembling experts from the industry, national metrology and designated institutes (NMIs and DIs), government agencies, IAEA (International Atomic Energy Agency) and BIPM (International Bureau of Weights and Measures) intergovernmental agencies, as well as academia to focus on the metrology aspects of isotope ratio measurements for greenhouse gases. Participant expertise spanned across research, atmospheric monitoring, paleoclimatology, energy gases, metrology, isotope reference material, specialty gas, and measurement technologies. A total of 26 NMIs and DIs participated of which half are engaged in isotope ratio metrology activities and are active participants of regional metrology programs and international comparison studies. The industry stakeholders were represented by both the optical and mass isotope ratio spectrometer manufacturers, specialty gas supplier and isotope testing laboratories. The workshop was held in a hybrid mode with 100 participants.

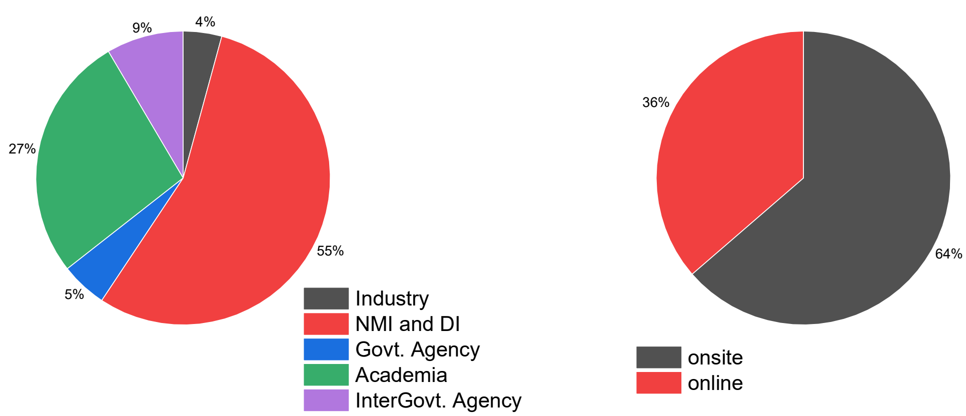
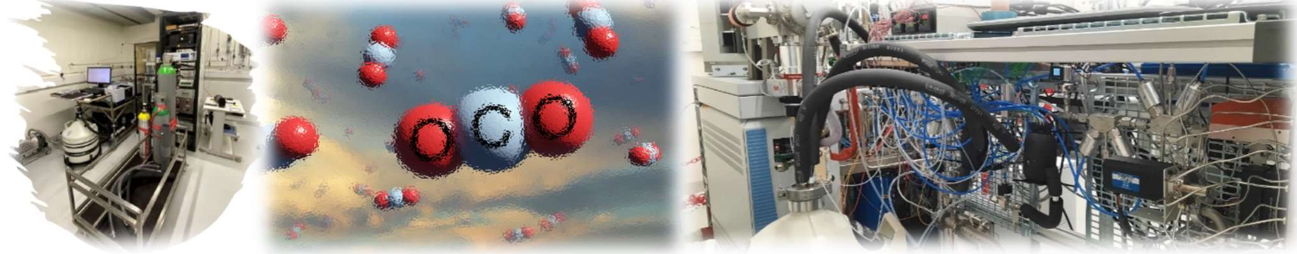


Fig 1. Distribution of participation

The workshop's primary objective [1] was to hear challenges and advances in CO_2 and CH_4 isotope ratio measurements to better identify the needs for attaining global comparability in isotope ratio measurements through traceability. Areas covered related primarily to atmospheric measurements but also delved into the stringent needs for ice-core measurements, advances in energy gases reference materials, emergence of ΔO17 proxy measurements and a path to SI traceability of isotope ratio.



A total of 33 presentations [2-34], (in long and short talk formats) were covered, broadly distributed over 1) Metrology and measurement infrastructure, 2) Measurement technologies and 3) Reference material and calibration topics. Several sub-topics including ongoing capacity building efforts, collaboration, comparison studies, global data compatibility critical to a robust global infrastructure were presented. The workshop provided a unique opportunity for instrument manufacturers and users to share advances in measurement technologies and address emerging challenges for standardization of measurements. As much of the standardization rides on availability of reference materials and calibration experts in specialty gas, specialist laboratories, academia and NMIs provided their unique perspective on isotope reference material (iRM) development, availability, stability, value assignment, traceability, and uncertainty estimation. To help introduce the metrology perspective to the participant community lying outside the CCQM fold a presentation on the "BIPM and CCQM overview and strategy for gas isotope metrology" was made by Dr. Robert Wielgosz of the BIPM [2]. Several global, regional and national GHG (greenhouse gas) monitoring programs were identified necessitating the need for isotope reference gases, achieving consistency in isotope ratio measurements, maintaining and identifying traceability chain for isotope ratio measurements, developing standardized calibration strategies for emerging optical isotope ratio instrumentation, reporting values on a common scale towards the development of a global infrastructure for GHG and related isotope ratio measurements.

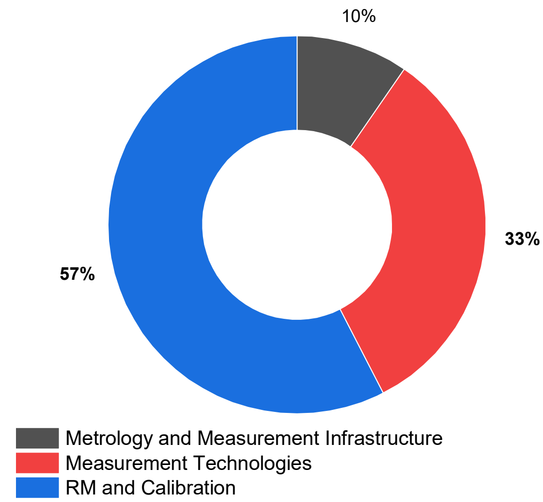
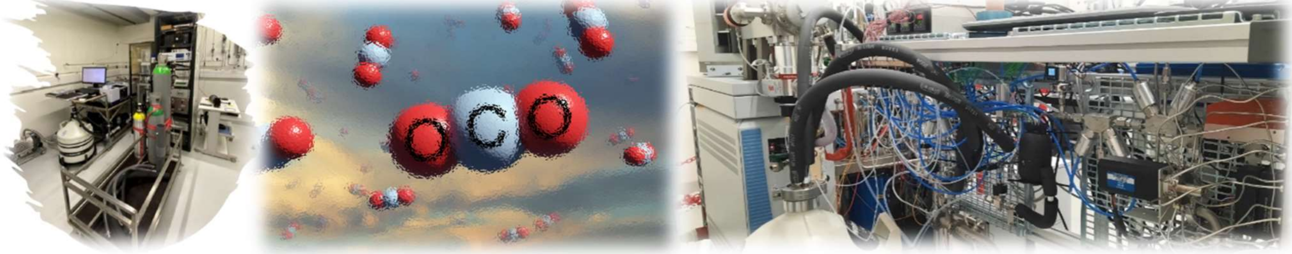


Fig 2. Distribution of topics

Guided by session rapporteur reports and ensuing discussions (please see rapporteur reports and discussion areas in Appendix 1) several issues and recommendations were identified for further action. Session synopsis and discussion recommendations are presented below.

