CIPM MRA
Comparison reports

CCQM-P239

CO_2 isotope ratios in CO_2 in air mixtures

PILOT STUDY

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CCQM-P239, CO_2 isotope ratios in CO_2 in air mixtures
Final Report

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Abstract

The pilot study CCQM-P239 aimed at evaluating the level of compatibility of laboratories' measurement capabilities to value assign isotope ratios (expressed as isotope delta*) of CO_2 ($\delta^{13}C$ vs. VPDB and $\delta^{18}O$ vs. VPDB-CO_2) in carbon dioxide in air gas mixtures. Such capabilities have been in development at: National Metrology Institutes (NMIs) and expert laboratories that have been developing CO_2 (isotope ratio) in air cylinder standards for calibrating optical spectroscopic techniques; the atmospheric community laboratories measuring isotope ratios of CO_2 in air, traditionally by mass spectrometry techniques (linked to the standards of the WMO-GAW Central Calibration Laboratory or other systems); and NMIs and expert laboratories developing CO_2 in air amount fraction standards that need CO_2 isotope ratios values for accurate amount fraction measurements.

Fourteen laboratories participated, submitting CO_2-in-air standards spanning a wide range of amount fractions and isotopic compositions. The comparison was organized by the BIPM as a Model 2 comparison, where CO_2 in air mixtures that have been value assigned by participants were sent to the BIPM for comparison against the BIPM Isotope Ratio Mass Spectrometry (IRMS) reference method for CO_2 isotopes in carbon dioxide in air mixtures. The BIPM used a cryogenic extraction system coupled to the Dual-Inlet IRMS, calibrated with two reference materials of gaseous CO_2 to provide reference values traceable to the VPDB and VPDB−CO_2 scales.

Previous studies [1] have shown that several calibration strategies can be employed for calibrating analysers that measure CO_2 isotope ratios in air, leading to the production of sets of

* The vocabulary « isotope ratio » may still appear in this report in place of the recommended "isotope delta" for the same quantity (δ). It follows the title of the comparison, agreed by the participants in 2022.

standards that either differ in their CO_2 isotope ratios and/or their CO_2 amount fractions. For this reason, the protocol required participants to submit a minimum of two and maximum of four standards that are representative of the standards they regularly work with over the CO_2 in air amount fraction range of 300 µmol mol^{-1} to 800 µmol mol^{-1} and CO_2 isotope ratios with $\delta(^{13}C)$ values in the range +2 ‰ to −43 ‰ vs. VPDB.

The report includes a description of the standards sent by participants, a summary of the measurements they performed in their laboratory and of the measurements performed at the BIPM before presenting the results of the comparison. It is followed by a deeper analysis of the results, examining dependencies on amount fraction, isotope delta value, analytical technique, and traceability, to deduce a series of conclusions.

The comparison confirms good overall consistency among laboratories, particularly for $\delta(^{13}C)$, where roughly 80% of measurements agree with values within stated uncertainties. No systematic difference was identified between IRMS and IRIS techniques. $\delta(^{18}O)$ results show greater dispersion, largely due to the higher sensitivity of oxygen-isotope measurements to extraction conditions in CO_2 traps. Laboratories that provided isotopic values of their CO_2 parent gases demonstrated excellent agreement with BIPM measurements, confirming that extraction—not analysis—is often the dominant source of bias for $\delta(^{18}O)$. Laboratories equipped with reliable trapping systems showed markedly better internal consistency.

The group of laboratories traceable to the JRAS−06 scale forms the most coherent subset, achieving standard deviations of about 0.031‰ for $\delta(^{13}C)$ and 0.055‰ for $\delta(^{18}O)$. This underscores the value of a shared calibration scale, identical treatment of samples and standards, and harmonized procedures, as implemented by the monitoring network under the GAW program of the WMO. On average, JRAS-06-anchored laboratories report $\delta^{13}C$(VPDB) values that are 0.064‰ more positive than those using other reference anchors, while $\delta^{18}O$(VPDB-CO_2) remains consistent across groups.

The BIPM facility demonstrated the stability, control, and traceability required for use as a central facility in on-demand comparisons. Routine calibration against gaseous CO_2 standards value-assigned relative to IAEA-603 provides a direct, well-maintained link to the VPDB and VPDB-CO_2 scales. The facility is ready for deployment as the central measurement laboratory in the planned BIPM.QM-K4 Key Comparison. Remaining limitations stem mainly from the carbonate-to-CO_2 acid reaction used to transfer delta values from primary carbonates standards. A dedicated Pilot Study with laboratories of similar capability will assess these uncertainties and potential biases, opening the path to re-assigning BIPM's CO_2 standard hierarchy with reduced uncertainties.

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2 Purpose and scope

The pilot study CCQM-P239 was aimed at evaluating the level of compatibility of laboratories' measurement capabilities to value assign isotope ratios in gaseous mixtures CO_2 in dry air, expressed as isotope–delta relative to the relevant international standards: $\delta(^{13}C)$ on the VPDB scale and $\delta(^{18}O)$ on the VPDB-CO_2 scale.

The comparison was classified as a Pilot Study (Track D) comparison in the terminology of CCQM comparisons. The results of the comparison were expected to provide a description of the current level of performance of laboratories and the state of the art to be achieved, and traceability chains in operation, as well as information for planning a future Key Comparison.

The comparison CCQM-P239 was organized within the Gas Analysis Working Group (GAWG) in close collaboration with the Isotope Ratio Working Group (IRWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM).

3 Measurands, quantities and Units

The measurands were the carbon–13 isotope–delta on the VPDB scale and the oxygen–18 isotope-delta on the VPDB-CO_2 scale, obtained via the ratio of the ^{13}C isotope to the most abundant isotope ^{12}C (R^{13}), and the ratio of the ^{18}O isotope to the main isotope ^{16}O (R^{18}) in gaseous CO_2. The quantity isotope delta is the relative difference between a specified isotope ratio in the sample and the same isotope ratio in a reference. The identity of the reference is agreed by consensus [2]. The quantity isotope delta takes numerical values close to 10^{-3}, is normally multiplied by 1000 and expressed in permil (‰). The notation adopted in this report for both quantities is $\delta_{VPDB}(^{13}C)$ and $\delta_{VPDB\text{-}CO2}(^{18}O)$ following the recommendation of [3].

4 Participants

The comparison was organised by the BIPM. It included 14 participants listed in the table displayed below. Five of the participating laboratories were invited as "guest laboratories" by the coordinators of the comparison, in view of their recognised expertise for the measurements involved here and following CCQM rules.

Table 1: list of participants sorted by acronym of the laboratory (Lab), analytical technique used (Tech.), and contact person(s). Rows with a blue background indicate guest laboratories in the comparison.

Lab	Tech.	Contact person(s)
BGC-isoLab	IRMS	Heiko Moossen
CSIRO	IRMS	Ray Langenfelds, Zoe Loh, Colin Allison
ECCC	IRMS	Lin Huang, Alina Chivulescu
IAEA	IRMS	Federica Camin
INRiM	IRIS	Francesca Rolle, Stefano Pavarelli, Michela Sega
IJS	IRMS	Bor Kranjc, Nives Ogrinc
INSTAAR	IRMS	Sylvia Michel
KRISS	IRMS	Kiryong Hong, Han Jun Eun
NIST	IRIS	Kimberly Harris
NPL	IRIS	Aimee Hillier, Christoph Nehrbass-Ahles
PTB	IRIS	Javis Nwaboh, Victor Xavier Da Silva
RUG	IRIS	Pharahilda Steur, Harro Meijer
UME	IRMS	Adnan Şimşek, Tanil Tarhan
VNIIM	IRMS	Ian Chubchenko, Anna Kolobova

5 Measurement schedule

The comparison was organised by the BIPM following the schedule (updated after the comparison) displayed in Table 2.

Table 2: schedule of events in CCQM-P239 organisation

Date	Event
30 January 2024	Distribution of final protocol and registration of participants
30 August 2024	Deadline for participants to ship standards to the BIPM
04 Nov. 2024	Start of measurements at the BIPM
05 March 2025	Last arrival of cylinders at the BIPM
15 March 2025	Last measurements at the BIPM
15 June 2025	Deadline to collect cylinders back from BIPM
01 Sept. 2025	Deadline for participants to send final results
06 Oct. 2025	Draft A.1 report distributed to participants
20-21 Jan. 2026	Meeting with participants to discuss Draft A.1 report
31 March 2026	Draft B report distributed to CCQM/GAWG and IRWG

6 Participants standards

A total of 37 cylinders filled with air mixtures at pressures between 7 MPa and 15 MPa were sent to BIPM by the participants. The mixtures were to be prepared and/or analysed by participants using their usual procedures, within the constraints detailed below. Participants

were required to submit a minimum of two and maximum of four standards that are representative of the standards they regularly work with over the CO_2 in air amount fraction range of 300 µmol mol^{-1} to 800 µmol mol^{-1} and carbon–13 isotope–delta values in the range +2 ‰ to −43 ‰ vs. VPDB. Constraints were provided in the protocol on the air composition, which was requested to be either dried scrubbed air or synthetic air with a similar composition. Participants were also asked to ensure that nitrous oxide amount fractions in their standards were either at nominally ambient levels (between 335 nmol mol^{-1} and 400 nmol mol^{-1}) or below 10 nmol mol^{-1} levels.

6.1 Preparation techniques

There are mainly two profiles of participants in this comparison, with the guest laboratories, experts in atmospheric monitoring forming one group, and the National Metrology Institute (NMIs) and Designated Institutes (DIs) in the other group. The group of guest laboratories has developed specific procedures and guidelines for their calibration work, which recommend the usage of scrubbed dry air as much as possible. Consistently, they sent large volume cylinders, typically 30 L (except RUG with a 10 L cylinder) prepared either in house or by another laboratory within their network by scrubbing and drying pure air and adding pure CO_2 after that if the target amount fraction is higher than in the air. In the second group, NMIs have developed expertise in gravimetric preparation and sent smaller volume cylinders ≤ 10 L with which they can reach smaller uncertainties in the amount fractions of the constituents. Consequently, all NMIs prepared the cylinders in-house, blending pure nitrogen, oxygen, argon, and CO_2 with optionally N_2O to match ambient levels. Three participants got their mixtures from others: PTB purchased the mixtures from NPL, and JSI and IAEA collaborated with INRiM to obtain their transfer standards, which were prepared by INRiM together with the cylinders sent to the BIPM.

6.2 Mixtures composition

Following the explanation provided above, all mixtures are composed of either scrubbed or synthetic air. Characteristics of the mixtures are listed in Table 3, indicating the number of cylinders as well. All mixtures in scrubbed air contained N_2O at ambient levels, while only two participants which sent synthetic mixtures added N_2O: NIST in their four mixtures and KRISS in one mixture only. A large majority of mixtures included CO_2 at an amount fraction close to ambient air, as can be seen in Figure 1 (see also Table 8). All participants sent at least one mixture at this level. Not surprisingly, a large majority of participants also sent mixtures with an isotopic composition close to ambient air, as can be seen on Figure 2. All mixtures except one were assigned with $\delta(^{13}C)$ values in the requested range. One mixture sent by NIST was assigned with a value of −50.42 ‰, which is outside the calibration range of the BIPM analytical instrument.

However, the distribution of $\delta(^{13}C)$ values also reflects different choices which are not necessarily correlated with the expertise of the laboratory in terms of mixtures preparation. For example, two guest laboratories (BGC-isoLab and ECCC) sent mixtures with $\delta(^{13}C)$ values lower than −30 ‰, while two NMIs (KRISS and PTB) only sent mixtures closer to air, with values between −20 ‰ and −8 ‰. More details on the mixtures can be found in the laboratory reports annexed to this report.

Table 3: type of air in the mixtures sent by participants (scrubbed air or synthetic) with the number of cylinders provided per laboratory (*n*), and the indication of the presence of N_2O and cylinder volume.

Laboratory	Scrubbed air (*n*)	Synthetic air (*n*)	N_2O presence	Volume / L
CSIRO	2		yes	29.5
RUG	2		yes	10.0
BGC-iso	3		yes	50.0
ECCC	3		yes	29.5
INSTAAR	4		yes	29.5
IAEA		2	no	5.0
JSI		2	no	5.0
KRISS		2	1 with/1 without	10.0
PTB		2	no	10.0
UME		2	no	5.0
VNIIM		2	no	5.0
INRiM		3	no	5.0
NIST		4	yes	10.0
NPL		4	no	10.0
Total	**14**	**23**		

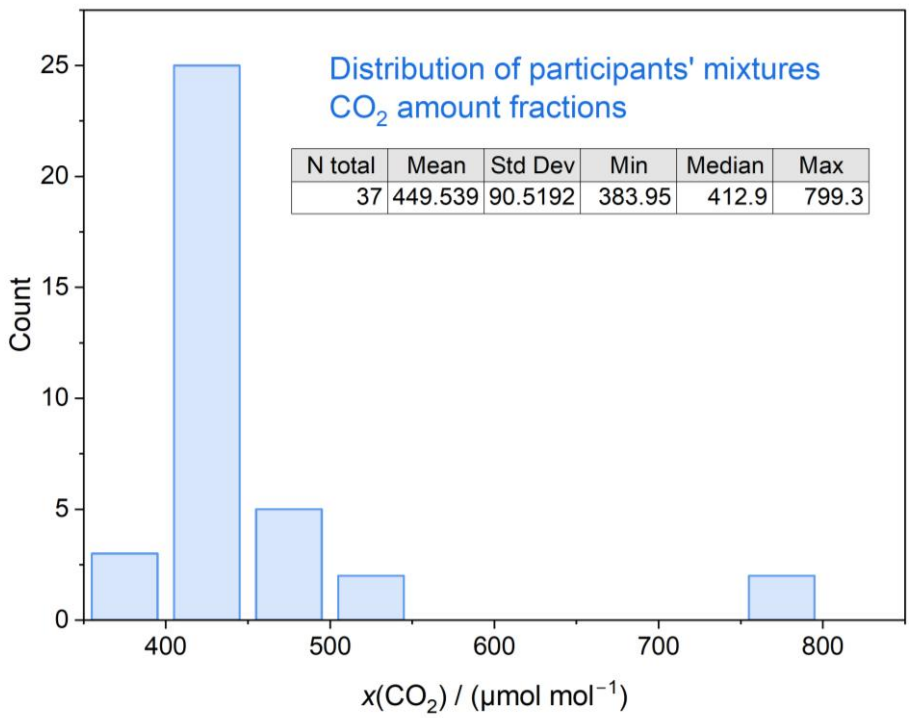


Figure 1: distribution of the participants' mixtures CO_2 amount fractions, on a total of 37 mixtures. The *y*-axis "count" is the number of mixtures .

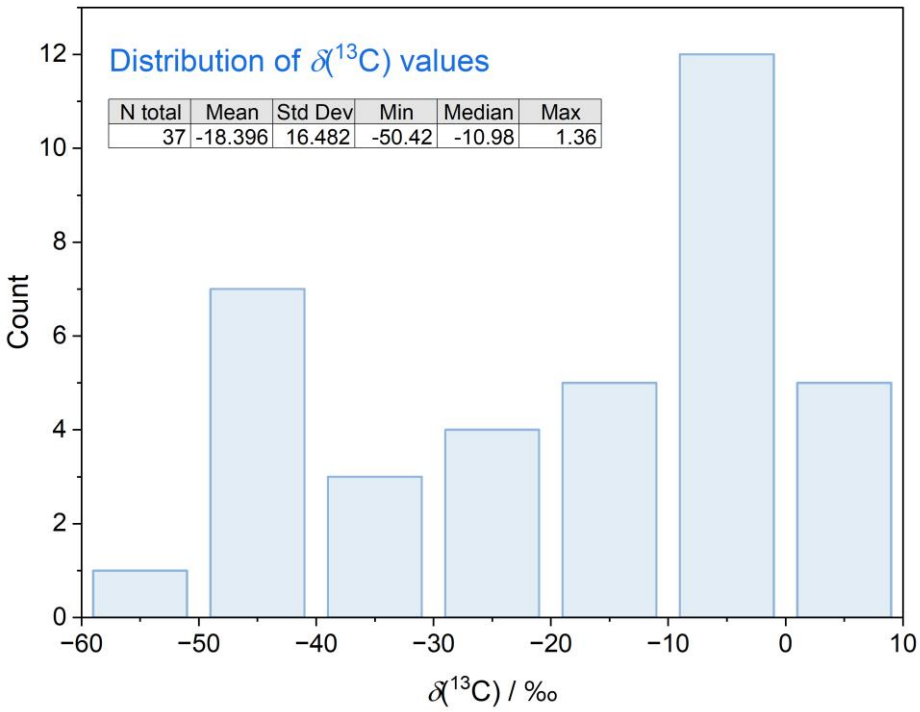


Figure 2: distribution of the ^{13}C isotope–delta values in the mixtures. The *y*-axis "count" is the number of mixtures .

7 Measurements performed by participants

7.1 Analytical techniques

According to the protocol, each participating laboratory was required to perform the measurements of the two measurands $\delta_{VPDB}(^{13}C)$ and $\delta_{VPDB\text{-}CO2}(^{18}O)$ in their mixtures with the analytical technique and method of their choice. Among the 14 participants, 9 used Isotope Ratio Mass Spectrometry (IRMS), and 5 used Isotope Ratio Infrared Spectroscopy (IRIS). The two acronyms are used in this report to group all techniques which rely on the same principle (mass spectrometry or light absorption spectroscopy), knowing that they are not fully identical and can vary in their application. The list of techniques is summarised in Table 4. More details on these techniques can be found in the participants' reports.

In the following section, the role of the analytical technique is considered more carefully, to make a distinction between instruments used to calibrate or to verify the values reported for the comparison.

7.2 Traceability of measurements

Participants were required to completely describe the calibration hierarchy they had employed in achieving their results, including descriptions of reference materials and methods, and any conventional numerical values and algorithms employed. This is a critical aspect of this comparison, as discussions are still going on about the traceability of CO_2 isotope deltas to the

same scale in the atmospheric monitoring community. A summary is provided in Table 4, where the following numbers are indicated:

- **Steps to VPDB or VPDB-CO_2**: number of calibration steps to the VPDB or VPDB-CO_2 scale, whatever the calibration process. Sample preparation steps (chemical reaction, gas mixing, cryogenic trapping) are not counted, even if they may impact the isotopic composition of the samples.
- **# Carb RMs**: number of carbonate reference materials included in the calibration chain. These numbers do not include materials which are used for validation (target values or other checks). It includes materials value assigned by the same laboratory or another one.
- **# Air RMs:** number of CO_2 in air mixture reference materials included in the calibration chain.
- **# Pure CO_2 RMs:** number of pure CO_2 gas reference materials included in the calibration chain.
- **Link with JRAS-06:** presence (yes) or absence (no) of a link with the JRAS−06 scale, maintained by BGC-IsoLab for measurements in ambient air and recommended for laboratories reporting isotope-delta values for the WMO/GAW program [4, 5]. In this comparison, several participants used BGC-isoLab services in their traceability. They are sorted in two groups according to the type of material value assigned by BGC-isoLab:
    - Air mixtures value assigned by BGC-isoLab with traceability reported to JRAS−06. Values reported on this scale are also considered traceable to VPDB, because BGC-isoLab calibrates its facility with reference air mixtures, previously calibrated with the NBS 19 reference material that defines the VPDB scale. More details on JRAS−06 are provided in section 11.4.
    - Pure CO_2 gas value assigned by BGC-isoLab and calibrated with CO_2 evolved from NBS 19 or IAEA-603 reference material. In that case the traceability to VPDB is more direct, meaning that fewer calibration steps are included.

From the table and reports of the participants, the following comments can be made:

- All participants having used DI-IRMS extracted CO_2 from the air mixtures with a liquid nitrogen trap, allowing direct comparison with their working reference gas (the gas injected in the second inlet of the instrument).
- Only one participant (UME) used GC-IRMS, in which case CO_2 in the mixtures was separated from the air matrix in a GC column and compared with the working reference gas.
- Five participants reacted carbonates reference materials with phosphoric acid in their laboratories to calibrate the DI-IRMS: ECCC, IAEA, JSI, UME and VNIIM. The carbonates reference materials are either NBS 19, IAEA-603, IAEA-610, IAEA-611 and IAEA-612 or a combination of them (see the reports for more details). It is understood that they all represent a strong link to the VPDB scale.
- All five participants having used IRIS sampled the air mixtures directly into the gas cell of the instrument. They typically calibrated the instrument response with a suite of different air mixtures, except PTB who used dynamic dilution of one CO_2 gas with CO_2−free air to obtain the calibration gases. However, one laboratory, NPL, used IRIS

to perform a validation of the values assigned on the CO_2 source gas, while others used IRIS to value assign the air mixtures sent for this comparison (INRiM, NIST, PTB, RUG).

- Four participants used air mixtures value assigned at BGC-isoLab to calibrate their DI-IRMS or IRIS: INRiM, INSTAAR, RUG, and CSIRO. Their values are clearly on JRAS-06 scale. BGC-isoLab can be added to this group, as the mixture sent for the comparison was also value assigned with the same method.
- Three participants sent synthetic air mixtures prepared in the same batch: three for INRiM (where the mixtures were prepared), two for IAEA and two for JSI. The same values can be expected for these seven mixtures.

Table 4: summary of the analytical techniques used by the participants, the number of calibration steps between their mixtures and the VPDB scale, the number of reference materials they used in their laboratory categorised by nature (carbonates, air, gaseous CO_2), and if their link to the VPDB scale includes the JRAS-06 system.

Participant	Technique	Steps to VPDB	# Carb RMs	# Air RMs	# Pure CO_2 RMs	Link with JRAS-06
BGC-IsoLab	DI-IRMS	2	1	1	0	Yes
BIPM (pilot)	DI-IRMS	2	0	0	2	No
ECCC	DI-IRMS	1	1	0	0	No
IAEA	DI-IRMS	1	1	0	0	No
INRiM	IRIS / CRDS	3	0	2	0	Yes
INSTAAR	DI-IRMS	2	0	3	0	Yes
JSI	DI-IRMS	2	0	0	1	No
KRISS	DI-IRMS	3	0	0	2	No
NIST	IRIS / TILDAS	2	0	0	3	No
NPL	IRIS / OA-ICOS	2	0	0	2	No
PTB	IRIS / TDLAS	2	0	0	2	No
RUG	IRIS / TILDAS	2	0	3	0	Yes
UME	GC-IRMS	1	1	0	0	No
VNIIM	DI-IRMS	1	4	0	0	No
CSIRO	DI-IRMS	2	0	1	0	Yes

Laboratories who prepare mixture by blending gases normally select the pure gases for their purity, but also for their isotopic composition when the target is to produce *isotopic reference materials*. Hence, they have some knowledge of the isotope delta values in the pure CO_2 gas before blending. This information appeared to be of great interest for the BIPM, who extracted that CO_2 from all mixtures to perform the analysis by IRMS. This additional information was shared by:

- NIST, with values traceable to VPDB via DI-IRMS measurements performed at NIST and calibrated with NIST gaseous CO_2 reference materials [6].
- KRISS, with values traceable to VPDB via DI-IRMS measurements performed at KRISS and calibrated with CO_2 reference gases value assigned by the BIPM.
- INRiM, with values traceable to VPDB via DI-IRMS measurements performed at BGC-IsoLab on flask samples of the same gas and calibrated with NBS 19 and IAEA-603 reference materials.

7.3 Values and uncertainties

Values and uncertainties as reported by the participants are displayed in Table 9 and Table 10 (section 15) Annex 2 – Tables. A graph showing the standard uncertainties sorted by participant is displayed below. The measurement uncertainty during the analysis at BIPM, without the scale uncertainty, is added for indication. The figure shows the quite large spread of uncertainty assigned by the participants, from a minimum of 0.004 ‰ (ECCC) to the maximum of 0.33 ‰ (NPL).

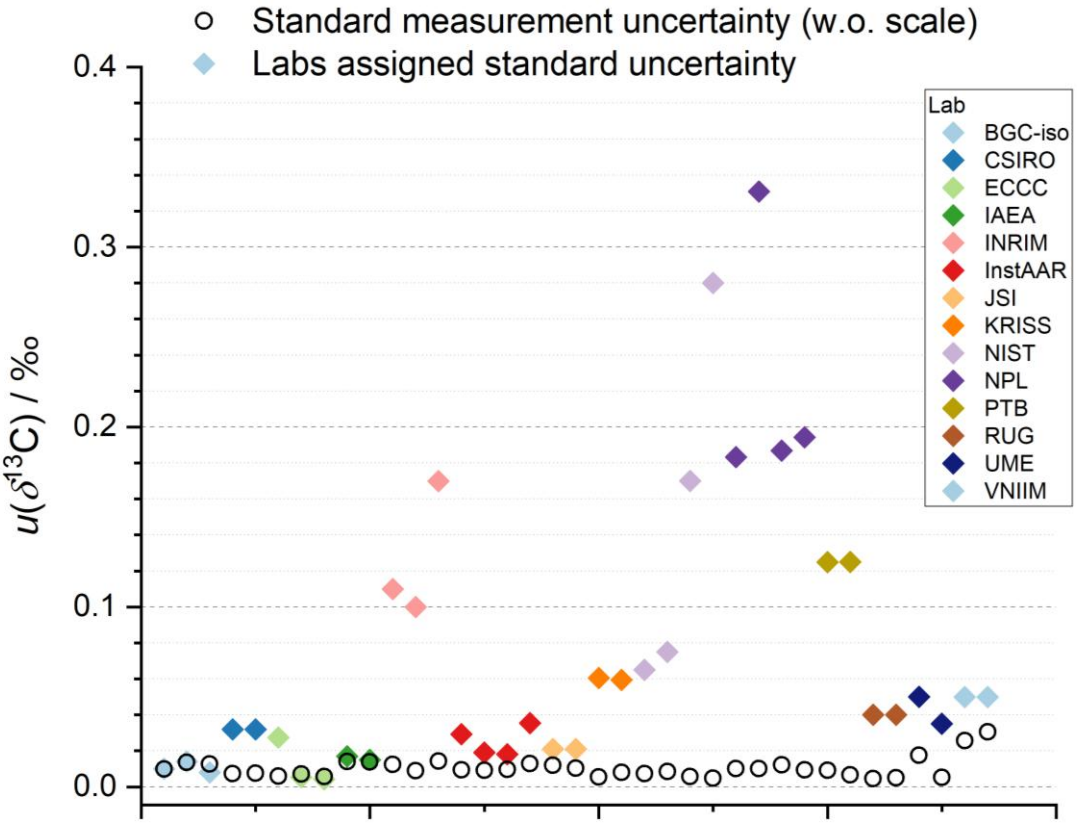


Figure 3: standard uncertainty $u(\delta(^{13}C))$ reported by the participants (coloured diamonds). The measurement uncertainty during the analysis at BIPM, without the scale uncertainty, is displayed with open circles for indication.

7.4 Verification of mixtures stability

Participants were given the opportunity to perform a second series of measurements on their mixtures after their return in their laboratory. Among the 14 participants, 7 could check the stability in their mixtures. Among them, 3 reported that the second set of values confirmed the first set, and 4 submitted modified values even if the second set was found in agreement with the first set. The approach is summarized in the table below. The submitted values considered as participants results in this report are those received after the stability verification when appropriate.

Table 5: list of participants having performed a second series of measurements and comments to indicate if the values changed or not.

Lab	2nd meas.	comments
BGC-iso	**yes**	O-18 drift in one mixture
CSIRO	**yes**	average on several years
ECCC	**yes**	average - O-18 drift in one mixture
IAEA	**yes**	different method - no drift observed
INRIM	**yes**	same values
INSTAAR	no	None
JSI	no	None
KRISS	no	None
NIST	no	None
NPL	**yes**	same values
PTB	no	None
RUG	**yes**	updated values but no drift
UME	no	None
VNIIM	**yes**	same values

8 BIPM comparison facility and reference materials

This comparison was a model 2 in the categories of the CCQM/GAWG because all participants sent their standards to a central facility at the BIPM. Measurements performed at the BIPM are also traceable to the VPDB scale for $\delta(^{13}C)$ and VPDB-CO_2 for $\delta(^{18}O)$, using the facility, reference materials, and method described below.

The comparison system at the BIPM was composed of a 16-port gas sampling system, to inject samples into a cryogenic facility with two air traps for the reproducible extraction of carbon dioxide (and nitrous oxide if present), its accumulation in a third trap followed by transfer into the dual inlet system of the IRMS. The sampling and cryogenic parts of the system were built on site and are controlled by a program developed in Labview. The DI-IRMS is a Thermo Scientific MAT253+, acquired in 2020 and used for all measurements reported in the report of the comparison CCQM-P204, with the same calibration method and reference materials [7]. Since the CCQM-P204 comparison, a method to correct for the presence of nitrous oxide in the gases extracted from air with the traps was also developed, including regular measurements of pure nitrous oxide gas injected in the DI-IRMS. Results of these measurements were used to estimate three parameters required for the correction: the relative ionisation efficiency between N_2O and CO_2, and the response of the instrument in terms of ratio between the signals detected at masses 45 and 46 against mass 44.

Prior to the comparison, the method was validated with six air mixtures produced by NPL, over the CO_2 amount fraction range of 380 µmol mol^{-1} to 800 µmol mol^{-1}, a $\delta(^{13}C)$ range of –43 ‰ to +1.5 ‰, and a $\delta(^{18}O)$ range of –35 ‰ to –7 ‰. The method demonstrated excellent results, with typical standard deviations of 0.005 ‰ and 0.05 ‰ for $\delta(^{13}C)$ and $\delta(^{18}O)$, respectively, comparable to the performance of the instrument on one mixture. The six mixtures contained the same N_2O amount fraction around ambient levels (335 nmol mol^{-1}), but different CO_2 amount fractions. The efficiency of the correction method was demonstrated by observing the good agreement between isotope-delta values obtained after correction compared to before correction, as expected for varying N_2O/CO_2 fractions.

BIPM establishes its metrological traceability to primary carbonate reference materials (IAEA-603) via a set of two calibrated gaseous CO_2 standards filled at the BIPM in early 2021 with gases originally provided by Air Liquide (AL CANISTER–5391), and SIAD (SIAD CANISTER–5386). A third canister (NMIJ CANISTER–5393) was filled with CO_2 gas provided by NMIJ (National Metrology Institute of Japan) and used as a target gas. These CO_2 standards are kept in 6L SilcoCans (referred to as canisters) with a filling pressure of 250 kPa and have been value assigned at the IAEA for the comparison CCQM–P204. The three canisters were constantly connected to the IRMS multiport and analysed during all measurement sequences reported here. The working reference gas injected in the right bellow of the IRMS was also a canister, filled from the same tank as AL CANISTER–5391. Its value was known but not used to calibrate the samples.

Quality controls of the measurements for this comparison also included systematic measurements, in all sequences, of two of the six air mixtures used during the validation, with the composition detailed below (averaged isotope-delta values provided):

Cylinder ID	$x(CO_2)$ / (µmol mol^{-1})	$x(N_2O)$ / (µmol mol^{-1})	$\delta_{VPDB}(^{13}C)$ / ‰	$\delta_{VPDB\text{-}CO2}(^{18}O)$ / ‰
D115537	798.40	0.336	1.22	–7.82
D193646	500.20	0.335	–42.13	–35.71

9 Measurements at the BIPM

The comparison was performed following the protocol sent to participants on 30 January 2024, with further details provided below.

9.1 Preparation of cylinders

On receipt by the BIPM, all cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders were then rolled for at least 1 hour to ensure homogeneity of the mixture.

Each cylinder was equipped with a pressure reducer and connected to one inlet of a 16-inlet automatic gas sampler connected to the IRMS analyser. The pressure reducer of each cylinder was flushed nine times with the mixture. The cylinder valve was then closed leaving the high-pressure side of the pressure reducer at the cylinder pressure and the low-pressure side of the pressure reducer at ~300 kPa. The cylinders were left to stand for at least 24 hours, to allow conditioning of the pressure reducers.

9.2 Trapping of CO_2 in the air mixtures

The BIPM Air Trapping system (BAT) samples about 8 L (at STP) of gas for one extraction/analysis of an air mixture with a CO_2 amount fraction of approximately 400 µmol mol^{-1}, and proportionally less for larger amount fractions. The appropriate volume of air was sampled by adjusting the sampling time, to produce the 80 µmol of CO_2 required for analysis by IRMS, observed via the pressure in the left bellow of the instrument.

The first extraction of gas was used for conditioning of the measurement system and did not contribute to the measurement results. Then three further extractions of CO_2 (and N_2O if present) were performed with three successive measurements of each sample on the IRMS.

Temperatures of the two first traps of the BAT were designed like the traps in the PVT–CO_2 system of the BIPM [1]. Their temperature was PID-controlled by adjusting the heating element and liquid nitrogen flow and set to values allowing first trapping of water only (evacuated at a later stage), then trapping of CO_2 (and N_2O) and evacuation of other gases, and eventually transfer of CO_2 in the third trap located close the IRMS inlet.

9.3 Series of IRMS analysis

The 37 standard mixtures submitted by the participants were analysed in ten batches of four, to match the typical measurement sequence followed at the BIPM. Each batch included the analysis of two air mixtures used as targets (cylinders D115537 and D193646), the analysis of two pure CO_2 calibration standards (AL CANISTER-R5391 twice and SIAD CANISTER-5386 once) and the pure CO_2 target gas (NMIJ CANISTER-R5393) (all described in section 8). AL CANISTER-R5391 was sampled twice to control the sequence stability, and to detect potential issues during the refill of the IRMS bellow containing the working gas (performed during analysis number 6). The result of the second analysis was used as calibration value for this standard. One typical sequence was setup as follow:

Analysis 1	2	3	4	5	6	7	8	9	10
AL CANISTER-R5391	SAMPLE 1	CONTROL D115537	SAMPLE 2	CONTROL D193646	AL CANISTER-R5391	SAMPLE 3	SAMPLE 4	NMIJ CANISTER-R5393	SIAD CANISTER -R5386

This sequence takes 16 to 20 hours and was repeated 2 more times during the same week. Typically, one week was devoted to the analysis of 4 samples, to allow some time for new cylinders connections and time for maintenance of the IRMS. The analysis of all samples in the comparison was performed between 4 November 2024 and 15 March 2025, as displayed in Table 11 (Annex 2). Samples from the same participants were analysed in the same sequence, adding BIPM samples to create a group of 4 when needed. The same sequence was repeated during another week if the first measurement results were judged non satisfactory and led to technical intervention, either on the BAT or the IRMS. In that case, only the second week of measurements were kept as final results. Two series of analysis of UME and VNIIM samples were recorded in November 2024, and repeated a third time early 2025 after having obtained further reduction of the noise of the IRMS. Only the last series of measurements was retained.

9.4 Calculation of assigned values and standard uncertainty

Starting from the two ratios of intensities R^{45} and R^{46} acquired with the IRMS control software ISODAT for each analysis of the sequence, the software developed in house for the comparison CCQM-P204 was used to treat the data. It includes corrections for cross-contaminations between samples, correction for the isobaric interferences between isotopologues of CO_2 having the same molecular mass (^{17}O correction), calibration on the VPDB scale using the two reference materials AL CANISTER-5391 and SIAD CANISTER-5386, and averaging of values acquired for the same sample. The correction for the interferences between isotopologues of CO_2 and N_2O was added to the software prior to this comparison, and introduced prior to the ^{17}O correction as recommended by Assonov [8]. It uses the equation introduced by Mook in 1983 [9], in its complete form, meaning with the dependency on $\delta(^{45}CO_2)$ and $\delta(^{46}CO_2)$. It involves the knowledge of the relative ionisation efficiency (RIE) between the two molecules, and the apparent isotope-delta values at masses 45 and 46 due to N_2O, $\delta(^{45}N_2O)$, and $\delta(^{46}N_2O)$. A standardised measurement routine (sequence in Isodat) had been designed for the long-term monitoring of RIE (including the pressure offset), $\delta(^{45}N_2O)$,

and $\delta(^{46}N_2O)$, with the injection of pure N_2O in the IRMS. Typical corrections and uncertainties are −0.245 ± 0.008 ‰ for $\delta(^{45}CO_2)_{corr}$ and −0.336 ± 0.009 ‰ for $\delta(^{46}CO_2)_{corr}$ for an air sample with 350 µmol mol^{-1} of CO_2 and 335 nmol mol^{-1} of N_2O. Note that the correction is smaller for higher CO_2 amount fractions at constant N_2O amount fractions as the ratio of the amount fractions becomes smaller.

The uncertainty of the values assigned by the BIPM was calculated to include only repeatability components and corrections due to the method. The full uncertainty budget of measurements traceable to the VPDB scale would include the uncertainty of the IAEA-603 reference material, which may already be accounted for in participants' uncertainties. More information is provided in Annex 3 – BIPM Uncertainty budget. To summarize, the uncertainty of the values assigned by the BIPM combines the standard deviation on three successive injections of the same sample, the average of the corresponding three values of the standard deviations on eight cycles of the dual inlet, and this value is averaged over the three days of measurements of the sample. A standard uncertainty associated with the cross-contamination estimation (typically 0.001 ‰) was also added, as well as the repeatability components of the measurements performed by IAEA on the two calibration standards, with values of 0.006 ‰ and 0.005 ‰ for $\delta(^{13}C)$, and 0.007 ‰ and 0.005 ‰ for $\delta(^{18}O)$. The standard uncertainty of the N_2O correction was considered constant (if N_2O was present) and equal to 0.008 ‰. Combining all sources resulted in uncertainty values between 0.012 ‰ and 0.015 ‰ for $\delta(^{13}C)$ and between 0.015 ‰ and 0.08 ‰ for $\delta(^{18}O)$.

