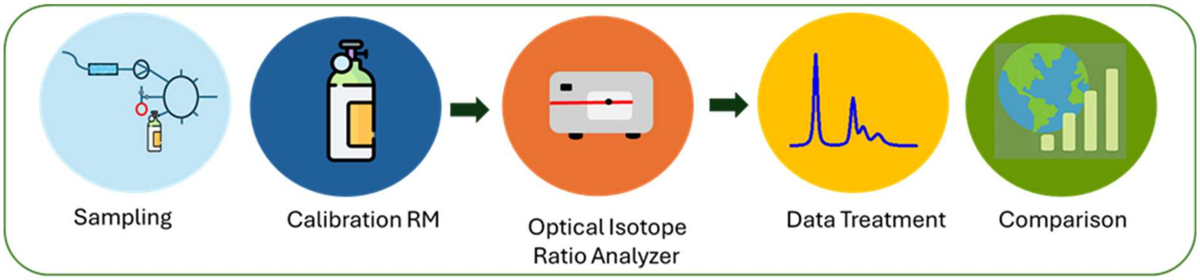
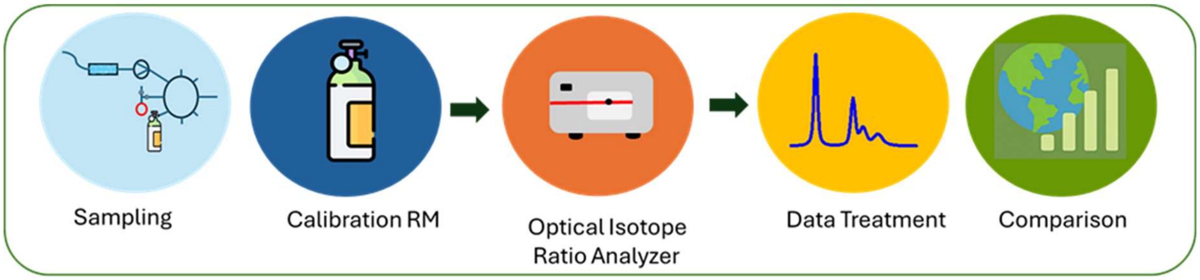


Harmonization of Optical Isotope Ratio Analyzer Calibration Practices in Atmospheric CO_2 and CH_4

CCQM GAWG-IRWG Isotope Ratio Task Group Online Workshop: 9 Sept 2025

Suggestions for Instrument Developers

The suggestions presented here are informed by discussions during the ***2025 OIRS Harmonization Online Workshop****, conducted by the* ***CCQM GAWG-IRWG joint isotope ratio task group (IRTG)*** *with participants from various NMIs and institutions. These are intended to support instrument developers in enhancing transparency, traceability, and usability of isotopic measurements.*



Purpose:

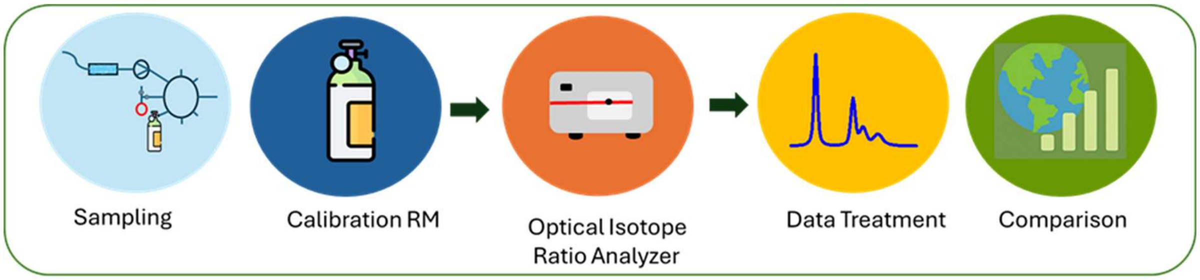
This document summarizes a set of suggestions aimed at improving transparency, calibration accuracy, and traceability in optical isotope analyzer measurements. The suggestions focus on a standardized classification of data levels, instrument data access, correction and calibration workflows, and environmental sensitivities. They are intended to help instrument developers present clear, accessible, and well-documented approaches to isotopologue data handling and δ(isotope delta)-value calibration, while acknowledging that many instruments already implement robust procedures.

