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Review

Developing calibration and measurement capabilities for atmospheric CH_4 stable isotope ratios at NMIs/DIs: metrology for global comparability

Abneesh Srivastava[1,*], **Michelle M G Chartrand**[2], **Federica Camin**[3], **Joachim Mohn**[4], **Peter Sperlich**[5], **Chris Rennick**[6], **Ruth Hill-Pearce**[6], **Stefan Persijn**[7], **Christoph Nehrbass-Ahles**[6] **and Javis Nwaboh**[8]

[1] National Institute of Standards and Technology, Gaithersburg, MD, United States of America
[2] National Research Council Canada, Metrology Research Center, Ottawa, ON, Canada
[3] International Atomic Energy Agency, Vienna, Austria
[4] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
[5] National Institute of Water and Atmospheric Research, Wellington, New Zealand
[6] National Physical Laboratory, Teddington, United Kingdom
[7] VSL, National Metrology Institute, Delft, The Netherlands
[8] Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

E-mail: abneesh@nist.gov

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Abstract

To establish robust calibration and measurement capabilities (CMCs) for atmospheric methane (CH_4) stable isotope ratios, National Metrology Institutes (NMIs) and Designated Institutes (DIs) need a comprehensive understanding of the underlying measurement techniques, reference materials (RMs), calibration hierarchies, value assignment, uncertainty evaluation, and inter-laboratory comparison activities. This review, developed by the CH_4 Task Team within the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) Gas Analysis Working Group (GAWG) and the Isotope Ratio Working Group (IRWG), provides key insights for developing these capabilities at NMIs/DIs. The World Meteorological Organization (WMO) recommended network compatibility goals for atmospheric methane stable isotope ratio monitoring, expressed as isotope delta values, are 0.02‰ for the stable carbon isotope delta (δ^{13}C) value and 1‰ for the stable hydrogen isotope delta (δ^{2}H) value, with extended targets of 0.2‰ for δ^{13}C and 5‰ for δ^{2}H. Global

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[*] Author to whom any correspondence should be addressed.

inter-laboratory comparisons have revealed offsets of up to 0.5‰ for $\delta^{13}C$ and 13‰ for δ^2H measurements, substantially exceeding the WMO targets. To address these discrepancies, steady progress is being made, particularly by expert isotope laboratories, with increasing engagement from NMIs/DIs. Improved measurement techniques and the use of common RMs are bringing measurements closer to the WMO goals. This overview not only reviews the components necessary for establishing NMI/DI CMCs but also provides actionable recommendations to further align global measurements, including the development of standardized protocols, adoption of the VPDB carbon isotope delta scale for atmospheric data harmonization, and international comparison studies to support NMI/DIs in their CMC claims. These actions are critical for achieving long-term consistency and advancing global standards for atmospheric methane stable isotope ratio measurements.

Keywords: atmospheric methane stable isotope ratio measurements,
WMO network comparability goal for atmospheric monitoring,
metrological traceability and global comparability,
national metrology institutes (NMIs) and designated institutes (DIs),
calibration and measurement capability (CMCs),
CCQM GAWG and IRWG joint isotope ratio task group (IRTG),
standardization and recommendations for methane isotope ratio measurements

1. Introduction

Monitoring the atmospheric methane (CH_4) amount fraction (x_{CH4}) and its stable isotopic composition (expressed as carbon isotope delta $\delta^{13}C$ and hydrogen isotope delta δ^2H values) are essential for global efforts to understand and mitigate methane emissions [1]. The World Meteorological Organization's Global Atmospheric Watch (WMO-GAW) has set rigorous goals for greenhouse gas (GHG) measurement quality and network compatibility, necessitating the expansion of monitoring sites and the adoption of standardized methodologies for calibration, measurement, data treatment, and modeling. The WMO network compatibility goals for atmospheric methane monitoring are 2 nmol mol^{-1} for the CH_4 amount fraction, 0.02‰ for $\delta^{13}C$, and 1‰ for δ^2H. The extended network compatibility goals, for regional-scale gradients, are 5 nmol mol^{-1} for CH_4 amount fraction, 0.2‰ for $\delta^{13}C$ of CH_4, and 2‰ for δ^2H of CH_4 [2]. Recently, the WMO introduced the global greenhouse gas watch (G3W) program [3], which proposes a high-resolution monitoring grid akin to global weather stations to enhance greenhouse gas flux monitoring. This new initiative builds upon ongoing global atmospheric measurement recommendations—including stable isotope ratio measurements of atmospheric methane—updated biennially at the Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT) meeting organized by the WMO and the International Atomic Energy Agency (IAEA) [2]. Together, these efforts provide the much-needed scientific and quality platform to integrate existing monitoring network activities.

Metrological traceability plays a key role in global standardization. The Meter Convention [4], established in 1875, led to the creation of the International Committee for Weights and Measures (CIPM) and the International Bureau of Weights and Measures (BIPM). The CIPM operates through several consultative committees, such as the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) [5], and is enabled by the BIPM to coordinate the development, improvement, and documentation of equivalence between national standards. The respective national standards are maintained by host National Metrology Institutes (NMIs), with support from Designated Institutes (DIs), to meet their nation's metrology traceability needs at the highest level [6].

Within the CCQM, two important working groups relevant to atmospheric gases and stable light isotope measurements are the Gas Analysis Working Group (GAWG) and the Isotope Ratio Working Group (IRWG). These groups in turn establish task groups to tackle specialized topics, fostering collaboration and advancements in metrology standards. Recently, the CCQM GAWG and IRWG formed a joint task group dedicated to carbon dioxide and methane stable isotope ratio measurements to support global metrology infrastructure for these measurements. This task group, known as the Isotope Ratio Task Group (IRTG) [7], aims to enhance activities at the NMI and DI levels and improve interactions within the atmospheric monitoring isotope ratio community. These structures facilitate the exchange of ideas and promote collaboration by organizing workshops and forming dedicated teams to address specific areas.

To identify the metrology needs in the atmospheric community, the 2022 Climate Action Workshop [8], hosted by the BIPM and the WMO, pinpointed 81 ongoing issues and made 126 recommendations to advance climate metrology through a measurement-based approach to greenhouse gas emission management and mitigation. Following this in October 2023, IRTG conducted an international workshop [9] involving stakeholders from international organizations, NMIs/DIs, industry, and academia. This workshop focused on assessing progress and identifying needs in metrological infrastructure, reference materials (RMs), calibration, and measurement technologies related to atmospheric carbon dioxide and methane stable isotope ratio measurements. Building on this targeted approach, the IRTG has formed specialized teams to address specific areas of interest, one of which is the CH_4 Task Team.

This paper presents insights from the activities of the CH_4 Task Team, offering an overview of the current state of atmospheric methane stable isotope ratio measurements. It aims to assist NMIs and DIs in enhancing their calibration and measurement capabilities (CMCs) to support the broader atmospheric monitoring community. The goal is to establish a global metrological infrastructure that ensures comparability across atmospheric methane stable isotope ratio studies. Additionally, these efforts aim to align with the WMO-GAW network compatibility goals for atmospheric monitoring. The content is structured into several sections, beginning with a definition of CMCs in the NMI/DI context, followed by discussions on measurement capabilities (including isotope delta scales and techniques such as isotope ratio mass spectrometry (IRMS) and optical isotope ratio spectroscopy (OIRS)), calibration components (calibration hierarchy, isotope RMs), uncertainty evaluation, ongoing activities, comparison protocol design, and concludes with recommendations for future action.

2. CMCs

CMCs relate a measured quantity to a reference through calibration, involving selecting techniques, developing procedures, using standards, and specifying the measurement range and uncertainty. Laboratories must demonstrate competency and comply with international standards like ISO/IEC 17025, ISO 17034, and ISO/IEC 17043.

NMIs and DIs ensure calibration certificate credibility through the CIPM Mutual Recognition Agreement (CIPM MRA) [6], confirming the international equivalence of standards. Currently, 251 institutes, including 97 NMIs, 150 DIs, and 4 international organizations (e.g. WMO and IAEA), participate in the CIPM MRA. CMC claims are listed in the BIPM Key Comparison Database (KCDB) [10], requiring peer-reviewed technical evidence and quality assessments.

A core principle of the CIPM MRA [6] framework is metrological traceability to the International System of Units (SI). For gas standards, this traceability is typically achieved using gravimetrically prepared RMs [11]. However, in atmospheric monitoring, artifact-based scales—such as the WMO X2004A [12] scale for CH_4 amount fraction—are used to meet the stringent WMO compatibility requirements. To address the limitations of artifact-based traceability, especially in terms of long-term stability, SI traceability is being integrated through ongoing collaboration between NMIs/DIs and laboratories maintaining these artifact-based scales [11].

Similarly, for gas isotope RMs, artifact-based scales provide greater precision than SI methods and are used to address WMO compatibility requirements. While SI traceability remains a priority for NMIs, the growing demand for isotope RMs has led to an allowance within the CIPM MRA, permitting [13] artifact-based traceability of isotope delta values using RMs recognized as international standards. Consequently, CMC claims for isotope RMs developed by NMIs and DIs are validated through this exception.

Currently, CMC claims for organic RMs used in stable isotope ratio measurements are listed in the KCDB [6]. However, additional work is needed to support the inclusion of gas stable isotope ratio related CMCs, particularly for methane and carbon dioxide. NMIs and DIs must therefore focus on measurement methods, RMs, traceability, uncertainty evaluation, inter-laboratory comparisons, and quality management to ensure robust capabilities.