Session 1 - Metrology and Measurement Infrastructure

This session had five talks [3-7] covering initiatives in the EURAMET SIRS and STELLAR projects for isotope gas reference material development, CCQM international comparison on pure CO_2, EURAMET isoMET metrology program for methane isotope emission in Europe, global data compatibility for $\delta^{13}C$ CO_2, several IAEA initiatives covering reference material development, guideline development for CH_4 isotope ratio analyzer and the establishment of a training center in Argentina to support the WMO-GAW program. Several

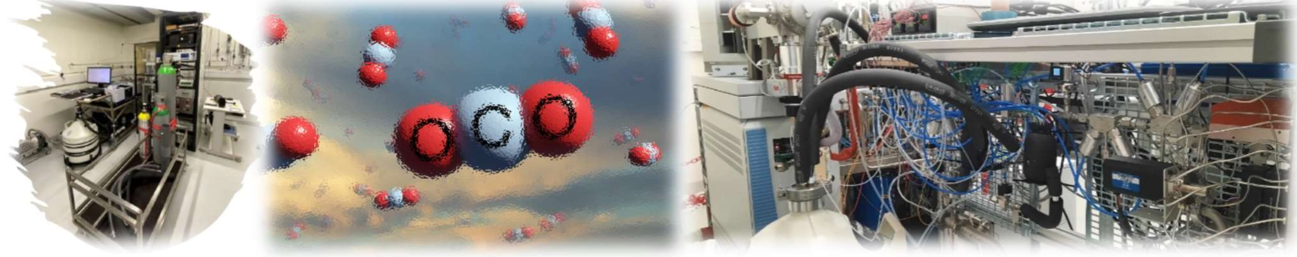


positives were brought to light including continued progress in 1) quantifying and achieving stability of iRM gas cylinder mixtures, 2) tuning of $\delta^{18}O$-CO_2 values in reference materials, 3) achieving comparability in iRM gas cylinder preparation across labs, 4) demonstrating the utility of having pure CO_2 isotope RMs as validation and harmonization standards, 5) the development of field measurement programs to support increased monitoring networks, 5) the ability to reduce scale offsets in decades of atmospheric isotope ratio data, as well as 6) the ongoing capacity building efforts for isotope ratio measurements in Latin America. Areas identified for continued addressal and innovative solutions included the quantification and rectification of variability in the carbonate extraction for realizing the VPDB scale via the primary iRM, providing a realistic representation of the underlying uncertainties, improving (reducing) the 18O stability (uncertainty) in gas cylinder CO_2 iRM mixtures, supporting efforts for the expansion and development of pure CO_2 iRMs as standardization tool, the maintenance of CO_2-air scale(s) stability, comparison and challenges in harmonizing and maintaining multiple non-SI traceable realizations of the isotope ratio scale.

Session 2- Measurement Technologies

This session had talks [8-14] from both manufacturers and researchers involved in isotope ratio measurements. The contributions from the manufacturers covered advances made in instrumentation, provided examples from various applications, shared aspects of performance assesment, instrumental and calibration challenges in mass spectrometer [8] as well as optical spectroscopy [12-14]. Talks [9-11] from NMI and academia addressed various facets and challenges of isotope ratio measurement including 1) the quantification of matrix interferences in optical analyzers, 2) development of custom interfaces and protocols for mass spectrometer and optical analyzer based ice core measurements of CH_4 amount fraction and isotope ratio, and 3) atmospheric ΔO17 measurements using laser absorption spectroscopy. While advances in measurement technologies are providing more options to the user, lack of standardized measurement procedures and appropriate reference materials impede their usage and applicability for attaining metrologically robust data.

In the area of ice-core CH_4 [9] calls for reference materials at lower amount fractions (400 nmol mol^{-1} for glacial air) compared to modern air (1850 nmol mol^{-1}) and standardization of custom-made continous flow methods for extraction and preconcentration from low volume ice core sample air (25 scc, nmol level) to achieve $\delta^{13}C$-CH_4 precision of < 0.1 ‰ were made. Additionally, absence of pure CO_2 iRMs at the biogenic source levels (c.a. -50 ‰) for referencing $\delta^{13}C$-CH_4 measurements (based on combustion to CO_2) was highlighted.
The application of direct 627 ($^{12}C^{16}O^{17}O$) isotoplogue measurements via optical methods to the study of oxygen isotope anamoly [11] as a promosing complement to IRMS based approaches for quantifying ΔO17 in the troposphere was introduced. Approaches of uncertainty estimation involving bracketing, isotoplogue amount fraction versus isotopologue ratio, extrapolation, interpolation methods were presented for data treatment of ΔO17 optical measurements.

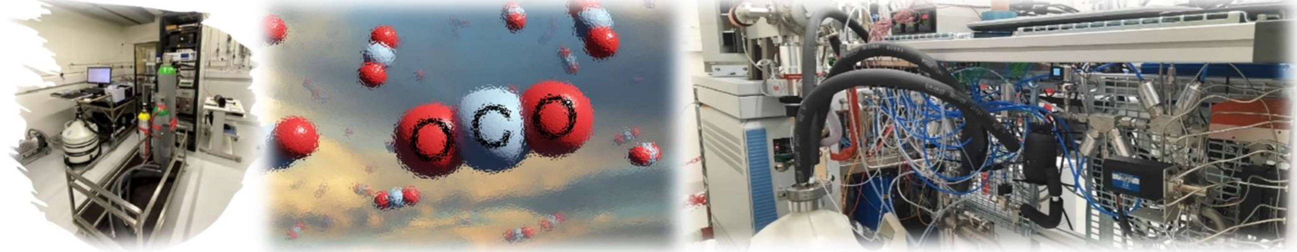


empirical correction schemes [10] for isotope matrix effect in optical measurements along with merits and demerits of isotopolgue amount fraction versus the isotope delta based calibration were discussed for CO_2 and CH_4 using commercial isotope optical analyzers.
It was clear that the metrology community and instrument manufacturers need to work in tandem for seamless integration of both instrument upgrades as well as the development of standardization protocols.

Session 3 – Reference Materials and Calibration

The reference material and calibration oral session had five talks [15-19] covering the development and verification of isotope RM mixtures in gas cylinders, recommendations from specialty gas supplier to avoid isotope fractionation in gas cylinder CO_2 delivery, development of CH_4 iRMs for standardizing CH_4 isotope ratio measurements, hydrocarbon reference mateirals for energy gases, and calibration approaches for triple oxygen measurements of atmopsheric CO_2. It is encouraging to see the continued improvement in gas isotope RM mixture preparation methods in cylinders with stabilities for $\delta^{13}C$-CO_2 in air approaching 0.01(0.02) ‰ over 1.5 years shelf life, development of realistic uncertainty budget schemes including gravimetric preparation and analytical measurement contributions [15]. Preliminary results [15] on fit-for-purpose isotope $\delta^{13}C$-CO_2 in air mixtures (obtained by physical mixing of parent gas isotope source materials) show agreement of the gravimetric predicted values with independent IRMS value assignments at the 0.1 ‰ level. Future work is expected to further test this method and hopefully quantify biases between physical and stochastic mixture values. In the absence of available ISO standards for preparation of gas isotope reference mixtures the ongoing progress in cylinder mixture preparation methods [15], its storage and delivery aspects [17] along with companion work in SIRS and STELLAR programs (covered in other sessions) could help the development of standardized protocols for preparation of gas isotope reference mixtures, in a manner similar to classical gravimetric standards for amount fraction production.

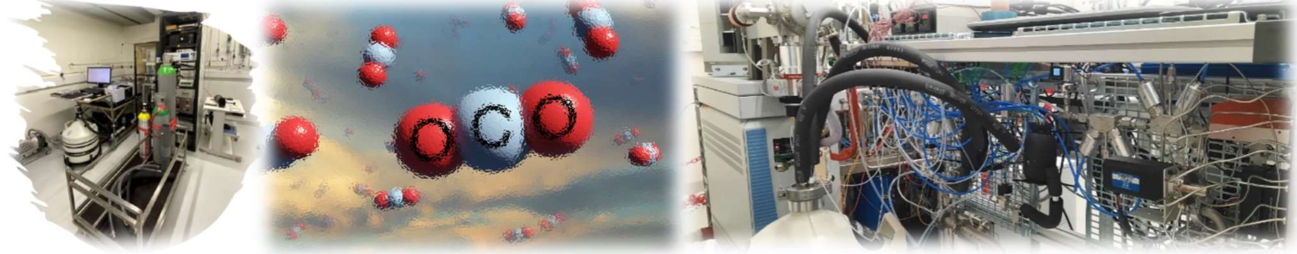
The problem in achieving 0.02 ‰ level compatability in $\delta^{13}C$-CH_4 isotope ratio measurements due to the absence of unifying CH_4 iRMs (leading to a scatter of 0.5 ‰ on count of several scale realizations in use) was presented [16]. Ongoing work on the development of suite of CH_4 iRMs and their mixtures in air has allowed harmonization of CH_4 isotope ratio measurements (much like the role played by JRAS iRMs for CO_2-air isotope ratio measurements). However, the stability, uncertainty, availability of super-light (< -50 ‰) CO_2 iRMs for anchoring biogenic CH_4 are some of the issues that need continued attention and collaboration.
The lack of iRMs for the emerging area of triple oxygen isotope research was presented [19] with needs for Δ'17O (CO_2) (^{17}O-excess) in the range of 400 per meg in contrast to the 50 per meg range covered by the currently VPDB and VSMOW-SLAP international iRMs for δ13C and δ18O measurements. An INTERCAP campaign like the INTERCARB effort undertaken by the clumped isotopes community was proposed to develop iRMs and achieve scale realizations to VPDB and VSMOW-SLAP.



