

Advances in the production of traceable amount fraction and isotope ratio gas reference materials to underpin climate monitoring

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Abstract. The National Physical Laboratory (NPL) in the United Kingdom provides traceable gas reference materials for calibration of atmospheric gas analysers where low uncertainty measurements of the amount fraction and/or stable isotope ratio of atmospheric components are required. Primary gas Reference Materials (PRMs) are available for amount fraction traceable to the SI and, for CO₂ amount fractions between 380 and 800 μmol mol⁻¹, can be linked to the WMO-CO₂-X2019 scale via the BIPM.QM-P5 comparison. Traceable stable isotope ratio PRMs for the most potent anthropogenic greenhouse gases and climate relevant species including carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and carbon monoxide (CO) are available and are traceable to current globally recognised isotope reference scales including VPDB for δ¹³C-CO₂, δ¹⁸O-CO₂ and δ¹³C-CH₄, VSMOW/SLAP for δ²H-CH₄ and δ¹⁸O-N₂O and Air N₂ for δ¹⁵N-N₂O. This paper details recent advances in the production of PRMs at NPL and outlines the PRMs and services currently being developed.

1 Traceability for primary gas reference materials (PRMs) for greenhouse gas amount fraction.

National Metrology Institutes (NMIs) as well as Designated Institutes (DIs) maintain and develop the highest-level primary measurement standards. For amount fraction of gases, these are typically primary reference gas materials (PRMs), prepared by precise gravimetry, providing traceability to the International System of Units (SI) [1]. The preparation and certification of PRMs establishes an unbroken, documented chain of comparisons, ensuring measurement results are accurate, comparable, and internationally recognised [2]. The NMIs/DIs then disseminate this traceability to end-users and secondary calibration laboratories.

The Bureau International des Poids et Mesures (BIPM) and NMIs/DIs organise intercomparisons. These key comparisons are crucial to ensure global consistency and traceability to the SI providing a method for NMIs to benchmark their capabilities in preparing and analysing gas reference materials [3]. Through comparing results across multiple laboratories systematic biases can be identified and corrected for, reported uncertainties can be verified and consistency in value assignment is improved [3].

International key comparisons including CCQM-K120 for CO₂ in air [4], CCQM-K82 for methane in air [5] and CCQM-K68 for N₂O in air [6], have played a critical role in enabling NMIs/DIs to demonstrate a

reduction in uncertainties in the amount fraction of gas mixtures towards those required by the user community. Achieved uncertainties are documented in the BIPM Key Comparison Database (KCDB) [7].

Due to the need to measure small changes in the amount fraction of greenhouse gases in the atmosphere, global greenhouse gas monitoring requires precise and comparable data between monitoring stations if the data is to be useful for modelling and flux studies [8]. The World Meteorological Organisation Global Atmospheric Watch (WMO-GAW) has published inter-laboratory compatibility goals which define the maximum bias for these measurements see Table 1 [8]. The requirements for the uncertainty of gas reference materials for global greenhouse gas monitoring are ideally an order of magnitude lower than the compatibility goals to enable monitoring stations to achieve the compatibility goals.

Despite the consistent reductions in uncertainty achieved [9,10] and documented in key comparisons [4-6], the extremely low uncertainties required continue to be challenging to achieve using the SI approach which evaluates the total uncertainty in amount fraction [13]. For gases such as CO₂, where reference materials for instrument calibration which are SI traceable currently does not provide sufficiently low uncertainty to meet the goals, the CO₂ reference gas materials scale system enables the production and value assignment of gas reference materials which have very small uncertainties in relationship to each other [13]. This low relative uncertainty leads to a high degree of internal consistency which is crucial for those atmospheric monitoring

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applications where small temporal and spatial changes are important. [8]

Table 1. Inter-laboratory compatibility goals published by the WMO-GAW [8].

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO ₂	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 - 520 ppm
CH ₄	± 2 ppb	± 5 ppb	1700 - 2100 ppb	300 - 2600 ppb
CO	± 2 ppb	± 5 ppb	30 - 300 ppb	20 - 500 ppb
N ₂ O	± 0.1 ppb	± 0.3 ppb	320 - 335 ppb	260 - 370 ppb
SF ₆	± 0.02 ppt	± 0.05 ppt	6 - 10 ppt	1.1 - 9.8 ppt
H ₂	± 2 ppb	± 5 ppb	450 - 600 ppb	140 - 1200 ppb
δ ¹³ C-CO ₂	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
δ ¹⁸ O-CO ₂	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
Δ ¹⁴ C-CO ₂	± 0.5‰	± 3‰	0-70‰	
Δ ¹⁴ C-CH ₄	± 0.5‰		50-350‰	
Δ ¹⁴ C-CO	± 2 molecules cm ⁻³		0-25 molecules cm ⁻³	
δ ¹³ C-CH ₄	± 0.02‰	± 0.2‰		
δD-CH ₄	± 1‰	± 5‰		
O ₂ /N ₂	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