3. Measurement capabilities

3.1. Isotope delta scale

Isotopic composition is commonly expressed as the relative difference between the amount of substance (N) isotope ratios (R) of a sample (sam) against a standard (std), using the isotope delta (δ) [14] notation:

$$\delta_{\mathrm{std}}\left({}^{i/j}\mathrm{E}\right)=\frac{R\left({}^{i/j}\mathrm{E}\right)_{\mathrm{sam}}}{R\left({}^{i/j}\mathrm{E}\right)_{\mathrm{std}}}-1=\frac{N\left({}^{i}\mathrm{E}\right)_{\mathrm{sam}}/N\left({}^{j}\mathrm{E}\right)_{\mathrm{sam}}}{N\left({}^{i}\mathrm{E}\right)_{\mathrm{std}}/N\left({}^{j}\mathrm{E}\right)_{\mathrm{std}}}-1$$

where ${}^{i/j}\mathrm{E}$ is ${}^{13/12}\mathrm{C}$ for carbon isotope delta, and ${}^{2/1}\mathrm{H}$ for hydrogen isotope delta (i and j refer to the heavy and light isotope, respectively of the element E). To express subtle variations in natural isotopic composition, differences in isotope ratios between sample and standard (as captured in the delta notation) are calculated. Isotope delta is a dimensionless quantity with an SI unit of 1. Its numerical values, which can be either positive or negative, is commonly small and expressed using the symbol ‰ (representing 10^{-3}). For example, $\delta_{\mathrm{std}}\left({}^{i/j}\mathrm{E}\right) = -0.0086$ is equivalent to -8.6×10^{-3} and -8.6‰ [15].

An isotope delta scale is defined using an international primary standard [16], ideally supplemented by a second international secondary standard to provide a two-point calibration, enhancing measurement comparability. The defining values of the scale are fixed and assigned zero uncertainty. (Note: As mentioned above, SI-traceable measurements of isotope ratios (R) for carbon and hydrogen currently lack the high precision (<0.01‰) required for atmospheric measurements. Therefore, metrological traceability for isotope delta values is established through materials recognized as international standards, in accordance with the exception granted by CIPM Decision CIPM/104-26 [13]. A list of these standards is provided by Brand *et al* [16, 17]).

For carbon two isotope delta scales are in use. Their definition has recently been agreed during an experts meeting at IAEA (Camin *et al*) [18] In brief the two scales are:

(1) VPDB scale:
NBS 19 (TS limestone): $\delta^{13}\mathrm{C} = +1.95(0)$‰ relative to VPDB.
and

(2) VPDB-LSVEC scale:
NBS 19 (TS limestone): $\delta^{13}C = +1.95(0)$‰ relative to VPDB.
LSVEC (Lithium carbonate): $\delta^{13}C = -46.6(0)$‰ relative to VPDB.

(Note: The uncertainty (shown in brackets) is zero per the scale definition above.)

Although LSVEC was selected in 2006 to anchor the carbon isotope VPDB scale, its instability was only recognized in 2016 [19, 20]. Consequently in 2017, it was recommended that its use be discontinued for VPDB-LSVEC scale realization [21]. However, the VPDB-LSVEC scale realization is still recognized, using RMs whose values [16] have been determined relative to the VPDB-LSVEC scale. Additionally, there is at least one study providing a scale conversion equation to relate the values on the VPDB-LSVEC scale to the VPDB scale [18, 22, 23].

For hydrogen the isotope delta scale is the VSMOW-SLAP scale defined by:

VSMOW (Vienna Standard Mean Ocean Water): $\delta^{2}H = 0(0)$‰
SLAP (Standard Light Antarctic Precipitation): $\delta^{2}H = -428(0)$‰ relative to VSMOW.

The isotope ratios (R) for $^{13}C/^{12}C$ VPDB, $^{2}H/^{1}H$ VSMOW, and $^{2}H/^{1}H$ SLAP have been measured in several exercises [24–37], providing a crucial link between the associated delta scale and the SI. However, higher precision is still needed for direct artifact-free SI traceable isotope delta value assignments. Measurement of these ratios remains an active research area, focusing on reducing uncertainty and establishing more representative and robust values using independent methods.

(Note: For clarity, $\delta_{\mathrm{VSMOW\text{-}SLAP}}(^{2/1}H)$ is written as $\delta^{2}H$, and $\delta_{\mathrm{VPDB}}(^{13/12}C)$ as $\delta^{13}C$. Additionally, the methane isotopologue CH_3^2H is represented as CH_3D.)

3.2. *Techniques*

To determine methane isotopic composition, two main measurement techniques are typically used: IRMS and OIRS. Each technique has distinct capabilities tailored to specific applications. IRMS, being the longer-established method, remains widely used, while OIRS, as a newer approach, offers advantages such as direct and continuous measurements, making it particularly suitable for atmospheric monitoring.

3.2.1. IRMS. Direct measurement of CH_4 isotopologues ($^{12}CH_4$, $^{13}CH_4$, CH_3D) is constrained by the relatively low mass resolution of traditional mass spectrometers with a value of ~200 for gases of moderate mass (mass resolution is defined as $m/\Delta m$, where m is the ion's mass and Δm is the ion peak width, which is typically expressed as the width of the peak at a height of 10%). Insufficient mass resolution can lead to isobaric interferences that introduce biases, obscuring the isotopologue signal of interest and making it especially difficult to quantify when analyzing radical ion fragments with low-resolution mass spectrometry. Consequently, determining the $\delta^{13}C$ and $\delta^{2}H$ isotopic composition of methane typically involves the chemical conversion of CH_4 into carbon dioxide (CO_2) and hydrogen (H_2), as these forms enable more accurate and robust isotopic analysis. The conversion process differs depending on the isotopes being measured: for $\delta^{13}C$ analysis, CH_4 combustion (C) to CO_2 is used; for $\delta^{2}H$ analysis, the process involves either combustion to H_2O (followed by its reduction to H_2 or exchange [38–40] with H_2), or by direct pyrolysis (P) of CH_4 to H_2. For ambient CH_4 isotope measurements in air, an additional step of extracting methane from the ambient air sample is required prior to the chemical conversion step described above, as well as an additional step involving chromatographic (GC) purification of the conversion products.

The measurement of atmospheric methane stable isotope ratios has advanced significantly, evolving from offline, high-sample-volume methods using dual-inlet (DI)-IRMS [41] to modern online continuous flow (CF)-IRMS [42] systems. These systems integrate extraction/preconcentration (precon), chemical conversion (via combustion or pyrolysis), and gas GC separation steps. They also feature a modified open-split injection technique that enables carrier gas-assisted CF of the analyte into the ion source. This integrated approach reduces both analysis time and the required air volume, and is commonly referred to by hyphenated terms such as precon-GC-C/P-IRMS. While DI-IRMS is the only existing technique capable of meeting the WMO network compatibility goal for $\delta^{13}C$, it comes with some trade-offs (see table 2). CF-IRMS, although having slightly lower precision, still meets the WMO's extended compatibility goals and has been largely adopted by the atmospheric community. CF-IRMS [40] approaches such as elemental analyzer (EA)-IRMS and high temperature conversion EA (TC/EA)-IRMS, largely used for solid and liquid samples [43], have also been adapted for gas inlet systems. These adaptations enable precise isotopic analysis of pure methane, specifically for $\delta^{13}C$ and $\delta^{2}H$ [44, 45].

For accurate isotope analysis, in addition to scale calibration, several corrections and quality controls [46] are essential. These include ^{17}O correction for $\delta^{13}C$ determination, the H_3^+ factor in $\delta^{2}H$ determination, and ensuring the removal of interfering substances both pre-conversion (such as H_2O, CO, N_2O, and non-methane hydrocarbons: NMHCs) and post-conversion (such as Kr and incompletely converted CH_4). Efficiencies of chemical conversions, along with each of the process workflow steps, including trapping and separation, must be carefully quantified, optimized, and monitored [45, 47, 48]. Although high-resolution ($m/\Delta m > 10\,000$) IRMS [49] shows promise for direct CH_4 isotopologue analysis (helping resolve individual CH_4 isotopologues and potential isobaric interferent mass-to-charge ions), its use is currently limited to a small number of laboratories. As a result, most methane isotope ratio measurements are conducted using indirect methods, as discussed above.

Table 1. Implementation of exemplary calibration strategies for methane isotope ratio measurements using commercial optical analyzers.

Isotope delta	Analyzer/company	Calibration strategy
$\delta^{13}C$	G2132-i, G2201-i, G-2210-i CRDS/Picarro Inc.	Ratio method [53, 55, 57, 59]. Multi-step correction for spectral interferences caused by water and ethane.
$\delta^{13}C$, $\delta^{2}H$	Dual laser TILDAS/Aerodyne Inc.	Preconcentration of air sample, ratio method, correction for CH_4 amount fraction, fractionation during preconcentration and calibration [51].
$\delta^{13}C$, $\delta^{2}H$	Dual laser TILDAS/Aerodyne Inc.	Preconcentration of air sample, isotopologue method [58].