The transition from NIST NGS (natural gas standards) to USGS HCG (hydrocarbon gases) iRMs for $\delta^{13}C$ and $\delta^{2}H$ isotope ratio measurements was presented [18] extending the isotopic range and covering methane, ethane and propane for natural gas, coal gas and biogenic needs in the energy sector. Both the DI-IRMS and CF-IRMS methods, the latter including both GC-IRMS and GC-CRDS approaches were presented. Areas of overlap with the atmopsheric isotope ratio community could lie in addressing common standardization issues of data treatment from optical isotope ratio analyzers.

Poster Session

A total of 14 posters were presented in the form of short talk (3 min) and follow-up poster displays. Five of the posters [20,21, 22, 25, 27] from the NMIs of NPL (National Physical Laboratory, UK), VSL (Van Swinden Laboratory, Netherlands) and TÜBITAK (The Scientific and Technological Research Institution of Turkey) highlighted the cylinder gas mixture isotope RM development work as well as the development of measurement facilities for dissemination of CO_2-air and CH_4-air primary isotope RMs occurring under the SIRS and STELLAR projects. Contributions from BIPM [23, 29], KRISS [26], and NPL [25] covered efforts on their carbonate and/or CO_2-air extraction reference facility for upcoming comparison studies. KRISS [26] (Korean Research Institute of Standards and Science) also shared plans around their recent purchase of 271 Ultra MS for both absolute and isotope ratio measurements of CO_2 and CH_4 as well as development of synthetic gravimetric mixtures for absolute isotope ratio gas standards. NPL [27] shared plans on their capacity building of a new measurement setup for stable isotope ratio of pure CH4. The National Institute of Standards and Technology (NIST) [24, 30] provided updates on their CO_2-air isotope RM cylinder development work as well as in-house developed optical techniques for the measurement of the 13C/12C absolute isotope ratio in CO_2-air ambient amount fraction mixtures and of the absolute isotope abundance of N_2O isotopocules in pure N_2O samples. NRC (National Research Council Canada) [28] presented a unique interconnected multi-CO_2 material measurement approach to independently value assign the IAEA-carbonates and NIST iRM CO_2 gases, showing an overall agreement within their reported uncertainties as well as identifying trends for continued studies. Institute for Marine and Atmospheric Research (IMAU) [31] discussed their approach to harmonize atmospheric $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 data across laboratories from same stations by calculating offsets of time series data and validating it against available round-robin exercises. Juan Lopa [32] presented joint efforts between University of Oklahoma and Uni National de San Agustínde Arequipa, Peru to develop isotope lab for studying hydrological, agriculture, climate change and soil isotope signatures in Peru. The unique requirements to advance ice core studies of past greenhouse gas values [33] were presented by the Australia Antarctic Division (representing the entire ice core gas measurement community) and included the need for low amount fraction calibration gas mixtures (to match glacial levels for both CO_2 and CH_4) as well as isotope RMs to better understand current $\delta^{13}C$-CO_2 offsets (0.1 ‰) between the Law Dome and West Antarctic ice sheet ice cores. Picarro [34] presented results of comparison of their combustion module interface aided cavity ringdown spectroscopy (CM-CRDS) isotope ratio method with the traditional EA-IRMS.



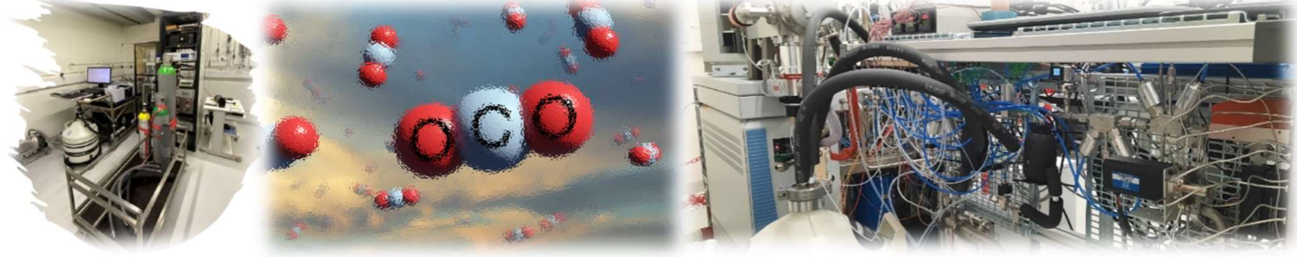
Discussion Recommendations

The rapporteur recommendations were condensed into 10 areas for the final discussion session (please see Appendix 1). The collated discussion recommendations and areas of continued interaction are presented below.

Carbonate: It is clear from the P204 comparison and STELLAR project studies that the carbonate reaction has variability across specialist laboratories at levels far exceeding their reported uncertainties. P204 studies [4] suggest variability of the order of 0.06 ‰ standard deviation amongst the specialist laboratories for δ13C-CO_2. STELLAR project [3] indicate differences upto 0.3 ‰ for δ18O-CO_2 across two specialist labs, exercising acid digestion of international reference carbonates. Discussions to harmonize and unpack the variables involved in acid digestion (phosphoric acid source, density, etc.) converged towards a proposal for developing a pilot CCQM comparison study for carbonate-CO_2 value assignment and its realistic uncertainty estimation. A model study based on circulation of P204 pure CO_2 gas samples for comparing carbonate-CO_2, derived from acid digestions, was proposed with a companion deliverable of a best practices document for carbonate acid digestion and its uncertainty estimation.

Pure CO_2: Returning to the P204 comparison study for context on the role played by pure CO_2 isotope RMs, data normalization with common pure CO_2 samples allowed harmonization of results across participant calibration and measurement approaches. Picking another example, pure CO_2 NIST iRMs (8562, 8563, 8564) have now been in circulation for over 15 years and served as a critical quality control, validation and harmonization tool (including the validation work in the recent development of IAEA carbonates). However, replacement pure CO_2 iRMs are not available as the existing iRMs reach depletion. In discussions on continuing the availability of ease-of-use pure CO_2 individual iRM development efforts at NMIs and other institutes need to be encouraged but be adequately vetted in their data quality, homogeneity, stability, uncertainty, batch production capabilities prior to building comparison protocols for arriving at consensus values and be covered by CMCs for dissemination. Notable efforts, include 1) IAEA's current effort to develop Cu tube based pure CO_2 iRMs (and potentially extending it to primary RM carbonate-CO_2) and 2) BIPM infrastructure to produce pure CO_2 iRMs (as demonstrated under the P204 comparison study).

CO_2-air: While the development of a unifying CO_2-air isotope RM in the form of JRAS (Jena Reference Air Standard) has helped improve the consistency in CO_2-air isotope ratio measurements (pre JRAS comparisons indicated variability in the 0.2 ‰ range) offsets within isotope labs using the common JRAS CO_2-air RMs at the 0.02 ‰ level (exceeding the WMO computability goal of 0.01 ‰ for δ13C-CO_2) have been observed and are currently being addressed [6]. Discussions on this topic during the workshop raised several issues including 1) Need to better understand JRAS stability, verification, value assignment protocols, 2) Calibration hierarchy and its maintenance for the JRAS, 3) Comparisons of VPDB scale realizations for CO_2-air, 5) Scale realization conversion factors, 6) Development of alternate CO_2-air iRMs for robustness, and 7) Usage of correct terminology in discussing scales and scale realizations. The planned 2024 CCQM pilot comparison study on CO_2-air [2, 23] is expected to help identify some of these

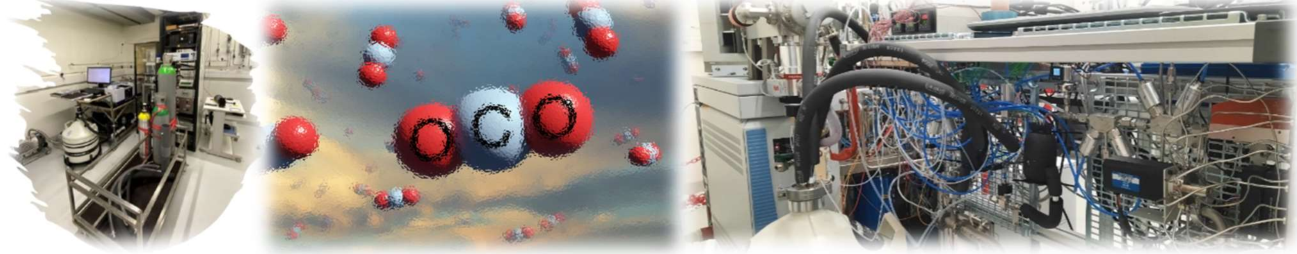


issues. However, further discussions on these and related items leading into the planned study would be useful.