The amount fraction of CO₂ in the atmosphere is traceable to the WMO-CO₂-X2019 CO₂ in air scale provided by the WMO [11]. The NOAA Global Monitoring Laboratory currently serves as the WMO-GAW Central Calibration Laboratory (CCL) for CO₂ and is responsible for maintaining the scale [11]. This scale has a reported consistency between tertiary standards of the order of 0.01 μmol mol⁻¹, with the SI traceability of their primary standards demonstrated in the CCQM-K120 comparison [11]. This relationship between reference materials in the scale approach is maintained in a database, and the value of any reference material can be traced back to the primary standard set defining the scale [11].

To reduce the burden on one laboratory, several NMIs/DIs are working toward providing scale traceable reference materials. The requirement for inter-compatible scales is that differences in scales must be close to the internal consistencies which are currently achieved by the WMO scale approach [12]. To minimise any potential scale bias, it is planned to maintain scale equivalence equations by using CIPM MRA on-going key comparisons [12, 8]. The comparisons of CO₂ in air scales (BIPM.QM-P5) will ensure consistency between the measurements traceable to the scales at the 0.01 μmol mol⁻¹ level [12].

The UK's National Physical Laboratory (NPL) has prepared the NPL 2023_CO₂ scale and tertiary reference materials traceable to this scale are currently being measured as part of BIPM.QM-P5 pilot comparison [12] which will provide algorithms to link amount fractions on each participating scale to the NOAA X2019 CO₂ scale. Thus, allowing participating NMIs, such as NPL, to provide PRMs and certified reference materials (CRMs) to the WMO monitoring community [13].

2 Traceability of PRMs for stable isotope ratio in greenhouse gases.

The measurement of the ratio of isotopes in atmospheric gases can be a powerful tool for investigating environmental processes including sources and sinks of greenhouse gases [14]. The large-scale adoption of

optical laser-based isotope ratio measurement techniques at greenhouse gas monitoring stations allow the apportionment of greenhouse gas fluxes to emission

sectors [14]. However, traceable PRMs or CRMs for calibration of optical isotope ratio analysers are limited in availability.

Under the CIPM Mutual Recognition Arrangement (CIPM MRA), a specific traceability exception exists for delta value isotope ratio measurements [15]. This exception allows measurements of isotope ratio to be made traceable to artefacts recognised as International Standards rather than directly to the SI. This is because, in the case of stable isotope ratio in gases, artefact-based scales currently provide lower measurement precision than existing SI-traceable methods [13]. Absolute isotope ratio measurements traceable to the SI [16, 17] have not yet achieved the desired low uncertainty required for greenhouse gas monitoring.

The internationally recognised consensus materials for stable isotope ratio relevant to greenhouse gases [18] are the Vienna Pee Dee Belemnite (VPDB) scale, typically realised through carbonate materials such as the now depleted NBS19 which is used for measurements of δ¹³C-CO₂ and δ¹³C-CH₄ and δ¹⁸O-CO₂; the Vienna Standard Mean Ocean Water and Standard Light Antarctic Precipitation scales (VSMOW/SLAP) for δ²H-CH₄ and δ¹⁸O-N₂O; and AirN₂ for δ¹⁵N-N₂O. The CCQM Isotope Ratio Working Group (IRWG) [19], established in 2018, is the primary body responsible for advancing traceability capabilities for stable isotope measurement and moving toward absolute SI-traceable ratios. They work in close collaboration with the Gas Analyses Working Group (GAWG) and have co-founded a new task group on Carbon Dioxide and Methane Stable Isotope Ratio Measurements (CCQM-GAWG-IRWG-TG-ISOTOP) established in 2023, to facilitate building a robust metrological support infrastructure for the measurement of stable isotope ratios in atmospheric greenhouse gases [20]. Worldwide consistency and traceability in measurements of isotope ratio in gases is challenging which can lead to differences in reported values of PRMs/CRMs used for calibration depending on which scale and institute the PRM/CRM producer is traceable to [21]. The BIPM stable isotopes of CO₂ pilot study (CCQM-P204) [22] evaluated the ability of different laboratories to accurately measure the isotope ratios in pure CO₂ gas

samples. This study highlighted the difficulties with primary realisation methods of the scale and the need for improved reference materials and consistency in methods and harmonised measurement practices. While no single reference value was calculated due to differences in the scales used by the participants, the study revealed offsets between participants which significantly exceed the WMO compatibility targets of 0.01‰ and 0.05‰ for $\delta^{13}\text{C}\text{-CO}_2$ and $\delta^{18}\text{O}\text{-CO}_2$ respectively. The challenges in achieving comparable measurements of the isotopic ratio of pure CO_2 is a fundamental challenge in the production of compatible diluted PRMs/CRMs.