3.2.2. OIRS. OIRS quantifies stable isotope ratios in CH_4 by directly measuring the amount fractions of individual isotopologues—$^{12}CH_4$, $^{13}CH_4$, and $^{12}CH_3D$—and calculating their ratios to determine the isotope delta value, similar to IRMS. Different wavelength-specific transitions for light absorption, light sources, detection schemes, and a range of spectral data reduction methods are applied for CH_4 isotope analysis by OIRS. This has led to a variety of optical techniques, including FTIR (Fourier transform infrared) spectroscopy, CRDS (cavity ringdown spectroscopy), OA-ICOS (off-axis-integrated cavity output spectroscopy), OF-CEAS (optical feedback-cavity enhanced absorption spectroscopy), TILDAS (tunable infrared laser direct absorption spectroscopy) [50–60]. While FTIR (conventionally implemented using an incoherent broadband light source) has been used to measure isotopes in atmospheric CO_2 [61, 62] the low abundance of $^{13}CH_4$ and $^{12}CH_3D$ results in low sensitivity at ambient amount fractions of isotopologues [50]. In contrast, laser spectroscopy, utilizing tunable coherent light sources, offers enhanced sensitivity and selectivity. When combined with sample preconcentration (for sample extraction) techniques and multipass absorption cells—such as in precon-TILDAS, or optical cavity resonators used as sample absorption cells (e.g. CRDS, OA-ICOS, OF-CEAS)—it enables precise measurement of atmospheric methane isotope ratios.

The successful implementation of commercial OIRS analyzers requires robust measurement protocols and calibration strategies (examples of which are provided in table 1). Two main approaches [58, 61, 63, 64] are used for calibration:

1. Isotopologue method: The isotopologue amount fractions of $^{13}CH_4$, $^{12}CH_3D$, and $^{12}CH_4$ are calibrated individually using accurate and high precision amount fraction gas RMs, derived from a single pure methane parent source of precisely known isotopic composition. This process does not require a range of isotope delta values in the calibration RMs. The ratios are then calculated based on these calibrations.
2. Isotope ratio method: The ratios of the measured instrument response of $^{13}CH_4$ to $^{12}CH_4$ and $^{12}CH_3D$ to $^{12}CH_4$ (similar to the IRMS approach) are calibrated using isotope RMs at near-identical amount fractions.

Since OIRS directly measures the absolute amount fraction of the individual isotopologues, the isotopologue method is the natural choice for its calibration [58, 61, 63, 64]. However, it depends on the availability of accurate and high precision amount fraction RMs. In contrast, the isotope ratio method, which requires RMs over a range of isotope delta values, is less stringent with respect to the accuracy of amount fractions. However, amount fraction dependence of the isotope delta calibration still needs to be carefully characterized and post-corrected. (Note: In traditional IRMS, a delta measurement of the sample ion signal ratio against that of an isotope RM is required, as part of the experimental design, to cancel out systematic biases, such as fractionation effects.)

Calibration and validation should be supported by a suite of carefully selected gas RMs for scale transfer, quality control, and reliable daily reference gases, as well as method-specific standards to account for CH_4 amount fraction, matrix composition, and potential interferents. As an alternative approach to quantifying and correcting spectral interference using custom calibration gases, albeit technically challenging, CH_4 can be separated from the air matrix and transferred into a consistent nitrogen carrier gas via a preconcentrator. This approach simplifies the calibration gas composition by eliminating the impact of interferents that vary [53] with the 'origin/source' of ambient air. However, careful testing is necessary [65] to quantify trapping, separation from co-adsorbed gases and control fractionation. OIRS measurements are also sensitive to temperature, with the effect varying by absorption line. Therefore, precise temperature control in the optical cell is essential to ensure consistent results. Recent technical documents from the IAEA [66] and EMPIR [67] (European Metrology Programme for Innovation and Research) initiatives provide valuable insights and best practices for OIRS measurements of CH_4 stable isotope ratios.

Due its maturity and wider use, IRMS is commonly used as a reference measurement method to link OIRS calibration RMs to the international isotope scale, and as a key benchmark for assessing the accuracy of OIRS techniques. Studies involving CRDS and TILDAS have demonstrated that OIRS measurement precision can achieve the WMO-GAW extended compatibility goals for atmospheric methane $\delta^{13}C$ values (0.2‰) and come close to the compatibility goal for the $\delta^{2}H$ values (1‰). Recent data [58] on preconcentrator-coupled TILDAS show a standard uncertainty of 0.07‰ for $\delta^{13}C$ and 0.9‰ for $\delta^{2}H$ values in atmospheric methane measurements, which are comparable to the precision reported [51] for CF-IRMS (0.07‰ for $\delta^{13}C$ and 0.7‰ for $\delta^{2}H$).

Measurement times for ambient air samples using OIRS vary: Some examples include, CRDS taking approximately 15 min [52] of spectral averaging to achieve robust results, while preconcentrator-coupled TILDAS requiring around 50 min [68] per sample.

Direct comparison between OIRS and IRMS measurements of identical atmospheric methane samples are limited and represent an area of increased activity. Field trials have shown that OIRS and IRMS meet extended compatibility goals, with reported differences of 0.20(33)‰ via CRDS [51] and 0.10(22)‰ to 0.26(7)‰ for δ^{13}C values using preconcentrator-coupled TILDAS [51, 58, 68]. Reported values for δ^{2}H available for preconcentrator-coupled TILDAS, are 2.1(3)‰ and 4.3(4)‰. [51, 58] (The values in brackets represent the reported uncertainties.) These offsets are suspected to result from scale propagation and instrumental issues, warranting further investigation. In comparison, δ^{13}Cand δ^{2}H measurement offsets between IRMS laboratories show spreads of 0.5‰ and 13‰, respectively, and are likely due to lab-specific calibration procedures and instrument corrections [69]. The measurement landscape for methane isotope ratio analysis is summarized in table 2, highlighting the need for multiple metrics to determine the most suitable measurement method.

4. Calibration

A successful calibration of the measurement system for atmospheric methane (and pure methane) stable isotope ratio requires a clear calibration hierarchy [14, 73], adherence to the principle of identical treatment, and access to appropriate RMs. The metrological traceability of δ^{13}C and δ^{2}H in atmospheric methane isotope delta measurements (figures 1 and 2 present some possible examples) depends on establishing an unbroken calibration chain linked to the international isotope delta scale reference. At the top of this hierarchy, IAEA-603 [74] serves as the RM for δ^{13}C (replacing the now-depleted NBS 19), while VSMOW2 and SLAP2 are used for δ^{2}H (replacing the previous VSMOW and SLAP RMs).

To ensure consistency, IUPAC [77] recommends the use of at least two RMs with distinct isotopic values. The IAEA has introduced three additional carbon isotope RMs [78]—IAEA-610, IAEA-611, and IAEA-612—providing multiple anchoring points (δ^{13}C values of −9.109(12)‰, −30.795 (13)‰, −36.722(15)‰, respectively) for the VPDB scale. (Note: The IAEA-610, −611, −612 RM series were specifically developed to serve as additional anchor points for the VPDB scale realization.). Additionally, USGS44 [76], a calcium carbonate RM developed by USGS (US Geological Survey) for δ^{13}C measurements, offers another potential anchor for the VPDB scale and the VPDB-LSVEC scale. In their studies, Qi and co-workers [76] reported δ^{13}C values of—42.08(1)‰ and −41.99(2)‰ on the VPDB scale and −42.21(5)‰ on the VPDB-LSVEC scale for USGS44 (with combined standard uncertainties reported in brackets). The use of multiple RMs is crucial for CF-IRMS to ensure accuracy, while for DI-IRMS, single-point calibration can be adequate for δ^{13}C value assignments once instrument-specific cross-contamination corrections are determined to account for scale contraction [46, 79, 80].

Nevertheless, material mismatches arise at the top of the calibration hierarchy, where methane must be made traceable to international standards. These mismatches introduce calibration offsets due to differing treatments and conversion steps required to generate CO_2 and H_2 for mass spectrometric detection. In DI-IRMS-based methods, varying conversion schemes (e.g. carbonate acid digestion versus methane combustion) can lead to significant offsets. This issue is minimized in CF-IRMS-based systems, which are developed to provide common conversion schemes (combustion or pyrolysis), ensuring more uniform treatment of methane and RMs. However, significant sources of bias remain uncontrollable due to the chemical differences between CH_4 and RMs, which is especially challenging for δ^{2}H and measurements of CH_4 and H_2O. While perfect alignment of treatments may be challenging due to the chemical forms of the materials, once the critical calibration step is established—resulting in the value assignment of a methane-in-air standard—this standard can be used to propagate the calibration chain without introducing significant material-specific offsets.

5. Gas RMs

The RM landscape relevant to atmospheric methane stable isotope ratio calibrations is shown in figure 3. The overall bulk isotopic composition of atmospheric methane is approximately [72] $\delta^{13}\mathrm{C} = -48$‰ and $\delta^{2}\mathrm{H} = -90$‰, with recorded gradients [2] in background air of 0.8‰ and 10‰, respectively. The primary sources of methane are biogenic, thermogenic, and pyrogenic. Currently available internationally RMs [16, 74, 76, 78] that can be used for δ^{13}C and δ^{2}H value assignments of methane come in various chemical forms, including carbonates, organics, and CO_2 gas for δ^{13}C, and water and organics for δ^{2}H. However, there are no international RMs specifically for stable isotope ratio measurements of gaseous methane, or atmospheric methane. This gap has led to the emergence of ad-hoc calibration strategies, each introducing associated biases in their application.

