# Final Report of CCQM-P225a and b, International Comparison on Carbon Dioxide in air and nitrogen at ambient levels (350 µmol/mol to 800 µmol/mol)

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## Summary

The pilot studies CCQM-P225a and b aimed at validating the performance of the *pVT*−$CO_2$ manometric reference facility maintained at the BIPM as a reference for the planned on-going comparisons BIPM.QM-K2a and b for $CO_2$ in air and nitrogen standards respectively over the range 350 µmol mol$^{-1}$ to 800 µmol mol$^{-1}$. The planned launch date of the BIPM.QM-K2a and b comparisons is 2024 and will enable NMIs and DIs to have access to on-demand comparisons for their $CO_2$ in air and nitrogen standards over the range 350 µmol mol$^{-1}$ to 800 µmol mol$^{-1}$.

The pilot studies supplemented the validation activities on the BIPM reference facility already reported in CCQM-P188, and on-going validation studies against NIST, NOAA and VSL gas standards. A description of the BIPM facility performance will be submitted for publication in a peer-reviewed journal in 2023, with a full uncertainty analysis showing that it can operate with standard uncertainty of 0.1 µmol mol$^{-1}$ over the amount fraction range of the comparison (Viallon et al. 2023b).

The comparison was organised using a sufficient number of independent standards, to demonstrate the performance of the BIPM system, whilst limiting the duration of the pilot study, allowing the key comparison to start as planned in 2024. Following discussions at the 44$^{th}$ GAWG meeting it was decided that comparisons with 3 independent standards at 3 nominal amount fraction values (380, 480 and 800 µmol mol$^{-1}$) in the two matrices (air and nitrogen) would be sufficient.

Results presented in this report show a good agreement between values assigned by participants and those measured at the BIPM, over the entire range of the comparison and for both matrices (air and nitrogen). The BIPM *pVT*−$CO_2$ facility is ready to act as reference facility for the on−going key comparison BIPM.QM−K2.

# Contents

# 1 Purpose and scope

The pilot studies CCQM-P225a and b aimed at validating the performance of the *pVT*− $CO_2$ manometric reference facility maintained at the BIPM as a reference for the planned on-going comparisons BIPM.QM-K2a and b for $CO_2$ in air and nitrogen standards respectively over the range 350 µmol mol$^{-1}$ to 800 µmol mol$^{-1}$.

The *pVT*− $CO_2$ facility of the BIPM quantifies the $CO_2$ amount fraction in air or nitrogen samples via measurements of the pressure and temperature of the sample and of the $CO_2$ extracted from it by cryogenic trapping. It was first described in the report of the pilot study CCQM-P188 (Flores et al. 2019b) conducted in parallel with the key comparison CCQM-K120 (Flores et al. 2019a). Since then, it underwent several improvements (Viallon et al. 2023b).

The comparisons were performed at 3 nominal $CO_2$ amount fractions and the following acceptable range at each nominal value: 380 µmol mol$^{-1}$ (acceptable range 350 to 430 µmol mol$^{-1}$); 480 (430 to 530 µmol mol$^{-1}$); 800 (530 to 800 µmol mol$^{-1}$). The standards were to contain $CO_2$ in a matrix of dry air (part a) or nitrogen (part b), with constraints imposed on the composition of this matrix. The $N_2O$ amount fractions was also to be reported by participants with standard uncertainties of 5 nmol/mol or better.

# 2 Measurand, quantities and Units

The measurand was the amount fraction of carbon dioxide in air (part a) and the amount fraction of carbon dioxide in nitrogen (part b), with measurement results being expressed in mol mol$^{-1}$ (or one of its multiples mmol mol$^{-1}$, µmol mol$^{-1}$ or nmol mol$^{-1}$).

# 3 Participants

The comparison included 5 participants listed below:

- Laboratoire National de métrologie et d'Essais (LNE)
- National Institute of Metrology (NIM)
- National Oceanic and Atmospheric Administration (NOAA)
- National Physical Laboratory (NPL)
- Dutch Metrology Institute (VSL).

# 4 Measurement schedule

The comparison was organised by the BIPM following the schedule (updated after the comparison) displayed in Table 1.

*Table 1: schedule of events in CCQM-P225 organisation*

| Due Date | Event |
|---|---|
| **01 March 2022** | Pre-study measurements on NOAA standards |
| **01 March 2022** | Distribution of Protocol for Comment to GAWG and confirmation of interest of potential participants |
| **26 April 2022** | Finalization of protocol and confirmation of participants |
| **15 May 2022** | Distribution of final protocol and results forms for comparisons |
| **30 September 2022** | Deadline for participants to ship standards to the BIPM and send their results forms |
| **15 October 2022** | Start of measurements at the BIPM |
| **15 January 2023** | Completion of measurements at the BIPM |
| **28 February 2023** | Deadline for retrieval of Standards from the BIPM |
| **28 February 2023** | Deadline for participants to confirm or modify uncertainties of their reported values |
| **15 April 2023** | Circulation of Draft A report to participants |

# 5 Standards prepared by participants

The mixtures were to be prepared and/or analysed by participants using their usual procedure, with the constraints on the nominal $CO_2$ amount fraction and on the matrix composition, as detailed in sections 5.1, 5.2 and 5.3. The two different approaches used by participants for value assignment of their standards are described in section 5.4, and section 5.5 summarises the values reported by participants and their uncertainties.

## 5.1 Nominal $CO_2$ amount fractions

Each participant was required to provide a standard for each of the nominal amount fractions summarized in Table 2, and in the matrix for the part (a - air or b - nitrogen) of the comparison they participate in.

*Table 2: Nominal amount fractions and acceptable ranges of standards to be submitted for measurement at the BIPM*

| Standard Submitted | $CO_2$ amount fraction nominal value ($\mu$mol mol$^{-1}$) | $CO_2$ amount fraction acceptable range ($\mu$mol mol$^{-1}$) |
|---|---|---|
| 1 | 380 | 350 to 430 |
| 2 | 480 | 430 to 530 |
| 3 | 800 | 530 to 800 |

Additional standards were provided by NOAA and VSL as part of validation studies started before this comparison. It was agreed with participants that the additional standards would also be included in the comparison.

## 5.2 Matrix composition for standards prepared in air (Part a)

Standards were requested to have a dry air matrix, which could be either *scrubbed real air* or *synthetic air* (blended from pure gases). The matrix was to contain the major constituents of air (nitrogen, oxygen, argon) and could contain nitrous oxide and methane at up to ambient amount fractions. The BIPM reference facility results are only weakly influenced by air composition (influence on compressibility factor of air) apart from nitrous oxide amount fraction. However, the comparison is at the level of uncertainty, where the air composition would influence the use of standards in calibrating spectroscopic methods. The limits of the amount fraction of the major constituents provided in Tables 3 and 4 are recommendations based on this limitation. In addition, participants were required to report the nitrous oxide amount fraction in their standards, reported with a standard measurement uncertainty of 5 nmol/mol or better.

*Table 3: Matrix composition limits for standards with $CO_2$ amount fractions below 530 $\mu$mol/mol*

| Species | 'Ambient' level amount fraction | Unit | Min amount fraction | Unit | Max amount fraction | Unit |
|---|---|---|---|---|---|---|
| $N_2$ | 0.7809 | mol/mol | 0.7804 | mol/mol | 0.7814 | mol/mol |
| $O_2$ | 0.2093 | mol/mol | 0.2088 | mol/mol | 0.2098 | mol/mol |
| Ar | 0.0093 | mol/mol | 0.0089 | mol/mol | 0.0097 | mol/mol |
| $N_2O$ | 335 | nmol/mol | 0 | nmol/mol | 400 | nmol/mol |
| $CH_4$ | 1900 | nmol/mol | 0 | nmol/mol | 1900 | nmol/mol |

*Table 4: Matrix composition limits for standards with $CO_2$ amount fractions above 530 $\mu$mol/mol*

| Species | Ambient level amount fraction | Unit | Min amount fraction | Unit | Max amount fraction | Unit |
|---|---|---|---|---|---|---|
| $N_2$ | 0.7809 | mol/mol | 0.7789 | mol/mol | 0.7829 | mol/mol |
| $O_2$ | 0.2093 | mol/mol | 0.2073 | mol/mol | 0.2113 | mol/mol |
| Ar | 0.0093 | mol/mol | 0.0078 | mol/mol | 0.0108 | mol/mol |
| $N_2O$ | 335 | nmol/mol | 0 | nmol/mol | 400 | nmol/mol |
| $CH_4$ | 1900 | nmol/mol | 0 | nmol/mol | 2000 | nmol/mol |

## 5.3 Matrix composition for standards prepared in nitrogen

Binary mixtures of $CO_2$ in nitrogen were requested to be prepared following the requirements of ISO 6142-1(ISO 2015) and ISO 19229 (ISO 2019) for preparation of gravimetric standards and purity respectively. A matrix composition table was asked with each cylinder submitted. In particular, attention was to be paid to nitrous oxide amount fractions, that were to be reported and should be below 10 nmol mol$^{-1}$ and reported with a standard uncertainty of 5 nmol mol$^{-1}$.