Following on from CCQM P204, the ongoing pilot study CCQM-P239 [23] for CO_2 in air or N_2 , provided samples containing CO_2 in the range of $380 \mu\text{mol mol}^{-1}$ to $800 \mu\text{mol mol}^{-1}$ and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}\text{-CO}_2$ values from 1‰ to -43‰ and -7‰ to -35‰, respectively to participants for measurement. Precise and comparable measurements of the isotope ratio of greenhouse gases in air are vital to studies of fractionation on dilution during the production of ambient amount fraction isotope ratio PRMs/CRMs

3 Recent developments in PRMs for amount fraction.

3.1 The importance of matrix gases

Reductions in the SI traceable uncertainty offered by NMIs for PRMs produced at the low amount fractions at which greenhouse gases exist in the atmosphere have primarily been driven by improvements to gravimetric preparation techniques and impurity analysis of matrix gases. Analysis of the trace amount fractions of greenhouse gases present in the Ar, O_2 and N_2 which comprise the matrix is challenging due to the very low

amount fractions but is critical for an accurate analysis of the final amount fraction in the PRM as the amounts can be significant due to the low amount fractions at which these PRMs are required.

Measurements of impurities in matrix gases are not only hampered by the limit of detection of analysers but also by the lack of traceable reference materials at trace level. Dynamic dilution [24] offers a practical methodology for producing gas reference materials at very low levels where adsorption effects present a significant issue. Preconcentration has also been developed at NPL [25] to enable lower limits of detection for purity analysis of matrix gases [10, 26] where the amount fraction of one or more isotopocules is often very low.

Collisions of the measured gas with matrix gases leads to changes in the adsorption profile due to pressure broadening [27]. Changing the matrix composition away from that of whole air can lead to biases in the reported amount fraction due to changes in the amount of pressure broadening which can significantly affect the reported amount fractions. The BIPM has published tolerances for matrix amount fraction [28] and also within [4-6], within which changes to pressure broadening are calculated to be negligible. NPL produces PRMs in air with amount fractions of Ar, O_2 and N_2 within the stated tolerances. The uncertainties offered by NPL for PRMs of CO_2 , CH_4 and N_2O in air are stated in table 2 and discussed in section 3.3

3.2 The NPL-2023- CO_2 scale

The NPL CO_2 scale comprises a suite of nine ‘super primaries’ with traceability to the SI, the NPL primary scale and the NPL secondary scale each with nine reference materials with amount fractions spanning $380 \mu\text{mol mol}^{-1}$ to $800 \mu\text{mol mol}^{-1}$. Tertiary reference materials are compared to the secondary scale and