9.5 Measurement results

The results of the comparison are the differences from the reference values sorted by laboratory, and they are formally presented in the next section. Another section presents the results with different approaches to highlight the impact of the parameters. This section includes control charts to show the stability of the system during the measurements, i.e. all measurement results for the two control mixtures D115537 and D193646. The first plot shows an average value of $\delta_{VPDB}(^{13}C)$ = +1.217 ‰ with no trend, while the second plot shows an average value of $\delta_{VPDB}(^{13}C)$ = –42.130 ‰ and could be fitted with a decreasing line with time, with a total loss of 0.01 ‰ during the 4.5 months of the comparison. This trend was observed on this mixture only, while no trend was found on the canister filled with CO_2 gas at a similar isotopic composition, SIAD CANISER-5386. Therefore, the trend was considered a property of the standard and not the measurement system, and no correction was applied to the assigned values.

Figure 4 also shows one series of three measurements on the control mixtures D115537 which could appear as outlier, recorded on 13 November 2024. While the second control mixture did not show a similar behaviour, the measurements of that week were discarded due to other observations, notably an increased noise in the instrument.

Figure 5 and Figure 7 show similar behaviour for $\delta(^{18}O)$ measurements on the two control mixtures. However, the values for $\delta(^{13}C)$ were close to the mean and none of the other quality control values were outside the expected boundaries. It was decided to keep the series of measurements of that week, corresponding to the analysis of ECCC samples.

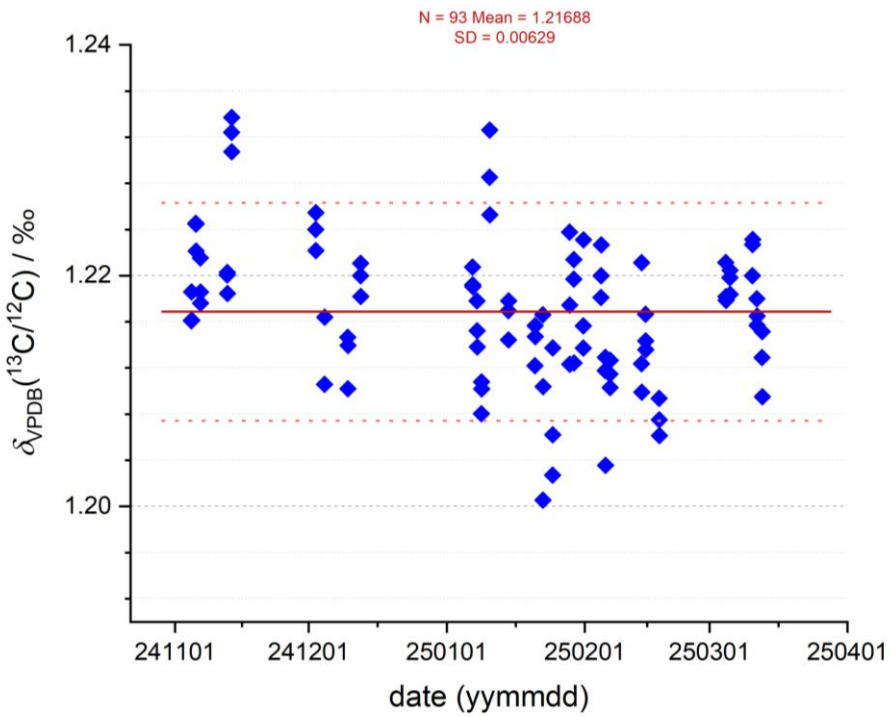


Figure 4: control chart showing all $\delta(^{13}C)$ values (n = 93) for cylinder D115537 (average $\delta(^{13}C)$ = +1.217 ‰).

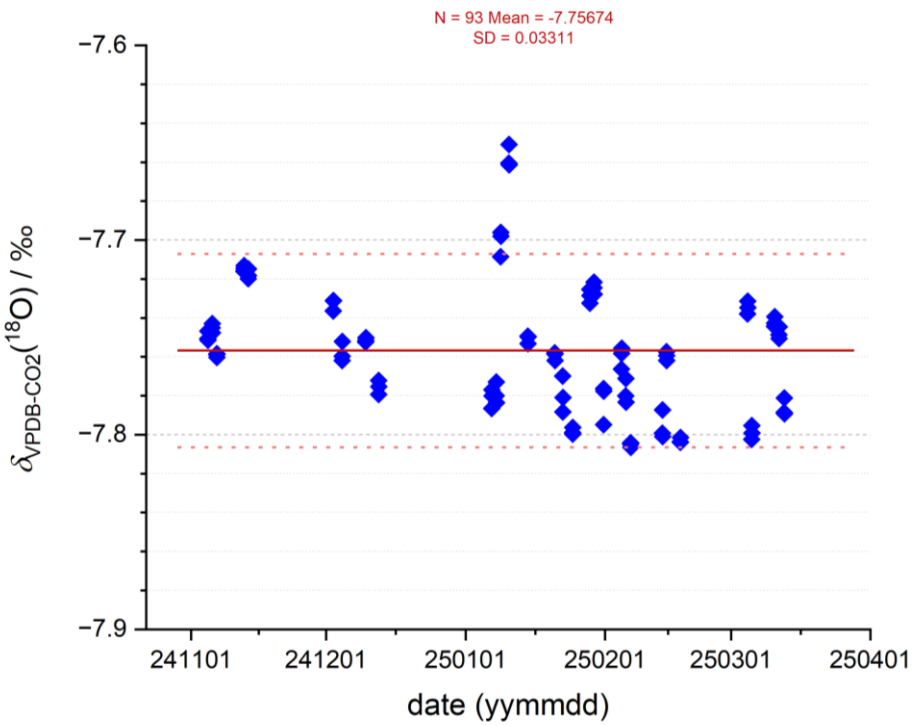


Figure 5: control chart showing all $\delta(^{18}O)$ values (n = 93) for cylinder D115537 (average $\delta(^{18}O)$ = −7.757 ‰).

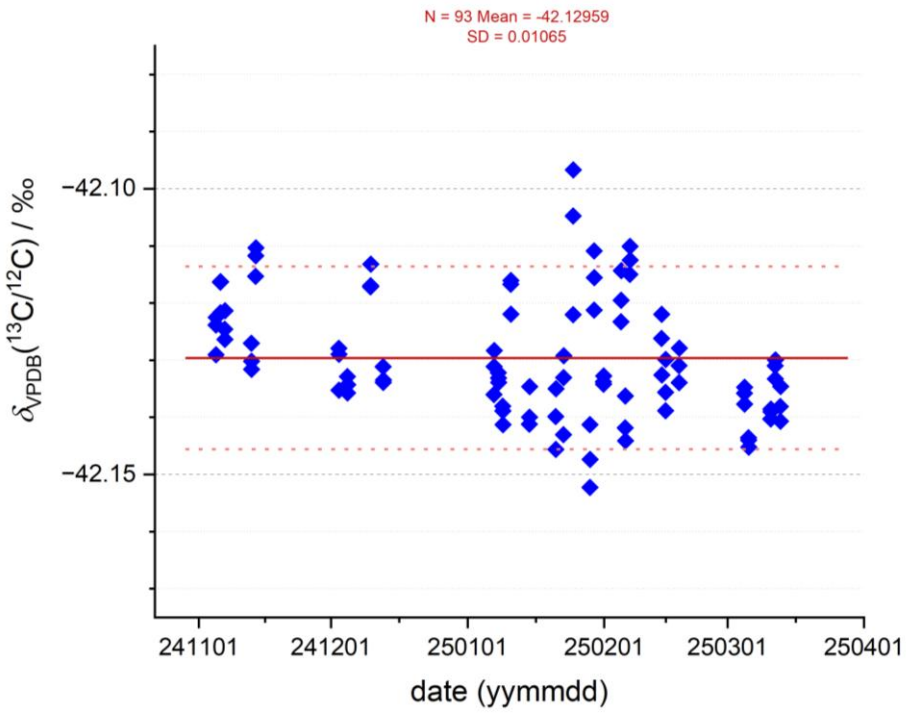


Figure 6: control chart showing all $\delta(^{13}C)$ values for cylinder D193646 (average $\delta(^{13}C)$ = −42.130 ‰).

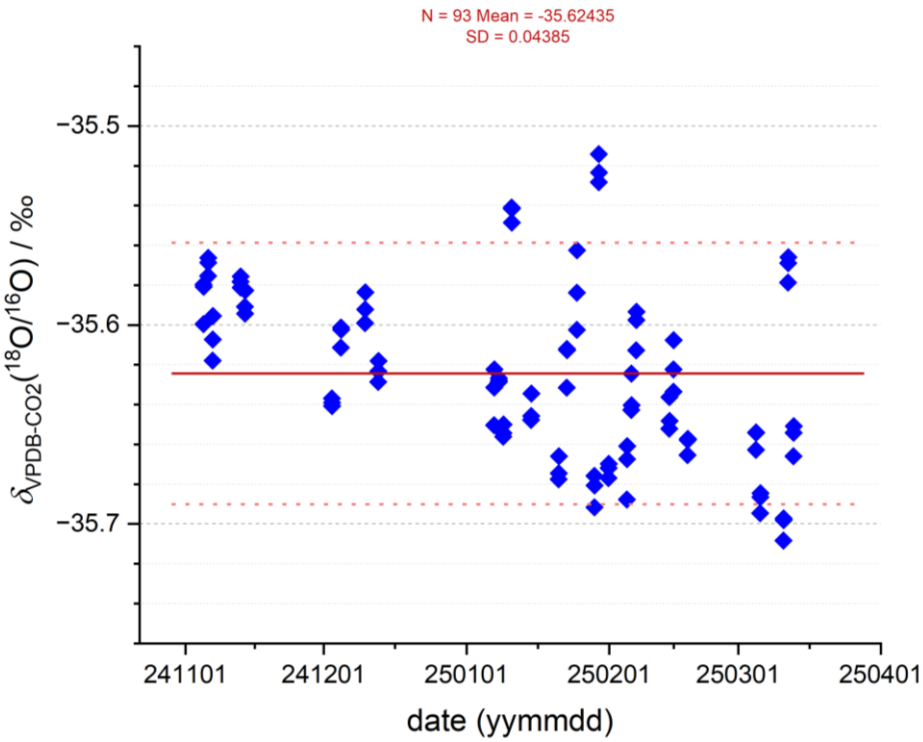


Figure 7: control chart showing all $\delta(^{18}O)$ values for cylinder D193646 (average $\delta(^{18}O)$ = −35.624 ‰).

10 Results of the comparison

Results of the comparison are presented here in two summary graphs showing the difference (Δ) between the values reported by the participants and those measured by the BIPM, for $\delta(^{13}C)$ on the VPDB scale, and $\delta(^{18}O)$ on the VPDB-CO_2 scale. Participants are indicated with different colours of the points and sorted alphabetically. The cylinder references are included as well on the *x*-axis. Two participants, INRiM and UME, did not report values for the oxygen−18 isotope, in which case the corresponding point does not appear.

10.1 Carbon−13 isotope

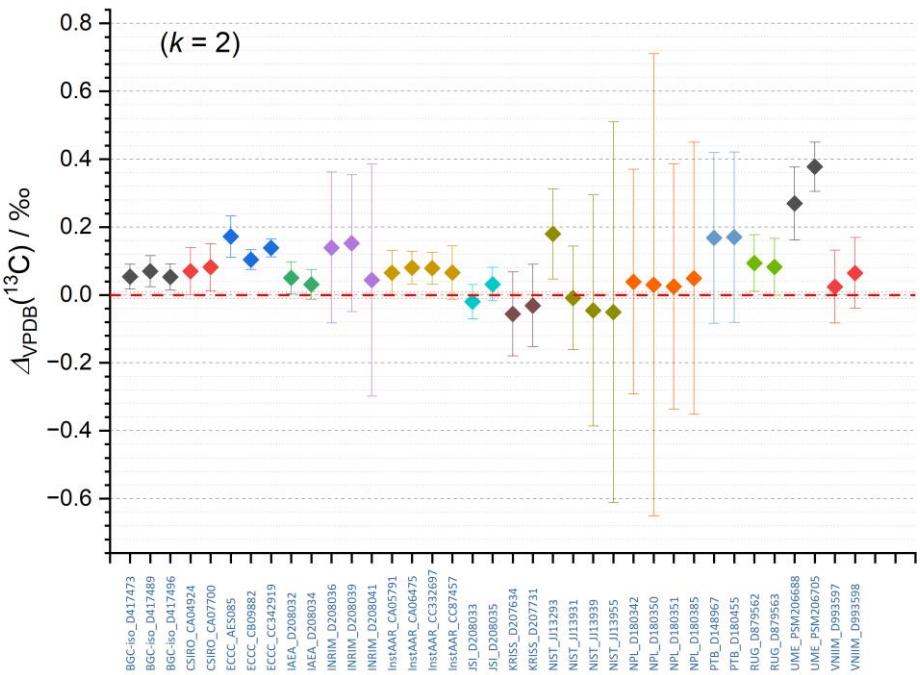


Figure 8: differences between $\delta(^{13}C)$ values reported by participants and values assigned by the BIPM, on the VPDB scale. Error bars are the reported uncertainties at 95% confidence level (k = 2).

10.2 Oxygen–18 isotope

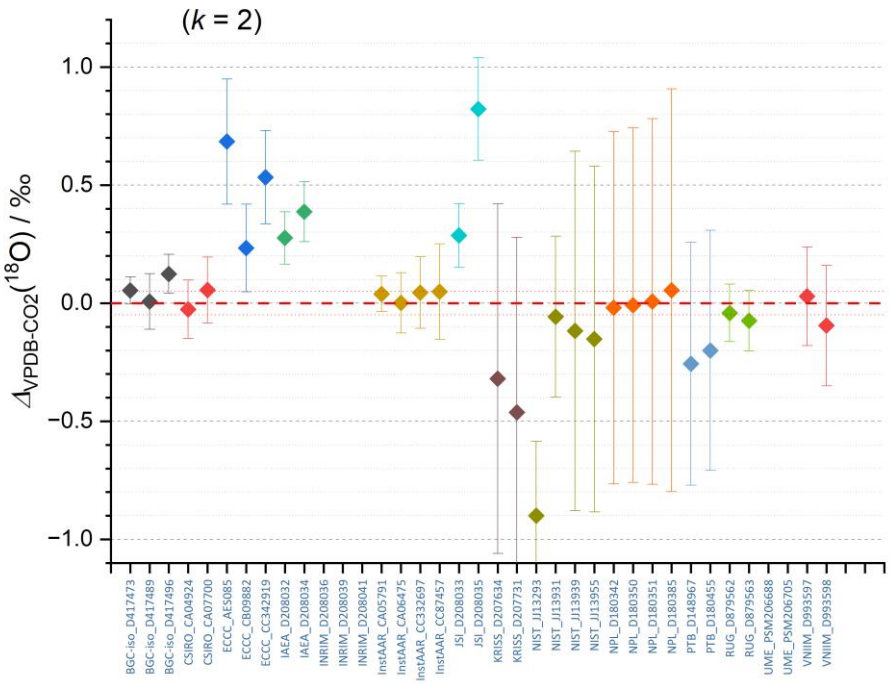


Figure 9: differences between $\delta(^{18}O)$ values reported by participants and values assigned by the BIPM, on the VPDB–CO_2 scale. Error bars are the reported uncertainties at 95% confidence level (k = 2).

11 Analysis of results

11.1 CO_2 amount fraction dependency

While the amount fraction of CO_2 in the mixture is not expected to impact the measurements results, there are some possible issues to consider, and the absence of dependency needs to be demonstrated.

Measurements performed by IRMS require extraction of CO_2 from air before injection in the analyser, which means that potentially the amount of CO_2 extracted can depend on the amount fraction in air. Dual inlet IRMS is sensitive to the gas amount, measured via the pressure in its variable bellows. Instruments typically include an automated process to balance the pressure in the two bellows of the Dual Inlets system, which works better if the sample pressure stays within a limited range. Therefore, the BAT system at the BIPM was conceived to trap CO_2 in air samples during a variable time, calculated before sampling, to obtain the same pressure independent of the amount fraction.

Measurements performed by IRIS are typically performed directly on the air mixtures, but non linearities in some instruments were reported to create a non-negligible dependency of the isotope delta with the amount fraction. This effect was first reported on CO_2 by Wen *et al*. [10], leading to a different calibration strategy being proposed to circumvent it, based on the amount fractions of all isotopologues detected by IRIS [11]. There are participants in this comparison who used the first method (NIST), and others who used the second method (RUG, NPL, PTB).

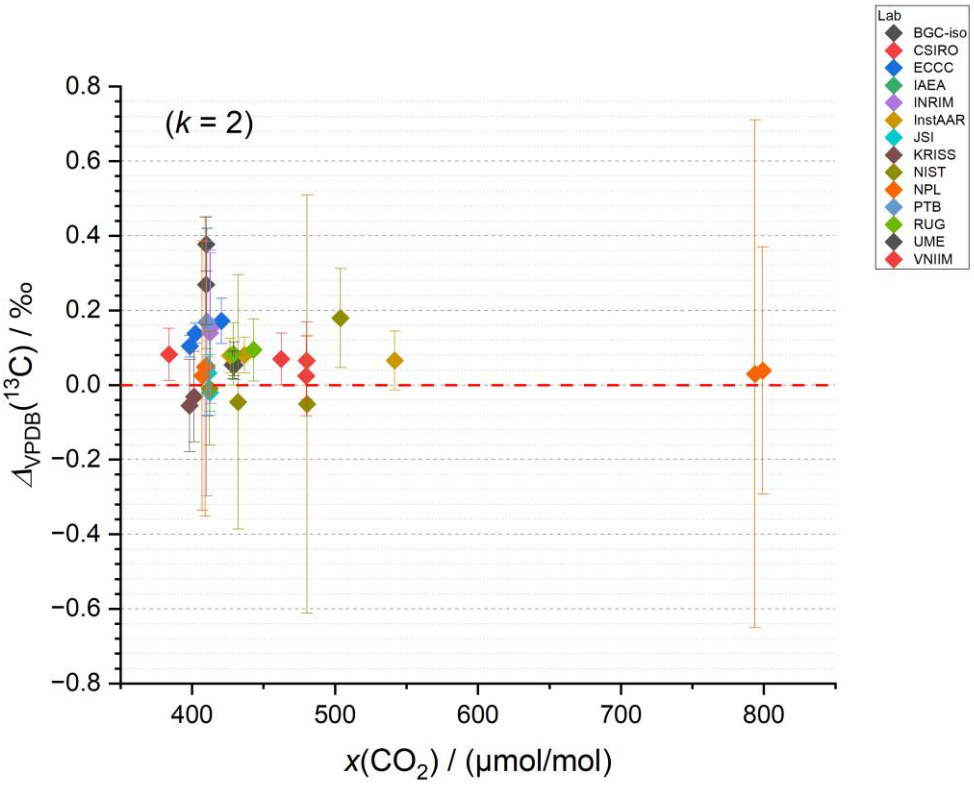


Figure 10: same as Figure 8 with results ordered by CO_2 amount fraction.

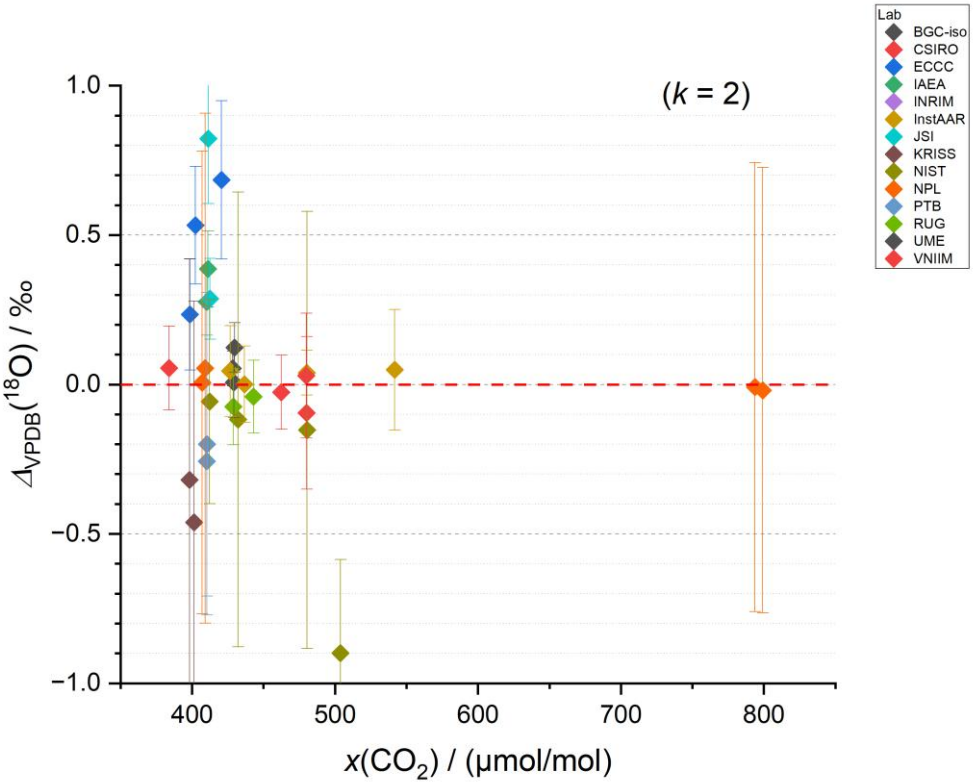


Figure 11: same as Figure 9 with results ordered by CO_2 amount fraction.

For the above reasons, the same results (difference between participants and the BIPM) are presented in this section against the CO_2 amount fraction in the mixtures. The two following figures show the results for carbon−13 and oxygen−18 isotopes independently. They show no general trend, which would have been attributed to biases in measurements performed at the BIPM. Likewise, no specific behaviour can be observed when looking at participants individually. Therefore, the conclusion is an absence of dependency of the results on the CO_2 amount fraction, at least within the range of values observed in the mixtures.

11.2 Isotope delta dependency

It is also of interest to observe the impact of the isotope delta value itself on the agreements between participants, as it can highlight biases in the measurement methods. By definition, the VPDB scale was constructed with one anchor point [2]. To achieve reliable measurements on the VPDB scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VPDB to minimize common sources of instrument measurement bias [3]. Deviations from this recommendation can lead to increasing biases when measuring away from the zero of the scale. defining material, which is NBS 19 ($\delta_{VPDB}(^{13}C) = +1.95‰$) for VPDB. This principle also applies to the VPDB−CO_2 scale for $\delta(^{18}O)$ values.

One specific effect which can lead to linear biases is the negligence of cross-contaminations in DI-IRMS instruments, due to the possibility of a fraction of gas from the sample bellows contributing to the gas from the reference bellows (and vice versa). The effect increases with the distance between the isotope delta values of the sample and the reference and is instrument dependent. Several methods have been proposed to estimate correction factors to be applied during the post-treatment of data recorded by IRMS control software, since the first publication on this effect [12], as summarised for example in the *Good Practice Guide for IRMS* edited by the FIRMS network [13]. These effects are often called “scale contraction effects” as the measured relative distances in isotope delta values appears smaller than the true distance.

For the above reasons, the same results (difference between participants and the BIPM) are presented in this section against the isotope delta value in the mixtures. Figure 11 and Figure 12 show the results for carbon−13 and oxygen−18 isotopes independently. They show no general trend, which would have been attributed to biases in measurements performed at the BIPM. Likewise, no specific behaviour can be observed when looking at participants individually, except for ECCC. The three points for ECCC show a linear decrease in the difference from BIPM results when $\delta_{VPDB}(^{13}C)$ increases, with a better agreement closer to the zero of the scale. The same observation can be made for ^{18}O isotope delta values. It should be highlighted that many participants sent mixtures with a limited range of isotope delta values, around values observed in the atmosphere. This reflects their decision to prioritise atmospheric measurements, which require high precision but a narrower range

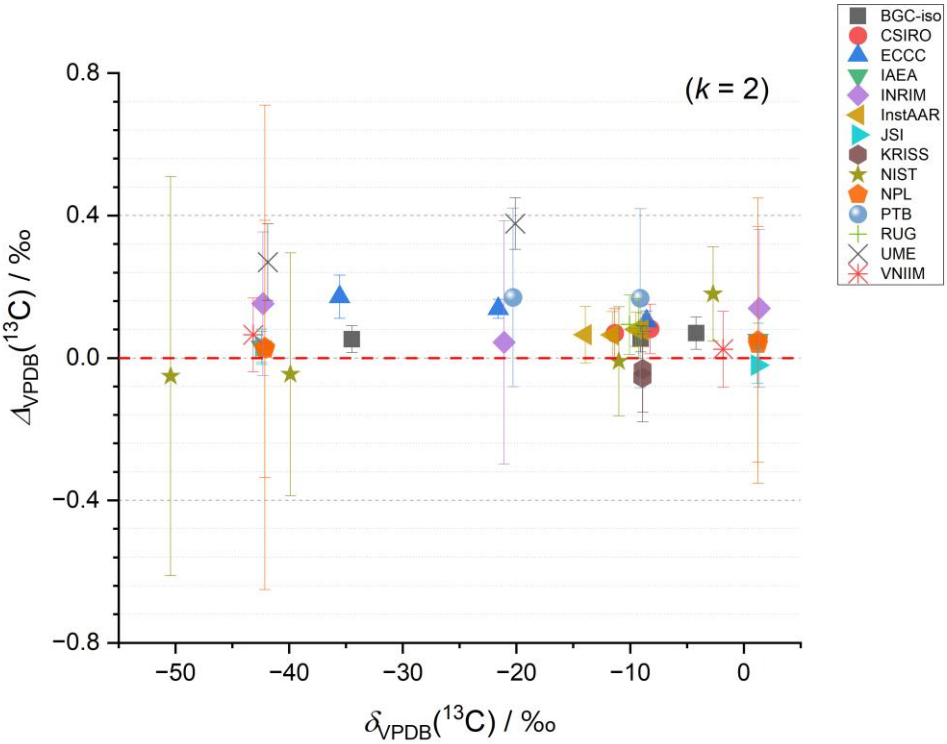


Figure 12: same as Figure 8 with results ordered by ^{13}C isotope delta, on VPDB scale.

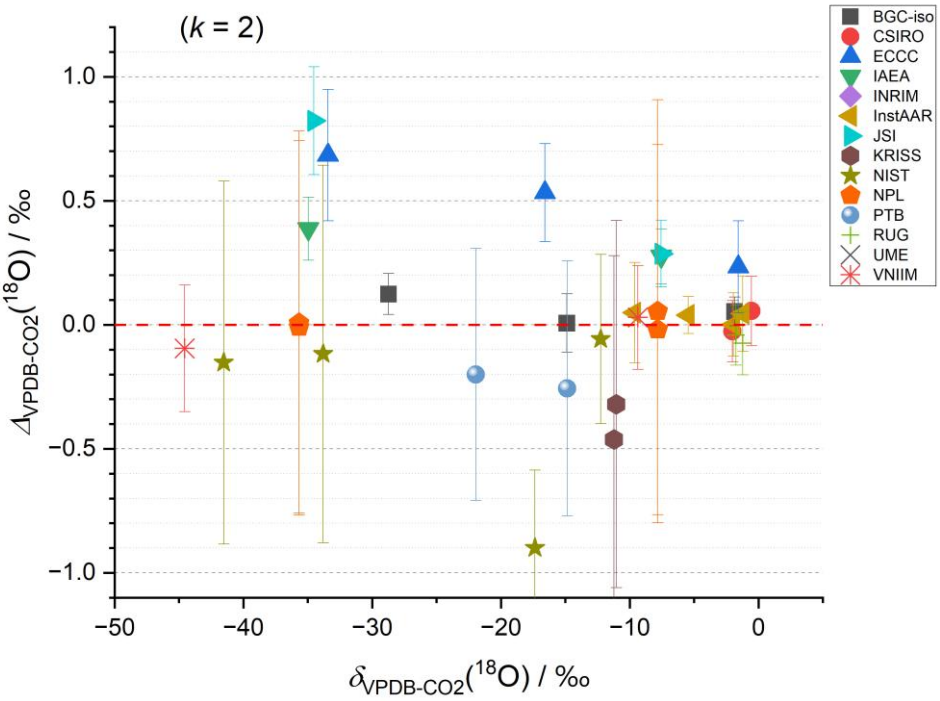


Figure 13: same as Figure 9 with results ordered by ^{18}O isotope delta, on VPDB−CO_2 scale. .

11.3 Analytical technique dependency

As detailed in section 7.1, participants used two major analytical techniques for their measurements: five used IRIS and ten used IRMS. The two following plots aim at observing differences between the two groups, keeping in mind that there are more variables than the technique itself, mainly due to differences in methods. Unlike the previous plots, the values of the difference between participants and the BIPM were sorted by order of magnitude, as it allows an easier observation of the difference between the two groups. Therefore, results for one participant can be separated from each other's and not grouped.

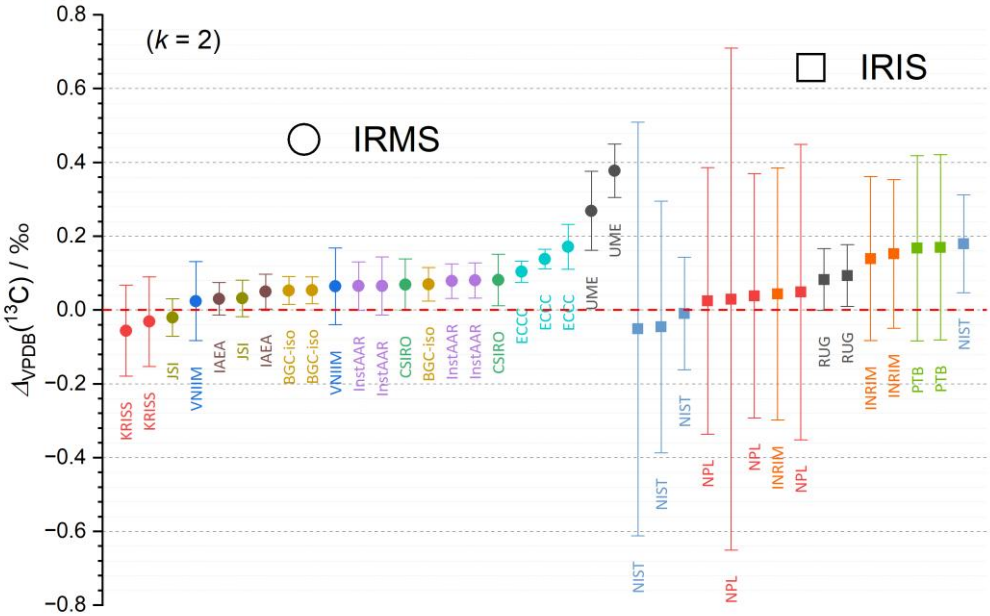


Figure 14: same as Figure 8 with results ordered by the magnitude of the difference $\Delta_{VPDB}(^{13}C)$ and separated in two groups according to the analytical technique of the participant.

From Figure 14 with results on ^{13}C analysis, several observations can be made:

- There is no significant difference between the two groups in terms of agreement with the reference BIPM value. The means of all results are very close: 0.08‰ for the IRMS group (n = 22) and 0.07‰ for the IRIS group (n = 15). This was expected, considering that the choice of reference materials and the calibration method are key to obtaining accurate results, more than the instrument.
- Participants who have used IRIS tend to estimate larger uncertainties than those who have used IRMS. This is consistent with reviews of techniques available in literature but could be challenged by a detailed analysis of the uncertainty budgets. DI-IRMS instruments associated with best practices can be very precise, with standard deviations of repeated delta values measurements lower than 0.01‰ for ^{13}C isotopes in air mixtures. However, they also require corrections (^{17}O interference, cross-contaminations, N_2O interferences) which come with uncertainties that are often neglected. Results of RUG show that IRIS instruments have the potential to compete with DI-IRMS for atmospheric observations when applied with state-of-the-art method and reference materials [14].

- Results of UME are statistically outliers within the IRMS group, and they are the only laboratory to have used GC-IRMS. However, it is not the technique itself that explains the observed bias, but rather the calibration scheme and the sample treatment steps. Indeed, UME used a GC to separate CO_2 from its air matrix in the mixture, to inject in the IRMS which is calibrated with CO_2 gas previously value assigned using an Elemental Analyser (EA-IRMS) calibrated with IAEA-603 reference materials. This calibration scheme differs from all others in the comparison. It involves two steps requiring careful manipulation (gas separation in the GC column and combustion of the carbonate reference material in the Elemental Analyser), meaning that the method is far from the recommendation of identical treatment of samples and references. The method also rely on only one carbonate reference material, when a minimum of two would be recommended.

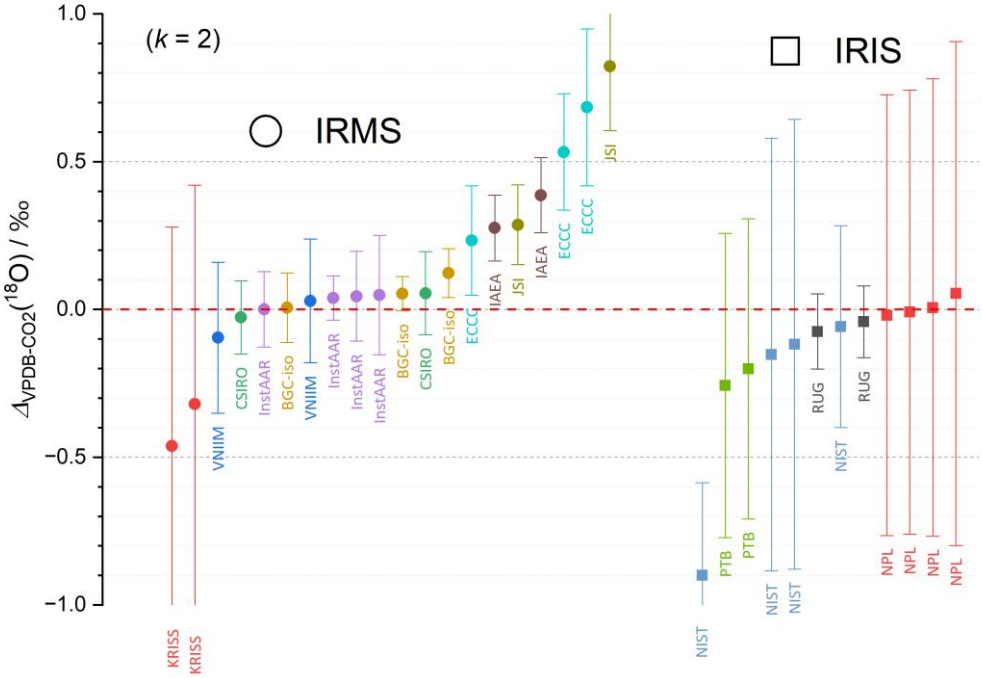


Figure 15: same as Figure 9 with results ordered by the magnitude of the difference $\Delta_{VPDB\text{-}CO2}(^{18}O)$ and separated in two groups according to the analytical technique of the participant.

From Figure 15 with results on ^{18}O analysis, different observations can be made:

- Unlike ^{13}C analysis, there seems to be a significant difference between the two groups in terms of agreement with the reference BIPM value. The means of all results are 0.12 ‰ for the IRMS group (n = 20) and −0.12 ‰ for the IRIS group (n = 12). But further screening of results is required as follows.
- The mean for the IRMS group is clearly influenced by some participants having measured values more than 0.2 ‰ greater than the BIPM: ECCC, JSI, and IAEA. The two former participants provided further explanation after the comparison was completed, pointing at issues in their CO_2 traps before their IRMS. Similar explanations were also provided by KRISS, who measured two values lower than the BIPM by more than 0.3 ‰. CO_2 traps for DI-IRMS analysis of air should indeed be designed with great care of the materials and the applied vacuum, to avoid residual gases being trapped with CO_2, as highlighted by BGC-IsoLab when they developed their BGC Air Trap [15]. No explanation could be found for

ECCC, and further investigations are under consideration. Without these four laboratories, the mean for the IRMS group reduces to 0.04 ‰ (n = 11), and the four participants and the BIPM agree within the uncertainties.

- In the IRIS group, one NIST result clearly appears as an outlier, and NIST could identify an error, reported orally after the comparison. Without this value, the mean of the IRIS group is −0.03 ‰ (n = 11), and the four participants and the BIPM agree within the uncertainties.
- As for ^{13}C analysis, participants who have used IRIS tend to estimate larger uncertainties than those who have used IRMS, except RUG. Given the similarity in agreement between the two groups, uncertainties with IRIS instruments may be overestimated.

11.4 Traceability and scales

A first analysis of the traceability of all participants shows more consistent approaches than in the comparison CCQM-P204, which focused on gaseous CO_2. Indeed, all participants of CCQM-P239 comparison could demonstrate traceability to VPDB for $\delta(^{13}C)$ and to VPDB−CO_2 for $\delta(^{18}O)$. However, the traceability chains differ in the number of calibration steps, and the analysis of participants reports described in section 7.2 highlighted important differences. One key aspect of the traceability of quantitative isotopic analysis of CO_2 in air is the existence of JRAS−06, recognised as a specific scale maintained by BGC-IsoLab [5].