Best practices, SOPs for optical analyzers and instrument support: The development of optical isotope ratio analyzers has undoubtedly paved way for isotopolgue specific, field-based high throughput measurements (abundantly demonstrated through the talks). However, to maximize their utility detailed SOPs (standard operating procedures) need to be developed to cover calibration gas requirements, data treatment procedures (quantifying matrix effects, temperature sensitivities, concentration dependence, isotopologue versus delta calibration approaches, uncertainty estimations), data reproducibility, data validation and quality control procedures to list a few. A joint effort between metrology institutes and optical instrument manufacturers is proposed for developing best practices. In this light IAEA recently completed a "Guideline for measurements of stable isotopes in atmospheric CH_4 to characterize CH_4 sources" document using Picarro isotope ratio analyzer that could be potentially expanded to the form of an SOP. Another ongoing effort is the EURAMET isoMET program [5] that will seek to harmonize isotopic CH_4 measurements from field optical isotope ratio analyzers. The recent call for WMO-coordinated global greenhouse monitoring infrastructure is expected to continue to increase demands for field optical isotope ratio analyzers and isotope RM gas cylinders to calibrate it. The community needs to work jointly on addressing the underlying challenges. For instrumentation hardware and software support a concerted effort between NMIs and manufacturer is needed for seamless support.

Quality management systems (QMS): Discussions on QMS continued the theme started in the SOP thread, i.e., the need for best practices as it would apply to isotope standard development, their maintenance as well as extension to data quality management for isotope ratio measurements. Examples from ICOS (integrated carbon observation system), ISO/REMCO (committee on reference materials), WCC (world calibration center) were discussed. There appears to be limited access to guidance documents for maintaining isotope reference materials and measurement quality in the "isotope" sphere within the GAW and ICOS network compared to "amount fraction" measurements and standards. In the case of CO_2 isotopes there is a CCL (central calibration lab) lab but no WCC directly addressing the needs for quality assurance and audit. For CH_4 isotopes both are missing. A move to further developing and sharing best practices between communities (QMS expertise of metrology institutes to the isotope ratio community), alignment with ISO 17025 and ISO 34 guidelines, developing ISO standards for isotope reference materials preparation much akin to the classical gravimetric methods, as well as defining the roles and expectations between various stakeholders is desirable.

CH_4: The metrology community needs to continue working closely with expert isotope labs to better understand the existing calibration hierarchy for CH_4 isotope ratio measurements, current scale realizations, ongoing gas iRM development work (its value assignments, uncertainty, quality control, stability), availability of transfer standards, measurement approaches towards developing a protocol for an international comparison study and infrastructure development.



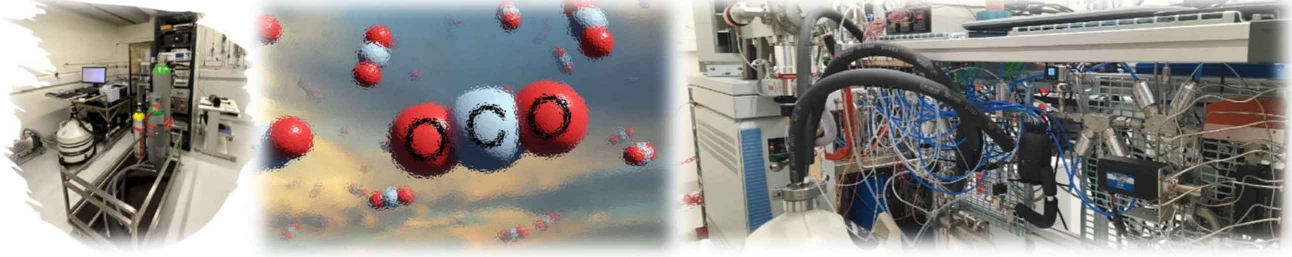
Others: Efforts to better understand and support the unique needs of ice core community, ΔO17 (CO_2) atmospheric measurements, overlap with energy gases and others need to be encouraged through active collaborations.

Conclusion

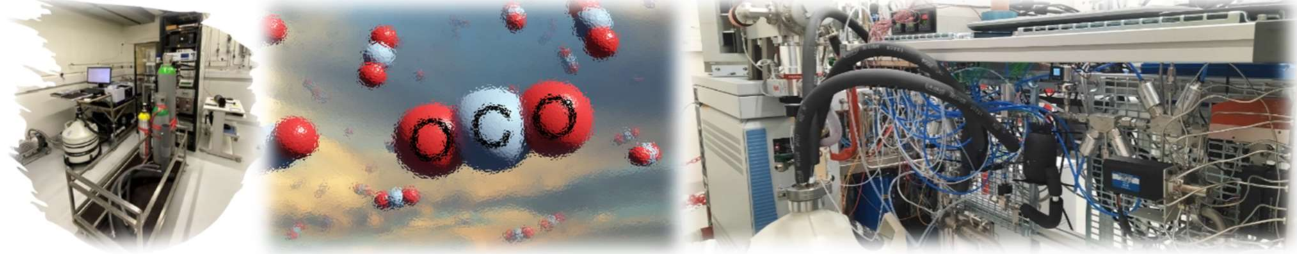
In conclusion the workshop succeeded in getting the isotope ratio and metrology communities together for constructive discussions on current standardization issues in gas isotope ratio measurements. The recommendations made will help the task group identify areas and partners for continued stakeholder engagement to support the CCQM gas analysis, isotope ratio working groups and BIPM towards the development of a global metrological infrastructure for gas isotope ratio measurements and standards. In instances where current support appears limited (e.g., ΔO17 (CO_2), ice core RMs, and others), collaboration efforts are encouraged.

Workshop Presentations

1. Workshop Goal, Abneesh Srivastava, NIST
2. BIPM and CCQM Overview and Strategy for Gas Isotope Metrology, Robert Wielgosz, BIPM
3. Advances in Isotope Ratio Gas Metrology: HIGHGAS, SIRS and STELLAR, Paul Brewer, NPL
4. Lessons learned from CCQM P204, CO_2 Isotope Ratios (δ13C and δ18O) in pure CO_2, J. Viallon, BIPM
5. Metrology for European emissions verification on methane isotopes, Javis Nwaboh, PTB
6. Can we achieve compatibility in measurements of atmospheric d13C CO_2, Sylvia Michel, INSTAAR, University of Colorado Boulder
7. INT7020 project: Developing Capacity towards the Wider Use of Stable Isotopic Techniques for Source Attribution of Greenhouse Gases in the Atmosphere, Federica Camin & M. Emilia Ruiz, IAEA & SMN Argentina
8. IRMS measurements of CO_2 and CH_4, Issaku Kohl and Nina Albrecht, Thermo Fisher
9. Towards measuring δ13C-CH_4 on <1 nmol CH_4 with < ± 0.1‰ reproducibility, Michael Döring, University of Copenhagen
10. Quantifying matrix effects for measurements of CO_2 and CH_4 amount fractions and 13/12C isotope ratios for two CRDS analyzers, Jelka Braden-Behrens, PTB
11. Δ17O measurements of atmospheric CO_2 using laser absorption spectroscopy, Pharahilda M. Steur, University of Gronigen
12. Measurement of isotopic ratios in atmospheric gases using precision laser spectroscopy: Instrumentation and applications, J. Barry McManus, Aerodyne Research Inc
13. Development of a Trace Carbon Dioxide Isotopologue Analyzer Performance Evaluation Study, Graham Leggett, Li-COR