Scope of Suggestions:

The suggestions are organized into five key areas:

1. **Classification of Isotopic Data Levels:** Establishing a common framework (Levels 0–4) to categorize the processing stages of various manufacturers, from raw digitizer output to calibrated values.
2. **Access to isotopologue raw data:** Ensuring users can access the fundamental measurement outputs (Levels 0 and 1) derived from optical spectra.
3. **Documentation of correction and calibration workflow:** Providing clarity on internal corrections, sensor-based cross-sensitivities, and the algorithmic transition from raw retrievals to internal outputs (Levels 2 and 3).
4. **Support for isotopologue-based and flexible ratio-based calibration methods:** Enabling both calibration strategies and mandatory concentration-dependent adjustments for the ratio method to achieve final traceability (Level 4).
5. **Sensitivity to environmental pressure and temperature:** Characterizing physical operational sensitivities to ambient conditions and providing guidance for site-specific monitoring and mitigation.

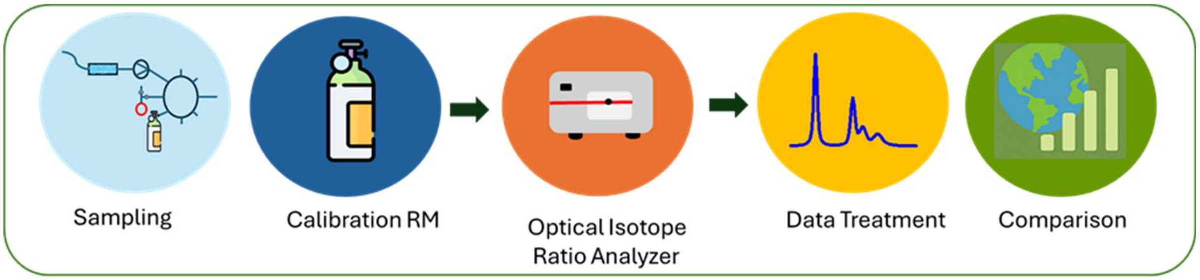
Each suggestion includes a **Rationale** emphasizing how these proposed practices support independent verification, inter-laboratory comparability, and high-accuracy measurements, while maintaining user-friendly workflows and respecting existing instrument capabilities.



1. Classification of Isotopic Data Levels Suggestion

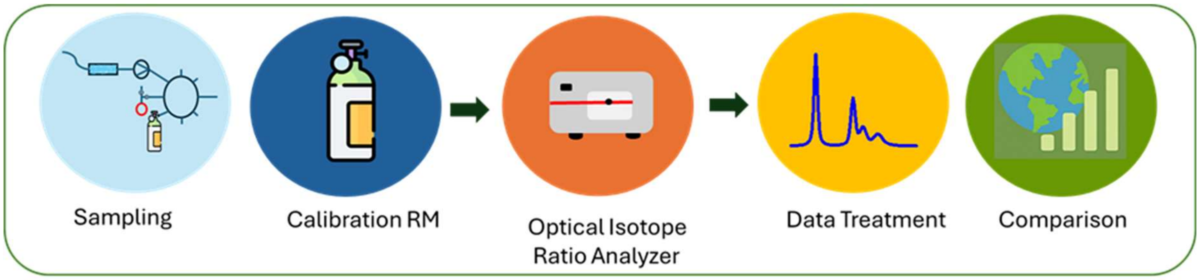
To harmonize documentation and data exchange across different manufacturers and measurement techniques, it is suggested that developers categorize data outputs into standardized "Levels." This framework helps categorize internal processes and provides a parallel set of levels for both isotopologue-based and ratio-based methods.