The JRAS−06 scale was proposed by Ghosh et al. [16] as a scale for isotopic measurements of atmospheric CO_2, within the narrow isotopic range of atmospheric values. The need for the JRAS-06 scale arises from the principle of identical treatment: to be able to make high precision isotope measurements, sample and standard should be identical in nature and be treated identically. The JRAS−06 scale was realized by assigning values of air mixtures that contained CO_2 evolved from two in-house carbonates, MAR-J1 and OMC-J1 against mixtures that contained CO_2 evolved from NBS 19, i.e. NBS 19-CO_2. Thereby it is linked to the VPDB scale via fixed values. The JRAS−06 scale has been maintained by BGC-IsoLab through high pressure air cylinders that are traceable back to the high-pressure cylinder that was used in the original measurements done in 2005.

Measurements anchored to JRAS−06 can therefore be expressed on the VPDB and VPDB−CO_2 scales. However, the procedure of evolving CO_2 from carbonates and mixing it into CO_2 free air can cause offsets between the two scales [17]. Additionally, a zero uncertainty was attributed to JRAS−06 scale anchors. If a user wants to express isotopic values that have been measured on the JRAS−06 scale, on the VPDB scale, then the numerical values are identical, however, the measurement uncertainty should be increased, as described in [17].

This said, it appears of interest to analyse the results of this comparison with a distinction between the group of laboratories anchored to JRAS−06 and others, because this group also applies harmonised methods recommended by experts in Greenhouse Gases measurements techniques who meet regularly in GGMT meetings [18, 19, 5].

The results are displayed in Figure 16 for ^{13}C and Figure 17 for ^{18}O. The most striking observation is the efficiency in minimising interlaboratory variability of using a common scale and standard operating procedure, which is the case for BGC-isolab, INSTAAR, CSIRO, and RUG. These laboratories form a very consistent group, and all of them are in good agreement for both isotopes within their claimed uncertainty, despite low standard uncertainty values (0.01 ‰ to 0.04 ‰ for $\delta(^{13}C)$, and 0.013 ‰ to 0.07 ‰ for $\delta(^{18}O)$.

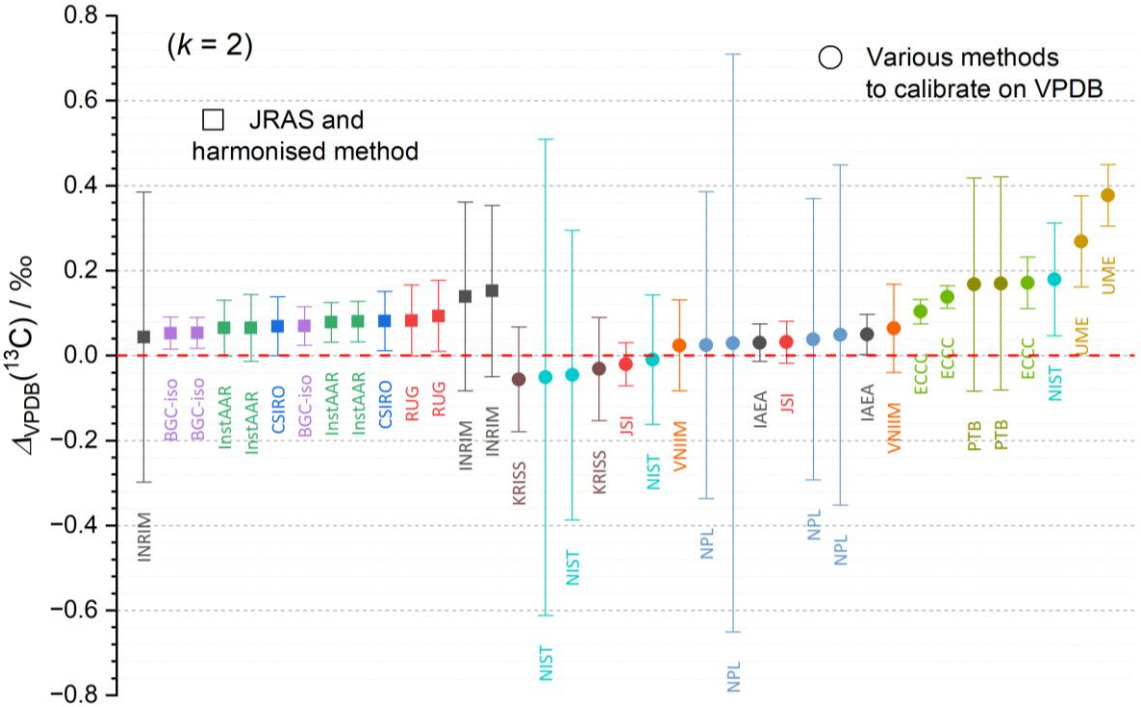


Figure 16: same as Figure 8 with results ordered by the magnitude of the difference $\Delta_{VPDB}(^{13}C)$ and separated in two groups according to the link with JRAS–06.

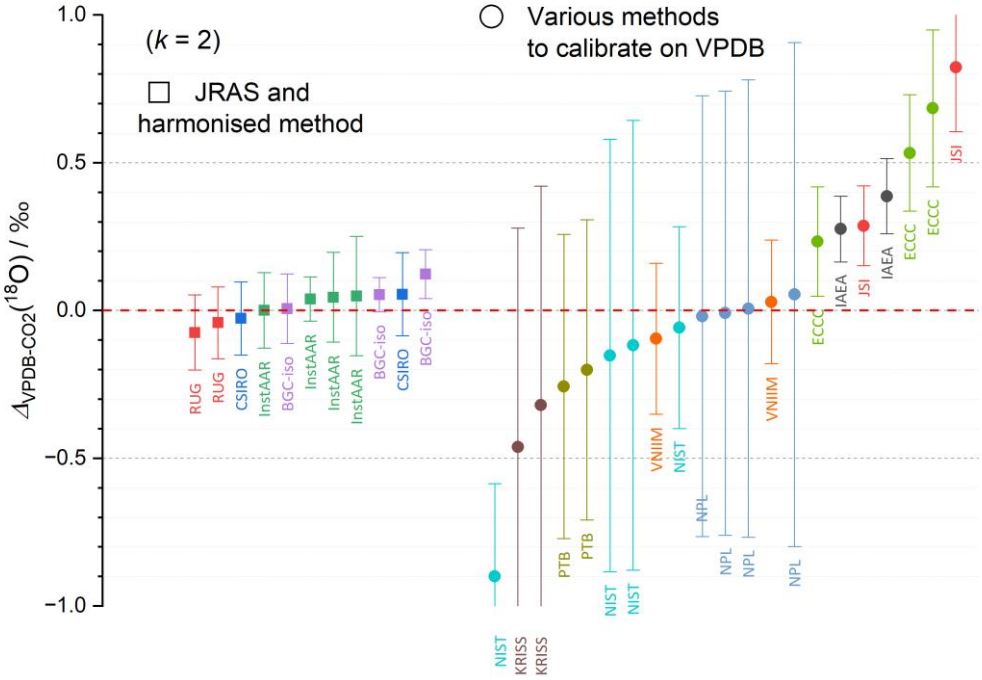


Figure 17: same as Figure 9 with results ordered by the magnitude of the difference $\Delta_{VPDB\text{-}CO2}(^{18}O)$) and separated in two groups according to the link with JRAS–06.

The second interesting observation is the weighted mean of the differences between the participants anchored to JRAS−06 and the BIPM, calculated with uncertainties as weights (See Table 6). The weighted means is equal to 0.066 ‰ (n = 14) for $\delta(^{13}C)$, and 0.001 ‰ (n = 11) for $\delta(^{18}O)$. By comparison, the weighted mean of the differences between other participants and the BIPM is 0.002 ‰ (n = 23) for $\delta(^{13}C)$, and −0.0002 ‰ (n = 21) for $\delta(^{18}O)$. Same results are obtained if the participants who reported issues with their CO_2 traps are rejected of the ^{18}O analysis.

The Birge ratio, or standard deviation calculated with uncertainties as weights, was also calculated for the two groups. It supports the good agreement of the JRAS−06 group within the claimed uncertainties, as it takes values below 2 for both $\delta(^{13}C)$ and $\delta(^{18}O)$. The Birge ratio for the second group is largely influenced by participants who used IRIS and estimated rather large uncertainties. The standard deviations without weights show more pronounced differences between the two groups. The observed standard deviations for the JRAS−06 group constitute a good achievement, considering the target compatibility goals of WMO for these measurements, equal to 0.01 ‰ for $\delta(^{13}C)$ and 0.05 ‰ for $\delta(^{18}O)$ [5].

Table 6: descriptive statistics on results of the comparison, highlighting a group of participants traceable to the JRAS−06 scale, considering the uncertainties as weight (weighted mean and Birge ratio) or not.

		n	Weighted Mean / ‰	Birge ratio / ‰	Mean / ‰	Standard deviation / ‰
$\Delta(^{13}C)$	JRAS−06	14	0.066	0.608	0.081	0.031
	Others	23	0.002	2.040	0.074	0.109
$\Delta(^{18}O)$	JRAS−06	11	0.001	1.965	0.021	0.055
	Others	21	−0.0002	2.050	0.035	0.391

These values demonstrate good agreement in general but raise the question of a better agreement with the JRAS−06 group when analysing oxygen isotopes compared to carbon isotopes. This could appear surprising at first glance, because anchoring oxygen isotope delta values on the VPDB−CO_2 scale is known to be problematic, as summarised in [2]. It was agreed more than three decades ago to define the VSMOW- SLAP scale as the primary oxygen isotope delta scale (CIAAW meeting in Lisbon, Portugal, 1993) and subsequently define the VPDB−CO2 scale in terms of the VSMOW- SLAP scale [20]. However, in this comparison, all measurements of oxygen isotopes are anchored to VPDB−CO_2 via analysis of pure CO_2 at some step. They could suffer from the variability attached to this method, but not from the biases with other methods based on equilibrium with water.

11.5 Comparison with the isotopic composition of the source CO_2

Several laboratories provided additional information on the isotopic composition of the CO_2 gas which was use as source gas to prepare the mixtures. Some laboratories have the capabilities to perform these measurements, some have this information from another laboratory, where the measurements were made. This additional information is of great interest, as it provides a tool to understand the source of biases observed on air mixtures measurements. Values are available in participants' reports attached as annexes to this report. In the two following figures, the difference was calculated between the ^{13}C and ^{18}O isotope delta values reported on the CO_2

source gases and the value measured at the BIPM, to allow direct comparison with the two figures of section 10 (results). A colour code and labels attached to the x-axis indicate the participating laboratory, and another set of labels attached to the values indicate the laboratory that value assigned the source gas. BGC appears on a total of 10 values, because they assigned values to the source gases for NPL, INRiM, JSI and IAEA mixtures. Three other laboratories provided the information on the source gas and performed the value assignment themselves: KRISS, NIST and VNIIM. All three used IRMS measurements on the pure CO_2, before it was diluted with air components to produce the mixtures.

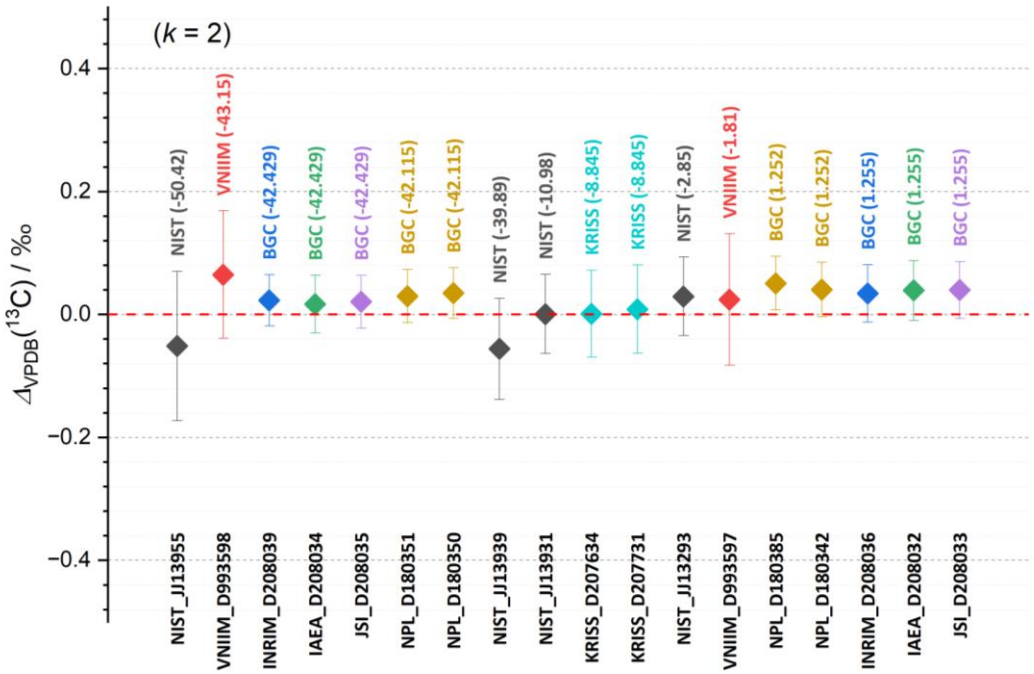


Figure 18: difference $\Delta_{VPDB}(^{13}C)$ between the isotope delta value assigned on the source CO_2 gas and the value measured by BIPM, sorted by measured value. The cylinders reference is indicated on the x-axis, and the name of the value assignment laboratory as label, with the assigned values in parenthesis (unit ‰). The diamonds are coloured according to the participating laboratory name.

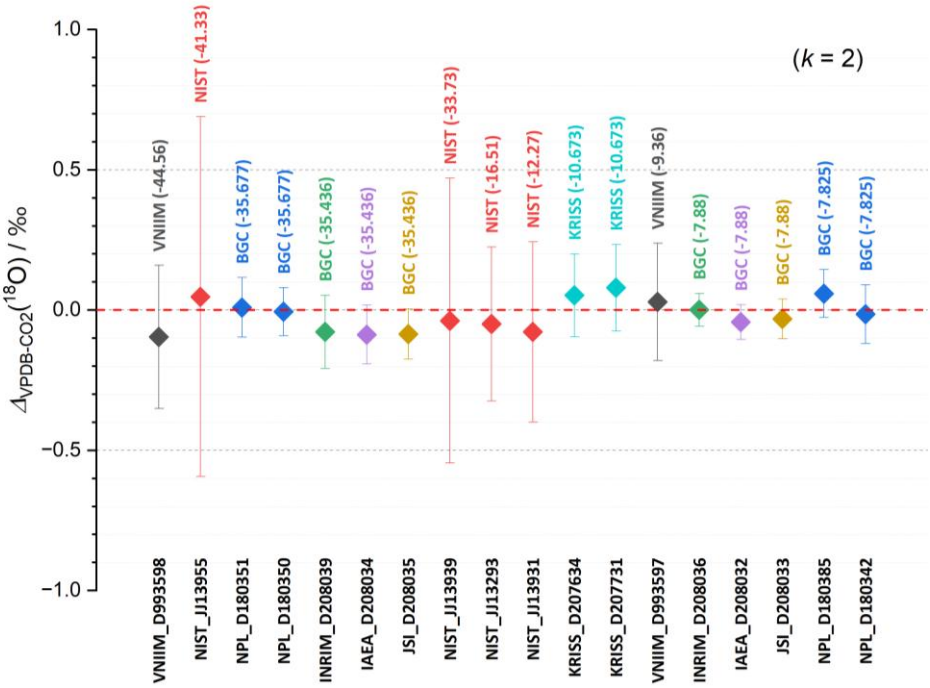


Figure 19: difference $\Delta_{VPDB\text{-}CO2}(^{18}O)$ between the isotope delta value assigned on the source CO_2 gas and the value measured by BIPM, sorted by measured value. The cylinders reference is indicated on the x-axis, and the name of the value assignment laboratory as label, with the assigned values in parenthesis (unit ‰).. The diamonds are coloured according to the participating laboratory name.

Table 7: descriptive statistics on the differences between the isotope delta value assigned on the source CO_2 gas and the value measured by BIPM, considering the uncertainties as weight (weighted mean and Birge ratio) or not.

	n	Weighted Mean / ‰	Birge ratio / ‰	Mean / ‰	Standard deviation / ‰
$\Delta(^{13}C)$	18	0.027	0.391	0.020	0.031
$\Delta(^{18}O)$	18	−0.018	0.436	−0.018	0.056

These data show a very good level of agreement and support the assumption that several participants encountered issues with their CO_2 traps, namely JSI, IAEA and KRISS. The agreement between VNIIM and BIPM is better than in the previous comparison CCQM−P204, with several reasons provided by VNIIM: improvements in the IRMS measurements, calibration with IAEA reference materials only where NBS 18 was used previously, and an efficient CO_2 extraction system designed after the publication of Werner *et al.* [15]. The agreement between NIST and BIPM has been maintained, as well as between BGC and BIPM. A deeper analysis of agreements between participants in CCQM-P204 and CCQM-P239 will be provided in a future publication.

12 Summary and conclusion

The CCQM-P239 pilot study evaluated the comparability of laboratories' capabilities to measure the carbon-13 and oxygen-18 isotope-delta values of CO_2 in air mixtures. Fourteen

laboratories—including National Metrology Institutes, Designated Institutes, and expert atmospheric laboratories—participated by preparing and submitting 37 cylinders of CO_2-in-air standards covering the range of 300–800 µmol mol^{-1} in CO_2 amount fraction, and a broad span of isotopic compositions. The mixtures were prepared either gravimetrically (mostly by NMIs) or by dilution of scrubbed natural air (mainly expert atmospheric laboratories).

All mixtures were analysed at the BIPM using a cryogenic CO_2 extraction system coupled to a dual-inlet IRMS, following a fully standardised measurement sequence including calibration with two BIPM CO_2 reference gases and embedded quality-control mixtures. Extensive validation and correction strategies were applied, notably for N_2O interference and isobaric effects, ensuring that all BIPM results remained traceable to the VPDB for $\delta(^{13}C)$ and VPDB–CO_2 for $\delta(^{18}O)$ scales. Measurements were performed over 4.5 months, during which stability of the analytical system was confirmed.

Participants measured their cylinders using their routine methods (mostly DI-IRMS or IRIS) and reported their assigned values with associated uncertainties and traceability chains. The study assessed comparability through differences between participant results and BIPM reference values, considering dependencies on amount fraction, isotopic composition, analytical technique, and traceability scheme. Additional information provided by several laboratories on the isotopic composition of the pure CO_2 source gases enabled a deeper analysis of consistency between measurements on parent-gas, highlighting the impact of CO_2 extraction systems.

The following conclusions can be stated, sorted by topic:

- Overall comparability across laboratories

For $\delta(^{13}C)$, 70% of participants have at least one result in agreement with BIPM values within reported expanded uncertainties ($k = 2$). For $\delta(^{18}O)$, the dispersion is larger, reflecting the higher sensitivity of oxygen-isotope measurements to extraction conditions, residual water, and trace gases.

- Influence of analytical technique (IRMS vs IRIS)

No global bias was observed between IRMS and IRIS for $\delta(^{13}C)$ when calibration was properly implemented. For $\delta(^{18}O)$, apparent differences disappear once results affected by trap issues are excluded. IRIS laboratories tend to report larger uncertainties, suggesting potential for optimisation in future work.

- Impact of CO_2 extraction systems

Some of the largest deviations in $\delta(^{18}O)$ originated from laboratories facing CO_2 extraction system issues. This was supported by laboratories that provided isotopic values of the CO_2 parent gas, which exhibited excellent agreement with BIPM's measurements. This finding highlights that the extraction step remains one of the dominant sources of bias for analysis of air mixtures, especially for $\delta(^{18}O)$. Laboratories with robust trapping systems demonstrated better consistency.

- Role of JRAS−06 traceability

Laboratories traceable to JRAS−06 form the most internally consistent group, with standard deviations of approximately 0.03 ‰ for $\delta(^{13}C)$ and 0.055 ‰ for $\delta(^{18}O)$. This demonstrates the effectiveness of a shared calibration scale and harmonised operating procedures, as implemented by the group of guest laboratories, which are all experts in atmospheric monitoring and reporting data for the same international programme GAW organised by the WMO.

- Relationship between JRAS−06 and VPDB

On average, with reported uncertainties considered as weights, the participants anchored to JRAS−06 appear to report $\delta_{VPDB}(^{13}C)$ values which are 0.064 ‰ more positive than the other participants, while $\delta_{VPDB\text{-}CO2}(^{18}O)$ values agree very well.

- Readiness of the BIPM Facility for use as a central facility in on-demand comparisons

The results of CCQM-P239 show that the BIPM reference methods and facility operates with the stability and measurement control needed for its use as a central facility in on-demand comparisons. Over the full measurement period, the cryogenic extraction system, dual-inlet IRMS, sampling manifold, and calibration scheme provided consistent measurements, as evidenced by the stability of the two control air mixtures measured throughout the campaign. The facility applies a uniform extraction and analysis sequence to all submitted mixtures, ensuring that values are obtained under consistent experimental conditions.

The system incorporates routine calibration with two gaseous CO_2 standards value-assigned relative to IAEA-603 at the IAEA in 2020, ensuring a direct link to the VPDB scale for $\delta(^{13}C)$ and VPDB–CO_2 scale for $\delta(^{18}O)$. Standard uncertainty of the measurements with this method is typically 0.017 ‰ for $\delta_{VPDB}(^{13}C)$, and 0.042 ‰ for $\delta_{VPDB\text{-}CO2}(^{18}O)$. The two calibration standards are part of an ensemble of six standards of the same kind, which constitute a hierarchy of standards (primaries, secondaries, tertiaries) with internal consistency better than 0.01 ‰ for $\delta_{VPDB}(^{13}C)$, and 0.02 ‰ for $\delta_{VPDB\text{-}CO2}(^{18}O)$, to ensure long term maintenance of the link with VPDB and VPDB-CO_2 scales. The demonstrated performance of the BIPM system, especially in terms of reproducibility, would allow it to be already used as a central facility for the planned on-demand Key Comparison BIPM.QM−K4. The measurement uncertainty achievable by the BIPM reference method is, however, limited by the transfer of delta values from carbonate primary reference materials to CO_2 gas using the reaction with over saturated phosphoric acid. The uncertainty, reproducibility and magnitude of potential biases from the acid reaction method will be validated in a Pilot Study with laboratories having similar capabilities, leading to the possibility of re-value assigning BIPM's hierarchy of CO_2 gas standards with smaller uncertainties.

13 References

[1] Viallon J., Meyer C., Moussay P., Schmidt J., Maxwell S., Arrhen F. and Wielgosz R.I., 2023, A high accuracy reference facility for ongoing comparisons of CO2 in air standards, *Metrologia*, **60**, 065014, 10.1088/1681-7575/ad0abe

[2] Camin F., Besic D., Brewer Paul J., Allison Colin E., Coplen Tyler B., Dunn Philip J.H., Gehre M., Gröning M., Meijer Harro A.J., Hélie J.-F., et al., 2025, Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting, *Rapid Communications in Mass Spectrometry*, **39**, e10018, https://doi.org/10.1002/rcm.10018

[3] Skrzypek G., Allison C.E., Böhlke J.K., Bontempo L., Brewer P., Camin F., Carter J.F., Chartrand M.M.G., Coplen T.B., Gröning M., et al., 2022, Minimum requirements for publishing hydrogen, carbon, nitrogen, oxygen and sulfur stable-isotope delta results (IUPAC Technical Report), *Pure and Applied Chemistry*, **94**, 1249-1255, doi:10.1515/pac-2021-1108

[4] Wendeberg M., Richter J.M., Rothe M. and Brand W.A., 2013, Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO_2 in air, *Atmos. Meas. Tech.*, **6**, 817-822, 10.5194/amt-6-817-2013

[5] Zellweger C., Brewer P., Crotwell A., Camin F., Sperlich P., Hammer S., Morgan E., Lan X., Hall B., Lee S., et al. WMO 2024 GAW Report No. 317, 22nd WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques, https://library.wmo.int/idurl/4/69756

[6] Srivastava A. and Verkouteren R.M., 2018, Metrology for stable isotope reference materials: 13 C/12 C and 18 O/16 O isotope ratio value assignment of pure carbon dioxide gas samples on the Vienna PeeDee Belemnite-CO 2 scale using dual-inlet mass spectrometry, *Analytical and bioanalytical chemistry*, **410**, 4153-4163,

[7] Viallon J., Choteau T., Flores E., Idrees F., Moussay P., Wielgosz R., Loh Z., Allison C., Huang L. and Chivelscu A., 2023, Final report of CCQM-P204, comparison on CO2 isotope ratios in pure CO2, *Metrologia*, **60**, 08026,

[8] Assonov S.S. and Brenninkmeijer C.A.M., 2006, On the N2O correction used for mass spectrometric analysis of atmospheric CO2, *Rapid Communications in Mass Spectrometry*, **20**, 1809-1819, https://doi.org/10.1002/rcm.2516

[9] Mook W.G., Van der Hoek S., Mook W.G. and Van der Hoek S., 1983, The N2O correction in the carbon and oxygen isotopic analysis of atmospheric CO2, *Chemical Geology*, **41**, 237-242, https://doi.org/10.1016/S0009-2541(83)80021-7

[10] Wen X.-F., Meng Y., Zhang X.-Y., Sun X.-M. and Lee X., 2013, Evaluating calibration strategies for isotope ratio infrared spectroscopy for atmospheric 13 CO 2/12 CO 2 measurement, *Atmospheric Measurement Techniques*, **6**, 1491-1501,

[11] Flores E., Viallon J., Moussay P., Griffith D.W.T. and Wielgosz R.I., 2017, Calibration strategies for FTIR and other IRIS instruments for accurate δ13C and δ18O measurements of CO2 in air, *Analytical Chemistry*, **89**, 3648-3655, 10.1021/acs.analchem.6b05063

[12] Meijer H.A.J., Neubert R.E.M. and Visser G.H., 2000, Cross contamination in dual inlet isotope ratio mass spectrometers, *International Journal of Mass Spectrometry*, **198**, 45-61, https://doi.org/10.1016/S1387-3806(99)00266-3

[13] Dunn P. J. H. B., C., Strak E., Carter J.F. 2025 Good practice guide for isotope ratio mass spectrometry, 3rd Edition.,

[14] Steur P.M., Scheeren H.A., Nelson D.D., McManus J.B. and Meijer H.A.J., 2021, Simultaneous measurement of δ13C, δ18O and δ17O of atmospheric CO2 – performance assessment of a dual-laser absorption spectrometer, *Atmos. Meas. Tech.*, **14**, 4279-4304, 10.5194/amt-14-4279-2021

[15] Werner R.A., Rothe M. and Brand W.A., 2001, Extraction of CO_2 from air samples for isotopic analysis and limits to ultra high precision $\delta^{18}O$ determination in CO2 gas, *Rapid Communications in Mass Spectrometry*, **15**, 2152-2167, 10.1002/rcm.487

[16] Ghosh P., Patecki M., Rothe M. and Brand W.A., 2005, Calcite-CO2 mixed into CO2-free air: a new CO2-in-air stable isotope reference material for the VPDB scale, *Rapid Communications in Mass Spectrometry*, **19**, 1097-1119, 10.1002/rcm.1886

[17] Brand W.A., Huang L., Mukai H., Chivulescu A., Richter J.M. and Rothe M., 2009, How well do we know VPDB? Variability of δ13C and δ18O in CO2 generated from NBS19-calcite, *Rapid Communications in Mass Spectrometry*, **23**, 915-926, 10.1002/rcm.3940

[18] Tans P.P. and Zellweger C. WMO 2016 GAW Report No. 229, 18th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques,

[19] Crotwell A.M. and Steinbacher M. WMO 2019 GAW Report No. 242, 19th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques,

[20] Coplen T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances (Technical Report), *Pure and Applied Chemistry*, **66**, 273-276, doi:10.1351/pac199466020273

[21] Brand W.A., Assonov S.S. and Coplen T.B. 2010 *Correction for the ^{17}O interference in δ(^{13}C) measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report)* vol 82 (Research Triangle Park, NC, ETATS-UNIS: Pure and applied chemistry)

[22] IUPAC Commission on Isotopic Abundances and Atomic Weights 2025 The isotopic composition of VPDB *Chemistry International* pp 34-35, doi:10.1515/ci-2025-0216

14 Annex 1 – Participants reports

All reports are displayed entirely in an annex (PDF version only).

15 Annex 2 – Tables

Four tables are displayed in the next pages:

- Table 8: composition of the air mixtures submitted by participants in terms of isotopic composition and amount fractions of CO_2 and N_2O.
- Table 9: comparison results for $\delta_{VPDB}(^{13}C)$, with the values reported by participants, the values measured by the BIPM, the difference between both and the uncertainties.
- Table 10: comparison results for $\delta_{VPDB\text{-}CO2}(^{18}O)$, with the values reported by participants, the values measured by the BIPM, the difference between both and the uncertainties.
- Table 11: schedule of measurements performed at BIPM

Table 8: composition of the air mixtures submitted by participants in terms of isotopic composition and amount fractions of CO_2 and N_2O.

Participant	Cylinder ID	$\delta_{VPDB}(^{13}C)$ / ‰	$\delta_{VPDB\text{-}CO2}(^{18}O)$ / ‰	$x(CO_2)$ / µmol mol^{-1}	$x(N_2O)$ / nmol mol^{-1}
BGC-iso	D417473	-9.060	-1.860	428.47	338.54
BGC-iso	D417489	-4.184	-14.890	429.3	337.42
BGC-iso	D417496	-34.477	-28.730	429.8	338.87
CSIRO	CA04924	-11.339	-2.030	462.44	358.86
CSIRO	CA07700	-8.235	-0.548	383.95	320.78
ECCC	AES085	-35.551	-33.438	420.58	334.4
ECCC	CB09882	-8.540	-1.561	398.47	358.09
ECCC	CC342919	-21.594	-16.573	402.43	359.44
IAEA	D208032	1.266	-7.562	410.3	--
IAEA	D208034	-42.415	-34.962	411.2	--
INRiM	D208036	1.360	--	412.6	--
INRiM	D208039	-42.300	--	412.9	--
INRiM	D208041	-21.080	--	410.2	--
INSTAAAR	CA05791	-11.554	-5.468	480.28	337.88
InstAAR	CA06475	-9.463	-1.946	436.74	337.87
InstAAR	CC332697	-8.925	-1.213	426.67	337.97
InstAAR	CC87457	-13.925	-9.622	541.85	337.8
JSI	D208033	1.195	-7.562	412.6	--
JSI	D208035	-42.418	-34.528	411.4	--
KRISS	D207634	-8.902	-11.046	398.26	341.25
KRISS	D207731	-8.885	-11.214	401.5	--
NIST	JJ13293	-2.700	-17.360	503.81	329.64
NIST	JJ13931	-10.990	-12.250	412.3	329.67
NIST	JJ13939	-39.880	-33.810	432.21	329.42
NIST	JJ13955	-50.420	-41.530	480.44	328.97
NPL	D180342	1.250	-7.830	799.3	--
NPL	D180350	-42.120	-35.680	793.85	--
NPL	D180351	-42.120	-35.680	407.12	--
NPL	D180385	1.250	-7.830	409.13	--
PTB	D148967	-9.115	-14.849	410.3	--
PTB	D180455	-20.295	-21.960	410.5	--
RUG	D879562	-10.052	-1.753	443.03	338.9
RUG	D879563	-9.240	-1.214	428.95	338.6
UME	PSM206688	-41.870	--	409.84	--
UME	PSM206705	-20.100	--	409.95	--
VNIIM	D993597	-1.810	-9.360	479.95	--
VNIIM	D993598	-43.150	-44.560	480.17	--

Table 9: comparison results for $\delta_{VPDB}(^{13}C)$, with the values reported by participants, the values measured by the BIPM, the difference between both and the uncertainties.

		Participant results		BIPM results		Difference	
Institute	**Cylinder ID**	$\delta_{VPDB}(^{13}C)$ / ‰	u (k=1) / ‰	$\delta_{VPDB}(^{13}C)$ / ‰	u (k=1) / ‰	$\Delta_{VPDB}(^{13}C)$ / ‰	U (k=2) / ‰
BGC-iso	D417473	-9.060	0.010	-9.114	0.015	0.054	0.037
BGC-iso	D417489	-4.184	0.014	-4.254	0.018	0.070	0.046
BGC-iso	D417496	-34.477	0.008	-34.530	0.017	0.053	0.038
CSIRO	CA04924	-11.339	0.032	-11.408	0.013	0.069	0.069
CSIRO	CA07700	-8.235	0.032	-8.317	0.014	0.082	0.070
ECCC	AES085	-35.551	0.028	-35.723	0.013	0.172	0.061
ECCC	CB09882	-8.540	0.005	-8.644	0.013	0.104	0.029
ECCC	CC342919	-21.594	0.004	-21.732	0.013	0.138	0.027
IAEA	D208032	1.266	0.017	1.216	0.016	0.050	0.047
IAEA	D208034	-42.415	0.015	-42.446	0.016	0.031	0.044
INRiM	D208036	1.360	0.110	1.220	0.015	0.140	0.222
INRiM	D208039	-42.300	0.100	-42.452	0.012	0.152	0.201
INRiM	D208041	-21.080	0.170	-21.124	0.016	0.044	0.342
InstAAR	CA05791	-11.554	0.029	-11.619	0.015	0.065	0.065
InstAAR	CA06475	-9.463	0.019	-9.544	0.015	0.080	0.048
InstAAR	CC332697	-8.925	0.018	-9.003	0.015	0.079	0.047
InstAAR	CC87457	-13.925	0.036	-13.991	0.017	0.066	0.079
JSI	D208033	1.195	0.021	1.215	0.014	-0.020	0.051
JSI	D208035	-42.418	0.021	-42.450	0.013	0.032	0.050
KRISS	D207634	-8.902	0.061	-8.846	0.013	-0.056	0.124
KRISS	D207731	-8.885	0.060	-8.854	0.011	-0.031	0.121
NIST	JJ13293	-2.700	0.065	-2.880	0.014	0.180	0.133
NIST	JJ13931	-10.990	0.075	-10.981	0.014	-0.009	0.153
NIST	JJ13939	-39.880	0.170	-39.834	0.013	-0.046	0.341
NIST	JJ13955	-50.420	0.280	-50.369	0.012	-0.051	0.561
NPL	D180342	1.250	0.165	1.211	0.013	0.039	0.331
NPL	D180350	-42.120	0.340	-42.150	0.013	0.030	0.680
NPL	D180351	-42.120	0.180	-42.145	0.015	0.025	0.361
NPL	D180385	1.250	0.200	1.201	0.012	0.049	0.401
PTB	D148967	-9.115	0.125	-9.282	0.012	0.168	0.251
PTB	D180455	-20.295	0.125	-20.465	0.010	0.170	0.251
RUG	D879562	-10.052	0.040	-10.146	0.012	0.094	0.084
RUG	D879563	-9.240	0.040	-9.323	0.012	0.083	0.084
UME	PSM206688	-41.870	0.050	-42.139	0.019	0.269	0.107
UME	PSM206705	-20.100	0.035	-20.478	0.010	0.378	0.073
VNIIM	D993597	-1.810	0.050	-1.835	0.019	0.025	0.107
VNIIM	D993598	-43.150	0.050	-43.215	0.014	0.065	0.104

Table 10: comparison results for $\delta_{VPDB\text{-}CO2}(^{18}O)$, with the values reported by participants, the values measured by the BIPM, the difference between both and the uncertainties.