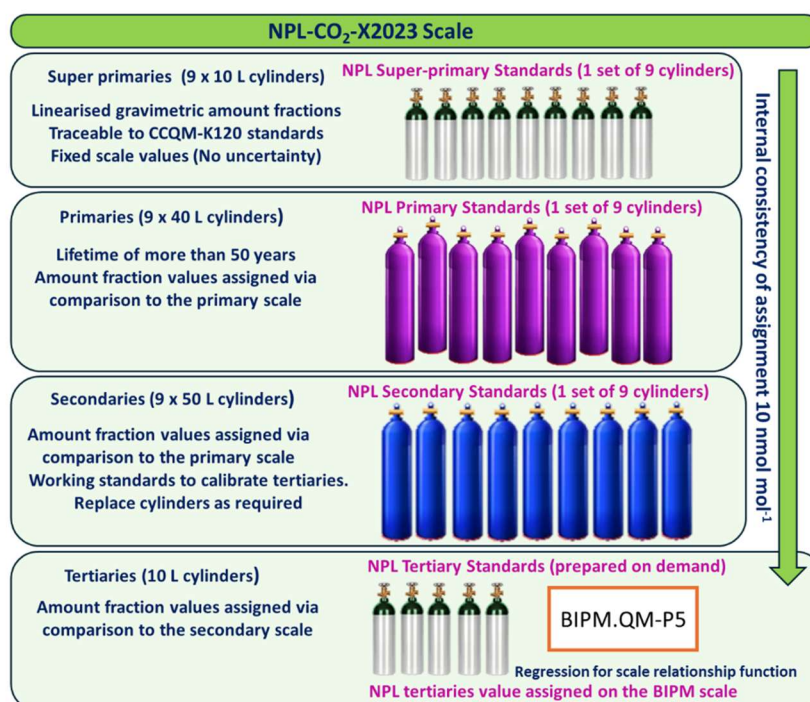


Fig. 1. Schematic showing the NPL-2023- CO_2 scale and comparisons within the BIPM.QM-P5 intercomparison.

distributed to monitoring stations for instrument calibration. Fig. 1. outlines the NPL CO₂ scale and the scale comparison BIPM.QM-P5 [29].

The super primary scale is traceable to the SI via comparison with reference materials evaluated in the CCQM K120 key comparison which span the amount fraction range of the CO₂ scale. The super primaries are produced by exchange dilution [30] to mitigate adsorption effects on the cylinder walls. The gravimetric values of the super primaries provide traceability for the NPL-2023-CO₂ scale via sequential certification of values for the primary and secondary scales.

The reproducibility of assignment of values to a suite of tertiary reference materials will be monitored through time to ascertain final values for scale transfer uncertainties. Stability of the suites of gas reference materials and the individual reference materials comprising each suite will be measured via the annual comparisons. Changes to the calibration function of each suite of reference materials may remain comparatively consistent even if drift in a single reference material occurs. The stability of the individual reference materials will be monitored through time by comparison of the residuals from the fitted function of the suite of reference materials.

3.3 Amount fraction greenhouse gas PRMs and CGMs currently available from NPL

NPL provides bespoke PRMs and certified gas reference materials (CGMs). Gas reference materials produced at the NPL are supplied in a synthetic air matrix comprising argon, oxygen and nitrogen at ambient amount fractions. These reference materials are suitable for calibrating a range of atmospheric gas analysers. Table 2. shows the PRMs and uncertainties currently available from NPL for ambient amount fraction greenhouse gases.

Component	Amount fraction range [μmol mol ⁻¹]	Typical amount fraction uncertainty (k=2) [%]	Matrix
CO ₂ *	380 - 800 **	0.2	Synthetic air. N ₂ available on request
CH ₄	1.8 - 2.5	0.2	Synthetic air. N ₂ available on request
N ₂ O	0.32 – 0.35	0.5	Synthetic air. N ₂ available on request

Table 2. SI traceable amount fraction greenhouse gas PRMs currently available from the NPL. * CO₂ gas reference materials traceable to the NPL 2023 CO₂ scale are expected to become available during 2026. Gas reference materials can be ordered and enquiries made by e-mailing gas_enquiries@npl.co.uk** Other amount fractions are available on request.

4 Recent development of PRMs/CRMs for isotope ratio.

Isotope ratio reference materials have been developed for calibration of optical isotope ratio analysers for the three most potent anthropogenic greenhouses: CO₂, CH₄ and N₂O. These isotopic PRMs are prepared from large volumes of natural pure source gases and have isotope ratios characterised by IRMS with traceability to VPDB for δ¹³C-CO₂, δ¹³C-CH₄ and δ¹⁸O-CO₂, VSMOW/SLAP for δ²H in CH₄ and δ¹⁸O in N₂O, and AirN₂ for δ¹⁵N-N₂O. The source gases were chosen to span a range of isotope ratios relevant for source attribution.

CO₂ sources cover the δ¹³C-CO₂ range of nominally + 2‰ to -42 ‰ with corresponding δ¹⁸O-CO₂ values of -8 ‰ to -36 ‰ [29]. Blends of CO₂ were produced to target specific δ¹³C values. The tuning of the δ¹⁸O CO₂ using enriched water has been demonstrated [31]. Further sources of CO₂ and CH₄ including biogenic sources are currently being evaluated for the purity and volume requirements required for long term supply of PRMs. Biogenic sources will enable the production of PRMs with certified δ¹⁴C ratios. Pure N₂O reference materials were obtained from Empa and match the isotope ratios of the reference materials marked RM1b, RM3a, RM3b and RM5 in J. Mohn *et al.* [32]. Further N₂O isotope ratios and larger volumes of reference materials are currently being developed in-house.