14. Measuring Stable Isotopes from the Atmosphere, Soil, and Even Hummingbird Breath All in One Instrument, Juan Carlos Guerrero, Picarro
15. Development and verification of gas reference materials of CO_2 in air for stable isotope determinations, Michael Sega, INRiM
16. Metrological challenges due to the absence of CRM for CH_4 isotopes, Peter Sperlich, NIWA
17. Delivery of Metrologically Robust Gas Isotope Reference Materials in Cylinders, Tracey Jacksier, Air Liquide
18. USGS hydrocarbon gas reference materials for stable carbon and hydrogen isotopic analyses, Geoffrey S Ellis, USGS
19. INTERCAP? A proposed (inter)calibration exercise for high-precision triple oxygen isotope analysis of CO_2 by optical spectrometry (and IRMS), Vincent J Hare, University of Cape Town, South Africa
20. Meeting the demand for δ13C CO_2, δ18O CO_2, δ 13C CH_4 and δ2H CH_4 Reference Materials for Climate Monitoring, Ruth Hill Pearce, NPL
21. Overview of the development of isotope ratio gas reference materials for δ13CH_4 and δ2H CH_4 within the Stellar Project, Stefan Persijn, VSL
22. Improvement of Static and Dynamic Stable Isotope Reference Gas Mixtures of CO_2 at 410 µmol/mol, Aylin Boztepe, TUBITAK
23. A reference facility for the comparison of CO_2 in Air isotope ratio standards, Edgar Flores, BIPM
24. CO_2 Air Gas Cylinder Isotope Reference Material Development, Kimberly J Harris, NIST
25. Progress towards an NMI based measurement facility for the dissemination of stable isotope measurements via CO_2 in air Primary Reference Materials, Eric Mussell Webber, NPL
26. Research plan and current progress for measurement of CO_2 and CH_4 isotopes in KRISS, Kiryong Hong, KRISS
27. Facility for the conversion of methane to carbon dioxide for linking of $\delta^{13}C$ CH_4 to $\delta^{13}C$ CO_2 using optical spectroscopy, Aimee Hillier, NPL
28. Independent Characterization of Carbon Dioxide and Carbonate Reference Materials for Improved Traceability to the VPDB, Michelle Chartrand, NRC
29. CO_2 isotope ratio reference gases: best achievable uncertainties on the VPDB scale, Joële Viallon, BIPM
30. Towards Artifact Free Measurements of Isotopic Composition of Key Greenhouse Gases, Michelle Bailey (presented by Abneesh Srivastava), NIST
31. Harmonization of atmospheric methane isotope ratio measurements from different laboratories: Procedures and Protocols, Bibhasvata Dasgupta IMAU
32. Implementation of a Laboratory for the analysis of stable isotope ratios at the National University of San Agustín de Arequipa Peru, Juan Lopa, Uni National de San Agustínde Arequipa
33. Advancing Stable Isotope Metrology for Ice Core Greenhouse Gas Studies, Daniel Baggenstos, AAD
34. Nature's Barcode: Molecular Tracking Using Carbon Stable Isotopes Measured by Picarro CM CRDS Examples of Food Adulteration Testing, Juan Carlos Guerrero, Picarro



Appendix 1: Rapporteur reports and discussion points

Session 1 - Metrology and Measurement Infrastructure (Rapporteur: Michela Sega)

- Development of Standard Operating Procedures for carbonate reaction systems
- Reference materials: harmonised guidelines for uncertainty evaluation; shared approach for selection and use
- Adopt best practices for gas standard stability, eg. For JRAS
- Organisation of further measurement comparisons among carbonate systems/linkage to gases? Extend CCQM-P204 for carbonate to CO_2 gas assesment, comparison

Session 2- Measurement Technologies (Rapporteur: Edgar Flores)

1- Approaches and challenges for atmospheric CO_2 and CH_4 isotope measurements: a Thermo Fisher Scientific perspective. Issaku Kohl, Qiong Li, Mario Tuthorn, Mieke Fischer, Nina Albrech

Issue and needs: Our user community of the MAT 253 requires that their instrument running under Qtegra has the same functionality as running under Isodata.

Recommendations : It is recommended that Thermo meets with the gas metrology community to understand their needs and requirements. The Gas metrology community recommends to Thermo to continue direct contact for producing an interface that will allow users to execute their applications as with ISODAT.

2- Towards measuring δ13C-CH_4 on <1 nmol CH4 with < ± 0.1‰ reproducibility, Michael Döring, Michael Dyonisius, Thomas Blunier

Issue and needs: Challenges in measuring CH_4 isotopes in ice cores include working with extremely small and limited samples, high costs associated with ice cores, and accessibility of significantly less sample compared to other methods.

Recommendations : The Gas metrology community urge underpin the work of the ice-core gas measuring community producing reference material covering the full range of glacial to inter-glacial amount fractions and stable isotope ratios

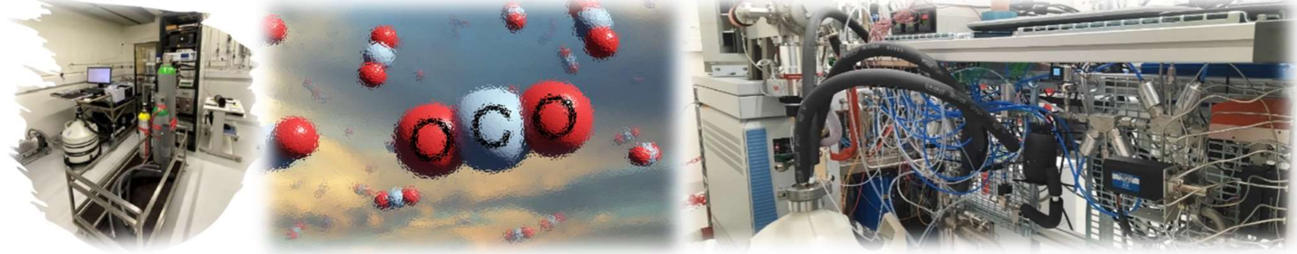
Wish list

Gas	Range mixing ratio	Isotope	Range iso 'need to have'	Range iso 'nice to have'	Scale
CO_2	150 to 450 ppmv	carbon-13	-10 to -5 ‰	-15 to -5 ‰	VPDB
CO_2	150 to 450 ppmv	oxygen-18	-10 to +2 ‰	-30 to +5 ‰	VSMOW+VPDB
CO_2	150 to 450 ppmv	oxygen-17	-10 to +2 ‰	*	VSMOW+VPDB
CH_4	300 to 2000 ppbv	carbon-13	-55 to -40 ‰	-65 to -35 ‰	VPDB
CH_4	300 to 2000 ppbv	hydrogen-2	-110 to -40 ‰	-150 to 0 ‰	VSMOW
N_2O	150 to 350 ppbv	nitrogen-15	+5 to +15 ‰	-5 to +30 ‰	air N_2
N_2O	150 to 350 ppbv	oxygen-18	+40 to +50 ‰	+30 to +60 ‰	VSMOW

3.- Quantifying matrix gas effects on ambient CO_2 and CH_4 amount fractions and 13/12C isotope ratios for two CRDS analyzers. Jelka Braden-Behrens, Anas Emad, Javis Nwaboh, Henning Bohlius, Volker Ebert

Issue and needs: Optical Isotope Ratio Spectroscopy (OIRS) analyzers that provide isotopic compositions based on calibration with reference materials, are sensitive to changes in gas matrix and concentration.

Recommendations: Urge the work presented in this talk is a good step forward to characterize and correct biases due to PBEs and focus on minor changes relevant to gas preparation . A peer review publication is encouraged including as reference Nara et al. 2012 paper.