		Participant results		BIPM results		Difference	
Institute	**Cylinder ID**	$\delta_{VPDB\text{-}CO2}(^{18}O)$ / ‰	u (k=1) / ‰	$\delta_{VPDB\text{-}CO2}(^{18}O)$ / ‰	u (k=1) / ‰	$\Delta_{VPDB\text{-}CO2}(^{18}O)$ / ‰	U (k=2) / ‰
BGC-iso	D417473	-1.860	0.016	-1.914	0.024	0.054	0.058
BGC-iso	D417489	-14.890	0.013	-14.897	0.058	0.007	0.118
BGC-iso	D417496	-28.730	0.022	-28.854	0.035	0.124	0.083
CSIRO	CA04924	-2.030	0.059	-2.004	0.019	-0.027	0.124
CSIRO	CA07700	-0.548	0.059	-0.603	0.038	0.055	0.140
ECCC	AES085	-33.438	0.126	-34.122	0.043	0.684	0.265
ECCC	CB09882	-1.561	0.089	-1.795	0.026	0.234	0.185
ECCC	CC342919	-16.573	0.090	-17.106	0.040	0.533	0.197
IAEA	D208032	-7.562	0.053	-7.838	0.017	0.276	0.111
IAEA	D208034	-34.962	0.050	-35.349	0.039	0.387	0.127
INRiM	D208036	--	--	-7.881	0.014	--	--
INRiM	D208039	--	--	-35.359	0.055	--	--
INRiM	D208041	--	--	-21.887	0.042	--	--
InstAAR	CA05791	-5.468	0.033	-5.508	0.017	0.039	0.075
InstAAR	CA06475	-1.946	0.034	-1.947	0.054	0.001	0.128
InstAAR	CC332697	-1.213	0.036	-1.257	0.067	0.045	0.152
InstAAR	CC87457	-9.622	0.075	-9.671	0.067	0.049	0.202
JSI	D208033	-7.562	0.063	-7.849	0.024	0.287	0.135
JSI	D208035	-34.528	0.105	-35.351	0.029	0.823	0.218
KRISS	D207634	-11.046	0.370	-10.726	0.015	-0.320	0.741
KRISS	D207731	-11.214	0.370	-10.753	0.025	-0.462	0.741
NIST	JJ13293	-17.360	0.150	-16.461	0.045	-0.899	0.313
NIST	JJ13931	-12.250	0.170	-12.192	0.015	-0.058	0.341
NIST	JJ13939	-33.810	0.365	-33.693	0.108	-0.117	0.761
NIST	JJ13955	-41.530	0.365	-41.378	0.025	-0.152	0.732
NPL	D180342	-7.830	0.370	-7.811	0.046	-0.019	0.746
NPL	D180350	-35.680	0.375	-35.671	0.022	-0.009	0.751
NPL	D180351	-35.680	0.385	-35.687	0.038	0.007	0.774
NPL	D180385	-7.830	0.425	-7.884	0.035	0.054	0.853
PTB	D148967	-14.849	0.250	-14.592	0.061	-0.257	0.515
PTB	D180455	-21.960	0.250	-21.759	0.046	-0.200	0.508
RUG	D879562	-1.753	0.050	-1.712	0.035	-0.041	0.122
RUG	D879563	-1.214	0.060	-1.140	0.021	-0.074	0.127
UME	PSM206688	--	--	-35.611	0.065	--	--
UME	PSM206705	--	--	-21.725	0.051	--	--
VNIIM	D993597	-9.360	0.095	-9.389	0.043	0.029	0.209
VNIIM	D993598	-44.560	0.095	-44.465	0.085	-0.095	0.255

Table 11: schedule of measurements performed at BIPM

week	Start date	Mixture Role	Group ID	Cylinder ID
45	2024-11-04	Sample 1	1	RUG_D879562
		Sample 2		RUG_D879563
		Sample 3		KRISS_D207634
		Sample 4		KRISS_D207731
46	2024-11-11	Sample 1	2	UME_PSM206688
		Sample 2		UME_PSM206705
		Sample 3		VNIIM_D993597
		Sample 4		VNIIM_D993598
49	2024-12-02	Sample 1	2	UME_PSM206688
		Sample 2		UME_PSM206705
		Sample 3		VNIIM_D993597
		Sample 4		VNIIM_D993598
50	2024-12-09	Sample 1	3	InstAAR_CA05791
		Sample 2		InstAAR_CA06475
		Sample 3		InstAAR_CC332697
		Sample 4		InstAAR_CC87457
2	2025-01-06	Sample 1	4	ECCC_AES085
		Sample 2		ECCC_CB09882
		Sample 3		ECCC_CC342919
		Sample 4		BIPM_D115537
3	2025-01-13	Sample 1	2	UME_PSM206688
		Sample 2		UME_PSM206705
		Sample 3		VNIIM_D993597
		Sample 4		VNIIM_D993598
4	2025-01-20	Sample 1	5	BGC-iso_D417473
		Sample 2		BGC-iso_D417489
		Sample 3		BGC-iso_D417496
		Sample 4		BIPM_D115537
5	2025-01-27	Sample 1	6	IAEA_D208032
		Sample 2		IAEA_D208034
		Sample 3		JSI_D208033
		Sample 4		JSI_D208035
6	2025-02-03	Sample 1	7	INRiM_D208036
		Sample 2		INRiM_D208039
		Sample 3		INRiM_D208041
		Sample 4		BIPM_D115537
7	2025-02-13	Sample 1	8	NPL_D180385
		Sample 2		NPL_D180342
		Sample 3		NPL_D180351
		Sample 4		NPL_D180350
10	2025-03-04	Sample 1	9	NIST_JJ13955
		Sample 2		NIST_JJ13939
		Sample 3		NIST_JJ13931
		Sample 4		NIST_JJ13293
11	2025-03-10	Sample 1	10	CSIRO_CA04924
		Sample 2		CSIRO_CA07700
		Sample 3		PTB_D148967
		Sample 4		PTB_D180455

16 Annex 3 – BIPM Uncertainty budget

16.1 Introduction

This document includes the details of the analysis of uncertainties associated with the measurements of isotope delta values $\delta_{VPDB}(^{13}C)$ and $\delta_{VPDB\text{-}CO2}(^{18}O)$ in gaseous mixtures of CO_2 in air by Isotope Ratio Mass Spectrometry (IRMS), at the BIPM, as calculated during the measurements performed for the Pilot Study CCQM-P239.

16.2 Setup and method

As described in the main body of CCQM-P239 report, the analytical instrument was a DI-IRMS manufactured by Thermo Scientific, model MAT253+, acquired in 2020 and already used for all measurements reported in the report of the comparison CCQM-P204, with the same calibration method and reference materials.

Since the CCQM-P204 comparison, it was completed by a 16-port gas sampling system and the BIPM Air Trap facility to extract CO_2 from the air mixtures. A method to correct for the presence of nitrous oxide in the gases extracted from air with the traps was also developed, including regular measurements of pure nitrous oxide gas injected in the DI-IRMS. Results of these measurements were used to estimate three parameters required for the correction: the relative ionisation efficiency between N_2O and CO_2, and the response of the instrument in terms of ratio between the signals detected at masses 45 and 46 against mass 44.

Raw data, consisting of the "big" isotope delta values Δ^{45} and Δ^{46} were further treated using an in-house software. The software performs a series of corrections: cross-contaminations between samples, presence of N_2O co-trapped with CO_2, and correction for the isobaric interferences between isotopologues of CO_2 having the same molecular mass (^{17}O correction). The final step is the calibration on the VPDB scale using the two reference materials AL CANISTER-5391 and SIAD CANISTER-5386 traceable to VPDB, and averaging of values acquired for the same sample

16.3 Measurement equation

There is no single measurement equation, but a series of calculations performed by the macro. The steps are listed below, starting from the raw values Δ^{45} and Δ^{46} measured for each analysis of one sequence:

- Calculate the cross-contamination correction

$$\eta_i = 0.5\left(1 - \frac{\Delta_m}{\Delta_t}\right) \quad (1)$$

where Δ_m is the measured value during one analysis (or the mean over n analysis) and Δ_t is the same quantity measured during the analysis of the most depleted gas with the longest idle time. This calculation was applied for each sequence, but a statistical analysis was performed after the completion of the pilot study CCQM-P204, and averages values were calculated. The averages values were the one included in the calculation of the final delta values.

- Correct all measured values $\Delta^i CO_2$. Requires the knowledge of η_i:

$$\Delta^i_{cor} = \Delta^i_m/(1 - 2\eta_i - \eta_i\Delta^i_m) \quad (2)$$

- Calculate the mean of Δ^{45} and Δ^{46} (versus the working reference) during the 4 analysis of the reference standard R2 in the sample bellow

- Calculate the Δ^{45} and Δ^{46} of the working reference versus R2
- Calculate all Δ^{45} and Δ^{46} for each analysis versus R2 using the formula:

$$\delta_{\mathrm{VPDB}} = \delta_{\mathrm{WS}} + \delta_{\mathrm{R}} + \delta_{\mathrm{WS}}\delta_{\mathrm{R}} \times 10^{-3} \quad (3)$$

- Calculate the N_2O corrections for the two quantities using the formulae:

$$\Delta_{\mathrm{c}}^{45} = \Delta^{45} + E_{\mathrm{N2O}} \frac{x(\mathrm{N_2O})}{x(\mathrm{CO_2})} (\Delta^{45} - \Delta_{\mathrm{N2O}}^{45}) \quad (4)$$

$$\Delta_{\mathrm{c}}^{46} = \Delta^{46} + E_{\mathrm{N2O}} \frac{x(\mathrm{N_2O})}{x(\mathrm{CO_2})} (\Delta^{46} - \Delta_{\mathrm{N2O}}^{46}) \quad (5)$$

Where:

- Δ^{45} and Δ^{46} are the value obtained in the previous step
- E_{N2O} is the relative ionisation efficiency of N_2O compared to CO_2,
- $x_{\mathrm{N2O}}/x_{\mathrm{CO2}}$ is the ratio between N_2O and CO_2 amount fractions in the air mixture,
- $\Delta^{45}{}_{\mathrm{N2O}}$ and $\Delta^{46}{}_{\mathrm{N2O}}$ are the apparent isotope-delta values at masses 45 and 46 due to N_2O

- Correct the above values and deduce the $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ values using a calculation loop to first calculate R^{18} and then deduce the other quantities:

$$R^{17} = k(R^{18})^{\lambda} \quad (6)$$

$$R^{13} = R^{45} - 2R^{17} \quad (7)$$

$$\delta^{18} = \left(\frac{R^{18}}{R_{VPDB}^{18}} - 1\right) \times 10^{3} \quad (8)$$

$$\delta^{13} = \left(\frac{R^{13}}{R_{VPDB}^{13}} - 1\right) \times 10^{3} \quad (9)$$

$$\delta^{17} = \left(\frac{R^{17}}{R_{VPDB}^{17}} - 1\right) \times 10^{3} \quad (10)$$

Where the reference values below, defining the scale, also need to be maintained. The set of reference values used for this comparison was from an IUPAC technical report published in 2010 [21]. Since December 2024, IUPAC has been recommending a new set of consensus values [22]. It was decided to keep the original set for this report, and it was checked that the impact on the comparisons results was insignificant.

$\lambda = 0.528$	$k = 0.01022461$	
$R^{13}{}_{\mathrm{VPDB}} = 0.01118$	$R^{17}{}_{\mathrm{VPDB}} = 0.0003931$	$R^{18}{}_{\mathrm{VPDB}} = 0.00208835$
$R^{45}{}_{\mathrm{VPDB}} = 0.0119662$	$R^{46}{}_{\mathrm{VPDB}} = 0.004185644$	

- linearize $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$ using the two end-points (standards R1 and R2)) and the function

$$\delta_{lin} = \delta_{R1} + \frac{(\delta_m - \delta_{R1,m})(\delta_{R2} - \delta_{R1})}{\delta_{R2,m} - \delta_{R1,m}} \quad (11)$$

- Calculate the average and standard deviation over all measurements of the same sample

16.4 Uncertainty components

16.4.1 Repeatability

Taking the example of $\delta_{VPDB}(^{13}C)$, which starts with the measurement of Δ^{45} by the IRMS, the experimental standard deviations $s45a$ calculated by the IRMS software for a series of 8 cycles of the dual inlet were recorded. Typical values observed were all around 5×10^{-3}. As one measurement sequence included two series of measurements for one sample, the standard deviation over the two measurements, $s45b$ was then computed. Values were typically of the same order. Additionally, the standard deviation $s13_{lin}$, obtained after the last steps of the algorithm described previously, was also recorded and compared. All three values were close to each other for all samples measured during the Pilot Study.

The two variances $s45a$ and s_{lin} were combined to obtain a conservative estimator of the repeatability. Typical values ranged between 3×10^{-3} and 9×10^{-3} for $\delta_{VPDB}(^{13}C)$, and between 3×10^{-3} and 1.2×10^{-2} for $\delta_{VPDB\text{-}CO2}(^{18}O)$ (using the same approach, with $s46$ and $s18_{lin}$).

16.4.2 Calibration

One final δ value is the result of a two-point calibration, using two standards which were both measured at IAEA against the same reference material IAEA-603. To avoid over estimation of the uncertainty of degrees of equivalence, which include uncertainties reported by participants who are also traceable to the same reference material, the uncertainty on isotope delta values of IAEA-603 was not included here. Only the repeatability of measurements performed at IAEA to value assign the gaseous standards maintained by the BIPM was accounted for, with values of $u(\delta_{VPDB}(^{13}C))$ = 0.005 ‰ for REF2 and $u(\delta_{VPDB}(^{13}C))$ = 0.006 ‰ for REF1.

The same rule was applied for $\delta_{VPDB\text{-}CO2}(^{18}O)$, with values of $u(\delta_{VPDB\text{-}CO2}(^{18}O))$ = 0.005 ‰ for REF2 and $u(\delta_{VPDB\text{-}CO2}(^{18}O))$ = 0.007 ‰ for REF1.

16.4.3 Cross-Contamination correction

The cross-contamination corrections were calculated for each sequence of analysis using the same method as for CCQM-P204, i.e. measuring the last injection of REF1 gas with a long idle time in the dual inlet of the IRMS to minimise cross-contamination. The values obtained were comparable than during CCQM-P204, with similar repeatability. Therefore the same uncertainty of 0.001 ‰ was kept.

16.4.4 N_2O correction

Equations 4 and 5 above include 4 input quantities. Uncertainties were estimated for each of them and further propagated to calculate the combined standard uncertainty on the correction, assuming no correlation, as follows:

- Δ^{45} and Δ^{46} were measured with a known uncertainty, from which only the repeatability component was taken at this stage.
- E_{N2O} was measured several times, and a conservative relative uncertainty of 1.5 % could be estimated.
- x_{N2O}/x_{CO2} : Conservative standard relative uncertainties of 0.1 % for $x(CO_2)$ and 0.5 % for $x(N_2O)$ were assumed. Many laboratories can obtain lower uncertainties but the sensitivity coefficient of this component in the budget is rather small.

- Δ^{45}_{N2O} and Δ^{46}_{N2O} : relative standard uncertainties of 3 % were estimated based on measurements and literature, as the exact knowledge of the isotopic composition of N_2O was missing.

Combining all components, standard uncertainties of 0.008 ‰ and 0.009 ‰ were estimated for the two corrections, i.e. on Δ^{45} and Δ^{46}.

16.5 Uncertainty budget

The uncertainty budget for $\delta_{VPDB}(^{13}C)$ measurements performed by the BIPM during the comparison CCQM-P239 was similar to the one applied during the comparison CCQM-P204, except that the uncertainty on the reference material IAEA-603 was not included, and that an uncertainty for the N_2O correction was added if relevant. An example of the uncertainty budget at a value close to REF1 is displayed in Table 12.

Table 12: typical uncertainty budget for $\delta_{VPDB}(^{13}C)$

y	**Value**	**Unit**	**Standard Uncertainty *u*(*y*)**			**Sensitivity coefficient**	**Contribution**
			Source	**Distribution**	***u*(*y*)**	C_i	u_i
d13m	−1.495	**‰**	Type A	normal	0.005	1	5×10^{-3}
ref1	−1.473	**‰**	Type A	normal	0.006	1	6×10^{-3}
ref2	−43.103	**‰**	Type A	normal	0.005	1	5×10^{-3}
η45	2.83×10^{-4}	**‰**	meas.	normal	0.001	1	1×10^{-3}
η46	1.16×10^{-3}	**‰**	meas.	normal	0.001	1	1×10^{-3}
						$u(\delta^{13}C$ / ‰)	**0.009**
If presence of N_2O :							
N_2O	−0.245	**‰**	estimation	Normal	0.008	1	8×10^{-3}
						$u(\delta^{13}C$ / ‰)	**0.012**

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**Max-Planck Institute for Biogeochemistry**
Contact	**Dr. Heiko Moossen**
Email	heiko.moossen@bgc-jena.mpg.de

Transfer Standards (cylinders) Information		
Number of standards	3.00	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D417473	2024-03-30		
2	D417489	2024-04-22		
3	D417496	2024-04-22		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D417473	-9.06	0.01	1 sigma
2	D417489	-4.18	0.01	1 sigma
3	D417496	-34.48	0.01	1 sigma
4	***			
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D417473	-1.86	0.02	1 sigma
2	D417489	-14.89	0.01	1 sigma
3	D417496	-28.73	0.02	1 sigma
4	=B15			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D417573	428.47	0.07	1 sigma
2	D417589	429.30	0.08	1 sigma
3	D417596	429.80	0.09	1 sigma
4	=B15			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D417573	338.54	0.10	
2	D417589	337.42	0.13	
3	D417596	338.87	0.15	
4	=B15			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1						
2						
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[*CCQM-P239_Result Form_Moossen*]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**Max-Planck Institute for Biogeochemistry**
Contact	**Dr. Heiko Moossen**
Email	**Heiko.moossen[at]bgc-jena.mpg.de**

Transfer Standards (cylinders) Information		
Number of standards	3	

Standard #	ID (Serial Number)
1	D417473
2	D417489
3	D417496
4	

Mandatory information

1) Traceability of the measurement results

- The BGC-IsoLab measures isotopes of CO_2 in air on the JRAS-06 scale (Ghosh et al., 2005, Wendeberg et al., 2013). The JRAS-06 was established in 2005 by reacting NBS 19 standard with phosphoric acid, and mixing the resulting CO_2 into CO_2 free air. These mixtures were used to calibrate CO_2 isotope measurements in high pressure tanks containing air. These NBS19 syntheses link the JRAS-06 scale to the VPDB scale. The same procedure was done with an in-house standard carbonate called "MAR-J1". This carbonate is used to verify the JRAS-06 scale to this day (Wendeberg et al., 2013). The JRAS-06 scale is realised using high pressure cylinders filled with air. The latest reference standard "Cosima" has $\delta^{13}C$- and $\delta^{18}O$-CO_2 values of -8.248 ± 0.004 ‰ and -0.865 ± 0.008 ‰ (standard error, 90 % confidence interval, n: > 200 analyses), respectively on the JRAS-06 scale. All analyses are calibrated against this reference standard using a 1-point calibration. "Cosima" is the third high pressure reference standard tank since Ghosh et al. (2005) calibrated the first tank against NBS19-CO_2.
- The following corrections are applied to all measurements, including the reference standard:
    - ^{17}O correction (Brand et al., 2010, Santrock, Studley, Hayes 1985)
    - Crimp-mismatch (Werner et al., 2001)
    - N_2O correction (Ghosh et al., 2004)
    - Drift correction
    - Scaling to JRAS-06 scale

2) Uncertainty budget

Each high-pressure cylinders is analysed once a day against the reference standard over a period of at least three weeks to obtain at least 10 individual measurements. The given uncertainty is the 1 sigma standard deviation of the average of all measurements that pass the quality control assessment.

Additional non-mandatory information

The three high pressure tanks were measured in two separate measurement campaigns, once in October 2024 and again in August 2025. The submitted data can be viewed in Table 1:

Table 1: measurements of CCQM P239 samples at Jena in October 2024 and August 2025

		October 2024			**July/August 2025**		
Standard #	Cylinder ID	δ13C permil	U(δ13C) permil	k	δ13C permil	U(δ13C) permil	k
1	D417473	-9.02463	0.01440593	1 sigma	-9.06	0.01	1 sigma
2	D417489	-4.164273	0.01570487	1 sigma	-4.184	0.014	1 sigma
3	D417496	-34.4325906	0.01486766	1 sigma	-34.477	0.008	1 sigma

Standard #	Cylinder ID	δ18O permil	U(δ18O) permil	k	δ18O permil	U(δ18O) permil	k
1	D417473	-1.91918063	0.01845708	1 sigma	-1.86	0.016	1 sigma
2	D417489	-14.847082	0.01529223	1 sigma	-14.89	0.013	1 sigma
3	D417496	-28.7406053	0.01481165	1 sigma	-28.73	0.022	1 sigma

There are small differences between the measurements that are discussed below:

1. All measurements are done on the JRAS-06 scale. This scale is specifically designed for the analyses of natural air samples. In accordance the instrument also usually analyses only air with natural isotope abundance of air samples. Where samples with isotope compositions are analysed that are isotopically distant from the standard, scale contraction effects may impact the measurements. In this case the samples with cylinder IDs D417489 and particularly D417496 could be affected by such scale contraction effects. To quantify and correct for such effects an eta correction is usually done. This was not done in this case due to the large time and personnel expenditure this would have required.

2. Since the tanks were transported to Paris and back between the two measurement episodes the regulators had to be removed from the tank after the first measurement episode. For the second measurement episode different regulators were then used. For high precision measurements regulators are usually “married” to the tanks as long as the tanks are analysed. Exchange of regulators can cause measurement offsets due to the intrinsic small differences in regulator geometries (even if regulators are the same make) that cause flow and temperature offsets between regulators.

3. Unfortunately, the analyses of the tanks with tank IDs D417496 and D417489 revealed initial measurement instabilities (e.g. Figure 1), i.e. a drift effect. Such drifts are usually observed

when the tank has not been sufficiently dried prior to filling or has been filled with air containing moisture. We suspect that the filling procedure of these two tanks was not ideal. Even though the outliers that make up the drift effect were removed prior to final data evaluation, moist air adversely affects measurement accuracy.

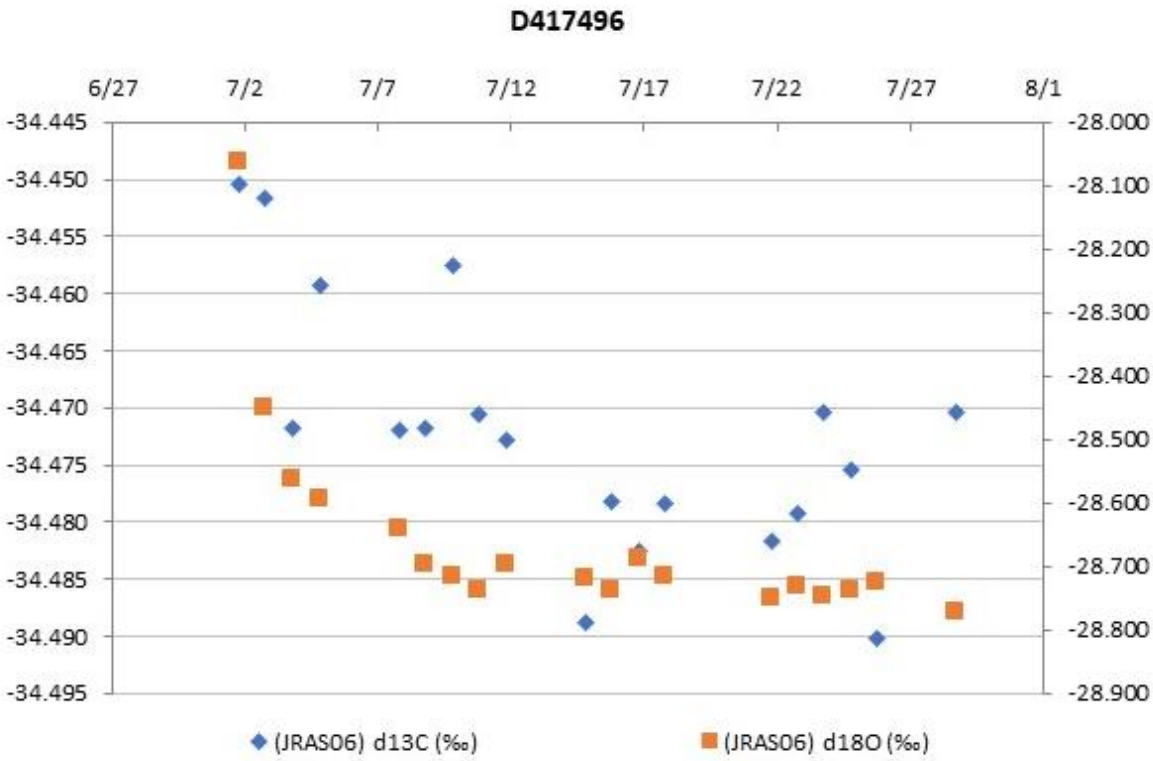


Figure 1: $\delta^{13}C$ (blue diamonds) and $\delta^{18}O$ (orange squares) in cylinder D417496 in cylinder D417496, showing the initial measurement drift

3) Mixtures composition

All three high pressure cylinders contain air collected from the institutes roof as a basis. D417573 is an unaltered air, while the CO_2 is removed from D417589 and D417596 and subsequently CO_2 with known high and low $\delta^{13}C$-CO_2 values was added. The pure CO_2 sources have a purity of 4.5.

4) Mixtures preparation

See above

5) Verification of mixtures

The stable isotope measurements of the atmospheric CO_2 of all three tanks were conducted between September and November 2024. All measurements are done using a MAT252 (Thermo Fisher, Bremen) isotope ratio mass spectrometer "Cora" equipped with a BGC-AirTrap (Werner et al., 2001).

The N_2O and CO_2 trace gas measurements were done at the GasLab (https://www.bgc-jena.mpg.de/servicegruppen/gaslab) using a GC-FID and GC-ECD. The CO_2 trace gas measurements are calibrated on the NOAA X2019 scale, and the N_2O measurements are calibrated on the X2006A scale (GAW Report No.255). The table below gives the measured concentrations of CO2 and N2O:

USN	FLASK	Avg cCO2 (NOAA X2019)	StDev cCO2 (NOAA X2019)	Avg cN2O (X2006A)	StDev cN2O (X2006A)
20240788	D417473	428.47	0.07	338.54	0.10
20240891	D417489	429.30	0.08	337.42	0.13
20240892	D417496	429.80	0.09	338.87	0.15

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**CSIRO**
Contact	**Elise-Andree Guerette**
Email	**Elise-Andree.Guerette@csiro.au**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	CA04924	2002-02-21	1830	psig
2	CA07700	2009-07-01	1800	psig
3	***	***		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	CA04924	-11.339	0.032	1
2	CA07700	-8.235	0.032	1
3	***			
4	***			
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	CA04924	-2.030	0.059	1
2	CA07700	-0.548	0.059	1
3	=B14			
4	=B15			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	CA04924	462.44	0.07	1
2	CA07700	383.95	0.04	1
3	=B14			
4	=B15			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	CA04924	358.86	0.15	1
2	CA07700	320.78	0.15	1
3	=B14			
4	=B15			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1	n/a (ambient)	n/a (ambient)	n/a (ambient)			
2	n/a (ambient)	n/a (ambient)	n/a (ambient)			
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

CCQM-P239_Result Form v0.1_CSIRO.xlsx

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**CSIRO**
Contact	**Elise-Andree Guerette**
Email	**Elise-Andree.Guerette@csiro.au**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)
1	CA04924
2	CA07700
3	
4	

Mandatory information

1) Traceability of the measurement results

[Instructions below may be removed]

As indicated in section 2 of the protocol, the measurands are $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the CO_2 gas in the carbon dioxide in air mixture expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO_2 scales respectively. Explain here how the measurement results reported in the result form are traceable to these scales, including information on:

- Number and kind of reference materials (gas mixture, pure gas, carbonate, …) used to ensure traceability to VPDB and VPDB-CO_2, including those employed inside the laboratory as well as outside if relevant (traceability obtained from another laboratory).
- Values of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the reference materials listed above, expressed preferably as isotope delta in per mil on the VPDB and VPDB-CO_2 scales.
- Name of any laboratory included in the traceability chain.
- Number of calibration steps between the higher order reference material (closest to the scale) and the transfer standards sent for CCQM-P239.
- Corrections applied to the isotope ratios as measured by your analytical instrument (for example ratios between signals measured at different masses by an IRMS, or ratios between the areas measured on two different peaks of the spectrum by an optical analyser).
- Values of reference data impacting the measurement results, for example conventional values of the isotope ratios included in the definition of the VPDB scale

CSIRO values for the transfer standards were based on i) measurements against a Working Reference gas analysed on the same dates and ii) periodic comparisons of the WR against a primary JRAS CO2-in-air standard supplied by the WMO CCL at MPI-BGC.

2) Uncertainty budget

[Instructions below may be removed]

Explain here how the uncertainties associated with the measurement results were obtained. Describe the sources of uncertainty identified, their values, and how they were combined. Examples of sources are the calibration performed by another laboratory, the repeatability of successive measurements, the reproducibility of measurements performed on different days, drift of the values, data treatment and corrections applied to the measurement results.

The uncertainty of each individual measurement is dynamically determined from a combination of the measurement uncertainty of the sample, the uncertainty assigned to the Working Reference gas on the analysis day, and the uncertainty of the value assigned to the WR gas on the VPDB-CO2 scale by the WMO CCL at MPI-BGC.

The components of uncertainty given below are: d13c (d18O).
TYPE B COMPONENTS

U1: Uncertainty assigned to the value of the Primary CO2-in-air standard assigned by MPI-BGC: 0.012 ‰ (0.018 ‰)

U2: Uncertainty assigned (standard error) to the Working Reference CO2-in-air standard (WR) by direct, or indirect, measurement against the Primary CO2-in-air standard, includes U1 assigned: 0.021 ‰ (0.042 ‰) – typical values that are fixed following calibration.

TYPE A COMPONENTS

U3: Uncertainty from variability (standard deviation) of aliquots of the WR during a sequence of measurements: 0.01 ‰ (0.02 ‰) - typical values.

U4: Uncertainty of measurement of a single sample (standard deviation of the repeat cycles of the measurement): 0.01 ‰ (0.02 ‰) – typical values.

TOTAL UNCERTAINTY

Total Uncertainty (U5) for a single measurement determined as: sqrt (U4*U4 +U3*U3 + U2*U2): 0.03 ‰ (0.05 ‰) – typical values.

Measurement Uncertainty for “tank value” from multiple measurements = stderr(n measurements) combined with average of U5 values: 0.03 ‰ (0.06 ‰) – typical values.

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

[Instructions below may be removed]

As explained in section 3.2 of the protocol, standards shall have a dry air matrix, which can be either *scrubbed real air* or *synthetic air* (blended from pure gases). Provide here any useful information on the gas mixture composition which is not already provided in the accompanying result form.

Cylinder CA04924 contains dry natural air. Cylinder CA07700 contains dry natural air spiked with small quantities of pure CO_2 and pure N_2O.

4) Mixtures preparation

[Instructions below may be removed]

If the mixtures were prepared in your laboratory, describe here the preparation method, including information on the sources of pure gases (with a particular attention to carbon dioxide), the purity of the gases, how they were mixed, and any relevant detail on materials or treatment employed to obtain the mixtures.

If the mixtures were prepared in another laboratory, report here the information provided by this laboratory regarding the mixtures' preparation.

Both mixtures were prepared at CSIRO's clean air facility at Cape Schanck, VIC, Australia, using a Rix-SA3 clean air compressor and magnesium perchlorate drying.

5) Verification of mixtures

[Instructions below may be removed]

As described in section 5 of the protocol, participants should perform a verification of their mixtures before and after shipment. Describe here the verification procedure, including information on the dates of the measurements, the analytical instruments, their calibration, the calculations performed to obtain the measurements results. A comprehensive description of the

isotope ratios measurements is the most important, but relevant information on the amount fractions measurements is also valuable.

Measurements reported for these mixtures were obtained using CSIRO's established isotope ratio mass spectrometry (CO_2 isotopes) and gas chromatography (CO_2 and N_2O) instruments. Isotopic values are the mean of all measurements over the life of the mixtures, i.e. from 2002-25 for CA04924 and 2009-25 for CA07700. They are reported on the VPDB-CO2 scale as established using a suite of ambient air tanks calibrated against a high-pressure tank of air that was value assigned on the VPDB-CO2 scale at MPI-BGC, the WMO CCL for CO2 stable isotopes, using their JRAS procedure.

Mole fraction values are the mean of measurements from 2024 for CA04924 and 2023-25 for CA07700. Their calibration traces back to CSIRO's primary standards that were calibrated at NOAA, with assignments on the WMO X2019 CO2 and NOAA-2006A N2O scales.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**Environment & Climate Change Canada (ECCC)**
Contact	**Lin Huang**
Email	lin.huang@ec.gc.ca; Alina.Chivulescu@ec.gc.ca

Transfer Standards (cylinders) Information		
Number of standards	3	

Standard #	ID (Serial Number)		Date of preparation		Pressure	(unit)
1	AES085		**2024.08.13**		**1700**	(psi)
2	CC342919		**2024.08.14**		**1750**	(psi)
3	CB09882		**2024.08.15**		**1660**	(psi)
4						

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239
Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)
This result form aims at recording measurement results
More details on standards and methods shall be reported in the CCQM-P239 Information Sheet
A complete version of this result form shall be sent ***prior to measurements at the BIPM.***
Measurements of the participant's standards by the BIPM will start only when this form is recived.
An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor k .

"The CO_2 from the three cylinders was extracted, sealed into ampoules, and analyzed on the MAT253 together with NBS19, NBS18, and two laboratory carbonate standards (Cal1 and Cal2). NBS19-CO2 is used, as the anchor to link the isotopic composition of air CO_2 to the primary VPDB-CO_2 scale, the results ($\delta^{13}C_{VPDB\text{-}CO2}$ & $\delta^{18}O_{VPDB\text{-}CO2}$) of the three cylinders were calculated. The procedures of extraction and IRMS analysis, for each individual cylinders, were performed three times between 2024 and 2025: (i) before sending to NOAA for concentration measurements (March 2024), (ii) after receiving from NOAA and before sending to BIPM (August 2024), and (iii) after receiving from BIPM (May 2025). The averages of these cylinders are reported below."

Average (all) 2004-2005, including all other lab's touchments.

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	k	$\delta^{18}O$	$U(\delta^{18}O)$	k
		permil	permil		permil	permil	
1	AES085 (n=7)	-35.551	0.028	1	-33.438	0.126	1
2	CC342919 (n=7)	-21.594	0.004	1	-16.573	0.090	1
3	CB09882 (n=7)	-8.540	0.005	1	-1.561	0.089	1

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

All the concentrations data below provided by NOAA in June 2024

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	AES085	420.58	0.23	1
2	CC342919	402.43	n/a	
3	CB09882	398.47	0.22	1

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

All the concentrations data below provided by NOAA in June 2024

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	AES085	334.40	1.04	
2	CC342919	359.44	n/a	
3	CB09882	358.08	1.11	

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells

(unit)

All the concentrations data below provided by NOAA in June 2024

Compound	N_2	O_2	Ar	CO (ppm)	CH4	Other
Standard #	(unit)	(unit)	(unit)	(ppm)	(ppb)	(unit)
1				297.40	2199.42	
2				143.20	1880.08	
3				349.50	2190.91	
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[CCQM-P239_Result Form v0.11_ECCC_20250917]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**ECCC** **Environment & Climate Change Canada**
Contact	**Lin Huang & Alina Chivulescu**
Email	**Lin.huang@ec.gc.ca; Alina.Chivulescu@ec.gc.ca;**

Transfer Standards (cylinders) Information		
Number of standards	3	

Standard #	ID (Serial Number)
1	AES085
2	CC342919
3	CB09882
4	

Mandatory information

1) Traceability of the measurement results

As indicated in section 2 of the protocol, the measurands are $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the CO_2 gas in the carbon dioxide in air mixture expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO_2 scales respectively. Explain here how the measurement results reported in the result form are traceable to these scales, including information on:

- Number and kind of reference materials (gas mixture, pure gas, carbonate, …) used to ensure traceability to VPDB and VPDB-CO_2, including those employed inside the laboratory as well as outside if relevant (traceability obtained from another laboratory).

  NBS19, NBS18, IAEA603, Cal1, Cal2,

- Values of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the reference materials listed above, expressed preferably as isotope delta in per mil on the VPDB and VPDB-CO_2 scales.

  NBS19:

  $\delta^{13}C_{NBS19/VPDB}$ = +1.95 ± 0.026 (2σ) permil
  $\delta^{18}O_{NBS19/PDB\text{-}CO2}$ = -2.2 ± 0.140 (2σ) permil

  NBS18:
  $\delta^{13}C_{NBS18/VPDB}$ = -5.059 ± 0.029 (2σ) permil
  $\delta^{18}O_{NBS18/PDB\text{-}CO2}$ = -22.947 ± 0.323 (2σ) permil

  Cal2:
  $\delta^{13}C_{Cal2/VPDB}$ = -2.598 ± 0.039 (2σ) permil
  $\delta^{18}O_{Cal2/PDB\text{-}CO2}$ = -12.650 ± 0.166 (2σ) permil

  Cal1:
  $\delta^{13}C_{Cal1/VPDB}$ = -45.810 ± 0.097 (2σ) permil
  $\delta^{18}O_{Cal1/PDB\text{-}CO2}$ = -22.125 ± 0.300 (2σ) permil

  The uncertainties above are based on the measurements of annual calibrations over 20 years.

  IAEA603 (2022-2025)
  $\delta^{13}C_{Cal1/VPDB}$ = 2.436 ± 0.020 (2σ) permil
  $\delta^{18}O_{Cal1/PDB\text{-}CO2}$ = -2.376 ± 0.173 (2σ) permil

  (The uncertainties for IAEA603 are based on the measurements of annual calibrations over 4 years; from 2022 to 2025).

- Name of any laboratory included in the traceability chain.

  N/A

- Number of calibration steps between the higher order reference material (closest to the scale) and the transfer standards sent for CCQM-P239.

  All the CCQM-P239 cylinders were measured against a working reference, pure CO_2 (APB2), together with the CO_2 from NBS19, NBS18, IAEA603, Cal1, and Cal2 carbonates, as well as JRAC-12 (a cylinder of air CO2 received on Sept. 17, 2011 from BGC-isoLab with assigned values: $\delta^{13}C_{VPDB\text{-}CO2}$ = 9.003± 0.011; $\delta^{18}O_{VPDB\text{-}CO2}$ = -2.287± 0.02).

  All the other standards, except for NBS19, are used quality control for the procedures. **Only NBS19** is directly used, as the primary anchor, in the calculation of CCQM-239 cylinders to link the measurements to the primary scale of VPDB-CO_2, as well as for other standards calculation, including JRAC-12.

  The JRAC-12 values relative to VPDB-CO_2 via using NBS19-CO_2 are -8.956 ± 0.012 (*k*=2), -2.089 ± 0.13 (*k*=2), respectively for $\delta^{13}C_{VPDB\text{-}CO2}$ and $\delta^{18}O_{VPDB\text{-}CO2}$. The differences between the assigned values by MPI-BGC-Isolab & ECCC measurements via NBS19 (2024-2025) are by ~ **0.05** permil for $\delta^{13}C_{VPDB\text{-}CO2}$, and ~ **0.2** permil for $\delta^{18}O_{VPDB\text{-}CO2}$.