## 5.4 Preparation and value assignment approaches

Participants were asked to prepare and value assign their standards using their usual approaches. Two approaches can be distinguished here, firstly the gravimetric method to prepare mixtures from pure gases, employed by all National Metrology Institutes (NMIs), and secondly an analytical method based on manometry applied to mixtures of purified dry air spiked with pure $CO_2$, employed by NOAA. They are briefly summarised below with further details on how the $CO_2$ amount fractions were assigned to the standards sent by participants.

### 5.4.1 Gravimetry and synthetic preparation of mixtures

Preparing $CO_2$ in air or nitrogen at the amount fractions chosen for this comparison is typically one of the core capabilities of NMIs, as summarised for example in (Brewer et al. 2019). The preparation involves the transfer of nominally pure starting materials into gas cylinders and the usage of automated weighing systems to determine the mass of each constituent. The purity of the starting materials will normally be assessed according to ISO 19229 with preparation, verification and value assignment of mixtures following ISO 6142-1 and ISO 6143 (ISO 2001). The mixtures prepared for this comparison present two specificities which require attention:

The first one is the air matrix, as the tolerance on air constituent described in the previous section can present a challenge. Composition of the air in NPL and NIM standards (see Annex 1) shows that the target was nicely reached, with nitrogen, oxygen, and argon fractions very close to air.

The second is the interaction between $CO_2$ and the cylinder surface, which can lead to part of the $CO_2$ being attached to the surface after the cylinder preparation, and starting to be desorbed when the pressure inside the cylinder decreases below a threshold estimated around 2 MPa (Leuenberger et al. 2014, Miller et al. 2015, Brewer et al. 2018, Schibig et al. 2018). Further details on this aspect were provided by NIM (see annex), with experiments performed before the comparison on similar cylinders. Their observations of the pressure effect are consistent with others, with an increase of 0.3 µmol mol$^{-1}$ observed below 2 MPa. They estimated a $CO_2$ adsorbed fraction of 0.02 µmol mol$^{-1}$, from which they deduced an uncertainty component and negligible correction. The issue was also considered by NPL, as already the case during their participation in the key comparison CCQM-K120 (Flores et al. 2019a). At that time, it had triggered discussions among participants and a decision to setup a cut-off standard uncertainty of 0.095 µmol mol$^{-1}$ on $CO_2$ amount fractions close to 400 µmol mol$^{-1}$. None of the participants of this pilot study have reported uncertainties lower than this threshold.

### 5.4.2 Manometry and natural air standards

NOAA is the Central Calibration Laboratory (CCL) for $CO_2$ standards in the Global Atmosphere Watch (GAW) of the WMO and designated in the CIPM-MRA framework by the international organization. NOAA has maintained the $CO_2$ scale for GAW since 1995, which, following a scale revision in 2021 (Hall et al. 2021), consists in a set of 19 standards containing $CO_2$ in dry natural air in the range 250-800 µmol mol$^{-1}$. The $CO_2$ amount fraction in these primary cylinders has been measured regularly by manometry, using a facility implemented in 1995 (Zhao et al. 1997), which provides SI−traceable values based on pressure, temperature and volume ratios as in the BIPM facility. NOAA had already sent 6 standards covering the range 350−500 µmol mol$^{-1}$ to the BIPM as part of a pre-validation work, and it was agreed with other participants that their measurements would be included in this pilot study. The standards sent by NOAA were at the tertiary level in their calibration hierarchy, traceable to their 19 primaries. They were value-assigned based on analysis versus secondary standards as described in (Zhao et al. 2006) using laser spectroscopy as the analytical technique as further described in (Hall et al. 2021) and references therein.

## 5.5 $CO_2$ amount fraction and uncertainties reported by participants.

All values submitted by participants are reported in Table 5. The $CO_2$ amount fractions were included in the nominal ranges imposed by the protocol. NOAA did not provide any standard in the higher range, which was not part of their scale until recently. But they provided 3 additional standards.

The composition of the air matrix for part a) can be found in the Annex and confirms that target values were reached. All standards except those provided by NOAA did not include $N_2O$ intentionally, and measurements showed values below 1 nmol mol$^{-1}$. NOAA standards are a blend of purified air and natural air, with $CO_2$ added as needed to achieve amount fractions higher than those found in the unpolluted atmosphere. They also contain $N_2O$ at typical ambient levels, around 300 nmol mol$^{-1}$.

The submitted uncertainties are very consistent for all standards prepared in air, whatever the value assignment approach, with typical values of 0.1 µmol mol$^{-1}$, slightly increasing with the $CO_2$ amount fraction. Standards prepared in nitrogen came with slightly lower uncertainties for NIM, with a minimum value of 0.08 µmol mol$^{-1}$, but also with larger values for LNE, up to 1.2 µmol mol$^{-1}$ for their standard at 800 µmol mol$^{-1}$.

# 6 BIPM comparison facility

The BIPM *pVT*-$CO_2$ system is maintained by the BIPM as a reference facility and will be further described in another publication (Viallon et al. 2023b). It aims at measuring the $CO_2$ amount fraction in a sample of air via the measurement of the pressure, volume, and temperature of that sample, and then of the $CO_2$ extracted from it by cryogenic trapping. For a given gas (air or $CO_2$), the three measurements of its pressure $p$, volume $V$ and temperature $T$ allow the calculation of its amount (amount of substance expressed in mole) $n$ via the real gas law (including the compressibility factor of gases measured). The amount fraction is then by definition the ratio between the amount of $CO_2$ and of air. When analysing samples which also contain $N_2O$, which is trapped together with $CO_2$ and cannot be separated, a final correction needs to be applied.

Before this Pilot Study, the *pVT*−$CO_2$ reference facility was validated across the $CO_2$ in air amount fraction range of (380 to 800) µmol mol$^{-1}$, using standards with values traceable to the reference value of the CCQM−K120 (2018) comparison, with the facility operating with a standard measurement uncertainty between 0.085 µmol mol$^{-1}$ and 0.17 µmol mol$^{-1}$ over this range. The results of this validation study will appear in the other publication (Viallon et al. 2023b).

*Table 5: participant's name (Lab), cylinder reference (REF), amount fraction of $CO_2$ assigned by participants ($x(CO_2)$), associated standard uncertainty ($u(CO_2)$), amount fraction of $N_2O$ assigned by participants ($x(N_2O)$), associated standard uncertainty ($u(N_2O)$).*

| Lab | REF | $x(CO_2)$ (µmol mol$^{-1}$) | $u(CO_2)$ (µmol mol$^{-1}$) | $x(N_2O)$ (nmol mol$^{-1}$) | $u(N_2O)$ (nmol mol$^{-1}$) |
|---|---|---|---|---|---|
| | | **Part a) air matrix** | | | |
| **NOAA** | CC91284 | 360.96 | 0.10 | 289.81 | |
| **NOAA** | CC309323 | 380.38 | 0.11 | 318.29 | |
| **NOAA** | CA01401 | 417.08 | 0.12 | 335.21 | |
| **NOAA** | CC71572 | 440.04 | 0.12 | 326.74 | |
| **NOAA** | CB11834 | 483.84 | 0.14 | 336.15 | |
| **NOAA** | CA05678 | 500.98 | 0.14 | 323.20 | |
| **NIM** | L220309064 | 380.06 | 0.10 | 0.79 | 0.15 |
| **NIM** | L220309053 | 480.47 | 0.11 | 0.79 | 0.15 |
| **NIM** | L220309060 | 801.35 | 0.13 | 0.79 | 0.15 |
| **NPL** | D050171 | 379.76 | 0.10 | 0.36 | 0.02 |
| **NPL** | D049869 | 479.68 | 0.12 | 0.36 | 0.02 |
| **NPL** | D049885 | 800.00 | 0.20 | 0.36 | 0.02 |
| | | **Part b) nitrogen matrix** | | | |
| **NIM** | L220309054 | 388.36 | 0.08 | 1.00 | 0.19 |
| **NIM** | L220309051 | 493.81 | 0.09 | 1.00 | 0.19 |
| **NIM** | L220309065 | 800.81 | 0.10 | 1.00 | 0.19 |
| **LNE** | APE1516250 | 362.43 | 0.72 | 0.50 | 0.29 |
| **LNE** | APE1126475 | 508.11 | 0.76 | 0.50 | 0.29 |
| **LNE** | D723204 | 787.07 | 1.19 | 0.50 | 0.29 |
| **VSL** | VSL210099 | 380.04 | 0.12 | < 1 | |
| **VSL** | VSL110105 | 479.85 | 0.15 | < 1 | |
| **VSL** | VSL110104 | 599.95 | 0.19 | < 1 | |
| **VSL** | VSL210103 | 700.13 | 0.22 | < 1 | |
| **VSL** | VSL110100 | 800.25 | 0.38 | < 1 | |

# 7 Measurements at the BIPM

The comparison was performed following the protocol sent to participants on 8 July 2022, described again below.

## 7.1 Preparation of the standards

After 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 before being transferred to the *pVT*− $CO_2$ laboratory. Cylinders were sequentially connected to the *pVT*−$CO_2$ system through a cylinder connector appropriate to the cylinder valve and a pressure reducer common to all cylinders.

## 7.2 Series of analysis

The *pVT*−$CO_2$ system samples 6 L of gas for each analysis. The first amount of gas sampled was used for conditioning of the measurement system and not as a measurement result. Standards were then sampled in successive series of $n \geq 9$ separate measurements. Standards from NOAA were measured almost 20 times because they were part of a validation series as well. The final value and uncertainty were calculated based on all $n$ measurements, taking the mean value and the standard deviation of the mean for the repeatability component of the uncertainty.