4.- The challenges and potential of doing **Δ**17O measurements of atmospheric CO_2 using laser absorption spectroscopy. Authors: Pharahilda M. Steur, Hubertus A. Scheeren and Harro A. J. Meijer, Centre for Isotope Research (CIO), University of Groningen, Groningen, the Netherlands
Issue and needs: Seasonal variations in **Δ**17O cannot be identified, presumably due to too high "uncertainties" in the measurement results
Recommendations: Support **Δ**17O measurements and RMs
5.- Measurement of isotopic ratios in atmospheric gases using precision laser spectroscopy: Instrumentation and applications. J. Barry McManus, David D. Nelson, Scott C. Herndon, J. Robert Roscioli, Tara Yakovitch, Christoph Dyroff, Rick Wehr, Elizabeth Lunny, Joanne Shorter, Mike Agnese, Mike Moore, Aerodyne Research Inc.
6.- Development of Trace Carbon Dioxide Isotopologue Analyzer - Performance Evaluation Study, BJ Clark, Graham Leggett, Doug Lynch, Mark Johnson, Anatoly Komissarov, Israel Begashaw, LI-COR Biosciences, Lincoln, Nebraska, USA.
7.- Measuring Stable Carbon Isotopes from the Atmosphere, Soil, and even Hummingbird Breath All in One Instrument – Picarro Isotopic Carbon Analyzer Author(s): Juan Carlos Guerrero, Picarro
Issue and needs: The Global Greenhouse Gas Watch (GGGW) requires to provide sustained delivery of consolidated, top-down, monthly, global estimates of net GHG fluxes into and out of the atmosphere at a 100 by 100 km resolution. This will provide critical and timely input to the:

- Global Stocktake;
- Work program for urgently scaling up mitigation ambition and implementation.
- IPCC Assessment Reports.
- Enhanced Transparency Framework.
- National Inventories.

No standardization procedures from instrument manufacturers. Recommend starting with SOP for atmospheric and moving onto less stringent applications

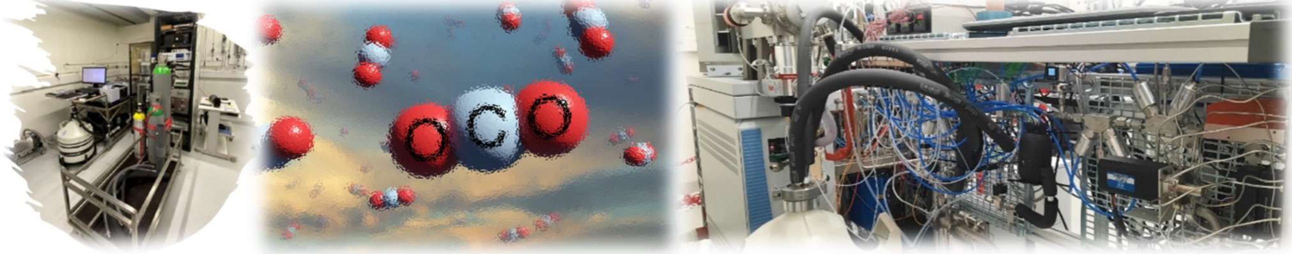
Session 3 – Reference Materials and Calibration (Rapporteur: Christina Cecelski)

Short version:

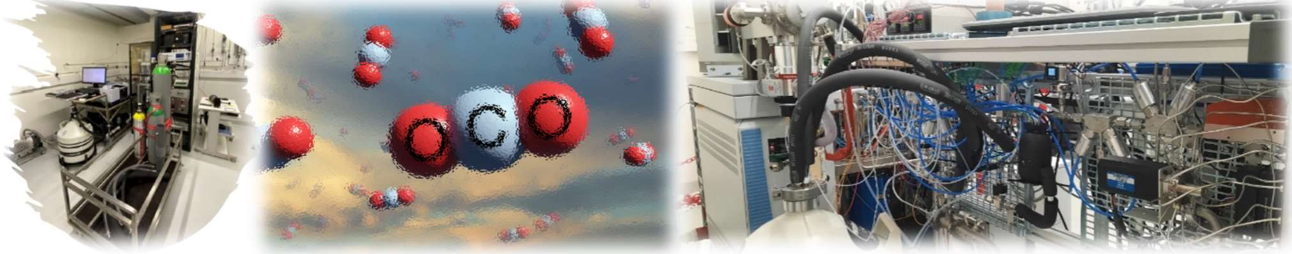
- Standards development underway with needs for further development:
    - Reduced uncertainties
    - Focus currently on carbon isotopes, less so on hydrogen, oxygen
    - Links to many different scales
- Common themes for developing effective reference gases:
    - Scale realization – harmonization efforts needed.
    - Uncertainties small enough to meet data quality objectives
    - Stability of reference materials

Detailed notes:
Michela Sega

- Gas reference material (RM) preparation, analysis by FTIR
- Involved in joint projects: SIRS and STELLAR (both NPL coordinated)

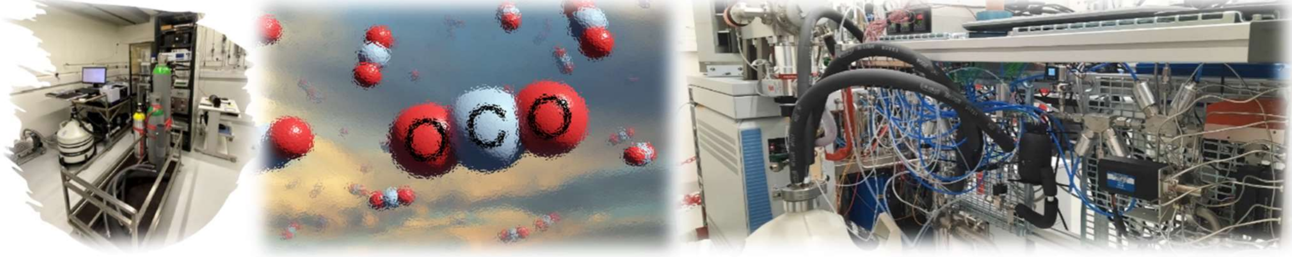


- Two methods: independent results, enables self-check
    - Gravimetric facility, verified by FTIR. Cylinders are conditioned at least 3x with matrix gas.
    - Dynamic dilution for calibration, used to prepare (400 to 500) µmol/mol and -48 ‰ to -8 ‰ for $\delta^{13}C$ and -27 ‰ to +2 ‰ for $\delta^{18}O$
- FTIR: Thermo Nicolet iS50, new MCT detector, 2 m cell, glove box for N2 flushing, BIPM software
- MALT/B-FOS for fitting spectra, certified amount fractions to optimize fitting parameters.
- ^{12}C Noise analysis (short term), dilute mixture and measure continuously
- Prep of RMs: blending mixtures with different δ values to get intermediate composition.
- Uncertainty contributors:
    - δ values of parent gases
    - ratios of parents
    - expanded uncertainty = 0.028 ‰ total
- 400 µmol/mol: start with pure CO_2, dilute to ambient. Starting compositions -42.15 ‰ and 1.22 ‰ $\delta^{13}C$-CO_2. Blend parent mixtures for total of three isotopic compositions at ambient amount fraction: -42.15 ‰, -19.58 ‰, and -19.58 ‰.
- SIRS uncertainty budget = 0.60 (k = 2); with STELLAR this uncertainty was reduced by half (0.34)
- Sample analysis by MPI (IRMS): 1 L flasks, fill with sample at 1 bar
- SIRS: 390.04 µmol/mol, -19.856 ‰; and 390.37 µmol/mol, -9.849 ‰ (U = 0.06)
- STELLAR: 404.72 µmol/mol and 409.46 µmol/mol (both at -42.148 ‰ (U = 0.03)
- Preliminary data: FTIR uncertainties very large compared with other verification. (Agrees, but is the large uncertainty hiding the bias?)
- New instrument: Picarro 2131-i for verification of CO2/air at ambient, to compare with FTIR verification. Goal is to reduce overall analytical uncertainties.
- Needs moving forward: continue with the uncertainty budget, tests with fitting spectral range, and improve analytical equipment
- Questions from the audience:
    - Zoltan asked about the preparation of the mixtures, Michela explained that they gravimetrically diluted 2 isotopic $\delta^{13}C$-CO_2 gases, then calculated new isotopic composition based on the gravimetry, then verified those values.
    - Edgar mentioned BIPM is using FTIR with uncertainties at 0.1 ‰. Instead of HITRAN they use two different amount fractions, same delta values, and at present they are making a calibration curve based on 3 points rather than bracket with 2 points, with the objective to improve the overall uncertainty.
    - Robert asked about the oxygen isotopes, limit is the distribution of oxygen with both starting gases, becomes important in some applications. Michela explained that the INRiM is satisfied with the agreement with MPI, cannot currently discriminate with the given uncertainties.