- Corrections applied to the isotope ratios as measured by your analytical instrument (for example ratios between signals measured at different masses by an IRMS, or ratios between the areas measured on two different peaks of the spectrum by an optical analyser).

  No drifting corrections are applied, except for ^{17}O correction, N_2O correction.

- Values of reference data impacting the measurement results, for example conventional values of the isotope ratios included in the definition of the VPDB scale

  $[R_{NBS19CO2}/R_{VPDBCO2}]^{45}$: 1.001756367325

  $[R_{NBS19CO2}/R_{VPDBCO2}]^{46}$: 0.997806231013

  $R^{45}_{VPDBCO2}$: 0.011998806684

  $R^{46}_{VPDBCO2}$: 0.004185401492

  $R^{13}_{VPDBCO2}$: 0.011237200000

  $R^{18}_{VPDBCO2}$: 0.002088349077

  $R^{17}_{VPDBCO2}$: 0.000380803342

2) Uncertainty budget

[Instructions below may be removed]

Explain here how the uncertainties associated with the measurement results were obtained. Describe the sources of uncertainty identified, their values, and how they were combined. Examples of sources are the calibration performed by another laboratory, the repeatability of successive measurements, the reproducibility of measurements performed on different days, drift of the values, data treatment and corrections applied to the measurement results.

The uncertainty budget should be very similar to that of CCQM-P204, as both share the same traceability. Specifically, the extracted CO_2 from the CCQM-P239 cylinders will be measured together with NBS19-CO_2, using the same reference (APB2: pure CO_2). The overall uncertainty budget for air CO_2 samples is approximately as follows:

- $\delta^{13}C_{VPDB}$: ~ 0.03 permil (k=2)
- $\delta^{18}O_{VPDB\text{-}CO2}$: ~ 0.20 permil (k=2)

It should be noted that these values are larger than the average standard deviations associated with the measurements, as the uncertainties identified above include not only the carbonate–acid reactions, CO_2 extraction from carbonates, but also the IRMS analysis, as well as extraction from air CO_2 and other lab's cylinder's handling, thereby representing the entire uncertainty on the traceability path and . However, the cylinder (AES085), which shows much more negative values, has been identified larger uncertainties (~0.06 ‰, k = 2, for $\delta^{13}C_{VPDB-CO2}$, and 0.3 ‰, k = 2, for $\delta^{18}{}_{OVPDB-CO2}$ respectively)

The procedure for isotope measurements of CCQM-P239 cylinders were performed as follows:

The CO_2 from the three cylinders was extracted, sealed into ampoules, and analysed on the MAT253 together with the CO_2 from NBS19, NBS18, and two laboratory carbonate standards (Cal1 and Cal2), as well as the JRAC-12 cylinder. NBS19-CO_2 is used, as the only anchor to link the isotopic composition of air CO_2 to the primary VPDB-CO_2 scale, the results ($\delta^{13}C_{VPDB\text{-}CO2}$ & $\delta^{18}O_{VPDB\text{-}CO2}$) of the three cylinders were calculated. The procedures of extraction and IRMS analysis, for each individual cylinders, were performed three times between 2024 and 2025: (i) before sending to NOAA for concentration measurements (March 2024), (ii) after receiving from NOAA and before sending to BIPM (August 2024), and (iii) after receiving from BIPM (May 2025). The averages (2024-2025) of these cylinders are reported to BIPM.

NBS18, Cal1 & Cal2 are used only for quality control.

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

[Instructions below may be removed]

As explained in section 3.2 of the protocol, standards shall have a dry air matrix, which can be either *scrubbed real air* or *synthetic air* (blended from pure gases). Provide here any useful information on the gas mixture composition which is not already provided in the accompanying result form.

Cylinders ID: AES085 (made by Scott-Marrin on March 11, 2013)

Pressure (PSI): 1710

CO_2 (ppm): 420.58

N_2O (ppb): 334.40

CH_4 (ppb): 2199.42

CO (ppm): 297.40

It was likely made from scrubbed real air (dry air) & mixed with fossil fuel CO_2, though the specific information for the matrix is not available.

Cylinders ID: CC342919 (made by Scott-Marrin in 2015)

Pressure (PSI): 1750

CO_2 (ppm): 402.43

N_2O (ppb): 359.44

CH_4 (ppb): 1880.08

CO (ppm): 143.20

It was likely made from scrubbed real air (very dry) and mixed with certain amount of fossil fuel CO_2, though the specific information for the matrix is not available.

Cylinders ID: CB09882 (made by NOAA on January 24, 2014)

Pressure (PSI): 1670

CO_2 (ppm): 398.47

N_2O (ppb): 358.09

CH_4 (ppb): 2190.91

CO (ppm): 349.50

It was made from scrubbed real air (very dry) at Niwot Ridge, Colorado, US

4) Mixtures preparation

[Instructions below may be removed]

If the mixtures were prepared in your laboratory, describe here the preparation method, including information on the sources of pure gases (with a particular attention to carbon dioxide), the purity of the gases, how they were mixed, and any relevant detail on materials or treatment employed to obtain the mixtures.

If the mixtures were prepared in another laboratory, report here the information provided by this laboratory regarding the mixtures' preparation.

See above in section 3.

5) Verification of mixtures

[Instructions below may be removed]

As described in section 5 of the protocol, participants should perform a verification of their mixtures before and after shipment. Describe here the verification procedure, including information on the dates of the measurements, the analytical instruments, their calibration, the calculations performed to obtain the measurements results. A comprehensive description of the isotope ratios measurements is the most important, but relevant information on the amount fractions measurements is also valuable.

- All the concentration data provided above in section 3 were performed by NOAA GHGs calibration group in June 2024.
- The results of $\delta^{13}C$ & $\delta^{18}O$ by ECCC are referred to the excel file: CCQM-P239 Results Form v0.11_ECCC_20250917

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**IAEA**
Contact	**Federica Camin**
Email	f.camin@iaea.org

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D208032 (INRiM 1A)	2024-07-01	100.00	bar
2	D208034 (INRiM 2A)	2024-07-05	100.00	bar
3	***	***		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D208032	1.266	0.017	1
2	D208034	-42.415	0.015	1
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D208032	-7.562	0.053	1
2	D208034	-34.962	0.050	1

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D208032 (IN	410.3	1.4	2
2	D208034 (IN	411.2	1.4	2
3				
4				

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D208032 (IN	\	\	
2	D208034 (IN	\	\	
3				
4				

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar			
Standard #	mol/mol	mol/mol	mol/mol			
1	0.7818	0.2085	0.0092			
2	0.7825	0.2079	0.0091			
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[*Name of result form*]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**IAEA**
Contact	**Federica Camin**
Email	**F.camin@iaea.org**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	**ID (Serial Number)**
1	D208032
2	D208034
3	
4	

Mandatory information

1) Traceability of the measurement results

- For each cylinder, three extractions of CO_2 were performed, with at least 3 replicates of analysis for each extraction, using DI-IRMS (MAT253).
- The extraction of CO_2 from the sample is achieved using an off-line vacuum line with liquid nitrogen cryotraps.
- The reference material used for calibration was CO_2 released from IAEA-603 using an acid-reaction based carbonate preparation system. The considered values are $\delta^{13}C$: +2.46 (0.01) ‰; $\delta^{18}O$ -2.37 (0.04) ‰, on the VPDB and VPDB-CO_2 scales.
- The corrections included on the dual-inlet system are:
    1. Cross-contamination corrections according to Meijer et al., 2000, with the longest idle time set at 250 s, and the idle time of the analysis method set at 15 s.
    2. ^{17}O corrections, according to Brand et al. (2010), with the iteration approach without approximations, using the following parameters:

λ	0.528
K	0.01022461
$^{13}R_{VPDB}$	0.01118
$^{17}R_{VPDB\text{-}CO2}$	3.931E-4
$^{18}R_{VPDB\text{-}CO2}$	2.08835E-3

    3. Drift effect was not significant, so the drift correction was not applied.

2) Uncertainty budget

The combined uncertainty derives from the standard deviation of repeatability when analysing the reference material (u_{rR}), the uncertainty of the reference material (u_{RM}), the uncertainty of the cross-contamination correction factor (u_{η}), and the standard deviation of repeatability when analysing the sample (u_{rS}).

Uncertainties of the different sources for the 3 extractions

ID	D208032		D208034	
Isotopes	U(δ^{13}C)	U(δ^{18}O)	U(δ^{13}C)	U(δ^{18}O)
urR	0.008	0.022	0.008	0.022
uRM	0.010	0.040	0.010	0.040
uη	0.000	0.001	0.001	0.002
urS	0.011	0.027	0.009	0.020
Combined U	**0.017**	**0.053**	**0.015**	**0.050**

To combine them, the root sum square of all the uncertainty was used.

$$\text{Combined U} = \sqrt{u_{rR}^2 + u_{RM}^2 + u_{\eta}^2 + u_{rS}^2}$$

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

Mixtures were prepared with dry synthetic air. It was proved to be without N_2O gas. Details are provided in the result form.

4) Mixtures preparation

The mixtures were prepared by INRiM, gravimetrically by adding CO_2 from a more concentrated parent mixture, and then sequentially adding Argon, O_2 and N_2.

5) Verification of mixtures

The composition of the mixture was not verified.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**Istituto Nazionale di Ricerca Metrologica (INRiM)**
Contacts	**Francesca Rolle, Stefano Pavarelli**
Email	**f.rolle@inrim.it, s.pavarelli@inrim.it**

Transfer Standards (cylinders) Information		
Number of standards	3	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D208036 (INRiM 1C)	2024-07-12	100	bar
2	D208039 (INRiM 2D)	2024-07-26	100	bar
3	D208041 (INRiM 12B)	2024-08-09	100	bar

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	**D208036 (INRiM 1C)**	1.36	0.22	2
2	**D208039 (INRiM 2D)**	-42.30	0.20	2
3	**D208041 (INRiM 12B)**	-21.08	0.34	2
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1		\		
2		\		
3		\		

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	**D208036 (INRiM 1C)**	412.6	1.4	2
2	**D208039 (INRiM 2D)**	410.2	0.8	2
3	**D208041 (INRiM 12B)**	412.9	1.3	2

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	\	\	\	
2	\	\	\	
3	\	\	\	

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	mol/mol	mol/mol	mol/mol	(unit)	(unit)	(unit)
1	0.7824	0.2080	0.0092			
2	0.7826	0.2079	0.0091			
3	0.7825	0.2078	0.0092			

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

CCQM-P239_Result Form INRiM_v1

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information			
Institute	**Istituto Nazionale di Ricerca Metrologica**	**INRiM**	
Contact	**Francesca Rolle**	***	**Stefano Pavarelli**
Email	**f.rolle@inrim.it**	***	**s.pavarelli@inrim.it**

Transfer Standards (cylinders) Information		
Number of standards	3	

Standard #	ID (Serial Number)
1	**D208036 (INRiM 1C)**
2	**D208039 (INRiM 2D)**
3	**D208041 (INRiM 12B)**
4	

Mandatory information

1) Traceability of the measurement results

The 3 gas mixtures were prepared for the comparison starting from 2 pure gas sources of CO_2, one having a depleted $\delta^{13}C$-CO_2 value and one having an enriched $\delta^{13}C$-CO_2 value. The CO_2 sources were purchased from SIAD (Italy), and the cylinders were filled to 30 bar, to keep the pure CO_2 in gaseous form to reduce possible fractionation inside the 50 L-cylinders.

The pure CO_2 sources had been previously sampled in 1 L-gas flasks, prior to the preparation of the diluted CO_2 mixtures in synthetic air, and these flasks were sent to the Max Planck Institute for Biogeochemistry (MPI-BGC) for the value assignment by IRMS and to obtain the traceability to the VPDB scale [1].

The assigned values of the two pure CO_2 sources measured at MPI-BGC and the associated expanded uncertainties are reported in table 1. The values for $\delta^{18}O$ are reported for completeness, even if it was not possible to measure them at INRiM in the CO_2 in synthetic air transfer standards prepared for the comparison.

Pure gas	**$\delta^{13}C$-CO_2 VPDB, [‰]**	**Expanded uncertainty $U(\delta^{13}C)$, [‰] (k = 2)**	**$\delta^{18}O$-CO_2 VPDB-CO2, [‰]**	**Expanded uncertainty $U(\delta^{18}O)$, [‰] (k = 2)**
Enriched CO_2 (1)	1.255	0.036	-7.880	0.052
Depleted CO_2 (2)	-42.429	0.034	-35.436	0.070

Table 1: assigned values of the two pure CO_2 sources measured at MPI-BGC and the associated expanded uncertainties (k = 2)

The pure sources were used for the preparation on the CO_2 in air gas standards, following the preparation scheme in Annex 1.

The certified values reported in table 1 were also used as reference for the subsequent analytical verification carried out by means of a Cavity Ring-Down spectrometer (CRDS G2131-i, Picarro, USA). This analyser allows the direct measurement of $\delta^{13}C$-CO_2, and requires a calibration with gas standards of CO_2 in air at known $\delta^{13}C$-CO_2. For the verification step, a calibration approach based on two gas standards bracketing the $\delta^{13}C$-CO_2 values of the prepared gas mixtures was applied. The analysis function was calculated according to the model equation (1), by using the Calibration Curves Computing (CCC) software, developed at INRiM [2]:

$$y = a + bx \qquad (1)$$

where:

y is the calculated value of $\delta^{13}C$-CO_2 (‰) in the transfer standard;

a is the intercept of the analysis curve;

b is the slope of the analysis curve;

x is the average of repeated readings (n = 100) of the CRDS analyser.

The $\delta^{13}C$-CO_2 values assigned to the transfer standards are the average of 4 repeated measurements for each mixture. Additional details are given in section 5. The information on the calibration mixtures used for each calibration curve is reported in table 6. The calibration mixtures were previously prepared at INRiM during the EMPIR projects 16ENV06 "SIRS" and 19ENV05 "STELLAR" in 5 L high-pressure cylinders, and their isotopic values were certified by IRMS at MPI-BGC on aliquots sampled in 1 L-glass flasks [3, 4]. The gas used for the calibration of the CRDS was sampled directly from the 5 L high-pressure cylinders, during each analysis sequence. The optimal gas flow to the CRDS was previously tested and was controlled by means of a calibrated Mass Flow controller. The stability of the calibration mixtures was tested over a period of 4 years, by periodically repeating the verification of their isotopic composition.

2) Uncertainty budget

For each of the 4 verifications carried out on the transfer standards, the measurement uncertainty was evaluated by applying the Law of propagation of uncertainty (LPU) to the eq. (1). The CCC software allows to calculate the uncertainties of the coefficients a and b of the analysis curve, taking into account the uncertainty of the calibration mixtures and the repeatability of the CRDS readings. The covariance term between the coefficients a and b was also considered.

An example of uncertainty budget for a single verification of a transfer standard is reported in table 2.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**	$\delta y/\delta x_i$	**Contribution to $u(y)$** $\lvert\delta y/\delta x_i\rvert \cdot u(x_i)$
$u(a)$	Uncertainty associated to the intercept of the linear regression (analysis curve)	0.059 ‰	1.0	0.059 ‰
$u(b)$	Uncertainty associated to the slope of the linear regression (analysis curve)	0.0088 ‰	2.8	0.025 ‰
$u(x)$	Uncertainty of measurement of the $\delta^{13}C$-CO_2 by CRDS	0.12 ‰	0.9	0.11 ‰
$cov(a, b)$	Covariance among the parameter of the analysis curve	0.00025		0.0014 ‰
$u_c(y)$				0.13 ‰
$U(y)$				0.26 ‰
y ($\delta^{13}C$-CO_2)				1.41 ‰

Table 2: Example of uncertainty budget for the $\delta^{13}C\text{-}CO_2$ value obtained from a single verification of mixture INRiM 1C (D208036), analytically determined via CRDS.

The uncertainty associated to the assigned $\delta^{13}C\text{-}CO_2$ for each transfer standard was evaluated by combining the contributions deriving from:

- the standard deviation of the 4 final values obtained from the verification by CRDS, to take into account the reproducibility of the CRDS, as dispersion of the 4 estimates of $\delta^{13}C\text{-}CO_2$ (s_{repr});

- the average of the standard deviation of the mean of each estimate (obtained from 100 data), to account for the repeatability of each measurement sequence by CRDS (s_{repeat}).

The following equation (2) was applied:

[redacted] (2)

In the following tables, the uncertainty budgets for the three cylinders sent to BIPM (INRiM 1C, INRiM 2D and INRiM 12B), are reported.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**
u_{repr}	Uncertainty associated to CRDS reproducibility	0.07 ‰
u_{repeat}	Uncertainty associated to CRDS repeatability	0.13 ‰
$u_c(y)$		0.11 ‰
$U(y)$ $(k = 2)$		0.22 ‰
y ($\delta^{13}C\text{-}CO_2$)		+1.36 ‰

Table 3: uncertainty budget for the transfer standard INRiM 1C (D208036)

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**
u_{repr}	Uncertainty associated to CRDS reproducibility	0.05 ‰
u_{repeat}	Uncertainty associated to CRDS repeatability	0.12 ‰
$u_c(y)$		0.10 ‰
$U(y)$ $(k = 2)$		0.20 ‰

y **($\delta^{13}C$-CO_2)**		-42.30 ‰

Table 4: uncertainty budget for the transfer standard INRiM 2D (D208039)

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty,** $u(x_i)$
u_{repr}	Uncertainty associated to CRDS reproducibility	0.20 ‰
u_{repeat}	Uncertainty associated to CRDS repeatability	0.14 ‰
$u_c(y)$		0.17 ‰
$U(y)$ **(*k* = 2)**		0.34 ‰
y **($\delta^{13}C$-CO_2)**		-21.08 ‰

Table 5: uncertainty budget for the transfer standard INRiM 12B (D208041)

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

The three cylinders prepared for the comparison are in synthetic air, made up from pure gases (Ar 7.0, O_2 6.0 and N_2 6.0). No N_2O was added to the air matrix.

The transfer standards prepared and submitted for the pilot study are representative of the reference gas mixtures prepared at INRiM to support laboratories carrying out measurements of the isotopic composition of CO_2 by means of spectroscopic techniques and to support, on a larger scale, measurements in the field of climate change monitoring. The tolerances on the matrix composition of the three standards are in agreement with the matrix composition requirements of the Key Comparison CCQM-K120.b, and in agreement with the most stringent requirement of the P239 protocol only for Ar. O_2 and N_2 are, at present, slightly out of these stringent ranges.

4) Mixtures preparation

Each pure source was diluted in pure N_2 to prepare a first parent mixture having a nominal amount fraction of 8 % mol/mol; a second parent mixture was then prepared to reach the nominal amount fraction of 0.5 % mol/mol. These two dilution steps were carried out using pure N_2 6.0 (Air Liquide) as matrix gas. The final mixture, having a nominal amount fraction of 410 µmol/mol, was then prepared in synthetic air by mixing pure Ar, O_2 and N_2. Ar was 7.0 purity grade (Linde), while O_2 and N_2 6.0 purity grade (Air Liquide). According to the manufacturers' specifications, pure gases have CO_2 impurities lower than 0.1 µmol/mol. No N_2O was added to the air matrix.

Following the above-mentioned procedure, two transfer standards were prepared, one from each pure CO_2 source (INRiM 1C, D208036, +1.3 % and INRiM 2D, D208039, -42 ‰). A third mixture (INRiM 12B, D208041) was prepared by blending the two CO_2 sources, targeting an intermediate $\delta^{13}C$ value (-21 ‰). The blending of the CO_2 was carried out by mixing gravimetrically aliquots of the two parent mixtures of CO_2/N_2 at 8 % mol/mol, to optimise the performances of the INRiM gravimetric facility and mass comparator.

5) Verification of mixtures

The verification of the transfer standards carried out before shipment was performed by means of CRDS. This analyser allows the direct measurement of $\delta^{13}C$-CO_2, and requires a calibration with gas standards of CO_2 in air at known $\delta^{13}C$-CO_2. For the verification step, a calibration approach based on two gas standards bracketing the $\delta^{13}C$-CO_2 values of the prepared gas mixtures was applied, as reported in section 1.

The details of the calibration standards for each calibration curve are reported in table 6. The $\delta^{13}C$-CO_2 values of the calibration mixtures were assigned via IRMS at MPI-BGC [3, 4] and are reported with their expanded uncertainties ($k = 2$).

	$\delta^{13}C$-$CO_{2\ VPDB}$, [‰]	**$U(\delta^{13}C$-$CO_{2\ VPDB})$, [‰]**
INRiM 1C		
Gas standard 1	1.314	0.026
Gas standard 2	-9.741	0.028
INRiM 2D		
Gas standard 1	-19.558	0.018
Gas standard 2	-42.033	0.020

INRiM 12B		
Gas standard 1	-9.741	0.028
Gas standard 2	-42.033	0.020

Table 6: details of the calibration standards used for the calibration of the CRDS. The $\delta^{13}C$-CO_2 values of the calibration mixtures were assigned via IRMS at MPI-BGC and are reported with their expanded uncertainties ($k = 2$).

The transfer standards were verified on different days in September 2024. The $\delta^{13}C$-CO_2 values assigned to the mixtures by CRDS show a bias of about 0.1 ‰ with respect to the values measured at MPI-BGC on the pure CO_2 parent gases. This phenomenon had already been observed for the measurements carried out within both SIRS and STELLAR projects, with different measurement techniques (IRMS and various OIRS techniques). The reason of this bias had not been clarified yet, but it could be related to fractionation effects occurring during the dilution process from pure CO_2 to the atmospheric amount fraction mixtures.

The CO_2 amount fraction of the 3 transfer standards was assigned gravimetrically following the prescriptions of the International Standard ISO 6142-1 [5]. The mixtures were verified by Non-dispersive infrared (NDIR) spectroscopy (URAS 14, ABB, Switzerland). The verification was carried out with a three-point calibration with independent calibration mixtures according to the International Standard ISO 6143 [6]. The associated uncertainty was evaluated by using the following equation (3), taken from [5].

$$u\left(x_{CO_2,cert}\right) = \frac{1}{2}\sqrt{u^2(x_{CO_2,prep}) + u^2(x_{CO_2,ver}) + (x_{CO_2,prep} - x_{CO_2,ver})^2}$$

Where:

$u(x_{CO2,cert})$ is the uncertainty associated to the amount fraction of the transfer standards;

$u(x_{CO2,prep})$ is the uncertainty of the gravimetric preparation value, $x_{CO2,prep}$;

$u(x_{CO2,ver})$ is the uncertainty of the NDIR verification value, $x_{CO2,ver}$.

References:

[1] H. Qi, H. Moossen, H.A.J. Meijer, et al "USGS44, a new high-purity calcium carbonate reference material for δ13C measurements", Rapid Commun Mass Sp, (2021), Volume 35, Issue 4, https://doi.org/10.1002/rcm.9006

[2] CCC Software: https://www.inrim.it/en/services/software-and-databases/ccc-software

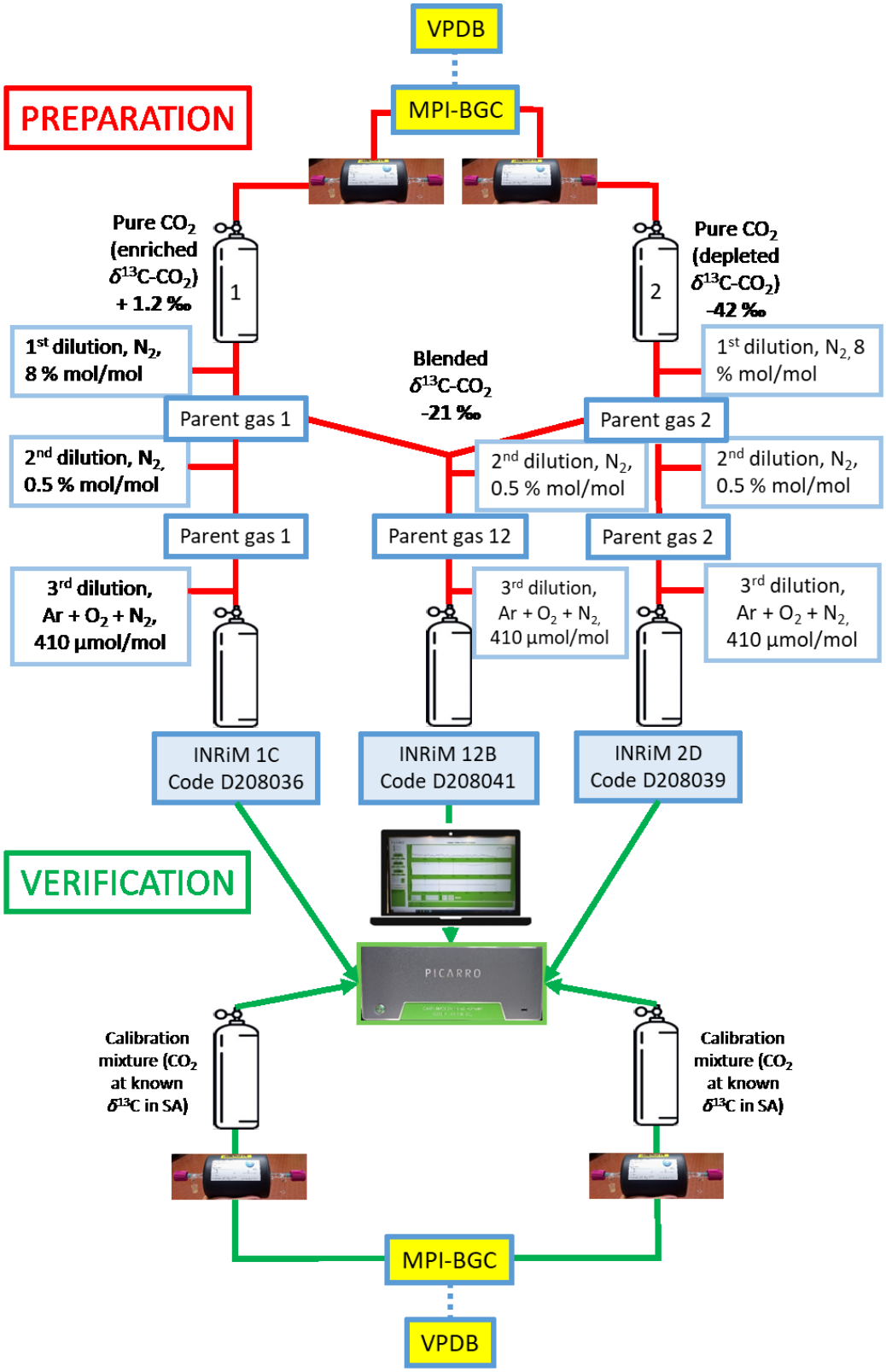
[3] M. Wendeberg, J.M. Richter, M. Rothe, W.A. Brand, "Jena reference air set (JRAS): a multi-point scale anchor for isotope measurements of CO_2 in air", Atmos Meas Tech. (2013), 6(3):817–822, doi:10.5194/amt-6-817-2013

[4] H. Moossen, "JRAS-06: keeping up with changing internationaly-distributed stable isotopic reference materials". 19th WMO/IAEA meeting on carbon dioxide, other greenhouse gases, and related measurement techniques (GGMT-2017); (2017), Empa Dubendorf. Switzerland: WMO; 2016

[5] International Standard ISO 6142-1:2015 “Gas analysis — Preparation of calibration gas mixtures. Part 1: Gravimetric method for Class I mixtures”, ISO, Geneva

[6] International Standard ISO 6143:2001 “Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”, ISO, Geneva

ANNEX 1:


VPDB
MPI-BGC
PREPARATION
Pure CO_2 (enriched $\delta^{13}C$-CO_2) + 1.2 ‰
1
Pure CO_2 (depleted $\delta^{13}C$-CO_2) -42 ‰
2
1st dilution, N_2, 8 % mol/mol
Blended $\delta^{13}C$-CO_2 -21 ‰
1st dilution, N_2, 8 % mol/mol
Parent gas 1
Parent gas 2
2nd dilution, N_2, 0.5 % mol/mol
2nd dilution, N_2, 0.5 % mol/mol
2nd dilution, N_2, 0.5 % mol/mol
Parent gas 1
Parent gas 12
Parent gas 2
3rd dilution, Ar + O_2 + N_2, 410 µmol/mol
3rd dilution, Ar + O_2 + N_2, 410 µmol/mol
3rd dilution, Ar + O_2 + N_2, 410 µmol/mol
INRiM 1C Code D208036
INRiM 12B Code D208041
INRiM 2D Code D208039
VERIFICATION
PICARRO
Calibration mixture (CO_2 at known $\delta^{13}C$ in SA)
Calibration mixture (CO_2 at known $\delta^{13}C$ in SA)
MPI-BGC
VPDB

ANNEX 2:

Measurement results at INRiM after shipping to BIPM

1) Verification of mixtures

A verification approach, based on the "exact matching", was applied for the measurements carried out after the return of the cylinders from BIPM in July-August 2025, following the equation (3):

$$\delta_{a,calc} = \frac{\delta_{a,meas} \cdot \delta_{ref,cert}}{\delta_{ref,meas}} \quad (3)$$

where:

$\delta_{a,calc}$ is the calculated $\delta^{13}C\text{-}CO_2$ value (‰) of the transfer standard;
$\delta_{a,meas}$ is the measured $\delta^{13}C\text{-}CO_2$ value (‰) of the transfer standard;
$\delta_{ref,cert}$ is the certified $\delta^{13}C\text{-}CO_2$ value (‰) of the mixture used as a reference;
$\delta_{ref,meas}$ is the measured $\delta^{13}C\text{-}CO_2$ value (‰) of the mixture used as a reference.

A prerequisite for the exact matching approach is that the reference mixture and the transfer standards have close $\delta^{13}C\text{-}CO_2$ and CO_2 amount fraction values within 10 %. Upon the return to INRiM of the transfer standards, they were verified with respect both to reference mixtures used in 2024 and to new reference mixtures prepared ad hoc by gravimetry in July 2025 at $\delta^{13}C\text{-}CO_2$ nominal values of +1.3 ‰ and -42 ‰. The following table reports the information on the gas mixtures used as reference for each transfer standard.

	$\delta^{13}C\text{-}CO_{2\ VPDB}$, [‰]	**$U(\delta^{13}C\text{-}CO_{2\ VPDB})$, [‰]**
INRiM 1C		
Gas standard 1	1.323	0.028
Gas standard 2	1.323	0.028
Gas standard 3(*)	1.355	0.030
INRiM 2D		
Gas standard 1	-42.048	0.026
Gas standard 2(*)	-42.329	0.040
INRiM 12B		
Gas standard 1	-19.578	0.028
Gas standard 2	-19.756	0.028

(*) Freshly prepared

The transfer standards were verified on different days in July-August 2025. The verification value of each transfer mixture is the weighted mean of 3 repetitions for mixtures at nominal values of +1.3 ‰ and -42 ‰ and 2 repetitions for the mixture at nominal value of -20 ‰. Each repetition was obtained by the average value of 3 analytical runs of 100 data.

2) Uncertainty budget

For each repetition on each transfer standard, the measurement uncertainty was evaluated by applying the Law of propagation of uncertainty (LPU) to the eq. (3), considering 3 analytical runs of 100 data each, as above mentioned. An example of uncertainty budget for 1 of the 3 $\delta^{13}C\text{-}CO_2$ values for the mixture INRiM 1C (D208036), analytically determined via CRDS, is reported in the following table.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty,** $u(x_i)$	$\delta y/\delta x_i$	**Contribution to** $u(y)$ $\lvert\delta y/\delta x_i\rvert \cdot u(x_i)$
$u(\delta_{a,meas})$	Uncertainty associated with the CRDS repeatability for the analysis of the transfer standard	0.075 ‰	0.774	0.058 ‰
$u(\delta_{ref,cert})$	Uncertainty associated with the certified value of the mixture used as a reference	0.014 ‰	1.029	0.014 ‰
$u(\delta_{ref,meas})$	Uncertainty associated with the CRDS repeatability for the analysis of the mixture used as a reference	0.062 ‰	-0.796	0.049 ‰
$u_c(\delta_{a,calc})$				0.077 ‰
$U(\delta_{a,calc})$				0.15 ‰
$\delta^{13}C\text{-}CO_2$ - $\delta_{a,calc}$				1.405 ‰

The weighted mean of the relevant repetitions (3 for mixtures at nominal values of +1.3 ‰ and -42 ‰, and 2 at nominal value of -20 ‰) was calculated together with the associated uncertainty, taking as weights the reciprocal of the corresponding square uncertainties. The consistency of the $\delta^{13}C\text{-}CO_2$ values that contribute to the weighted mean was checked by using the χ^2 test in accordance with [1]. This gave successful results for all the transfer standards. The following table reports an example of the calculations carried out to obtain the final $\delta^{13}C\text{-}CO_2$ value, δ_a, and its associated uncertainty for the transfer standard INRiM 1C (D208036).

$\delta^{13}C\text{-}CO_2$ - $\delta_{a,calc}$ ‰	$u(\delta_{a,calc})$ ‰	$1/u(\delta_{a,calc})^2$	$\delta_{a,calc} \cdot 1/u^2$	$(\delta_{a,calc} - \delta_a)^2/u^2$
1.345	0.081	152.4158	204.9992	0.003055
1.326	0.052	369.8225	490.3846	0.203834
1.405	0.077	168.6625	236.9708	0.519954
χ^2_{obs}				0.73
Degrees of freedom ν				2
$Pr(\chi^2(\nu) < \chi^2_{obs})$				0.70 (> 0.05)
$u_c(\delta_a)$				0.038 ‰
$U(\delta_a)$				0.076 ‰
$\delta^{13}C\text{-}CO_2$ - δ_a				1.349 ‰

References:

[1] M. G. Cox "The evaluation of key comparison data", Metrologia, (2002), Volume 39, 585-595. doi: 10.1088/0026-1394/39/6/10

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**INSTAAR**
Contact	**Sylvia Michel**
Email	sylvia.michel@colorado.edu

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	CC332697	2024 2 15	not recorded	
2	CA05791	2024 3 13	roughly ~2000 psi for all	
3	CA06475	2024 3 4		
4	CC87457	2024 3 13		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	CC332697	-8.92	0.02	
2	CA05791	-11.55	0.03	
3	CA06475	-9.46	0.02	
4	CC87457	-13.93	0.04	
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	CC332697	-1.21	0.04	
2	CA05791	-5.47	0.03	
3	CA06475	-1.95	0.03	
4	CC87457	-9.62	0.08	

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	CC332697	426.7		
2	CA05791	480.3		
3	CA06475	436.7		
4	CC87457	541.8		

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	CC332697	338.0		
2	CA05791	337.9		
3	CA06475	337.9		
4	CC87457	337.8		

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1	These cylinders are all natural air; some have additional CO2.					
2						
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

INSTAAR_CCQM-P239_Result Form v0.1 1.xls

Additional data can be seen in: INSTAAR_ccqm_2025.xls

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**Intitute of Arctic and Alpine Research**
Contact	**Sylvia Englund Michel**
Email	**Sylvia.michel@colorado.edu**

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	ID (Serial Number)
1	CC332697
2	CA05791
3	CA06475
4	CC87457

Mandatory information

1) Traceability of the measurement results

All INSTAAR d13CCO2 and d18OCO2 data are now reported on the JRAS-06 realization of the VPDB-CO2 scale. We have three primary working standards (WS) that have had three calibration episodes at the Max-Planck Institute for Biogeochemistry in Jena, Germany. They are

INSTAAR name	serial number	d13C	error	d18O	error
DEWY-001	CC324174	-8.61	0.017	-3.44	-0.018
LOUI-001	CA02758	-13.69	0.014	-12.22	-0.033
HUEY-001	ALM-052786	-45.37	0.012	-15.91	-0.028

The error in these cylinders is the pooled standard deviation of the three measurement episodes.

Our CCQM-P239 cylinders were measured directly against these standards.

Our data have five processing steps:

1) We correct for the fractionation of the monitoring gas as it is depleted from the reference bellows. The working standard (in this case DEWY-001), changes throughout the run because of fractionation through the dual inlet capillaries; therefore we correct for this drift.

2) Because N_2O is frozen in our trap along with CO_2 and is isobaric with CO_2, we apply a correction which is based on the N_2O/CO_2 ratio in our samples and standards. Because we are measuring CO_2-in-air samples against CO_2-in-air working standards, and because CO_2 and N_2O mole fractions are very accurately measured, this correction is quite small and extremely accurate.

3) We adjust our 'raw' values to VPDB-CO_2 using the assigned $\delta 45$ and $\delta 46$ values INSTAAR primary standards (prior to the oxygen-17 correction).

4) We correct for oxygen-17 in samples and standards using recommendations in Assonov and Brenninkmeijer (2003a,b). (This is indistinguishable from the Brand, Coplen, Assonov, 2010 algorithm.)

The values included in the calculation are as follows:

^{13}Rvpdb = 0.011180

^{17}Rvpdb = 0.0003931

^{18}Rvpdb = 0.00208835

lamda=0.528

5) We correct for scale contraction using our scale span standard, in this case, LOUI-001. (The other INSTAAR primary WS, HUEY-001, was used to calculate the uncertainty in the scale contraction.)

2) Uncertainty budget

The uncertainty in our tie to JRAS-06 is determined by the pooled standard deviation of the measurement episodes of the cylinders. I do not address the uncertainty of JRAS-06 to VPDB-CO_2.