## 7.3 Analysis of $N_2O$ amount fractions in standards with air matrix

For those standards including nitrous oxide, the amount fractions in $CO_2$ in air mixtures were verified by the BIPM using its GC-ECD facility (comparison facility which was used in the comparison CCQM-K68.2019 (Viallon et al. 2023a)) allowing measurement of amount fractions with standard uncertainties of 1 nmol $mol^{-1}$. This was the case for NOAA cylinders only, and the measurements of the BIPM confirmed the values provided by NOAA.

## 7.4 Measurement results

The results of measurements performed with the *pVT*−$CO_2$ facility are summarised in Table 6. The number of measurements per series is indicated for information, as well as the value of the standard deviation of the mean, for which values lay between 0.01 µmol $mol^{-1}$ and 0.02 µmol $mol^{-1}$, showing good repeatability of the system. The combined standard uncertainty is similar to that obtained during the validation study, with the same uncertainty budget being applied.

The same information is available in participants' reports added in Annex, which were also distributed to participants after the completion of measurements.

*Table 6: participant's name (Lab), cylinder reference (REF), amount fraction of $CO_2$ measured by the BIPM ($x(CO_2)$), associated standard uncertainty ($u(CO_2)$),number of repeats ($n$), standard deviation of the mean ($\sigma$).*

| Lab | REF | $x$ ($CO_2$) (µmol mol$^{-1}$) | $u$($CO_2$) (µmol mol$^{-1}$) | $n$ | $\sigma$ / (µmol mol$^{-1}$) |
|---|---|---|---|---|---|
| **Part a) air matrix** | | | | | |
| **NOAA** | CC91284 | 360.92 | 0.08 | 18 | 0.02 |
| **NOAA** | CC309323 | 380.35 | 0.09 | 10 | 0.02 |
| **NOAA** | CA01401 | 417.02 | 0.09 | 12 | 0.01 |
| **NOAA** | CC71572 | 439.98 | 0.10 | 11 | 0.01 |
| **NOAA** | CB11834 | 483.84 | 0.11 | 11 | 0.01 |
| **NOAA** | CA05678 | 500.99 | 0.11 | 19 | 0.01 |
| **NIM** | L220309053 | 480.57 | 0.10 | 10 | 0.01 |
| **NIM** | L220309064 | 380.14 | 0.08 | 10 | 0.02 |
| **NIM** | L220309060 | 801.74 | 0.17 | 10 | 0.02 |
| **NPL** | D050171 | 379.79 | 0.08 | 11 | 0.01 |
| **NPL** | D049869 | 479.75 | 0.10 | 10 | 0.01 |
| **NPL** | D049885 | 799.95 | 0.17 | 10 | 0.02 |
| **Part b) nitrogen matrix** | | | | | |
| **NIM** | L220309054 | 388.52 | 0.09 | 10 | 0.01 |
| **NIM** | L220309051 | 493.98 | 0.11 | 11 | 0.01 |
| **NIM** | L220309065 | 801.17 | 0.17 | 10 | 0.01 |
| **LNE** | APE1516250 | 362.28 | 0.08 | 11 | 0.02 |
| **LNE** | APE1126475 | 507.93 | 0.11 | 10 | 0.02 |
| **LNE** | D723204 | 786.80 | 0.17 | 10 | 0.01 |
| **VSL** | VSL210099 | 379.95 | 0.08 | 11 | 0.01 |
| **VSL** | VSL110105 | 479.84 | 0.10 | 9 | 0.02 |
| **VSL** | VSL110104 | 600.19 | 0.13 | 12 | 0.02 |
| **VSL** | VSL210103 | 700.52 | 0.15 | 10 | 0.02 |
| **VSL** | VSL110100 | 800.29 | 0.17 | 14 | 0.02 |

# 8 Agreement between participants and the BIPM

As planned in the protocol, participants' results are compared against BIPM values, as a common reference for all measurements. The differences and their uncertainties are plotted in two figures, because of the difference between the magnitude of the uncertainties in parts a) and b) of the comparison. The values themselves can be found in the report forms of each participant, added in the Annex. The two figures below show the difference $d_i = x_{i,\text{lab}} - x_{i,\text{R}}$, where $x_{i,\text{lab}}$ are the $CO_2$ amount fractions reported by participants and $x_{i,\text{R}}$ the same quantity measured by the BIPM. They are plotted against the $CO_2$ amount fraction to highlight any issue with the linearity of the system.

The associated expanded uncertainties are defined as

$$U(d_i) = 2\sqrt{u(x_{i,\text{lab}}) + u(x_{i,\text{R}})}$$

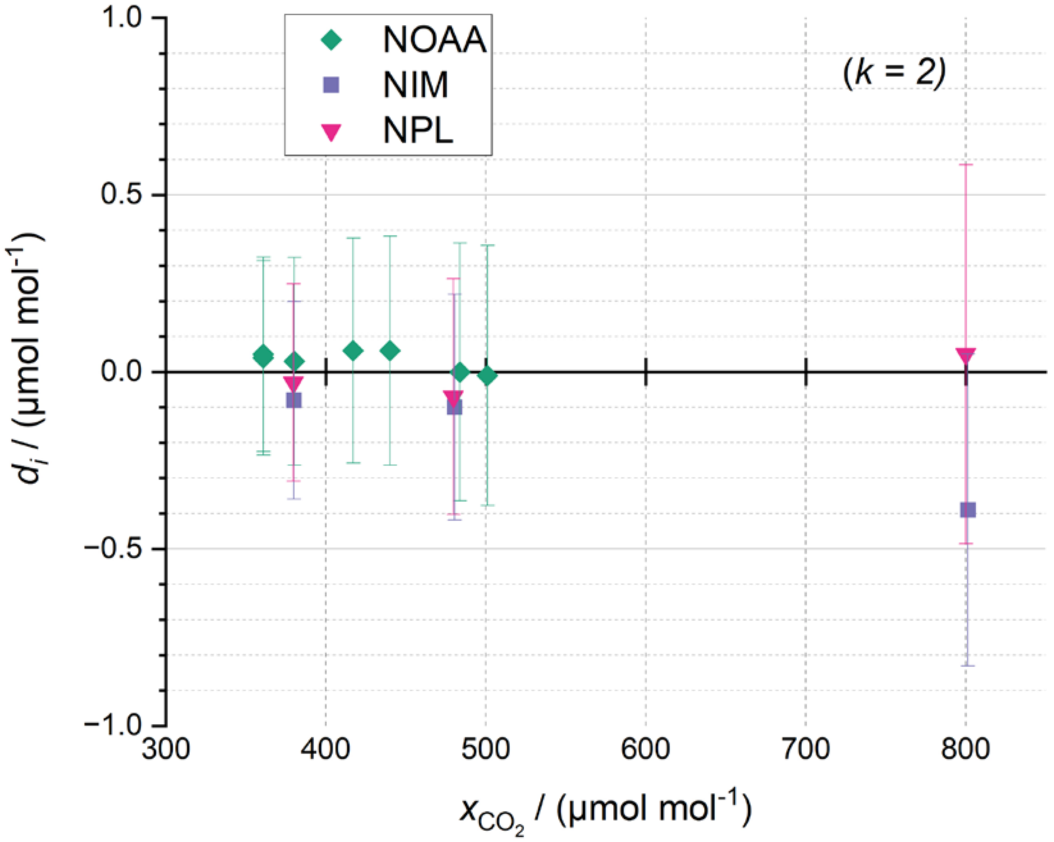


*Figure 1: difference between $CO_2$ amount fractions in air measured by participants and by the BIPM for CCQM−P225.a*