Peter Sperlich

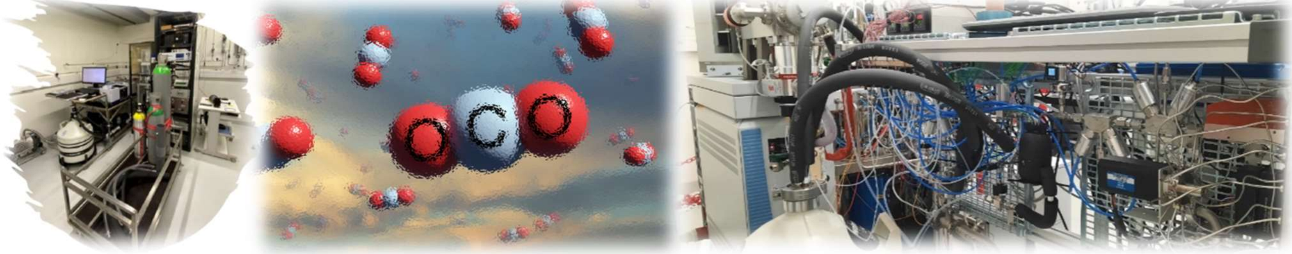
- CRMs for isotopes in CH_4 are not available, labs develop local solutions (local scale realizations), resulting in measurement offsets from the NIWA DI-IRMS value
- The spread is huge, ~0.5 ‰, but the DQO is 0.02 ‰
- Broad range of CRMs for $\delta^{13}C$-CH_4: carbonate, calcite, CO_2
- Many scale realizations, many labs don't measure at all, no impact from LSVEC (deemed unstable, not widely used)
- Scales maintained as cylinders with CH_4 in air
- PIT: Principle of Identical Treatment – to cancel out fractionation effects
- But CRMs use totally different materials for CH_4, fail the PIT
- 2016 PIT $\delta^{13}C$-CH_4 calibrations: EA-IRMS, autosampler for liquid/solid samples, combustion, inject CH_4 in between
- 2020 – built the same system, same method, CRMs, good agreement
    - Wide-spread USGS standard
    - CH_4 always out of range of CRM, extrapolate ~30 ‰
    - Need something at -60 to -70 ‰ range
- 2022 – remeasured because USGS paper indicated discontinuity
    - Within available CRMs, CH_4 calibrations are robust
    - USGS issue to be resolved, put all in agreement?
- 6 CRMs, primary $\delta^{13}C$-CH_4 calibrations (~44 ‰ range), measure with wide range (-39 to -70) ‰
- Suggestion: how can we make effective reference gases for the community?
    - Primary (wide range del value) -> dilute -> NIWA/MPI scale realization -> secondary mixtures (analyze vs primary with DI-IRMS) -> secondary gases for community with ≤0.02 ‰ agreement
- Round Robin (RR-CH_4-i)
    - INSTAAR/NIWA, four 30 L cylinders, NH air, 1 ppm CH_4
    - 9 ‰ spike $\delta^{13}C$-CH_4, 2 ppm Kr
    - Kr interference effect mostly controlled
- RR-CH_4-I results
    - NH air: 1900 ppb, 1 ppm Kr – good agreement
    - Kr spike: 1800 ppb, 2 ppm Kr – similar agreement
    - Isotope spike: 1850 ppb, 1 ppm Kr – offset changes (scale compression?)
    - 50 % CH_4: 1000 ppb, 1 ppm Kr – offset
- INSTAAR->NIWA conversion (NH air), plot NIWA vs INSTAAR -> curve used for conversion ("common scale")
- Compare "common scale" scale transfer – good agreement, 50 % of labs agree within compatibility goal of 0.02 ‰
- Equations to convert atmospheric data, adjusted agreement suggests well controlled continuity.



- Smoothed measurements of monthly means, compared agreement via scale transfer, similar seasonal pattern suggests the correction works and is stable; lso BGC IsoLab (GVN) applied correction from RR
- Questions from audience:
    - Paul asked about dilutions of methane and purity of CH_4 in the matrix gas. They tried a few approaches and the best was cryo air, but not available. They are developing a system to make their own CH_4-free air, but want to know how to measure CH_4 at such levels. Right now, no idea what the real concentration is because it is so low. Paul also mentioned WMO infrastructure, not aware of formalizing.
    - Tracey touched on how many labs are offset, use their own preparation. Once community comes up with “metrologically traceable RMs” how will this result in agreed value? Community is willing to do what it takes to get agreement. Goals show continuity, stability, but don’t have a product.
    - Sylvia pointed out there is no presumption of accuracy, but rather known and demonstrated stability. It is easy to transfer data to any new scale agreed upon by the community, easy to do with how they handle their data.
    - Robert asked if CO_2 would be useful to convert to CH_4 to meet the range needed
    - Stefan asked if they worked on H_2. Yes, more challenging, exclusively at Max Planck, NIWA does not have the facilities. RR included H_2, only three labs reported results (not shown in this presentation).
    - Javis asked about 2 optical systems, second one didn’t report, or data too noisy, or biased.

Tracey Jacksier

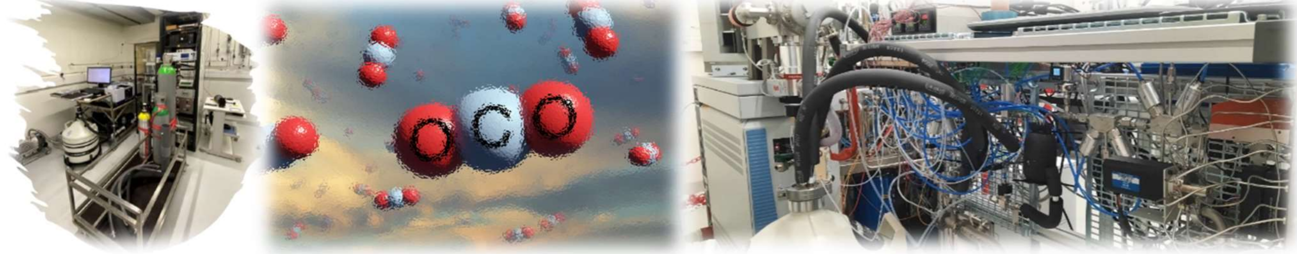
- Robust standards (pure or mixtures)
    - Need to be homogeneous.
    - Need to be sufficiently stable for use, storage – many believe stable isotopes are not stable issues with pressure reduction, fractionation.
    - Can regulators be used? (Fractionation)
    - Does it matter if more than one phase?
    - How to store the cylinder, shelf life
- Pressure reduction, CO2 multiphase – if you draw too fast then you get droplets.
- Air Liquide did transfer tests with and without regulator. $\Delta^{13}C$ different between regulated and unregulated flow
    - Piston, low dead volume regulator preferred, reaches steady state faster with less surface interactions.
- Looked at variations in $\delta^{13}C$ and $\delta^{18}O$ at different T/P/phases.
    - Used freezer or put cylinders directly outside (Cyl A gas, Cyl B supercritical)
    - Took headspace (3-5 psig) so only gas
    - Three cylinders: A (34 bar), B (57 bar), C (control, 57 bar)



  - When removed from the freezer, $\delta^{13}C$ increased and $\delta^{18}O$ decreased. But once warmed up, came back to agreement.
  - Slightly opposite trend when removed from heat exposure, but not significant given the overall uncertainties.
- Stability: Oxygen in CO_2 can exchange with oxygen in H_2O, T/P dependent
  - Filled cylinders to 34 bar (no liquid), depleted at constant rate until empty. The δ values remained constant, so does this just mean no moisture?
- Suggestions for eliminating/minimizing fractionation:
  - Carefully select regulator, low dead volume stainless steel
  - Good cylinder prep, low moisture
  - Store cylinders indoors, minimize temperature fluctuations.
  - Maintain single phase (less than ~34 bar)
- Questions from audience:
  - Frederica asked about the need to keep cylinder horizontal to avoid fractionation. This was not studied but Tracey assumes this is probably not an issue. Likely the issue is related to contact with the cold floor (she keeps cylinders on wooden pallets to prevent this?).