We correct for the drift in the monitoring gas over the course of the run. This is typically on the order of a 0.1-0.2 ‰ correction over 50-60 samples. We do not correct for error in this correction in our uncertainty calculation, because we think it is very small.

Because the N_2O correction is so small, and because it is quite accurate (both the measurements of N_2O and CO_2 are accurate and precise, and the effect of ionization efficiency is so small), we do not explicitly account for the uncertainty here.

The oxygen-17 correction is as accurate as we can get it, and we do not account for its uncertainty explicitly.

We correct for known scale contraction using a secondary standard calibrated at MPI-BGC that has values depleted in the heavy isotopes of carbon and oxygen. To account for the error in the scale contraction, I used two different standards: first LOUI-001, and then HUEY-001. I calculated the difference between the two measurements, and used the standard deviation as the error in the scale contraction correction.

In a typical run, we use the reproducibility of a surveillance cylinder to account for analytical issues that cause measurement noise. In this case, we use the standard deviation of the measurement episodes. This accounts for trapping efficiency, heating/cooling of the trap, source cleanliness, pumping efficiency etc, as well as any small error in the drift, N_2O, and oxygen-17 correction.

Error due to the tie to JRAS-06, the scale contraction, and analytical reproducibility are added in quadrature to obtain the combined uncertainty.

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

INSTAAR measurements of $\delta^{13}C_{CO2}$ and $\delta^{18}O_{CO2}$ are described in Trolier et al., (1996), Vaughn et al. (2004) and a forthcoming publication (Michel et al., in preparation) but are described briefly here:

Air from a cylinder or flask is pulled through a mass flow controller set to 40 sccm for 10 min, through a beaded water trap in an ethanol bath chilled by an immersion cooler to -90° C, and into a cold trap at liquid nitrogen temperatures where CO_2 (and N_2O) are frozen onto a ¼" stainless steel trap. Other air components are pulled away by a scroll vacuum pump. After a ten-minute extraction period, followed by a turbo-vacuum "cleanup" of residual air over the frozen sample, the trap is heated by a resistive heating wire and the sample is expanded into the sample bellows of an Isoprime (Elementar) dual inlet mass spectrometer. The sample is allowed into the mass spectrometer and the bellows are compressed to reach a target beam of 5 nA (in times of low instrument sensitivity we target 4.0 or 4.5 nA). The reference bellows monitoring gas (CO_2 extracted from a cylinder of clean air collected at Niwot Ridge, Colorado) meets the target beam, and then reference and sample gases are iteratively sent into the ion source for isotopic measurement. Measurement consists of 12 ref/sam switches, with 20 seconds to waste, and 12 seconds of measurement. During each 6.5 minute measurement, extraction of the next sample begins, which maximizes efficiency. Following the principle of identical treatment, both samples and working standard (WS) follow the same extraction path and procedure.

3) Mixtures composition

Our standards are Niwot Ridge Air prepared by Stephen Devogel of NOAA GML. We targeted different isotopic ratios by spiking the cylinders with CO_2 depleted in the carbon-13 isotope. More information on cylinders can be found on the GML website (https://gml.noaa.gov/ccl/services.html) or by email request to Stephen.devogel@noaa.gov.

4) Mixtures preparation

[Instructions below may be removed]

If the mixtures were prepared in your laboratory, describe here the preparation method, including information on the sources of pure gases (with a particular attention to carbon dioxide), the purity of the gases, how they were mixed, and any relevant detail on materials or treatment employed to obtain the mixtures.

If the mixtures were prepared in another laboratory, report here the information provided by this laboratory regarding the mixtures' preparation.

Replace this text with your reply.

More information on mixtures preparation can be found on the GML website (https://gml.noaa.gov/ccl/services.html) or by email request to Stephen.devogel@noaa.gov.

5) Verification of mixtures

When our cylinders are returned, we will measure them on whatever instruments are available and running reliably, and we will use our INSTAAR primary standards. If there is any indication of drift, we will consider sending them back to NOAA for measurement of CO_2 and CH_4 mole fraction. In the case of any anomalous measurements, we would also consider measuring them on different instruments, in case the measurements indicate a new problem.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**Jožef Stefan Institute (JSI)**
Contact	**Bor Krajnc**
Email	bor.krajnc@ijs.si

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D208033 (INRiM 1B)	1.July 2024	130	bar
2	D208035 (INRiM 2B)	5. July 2024	105	bar
3	***	***		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D208033 (INRiM 1B)	1.20	0.02	1.00
2	D208035 (INRiM 2B)	-42.42	0.02	1.00
3	***			
4	***			
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D208033 (INRiM 1B)	-7.56	0.06	1.00
2	D208035 (INRiM 2B)	-34.53	0.11	1.00
3	***			
4	***			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D208033 (INRiM 1B)	412.6	1.4	2
2	D208035 (INRiM 2B)	411.4	1.4	2
3	***			
4	***			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D208033 (INRiM 1B)	\	\	\
2	D208035 (INRiM 2B)	\	\	\
3	***			
4	***			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1	0.7820	0.2084	0.0092			
2	0.7827	0.2077	0.0091			
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

CCQM-P239_Result Form v0.1 1_JSI

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**Jožef Stefan Institute**
Contact	**Bor Krajnc**
Email	**bor.krajnc@ijs.si**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)
1	D208033 (INRiM 1B)
2	D208035 (INRiM 2B)
3	
4	

Mandatory information

1) Traceability of the measurement results

Analyses was performed on Dual Inlet IRMS using one-point calibration with cross contamination correction as means for eliminating scale contraction/expansion

- Reference material for the analysis was pure CO_2 standard "Yoshi" calibrated against IAEA-603 via carbonate H_3PO_4 (104%) reaction at 25 °C. Three repetitions of refence material were measured during the daily sequence. "Yoshi" standard was calibrated at IAEA TERCL laboratories.

- The $\delta(^{13}C)$ and $\delta(^{18}O)$ values of the reference material used are −3.50 ± 0.03 ‰ (VPDB, k=2) for and −14.77 ± 0.12 ‰ (VPDB-CO_2, k=2) for carbon and oxygen, respectively.

- Calibration steps: IAEA-603 -> pure CO_2 RM "Yoshi" -> gas mixture standards sent for CCQM-P239.

- Final delta values were calculated from the IsoDat 2.0 output d45CO2/44CO2 and d46CO2/44CO2.

    - 1-point calibration according to Srivastava and Verkouteren (2018).

    - Cross-contamination correction: In accordance to Meijer et al., 2000. With 250 s idle time set as "true" value while 15 s was the idle time of the method for the analysis

    - ^{17}O correction: In accordance Brant et al. (2010) with the iteration approach without approximations and with the parameters (λ, K , scale zero point ratios) recommended.

- Conventional values of the isotope ratios included in the definition of the VPDB scale used for calculations were:
    - $\lambda = 0.528$
    - $K = 0.01022461$
    - $^{13}R_{VPDB} = 0.01118$
    - $^{17}R_{VPDB\text{-}CO2} = 0.0003931$
    - $^{18}R_{VPDB\text{-}CO2} = 0.00208835$

2) Uncertainty budget

Uncertainty components considered for combined uncertainty were the following:

- **Repeatability of reference material (u_{rR}^2):** Standard deviation of repetitions of measured RMs measured with the sample sequence

- **Uncertainty of the value of the reference material (u_{RM}^2):** The uncertainty assigned to the RM during its value assignment

- **Uncertainty of the cross-contamination correction factor (u_{η}^2):** Uncertainty of the cross-contamination correction factor (Srivastava and Verkouteren, 2018)

- **Repeatability of samples(u_{rS}^2):** Standard deviation of repetitions of measured samples

Uncertainty components were combined using the root of sum of squares:

$$\text{Combined U} = \sqrt{u_{rR}^2 + u_{RM}^2 + u_{\eta}^2 + u_{rS}^2}$$

D208033 Nominal $\delta(^{13}C)$ value: +1.4 ‰

	***U*(*δ*^{13}C)**	***U*(*δ*^{18}O)**
Repeatability of Reference material	0.014	0.012
Uncertainty of the value of the reference material	0.013	0.061
Uncertainty of the cross-contamination correction factor	0.000	0.003
Repeatability of samples	0.009	0.008
Combined	**0.021**	**0.063**

D208035 Nominal $\delta(^{13}C)$ value: −42.2 ‰

	***U*(*δ*^{13}C)**	***U*(*δ*^{18}O)**
Repeatability of Reference material	0.002	0.008
Uncertainty of the value of the reference material	0.013	0.061
Uncertainty of the cross-contamination correction factor	0.004	0.015
Repeatability of samples	0.016	0.084
Combined	**0.021**	**0.105**

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

Mixtures were prepared by Instituto Nazionale di Ricerca Metrologica (INRiM). Besides the information in the results form we have not much more information about the mixture composition and preparation. Except that they were prepared in the exactly same way as 16ENV06 SIRS project. If needed an internal report form the project exist and may be obtainable.

4) Mixtures preparation

As in previous section (Section 3)

5) Verification of mixtures

Preconcentration step:

Precontraction of CO_2 form the gas mixture was done on the vacuum line using liquid nitrogen (LN) cryotraps.

Setup was adopted after Werner and Brand (2001) but is modified in a way that last trap is detachable and the trapped sample is manually transported to the inlet of the IRMS.

The flow was controlled by a needle valve positioned after the regulator of the high-pressure cylinder. Gas mixture travelled first trough the water trap kept at −70 °C than trough LN trap for catching CO_2. After letting the right amount of gas mixture through, the trap was left on vacuum for to pump away the non-condensable gases. After that the trap was lifted from liquid nitrogen and left for thawing on room temperature for 20 minutes. A third, detachable trap, was than submerged into LN and valves were open to enable the transfer of CO_2 from the second trap. This trap was than detached from the vacuum line and after thawing it was attached to the inlet of the left bellow.

Amount of gas mixture needed to flow trough the trap was assessed from the pressure difference in a canister of a known volume and the time needed to achieve that difference. 6 L (laboratory conditions) of gas mixture was used for one sample.

Unfortunately, we have issues with the turbo pump therefore just rotary pump was used for the vacuum line. However, an additional liquid nitrogen trap was positioned on the way to the pump to enhance the line cleanings and to minimize the possibility of contamination.

Measurement:

Analysis of reference gas mixtures was performed on the Dual Inlet IRMS Thermo Finnigan™ DELTA^{plus}XP. The analysis was done in the week from 22 of November to 26 November 2024.

High voltage was set to 2.2 kV and the pressure of the sample in the bellows was set to maintain signal of 4000 mV on the mass 44.

Idle time was set to 15 s and integration time was set to 8 s. Number of cycles was set to 10.

All measurements were measured against working reference-CO_2 (WR-CO_2) gas filled in the reference bellow.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**KRISS**
Contact	**Han Jun, Eun**
Email	hjeun@kriss.re.kr

Transfer Standards (cylinders) Information		
Number of standards		

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D207634	2024-07-11	7.6	MPa
2	D207731	2024-07-11	8.8	MPa
3				
4				

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D207634	-8.90	0.12	2.00
2	D207731	-8.89	0.12	2.00
3				
4				
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D207634	-11.05	0.74	2.00
2	D207731	-11.21	0.74	2.00
3				
4				

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D207634	398.26	0.05	2.00
2	D207731	401.50	0.05	2.00
3				
4				

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D207634	341.25	0.11	2.00
2	D207731			
3				
4				

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells cmol/mol

Compound	N_2	O_2	Ar	CH_4	H_2O	Other
Standard #	cmol/mol	cmol/mol	cmol/mol	nmol/mol	µmol/mol	(unit)
1	78.03	20.98	0.95	1.99	0.29	
2	78.05	20.97	0.94	2.00	0.25	
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[CCQM-P239_Result Form v0.1 _KRISS.xlsx]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information		
Institute	**KRISS**	
Contact	**Kiryong, Hong**	**Han Jun, Eun**
Email	**khong@kriss.re.kr**	**hjeun@kriss.re.kr**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)
1	D207634
2	D207731

Mandatory information

1) Traceability of the measurement results

Reference material used in this measurement

The reference materials used in this measurement were prepared and filled with pure CO_2 at the BIPM between April 20 and May 2, 2023. The source materials were analyzed by the IAEA against the IAEA-603 carbonate reference material. The details are listed in Table 1.

Table 1. Isotope delta values of reference materials measured by the IAEA.

Cylinder	$\delta^{13}C_{VPDB}$	u_{anal} (k = 1)	$\delta^{18}O_{VPDB\text{-}CO2}$	u_{anal} (k = 1)
AL 44050	-1.473	0.015	-9.283	0.034
SIAD S0833813	-43.103	0.017	-36.108	0.037

* All values are expressed in ‰.

** The uncertainty does not include the uncertainty associated with the IAEA-603.

After the filling was completed, the isotope delta values for $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB\text{-}CO2}$ were re-analyzed by the BIPM. The re-analyzed isotope delta values for the reference material measured at the BIPM are shown in Table 2.

Table 2. Re-analyzed isotope delta values of reference materials assigned by the BIPM.

Cylinder	$\delta^{13}C_{VPDB}$	u_{anal} (k = 1)	$\delta^{18}O_{VPDB\text{-}CO2}$	u_{anal} (k = 1)
R9933 (from AL44050)	-1.479	0.009	-9.269	0.011
R9983 (from SIAD S0833813)	-43.107	0.009	-36.089	0.011

* All values are expressed in ‰.

** The uncertainty does not include the uncertainty associated with the IAEA measurements.

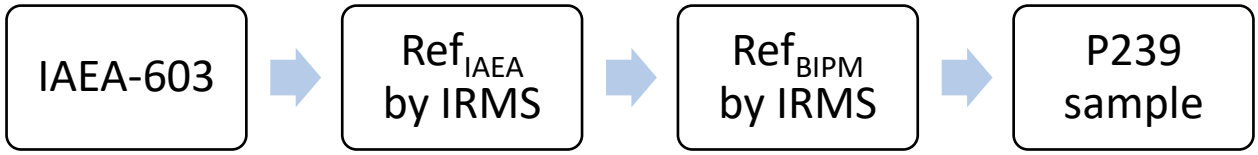


Figure 1. Traceability chain for isotope delta values of samples prepared by KRISS.

Ion corrections

To measure isotope delta values, the isotope ratio mass spectrometer (271 Ultra, Thermo Fisher) was used. Ideally, the assignment of the isotope delta values (δ values) would require measuring all

relevant isotopologues. However, in practice, only the mass-to-charge (m/z) ratios from 44 to 46 are typically measured, and the isotope delta values are calculated based on these measurements

The m/z 45 and 46 signals include isotopologues originating from the minor isotope ^{17}O. For example, the 45 m/z signal includes contributions from both $^{13}C^{16}O^{16}O$ and $^{12}C^{17}O^{16}O$, while the m/z 46 signal include contributions from both $^{12}C^{16}O^{18}O$, $^{13}C^{17}O^{16}O$, and $^{12}C^{17}O^{17}O$. To account for these contributions, an ion correction for ^{17}O was applied.

Accurately assigning isotope ratios requires corrections for minor isotopes, which significantly affect the signals at m/z 45 and 46. The calculation process is based on specific relationships between the isotope ratios.

- Relationship at 45 m/z (^{45}R): the contribution from the isotopologues $^{13}C^{16}O^{16}O$ and $^{12}C^{17}O^{16}O$.

$$^{45}R = {}^{13}R + 2\,{}^{17}R$$

- Relationship at 46 m/z (^{46}R): the contribution from $^{12}C^{16}O^{18}O$, $^{13}C^{17}O^{16}O$, and $^{12}C^{17}O^{17}O$.

$$^{46}R = 2\,{}^{18}R + 2\,{}^{17}R \cdot {}^{13}R + ({}^{17}R)^2$$

- Relationship between ^{17}R and ^{18}R:

$$^{17}R = k \cdot ({}^{18}R)^{\lambda}$$

Here, k and λ are constants that describe the empirical relationship between ^{17}R and ^{18}R.

- Calculation of ^{13}R: the contribution from $^{13}C^{16}O^{16}O$ at 45 m/z.

$$^{13}R = {}^{45}R - 2\,{}^{17}R$$

These equations are integrated into an iterative correction process, beginning with an initial estimate for ^{18}R. Each step recalculates ^{17}R, ^{13}R, and ^{46}R until the ratios converge to consistent values. Once the corrected isotope ratios (^{13}R, ^{18}R, and ^{17}R) are determined, they are converted into isotope delta values relative to the VPDB scale using the following equations:

$$\delta^{13}\mathrm{C} = \left(\frac{^{13}R}{^{13}R_{\mathrm{VPDB}}} - 1\right) \cdot 1000$$

$$\delta^{18}\mathrm{O} = \left(\frac{^{13}R}{^{13}R_{\mathrm{VPDB}}} - 1\right) \cdot 1000$$

This correction process ensures that the effects of minor isotopes are properly accounted for, providing precise and reliable isotope delta values.

Scale linearization correction

To reduce bias and ensure measurement accuracy, a scale linearization correction was applied. The isotope delta values were calibrated using two reference materials (RMs) with $\delta^{13}C_{VPDB}$ values of -1.48 ‰ and -43.11 ‰, assuming a linear response. The correction was specifically applied to the isotope delta values $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB-CO2}$. This approach effectively minimizes bias caused by non-linearity and ensures that the instrument's measurements remain accurate across the calibration range.

N_2O correction

During the extraction of CO_2 from air, one critical factor that must also be addressed is the presence of trace amounts of N_2O in the air samples. N_2O interferes with the measurement of isotope delta values ($\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2) due to its similar mass and freezing point (around 128 K under sub-mbar pressures), both of which are comparable to those CO_2. These factors make separating N_2O from CO_2 during extraction extremely challenging.

Therefore, it is common practice to allow N_2O to enter the IRMS alongside CO_2 without attempting separation. However, the presence of N_2O introduces a bias in the resulting stable isotope ratios, which requires a correction. The N_2O correction is calculated using the following equations:

$$\delta^{13}\mathrm{C}_{\mathrm{N2O\ corr}} = \delta^{13}\mathrm{C} + \mathrm{RIE} \cdot \ \delta^{13}\mathrm{N_2O} \cdot \frac{[\mathrm{N_2O}]}{[\mathrm{CO_2}]}$$

$$\delta^{18}\mathrm{O}_{\mathrm{N2O\ corr}} = \delta^{18}\mathrm{O} + \mathrm{RIE} \cdot \ \delta^{18}\mathrm{N_2O} \cdot \frac{[\mathrm{N_2O}]}{[\mathrm{CO_2}]}$$

Where RIE represents the Relative ionization efficiency of N_2O relative to CO_2, $\delta^{13}(N_2O)$, $\delta^{18}(N_2O)$ refers to the isotope delta values indicating how N_2O is interpreted by the CO_2 working reference and includes the amount fractions of the two greenhouse gases (N_2O and CO_2) in the sourcing sample cylinder.

The RIE used in this study is 0.792 ± 0.004 (k = 2). The values of $\delta^{13}N_2O$ and $\delta^{18}N_2O$ are −323 ± 6 (k = 2) and -490 ± 2 (k = 2), respectively.

Values of reference data impacting the measurement results

$\lambda = 0.528$

k = 0.01022461

$^{13}R_{VPDB}$= 0.01118

$^{17}R_{VPDB}$ = 0.0003931

$^{18}R_{VPDB}$ = 0.00208835

$^{45}R_{VPDB}$ = 0.0119662

$^{46}R_{VPDB}$ = 0.004185644

Bibliography

Werner, R. & Brand, W. (2001). Referencing strategies and techniques in stable isotope ratio analysis, *Rapid Commun. Mass Spectrom.*, 15, 501–519.

Brand, W., Assonov, S. and Coplen, T. (2010). Correction for the 17O interference in δ(13C) measurements when analyzing CO2 with stable isotope mass spectrometry (IUPAC Technical Report). *Pure and Applied Chemistry*, *82*(8), 1719-1733.

Assonov, S. S., & Brenninkmeijer, C. A. M. (2006). On the N_2O correction used for mass spectrometric analysis of atmospheric CO_2. *Rapid Commun. Mass Spectrom., 20*(14), 1809–1819.

2) Uncertainty budget

Measurement sequence

The Dual inlet system was used for measurement. The ionization source was an open-type design, unlike the standard closed-type ionization source used in typical IRMS instruments (253 Plus, Thermo Fisher), and had relatively low ionization efficiency. As a result, 65 mbar of gas sample was introduced for each analysis.

The sequence of analyses was performed manually due to the absence of a multi-port option and the inability of the IRMS software (Qtegra, Thermo Fisher) to synchronize with the home-made CO_2 extraction system, all sampling was conducted manually. To minimize the waste and fractionation of WR (working reference) gas during the time intervals between each sample analysis, the WR valve was closed after each analysis, and the gas in the cross section was evacuated.

Each analysis consisted of eight measurement cycles, with 60 seconds allotted for equilibration and 33 seconds for signal integration. The entire analysis was repeated six times for consistency. The bellows of the dual inlet were adjusted after every three analyses.

Two-point calibration was conducted using RMs with $\delta^{13}C$ values of -1.48 ‰ and -43.11 ‰. An internal standard with a $\delta^{13}C$ value of -34.29 ‰ was also used to assess reproducibility uncertainty.

Table 3. Information on the measurement sequence.

Information on measurement sequence	
Number of measurement cycles in one analysis	8
Instrument IDLE time	60 sec
Instrument integration time	33 sec
Number of successive repeats of one analysis	3
Number of unknown samples per sequence	1
Number of standards per sequence	3

The raw data for the 44, 45, and 46 m/z signals with background correction were obtained from Qtegra. These data were measured in CPS (counts per second) and calibrated through the amplifier calibration process performed within Qtegra; subsequently, all calculations were carried out manually.

Instrument stability

To evaluate the measurement stability of the IRMS, zero-enrichment analyses were conducted in addition to the regular measurement schedule under controlled conditions. In this process, pure CO_2 gas was introduced into both bellows of the IRMS, and all connected valves were opened to equilibrate the CO_2 gas between the bellows by alternately compressing and expanding them.

To assess instrument stability, six zero-enrichment analyses were conducted between August 2024 and October 2024. The standard deviations of isotope delta values ($\delta^{13}C$ and $\delta^{18}O$) were calculated as follows:

$1\sigma_{mean}$ ($\delta^{13}C$) = 0.006 ‰

$1\sigma_{mean}$ ($\delta^{18}O$) = 0.013 ‰.

Additionally, the zero-enrichment analyses conducted during sample measurements met the criteria outlined above.

Uncertainty budget

The measurement values and their associated expanded uncertainties for the samples are summarized in the table and graph below.

Table 4. Measurement results and expanded uncertainties for KRISS samples.

Cylinder	$\delta^{13}C_{VPDB}$	U_{anal} (k = 2)	$\delta^{18}O_{VPDB-CO2}$	U_{anal} (k = 2)	*Description*
D207731	-8.885	0.088	-11.214	0.392	Without N_2O
D207634	-8.902	0.084	-11.046	0.391	With N_2O
CC768120	-8.845	0.068	-10.673	0.145	Source Gas

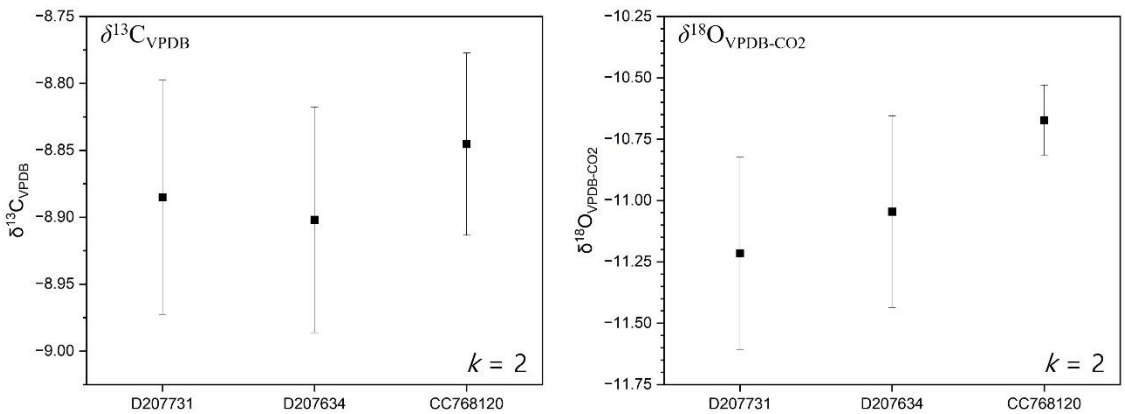


Figure 2. Isotope Delta Values for Measured Samples.

The total uncertainty (u_{total}) is calculated by combining the analytical uncertainty (u_{anal}) and the reference material uncertainty ($u_{reference}$) as follows:

$$u_{total} = \sqrt{u_{anal}^2 + u_{reference}^2}$$

The analytical uncertainty (u_{anal}) accounts for repeatability, reproducibility, and uncertainties arising from sample preparation and extraction, as follows:

$$u_{anal} = \sqrt{u_{repeat1}^2 + u_{repeat2}^2 + u_{reproduce}^2 + u_{extraction}^2}$$

$u_{repeat1}$ represents the standard deviation derived from eight cycles of dual inlet measurements.

$u_{repeat2}$ represents the standard deviations of values obtained after applying linearization to repeated measurements of the same sample using two reference materials

$u_{\mathbf{reproduce}}$ represents the reproducibility uncertainty. Since the CO_2 in the air sample was measured only once, the reproducibility value could not be directly determined. Therefore, it was derived from measurements of an internal standard material, which was measured four times.

The graph below represents the measurement results of the internal standard material, with corresponding uncertainties of 0.019 (k = 1) and 0.028 (k = 1), respectively.

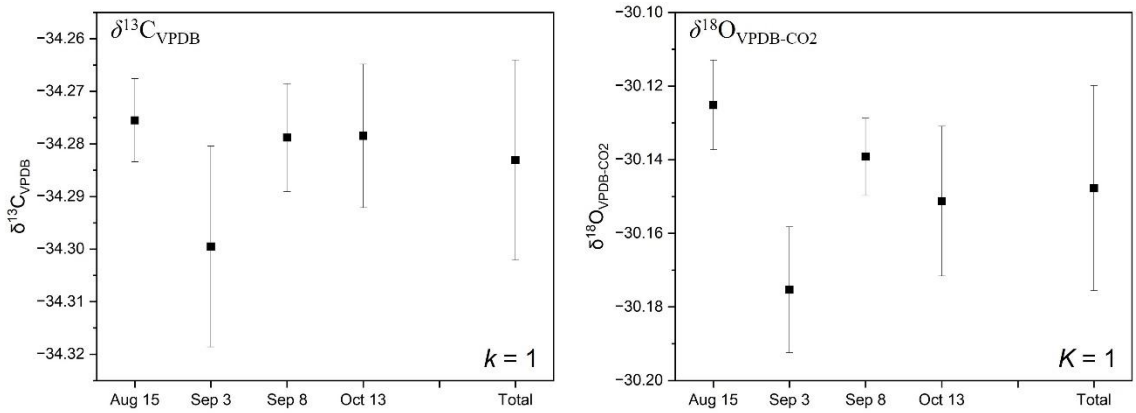


Figure 3. Isotope delta values for the internal standard material used in this measurement.

$u_{\mathbf{extraction}}$ represents the measurement uncertainty associated with the process of extracting CO_2 from air samples. Notably, the isotope delta value $\delta^{18}O_{VPDB\text{-}CO2}$ between the source gas and the extracted CO_2 is approximately ten times larger than that of $\delta^{13}C_{VPDB}$. According to Werner et al., fractionation of $\delta^{18}O$ can occur during the extraction process due to freezing and release cycles, interactions with trap surfaces, and the presence of residual impurities.

Since the sample does not contain CO_2 from other sources, it is expected to have isotope delta values identical to the source CO_2. Therefore, $u_{\mathbf{extraction}}$ was determined using a rectangular distribution, based on the measured differences in isotope delta values between the source CO_2 and the extracted CO_2.

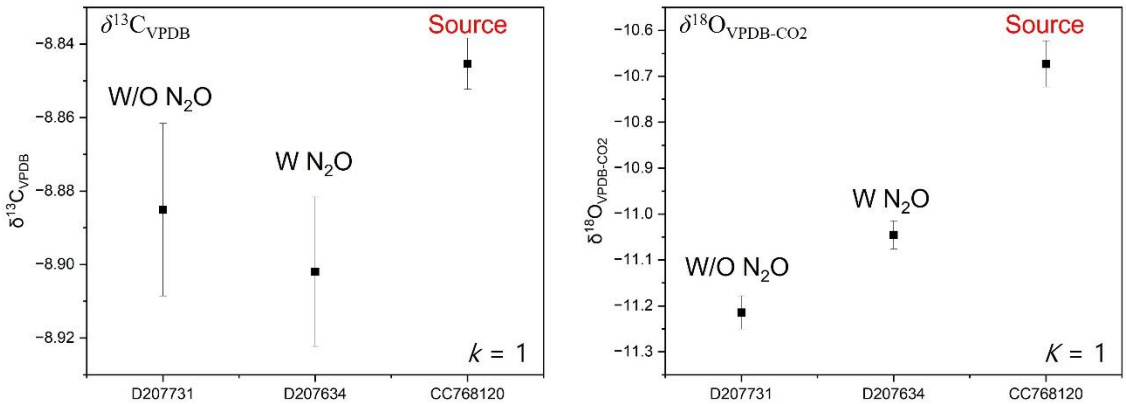


Figure 4. Isotope ratio values for the source CO_2 and extracted CO_2

The reference material uncertainty ($\boldsymbol{u}_{\mathbf{reference}}$) combines the uncertainties of multiple reference materials and their respective analyses, calculated as:

$$\boldsymbol{u}_{\mathbf{reference}} = \sqrt{\boldsymbol{u}^2_{\mathbf{IAEA-603}} + \boldsymbol{u}^2_{\mathbf{ref_1IAEA}} + \boldsymbol{u}^2_{\mathbf{ref_2IAEA}} + \boldsymbol{u}^2_{\mathbf{ref_1BIPM}} + \boldsymbol{u}^2_{\mathbf{ref_2BIPM}}}$$

$\boldsymbol{u}_{\mathbf{IAEA-603}}$ represents the uncertainty associated with IAEA-603, a reference material used by the IAEA when measuring BIPM reference materials.

$\boldsymbol{u}_{\mathbf{ref_1IAEA}}$ and $\boldsymbol{u}_{\mathbf{ref_2IAEA}}$ represent the analytical uncertainties of the reference materials measured by the IAEA. These uncertainties are sourced from the P204 report, excluding the uncertainty of IAEA-603. These two calibrants were used for linearization after being measured by the BIPM.

$\boldsymbol{u}_{\mathbf{ref_1BIPM}}$ and $\boldsymbol{u}_{\mathbf{ref_2BIPM}}$ represent the analytical uncertainties of reference materials provided by the BIPM.

Table 5. Uncertainty budget for the D207731 cylinder.

D207731 (without N_2O)		$\delta^{13}C_{VPDB}$		$\delta^{18}O_{VPDB\text{-}CO2}$	
		u_i	Contribution	u_i	Contribution
$\boldsymbol{u}_{\mathbf{anal}}$					
	$\boldsymbol{u}_{\mathbf{repeat1}}$	0.005	1.4	0.011	0.3
	$\boldsymbol{u}_{\mathbf{repeat2}}$	0.013	8.5	0.021	1.1

	$u_{\mathrm{reproduce}}$	0.019	18.9	0.028	2.0
	$u_{\mathrm{extraction}}$	0.024	30.7	0.181	85.3
$u_{\mathrm{reference}}$					
	$u_{\mathrm{IAEA\ 603}}$	0.010	5.6	0.040	4.2
	$u_{\mathrm{ref1_IAEA}}$	0.015	12.7	0.034	3.0
	$u_{\mathrm{ref2_IAEA}}$	0.017	16.3	0.037	3.6
	$u_{\mathrm{ref1_BIPM}}$	0.009	4.6	0.011	0.3
	$u_{\mathrm{ref2_BIPM}}$	0.009	4.6	0.011	0.3
u_{total}		0.044		0.196	
Expanded uncertainty (k = 2)	U(x)	0.088		0.392	

Table 6. Uncertainty budget for the D207634 cylinder.

D207634 (with N_2O)		$\delta^{13}C_{VPDB}$		$\delta^{18}O_{VPDB\text{-}CO2}$	
		u_i	Contribution	u_i	Contribution
u_{anal}					
	u_{repeat1}	0.006	2.3	0.008	0.1
	u_{repeat2}	0.003	0.6	0.010	0.3
	$u_{\mathrm{reproduce}}$	0.019	20.4	0.028	2.0
	$u_{\mathrm{extraction}}$	0.024	33.0	0.181	86.1

$u_{\text{reference}}$					
	$u_{\text{IAEA 603}}$	0.010	5.6	0.040	4.2
	$u_{\text{ref1_IAEA}}$	0.015	12.7	0.034	3.0
	$u_{\text{ref2_IAEA}}$	0.017	16.3	0.037	3.6
	$u_{\text{ref1_BIPM}}$	0.009	4.6	0.011	0.3
	$u_{\text{ref2_BIPM}}$	0.009	4.6	0.011	0.3
u_{total}		0.042		0.195	
Expanded uncertainty (k = 2)	U(x)	0.084		0.391	

Table 7. Uncertainty budget for the CC768120 cylinder.

CC768120 (Source CO_2)		$\delta^{13}C_{VPDB}$		$\delta^{18}O_{VPDB\text{-}CO2}$	
		u_i	Contribution	u_i	Contribution
u_{anal}					
	u_{repeat1}	0.004	1.2	0.006	0.7
	u_{repeat2}	0.003	0.6	0.007	0.9
	$u_{\text{reproduce}}$	0.019	31.3	0.028	14.8
$u_{\text{reference}}$					
	$u_{\text{IAEA 603}}$	0.010	8.6	0.040	30.6
	$u_{\text{ref1_IAEA}}$	0.015	19.4	0.034	22.1

	$u_{\mathrm{ref2_IAEA}}$	0.017	24.9	0.037	26.2
	$u_{\mathrm{ref1_BIPM}}$	0.009	7.0	0.011	2.3
	$u_{\mathrm{ref2_BIPM}}$	0.009	7.0	0.011	2.3
u_{total}		0.034		0.072	
Expanded uncertainty (k = 2)	U(x)	0.068		0.145	

Bibliography

Werner, R.A., Rothe, M. and Brand, W.A. (2001), Extraction of CO2 from air samples for isotopic analysis and limits to ultra high precision δ18O determination in CO2 gas. *Rapid Commun. Mass Spectrom.*, 15: 2152-2167

Information added after Draft A circulation

This section is added to describe how KRISS evaluated the potential fractionation of CO_2 isotopes during gravimetric preparation using three different preparation processes with two different isotope ratio measurement methods (e.g., DI-IRMS and IRIS). KRISS investigated the fractionation in three different scenarios: the first scenario simulates gravimetric preparation with DI-IRMS measurements; the second involves gravimetric preparation (more like volumetric preparation) with IRIS measurements; and the third is actual gravimetric preparation with IRIS measurements.

-**Simulation of gravimetric preparation with DI-IRMS measurements (done before reporting**): An intermediate CO_2 gas mixtures in nitrogen at (2 – 5) cmol/mol needed to be prepared to develop atmospheric CO_2 in synthetic air. An intermediate CO_2 gas mixture (10 L cylinder) was prepared by transferring a certain amount of pure CO_2 in source cylinder to an empty 10 L cylinder, but it was not diluted with pure nitrogen. Thus, the simulated intermediate mixture contained only a certain amount of pure CO_2, which is equivalent to the CO_2 amount in a CO_2 gas mixture at (2 -5) cmol/mol. KRISS analyzed pure CO_2 in both the source cylinder and intermediate cylinder using DI-IRMS to evaluate the potential fractionation of CO_2 isotopes. Results from DI-IRMS measurements showed that difference between the two pure CO_2 gases was 0.0025 ‰ ± 0.01 ‰ (k=2) for δ^{13}C and 0.005 ‰ ± 0.01 ‰ (k=2) for δ^{13}O. Thus, significant fractionation of CO_2 isotopes was not observed during the

transfer of pure CO_2 from source cylinder to the empty cylinder (i.e., the simulated intermediate gas mixture).

-**Simulation of gravimetry preparation with IRIS measurements (done after reporting**): To prepare atmospheric CO_2 gas mixtures, pure CO_2 needs to be dilute to an intermediate level at cmol/mol and then further diluted to atmospheric level. A pure CO_2 cylinder (30 L) , the original cylinder, was decanted into another empty cylinder (30 L), the second cylinder, which was then further decanted into a third empty cylinder (30 L). Pure CO_2 in the three 30 L cylinders were diluted by directly filling home-made scrubbed dry air into the same three cylinders to prepare intermediate CO_2 gas mixtures at about 4 cmol/mol. One atmospheric CO_2 gas mixture in scrubbed dry air at about 800 µmol/mol was prepared from each of the intermediate CO_2 gas mixtures, resulting in a total of three atmospheric CO_2 gas mixtures being prepared from the original pure CO_2 source. The first atmospheric CO_2 gas mixture underwent two decanting processes, and the second mixture underwent two decanting processes, and the third gas mixture underwent three decanting processes. If CO_2 isotope fractionation occurred during decanting, the third mixture is expected to be most affected by the fractionation. The three atmospheric CO_2 gas mixtures were analyzed using IRIS (CRDS, G2131-i), which provides only carbon isotope delta values. The potential fractionation of CO_2 isotopes was evaluated by comparing the carbon isotope delta values (delta ratio method, not isotopologue amount fraction method) against each other. Biases due to the amount fraction (i.e., concentration) -dependent delta ratio method were not expected since the three atmospheric CO_2 gas mixture were prepared at about 800 µmol/mol. Results showed that the carbon isotope delta values agree well within the analytical uncertainties ($U \approx 0.094$ ‰).