Level	Definition	Example (Spectroscopic Context)
Level 0	**Digitizer output:** Raw signal for a single measurement.	1-second average spectrum (several thousand laser scans) provided as detector voltage vs. channel number.
Level 1	**Primary Retrieval:** Quantities proportional to the amount fraction of targeted species.	Amount fractions derived from spectral fitting (using HITRAN, path length, ***P***, and ***T***).
Level 2	**Intermediary Corrections:** Level 1 data adjusted for known interfering species.	Amount fractions corrected for H_2O (dilution and broadening) **and** other spectral overlaps from interfering species.
Level 3	**Internal Amount Fraction:** High-frequency outputs using internal factory factors.	**Level 2** corrected values with factory-supplied scaling factors applied; recorded at 1-second intervals to the data file.
Level 4	**Calibrated Isotope Ratio:** Final traceable isotope ratios.	δ-values calculated from **Level 3** data following external calibration using reference standards.



Rationale

Defining data levels allows users to identify exactly where in the processing chain they are accessing data. This framework supports transparency by distinguishing between raw physical observables and the algorithmic layers applied by the manufacturer, enabling better comparison between different instrument models.



2. Access to isotopologue raw data (Level 0 and 1)

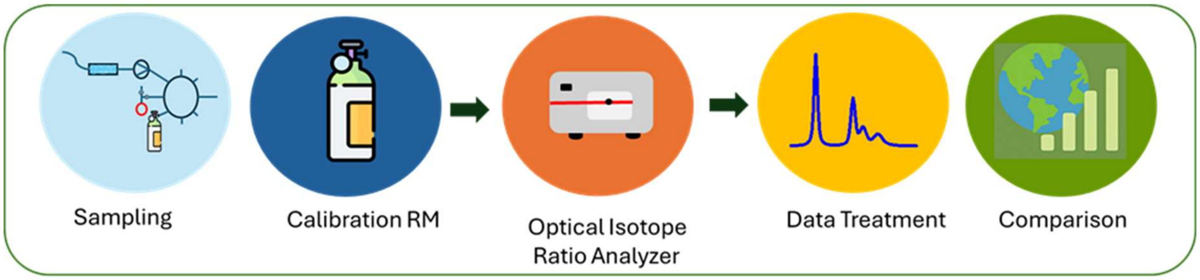
Suggestion

Provide clearly documented access to **Level 0** and **Level 1** data derived from optical spectra, including:

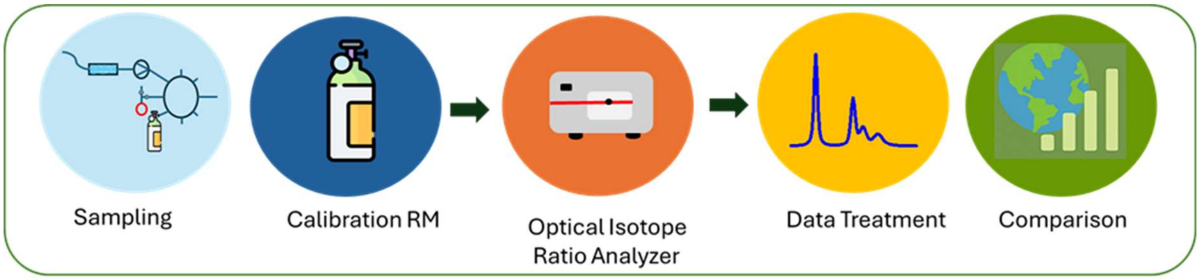
- **Absorption spectral data:** Absorption coefficient vs. frequency (e.g., ring-down time for CRDS or transmittance for multipass cells) with a brief baseline treatment description.
- **Isotopologue-specific amount fractions:** Fundamental observables (e.g., baseline-corrected peak height/area or fitted amplitude) treated as functionally related to isotopologue amount fraction and used in downstream correction and calibration steps.
- **Units and metadata:** Data format, file location, and optical cell conditions (pressure and temperature).
- **Versioning for Long-Term Integrity:** To ensure the integrity of long-term data records (e.g., multi-year timeseries), provide clear version identification for both the data processing software and instrument hardware. This enables users to track and reconcile changes in internal retrieval processes across software updates and instrument generations.
- **Fitting Approach:** For fitted quantities, briefly describe the fitting approach (e.g., line shape, window, weighting, constraints).
- **Spectroscopic Details:** Wavelength regions and targeted ro-vibrational lines for each isotopologue and co-measured species, including potential spectral overlaps (e.g., H_2O) used to assess interference.