The pure source gases are diluted to a range of near ambient amount fractions in an air matrix comprising Ar, O₂ and N₂ at ambient amount fractions to avoid biases when measuring with whole or synthetic air on optical isotope ratio analysers due to pressure broadening. The isotope ratios of the pure and ambient reference materials are measured by Isotope Ratio Mass Spectrometry (IRMS) to investigate potential fractionation on dilution and to provide traceability to existing isotope ratio scales [31].

Further PRMs are measured in house using Optical Isotope Ratio Spectroscopy (OIRS) to assign isotope ratios and ensure consistency between newly produced diluted PRMs and those measured by IRMS. Calibration protocols have been developed for OIRS to enable traceable calibration using PRMs with certified isotope ratios alongside uncertainty evaluations for the calibration procedures.

Multi component PRMs can be produced with certified isotope ratios for CO₂, CH₄ and N₂O. Additional components are added as required to address the sensitivities of the measurement techniques, for example, Kr and CO have been added to PRMs for measurements of the isotope ratio of CO₂ by IRMS and for measurements of the isotope ratio of N₂O by OIRS.

4.1 Large scale production of CH₄ isotope ratio PRMs.

A recent comparison study which formed part of the EMPIR 21GRD04 isoMET project required the production of over 30 calibration reference materials with a range of near ambient δ¹³C-CH₄ isotope ratios for a comparison of measurement compatibility at seven institutes. The institutes used a range of isotope ratio measurement instruments including IRMS and OIRS with and without preconcentration. Harmonised measurement protocols were developed [33]. Each

partner received a suite of calibration PRMs to ensure traceability to VPDB and VSMOW/SLAP. The calibration PRMs were gravimetrically produced from four isotopically characterised fossil CH₄ sources with near ambient δ¹³C. Where requested, ambient amount fraction CO₂ and N₂O were added as the presence of these gases may cause changes to the reported isotope ratio measurements for OIRS techniques. Higher amount fraction CH₄ in N₂ reference materials (500 - 600 μmol mol⁻¹) were produced for calibration of OIRS instruments which utilised preconcentration of ambient amount fraction samples. Ambient amount fraction PRMs were produced as travelling standards which were then measured at each institute. Results of the comparison are being prepared for publication [34]

4.2 Currently available Isotope ratio PRMs from NPL

Table 3 provides information on the standard traceable isotope ratio PRMs currently available from NPL for greenhouse gases.

Table 3. Traceable isotope ratio PRMs currently available from the NPL.

Component	Amount fraction range [μmol mol ⁻¹]	Typical amount fraction uncertainty (<i>k</i> =2) [%]	Matrix	Isotopic values available [‰]	Isotope ratio traceability
CO ₂	400 – 420, 800	0.2	Synthetic air	δ ¹³ C: +2, -42, -20, -9 δ ¹⁸ O: -8, -36, -22, -15	VPDB
CH ₄	1.8 – 2.5	0.2	Synthetic air	δ ¹³ C: -39 δ ² H: -195	VPDB, VSMOW/SLAP
N ₂ O	0.32 – 0.35	0.5	Synthetic air	δ ¹⁵ NSP: 1, -4, -0.7, 20 δ ¹⁵ N: 0.2, 53, 16, 33 δ ¹⁸ O: 39, 103, 55, 40	Air N ₂ , VSMOW/SLAP

Further amount fractions and isotope ratios may be available on request at gas_enquiries@npl.co.uk and online at <https://www.npl.co.uk/products-services/gas/climate-monitoring>. The webpage will be updated with new products and services as they become available. The isotope ratio values provided for N₂O and CH₄ reference materials are those of the pure gases used to prepare the PRMs. Validated isotope ratio of ambient amount fraction PRMs traceable to VPDB are available for CO₂ with typical uncertainties of 0.2 -0.5 ‰ (*k*=2).

5 Summary

Large volume PRMs with traceability to the SI for amount fraction and to existing scales for isotope ratio have been developed at NPL for use as calibration standards for greenhouse gas monitoring. The NPL-2023-CO₂ scale will enable the provision of amount fraction CO₂ PRMs with equations to link the amount fraction to the WMO-CO₂-X2019 scale. This will

improve accessibility to traceability and ensure redundancy, help to monitor long term drift in existing scales and ensure international traceability is not dependent on one institute.

Further developments aim to reduce uncertainties to achieve the network comparability goals set by the WMO-GAW for amount fraction and isotope ratio and extend the range of isotope ratios available to customers. This work lays the foundations for the establishment of an international metrology support infrastructure for enhancing data quality and comparability of the amount fraction and isotope ratio of greenhouse gas measurements and enable to identification of sources and sinks of GHG emissions.

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