- **Actual gravimetry preparation with IRIS measurements (done after reporting**): for the KRISS CO_2 scale, KRISS prepared atmospheric CO_2 gas mixtures (from 350 µmol/mol to 800 µmol/mol) in synthetic air using gravimetry (hereafter, gravimetric CO_2 gas mixtures), which were used as references to value-assign CO_2 gas mixtures at the primary level of the KRISS CO_2 scale. Thus, it is important to evaluate any potential CO_2 isotope fractionation during gravimetry preparation for accurate value-assignment. If significant fractional did not occur during gravimetric preparation, the isotope delta values should be the same since a single pure CO_2 source was used to prepare the gravimetric CO_2 gas mixture. The gravimetry CO_2 gas mixtures were analyzed using IRIS (CRDS, G2131-i). the carbon isotope delta values were calculated by applying isotopologue method. the carbon isotope delta values from the IRIS isotopologue method were compared with that of the pure CO_2 source measured by DI-IRMS. First of all, results show that the carbon isotope delta values of the gravimetric CO_2 gas mixtures agree well within the uncertainties ($U \approx 0.07$ ‰) and are also consistent with that of the pure CO_2 source from DI-IRMS ($\delta^{13}C$ = -8.845 ‰ ± 0.068 ‰, k=2). Thus, a significant CO_2 isotope fractionation was not observed, considering the consistencies among the gravimetry CO_2 gas mixtures and their pure CO_2 source.

- **Rationale for the extra uncertainty of the KRISS CO2 extraction system**): KRISS added the extra uncertainty in the report regarding its CO_2 extraction system based on the results from the

simulation of gravimetric preparation with DI-IRMS. The results from the two additional evaluations with IRIS, which do not require CO_2 extraction, confirmed that significant CO_2 isotope fractionation did not occur during gravimetric preparation. In addition, the fact that the delta values of KRISS CO_2 source gas agree well with those of the BIPM measurement results of the two KRISS comparison samples (gravimetrically prepared in synthetic air) also supports little isotope fractionation during KRISS gravimetry preparation.

KRISS CO_2 source gas measured by KRISS;

$\delta^{13}C$ = -8.845 ‰ ± 0.068 ‰, $\delta^{18}O$ = -10.673 ‰ ± 0.145 ‰

BIPM measurement results;

KRISS comparison sample I (D207634): $\delta^{13}C$ = -8.902 ‰ ± 0.026 ‰, $\delta^{18}O$ = -10.726 ‰ ± 0.030 ‰;

KRISS comparison sample II (D207731): $\delta^{13}C$ = -8.854 ‰ ± 0.022 ‰, $\delta^{18}O$ = -10.753 ‰ ± 0.050 ‰

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**NIST**
Contact	**Kimberly Harris**
Email	kimberly.harris@nist.gov

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	JJ13293	2024-06-17	10.69	mpa
2	JJ13931	2021-10-08	7.24	mpa
3	JJ13939	2024-04-13	9.65	mpa
4	JJ13955	2024-04-23	11.03	mpa

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	JJ13293	-2.70	0.13	2.00
2	JJ13931	-10.99	0.15	2.00
3	JJ13939	-39.88	0.34	2.00
4	JJ13955	-50.42	0.56	2.00
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	JJ13293	-17.36	0.30	2.00
2	JJ13931	-12.25	0.34	2.00
3	JJ13939	-33.81	0.73	2.00
4	JJ13955	-41.53	0.73	2.00

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	JJ13293	503.807	0.232	2.00
2	JJ13931	412.302	0.155	2.00
3	JJ13939	432.207	0.200	2.00
4	JJ13955	480.443	0.224	2.00

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	JJ13293	329.64	0.50	2.00
2	JJ13931	329.67	0.60	2.00
3	JJ13939	329.42	0.42	2.00
4	JJ13955	328.97	0.37	2.00

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	%mol/mol	%mol/mol	%mol/mol	(unit)	(unit)	(unit)
1	78.0730 ± 0.0150	20.9391 ± 0.008	0.9374 ± 0.0056			
2	78.0739 ± 0.0238	20.97403 ± 0.01	0.9446 ± 0.0094			
3	78.0667 ± 0.313	20.9795 ± 0.194	0.9405 ± 0.0098			
4	78.0909 ± 0.0161	20.9224 ± 0.004	0.9387 ± 0.0103			

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[*CCQM-P239_Result Form v0.1 1_NIST.xlsx*]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**NIST**
Contact	**Kimberly Harris**
Email	**Kimberly.harris@nist.gov**

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	ID (Serial Number)
1	JJ13293
2	JJ13931
3	JJ13939
4	JJ13955

Mandatory information

1) Traceability of the measurement results

The source materials listed in Table 1 were value assigned using a Thermo MAT 253 isotope ratio mass spectrometer (IRMS) following measurement procedures described in the 2018 publication by A. Srivastava and M. Verkouteren (1). To perform these analyses, an aliquot of each CO_2 source was transferred into a 50 ml chamber and directly compared against NIST pure CO_2 isotopic RMs 8562, 8563, and 8564. The final value assignment of this material is listed in Table 1.

Table 1. Source material delta value assignment (k = 2).

	δ^{13}C VPDB-CO2	δ^{18}O VPDB-CO2
EX0013341	- 2.85 ± 0.06 ‰	- 16.51 ± 0.26 ‰
EX0013330	- 10.98 ± 0.06 ‰	- 12.27 ± 0.32 ‰
FF59918	- 39.89 ± 0.08 ‰	- 33.73 ± 0.46 ‰
FF59930	- 50.42 ± 0.12 ‰	- 41.33 ± 0.64‰

Ambient level mixtures were then prepared through a two-step dilution scheme. The first step ranged from a nominal [1 – 2] % mol/mol CO_2 in synthetic air (defined in Table 5) while the second step ranged from a nominal [400 – 500] µmol/mol CO_2 in synthetic air. As shown in Figure 1, three ambient-level mixtures were prepared from each CO_2 source, one of these was value assigned using the technique described below (2). A more detailed description of the preparation process is included in Section 4.

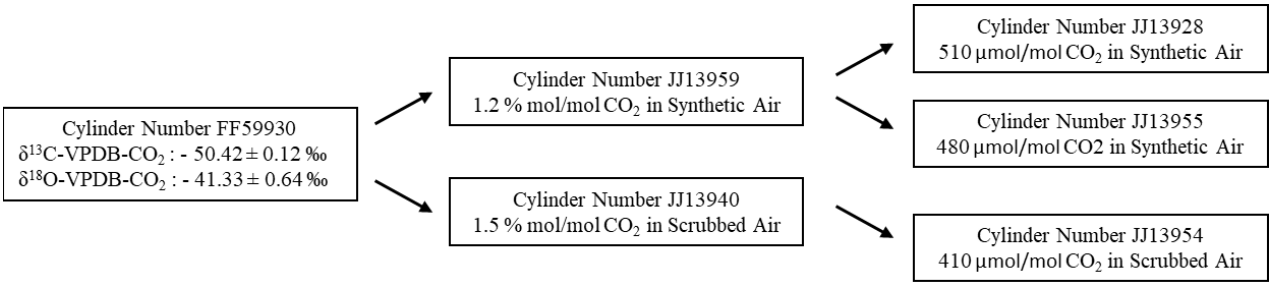


Figure 1. Example dilution scheme from value assigned source material to ambient level mixtures. Uncertainties are expanded.

Analyses were then performed using Aerodyne tuneable infrared laser direct absorption spectroscopy (TILDAS, NIST # N116423) to establish an 8-point response curve. The delta values of these standards are listed in Figures 2 and 3 while the amount fractions are listed in Section 4, Table 6. This analyzer is equipped with two lasers, at 2310 cm^{-1} and 2350 cm^{-1}, covering the spectral range of 626, 636, and 628, or 627 respectively. A 3-minute sweep wait was performed before a 60 second average was collected for each isotopologue listed above. A response ratio of the sample to the analytical control, as described in Section 5, was calculated for each isotopologue

individually. The corrected response ratios were then used to calculate a 636/626 or 628/626 response ratio.

The response curve was composed of two primary standards mixtures from each source material listed in Table 1 for a total of eight standards. To do so, the IRMS delta value assignment was converted to isotopes ratios following equations 1 and 2 for δ^{13}C-VPDB-CO_2 and δ^{18}O-VPDB-CO_2 respectively and the isotopologue abundance method was to establish the calibration curve.

$$\frac{636}{626} = \left(\frac{\delta 13C}{1000} + 1\right) \times 0.01118 \tag{1}$$

$$\frac{628}{626} = \left(\frac{\delta 18O}{1000} + 1\right) \times 0.00208835 \tag{2}$$

The general least squares regression analyses, shown in Figure 2 and 3, were used to assign an isotope ratio to the samples submitted (3,4).

Data to be fit to a function using ISO 6143 compliant GenLine

Value of Standards		Analytical Response			Evaluation Data Responses	
Y-Values	Y-uncertainty	X-Values	X-uncertainty	<-Cylinder	X-Values	X-uncertainty
0.01115	0.00003	1.00589	0.00044	*JJ13951*	1.00000	
0.01062	0.00003	0.95743	0.00048	JJ13954	0.96806	0.00011
0.01106	0.00003	0.99780	0.00022	JJ13924	0.99771	0.00057
0.01073	0.00003	0.96820	0.00032	JJ13923	0.99753	0.00020
0.01115	0.00003	1.00592	0.00029	JJ13956	0.99771	0.00016
0.01062	0.00003	0.95752	0.00075	JJ13928	0.99759	0.00016
0.01073	0.00003	0.96817	0.00037	JJ13938	0.96819	0.00031
0.01106	0.00003	0.99769	0.00013	JJ13947	0.96824	0.00030
					0.96820	0.00031
					1.00605	0.00056
					1.00630	0.00055
					1.00598	0.00058
					0.95755	0.00053
					0.95751	0.00059
					0.95750	0.00053
					0.95742	0.00057
					0.95746	0.00054

Execute **Degree = 1** K=1

GENLINE - Linear (y=b0+b1*x)

	Value	Std Error
b0	0.0001152	0.00047966
b1	0.01096756	0.00048843
cov(b0,b1)		-2.342E-07
rms residual error		0.02671059

X	Y	X-Solution	Y-Solution	uTest
1.005892	0.01114814	1.00589353	0.011147	PASS
0.957433	0.0106163	0.9574343	0.010616	PASS
0.997799	0.01105724	0.99779821	0.011059	PASS
0.968202	0.01073403	0.9682025	0.010734	PASS
1.005922	0.01114814	1.0059227	0.011148	PASS
0.957519	0.0106163	0.9575151	0.010617	PASS
0.968166	0.01073403	0.96816661	0.010734	PASS
0.997688	0.01105724	0.99768801	0.011057	PASS

	Xin	uXin	Yeval	uYeval
1720-A-18	1	0	0.01108275	1.32E-05
FB04278	0.968064	0.00010594	0.01073249	1.19E-05
JJ13931 - 9/13/2024	0.997707	0.00056776	0.0110576	1.39E-05
JJ13931-9/12/2024	0.997534	0.00019736	0.0110557	1.26E-05
JJ13931-9/19/2024	0.997706	0.00015631	0.01105759	1.26E-05
JJ13931-9/25/2024	0.997592	0.00015648	0.01105635	1.26E-05
JJ13939-9/12/2024	0.968193	0.00031327	0.01073391	1.23E-05
JJ13939-9/19/2024	0.968239	0.00029985	0.01073441	1.23E-05
JJ13939-9/25/2024	0.9682	0.00030822	0.01073398	1.23E-05
JJ13293-9/18/2024	1.006055	0.00055801	0.01114916	1.65E-05
JJ13293-9/19/2024	1.006303	0.00055231	0.01115188	1.66E-05
JJ13293-9/24/2024	1.005977	0.00058153	0.0111483	1.66E-05
JJ13955-9/04/2024	0.95755	0.00053203	0.01061717	1.64E-05
JJ13955-9/12/2024	0.957507	0.00058637	0.0106167	1.67E-05
JJ13955-9/18/2024	0.957499	0.0005307	0.01061662	1.65E-05
JJ13955-9/24/2024	0.957416	0.00056687	0.01061571	1.66E-05
JJ13955-10/02/2024	0.957458	0.00054186	0.01061617	1.65E-05

Figure 2. General least squares regression for 636/626 isotope ratio. Uncertainties are combined.

Data to be fit to a function using ISO 6143 compliant GenLine

Value of Standards		Analytical Response			Evaluation Data Responses	
Y-Values	Y-uncertainty	X-Values	X-uncertainty	<-Cylinder	X-Values	X-uncertainty
-0.00205	0.00002	0.98586	0.00039	*JJ13951*	1.00000	
-0.00200	0.00002	0.96116	0.00045	JJ13954	0.97165	0.00010
-0.00206	0.00003	0.98869	0.00022	JJ13924	0.98467	0.00054
-0.00205	0.00002	0.98518	0.00028	JJ13956	0.98458	0.00054
-0.00200	0.00002	0.96020	0.00073	JJ13928	0.98473	0.00056
-0.00202	0.00001	0.96941	0.00037	JJ13938	0.98957	0.00050
-0.00206	0.00003	0.98952	0.00012	JJ13947	0.98967	0.00019
					0.98983	0.00015
					0.98966	0.00015
					0.96879	0.00032
					0.96810	0.00032
					0.96849	0.00030
					0.96846	0.00031
					0.96065	0.00054
					0.96064	0.00057
					0.96132	0.00053
					0.96084	0.00056

Execute **Degree = 1** K=1

GENLINE - Linear (y=b0+b1*x)

	Value	Std Error
b0	3.71E-05	0.0005733
b1	-0.002122	0.00058834
cov(b0,b1)		-3.373E-07
rms residual error		0.08582038

X	Y	X-Solution	Y-Solution	uTest
0.985861	-0.002054	0.98586046	-0.002055	PASS
0.961164	-0.002002	0.96116372	-0.002002	PASS
0.988694	-0.002063	0.98869435	-0.002061	PASS
0.985176	-0.002054	0.98517656	-0.002053	PASS
0.960202	-0.002002	0.96020924	-0.002	PASS
0.969408	-0.002018	0.96940538	-0.00202	PASS
0.989522	-0.002063	0.98952185	-0.002062	PASS

Xin	uXin	Yeval	uYeval
1720-A-18	1	0	-0.0020846	1.657E-05
FB04278	0.971649	9.58E-05	-0.0020245	7.023E-06
JJ13293-9/18/24	0.984669	0.000542	-0.0020521	9.215E-06
JJ13293-9/19/24	0.984582	0.000539	-0.0020519	9.18E-06
JJ13293-9/24/24	0.984727	0.000562	-0.0020522	9.242E-06
JJ13931-9/13/24	0.98957	0.000502	-0.0020625	1.132E-05
JJ13931-9/12/24	0.989672	0.000188	-0.0020627	1.132E-05
JJ13931-9/19/24	0.989827	0.000147	-0.0020631	1.139E-05
JJ13931-9/25/24	0.989664	0.000146	-0.0020627	1.131E-05
JJ13939-9/12/24	0.968792	0.000317	-0.0020184	7.609E-06
JJ13939-9/17/24	0.968097	0.000319	-0.002017	7.794E-06
JJ13939-9/19/24	0.968488	0.000299	-0.0020178	7.685E-06
JJ13939-9/25/24	0.968463	0.000306	-0.0020177	7.692E-06
JJ13955-9/4/2024	0.960654	0.000535	-0.0020012	1.063E-05
JJ13955-9/12/2024	0.960638	0.000572	-0.0020011	1.065E-05
JJ13955-9/18/2024	0.961324	0.00053	-0.0020026	1.033E-05
JJ13955-9/24/2024	0.960842	0.000562	-0.0020016	1.055E-05

Figure 3. General least squares regression of 628/626 isotope ratio. Uncertainties are combined.

The assigned isotope ratio was then converted to a delta value using the inverse of the equations listed above.

The traceability chain described here suggests the delta value assignment is four steps removed as illustrated in Figure 4.

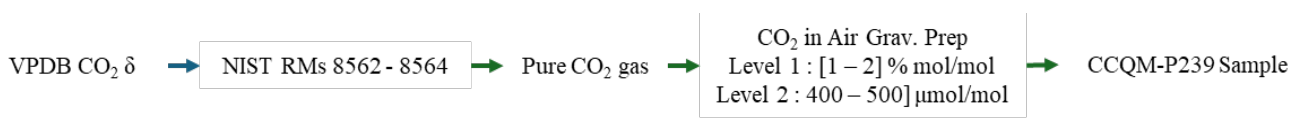


Figure 4. Traceability chain between source material value assignment by IRMS, the dilution scheme, and optical analyses.

2) Uncertainty budget

Uncertainties were calculated using guidance outlined in IAEA-TECDOC-2066 (5). A list of each component is included below.

IRMS value assignment (u_{cali}): Table 1 lists the IRMS value assignment and expanded uncertainty of the source material. This value includes the δ^{18}O and δ^{13}C uncertainty for NIST RMs 8562, 8563, and 8564, the IRMS measurement repeatability, the isotope data reproducibility for the respective ion, and cross contamination.

Response ratio (u_R): The relative standard deviation for each sample or control analysis was calculated using the standard deviation of instrument response (σ) divided by the 60-second average $\bar{x}$. The relative standard deviation of the sample and corresponding control runs were then combined according to equation 3.

$$u_r = \sqrt{\left(\frac{\sigma_{ctrl1}}{\bar{x}_{ctrl1}}\right)^2 + \left(\frac{\sigma_{sample}}{\bar{x}_{sample}}\right)^2 + \left(\frac{\sigma_{ctrl2}}{\bar{x}_{ctrl2}}\right)^2} \quad (3)$$

A minimum of four response ratios were collected on each analytical day, the response ratio uncertainties and standard deviation were then combined in quadrature for an uncertainty the analytical day equation 4.

$$u_R = \sqrt{u_{r1}^2 + u_{r2}^2 + u_{r3}^2 + \cdots + u_{rn}^2 + \sigma_{ratio}} \quad (4)$$

Instrument response function based on total amount fraction (u_{626}): Using the same type of laser absorption spectrometer, Steur et al. (6) reported fit residuals in spectroscopic measurements of the 626, 636, and 627 isotopologues which varied with CO2 amount fraction for concentration ranges exceeding 100 µmol/mol. However, they reported that residuals for the 638 isotopologue were insensitive to CO2 amount over the range [400 – 1000] µmol/mol. Their observed variations in residuals with CO2 amount fraction were ascribed to nonlinearities in the measurement over the considered concentration range. We note that the total CO2 amount fraction in the primary standards listed in Table 6 range from [400 – 500] µmol/mol corresponds to the concentration range reported in Fig. 5c of Steur et al. (6). In this figure, fit residuals for the 636 isotopologue span nominally [0.1 – 0.4] ‰. Here, we use this result to estimate an upper bound on the uncertainty caused by nonlinearity in our system. Assuming a uniform probability distribution of width 0.3 ‰, the corresponding effective standard deviation of these fit residuals is calculated according to the GUM [7], using equation 5.

$$u_{626} = \frac{0.3}{2\times\sqrt{3}} \quad (5)$$

Methane interference ($u_{GM,CH4}$): The analytical control was an SRM 1720 Northern Hemisphere Air sample with ambient level methane while the primary standards described had trace amounts. The laser used for the 626, 636, and 628 measurements operated at a spectral rage of 2310 cm^{-1}. There is minimal interference of CH_4 at each spectral band of interest, the intensity of this peak was calculated using the total amount fraction of methane in each cylinder of interest and the HITRAN2020 line list. While this was included in the uncertainty budget, the change to the final value assignment was negligible.

Table 2. Spectral overlap of CH_4 and CO_2 from HITRAN2020.

Isotopologue	Frequency (cm^{-1})	Max loss CH_4/Max loss CO_2
626	2310.29900	1.049×10^{-7}
628	2310.26582	1.082×10^{-7}
636	2310.04742	7.049×10^{-8}

Total uncertainty per analytical day (u_n): The components listed above were then combined in quadrature following equation 6 and assigned to the response ratio within Genline. This calculation is repeated for each analytical day noted as the subscript 1 - 3.

$$u_n = \sqrt{u_{cali}^2 + u_R^2 + u_{GM,CH4}^2 + u_{626}^2} \tag{6}$$

Final Uncertainty Equation: The uncertainty of each analytical day and the distribution of assigned delta values were combined in quadrature following equation 7. Sigma is the standard deviation of delta value assignment across multiple analytical days. The final expanded uncertainty was reported as $k = 2$.

$$U = k \times \sqrt{u_1^2 + u_2^2 + u_3^2 + \sigma_\delta^2} \tag{7}$$

Additional non-mandatory information

3) Mixtures composition

The mixtures submitted were prepared in synthetic air of ambient level oxygen, argon, and nitrous oxide in a balance of nitrogen.

4) Mixtures preparation

The submitted samples were gravimetrically prepared at NIST and range in nominal amount fraction from [400 – 510] µmol/mol CO_2 in synthetic air. Each of those mixtures was prepared from a different CO_2 source through a 2-step dilution scheme. The dilution hierarchy and corresponding amount fractions are list in Table 3 while the impurity analyses of the source materials are listed in Table 4.

Table 3. Dilution hierarchy from pure CO_2 source to final ambient level mixture. Total amount fraction uncertainties are expanded.

Source Material	Level 1 (% mol/mol)		Level 2 (µmol/mol)	
EX0013341	JJ13937	1.2779 ± 0.00037	JJ13293	503.807 ± 0.232
EX0013330	JJ13926	1.4606 ± 0.0004	JJ13931	412.302 ± 0.155
FF59918	JJ13952	1.7983 ± 0.0004	JJ13939	432.207 ± 0.200
FF59930	JJ13959	1.1651 ± 0.0004	JJ13955	480.443 ± 0.224

Table 4. Source CO_2 impurity analyses. Uncertainties are expanded.

	EX0013341	EX0013330	FF59918	FF59930
Nitrogen (N_2, % mol/mol)	0.00086 ± 0.00086	0.00036 ± 0.00036	0.00016 ± 0.00016	0.00489 ±0.00489
Oxygen (O_2, µmol/mol)	0.003 ± 0.002	0.003 ± 0.002	0.004 ± 0.009	0.006 ± 0.004
Argon (Ar, µmol/mol)	4.8 ± 1.0	2.0 ± 0.3	1.1 ± 0.1	1.6 ± 0.2

In each case, cylinders were connected to the fill manifold and evacuated before a minimum of ten mass measurements were performed by a KRISS balance system (KRISS # 1, NIST # 634407). Cylinders were then reconnected to the manifold system and a predetermined mass of parent gas was transferred into the evacuated daughter cylinder. Level 1 mixtures were allowed to temperature equilibrate before being transferred to the balance while Level 2 mixture underwent mother-daughter testing using an Agilent 6890 GC-TCD (NIST # 632010) prior to weighing. In both cases the cylinders were allowed a minimum of 10 hours to temperature equilibrate before ten mass measurements were performed.

Cylinders were then reconnected to the fill manifold and a predetermined amount of synthetic air was transferred. To achieve the final pressure cylinders were filled with multiple synthetic air cylinders. A mass measurement was performed after each balance gas transfer to determine the final balance gas composition within each cylinder. An assay of those balance air cylinders is listed in Table 5.

Table 5. Balance air mole fraction composition. Uncertainties are expanded (*k*=2).

Cylinder #	TW04-653914	1016422y	566047y	TW04-654017	O-2675
O_2 (mol/mol)	0.20916 ± 0.00028	0.20963 ± 0.00025	0.20987 ± 0.00034	0.20932 ± 0.00002	0.20958 ± 0.00009
Ar (mo/mol)	0.00932 ± 0.00006	0.00940 ± 0.00004	0.00943 ± 0.00008	0.00950 ± 0.00010	0.009389 ± 0.000053
N_2O (nmol/mol)	329.458 ± 1.005	330.166 ± 0.315	329.979 ± 0.259	329.101 ± 0.122	332.101 ± 0.122
CO_2 (µmol/mol)	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01

5) Verification of mixtures

Isotope analyses were performed using an Aerodyne tuneable infrared laser direct absorption spectroscopy (TILDAS, NIST # N116423) equipped with 2-way gas sampling valve. Pressure within the TILDAS was maintained at [30.09 ± 0.01] torr using an Agilent SH 110 scroll pump while temperature was held at 23 °C using an Oasis three cooling system. Throughout analyses the 425 sccm flow rate was monitored using an Aalborg mass flow meter. The sampling valve oscillated between the analytical control and sample cylinder on 4-minute intervals.

In all cases a 240 second sweep wait was performed prior to a 60 second average of instrument response for each isotope (626, 636, 628, and 627). A minimum of six repetitions of the sampling sequence (control, sample, control) constituted one analytical sequence. The instrument response was corrected in this way to account for instrument offset and drift. A response ratio of sample to analytical control was then calculated for each isotopologue according to equation 8 using an SRM 1720 Northern Hemispheric air sample, 1720-A-18, as the analytical control.

$$R_i = \frac{r_s}{Average(r_{c1}, r_{c2})} \tag{8}$$

The response ratio of each isotopologue was then used to calculate an isotope ratio of 636/626 and 628/626 as shown in equation 9 and a daily average was calculated.

$$R_{636/626} = \frac{R_{636}}{R_{626}} \tag{9}$$

These results were then averaged, and the sequence was repeated over three analytical days to produce three sets measurement results. A general least squares regression was used to assign the value of submitted samples. For those primary standards used the IRMS value assignment was used for each of those establishing the curve, these values were then used to value assign the submitted samples. Genline was performed using the calculated ratio of 636/626, or 628/636, and then converted back to the per mil scale for the final value reported here.

Table 6. Ambient level carbon dioxide in synthetic air primary standard mixtures and the respective source material (µmol/mol, $k = 2$).

Source Material	Standard # 1	Standard # 2
EX0013341	JJ13951 : 400.011 ± 0.163	JJ13956 : 441.273 ± 0.209
EX0013330	JJ13924 : 426.879 ± 0.160	JJ13947 : 433.204 ± 0.175
FF59918	JJ13923 : 433.394 ± 0.210	JJ13938 : 444.690 ± 0.194
FF59930	JJ13954 : 410.524 ± 0.194	JJ13928 : 511.176 ± 0.254

Measurements were validated through comparison to an SRM 1720 Northern hemisphere air sample and a participant cylinder from CCQM-K120b, value assigned by NOAA and BIPM respectively. The results are displayed in Table 7 and Table 8.

Table 7: Validation of δ^{13}C-VPDB-CO_2 value assignment using the Aerodyne TILDAS. Uncertainties are expanded.

Cylinder #	Sample #	NIST Analysis (‰)	External Org	Assigned Value (‰)	Diff.
CC324298	1720-A-18	- 8.70 ± 0.12	NOAA	- 8.6 ± 0.1*	- 0.098
FB04278	CCQM-K120	- 40.03 ± 0.15	BIPM	-39.83 ± 0.36	+ 0.073

Table 8: Validation of δ^{18}O-VPDB-CO_2 value assignment using the Aerodyne TILDAS. Uncertainties are expanded.

Cylinder #	Sample #	NIST Analysis (‰)	External Org	Assigned Value (‰)	Diff.
CC324298	1720-A-18	- 1.77 ± 0.18	NOAA*	- 1.95 ± 0.1*	+ 0.186
FB04278	CCQM-K120	- 30.58 ± 0.27	BIPM	- 30.92 ± 0.96	- 0.401

*NOAA uncertainties are expressed as standard deviations

References

1. A. Srivastava, R.M. Verkouteren, Metrology for stable isotope reference materials: $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratio value assignment of pure carbon dioxide gas samples on Vienna PeeDee Belemnite-CO2 scale using dual-inlet mass spectrometry, *Analytical and Bioanalytical Chemistry* (411) 2743 (2019).

2. International Organization for Standardization, ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures.

3. C. Cecelski, K. Harris, C. Goodman, W. Kimes, P. Liu, W. Miller Jr., and J. Carney, Certification of NIST Gas Mixture Standard Reference Materials, Special Publication (NIST SP) 260-222, National Institute of Standards and Technology, Gaithersburg, MD, https://doi.org/10.6028/NIST.SP.260-222.

4. M.J.T. Milton, P.M. Harris, I.M. Smith, A.S. Brown, and B.A. Goody, Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures, *Metrologia*, 4(4), S291–S298 (2006).

5. Measurement of Stable Carbon Isotope Ratio in Atmospheric CH_4 Using Laser Spectroscopy for CH4 Source Characterization, *IAEA-TECDOC* No. 2066 (2024).

6. P.M. Steur, H.A. Scheeren, D. D. Nelson, J. J. McManus, and H. A.J. Meijer, Simultaneous measurement of $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2 – performance assessment of a dual-laser adsorption spectrometer, *Atmospheric Measurement Technology* (14), 4279-4304 (2021).

7. JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (Gum 1995 with minor corrections), Joint Committee for Guides in Metrology, BIPM, Sèvres, France (2008); http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**NPL**
Contact	**Aimee Hillier**
Email	aimee.hillier@npl.co.uk

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D180351	2024-07-31	100	bar
2	D180385	2024-07-31	103	bar
3	D180350	2024-07-31	106	bar
4	D180342	2024-08-13	106	bar

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D180351	-42.12	0.36	2
2	D180385	1.25	0.40	2
3	D180350	-42.12	0.68	2
4	D180342	1.25	0.33	2
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D180351	-35.68	0.77	2
2	D180385	-7.83	0.85	2
3	D180350	-35.68	0.75	2
4	D180342	-7.83	0.74	2

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D180351	407.12	0.24	2
2	D180385	409.13	0.25	2
3	D180350	793.85	0.40	2
4	D180342	799.30	0.40	2

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D180351	<1		
2	D180385	<1		
3	D180350	<1		
4	D180342	<1		

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	%	%	%	(unit)	(unit)	(unit)
1	78.25	20.78	0.93			
2	78.16	20.87	0.93			
3	78.23	20.76	0.93			
4	78.07	20.92	0.94			

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[*CCQM-P239_Result Form v0.1 2_NPL*]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**NPL**
Contact	**Aimee Hillier**
Email	**aimee.hillier@npl.co.uk**

Transfer Standards (cylinders) Information		
Number of standards	4	

Standard #	**ID (Serial Number)**
1	D180351
2	D180385
3	D180350
4	D180342

Mandatory information

1) Traceability of the measurement results

The pure CO_2 used to prepare the P239 RMs and the suites of calibration standards was certified by MPI-BGC (Max Planck Institute for Biogeochemistry). The measured isotope ratios and associated uncertainties is described in Table 1.

Table 1: $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ of the pure CO_2 used to prepare the NPL RMs and calibration suites. Uncertainties represent the combined expanded (k=2) uncertainties in measured isotope ratio.

Source	$\delta^{13}C_{VPDB}$ / ‰	$\delta^{18}O_{VPDB}$ / ‰
1	-42.115 ± 0.031	-35.677 ± 0.074
2	+1.252 ± 0.036	-7.825 ± 0.048

The pure CO_2 was sampled into 1 L glass flasks (Normag) at NPL and the $\delta^{13}C$-CO_2 was characterised using DI-IRMS (Dual Inlet Isotope Ratio Mass Spectrometry). Samples were measured against an aliquot of working standard CO_2 gas 'Cecily2015' which had previously been measured against CO_2 evolved from NBS 19. The average isotope ratio from three distinct measurements provided a $\delta^{13}C_{VPDB}$ assignment for the pure CO_2. The standard uncertainty for each measurement was calculated by combining the standard error for both the sample and standard gases.

The MPI-BGC measured isotope ratios and associated uncertainties have been used for the suites of calibration standards and the P239 reference materials. The $\delta^{13}C$ and $\delta^{18}O$ of the P239 reference materials have been certified against a suite of calibration standards to confirm agreement with the MPI-BGC certification of the pure CO_2 source within combined (k=2) uncertainties.

2) Uncertainty budget

Uncertainty in calibration suite standards

The measured isotope ratio and associated uncertainty of the pure CO_2 used to prepare the P239 RMs and calibration suite standards is detailed in Table 1. The uncertainty in measured isotope ratio inputs to determine the uncertainty in isotopic abundance according to the equation:

$$X^{12}C = \frac{1}{(1 + R^{13} + R^{13} * \frac{\delta^{13}C}{1000})}$$

An example uncertainty budget for the determination of $X^{12}C$ for the pure CO_2 is detailed in Table 2.

Table 2: Example uncertainty budget for the determination of isotopic abundance

Quantity	Units	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
$\delta^{13}C_{VPDB\text{-}CO2}$	‰	1.252	0.018	-1.09E-02	-1.97E-07
$R^{13}{}_{VPDB\text{-}CO2}$		0.011	0.00		0.00E+00
$X^{12}C$		**0.9889**			**1.97E-07**

The isotopologue amount fraction and associated uncertainty for each calibration suite standard is derived from the gravimetric amount fraction and isotopic abundance according to the equation:

$$x_{626_R} = xCO_2 * X^{12}C * X^{16}O * X^{16}O$$

An example uncertainty budget for the determination of x_{626_R} for one of the calibration suite standards is detailed in Table 3.

Table 3: Example uncertainty budget for the determination of isotopologue amount fraction for the calibration suite standards, combining gravimetric amount fractions with isotopic abundances.

Quantity	Units	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
xCO_2	µmol/mol	3.80E+02	9.50E-02	9.84E-01	9.34E-02
$X^{12}C$		9.89E-01	1.97E-07	3.78E+02	7.44E-05
$X^{16}O$		9.98E-01	25.48E-08	7.49E+02	4.11E-05
x_{626_R}		**373.76**			**0.09**

Uncertainty in unknown RMs

A linear regression was established for each isotopologue using the XLgenline software from the calculated isotopologue amount fractions (x-axis) and raw analytical response (y-axis) including the associated uncertainties in both data sets. The uncertainties in the y-axis is the standard error of the mean (SEM) of the four repeat measurements of each cylinder.

The certified isotopologue amount fractions and associated uncertainties for the P239 RMs determined from the linear regression. The isotope ratio of the unknown P239 RMs ($R^{13}{}_u$) is determined from the certified isotopologue amount fractions according to the equation:

$$R^{13}{}_u = \frac{x_{626}}{x_{636}}$$

An example uncertainty budget for the determination of $R^{13}{}_u$ is detailed in Table 4.

Table 4: Example uncertainty budget for the calculation of isotope ratio $R^{13}{}_u$ of the P239 RM, from the certified isotopologue amount fractions.

Quantity	Units	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
x_{626}	µmol/mol	400.81	0.07	-2.67E-05	-1.77E-06
x_{636}	µmol/mol	4.2922	0.0010	2.49E-03	2.62E-06
$R^{13}{}_u$		**1.071E-02**			**3.158E-06**

The isotope ratio is determined from $R^{13}{}_u$ according to the equation:

$$\delta^{13}C = \left(\frac{R^{13}{}_u}{R^{13}_{vpdb-CO2}} - 1\right) * 1000$$

An example uncertainty budget for the determination of $\delta^{13}C$ is detailed in Table 5.

Table 5: Example uncertainty budget for the determination of $\delta^{13}C$ for the P239 RMs.

Quantity	Units	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
R^{13}_{u}		1.07E-02	3.16E-06	8.94E+04	2.82E-01
$R^{13}_{VPDB\text{-}CO2}$		0.0111802	0.0000	-8.57E+04	0.00E+00
$\delta^{13}C$	‰	**-42.16**			**0.28**

Combined uncertainties

Three independent certifications were performed on each P239 RM. The three repeat measurements were combined by taking a weighted average, according to the uncertainty in each measurement. Sensitivity coefficients are given to provide an equal input from each measurement. An example uncertainty budget for the combination of the three measurement repeats is detailed in Table 6.

Table 6: Example uncertainty budget for the combination of independent measurement results for the certification of $\delta^{13}C$ of one of the P239 RMs

Date	Units	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution
25/09/2024	‰	-42.16	0.28	0.33	0.094
02/10/2024	‰	-42.15	0.23	0.33	0.077
08/10/2024	‰	-42.24	0.43	0.33	0.142
$\delta^{13}C$	**‰**	**-42.17**			**0.19 (*k* = 1)**
					0.37 (*k* = 2)

The certified $\delta^{13}C$ and $\delta^{18}O$ of each P239 RM agree with the MPI-BGC certified values of the pure source within the combined (k=2) uncertainties.

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

The compositions of Ar, O_2 and N_2 within the four P239 RMs is calculated from the gravimetry and are detailed in the results form. The amount fraction of O_2 and N_2 is slightly outside of the matrix composition limits for cylinders D180351, D180385, and D180350 described in Table 1 of the protocol but deemed to have a negligible impact on the laser spectroscopic measurement of the x_{636}/x_{626} ratio.

A synthetic air cylinder prepared from the same pure oxygen cylinder used to prepare the P239 RMs and calibration suite reference materials was purity analysed for trace N_2O impurities using standard addition. A PRM with traceability through NPL's hierarchy containing nominally 360 nmol mol^{-1} N_2O in synthetic air was diluted with synthetic air using a custom-built dilutor based on critical flow orifices[1]. A linear regression was generated using the XLgenline software, the N_2O impurity in the synthetic air was certified as < 1 nmol mol^{-1} including uncertainty in certified amount fraction.