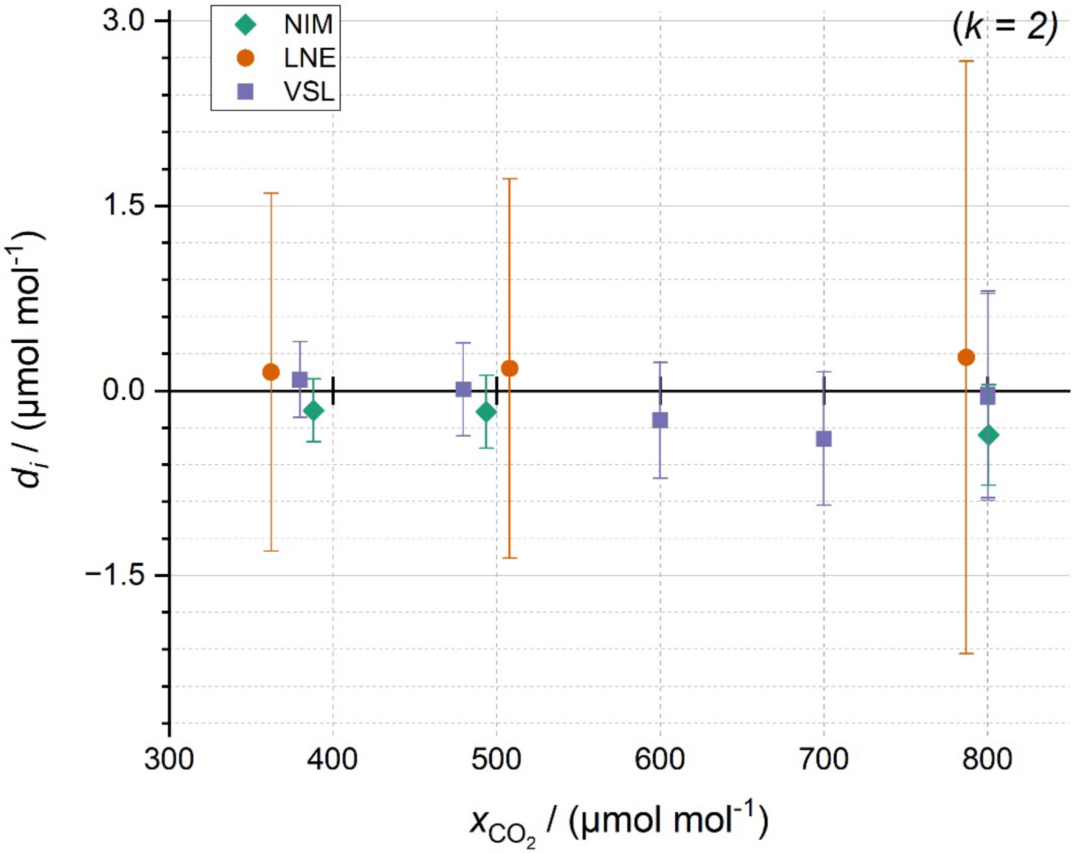


*Figure 2: difference between $CO_2$ amount fractions in nitrogen measured by participants and by the BIPM for CCQM−P225.b*

All results show good agreement between the values assigned by participants and by the BIPM *pVT*-$CO_2$ facility, within their combined uncertainties. There is no obvious dependency on amount fraction of the results, and the BIPM values are very reproducible. For example, the BIPM measured the VSL standard at 800 µmol mol$^{-1}$ before and after the standards at 600 µmol mol$^{-1}$ and 700 µmol mol$^{-1}$ with repeat measurements in very good agreement and the average of 14 repeats from both measurement runs being used for the final result.

# 9 Past comparisons

Results of this Pilot Study are compared with the results of the key comparison CCQM−K120 in Figure 3, for measurements performed on standards at the $CO_2$ amount fraction nominal value of 380 µmol mol$^{-1}$. The agreement is as good or sometimes better in this study, even if the measurement technique employed by the BIPM was very different. In CCQM−K120 (2018), the BIPM acted as comparator and measured all $CO_2$ amount fractions by Fourier Transformed Infrared Spectroscopy (FTIR), including a correction to reflect differences in the isotopic composition of $CO_2$ among participants. The spectrometer was maintained under repeatability conditions and calibrated by all participants selected for the calculation of the Key Comparison Reference Values (KCRVs), allowing to obtain KCRVs with typical uncertainties around 0.05 µmol mol$^{-1}$. The *pVT*−$CO_2$ system is capable of a similar performance in terms of repeatability, whilst producing SI-traceable values, independent of the method employed by most NMIs, and with a combined uncertainty around 0.1 µmol mol$^{-1}$.

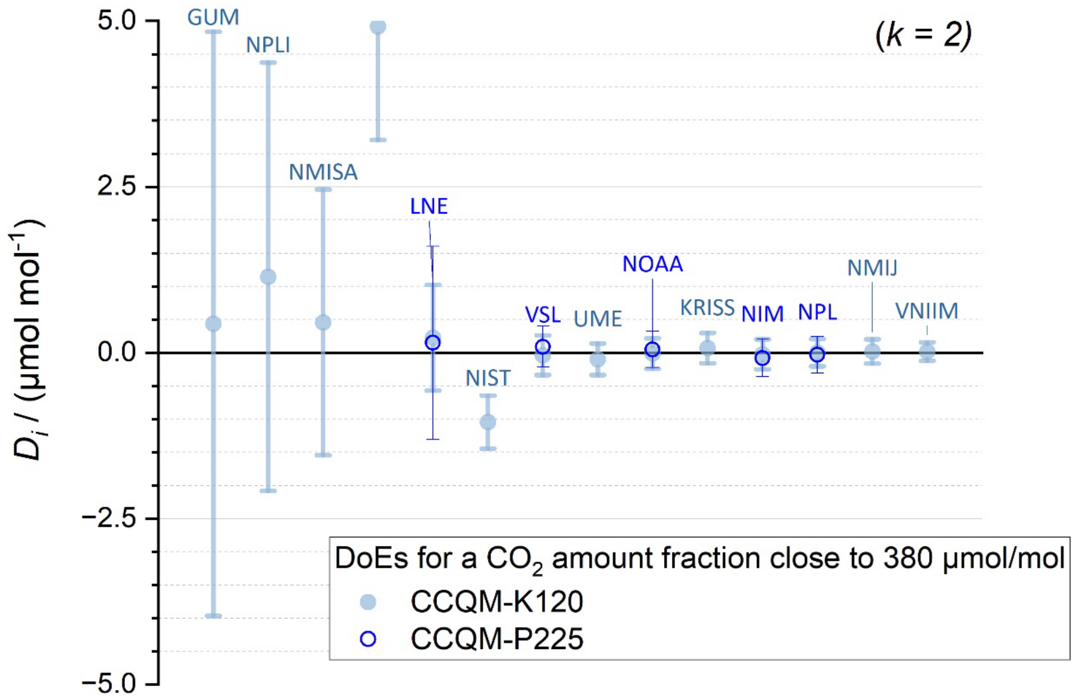


*Figure 3: Degree of equivalence in the Key Comparison CCQM−K120 (full light blue dots) and difference from the reference value in CCQM−P225 (open blue dots), at the nominal $CO_2$ amount fraction of 380 µmol mol$^{-1}$.*

# 10 Conclusion

The results of the Pilot Study CCQM-P225 show good agreement between all participants and the BIPM, both for part a (standards in air) and part b (standards in nitrogen). The participants were selected based on their previous track record for these standards, as demonstrated by their low uncertainty combined with good agreement with the reference value in the Key Comparison CCQM-K120 (2018), in which BIPM acted as coordinator. At that time, the BIPM compared the standards of 14 laboratories using an FTIR spectrometer operated under reproducibility conditions. The *pVT*-$CO_2$ facility was also included for the first time in a parallel Pilot Study CCQM−P188, showing agreement within the uncertainties, including values between 0.14 µmol mol$^{-1}$ and 0.20 µmol mol$^{-1}$ for the facility. Since then, the system was improved and its standard uncertainty reduced, but the agreement with other standards was maintained. The *pVT*−$CO_2$ will be ready to act as central facility for the on−demand key comparisons BIPM.QM−K2a and BIPM.QM−K2b, starting in 2024. The comparisons will underpin the capabilities of National Metrology Institutes and Designated Institutes to produce and/or value assign gas standards of $CO_2$ in air (part a) and in nitrogen (part b).

# 11 Annex 1 – Participants reports

All reports are displayed entirely in the following pages (PDF version only).

# 12 References


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Viallon J, et al. (2023b). "A high accuracy reference facility for ongoing comparisons of CO2 in air standards." *to be published*.

Zhao CL and Tans PP (2006). "Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air." *Journal of Geophysical Research: Atmospheres* **111**(D8): D08S09. http://dx.doi.org/10.1029/2005JD006003.

Zhao CL, Tans PP and Thoning KW (1997). "A high precision manometric system for absolute calibrations of CO2 in dry air." *Journal of Geophysical Research: Atmospheres* **102**(D5): 5885-5894. http://dx.doi.org/10.1029/96JD03764.

# Result Form for the comparison

## CCQM-P225.a and b, Carbon Dioxide in air (a) or nitrogen (b)

| Participating institute information | |
|---|---|
| **Institute** | **NOAA-GML** |
| **Address** | **325 Broadway, Boulder, CO 80305 USA** |
| **Contact** | **Andrew Crotwell** |
| **Email** | andrew.crotwell@noaa.gov |
| **Telephone** | **720-310-5424** |
| | |
| **Comparison part (a/b)** | **A** |

| Transfer Standards (cylinders) Information | | |
|---|---|---|
| **Number of standards** | 6.00 | |

| Standard # | ID (Serial Number) | Date of preparation | Pressure | (unit) |
|---|---|---|---|---|
| 1 | CC91284 | 2021-12-09 | 1900.00 | psi |
| 2 | CC309323 | 2012-10-18 | 1700.00 | psi |
| 3 | CA01401 | 2021-12-09 | 1900.00 | psi |
| 4 | CC71572 | 2014-02-20 | 1600.00 | psi |
| 5 | CB11834 | 2021-12-03 | 1800.00 | psi |
| 6 | CA05678 | 2015-07-02 | 1800.00 | psi |

### Content of the form



***This result form is to be completed by participants in CCQM-P225***

*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)*

*Additional pages can be added if there is not enough space to report information*

## Cylinders 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 | CC91284 | 360.96 | 0.20 | 2.00 |
| 2 | CC309323 | 380.38 | 0.21 | 2.00 |
| 3 | CA01401 | 417.08 | 0.23 | 2.00 |
| 4 | CC71572 | 440.04 | 0.24 | 2.00 |
| 5 | CB11834 | 483.84 | 0.27 | 2.00 |
| 6 | CA05678 | 500.98 | 0.28 | 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 | CC91284 | 289.81 | Informational value only | |
| 2 | CC309323 | 318.29 | Informational value only | |
| 3 | CA01401 | 335.21 | Informational value only | |
| 4 | CC71572 | 326.74 | Informational value only | |
| 5 | CB11834 | 336.15 | Informational value only | |
| 6 | CA05678 | 323.20 | Informational value only | |