Geoffrey Ellis

- HC gas RMs, stable C and H isotopic analysis
- History of standards
  - 1980s: Chevron/IAEA round robin with coal, oil, biogenic natural gas
  - 1900s: Chevron donated gases to NIST, NIST certified composition
  - 2000s: NIST discontinued standards
- New standards – brought together stakeholders, advisory committee
  - Target composition methane, ethane and propane, no butanes or heaver HCs
  - "Equimolar", i.e., same concentration for all 3 compounds
  - "Synthetic" vs natural gas: pure gases better, fewer impurities
  - Picked gases with intermediate isotopic composition, some "spiked" using biogenic gas from Denver Basin
- Dual inlet IRMS
  - $\delta^{13}C$ measured vs NBS-19 and LSVEC carbonate
  - $\delta^{2}H$ measured against VSMOW and SLAP
- 16 cylinders
  - Continuous flow round robin, 6 labs (5 IRMS and 1 CRDS) – only dual inlet results used to derive values
- Replicate analysis of LSVEC were highly reproducible, first report shows that the values have shifted. IAEA no longer reports $\delta^{13}C$ values for LSVEC.
- Comparison with recommended values

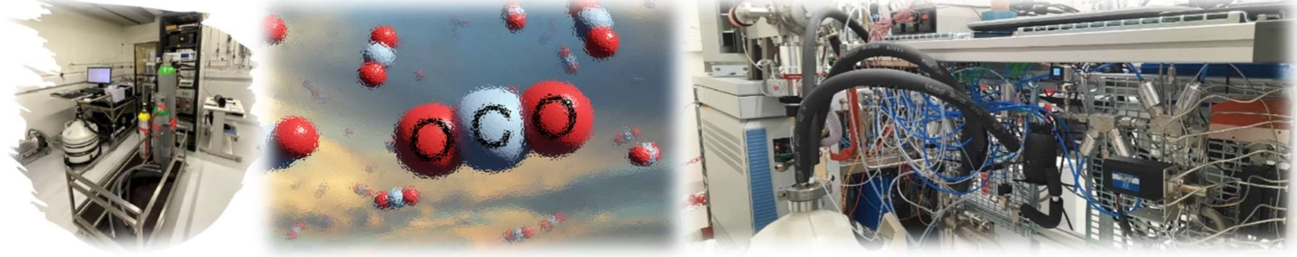


- Dual inlet vs continuous flow – dual inlet better precision, better standardization across labs should improve
- NIST only provides informational value for H isotopes

- Questions from the audience:
    - Abneesh asked about what standards are being used for continuous flow. They run 40 % standards, 60 % samples, he thinks there might be problems with not analyzing standards enough, or that in-house standards disagree.
    - Frederica asked about how they do the HC analysis by dual inlet. Geoff discussed offline vacuum, combustion furnace, separation of water/CO_2, the water is used to activate [?] (didn't catch this)
    - Barry asked what "wet" biogenic gas means, this is just a term used for heavier HCs
    - Sylvia mentioned isoprime(?) scale contraction issues, they monitor and correct for this
    - Ruth mentioned she would like to know more about the pure gases used to make the RMs

Vincent Hare

- Triple oxygen isotope analysis of CO_2 by IRMS
- CAP17 – difference between $\delta^{17}O - \lambda\delta^{18}O$
- Oxygen-17 rarest form
- Variation in $\Delta^{17}O$ very small, very hard to measure
- Much of triple oxygen is concerned with water, here we are concerned with CO_2
- For CO_2 from carbonates, need to covert to O_2, 10 mg carbonate, 4 + hours
- Primary traceability to VPDB/SLAP
- $\Delta'^{17}O$ CO_2 potential top-down constraint: carbon flux, GPP, source apportionment; stable analog to radiocarbon
- Uncertain how to relate δ, Δ to $R^{18}O$, $R^{17}O$, how to relate to common isotope abundance
- Requirements for high-precision $\Delta'^{17}O$ (CO_2)
    - Traceability (to VPDB or VSMOW)
    - Rapid throughput
    - Small sample sizes
    - No water at ppm level
    - Temp and laser predictability
    - Available absorption features
- Drift in closed cells, static measurement, regular variations in phase with lab air conditioning -> temperature dependent
    - Reference gas eliminates drift, "dual inlet"
- Reproducibility without conversion steps is a game changer
- Workflow relates samples to IA603
    - Dilute CO_2 in N_2 (mix to correct for fractionation)
- For traceability, what is wanted is CO_2 on the VSMOW-VSLAP scale to calibrate optical analyzers directly (rather than CO_2 from carbonates on VPDB normalized to VSMOW)



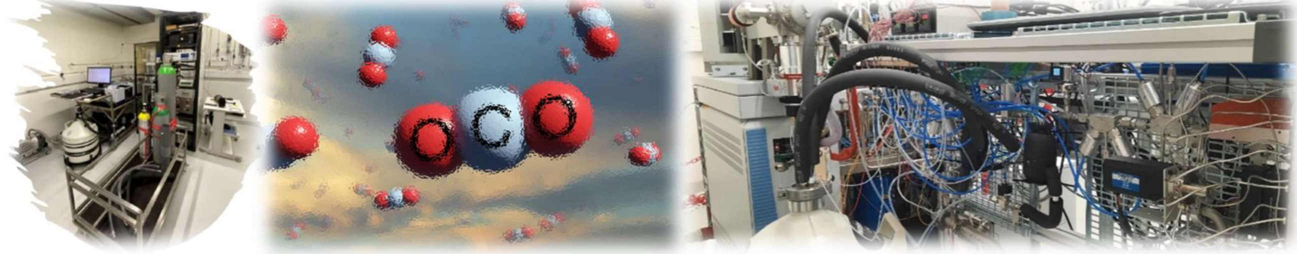
- Primary standards for VSMOW-SLAP are not designed with ^{17}O in mind, how can we overcome this?
    - CO_2 “calcite like”(?), stands very different from atmospheric CO_2, even when converted. For most samples, standards might need to be rethought.

Summary (Session 3)

- RMs are needed, standards development underway but not there yet
    - Most of the focus is on C isotopes, but more work needed for O and H
    - Uncertainties currently do not meet DQO, compatibility goals
    - Links to multiple local scales, realizations
- There is a need to better understand what the community needs, and define what is required in order to provide effective, fit-for-purpose reference gas mixtures. Things to consider:
    - Traceability
    - Small uncertainties
    - One scale realization
    - All isotopes vs “most important” (one is faster, the other more accurate)
    - Formalization
- We should aim to establish some understanding of common goals of the NMIs vs the isotope community, find a middle ground which is most impactful for stakeholders and for decision-making
    - Traceability vs consistency – what is more important: an accurate link to the SI, or to be able to track small changes over time?
    - How to ensure stability of reference(s) used
    - One common reference vs multiple references –max compatibility vs being able to co-check, validate

Discussion/Recommendations (All Sessions)

- Comparison for carbonate extraction
    - Discussion, protocol development, to ensure that it is executed in a sound (and similar) manner
    - Summarize, publicize best practice: expert labs present methods -> common procedures
    - Need to assign project lead
- Scale realization
    - JRAS developed but not maintained, need more information on it
    - Terminology clarification – different scales? Different scale realizations?
    - Calibration hierarchy
- Calibration of optical analyzers
    - Move from guidelines to SOPs
- Quality management system
    - CCLs
    - Already a system in ICOS network
- Instrument support
    - Maintain continuity with instrument manufacturers
- Methane
    - Hierarchy of traceability, protocols



Discussion session: The rapporteur recommendations were condensed into 10 areas for the discussion session.

1- **Carbonate extraction**: SOP, IAEA materials in line with CMC requirements, comparison, uncertainty estimate
2- Availability of pure CO_2 RMs for normalization (**ease of use**) linked to carbonate with low uncertainty and from NMIs.
3- CO_2-Air traceability model: **understand traceability, develop infrastructure to compare scale realizations.**
4- More than one scale: international scale comparison: JRAS scale, SIO, NMI scale?,..
5- **SOP for calibration of optical analyzers** to support GGMT and GGGW networks (Ground based GHG measurement top priority 1x1 degree matrix)- gases, range, data treatment, Quality control ,..
6- Support development of **Quality management system** for calibration gas RM production/dissemination/validation/re-certification to support GGGW networks: CO_2 in Air, CH_4 in Air
7- **Instrument support**: Understand community requirements in maintaining continuity software/hardware.
8- **Gas Kits: Support RM producers to have high quality** transparent systems: corrections, traceability.
9- **Dissemination strategy** of CH_4 in air for d13 by NIWA/MPI: when? Prerequisites, QMS, …
10- Work with expert community on **CH4 traceability** and comparison protocol