Addressing these biases has been a significant focus in the atmospheric methane stable isotope ratio measurement community. Inter-laboratory comparison studies, such as the one by Umezawa *et al* [69], as indicated earlier, have revealed discrepancies of up to 0.5‰ in δ^{13}C values and 13‰ in δ^{2}H values for atmospheric methane isotope ratio measurements across 16 global laboratories. To address these biases Sperlich *et al* [45, 81] proposed and developed a suite of isotope reference gases for atmospheric methane (shown under ongoing efforts in figure 3), aiming to help establish a universal scale anchor for δ^{13}C and δ^{2}H isotope measurement of methane. Although an international comparison study using these reference gases hasn't been reported yet, bilateral comparisons in 2020 between the Max Planck

Table 2. Performance matrix of measurement techniques used for methane isotope ratio measurements. (Major contributors listed).

		CF-IRMS		OIRS		
Metric↓Technique→	DI-IRMS (external sample preparation line needed)	GC-C/P-IRMS	EA-IRMS, TC/EA-IRMS	CRDS	Precon-TILDAS	Takeaways
Throughput	Low	High	High	High	High	CF-IRMS, OIRS preferred methods (15–50) min [52, 68] DI-IRMS: Long (several hours) due to typically additional offline preparations involved
Volume	20 l to 100 l STP (ambient air) [69, 70] (gas cylinder will not last long)	100 ml STP (ambient air)	250 nl STP	∼1 l STP (at 80 sccm, 15 min)[52]	5 l to 10 l [51, 58] STP preconc needed	DI-IRMS sample intensive
Precision ‰ $(\delta^{13}C, \delta^{2}H)$	0.02 [71][a]	0.06 [48][a], 1.0 [48][a]	0.04 [45], 0.7 [45]	0.24 [53][b]	0.05(0.02[c]) [58], 0.27(0.11[c]) [58]	Strategize DI-IRMS and CF-IRMS usage based on compatibility, throughput, volume demands.
Peripherals	Combustion, separation, reduction, preconcentration		Combustion, separation, reduction	Separation of potential spectral interferents [66]	Preconcentration trap	CRDS less processing, online CF-IRMS: online Precon-TILDAS: online DI-IRMS: offline
Interferences	CO_2 analysis: $m/z = 44$ (combustion by product from unseparated sample impurities, unseparated $^{86}Kr^{2+}$ tail, N_2O), $m/z = 45$ ($CO^{17}O$, CO_2H (CO_2 + uncombusted CH_4), unseparated $^{86}Kr^{2+}$ tail), $m/z = 46$ (unseparated $^{86}Kr^{2+}$ tail). H_2 analysis: $m/z = 2$ (reduction byproduct from unseparated sample impurities), $m/z = 3$ (H_3^+ source protonation reaction, HD impurity in carrier He)			Wavelength-specific spectral interferences; deviations in gas matrix composition [66]		Method dependent

(Continued.)

Table 2. (Continued.)

		CF-IRMS		OIRS		
Metric↓Technique→	DI-IRMS (external sample preparation line needed)	GC-C/P-IRMS	EA-IRMS, TC/EA-IRMS	CRDS	Precon-TILDAS	Takeaways
Biases	Incomplete combustion, separation, reduction, interference correction, scale contraction, ^{17}O correction algorithm, [Kr]/[CH_4], signal linearity, blank (GC-IRMS for CH_4-air, EA-IRMS and TC/EA-IRMS for pure CH_4), memory effect			Sample-reference mismatch related matrix pressure broadening and spectral interference correction, amount fraction dependence, linearity	Incomplete separation of O_2 results in matrix pressure broadening, amount fraction dependence, linearity	
Gas RM needs	CH_4-air	CH_4-air	Pure CH_4	CH_4-air		Pure CH_4, CH_4-air 'international standards' needed, current non-CH_4 international standards include carbonate, water, CO_2, organics.
Cal gases requirements	δ^{13}C of CH_4 (-70‰ to -20‰) common CH_4 in air standards for atmospheric studies. (Additional custom mixtures required for method validation) δ^{2}H of CH_4 (-120‰ to -70‰) (overall bulk atmosphere composition: δ^{13}C of $CH_4 = -48$‰, δ^{2}H of $CH_4 = -90$‰) [72]					Purity, standardized spiking protocols, verification methods to quantify artifacts by enriched clumped isotopologues. Requirement for biogenic ^{13}C depleted CH_4 sources, commutability, QC
Traceability	VPDB or VPDB-LSVEC isotope delta scales for C and VSMOW-SLAP isotope delta scale for H), OIRS traceability is dependent on IRMS measurements of primary RMs					C and H isotope delta scales, OIRS dependent on IRMS for traceability

[a] one standard deviation.

[b] Allan deviation (15 min).

[c] estimated based on reported Allan deviation (100 s).

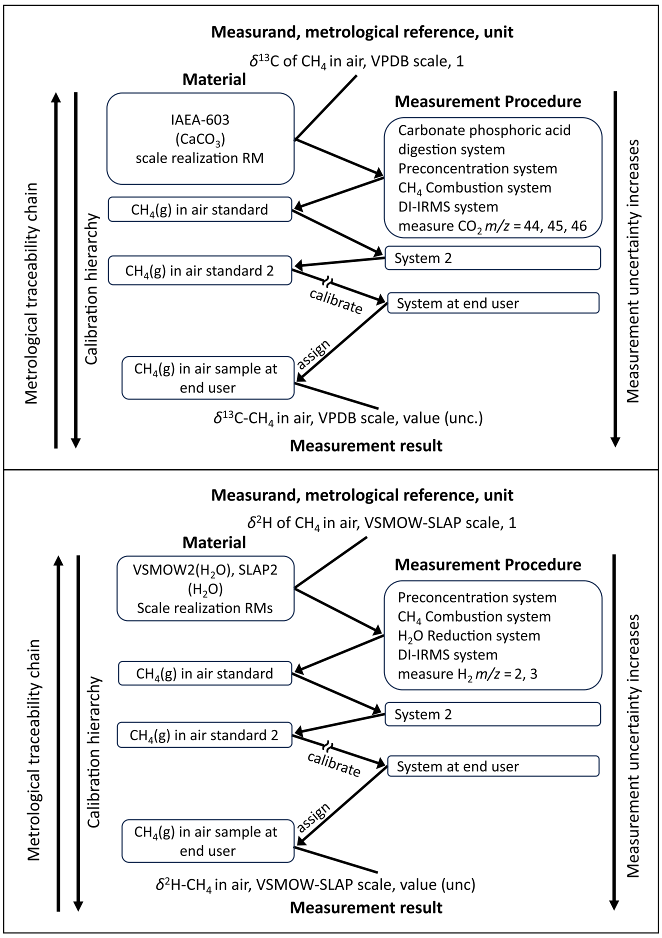

Figure 1. Example of calibration hierarchy for CH_4 in air using DI-IRMS: (top panel) $\delta^{13}C$ on the VPDB scale, and (bottom panel) δ^2H on the VSMOW-SLAP scale. IAEA-603 (for $\delta^{13}C$) and VSMOW2 and SLAP2 (for δ^2H) serve as calibrators at the top of the hierarchy. The value assignment of a CH_4 in air standard at the top of the chain enables stringent adherence to the principle of identical treatment [75] further down (depicted as ≈) the traceability chain, significantly reducing calibration offsets. However, potential offsets at the top level due to the differing chemical conversion schemes used to obtain CO_2 or H_2 can introduce variability.

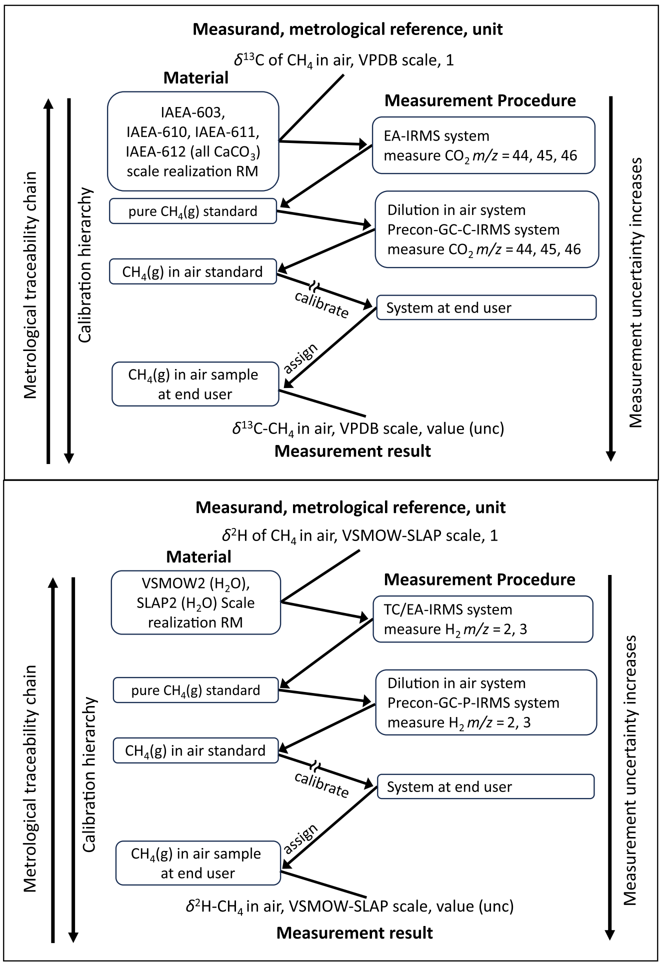

Figure 2. Example of calibration hierarchy for CH_4 in air using CF-IRMS: (top panel) $\delta^{13}C$ on the VPDB scale (as shown) or VPDB-LSVEC scale (not shown), and (bottom panel) δ^2H on the VSMOW-SLAP scale. IAEA-603 and IAEA-610, −611, and −612 (for $\delta^{13}C$) and VSMOW2 and SLAP2 (for δ^2H) serve as calibrators at the top of the hierarchy. The value assignment of a CH_4 in air standard at the top of the chain ensures stringent adherence to the principle of identical treatment further down (depicted as ≈) the traceability chain, significantly reducing calibration offsets. The potential offsets at the top level are minimized using common chemical conversion systems for obtaining CO_2 or H_2, ensuring greater consistency. For $\delta^{13}C$, USGS44 can also be used instead of the IAEA-610, −611, −612 series. When using USGS44, depending on the assigned values used (see Qi *et al* [76]), $\delta^{13}C$ VPDB or VPDB-LSVEC scale is realized.