### CCQM-P225.a ($CO_2$ in air) - 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 | Natural air matrix | | | | | |
| 2 | Natural air matrix | | | | | |
| 3 | Natural air matrix | | | | | |
| 4 | Natural air matrix | | | | | |
| 5 | Natural air matrix | | | | | |
| 6 | Natural air matrix | | | | | |

## Results of the comparison

## $CO_2$ amount fraction measured at BIPM

$CO_2$ amount fractions measured by the PVT-CO2 system

*x* = mean of all repeats

*n* = number of repeats,

*σ* = standard deviation of the mean

*U* = expanded uncertainty of the result

*The PVT-CO2 uncertainty budget will be detailed in the comparison report*

| Standard # | Cylinder ID | $x_{CO2}$ | *n* | *σ* | $U(x_{CO2})$ | *k* |
|---|---|---|---|---|---|---|
| | | µmol/mol | | µmol/mol | µmol/mol | |
| 1 | CC91284 | 360.92 | 18 | 0.02 | 0.16 | 2 |
| 2 | CC309323 | 380.35 | 10 | 0.02 | 0.17 | 2 |
| 3 | CA01401 | 417.02 | 12 | 0.01 | 0.18 | 2 |
| 4 | CC71572 | 439.98 | 11 | 0.01 | 0.19 | 2 |
| 5 | CB11834 | 483.84 | 11 | 0.01 | 0.21 | 2 |
| 6 | CA05678 | 500.99 | 19 | 0.01 | 0.22 | 2 |

## Difference from BIPM value

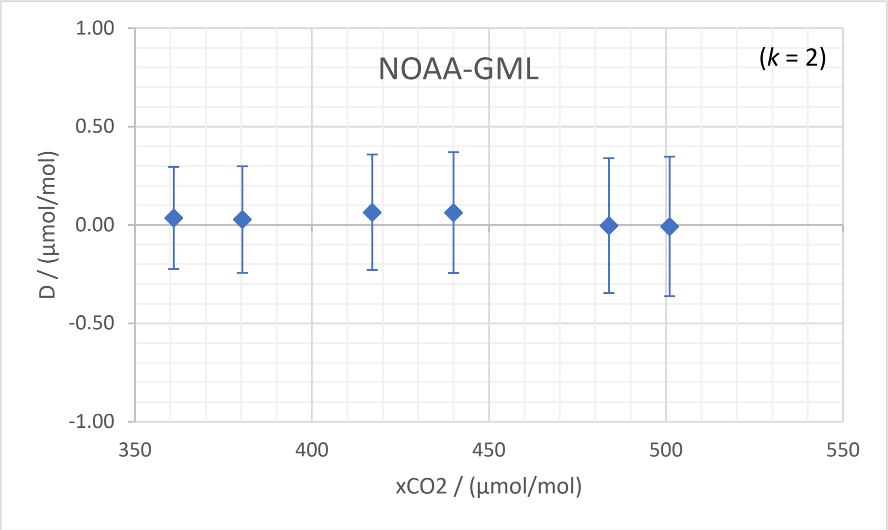
| Standard # | Cylinder ID | $x_{CO2}$ | *D* | *U(D)* |
|---|---|---|---|---|
| | | µmol/mol | µmol/mol | µmol/mol |
| 1 | CC91284 | 360.92 | 0.04 | 0.26 |
| 2 | CC309323 | 380.35 | 0.03 | 0.27 |
| 3 | CA01401 | 417.02 | 0.06 | 0.29 |
| 4 | CC71572 | 439.98 | 0.06 | 0.31 |
| 5 | CB11834 | 483.84 | 0.00 | 0.34 |
| 6 | CA05678 | 500.99 | -0.01 | 0.36 |

## Plot

title NOAA-GML

x-axis title xCO2 / (µmol/mol)

y-axis title D / (µmol/mol)



## Uncertainty budget

Describe your uncertainty budget in the text box below with as much details as possible, indicating for example the part of the uncertainty due to the preparation and to the validation

Uncertainties described in Hall et. al. 2021 (Atmos. Meas. Tech., 14, 3015–3032, 2021 https://doi.org/10.5194/amt-14-3015-2021) section 8 and suplemental information.

# Result Form for the comparison

# CCQM-P225.a and b, Carbon Dioxide in air (a) or nitrogen (b)

| Participating institute information | |
|---|---|
| **Institute** | **LNE** |
| **Address** | **1 rue Gaston Boissier** |
| **Contact** | **Christophe Sutour** |
| **Email** | christophe.sutour@lne.fr |
| **Telephone** | **0140433749** |
| | |
| **Comparison part (a/b)** | **b** |

| Transfer Standards (cylinders) Information | | |
|---|---|---|
| **Number of standards** | 3 | |

| Standard # | ID (Serial Number) | Date of preparation | Pressure | (unit) |
|---|---|---|---|---|
| 1 | D723204 | 2022-09-09 | 130 | Bar |
| 2 | APE1126475 | 2022-09-12 | 130 | Bar |
| 3 | APE1516250 | 2022-09-13 | 130 | Bar |
| 4 | *** | *** | *** | *** |
| 5 | *** | *** | *** | *** |
| 6 | *** | *** | *** | *** |

## Content of the form



***This result form is to be completed by participants in CCQM-P225***

*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)*

*Additional pages can be added if there is not enough space to report information*

# Cylinders 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 | D723204 | 787.07 | 2.37 | 2.00 |
| 2 | APE1126475 | 508.11 | 1.52 | 2.00 |
| 3 | APE1516250 | 362.43 | 1.44 | 2.00 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

## $N_2O$ 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 | D723204 | 0.50 | 0.58 | 2.00 |
| 2 | APE1126475 | 0.50 | 0.58 | 2.00 |
| 3 | APE1516250 | 0.50 | 0.58 | 2.00 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

## CCQM-P225.a ($CO_2$ in air) - 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 | | | | | | |
| 5 | | | | | | |
| 6 | | | | | | |

# Results of the comparison

## $CO_2$ amount fraction measured at BIPM

$CO_2$ amount fractions measured by the PVT-CO2 system

$x$ = mean of all repeats

$n$ = number of repeats,

$\sigma$ = standard deviation of the mean

$U$ = expanded uncertainty of the result

*The PVT-CO2 uncertainty budget will be detailed in the comparison report*

| Standard # | Cylinder ID | $x_{CO2}$ | $n$ | $\sigma$ | $U(x_{CO2})$ | $k$ |
|---|---|---|---|---|---|---|
| | | µmol/mol | | µmol/mol | µmol/mol | |
| 1.00 | D723204 | 786.80 | 10.00 | 0.01 | 0.34 | 2.00 |
| 2.00 | APE1126475 | 507.93 | 10.00 | 0.02 | 0.22 | 2.00 |
| 3.00 | APE1516250 | 362.28 | 11.00 | 0.02 | 0.16 | 2.00 |
| 4.00 | *** | | | | | |
| 5.00 | *** | | | | | |
| 6.00 | *** | | | | | |

## Difference from BIPM value

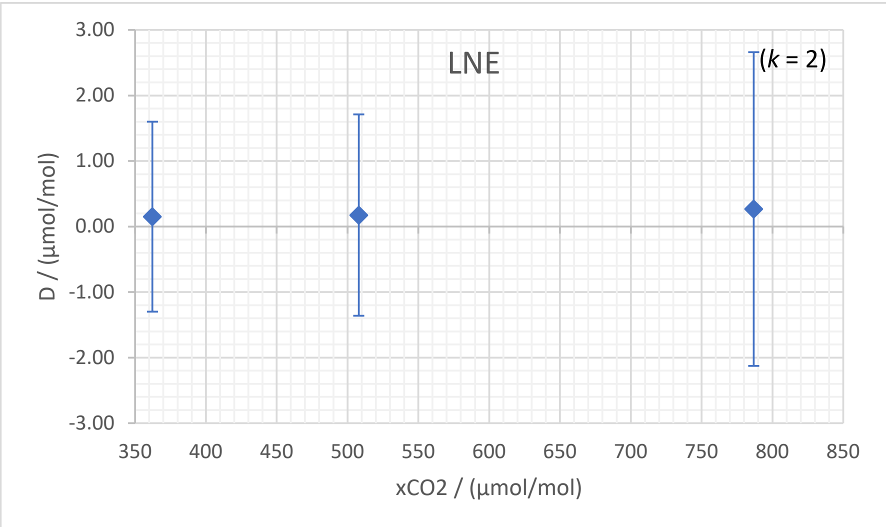
| Standard # | Cylinder ID | $x_{CO2}$ | $D$ | $U(D)$ |
|---|---|---|---|---|
| | | µmol/mol | µmol/mol | µmol/mol |
| 1 | D723204 | 786.80 | 0.27 | 2.39 |
| 2 | APE1126475 | 507.93 | 0.18 | 1.54 |
| 3 | APE1516250 | 362.28 | 0.15 | 1.45 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

## Plot

title LNE

x-axis title xCO2 / (µmol/mol)

y-axis title D / (µmol/mol)



## Uncertainty budget

Describe your uncertainty budget in the text box below with as much details as possible, indicating for example the part of the uncertainty due to the preparation and to the validation

The reference gas mixtures of $CO_2$ in nitrogen were prepared by gravimetric method according to the ISO 6142-1 standard from pure carbon dioxide and pure nitrogen. Two premix gas mixtures were produced to prepare the three final reference gas mixtures (RGM).
After the preparation the RGM were validated by analytical verification using a Brüker Matrix FTIR and a RGM diluted by a Sonimix 2106 as reference gas mixture.
The final expanded uncertainty is the combined standard uncertainties of the amount fractions from gravimetric preparation and from the analytical validation.