Rationale

Optical isotope analyzers retrieve isotopologue-resolved quantities prior to interference corrections or calibration. These are the fundamental observables for all downstream data processing. Transparent access, with high-level documentation of retrieval methods, enables independent calibration, method development, inter-laboratory comparison, and



traceability. Crucially, documenting the evolution of internal processing versions ensures that long-term data records remain comparable even as proprietary algorithms and hardware models are upgraded.



3. Documentation of correction and calibration workflow (Level 2 and 3)

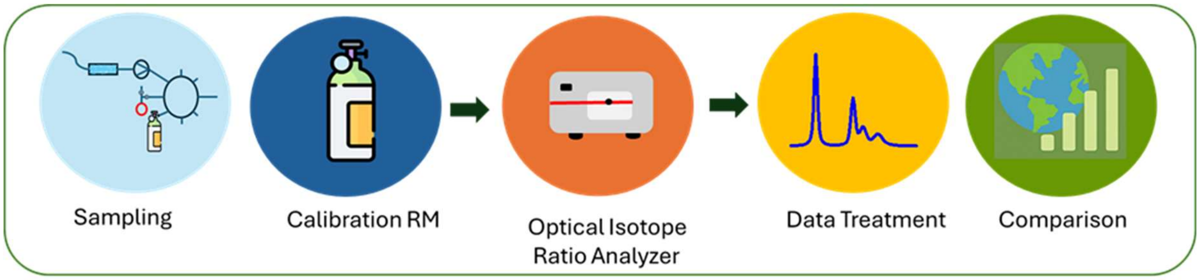
Suggestion

Provide clear, non-proprietary documentation describing the sequence of processing steps used to transform **Level 1** spectroscopic fits into **Level 3** internal outputs, including:

- **Algorithmic Sequence:** The order of operations for all post-corrections applied to raw isotopologue amount fractions.
- **Spectral Interferences:** Identification of corrections for H_2O spectral overlap, dilution, and induced line broadening.
- **Sensor-Based Cross-Sensitivities:** Documentation of cases where one measured variable is used to correct another, for example, using retrieved water vapor to adjust for pressure sensor bias (Reum et al., 2019).
- **Validation Limits:** The concentration and operating ranges (***P***, ***T***, humidity) over which individual corrections were developed and tested, including operational limits.
- **Workflow Schematic:** A flow diagram illustrating the processing chain, indicating exactly where intermediate quantities (**Level 2**: "corrected but uncalibrated") are generated.

Rationale

Manufacturers apply multiple internal corrections to optimize routine performance and ensure instrument stability. Transparency about the nature, scope, and validity of these corrections is essential for independent verification, inter-laboratory comparison, and traceability. Clear documentation helps standard users understand instrument behavior while enabling expert users to assess the impact of software updates on multi-year timeseries or test alternative correction strategies (e.g., Havsteen et al., 2025; IAEA-TECDOC-2066, 2024).



4. Support for isotopologue-based and flexible ratio-based calibration methods (Level 4)

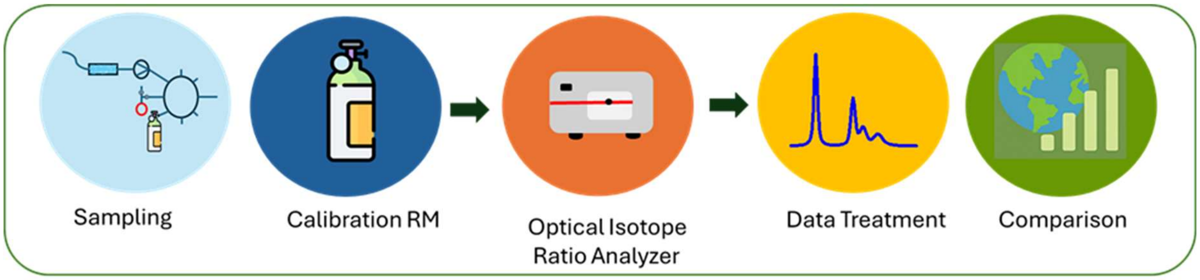
Suggestion

Provide support for isotopologue-based calibration in addition to flexible ratio-based calibration workflows to transform **Level 3** data into **Level 4** calibrated isotope ratios, including:

- **Isotopologue Method (IM):** Individual isotopologue amount fractions are calibrated independently over an appropriate range, with δ-values derived only after isotopologue-level calibration.
- **Ratio/Delta Method (R/DM) with flexible calibration:** Raw delta values calculated from the spectroscopic data are calibrated against calibrated delta values. δ-based calibrations must account for the inherent concentration-dependence of the ratio measurement. The workflow should allow for amount-fraction-dependent terms (linear or non-linear) to correct for these effects and achieve parity with isotopologue-level calibration.
- **Software support:** Maintain both IM and RM workflows within the instrument software to allow for comparison, benchmarking, and backward compatibility with legacy datasets.

Rationale

The fundamental measured quantities in optical isotope analysis are individual isotopologue amount fractions. RM and IM represent two valid calibration strategies. However, the RM inherently causes a concentration-dependence in the resulting ratios that must be characterized and calibrated separately (Griffith, 2012; Wen et al., 2013). By contrast, the IM reduces these biases by calibrating each species independently, which aligns more directly with the physical measurement process and often requires fewer correction steps. Supporting both approaches improves transparency, enables cross-validation, and allows concentration-dependent biases to be effectively mitigated (Griffith, 2018; Wen et al., 2013; Steur et al., 2021; Li et al., 2025).



5. Sensitivity to environmental pressure and temperature

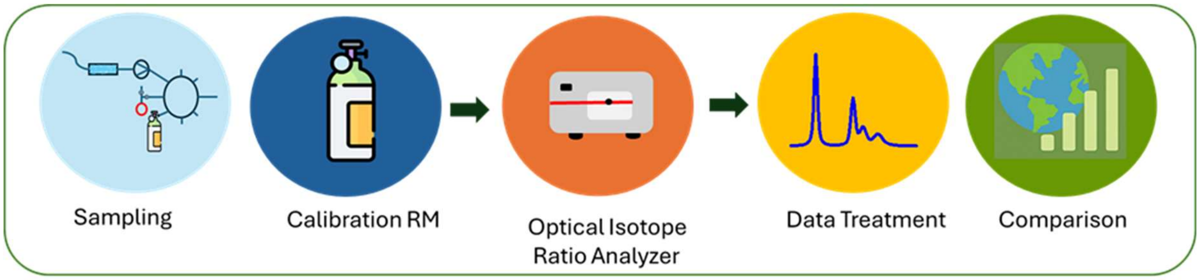
Suggestion

Characterize and document the physical sensitivity of the instrument to external environmental conditions at the monitoring site, specifically:

- **Ambient Pressure & Temperature:** The impact of room temperature fluctuations and station-level pressure on the stability of optical components, laser tuning, and internal electronics.
- **Site-Altitude Performance:** Characterization of instrument stability and noise levels across the pressure regimes typical of diverse monitoring networks (e.g., performance at **800 hPa vs. 1015 hPa**).
- **Residual Sensitivity:** Documented drift or bias remaining after internal hardware stabilization (such as cell temperature control) has reached its operational limit.
- **Monitoring and Mitigation:** Recommended field-proven strategies for station operators to minimize these effects, such as localized thermal insulation, rack-pressure regulation, or specific laboratory climate control requirements.