Institute for Biogeochemistry (MPI-BGC) IsoLab, which is also the WMO central calibration laboratory [84] for CO_2 isotope ratio measurements, and the National Institute for Water and Atmospheric Research (NIWA) on pure CH_4 gases showed agreement at the 0.05‰, approaching the WMO network compatibility goal of 0.02‰. The objective of this approach is to develop a robust method for the calibration of pure CH_4 gases. These can then be diluted to ambient atmospheric levels with CH_4-free air in the subsequent step. This would provide CH_4-in-air mixtures with precisely known $\delta^{13}C$ and δ^2H values of the highest possible calibration level. Lower-level mixtures could then be value-assigned against these primary mixtures and be disseminated within the atmospheric community.

Developing CH_4 gas RMs on a scale sufficient to support the global community is a logical next step [11]. However, this development faces unique challenges related to scaling, distribution, preparation, packaging, purity, availability, and standardization. Pressurized gas cylinders have been used for instrument calibration in the atmospheric community for several decades, which has demonstrated the desired robustness and stability criteria required for RMs for stable isotopes in atmospheric methane. NMIs, particularly those with expertise in gravimetric cylinder standards, are well-positioned to address this need, especially for field-deployed OIRS. Successful implementation by NMI/DI gas metrology groups requires establishing robust calibration and measurement

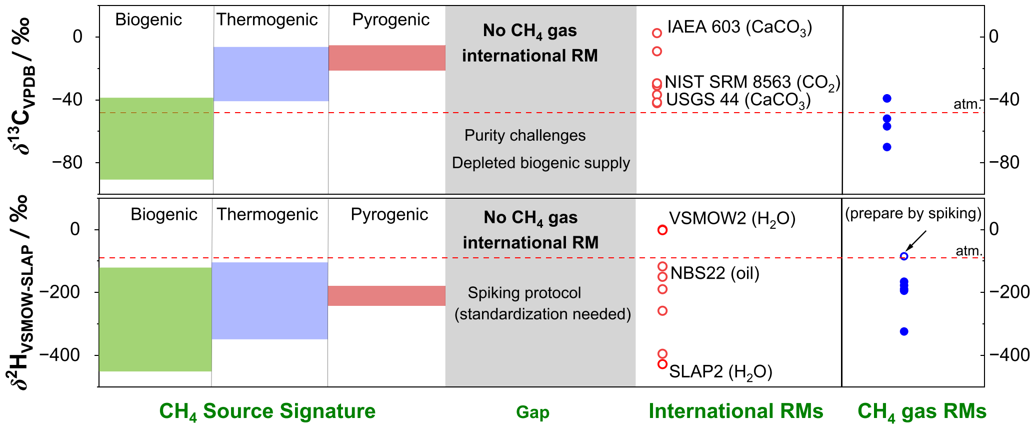

Figure 3. Reference material landscape for stable isotope composition (δ^{13}C and δ^2H) of atmospheric methane. The *y*-axis shows isotope composition, while the *x*-axis is divided into four panels: span of natural CH$_4$ source signatures (leftmost), current gaps in international CH$_4$ RMs, partial list of available international RMs [16, 74, 76, 78] and their forms, and current efforts to develop CH$_4$ gas RMs (rightmost). The overall atmospheric CH$_4$ bulk isotope composition ($\delta^{13}C = -48$‰, $\delta^2H = -90$‰) is compared with isotope delta values of some of the available international reference materials used to assign δ^{13}C and δ^2H values of CH$_4$. Although no international CH$_4$ gas RMs are currently available, several ongoing efforts within the community are underway to develop them [45, 81–83].

infrastructure, often necessitating filling gaps in isotope ratio measurement capabilities through active collaborations with expert laboratories. Although this process is gradual, the progress being made is encouraging.

The NMIs of the UK (NPL) and Netherlands (VSL), as part of the European project 19ENV05 (STELLAR [82]), have successfully demonstrated the production of large cylinders (5 l–10 l, at 120 bar) containing methane in air at ambient concentrations (1.85 µmol mol^{-1}), with isotopic compositions traceable to VPDB and VSMOW-SLAP. The methane sources, which were derived from both biogenic and fossil origins, spanned a wide range of δ^{13}C (from −39.07‰ to −56.82‰) and δ^2H (from −189.06‰ to −323.9‰), offering a diverse selection of isotopic compositions (shown as CH$_4$ gas RMs in figure 3) that could be used for atmospheric calibration needs. These RMs were diluted with synthetic air and certified for their isotopic composition at MPI-BGC IsoLab [44, 45], with no fractionation observed between pure and diluted materials. This collaboration underscores the value of NMIs and atmospheric isotope laboratories working together to advance stable isotope calibration and provide reliable RMs for global measurement needs.

In addition to their traceable isotopic composition, these RMs are distinguished by their SI-traceable amount fraction, established gravimetrically, and an isotope delta value referenced to the international isotope scale. These methane RMs have been compared with the WMO methane amount fraction scale (X2004A scale) at Empa during the STELLAR [82] project, as well as in international key comparisons (CCQM K82 [85]) involving NOAA as an additional participant. With the introduction of the international key comparison BIPM QM-K5 [86] for CO$_2$ in air scale standards and plans to extend this to methane, participating NMIs will be uniquely positioned to offer both amount fraction and isotope ratio RMs linked to international standards. The need for such dual-tracer RMs with high-precision methane amount fraction and δ^{13}C isotope delta values is also critical for inversion models such as CarbonTracker-CH$_4$ [87], which use both atmospheric CH$_4$ amount fraction and δ^{13}C data to estimate methane emissions, improving predictability and alignment with observed patterns. These RMs are essential for OIRS calibration, as they provide data on both methane amount fraction and isotope composition. This information will help refine our understanding of methane sources and sinks worldwide.

Challenges in the large-scale production and dissemination of isotopic CH$_4$ RMs include sourcing biogenic gas with high ^{13}C depletion (δ^{13}C values approximately −70‰) and preparing standards that cover the full atmospheric δ^2H range (approximately −90‰ ± 10‰). The availability of such ^{13}C depleted biogenic sources depends on gas wells [88] with sufficient microbial activity, and furthermore, these gases must be compressed into high-pressure tanks and purified cost-effectively in large volumes. Biogas plants can also provide valuable sources of δ^{13}C depleted CH$_4$ (around −50‰ to −65‰) [89], but significant purification is required to remove impurities like N$_2$, CO$_2$, H$_2$S, NH$_3$, siloxanes, and higher alkanes [90]. While fossil methane sources are widely available at high purity, a larger supply of high-purity biogenic methane would expand the range of isotopic values for δ^{13}C. With the growing production of bio-liquefied natural gas (Bio-LNG) for transportation fuel, it could become a key source for CH$_4$ in the future. Despite the relatively lenient European biomethane standards (EN167223-2, $CO_2 + O_2 + N_2 < 5$ cmol mol^{-1}), most Bio-LNG methane is expected to have higher purity. However, standardization of purity analysis [91, 92] for both parent and balance [93] gases is needed to guide source material suppliers and RM producers for minimizing impurity driven uncertainties in light of the stringent WMO requirements. When natural CH$_4$ sources are unavailable (illustrated in figure 3), particularly for methane δ^2H values in ambient air, spiking with ^{2}H enriched CH$_4$ is an option used to match the atmospheric isotopic composition. Further research into spiking techniques and their standardization is required to address challenges such as the potential introduction of non-natural levels of clumped isotopes [82], as well as the long-term isotopic stability of the methane mixtures produced using this method.

To maintain uniformity and adhere strictly to the principle of identical treatment [75], synthetic methane-in-air reference gases generally require the inclusion of air components such as Kr, N_2O, CO_2, CO in addition to atmospheric levels of N_2, O_2, and Ar. High purity levels in the balance gas/zero gas (synthetic air) are necessary to avoid potential biases in the isotopic composition of the final CH_4 in-air mixture. These purity challenges, estimated in one study, can result in biases of up to 0.04‰ for δ^{13}C values and 0.007‰ for δ^{2}H values at nmol mol^{-1} level addition of CH_4 impurity in the final ambient amount fraction level mixture [45].