**Gravimetric uncertainty budget of CO2/N2 0072 D723204**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Mass of premix | g | 2.3772E+02 | 1.40E-02 | 2.79E+00 | 3.91E-02 | 2.18% |
| premix | mol/mol | 4.9998E-03 | 1.66E-06 | 1.57E+05 | 2.61E-01 | 97.69% |
| Molar mass of CO2 | g/mol | 4.4010E+01 | 9.10E-04 | -1.18E-01 | -1.07E-04 | 0.00% |
| Molar mass of N2 | g/mol | 2.8013E+01 | 9.90E-05 | 1.85E-01 | 1.84E-05 | 0.00% |
| N2 purity | mol/mol | 1.0000E+00 | 1.00E-10 | -6.63E+02 | -6.63E-08 | 0.00% |
| Mass of N2 | g | 1.2687E+03 | 1.80E-02 | -5.23E-01 | -9.41E-03 | 0.13% |

$CO_2$ amount fraction 787,07 ± 0,53 µmol/mol (k=2)

**Final uncertainty budget of CO2/N2 0072 D723204**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Preparation | µmol/mol | 787.068 | 2.64E-01 | 5.00E-01 | 1.32E-01 | 1.25% |
| Verification | µmol/mol | 786.401 | 2.25E+00 | 5.00E-01 | 1.13E+00 | 90.71% |
| Prep-Verification | µmol/mol | 0.667 | 6.70E-01 | 5.00E-01 | 3.35E-01 | 8.04% |

$CO_2$ amount fraction 787,07 ± 2,37 µmol/mol (k=2)

**Gravimetric uncertainty budget of CO2/N2 0073** **APE1126475**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Mass of premix | g | 1.5394E+02 | 1.40E-02 | 2.97E+00 | 4.15E-02 | 5.70% |
| premix | mol/mol | 4.9998E-03 | 1.66E-06 | 1.01E+05 | 1.69E-01 | 94.16% |
| Molar mass of CO2 | g/mol | 4.4010E+01 | 9.10E-04 | -8.12E-02 | -7.39E-05 | 0.00% |
| Molar mass of N2 | g/mol | 2.8013E+01 | 9.90E-05 | 1.28E-01 | 1.26E-05 | 0.00% |
| N2 purity | mol/mol | 1.0000E+00 | 1.00E-10 | -4.56E+02 | -4.56E-08 | 0.00% |
| Mass of N2 | g | 1.3569E+03 | 1.90E-02 | -3.36E-01 | -6.39E-03 | 0.14% |

$CO_2$ amount fraction 508,11 ± 0,35 µmol/mol (k=2)

**Final uncertainty budget of CO2/N2 0073** **APE1126475**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Preparation | µmol/mol | 508.112 | 1.73E-01 | 5.00E-01 | 8.60E-02 | 1.29% |
| Verification | µmol/mol | 508.662 | 1.41E+00 | 5.00E-01 | 7.04E-01 | 85.62% |
| Verification-Prep | µmol/mol | 0.550 | 5.50E-01 | 5.00E-01 | 2.75E-01 | 13.08% |

$CO_2$ amount fraction 508,11 ± 1,52 µmol/mol (k=2)

**Gravimetric uncertainty budget of CO2/N2 0074** **APE1516250**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Mass of premix | g | 1.10E+02 | 1.40E-02 | 3.06E+00 | 4.29E-02 | 11.27% |
| Amount fraction of prem | mol/mol | 5.00E-03 | 1.66E-06 | 7.23E+04 | 1.20E-01 | 88.62% |
| Molar mass of CO2 | g/mol | 4.40E+01 | 9.10E-04 | -5.98E-02 | -5.44E-05 | 0.00% |
| Molar mass of N2 | g/mol | 2.80E+01 | 9.90E-05 | 9.40E-02 | 9.30E-06 | 0.00% |
| N2 purity | mol/mol | 1.00E+00 | 1.00E-10 | -3.36E+02 | -3.36E-08 | 0.00% |
| Mass of N2 | g | 1.40E+03 | 1.80E-02 | -2.40E-01 | -4.32E-03 | 0.11% |

| | |
|---|---|
| $CO_2$ amount fraction | 362,43 ± 0,26 µmol/mol (k=2) |

**Final uncertainty budget of CO2/N2 0074** **APE1516250**

| Variable | Unit | Value | u(Xi) | Sensib, C(Xi) | C(Xi),u(Xi) | Contribution |
|---|---|---|---|---|---|---|
| Preparation | µmol/mol | 362.43 | 1.30E-01 | 5.00E-01 | 6.50E-02 | 0.82% |
| Verification | µmol/mol | 363.43 | 1.02E+00 | 5.00E-01 | 5.12E-01 | 50.79% |
| Prep-Verification | µmol/mol | 1 | 1.00E+00 | 5.00E-01 | 5.00E-01 | 48.39% |

| | |
|---|---|
| $CO_2$ amount fraction | 362,43 ± 1,44 µmol/mol (k=2) |

[redacted]

# Result Form for the comparison

## CCQM-P225.a and b, Carbon Dioxide in air (a) or nitrogen (b)

| Participating institute information | |
|---|---|
| Institute | **National Institute of Metrology, China** |
| Address | **Building 17, Room 217**<br>**18, Beisanhuandonglu, Chaoyang District, 100029, Beijing** |
| Contact | **Zhe Bi** |
| Email | bizh@nim.ac.cn |
| Telephone | **86-10-64525345** |
| | |
| Comparison part (a/b) | **a & b** |

| Transfer Standards (cylinders) Information | | |
|---|---|---|
| Number of standards | 6 | |

| Standard # | ID (Serial Number) | Date of preparation | Pressure | µmol/mol |
|---|---|---|---|---|
| 1 | 200220309054 | 01/08/2022 | 16Mpa | 388.36 |
| 2 | 200220309051 | 29/07/2022 | 15 Mpa | 493.81 |
| 3 | 200220309065 | 28/07/2022 | 12 Mpa | 800.81 |
| 4 | 200220309064 | 03/08/2022 | 16Mpa | 380.06 |
| 5 | 200220309053 | 09/08/2022 | 15Mpa | 480.47 |
| 6 | 200220309060 | 11/08/2022 | 15Mpa | 801.35 |

### Content of the form



***This result form is to be completed by participants in CCQM-P225***
*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)*
*Additional pages can be added if there is not enough space to report information*

## Cylinders 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 | 20022030905 | 388.36 | 0.16 | 2 |
| 2 | 20022030905 | 493.81 | 0.18 | 2 |
| 3 | 20022030906 | 800.81 | 0.20 | 2 |
| 4 | 20022030906 | 380.06 | 0.20 | 2 |
| 5 | 20022030905 | 480.47 | 0.22 | 2 |
| 6 | 20022030906 | 801.35 | 0.26 | 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 | 20022030905 | 1.00 | 0.39 | 2 |
| 2 | 20022030905 | 1.00 | 0.39 | 2 |
| 3 | 20022030906 | 1.00 | 0.38 | 2 |
| 4 | 20022030906 | 0.79 | 0.30 | 2 |
| 5 | 20022030905 | 0.79 | 0.30 | 2 |
| 6 | 20022030906 | 0.79 | 0.29 | 2 |

### CCQM-P225.a ($CO_2$ in air) - 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 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | 0.7812 | 0.2093 | 9.107E-3 | | | |
| 5 | 0.7812 | 0.2092 | 9.151E-3 | | | |
| 6 | 0.7810 | 0.2091 | 9.104E-3 | | | |

## Results of the comparison

### $CO_2$ amount fraction measured at BIPM

$CO_2$ amount fractions measured by the PVT-CO2 system

$x$ = mean of all repeats

$n$ = number of repeats,

$\sigma$ = standard deviation of the mean

$U$ = expanded uncertainty of the result

*The PVT-CO2 uncertainty budget will be detailed in the comparison report*

| Standard # | Cylinder ID | $x_{CO2}$ | $n$ | $\sigma$ | $U(x_{CO2})$ | $k$ |
|---|---|---|---|---|---|---|
| | | µmol/mol | | µmol/mol | µmol/mol | |
| 1.00 | 20022030905 | 388.52 | 10 | 0.01 | 0.17 | 2.00 |
| 2.00 | 20022030905 | 493.98 | 11 | 0.01 | 0.21 | 2.00 |
| 3.00 | 20022030906 | 801.17 | 10 | 0.01 | 0.34 | 2.00 |
| 4.00 | 20022030906 | 380.14 | 10 | 0.02 | 0.17 | 2.00 |
| 5.00 | 20022030905 | 480.57 | 10 | 0.01 | 0.21 | 2.00 |
| 6.00 | 20022030906 | 801.74 | 10 | 0.02 | 0.34 | 2.00 |