4) Mixtures preparation

The four NPL reference materials were prepared by gravimetry in accordance with ISO 6142-1 in 10 L aluminium cylinders treated with Spectraseal™ (BOC) internal passivation process[2]. Nominally 4000 µmol mol^{-1} carbon dioxide in nitrogen reference materials were prepared from dilution of pure CO_2 of known isotope ratio. The CO_2 was added via an indirect transfer vessel addition to minimise the uncertainty associated with small mass additions. The NPL RMs were prepared by direct addition of the CO_2 intermediate mixture and dilution with argon (BIP, Air Products), oxygen (N6.0, BOC) and nitrogen (Alphagaz 2, Air Liquide) to target atmospheric blending ratios. The argon was added from a nominally 30 cmol mol^{-1} argon in nitrogen parent mixture. Two suites of calibration reference materials were prepared in the same way from the pure CO_2 source with $\delta^{13}C_{VPDB}$ 1.25 ‰ to cover the amount fraction ranges of 380-420 µmol mol^{-1} and 750-810 µmol mol^{-1}.

The dilution hierarchy is detailed in Figure 1.

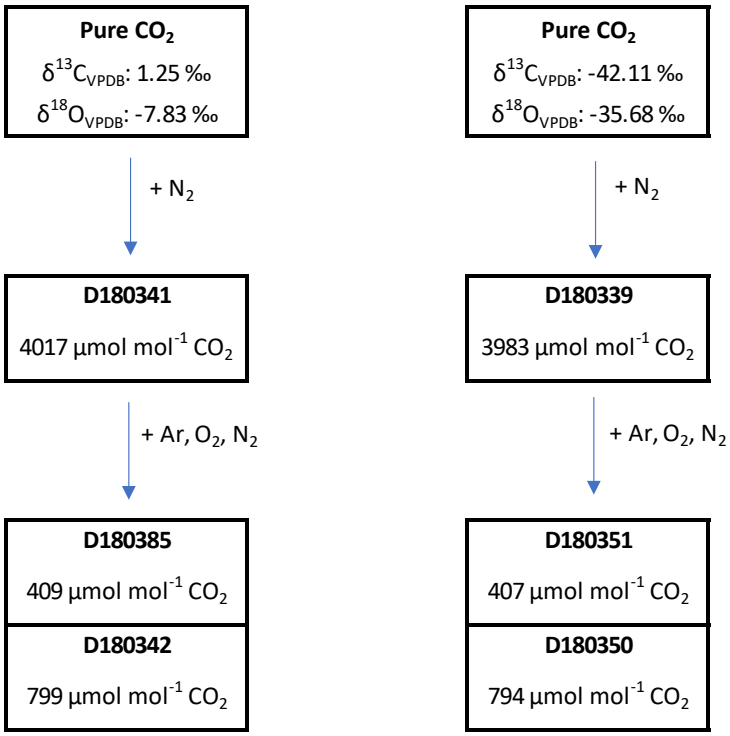


Figure 1:Dilution hierarchy for the preparation of the four NPL P239 RMs including the isotope ratio of the pure CO_2 source.

5) Verification of mixtures

Pure CO_2 with a nominal isotope ratio of $\delta^{13}C$ 1.25 ‰ and $\delta^{18}O$ -7.83 ‰ was used to prepare calibration suites consisting of three CO_2 in synthetic air reference materials in the amount fraction ranges of 380-420 µmol mol^{-1} and 750-810 µmol mol^{-1}. The calibration suite of CO_2 reference materials and the PRMs were sampled by the OA-ICOS analyser (Off-Axis Integrated Cavity Output Spectrometer; ABB Los Gatos Research (LGR), CCIA-43r-EP) at ambient pressures and with an overflow between 200-300 mL min^{-1} to prevent contamination with laboratory air. Each reference material was sampled for 5 minutes, and the sequence repeated four times.

The OA-ICOS analyser simultaneously records the amount fractions of the most abundant CO_2 isotopologues ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{17}O^{16}O$ and $^{12}C^{16}O^{18}O$). The $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 of each PRM was certified using a calibration curve approach in which a linear regression is performed for each CO_2 isotopologue against the suite of CO_2 in synthetic air reference materials which cover the amount fraction range of each isotopologue of the combustion output. The polynomial fitting software XLgenline was used to establish a linear regression of the calculated isotopologue amount fractions (x-axis) against the analytical response to each isotopologue (y-axis)[3]. Isotopologue amount fractions were determined from the traceable isotope ratios for the pure CO_2 and the gravimetric amount fraction of CO_2 for each in synthetic air reference material[4]. The certified amount fractions of the $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ isotopologues, as calculated from the linear

regressions were ratioed to determine the certified $\delta^{13}C$-CO_2 of each PRM. The certified $\delta^{18}O$-CO_2 was determined through the same method using the certified amount fractions of $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$. The certification of $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 for each PRM was repeated on three separate dates between 25/09/2024 and 15/10/2024.

References:

1. Hill-Pearce, R. E.; Resner, K. V.; Worton, D. R.; Brewer, P. J., Synthetic Zero Air Reference Material for High Accuracy Greenhouse Gas Measurements. *Analytical chemistry* **2018,** *91* (3), 1974-1979.
2. ISO, 6142-1: Gas analysis-Preparation of calibration gas mixtures-Part 1: Gravimetric method for Class I mixtures. *Geneva, Switzerland* **2015**.
3. (NPL), N. P. L., XLGENLINE V1.1. https://www.npl.co.uk/resources/software/xlgenline-and-xgenline 2014.
4. Flores, E.; Viallon, J.; Moussay, P.; Griffith, D. W.; Wielgosz, R. I., Calibration strategies for FT-IR and other isotope ratio infrared spectrometer instruments for accurate $\delta^{13}C$ and $\delta^{18}O$ measurements of CO_2 in air. *Analytical chemistry* **2017,** *89* (6), 3648-3655.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**Physikalisch-Technische Bundesanstalt**
Contact	**Dr. Javis Nwaboh**
Email	Javis.Nwaboh@ptb.de

Transfer Standards (cylinders) Information		
Number of standards	**2**	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D148967	2024-08-29	80	bar
2	D180455	2024-08-29	80	bar
3	***	***		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D148967	-9.1145	0.2500	2
2	D180455	-20.2946	0.2500	2
3	***			
4	***			

Standard #	Cylinder ID	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D148967	-14.8490	0.5000	2
2	D180455	-21.9597	0.5000	2
3	***			
4	***			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D148967	410.30	0.80	2
2	D180455	410.50	0.80	2
3	***			
4	***			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D148967	< 10		
2	D180455	< 10		
3	***			
4	***			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1	78.09	20.95	0.93			
2	78.12	20.92	0.92			
3						
4						

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	***
Contact	***
Email	***

Transfer Standards (cylinders) Information		
Number of standards		

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D87 9562	2024-01-17	172	hPa
2	D87 9563	2023-08-11	165	hPa
3	***	***		
4	***	***		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D87 9562	-10.05	0.04	1.00
2	D87 9563	-9.20	0.04	1.00
3	***			
4	***			
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	=B12	-1.75	0.05	1.00
2	=B13	-1.21	0.06	1.00
3	=B14			
4	=B15			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D87 9562	443.03	0.07	1.00
2	D87 9563	428.95	0.07	1.00
3	***			
4	***			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D87 9562	338.90	0.50	1.00
2	D87 9563	338.60	0.30	1.00
3	***			
4	***			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(unit)	(unit)	(unit)	(unit)	(unit)	(unit)
1						
2						
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

Results UGv1

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**University of Groningen**
Contact	**Pharahilda Steur**
Email	**p.m.steur@rug.nl**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)
1	D87 9562
2	D87 9563
3	
4	

Mandatory information

1) Traceability of the measurement results

For our CO_2 isotope ratio measurements, we use five high-pressure gas tanks (40 L Luxfer aluminum, alloy 6061, max. pressure of 200 bar) in the standard measurement procedure of our Stable Isotopes of CO_2 Absorption Spectrometer (SICAS) instrument used in these analyses. Our gas tanks are filled with dry ambient air collected from the roof of our institute and compressed with our in-house compressor system. One of the tanks contains the working gas and is used for drift correction and calibration. One of the tanks is the quality control gas which is treated as a sample for the long-term quality control of the instrument. The other 3 reference tanks are calibration gases which have a low, high and medium CO_2 mole fraction and a range of modern ^{13}C-CO_2 and ^{18}O-CO_2 isotopic compositions. Aliquots of the SICAS reference tanks have been analyzed at the Max Planck Institute for Biogeochemistry in Jena (MPI-BGC) by Isotope Ratio Mass Spectrometry (IRMS) to link the $\delta^{13}C$ and $\delta^{18}O$ values of our reference tanks directly to the JRAS-06 scale (Jena Reference Air Set for isotope measurements of CO_2 in air (VPDB/VPDB-CO_2 scale)).

CO_2 mole fractions are measured on a Picarro G2401 CRDS gas mole fraction analyzer and calibrated using 4 in-house working standards, calibrated themselves against 3 primary standards provided by the ICOS Central Analytical Laboratories (CAL) in Jena (hosted by the Max Planck Institute for Biogeochemistry) that are directly linked to the WMO X2019 scale for CO_2.

Table 1. The reference gases on the SICAS used in this experiment. The measurement error represents the total uncertainty from the combined measurement precision of the reference samples and the scale uncertainty.

Cyl. #	SICAS reference gases	CO2 (ppm)	d13C VPDB (per mille)	d18O VPDB (per mille)	d17O VSMOW (per mille)	CO2 scale	d13C VPDB scale	d18O VPBD scale
8164	Working Gas	405.94±0.07	-8.630±0.014	-4.050±0.019	19.28±0.019	WMO-X2019	JRAS	JRAS
4318	Quality Control	417.31±0.07	-9.130±0.018	-3.250±0.018	19.69±0.018	WMO-X2019	JRAS	JRAS
4315	Reference1	424.75±0.07	-9.434±0.014	-3.637±0.022	19.48±0.027	WMO-X2019	JRAS	JRAS
6185	Reference2	443.40±0.07	-9.899±0.010	-3.122±0.064	/	WMO-X2019	JRAS	JRAS
4330	Reference3	463.90±0.07	-9.686±0.009	-1.974±0.028	/	WMO-X2019	JRAS	JRAS

A second order polynomial calibration curve is derived from the assigned and the measured isotopologue mole fractions of the working gas and the three references gases. Calibrated isotopologue mole fractions are calculated for the measured transfer standards, and subsequently calibrated delta values are calculated from the calibrated mole fractions. The $\delta^{17}O$ values of the working gas, quality control and reference 1 have been assigned by using measurements of the $\delta^{17}O$-$\delta^{18}O$ relation of the reference gases at the Institute for Marine and Atmospheric Research in

Utrecht (IMAU). These assigned values are included in the calibration, while for the other cylinders the $\ln(\delta^{17}O)/\ln(\delta^{18}O)$ relation is assumed to be 0.5229, being the value measured for CO_2 calibrated with water (Barkan and Luz, 2012). All the SICAS oxygen isotope measurements are expressed on the VSMOW scale. We convert the VPDB-CO_2 $\delta^{18}O$ values derived from the MPI-BGC measurements to the VSMOW scale with the following equation:

$\delta^{18}O$ VSMOW = $\delta^{18}O$ VPDB*1.0414869+($\delta^{18}O$ VPDB -1)

The following ratio values are used for the calculation of the assigned isotopologue mole fractions:

R^{13}(VPDB) = 0.01118 (Chang & Li, 1990)

R^{17}(VSMOW) = 0.00038672 (Assonov & Brenninkmeijer, 2003)

R^{18}(VSMOW) = 0.0020052 (Allison et al.,1995; Baertschi, 1976)

Our SICAS $\delta^{18}O$ results on the VSMOW scale are for this intercomparison converted to the VPDB-CO_2 scale by the following equation:

$\delta^{18}O$ VPDB-CO_2 = $\delta^{18}O$ VSMOW-41.49/ 1.04149

The traceability chain can thus be listed as follows:

1. Transfer standards are calibrated using the SICAS reference cylinders as listed in table 1.

2. The SICAS reference cylinders are directly linked to the JRAS-06 scale as aliquots of the cylinder gases were sent to the MPI-BGC in Jena and measured on IRMS against JRAS-06 CO_2 in air mixtures. Aliquots of several reference cylinders were also measured for their $\delta^{17}O$-$\delta^{18}O$ relation at the IMAU so $\delta^{17}O$ values can be assigned as well.

3. The JRAS-06 scale is linked to the VPDB(-CO_2) scale by the use of CO_2 released from the MARJ-1 calcite, that was determined against primary reference materials, that is mixed into CO_2 free air. (Wendeberg et al., 2013).

2) Uncertainty budget

The standards 1 and 2 were measured on the SICAS in two measurement series at two consecutive days. There were in total 6 and 2 individual measurements of standards 1 and 2, respectively. An individual measurement consists of 9 iterations of sample and working gas measurements, where the working gas measurements are used to do a drift correction. The uncertainty reported in the results includes the average of the combined uncertainties and the standard error of the individual measurements. The standard errors for the $\delta^{13}C$ measurements are 0.007 and 0.001 ‰ for standards 1 and 2, respectively. The standard errors for the $\delta^{18}O$ measurement are 0.003 and 0.024 ‰ for standards 1 and 2, respectively.

The combined uncertainty consists of various values that express different sources of uncertainty, which are explained bellow:

- Instrumental repeatability: a quality control tank is measured 4 times in one measurement series and is used to determine the repeatability of the measurement series by calculating the standard deviation of the 4 measurements (k=1). The instrumental repeatability of the measurements ranges between 0.006 and 0.011 for both the $\delta^{13}C$ and $\delta^{18}O$ measurements.

- Introduced uncertainty: the distance in CO_2 mole fraction of the sample from the calibration gas will influence the uncertainty of the calibrated value. For both cylinders an uncertainty of 0.03 is assigned to the calibrated values.

- Scale uncertainties: scale uncertainties for all calibration gases are shown in table 1. The uncertainties are determined from the measurements conducted by the MPI-BGC, including the standard error and the average measurement uncertainty of the aliquot measurements.

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

The two standards are both natural air taken from the roof of our institute, scrubbed from water to mole fractions >5 ppm.

4) Mixtures preparation

The cylinders were filled with natural air using a two stage Resato air driven gas booster type RBS-160-5-30-D-B. Water is removed in four steps. In step 1 the air is pumped through a chemical dryer cartridge containing 500 g of Drierite ($CaSO_4$), after which the air contains about 0.9 % water. In step 2 water is removed using a Parker Hiross cooler dryer, reducing the water content to 0.1%. In step 3 the air goes through a Midland coalescent dryer. The fourth step is water removal by pumping the air through 2 chemical drier tubes (60 cm x ¾") both containing 75 g of $Mg(ClO_4)_2$. These last two drying steps reduce the water content to >0.0005 %.

5) Verification of mixtures

Both cylinders were extensively measured for their composition on different instruments in our lab, which we will repeat after the comparison. The results from different instruments are listed below in table 2.

Table 2. Results of various trace gases and isotope composition measurements that were conducted for verification of the mixtures.

Species	cyl #9563	cyl #9562	scale	scale error	instrument	Date
N2O ppb	338.6	338.9	WMO 2006A	0.26	GC-PDHID	23/07/24
sd	0.1	0.4		0.49370134	0.27490467	
H2 ppb	602.1	952.7	MPI 2009	1.5	GC-PDHID	23/07/24
sd	3.1	4.7				
SF6 ppb	11.88	12.24	WMO X2006	0.07	GC-PDHID	23/07/24
sd	0.01	0.07				
CO2 ppm	428.95	443.03	WMO X2019A	0.07	CRDS	17/07/24
sd	0.01	0.01		0.07155667		
CH4 ppb	2307.68	2259.91	WMO X2004A	1	CRDS	17/07/24
sd	0.13	0.07				
CO ppb	208.46	270.16	WMO X2014A	2	CRDS	17/07/24

sd	0.47	0.50				
d13C-CO2	-9.240	-10.055	VPBD	0.035	TILDAS	25/07/24
sd	0.006	0.005				
d18O-CO2	-1.186	-1.753	VPBD	0.05	TILDAS	25/07/24
sd	0.007	0.004				
H2O	<5 ppm	<5 ppm	n.a.	n.a.	CRDS	17/07/24

References:

Allison, C. E., & Francey, R. J. (1995). High precision stable isotope measurements of atmospheric trace gases. *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, 131-153.

Assonov, S. S., & Brenninkmeijer, C. A. (2003). A redetermination of absolute values for 17RVPDB-CO2 and 17RVSMOW. *Rapid Communications in Mass Spectrometry*, *17*(10), 1017-1029.

Baertschi, P. (1976). Absolute18O content of standard mean ocean water. *Earth and Planetary Science Letters*, *31*(3), 341-344.

Barkan, E., & Luz, B. (2012). High-precision measurements of 17O/16O and 18O/16O ratios in CO2. *Rapid communications in mass spectrometry*, *26*(23), 2733-2738.

Wendeberg, M., Richter, J. M., Rothe, M., & Brand, W. A. (2013). Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO 2 in air. *Atmospheric Measurement Techniques*, *6*(3), 817-822.

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**TUBITAK UME**
Contact	**Adnan Şimşek, Aylin Boztepe, Tanıl Tarhan**
Email	**adnan.simsek@tubitak.gov.tr, aylin.boztepe@tubitak.gov.tr, tanil.tarhan@tubitak.gov.tr**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	PSM206705	2024-05-28	110	bar
2	PSM206688	2024-05-28	115	bar
3				
4				

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	PSM206705	-20.10	0.07	2
2	PSM206688	-41.87	0.10	2
3				
4				
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1				
2				
3				
4				

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	PSM206705	409.95	0.82	2
2	PSM206688	409.84	0.82	2
3				
4				

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1				
2				
3				
4				

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar			
Standard #	(µmol/mol)	(µmol/mol)	(µmol/mol)			
1	788625.05	210903.63	60.82			
2	788626.55	210902.84	60.22			
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

[*CCQM-P239_Result Form v0.1_TUBITAK_UME_2024_9_19*]

Participating institute information	
Institute	**TUBITAK UME**
Contact	**Adnan Şimşek, Aylin Boztepe, Tanıl Tarhan**
Email	**adnan.simsek@tubitak.gov.tr, aylin.boztepe@tubitak.gov.tr, tanil.tarhan@tubitak.gov.tr**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	**ID (Serial Number)**	
1	PSM206705	
2	PSM206688	

1) Traceability of the measurement results

The instrument information used in CCQM P-239 comparison was given in Table 1.

Table 1. Information on the instrument

Technique	GC-IRMS, EA
Brand	Thermo Finnigan
Model	MAT 253
Control software name and version	Isodat NT Ver. 3.0

IAEA-603 (calcite) produced by International Atomic Energy Agency was used as the reference material for the calibration of reference CO_2 gas used in GC-IRMS. The traceability of the measurements ensured with this reference material.

Table 2. Calcite reference material certificate value

IAEA-603 (calcite)	
$\delta^{13}C$ Value	+2.46
Uncertainty (U, k=2)	0.01

For the calibration of the reference CO_2 gas, IAEA-603 was measured with Elemental Analyser (EA-IRMS) 6 times using solid autosampler. $\delta^{13}C$ value of the CO_2 reference gas was determined using these measurements. Then, this $\delta^{13}C$ value of the reference CO_2 gas was used in GC-IRMS method using the same reference CO_2 gas.

In sample measurements, CO_2 in air was separated by using gas column (HP PLOT-Q) in GC coupled to IRMS. The air was removed from the system by using backflush mode in GC method and $\delta^{13}C$ value of CO_2 in the gas cylinders coded PSM206705 and PSM206688 was measured. The $\delta^{13}C$ measurements of the cylinders were performed on 2 different days. 6 injections of each cylinders were carried out through the GC-IRMS gas autosampler.

Corrections applied to the $\delta^{13}C$ isotope ratios were carried out using the CO2_SSH evaluation type available in the IRMS software.

2) Uncertainty budget

The values and uncertainties for the standards were calculated using single point calibration with IAEA-603 reference material. The measurements of the cylinders coded PSM206705 and PSM206688 were carried out on two different days without any drift corrections.

The combined uncertainty of the standards reported $\delta^{13}C$ values include contributions from:

- Standard uncertainty from repeatability of the sample measurements

- Standard uncertainty of RM (IAEA-603) from certificate value

- Standard uncertainty from repeatability of the reference CO_2 gas calibrated with IAEA-603

The standard uncertainty in $\delta^{13}C$ was calculated using the Equation 1.

$$u = \frac{stdev}{\sqrt{n}} \qquad \text{Eq. 1}$$

stdev : standard deviation of n measurements

n : number of measurements

The combined standard uncertainty was determined by the following equation:

$$u_c = \sqrt{{u_1}^2 + {u_2}^2 + {u_3}^2 + {u_4}^2} \qquad \text{Eq. 2}$$

where

u_1, standard uncertainty from measurement of sample in day 1

u_2, standard uncertainty from measurement of sample in day 2

u_3, standard uncertainty of RM (IAEA-603) from certificate value

u_4, standard uncertainty from repeatability of the reference CO_2 gas calibrated with IAEA-603

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

Results of the standards on two different days are presented in Table 3.

Table 3. $\delta^{13}C_{VPDB}$ results of the standards

Standards	$\delta^{13}C_{VPDB}$, ‰ Day 1	$\delta^{13}C_{VPDB}$, ‰ Day 1 Mean	$\delta^{13}C_{VPDB}$, ‰ Day 2	$\delta^{13}C_{VPDB}$, ‰ Day 2 Mean	$\delta^{13}C_{VPDB}$, ‰ Overall Mean	Uncertainty, k=2
PSM206705	-20.28	-20.21	-20.00	-19.98	-20.10	0.07
	-20.29		-19.96			
	-20.21		-19.92			
	-20.18		-19.94			
	-20.14		-20.04			
	-20.15		-20.05			
PSM206688	-41.81	-41.87	-41.78	-41.86	-41.87	0.10
	-41.90		-41.87			
	-41.78		-41.85			
	-42.00		-41.82			
	-41.78		-41.88			
	-41.96		-41.98			

3) Mixtures composition

Pure CO_2 gases with different isotopic compositions were supplied from SIAD company. Dry air containing N_2, O_2, and Ar were supplied from HABAŞ Gas (Turkish Company). CO_2 amount fraction in dry air has been checked and found to be less than 0.6 µmol mol^{-1}. A filter (SAES Pure Gas/ Micro Torr, SP600-906F) was utilised for dry air during mixture preparation to remove CO_2 to < 1 nmol mol^{-1}. The amount fraction of N_2O in the air and mixtures could not be determined due to lack of infrastructure.

4) Mixtures preparation

CO_2 gas mixtures at ambient amount fractions (410 µmol mol^{-1}) were prepared gravimetrically by the dilution of pure CO_2 gases with dry air.

Mixtures were prepared in three steps. In the first step, pure CO_2 was diluted to 6 cmol mol^{-1} with dry air. In the second step, this pre-mixture was diluted to 0.5 cmol mol^{-1}. In the final step, 0.5 cmol mol^{-1} mixtures were used to produce 410 µmol mol^{-1} CO_2/air mixtures.

All gas fillings were performed in accordance with ISO 6142-1:2015 standard [1] by TUBITAK UME Gas Metrology Laboratory.

5) Verification of mixtures

The carbon dioxide (CO_2) in air mixtures were analyzed on a cavity ring-down spectroscopy (CRDS) instrument, i.e., Picarro G2401 $CO/CO_2/CH_4/H_2O$ Analyzer equipped with 16-Port Distribution Manifold. Verification of the mixtures was carried out using own standards. Cylinders were equipped with pressure reducers and connected to 16-port distribution manifold. They were flushed three times before the first measurement.

Each cylinder was measured for 5 minutes which is a sufficient time to obtain stable results. The measurement data was collected using CRDS software. Software takes about 404 readings for 5 minutes. During the data evaluation of cylinders, total number of 92 readings in between 3-4 minutes has been used for determination of average values and uncertainties for each cylinder at each measurement.

The measurement uncertainty of samples was determined according to ISO 6143:2001 [2], using the CurveFit software. The value for goodness of fit in each measurement was found to be less than 2 in each case for linear function.

References

[1] International Organization for Standardization, ISO 6142-1:2015 “Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures”

[2] International Organization for Standardization, ISO 6143:2001 “Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures”

Result Form for the comparison

CCQM-P239 - Pilot Study on isotopes of CO_2 in air mixtures

Participating institute information	
Institute	**D.I.Mendeleyev Institute for Metrology (VNIIM)**
Contact	**Dr. Ian Chubchenko**
Email	ycc@b10.vniim.ru

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	D993597	2024-06-10	115	bar
2	D993598	2024-06-10	110	bar
3	-	-		
4	-	-		

Content of the form

page 1	General information
page 2	Results
page 3	Standards Composition

This result form is to be completed by participants in CCQM-P239

Please complete the cells according to their format:

	A numerical value is expected
***	*Text is expected*

After completion of the appropriate section of this report, please send to Joële Viallon by email (jviallon@bipm.org)

This result form aims at recording measurement results

More details on standards and methods shall be reported in the CCQM-P239 Information Sheet

A complete version of this result form shall be sent ***prior to measurements at the BIPM.***

Measurements of the participant's standards by the BIPM will start only when this form is recived.

An updated version may be sent after verification measurements by the participant.

Measurement results - isotope ratios

Complete the cells below with your final measurement results :
Value of the isotope ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measured in each standard
expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO2 scales respectively.
with their associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	$\delta^{13}C$	$U(\delta^{13}C)$	*k*
		permil	permil	
1	D993597	-1.81	0.10	2
2	D993598	-43.15	0.10	2
3	***			
4	***			
Standard #	**Cylinder ID**	$\delta^{18}O$	$U(\delta^{18}O)$	*k*
		permil	permil	
1	D993597	-9.36	0.19	2
2	D993598	-44.56	0.19	2
3	=B14			
4	=B15			

Standards composition

CO_2 amount fraction

Complete the highlighted cells below with the value of the amount fraction of carbon dioxide measured in each cylinder, expressed in µmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{CO2}	$U(x_{CO2})$	*k*
		µmol/mol	µmol/mol	
1	D993597	479.95	0.19	2
2	D993598	480.17	0.20	2
3	=B14			
4	=B15			

N_2O amount fraction

Complete the highlighted cells below with the value of the amount fraction of nitrous oxide measured in each cylinder, expressed in nmol/mol,
the associated expanded uncertainty and its coverage factor *k*

Standard #	Cylinder ID	x_{N2O}	$U(x_{N2O})$	*k*
		nmol/mol	nmol/mol	
1	D993597	< 8,3	4.8	2
2	D993598	< 8,3	4.8	2
3	=B14			
4	=B15			

Matrix Gas

Complete the cells below with the composition of the matrix gas
Indicate the amount fractions of the three major compounds
Compounds at trace levels may be indicated as well in the columns (other)
Indicate the unit in the cells (unit)

Compound	N_2	O_2	Ar	Other	Other	Other
Standard #	(%)	(%)	(%)	(unit)	(unit)	(unit)
1	78.0892	20.9274	0.93541			
2	78.0899	20.9318	0.93025			
3						
4						

Information Sheet
CCQM-P239, CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures

Please complete one information sheet per participant, providing at least the information which is listed as mandatory. The replies can replace the text provided as instructions, which will be deleted in the final report of the comparison.

This information sheet completes the result form (Excel Spreadsheet), in which results of measurement are to be reported. Please indicate here the name of the result form, with the different versions if applicable:

[*CCQM-P239_Result Form v0.1 1-VNIIM*]

Measurements of the participant's standard by the BIPM will start only when a complete version of the result form is received. This information sheet can be sent later, but in any case, prior to the drafting of the comparison report. The measurements results of the participant will not be included in the comparison report if the information sheet is missing.

Send an electronic version by email to Dr. Joële Viallon (jviallon@bipm.org).

Participating institute information	
Institute	**D.I.Mendeleyev Institute for Metrology (VNIIM)**
Contact	**Dr. Ian Chubchenko**
Email	**ycc@b10.vniim.ru**

Transfer Standards (cylinders) Information		
Number of standards	2	

Standard #	**ID (Serial Number)**
1	D993597
2	D993598
3	-
4	-

Mandatory information

1) Traceability of the measurement results

[Instructions below may be removed]

As indicated in section 2 of the protocol, the measurands are $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the CO_2 gas in the carbon dioxide in air mixture expressed as $\delta^{13}C$ and $\delta^{18}O$ values in per mil (‰) on the VPDB and VPDB-CO_2 scales respectively. Explain here how the measurement results reported in the result form are traceable to these scales, including information on:

- Number and kind of reference materials (gas mixture, pure gas, carbonate, …) used to ensure traceability to VPDB and VPDB-CO_2, including those employed inside the laboratory as well as outside if relevant (traceability obtained from another laboratory).

  Calibration hierarchy:

RMs (carbonates):IAEA-603, IAEA-610, IAEA-611, IAEA-612

*

↓

Working ref. (pure CO_2): D157908, D158049

**

↓

Transfer standards (CO_2 in air): D993597,D993598

Footnote	Description
*	The reaction of carbonates with orthophosphoric acid is carried out. Carbonate aliquots (0.5 mg) is reacted with 0.1 ml H_3PO_4 (1.93 g/cm^3 density) at 25±0.1 ºC for 24 hours. H_3PO_4 (>85 %, Merck, CAS-no: 7664-38-2, ACS, ISO and Reag. PhEur) and P_2O_5 (>99 %, Merck, CAS-no: 1314-56-3, ACS, ISO and Reag. PhEur) are used for the preparation of concentrated acid. Other parameters of this reaction are given in 10.1002/rcm.1886, 10.1002/rcm.8867. CF-IRMS is used for the measurements.
**	The CO_2 extraction system is used for the measurements. The system is carefully described in https://doi.org/10.1016/B978-044451114-0/50016-8. DI-IRMS is used for the measurements.

- Values of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios in the reference materials listed above, expressed preferably as isotope delta in per mil on the VPDB and VPDB-CO_2 scales.

Carbonates Reference Materials	
RM1 description	IAEA-603

Use in the calibration hierarchy	Calibration of working ref. for DI-IRMS
δ13C in per mil (‰) on the VPDB scale	2,46
δ18O in per mil (‰) on the VPDB-CO2 scale	-2,37
RM2 description	IAEA-610
Use in the calibration hierarchy	Calibration of working ref. for DI-IRMS
δ13C in per mil (‰) on the VPDB scale	-9,109
δ18O in per mil (‰) on the VPDB-CO2 scale	-18,834
RM3 description	IAEA-611
Use in the calibration hierarchy	Calibration of working ref. for DI-IRMS
δ13C in per mil (‰) on the VPDB scale	-30,795
δ18O in per mil (‰) on the VPDB-CO2 scale	-4,224
RM4 description	IAEA-612
Use in the calibration hierarchy	Calibration of working ref. for DI-IRMS
δ^{13}C in per mil (‰) on the VPDB scale	-36,722
δ^{18}O in per mil (‰) on the VPDB-CO_2 scale	-12,079
Gaseous Reference Materials of pure CO2	
RM5 description	Pure CO2 in Luxfer cylinder #D158049
Use in the calibration hierarchy	Working ref. for DI-IRMS
δ13C in per mil (‰) on the VPDB scale	-1,81
δ18O in per mil (‰) on the VPDB-CO2 scale	-9,36
RM6 description	Pure CO2 in Luxfer cylinder #D157908
Use in the calibration hierarchy	Working ref. for DI-IRMS
δ13C in per mil (‰) on the VPDB scale	-43,15
δ18O in per mil (‰) on the VPDB-CO2 scale	-44,56

- Name of any laboratory included in the traceability chain.

  None

- Number of calibration steps between the higher order reference material (closest to the scale) and the transfer standards sent for CCQM-P239.

  One

- Corrections applied to the isotope ratios as measured by your analytical instrument (for example ratios between signals measured at different masses by an IRMS, or ratios between the areas measured on two different peaks of the spectrum by an optical analyser).

Information on data treatment	
Were the data treated with the control software, in-house software, or both?	Control software
Correction for cross-contamination ("eta" value) (yes/no)?	no
^{17}O Correction (yes/No)?	yes
If yes, reference to a publication where the method is described	Craig, H. (1957). Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide Geochimica et Cosmochimica Acta 12: 133-149.
Linearization (calibration assuming linear behavior) of δ values (yes/no)?	yes
If yes, number of standards (eg NBS19/LSVEC) used to linearize and their values?	4

- Values of reference data impacting the measurement results, for example conventional values of the isotope ratios included in the definition of the VPDB scale

  None

2) Uncertainty budget

[Instructions below may be removed]

Explain here how the uncertainties associated with the measurement results were obtained. Describe the sources of uncertainty identified, their values, and how they were combined. Examples of sources are the calibration performed by another laboratory, the repeatability of successive measurements, the reproducibility of measurements performed on different days, drift of the values, data treatment and corrections applied to the measurement results.

The analytical standard uncertainty was obtained by using the following equation:

$$u_{delta} = \sqrt{u_{rep}^2 + u_{cal}^2}$$

where u_{rep} is the contribution of the reproducibility between measurements on DI-IRMS, u_{cal} is the uncertainty of the working ref. for DI-IRMS. Working ref. is pure CO_2 gas traceable to the CCQM-P204.

Table 1: Uncertainty budget for the analysis of $\delta^{13}C$

Source of uncertainty	Standard uncertainty, ‰

Reproducibility (u_{rep})	0,003
RM (u_{cal})	0,049
Combined standard uncertainty (u_{delta})	0,049
Expanded uncertainty k=2 (U_{delta})	0,10

Table 2: Uncertainty budget for the analysis of $\delta^{18}O$

Source of uncertainty	Standard uncertainty, ‰
Reproducibility (u_{rep})	0,019
RM (u_{cal})	0,093
Combined standard uncertainty (u_{delta})	0,095
Expanded uncertainty k=2 (U_{delta})	0,19

Additional non-mandatory information

Participants are invited to further describe their standards and methods below. References to articles published in peer-reviewed journals may be provided. The provided information will be added as annex to the comparison report and referred to when relevant to explain the comparison's results.

3) Mixtures composition

[Instructions below may be removed]

As explained in section 3.2 of the protocol, standards shall have a dry air matrix, which can be either *scrubbed real air* or *synthetic air* (blended from pure gases). Provide here any useful information on the gas mixture composition which is not already provided in the accompanying result form.

All details are provided in the accompanying result form

4) Mixtures preparation

[Instructions below may be removed]

If the mixtures were prepared in your laboratory, describe here the preparation method, including information on the sources of pure gases (with a particular attention to carbon dioxide), the purity of the gases, how they were mixed, and any relevant detail on materials or treatment employed to obtain the mixtures.

If the mixtures were prepared in another laboratory, report here the information provided by this laboratory regarding the mixtures' preparation.

We used the gravimetric preparation method according to ISO 6142. Two sources of CO2 indicated in table below were used for the preparation.

Standard #	Source of CO2	CO2 mole fraction of the source, %	Nominal $\delta^{13}C$, ‰
D993597	7481	99,999322	-1,8
D993598	14509448	99,9999575	-43,2

5) Verification of mixtures

[Instructions below may be removed]

As described in section 5 of the protocol, participants should perform a verification of their mixtures before and after shipment. Describe here the verification procedure, including information on the dates of the measurements, the analytical instruments, their calibration, the calculations performed to obtain the measurements results. A comprehensive description of the isotope ratios measurements is the most important, but relevant information on the amount fractions measurements is also valuable.

Isotope ratios measurements

The dates of the measurements:

Operator	Ian Chubchenko
Start date (first measurements)	19.08.2024
End date (last measurements)	26.08.2024

The analytical instruments:

Technique (Dual Inlet, Continuous Flow, …)	Dual Inlet

Brand	Elementar
Model	isoprime precisION
Control Sotfware name and version	ionOS 4.5.8.26

Information on measurement sequences, all sequences were identical in structure

Number of measurement cycles in one analysis	12
Instrument IDLE time	30 sec
Instrument integration time	30 sec
Number of successive repeats of one analysis	10
Duration of one sequence	12 min
Number of unkown samples per sequence	1
Number of standards per sequence	1
Number of measurement sequences per sample	10
Total number of analysis per sample	120

The results of isotope ratios measurements are shown in attached excel files.

Amount fractions measurements

The dates of the measurements:

Operator	Ian Chubchenko
Start date (first measurements)	01.07.2024
End date (last measurements)	08.07.2024

The analytical instruments:

Technique	CRDS
Brand	Picarro
Model	G2131i

Two mixtures with the same nominal mole fraction of CO_2 were prepared gravimetrically in the same type of cylinders. The measurement results are shown in the table below.

Cylinder ID	Nominal $\delta^{13}C$, ‰	X_{CO2}, µmol/mol	$U(X_{CO2})$, k=2, µmol/mol	Measurement result, µmol/mol	SD, µmol/mol	Number of measurements	Verification is successful?
D993597	-1,8	479,95	0,19	480,01	0,05	6	Y

D152690	-1,8	480,05	0,19	-	-	-	-
D993598	-43,15	480,17	0,20	480,32	0,05	6	Y
D152689	-43,15	480,18	0,20	-	-	-	-