In preparing synthetic mixtures, methane amount fraction levels may also need to be prepared at lower levels (1 µmol mol^{-1} or lower) to accommodate measurements relevant to stratospheric or ice core samples [94, 95]. However, due to the variety of measurement approaches within IRMS and OIRS, method-specific biases exist, and the commutability [96] of gas RMs must be clearly established. In addition to common reference gases, customized mixtures are employed for method validation and calibration corrections, Examples include methane at 500 µmol mol^{-1} levels in pure N_2 for preconcentrator-based OIRS systems and high amount fraction methane in synthetic air for establishing concentration dependence using the isotope ratio calibration method [51, 58, 68]. An added benefit of using CH_4 RM, beyond meeting the principle of identical treatment, is that it enables the calibration of both δ^{13}C and δ^{2}H measurements. This feature is largely absent in current international RMs, except for NBS22 oil [97] and IAEA-CH-7 polythene [98], which provide both δ^{13}C and δ^{2}H values but are chemically distinct from CH_4.

6. Uncertainty evaluation

Reported uncertainties for isotope delta values often address only statistical uncertainties (Type A evaluation), neglecting non-statistical uncertainties (Type B evaluation), such as those from calibration RM certificates. For δ^{13}C and δ^{2}H measurements conducted under repeatability conditions for atmospheric methane, reported statistical uncertainties could vary from 0.02‰ to 0.3‰ and from 1‰ to 3‰, respectively, based on IRMS data compiled from 16 laboratories [69]. Including the uncertainty of calibration materials (Type B evaluation) in the combined standard uncertainty requires an accurate assessment of all RMs in the calibration hierarchy, as well as consideration of correlations arising from common calibrators.

The need for guidance on uncertainty evaluation has long been recognized and was formalized in the Guide to the Expression of Uncertainty in Measurement (GUM) [99], developed following a 1993 call by the CIPM. Determining the delta values of isotope RMs and their uncertainties often requires multi-laboratory comparisons against a set of higher-order RMs. However, these evaluations may under-represent or overlook Type B uncertainties associated with higher-order RMs. Gröning's [100] recent re-evaluations of RM value uncertainty estimates, conducted in line with GUM principles, suggest potential revisions of uncertainties for several RMs. In one instance, relevant to δ^{13}C assignments via the NBS22 oil RM, revised uncertainty estimates were found to be up to three times higher. The study also underscored the challenges of retroactive adjustments, such as the availability of raw data.

An example of incorporating correlations into the combined uncertainty when addressing multi-laboratory studies is provided by Meija and Chartrand [101] who showed that in a four-laboratory study of three common higher-order RMs, correlations increased the uncertainty of the δ^{13}C value for BEET-1 sugar RM from 0.03‰ (no correlations) to 0.05‰ (with correlations). Such evaluations assume importance in interpreting inter-laboratory comparison differences, establishing consensus estimates, and developing accurate atmospheric source apportionment models. Proper treatment of the correlation between calibrated isotope delta values sharing common calibration RMs requires calculating the variance-covariance matrix [102] and its off-diagonal terms. The underlying mathematical procedures can be quite involved and challenging for large matrix sizes. Resorting to accessible computational tools like the Monte Carlo method (MCM) can be a useful aid in simplifying and including the quantification of correlations [103]. Additionally, it is desirable to design assessment studies with well-defined protocols for both measurement and calibration methods.

Multi-point calibration is increasingly recommended for robust assignment of isotope delta values in samples [104, 105]. The calibration method, typically constructed as a linear calibration curve with certified (y) versus measured (x) data, must account for uncertainty associated with the employed RMs (Type B from certificates) when applied to evaluate sample uncertainty. Instead of the common ordinary linear regression approach—which overlooks RM uncertainty (Type B uncertainty, obtained from RM certificate)—a fitting model that incorporates errors-in-variables is therefore essential. Here, as indicated earlier, sampling-based uncertainty analysis using iterative MCM provides a straightforward way to estimate uncertainties when applying the errors-in-variables model, while also considering correlations between values [80, 102, 104, 106].

The potential instability of RMs, a prominent example being LSVEC—initially deemed stable but later found to be unreliable and discontinued from use for stable carbon isotope measurements [21]—complicates uncertainty evaluations. For instance, while Sperlich *et al* [45] used an uncertainty value of 0.15‰, it could potentially be as high as 0.30‰ according to the IAEA Reference Sheet for LSVEC. This instability necessitates retroactive corrections to measurement data associated with these standards [107].

To standardize data treatment and promote its application, the development of web-based software tools [103, 108]

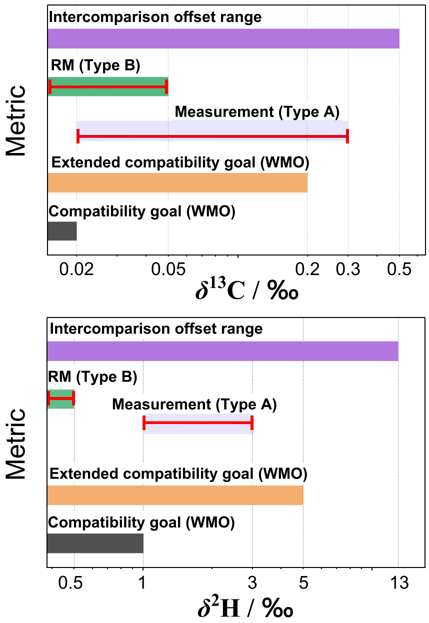

Figure 4. Figure of merit for atmospheric CH_4 stable isotope ratio measurements, showing WMO targets, uncertainty components, and data offsets (derived from Umezawa *et al* [69]). Measurement (Type A evaluation) and RM (Type B evaluation) uncertainties are represented by their spread (solid red line) across laboratories. The WMO compatibility (extended compatibility) goals are 0.02(0.2)‰ for δ^{13}C values and 1(5)‰ for δ^{2}H values, respectively. The reported intercomparison offset range is 0.5‰ and 13‰ for δ^{13}C and δ^{2}H, respectively.

and the increasing number of publications highlighting their importance (e.g. IUPAC 2022 [77]) are helping to improve the accuracy of assessments and ensure better agreement across global datasets. Harmonizing datasets requires careful consideration of systematic biases [109], which can arise from differences in methods, laboratories, scale realization or history thereof, sample processing, or instrument performance. These biases [69] can often be significantly larger than the combined uncertainties previously discussed (see figure 4), exceeding the WMO network atmospheric methane measurements compatibility targets of 0.02‰ for δ^{13}C values and 1‰ for δ^{2}H values, as well as the extended compatibility goals of 0.2‰ and 5‰, respectively. Collaborative efforts, including the development of common gas RMs, intercomparison studies, and best practices, aim to minimize these issues. The largest component of lab-to-lab offsets stems from differences [69] in local scale realizations of CH_4 against available (non-CH_4 gas) isotope RMs. These offsets are typically corrected through linear calibration scale transfer transformations, which help harmonize datasets. They also underscore the need for continued development of common gas isotope RMs and transparent methodologies to further minimize the offsets.

7. Ongoing activities

Several comparison and capacity-building activities are currently underway to support the goals of atmospheric methane isotope ratio measurements, with growing participation from NMIs and DIs. Other key contributors, including the IAEA, the expert isotope laboratories, and the GGMT atmospheric monitoring community, remain actively involved.

7.1. Comparison studies

Following the 2018 Umezawa *et al* [69] study, which provided global comparability across 16 major laboratories engaged in stable isotope ratio measurements of atmospheric methane, new studies have been undertaken to address the identified gaps. These efforts, tabulated in table 3, include round-robin (RR) initiatives led by NIWA and INSTAAR/NOAA (Institute of Arctic and Alpine Research/National Oceanic and Atmospheric Administration), the isoMET [83] project, the upcoming EPM (European Partnership on Metrology) MetHIR Joint Research Project, and a bilateral comparison between the stable isotope laboratories at NIWA and MPI-BGC IsoLab [44].

The 2019 RR study involved 16 global laboratories using both IRMS and OIRS techniques. The experimental design included cylinders with northern hemisphere air, as well as those for testing comparability with spiked Kr, isotopically spiked CH_4, and varying methane amount fractions. Preliminary results [9, 110] indicate that laboratory offset dependence in IRMS measurements varies with factors such as the Kr/CH_4 ratio, scale contraction, and methane amount fraction. It is also suggested that OIRS may exhibit different measurement dependencies, highlighting the need for specific comparison test protocols to fully characterize these variations.

While a comprehensive report is forthcoming, the study demonstrates the effectiveness of using common reference gases to correct lab-to-lab data offsets, achieving convergence within the WMO compatibility goal of 0.02‰ for δ^{13}C isotope ratio measurements in a data harmonization experiment using round robin data.

A key project focused on further exploring OIRS methodologies, particularly for field deployment, is the newly launched EPM isoMET [83] Joint Research Project. This initiative seeks to enhance methane estimation models in Europe using CH_4 isotope ratios and brings together experts from various fields, including national metrology institutes. Key components of the project include developing calibration protocols for field-deployed OIRS, identifying the potential of clumped isotope measurements for source identification [111], and harmonizing datasets to improve emission estimates. The field-OIRS test protocol leverages advancements made during the European 19ENV05 STELLAR [82] Joint Research Project, which developed ambient methane RMs with isotope composition. Such efforts will be further explored in the upcoming EPM MetHIR Joint Research Project.

7.2. Gas RMs

The NMIs NPL and VSL have developed large-volume gas isotope RMs for ambient methane in air, prepared gravimetrically and covering a useful isotopic range (δ^{13}C

Table 3. Comparison studies relevant to atmospheric methane stable isotope ratio measurements.