### Difference from BIPM value

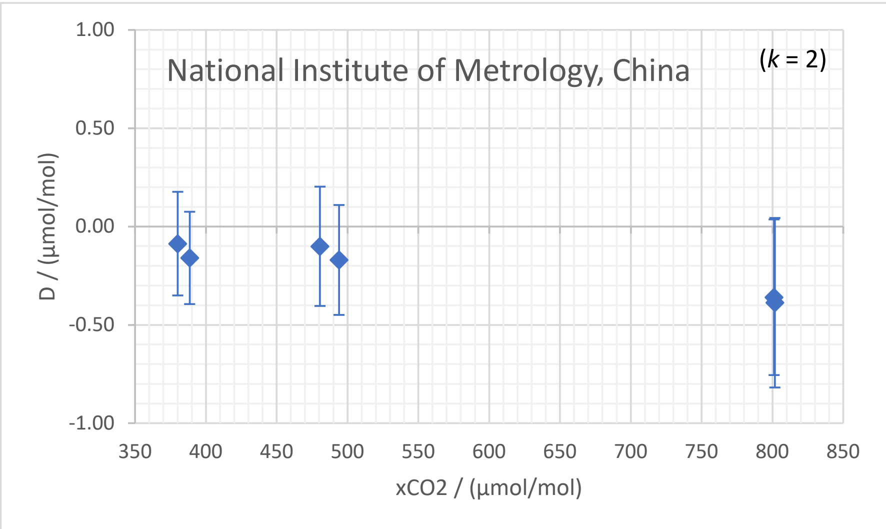
| Standard # | Cylinder ID | $x_{CO2}$ | $D$ | $U(D)$ |
|---|---|---|---|---|
| | | µmol/mol | µmol/mol | µmol/mol |
| 1 | 20022030905 | 388.52 | -0.16 | 0.23 |
| 2 | 20022030905 | 493.98 | -0.17 | 0.28 |
| 3 | 20022030906 | 801.17 | -0.36 | 0.40 |
| 4 | 20022030906 | 380.14 | -0.09 | 0.26 |
| 5 | 20022030905 | 480.57 | -0.10 | 0.30 |
| 6 | 20022030906 | 801.74 | -0.39 | 0.43 |

### Plot

title National Institute of Metrology, China

x-axis title xCO2 / (µmol/mol)

y-axis title D / (µmol/mol)



## Uncertainty budget

Describe your uncertainty budget in the text box below with as much details as possible, indicating for example the part of the uncertainty due to the preparation and to the validation

| Cylinder | Gravimetric value/μmol/mol | Component | Distribution | Standard uncertainty/μmol/mol |
|---|---|---|---|---|
| 200220309054 | 388.36 | Purity of source gases | Normal | 0.02 |
| | | Molar mass | Normal | 0.0004 |
| | | Weighing of gas | Normal | 0.03 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.063 |
| | | Repeatability of the | Normal | 0.03 |
| | | Consistency of measurement | Normal | 0.02 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.08** |
| 200220309051 | 493.81 | Purity of source gases | Normal | 0.03 |
| | | Molar mass | Normal | 0.0003 |
| | | Weighing of gas | Normal | 0.02 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.07 |
| | | Repeatability of the | Normal | 0.03 |
| | | Consistency of measurement | Normal | 0.03 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.09** |
| 200220309065 | 800.81 | Purity of source gases | Normal | 0.04 |
| | | Molar mass | Normal | 0.0004 |
| | | Weighing of gas | Normal | 0.03 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.08 |
| | | Repeatability of the | Normal | 0.04 |
| | | Consistency of measurement | Normal | 0.02 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.10** |
| 200220309064 | 380.06 | Purity of source gases | Normal | 0.03 |
| | | Molar mass | Normal | 0.004 |
| | | Weighing of gas | Normal | 0.02 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.09 |
| | | Repeatability of the | Normal | 0.03 |
| | | Consistency of measurement | Normal | 0.02 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.10** |
| 200220309053 | 480.47 | Purity of source gases | Normal | 0.02 |
| | | Molar mass | Normal | 0.004 |
| | | Weighing of gas | Normal | 0.03 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.10 |
| | | Repeatability of the | Normal | 0.03 |
| | | Consistency of measurement | Normal | 0.02 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.11** |
| 200220309060 | 801.35 | Purity of source gases | Normal | 0.06 |
| | | Molar mass | Normal | 0.004 |
| | | Weighing of gas | Normal | 0.05 |
| | | Adsorption and Fractionation effect of two step dilution | Normal | 0.10 |
| | | Repeatability of the | Normal | 0.04 |
| | | Consistency of measurement | Normal | 0.02 |
| **Combined standard uncertainty (*k*=1)** | | | | **0.13** |

# Result Form for the comparison

# CCQM-P225.a and b, Carbon Dioxide in air (a) or nitrogen (b)

| Participating institute information | |
|---|---|
| **Institute** | **NPL** |
| **Address** | **Hampton Road, Teddington, TW11 0LW, U.K.** |
| **Contact** | **Ruth Hill-Pearce** |
| **Email** | ruth.pearce@npl.co.uk |
| **Telephone** | **+44 20 8943 7165** |
| | |
| **Comparison part (a/b)** | **a** |

| Transfer Standards (cylinders) Information | | |
|---|---|---|
| **Number of standards** | 3 | |

| Standard # | ID (Serial Number) | Date of preparation | Pressure | (unit) |
|---|---|---|---|---|
| 1 | D050171 | 2022-08-26 | 110 | bar |
| 2 | D049869 | 2022-08-26 | 110 | bar |
| 3 | D049885 | 2022-08-26 | 110 | bar |
| 4 | *** | *** | | |
| 5 | *** | *** | | |
| 6 | *** | *** | | |

## Content of the form



***This result form is to be completed by participants in CCQM-P225***

*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)*

*Additional pages can be added if there is not enough space to report information*

## Cylinders 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 | D050171 | 379.76 | 0.19 | 2.00 |
| 2 | D049869 | 479.68 | 0.24 | 2.00 |
| 3 | D049885 | 800.00 | 0.40 | 2.00 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

### $N_2O$ 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 | D050171 | 0.36 | 0.03 | 2.00 |
| 2 | D049869 | 0.36 | 0.03 | 2.00 |
| 3 | D049885 | 0.36 | 0.03 | 2.00 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

### CCQM-P225.a ($CO_2$ in air) - 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 # | cmol/mol | cmol/mol | cmol/mol | (unit) | (unit) | (unit) |
| 1 | 78.09 | 20.94 | 0.94 | | | |
| 2 | 78.09 | 20.92 | 0.94 | | | |
| 3 | 78.07 | 20.92 | 0.93 | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | | | | | |

## Results of the comparison

### $CO_2$ amount fraction measured at BIPM

$CO_2$ amount fractions measured by the PVT-CO2 system

$x$ = mean of all repeats

$n$ = number of repeats,

$\sigma$ = standard deviation of the mean

$U$ = expanded uncertainty of the result

*The PVT-CO2 uncertainty budget will be detailed in the comparison report*

| Standard # | Cylinder ID | $x_{CO2}$ | $n$ | $\sigma$ | $U(x_{CO2})$ | $k$ |
|---|---|---|---|---|---|---|
| | | μmol/mol | | μmol/mol | μmol/mol | |
| 1.00 | D050171 | 379.79 | 11.00 | 0.01 | 0.17 | 2.00 |
| 2.00 | D049869 | 479.75 | 10.00 | 0.01 | 0.21 | 2.00 |
| 3.00 | D049885 | 799.95 | 10.00 | 0.02 | 0.34 | 2.00 |
| 4.00 | *** | | | | | |
| 5.00 | *** | | | | | |
| 6.00 | *** | | | | | |

### Difference from BIPM value

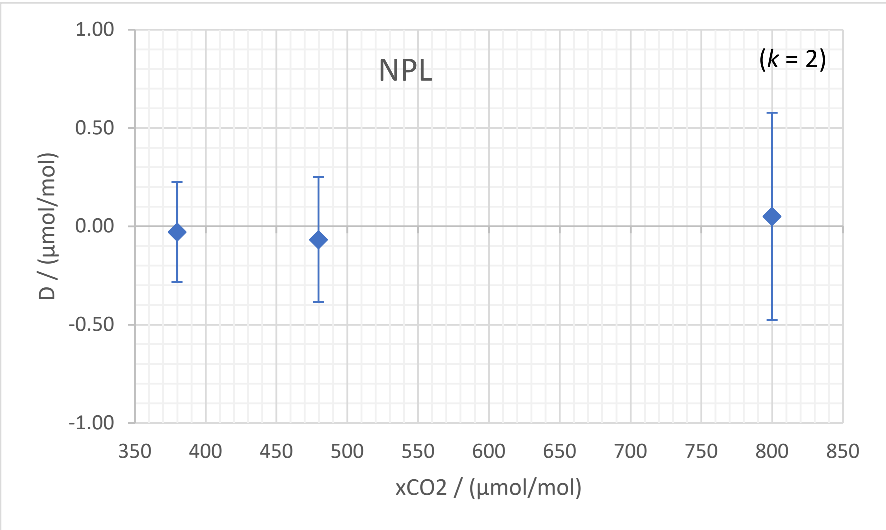
| Standard # | Cylinder ID | $x_{CO2}$ | $D$ | $U(D)$ |
|---|---|---|---|---|
| | | μmol/mol | μmol/mol | μmol/mol |
| 1 | D050171 | 379.79 | -0.03 | 0.25 |
| 2 | D049869 | 479.75 | -0.07 | 0.32 |
| 3 | D049885 | 799.95 | 0.05 | 0.53 |
| 4 | *** | | | |
| 5 | *** | | | |
| 6 | *** | | | |