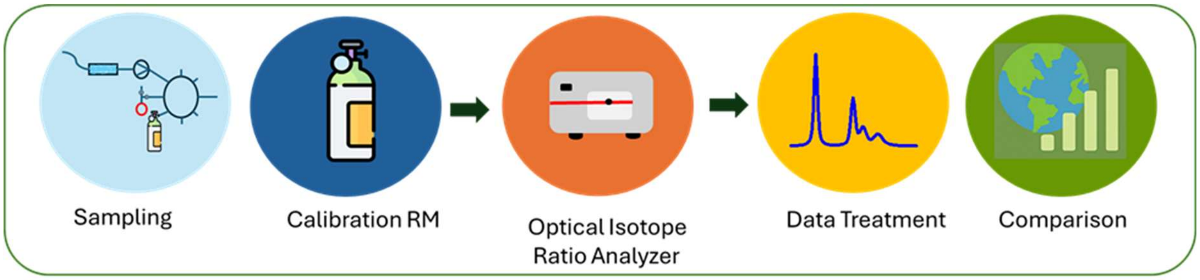
Rationale

Environmental effects vary significantly depending on site location. For example, a low-elevation station in southern Europe may experience temperature and air pressure cycles very different from those at a high-altitude northern site. Because a ±10 hPa pressure swing represents a larger relative change at a mountain site (1.25 % at 800 hPa) than at a sea-level site (0.98 % at 1015 hPa), site-specific characterization is essential. Relying solely on hypothetical “standard” laboratory conditions can lead to site-dependent biases and inconsistencies in global monitoring networks. Quantifying these sensitivities supports robust uncertainty evaluation and ensures long-term reliability across varying climates and altitudes (Rella et al., 2013; Miles et al., 2018).



Bibliography:

1. Griffith DWT, Deutscher NM, Caldow C, Kettlewell G, Riggenbach M, Hammer S. A Fourier transform infrared trace gas and isotope analyser for atmospheric applications. Atmospheric Measurement Techniques. 2012 Oct 24;5(10):2481-98.
2. Griffith DWT. Calibration of isotopologue-specific optical trace gas analysers: a practical guide. Atmospheric Measurement Techniques. 2018 Nov 15;11(11):6189-201.
3. Flores E, Viallon J, Moussay P, Idrees F, Wielgosz RI. An FTIR method for accurate CO_2 mole fraction measurements with correction for differences in isotopic composition of gases. Metrologia. 2019 Jul 2;56(4):044005.
4. Steur PM, Scheeren HA, Nelson DD, McManus JB, Meijer HA. Simultaneous measurement of $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2–performance assessment of a dual-laser absorption spectrometer. Atmospheric Measurement Techniques. 2021 Jun 9;14(6):4279-304.
5. Li J, Chi X, Ding A, Ju W, Zhang Y, Chen JM, Chen H. Evaluation of Calibration Strategies for Accurate δ 13 CH 4 Measurements in Dry and Humid Air. EGUsphere. 2025 Nov 19;2025:1-23.
6. Havsteen JC, Fatima M, Brunamonti S, Pogány A, Hausmaninger T, Wolf B, Well R, Mohn J. Correction and Calibration Protocol for Isotope Data via CRDS: A Study Case for N_2O and Other Isotope Systems. EGUsphere. 2025 Nov 6;2025:1-37.
7. IAEA-TECDOC-2066. Measurement of the Stable Carbon Isotope Ratio in Atmospheric CH_4 Using Laser Spectroscopy for CH_4 Source Characterization. International Atomic Energy Agency; 2024.
8. Reum F, Gerbig C, Lavric JV, Rella CW, Göckede M. Correcting atmospheric CO 2 and CH 4 mole fractions obtained with Picarro analyzers for sensitivity of cavity pressure to water vapor. Atmospheric Measurement Techniques. 2019 Feb 15;12(2):1013-27.
9. Rella CW, Chen H, Andrews AE, Filges A, Gerbig C, Hatakka J, Karion A, Miles NL, Richardson SJ, Steinbacher M, Sweeney C. High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air. Atmospheric Measurement Techniques. 2013 Mar 27;6(3):837-60.
10. Miles NL, Martins DK, Richardson SJ, Rella CW, Arata C, Lauvaux T, Davis KJ, Barkley ZR, McKain K, Sweeney C. Calibration and field testing of cavity ring-down laser



spectrometers measuring CH_4, CO_2, and $\delta^{13}CH_4$ deployed on towers in the Marcellus Shale region. Atmospheric Measurement Techniques. 2018 Mar 5;11(3):1273-95.

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