Study	Comparison	Material	Period	Labs	IRMS	OIRS	Takeaways
Umezawa *et al* [69]	Inter-laboratory	CH_4-air	1991–2018	16	16	2	$\delta^{13}C(\delta^2H)$ offset large: 0.5(13)‰.
Post Umezawa *et al* [69]	Round robin (INSTAAR/NOAA, NIWA)	CH_4-air	2019-	16	11	5	With common reference gases, 50% achieve $\delta^{13}C$ agreement at 0.02‰. Kr bias reduced; scale compression is a problem. Lab offset used to merge datasets. IRMS, OIRS issues vary.
	Intercomparison of field OIRS (isoMET EPM), MetHIR (EPM)	CH_4-air	2024-	7	0	7	Ongoing, leveraging STELLAR ambient CH_4-air gas isotope RMs development work.
	Lab comparison for $\delta^{13}C$-pure CH_4 (NIWA, MPI-BGC IsoLab)	Pure CH_4	2020	2	2	0	Agreement within 0.1‰. Three-point calibration is more robust. MPI-BGC IsoLab and NIWA analytical systems provide 'fundamental capability' to calibrate pure CH_4.

values of −39.07(0.09)‰ and −56.82(0.04)‰, and δ^2H values from −189.06(1.55)‰ to −323.9(1.90)‰) as part of the ENV05 STELLAR [82] project. Within the isoMET [83] project, NPL has scaled up production, producing approximately 40 pressurized gas cylinders, each providing 1000 standard liters of CH_4 in air. These materials include customized mixtures with CO_2 and N_2O added to synthetic air (Ar, O_2, N_2). The CH_4 is sourced from commercially available fossil methane (99.9999% purity), providing a range of $\delta^{13}C$ and δ^2H values traceable to VPDB and VSMOW-SLAP scales via IRMS [44, 45, 82]. The RMs cover methane amounts from 1.7 µmol mol^{-1} in air to 600 µmol mol^{-1} in nitrogen (for OIRS coupled to preconcentration systems) and are traceable to the SI with a nominal relative uncertainty ($k = 2$) of 0.2%. NPL now offers [112] these RMs for climate monitoring applications.

7.3. Pure CH_4 reference gases

To provide pure CH_4 isotopic reference gases, similar to the existing pure CO_2 NIST SRMs (8562, 8563, and 8564) [113], available in glass ampoules, the IAEA is evaluating the feasibility of packaging and distributing two pure CH_4 RMs: one of fossil origin and another of biogenic origin. (Note: The IAEA is also in the process of releasing three pure CO_2 RMs with different $\delta^{13}C_{VPDB}$ isotopic values: IAEA-615, IAEA-616, IAEA-617, packaged in copper tubes.) Additionally, NPL and VSL have established the capability to provide pure CH_4 RMs (of fossil and biogenic origins), which have been isotopically assigned and used as starting material for their CH_4-in-air gas cylinder preparations.

7.4. Measurement capabilities

The National Research Council of Canada (NRC, Canada's NMI) is developing the capability to measure hydrogen and carbon isotope ratios in pure methane using TC/EA-IRMS for hydrogen and EA-IRMS for carbon. Hydrogen isotope measurements are traceable to the VSMOW-SLAP scale through RMs VSMOW2, SLAP2, USGS45, USGS46, and USGS47, while carbon isotope measurements are traceable to the VPDB scale using in-house CO_2 reference gases, calibrated against NBS19, IAEA-603, IAEA-610, IAEA-611, and IAEA-612. Additionally, Physikalisch-Technische Bundesanstalt (PTB, German NMI), VTT MIKES (Finnish NMI) and NPL are actively involved in developing metrologically robust OIRS methodologies for stable isotope ratio measurements, alongside the GGMT community [83].

8. Leveraging natural gas isotopic RMs

Although this work focuses on CMC requirements for atmospheric methane, valuable insights and resources can be drawn from the development of natural gas isotopic RMs for the oil and gas industry. In 1984, collaborative efforts between the oil industry, academia, and the IAEA led to the creation of three natural gas RMs [114]. Labeled as NGS-1, NGS-2, and NGS-3, these materials were derived from coal, petroleum, and biogenic sources, with methane molecular compositions of over 80%, 50%, and 95%, respectively. The $\delta^{13}C$ (VPDB scale) nominal values for methane were −29‰, −44‰, and −72‰, respectively.

In 1992, these gases were transferred to NIST, which conducted detailed characterization and intercomparison studies, subsequently distributing them as RM8559, RM8560, and RM8561 in 50 cm^3 pressurized (5 MPa) stainless steel cylinders [115]. These gases served the research and technology needs in the energy gas industry for over a decade, significantly reducing the combined expanded uncertainties ($k = 2$ coverage factor), notably from 1.31‰ to 0.09‰ for NGS-3(RM 8561) for $\delta^{13}C$ values.

To address the continued need for RMs in the energy gas sector, the USGS led efforts in 2021 [116] to develop three light hydrocarbon (methane, ethane, propane) reference gases. Labeled as HCG-1, HCG-2, and HCG-3, these materials were derived through a hybrid method involving synthetic mixing, isotope spiking, and natural samples, with methane amount fraction compositions near 46%, 59%, and 94%, respectively. Available in pressurized (350–500) kPa 50 cm^3 stainless steel cylinders, the corresponding $\delta^{13}C$ nominal values are -1.5‰, -43‰, and -61‰, with combined expanded ($k = 2$) uncertainties between 0.1‰ and 0.15‰.

Though the depleted $\delta^{13}C$ biogenic methane source did not reach the low levels of the NGS series, both the $\delta^{13}C$ and $\delta^{2}H$ ranges were expanded for the HCG series to meet the energy sector's needs. In the case of HCG-1, developed by mixing natural and ^{13}C- and ^{12}C-enriched hydrocarbons, the necessity for full equilibration of the prepared methane mixture was emphasized [116]. This mirrors the current challenges in atmospheric methane reference gas development, i.e., limited sources of depleted biogenic methane and the need to employ synthetic mixing and isotope spiking to achieve the desired isotope composition.

In the NIST campaign, measurements used both DI-IRMS (with offline preparation) and GC-C-IRMS for $\delta^{13}C$, employing RM 8563 and RM 8564 as reference gases. The USGS campaign reported $\delta^{13}C$ and $\delta^{2}H$ using DI-IRMS (with offline preparation), referenced against NBS-19 and LSVEC for carbon, and VSMOW2 and SLAP2 for hydrogen.

The natural gas or hydrocarbon gas series could potentially be used, either pure or diluted, for method development, as anchor RMs, or as secondary reference gases by NMIs and DIs planning to work in the atmospheric and/or energy gas sectors.

9. Comparison protocol

The CCQM working groups, namely the GAWG and IRWG, supported by the BIPM and expert laboratories, are actively addressing the needs for isotope ratio metrology across sectors such as climate & environment, food safety, and energy. These efforts often involve developing appropriate infrastructure at member NMIs/DIs and the BIPM, with close coordination among expert laboratories and international organizations like the WMO and IAEA. In recent years, these collaborative efforts have led to the organization of several international stable isotope ratio comparison studies coordinated by CCQM. As shown in table 4, these studies cover pure CO_2 and CO_2 in air, which are relevant to atmospheric isotope ratio measurements, as well as vanillin (solid) and honey (liquid), which are crucial for food safety. The comparisons primarily involve measurements of the light stable isotopes $\delta^{13}C$ and $\delta^{18}O$.

Two primary models [117] are typically used in designing these comparison studies:

Model 1: A suite of 'travelling' standards, value-assigned by the coordinating laboratory, is distributed to all participants for measurement. This allows for the assessment of their CMCs for value assignment.

Model 2: Participants send their RMs to the coordinating laboratory, where their value assignments are compared with those of the coordinating laboratory. This model assesses the capabilities of NMIs/DIs in producing RMs and making their value assignments.

In developing a CCQM international comparison of pure CH_4 and CH_4 in air standards for $\delta^{13}C$ and $\delta^{2}H$ related isotope ratio measurements, insights from past studies can guide the design. The CH_4 comparison test protocol can benefit from findings in the CO_2 CCQM studies due to similarities in atmospheric isotope ratio methods. Additionally, expertise in the EA-IRMS technique could involve participants from honey and vanillin studies, enabling the use of organic international standards while adhering more closely to the principle of identical treatment. Leveraging RR designs from the international community will aid in selecting appropriate sample types.

For pure CH_4 gases, a suite of four gases, detailed in table 5, can be selected to assess agreement under various scenarios. This includes evaluating scale contraction using gases with a large isotopic delta span (Gas 1 and Gas 3 for $\delta^{13}C$). Given the lack of international isotopic RMs in the highly depleted $\delta^{13}C$ region of -70‰, multipoint calibration with extrapolation is essential. Including Gas 4 allows for the evaluation of participants' multipoint calibration procedures and the inherent scale contraction in their measurements. To assess performance at atmospheric levels, Gas 2 is included. As there are no sources of pure CH_4 with atmospheric hydrogen isotope delta levels, a synthetic approach using spiking with isotopically enriched samples (CH_3D) will test the preparation of spiked mixtures. Additionally, Gas 1 and Gas 3 can normalize data across participants, helping to determine how agreement for Gas 2 and Gas 4 improves. Challenges include sourcing a highly depleted pure CH_4 for Gas 4, as well as ensuring purity, stability, homogeneity, and proper characterization. While pure CH_4 isotope ratio measurements are not typically performed by atmospheric laboratories, establishing their traceability is crucial for both developing CH_4 in air standards and maintaining an unbroken calibration chain to international standards (figure 2).