### Plot

title NPL

x-axis title xCO2 / (μmol/mol)

y-axis title D / (μmol/mol)



## Uncertainty budget

Describe your uncertainty budget in the text box below with as much details as possible, indicating for example the part of the uncertainty due to the preparation and to the validation

The estimated uncertainty for the measurement contains the following components:
- Purity analysis of $CO_2$ and synthetic air components.
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analytical validation

The table details the uncertainty analysis. The preparation component includes estimated uncertainty from purity analysis, weighing and atomic weights.

| | | Relative Uncertainty (%) | | |
|---|---|---|---|---|
| **Identifier** | **Component** | **Preparation (*k*=1)** | **Validation (*k*=1)** | **Total (*k*=2)** |
| D050171 | $CO_2$ | 0.016 | 0.02 | 0.05 |
| D049869 | $CO_2$ | 0.013 | 0.02 | 0.05 |
| D049885 | $CO_2$ | 0.010 | 0.02 | 0.05 |

To calculate the combined uncertainty, the uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of *k*=2, providing a level of confidence of approximately 95%.

# Result Form for the comparison

## CCQM-P225.a and b, Carbon Dioxide in air (a) or nitrogen (b)

| Participating institute information | |
|---|---|
| **Institute** | **VSL** |
| **Address** | **Thijsseweg 11, 2629 JA Delft, The Netherlands** |
| **Contact** | **Adriaan Van der Veen** |
| **Email** | avdveen@vsl.nl |
| **Telephone** | **+31612021712** |
| | |
| **Comparison part (a/b)** | **b** |

| Transfer Standards (cylinders) Information | |
|---|---|
| **Number of standards** | 5.00 |

| Standard # | ID (Serial Number) | Date of preparation | Pressure | (unit) |
|---|---|---|---|---|
| 1 | VSL210099 | 22-9-2022 | 11.50 | MPa |
| 2 | VSL110105 | 19-4-2022 | 11.80 | MPa |
| 3 | VSL110104 | 29-4-2022 | 11.30 | MPa |
| 4 | VSL210103 | 23-9-2022 | 11.40 | MPa |
| 5 | VSL110100 | 22-4-2022 | 11.30 | MPa |
| 6 | *** | *** | | |

### Content of the form



***This result form is to be completed by participants in CCQM-P225***

*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)*

*Additional pages can be added if there is not enough space to report information*

## Cylinders 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 | VSL210099 | 380.04 | 0.23 | 2.0 |
| 2 | VSL110105 | 479.85 | 0.29 | 2.0 |
| 3 | VSL110104 | 599.95 | 0.38 | 2.0 |
| 4 | VSL210103 | 700.13 | 0.43 | 2.0 |
| 5 | VSL110100 | 800.25 | 0.76 | 2.0 |
| 6 | *** | | | |

### $N_2O$ 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 | VSL210099 | < 1 | | |
| 2 | VSL110105 | < 1 | | |
| 3 | VSL110104 | < 1 | | |
| 4 | VSL210103 | < 1 | | |
| 5 | VSL110100 | < 1 | | |
| 6 | *** | | | |

### CCQM-P225.a ($CO_2$ in air) - 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 | H2O | H2 | CO |
|---|---|---|---|---|---|---|
| Standard # | mol/mol | mol/mol | mol/mol | mol/mol | mol/mol | mol/mol |
| 1 | 0.999615 | 5.008E-09 | 4.998E-06 | 1.060E-08 | 2.499E-08 | 9.996E-10 |
| 2 | 0.999515 | 5.010E-09 | 4.998E-06 | 1.076E-08 | 2.499E-08 | 9.995E-10 |
| 3 | 0.999395 | 5.013E-09 | 4.997E-06 | 1.095E-08 | 2.499E-08 | 9.994E-10 |
| 4 | 0.999295 | 5.015E-09 | 4.997E-06 | 1.111E-08 | 2.498E-08 | 9.993E-10 |
| 5 | 0.999195 | 5.017E-09 | 4.996E-06 | 1.127E-08 | 2.498E-08 | 9.992E-10 |
| 6 | | | | | | |

## Results of the comparison

### $CO_2$ amount fraction measured at BIPM

$CO_2$ amount fractions measured by the PVT-CO2 system

*x* = mean of all repeats

*n* = number of repeats,

*σ* = standard deviation of the mean

*U* = expanded uncertainty of the result

*The PVT-CO2 uncertainty budget will be detailed in the comparison report*

| Standard # | Cylinder ID | $x_{CO2}$ | *n* | *σ* | $U(x_{CO2})$ | *k* |
|---|---|---|---|---|---|---|
| | | μmol/mol | | μmol/mol | μmol/mol | |
| 1.00 | VSL210099 | 379.95 | 11.00 | 0.01 | 0.17 | 2.00 |
| 2.00 | VSL110105 | 479.84 | 9.00 | 0.02 | 0.21 | 2.00 |
| 3.00 | VSL110104 | 600.19 | 12.00 | 0.02 | 0.26 | 2.00 |
| 4.00 | VSL210103 | 700.52 | 10.00 | 0.02 | 0.30 | 2.00 |
| 5.00 | VSL110100 | 800.29 | 28.00 | 0.02 | 0.34 | 2.00 |
| 6.00 | *** | | | | | |

### Difference from BIPM value

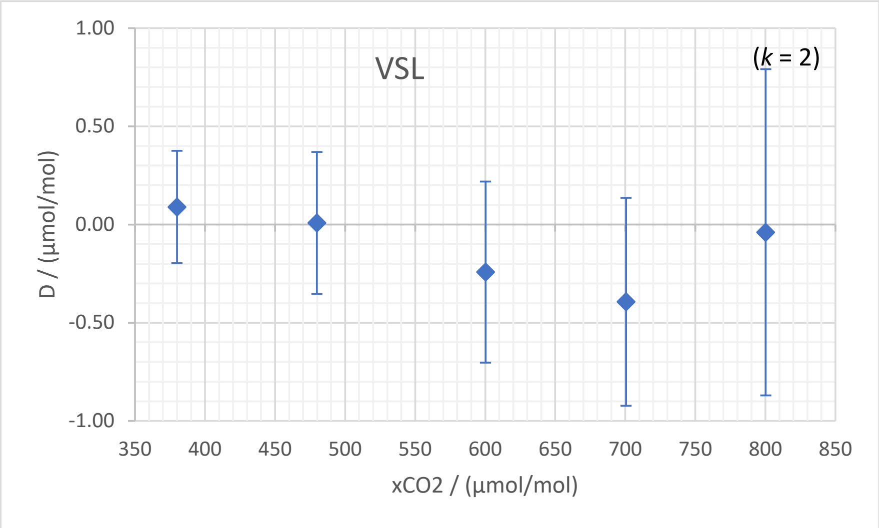
| Standard # | Cylinder ID | $x_{CO2}$ | *D* | *U(D)* |
|---|---|---|---|---|
| | | μmol/mol | μmol/mol | μmol/mol |
| 1 | VSL210099 | 379.95 | 0.09 | 0.29 |
| 2 | VSL110105 | 479.84 | 0.01 | 0.36 |
| 3 | VSL110104 | 600.19 | -0.24 | 0.46 |
| 4 | VSL210103 | 700.52 | -0.39 | 0.53 |
| 5 | VSL110100 | 800.29 | -0.04 | 0.83 |
| 6 | *** | | | |

### Plot

title VSL

x-axis title xCO2 / (μmol/mol)

y-axis title D / (μmol/mol)



## Uncertainty budget

Describe your uncertainty budget in the text box below with as much details as possible, indicating for example the part of the uncertainty due to the preparation and to the validation

The uncertainty budget is obtained from the static gravimetry in accordance with ISO 6142-1 and the verification in accordance with ISO 6143. Considering the compatibility between VSL's primary standard gas mixtures, the verification uncertainty, expressed as standard uncertainty is set at 0.03 %. This figure is in line with the long-term data from the method and standards (https://www.vsl.nl/wp-content/uploads/2022/12/CMCs-for-carbon-dioxide-in-nitrogen-and-air.pdf) and comparable to the performance demonstrated by VSL in the key comparison CCQM-K120.

The purity data for nitrogen and carbon dioxide have been obtained in accordance with ISO 19229. The purity tables are the same as those used in CCQM-K120. As nitrous oxide may interfere with the *pVT* measurement of the BIPM, the gases and some mixtures have been checked for the presence of this component. The method and results are the same as for CCQM-K68.2019, in which it was demonstrated that the nitrogen contained less than 1 nmol/mol nitrous oxide. In the mixtures assessed, the amount fraction nitrous oxide did not differ from that of the nitrogen used.

The final expanded uncertainty has been obtained by assuming a normal distribution and using a coverage factor $k$ = 2. These uncertainties are comparable to those of CCQM-K120.