In contrast, a CH_4 in air comparison test protocol should include mixtures that account for common interferents and concentration dependencies found in isotope ratio measurements of atmospheric CH_4. The selection of balance gas may

Table 4. CCQM comparison initiatives in stable isotopes for δ^{13}C and δ^{18}O measurements.

Comparison study	Light stable isotope	Material	NMI/DI	Guest Labs	Mode	Year	WG	Technique
CCQM-K140/P175 [118]	δ^{13}C	Honey (liquid)	5	0	1	2015–2016	IAWG[a]	EA-IRMS
CCQM- K167 [119] /P211 [106]	δ^{13}C	Vanillin (solid)	8/1	0/3	1	2019–2020	IRWG	EA-IRMS and one CM-OIRS
CCQM-P212 [105]	δ^{13}C	Vanillin (solid)	6	1	1	2019–2022	IRWG	EA-IRMS[b], CM-OIRS
CCQM-P204 [120]	δ^{13}C, δ^{18}O	Pure CO_2 (gas)	14	5	1	2019–2022	GAWG	DI-IRMS[b], EA-IRMS, GC-IRMS, OIRS
CCQM-P239 [121]	δ^{13}C, δ^{18}O	CO_2 in air (gas)	TBD	TBD	2	2024	GAWG	TBD

(Additional studies include a key comparison organized by IAEA and NIST on one pure organic material, two pure inorganic materials, and one real-world material for C and N isotope ratio analysis (2024–2025) within the IRWG, as well as plans for pilot studies on carbonates by BIPM and IAEA).

[a] Conducted by the IAWG, inorganic analysis working group.

[b] Majority of participants.

need to be tailored to address the specific dependencies of CF-IRMS and OIRS. For instance, incorporating Kr (krypton, an interferent in IRMS) versus CO_2, C_2H_6, N_2O (spectral interferents in OIRS) could be crucial for assessing compatibility both within and across techniques.

10. Conclusion and recommendations

In summary, this document presents key insights and recommendations from the *CH_4 Task Team of the Isotope Ratio Task Group* aimed at developing robust CMCs for atmospheric methane stable isotope ratio measurements. These efforts are designed to enhance national metrology capabilities and foster collaboration among metrology, atmospheric science, industry, and user communities. As OIRS gains traction, the demand for RM gases in high-volume gas cylinders for atmospheric methane will increase. NMIs/DIs with expertise in gravimetric standard preparation are well-positioned to produce materials that provide both amount fraction and isotope ratio values traceable to appropriate scales. This transition will alleviate the burden on current expert isotope laboratories multitasking in atmospheric monitoring, standard development, and scale maintenance. However, developing NMI/DI gas standards presents its own challenges, including the need to establish in-house measurement capabilities for stable CH_4 isotope ratios, demonstrate the ability to achieve required precision and long-term stability, or rely on specialized isotope laboratories. This underscores the continued need for collaboration between the two communities.

Atmospheric methane calibration and measurement practices are evolving but present challenges, including the limited availability of highly depleted δ^{13}C CH_4 biogenic sources, preparation of standards with ambient δ^{2}H CH_4 values, and the need to ensure low hydrocarbon impurity load in source methane. These factors complicate the development of methane gas isotope RMs. Alternative solutions, such as spiking with isotopically enriched methane, face difficulties [67] due to the artificial and unknown distribution of isotopes between molecules and require more research and standardized protocols. Promising approaches to calibration include creating a range of standards with fixed, accessible isotope delta values across various amount fractions, which are being pursued to enable accurate calibration of OIRS through the isotopologue method. Additionally, the development of gas EA-IRMS and TC/EA-IRMS methods for pure CH_4 gas holds promise for broadening access to isotope RMs while striving to adhere to the principles of identical treatment and multipoint calibration.

To address these challenges and capitalize on emerging opportunities, the following recommendations are proposed to NMIs, DIs, expert laboratories, standardization bodies, and the global atmospheric science community:

1. **Enhance NMI/DI measurement capabilities**: Strengthen the stable CH_4 isotope ratio measurement capabilities of NMIs and DIs, ensuring precision, stability, and traceability to internationally recognized isotopic scales.
2. **Develop high-quality gas RMs:** Expand the development of pure CH_4 and CH_4 in air RMs across NMIs and DIs, ensuring traceability to international standards. Address challenges like limited biogenic δ^{13}C methane sources and ensure impurity control in both parent methane and balance gas. Explore alternatives, such as isotopically enriched methane, with standardized protocols.
3. **Develop ISO standards for methane isotope materials and zero gas:** Advocate for the creation of ISO standards for methane isotope RMs and zero gas (balance gas), with an emphasis on impurity specifications, in collaboration with ISO TC/158 [123] to ensure global consistency.
4. **Standardize calibration protocols:** Support the development of robust, standardized calibration strategies for both OIRS and IRMS, including methods like the isotopologue approach for OIRS calibration and gas-based EA-IRMS for the calibration of pure methane. Emphasize multipoint calibration and adherence to the principle of identical treatment.
5. **Update RM value assignment and uncertainty:** Update the IUPAC list [17] of RMs (Brand *et al* [16]) to reflect currently accepted values, ensuring both VPDB and VPDB-LSVEC values are provided for δ^{13}C to avoid potential biases and maintain consistency in usage [18]. (Note: The

Table 5. Example design of a pure CH_4 isotope ratio comparison test using four gases.

Gas	($\delta^{13}C$, $\delta^{2}H$)[a] ‰	Purpose	Source [122]	Additional
Gas 1	(−40, −180)	High $\delta^{13}C$	Fossil	Gas 1 and Gas 3 can also be used to normalize Gas 2 and Gas 4, allowing for a comparison with common reference gases to test for agreement.
Gas 2	(−48, −98)	Mimic atmosphere	Preparation by spiking CH_3D	
Gas 3	(−50, −200)	Intermediate $\delta^{13}C$	Fossil	Gas 2 mimics atmosphere.
Gas 4	(−70, −300)	Low $\delta^{13}C$	Biogenic	No RMs in Gas 4 range, test of multipoint calibration to extrapolate.

[a] Nominal values.

IUPAC list is currently under revision by the CIAAW Subcommittee on Stable Isotope RM Assessment, IUPAC Project 2014-002-1-200 [124]).

6. **Adopt the minimum requirements established by IUPAC** [14]: End users should state the RM values used to calibrate isotope delta values and, for carbon, specify if they are traceable to the VPDB or the VPDB-LSVEC scale.
7. **Adopt the δ^{13}C VPDB Scale for atmospheric methane:** Prioritize the δ^{13}C VPDB scale over the VPDB-LSVEC scale to (a) align with WMO compatibility goals, (b) avoid biases from LSVEC instability, and (c) ensure consistency with atmospheric CO_2 measurements, which are also referenced to the VPDB scale. This approach also promotes transparency in data reporting.
8. **Establish quality management systems (QMS):** Ensure that QMS are in place for the production, calibration, and maintenance of isotope RMs, in alignment with CMC criteria.
9. **Create a WMO central calibration laboratory for CH_4 isotope ratios:** Establish a central calibration laboratory for CH_4 isotope ratio measurements, similar to the carbon dioxide [84] initiative, to standardize global practices.
10. **Initiate CCQM comparison studies:** The CCQM-GAWG and CCMQ-IRWG are encouraged to include methane stable isotope ratio measurements in their strategic plans and help support comparison studies to aid global consistency in methane isotope ratios.
11. **Support CMC claims on gas isotope ratio RMs and measurements:** NMIs/DIs are encouraged to apply for CMC claims [10] on gas isotope ratio RMs and measurements, specifically focusing on methane and carbon dioxide, to support the reliability and traceability goals of atmospheric and related studies.
12. **Promote data harmonization:** Regularly update calibration scale transfer relationships through intercomparisons, reduce systematic biases, and document metrological traceability at all stages to ensure consistency in data comparisons.
13. **Foster ongoing collaboration and knowledge sharing:** Promote ongoing collaboration between NMIs, DIs, expert laboratories, and the atmospheric science community to enhance knowledge sharing and streamline development.

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Conflict of interest

The authors declare no conflict of interest. This paper identifies certain commercial equipment, instruments, and materials to clearly specify commonly used experimental methods. This identification does not constitute a recommendation or endorsement, nor does it suggest that the identified materials or equipment are the best options available for their intended purpose. No financial support was received from any funding agency for the preparation of this paper.

ORCID iDs

Abneesh Srivastava https://orcid.org/0000-0002-8527-112X
Michelle M G Chartrand https://orcid.org/0000-0003-3398-7246
Federica Camin https://orcid.org/0000-0003-0509-6745
Joachim Mohn https://orcid.org/0000-0002-9799-1001
Peter Sperlich https://orcid.org/0000-0003-1455-0903
Chris Rennick https://orcid.org/0000-0003-4993-0156
Ruth Hill-Pearce https://orcid.org/0000-0002-5515-0909
Stefan Persijn https://orcid.org/0000-0002-4356-4266
Christoph Nehrbass-Ahles https://orcid.org/0000-0002-4009-4633
Javis Nwaboh https://orcid.org/0000-0001-5251-5215

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