Protocol for the Key Comparison BIPM.QM-K2.a and b, Carbon Dioxide in air or nitrogen, ambient levels (350 µmol mol^{-1} to 800 µmol mol^{-1})

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1 Purpose and scope

The Key Comparisons BIPM.QM-K2.a and b are aimed at underpinning the capabilities of the participants to value assign the amount fraction of CO_2 in air (part a) or in nitrogen (part b) in gas standards over the amount fraction range from 350 μmol mol^{-1} to 800 μmol mol^{-1}, with a method ensuring traceability of the measurements to the SI. The standards to be sent by the participants are reference gas mixtures in high pressure cylinders, further described in section 5 of this protocol.

The comparison is run as a series of bilateral comparisons between each participant and the BIPM. The facility maintained by the BIPM (the so called the CO_2-PVT facility) provides the Key Comparison Reference Value (KCRV) in each case and quantifies CO_2 amount fractions 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. Its performance have been validated during the Pilot Study CCQM-P225 [1], and described in detail in a publication [2].

Participants can select one or up to all three of the nominal amount fraction of CO_2 covered by the comparison: 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 shall contain CO_2 in a matrix of dry air (part a) or nitrogen (part b), with constraints imposed on the composition of this matrix (see section 5), and in particular the N_2O amount fractions shall be reported by participants with standard uncertainties of 5 nmol mol^{-1} or better.

2 Participants

BIPM.QM-K2 is open to laboratories listed in Appendix A of the CIPM MRA, available on the BIPM website (https://www.bipm.org/en/cipm-mra/participation).

3 Measurement schedule and registration

Laboratories wishing to participate should register their interest using the registration form provided (BIPM.QM-K2-R1) and return this to the coordinator at least three months before the requested comparison date. A date will then be agreed between the laboratory and the coordinator, which may differ from the proposal depending on the workload of the BIPM.

The minimum period for completion of measurements at the BIPM is one week with a maximum of one month. In the event of technical issues which would extend this duration, the coordinator will contact the participant to agree on the way forward. The laboratory should take into account the time for the transport of cylinders to and from the BIPM based on its knowledge of dangerous goods' shipments between its country and France. More details regarding transport of cylinders are provided in section 8.

4 Measurand, quantities and units

The measurand is the amount fraction of carbon dioxide in air (part a) and 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}).

5 Preparation of mixtures by participants

The mixtures are to be prepared and/or analysed by participants using their usual procedure, with the constraints detailed below:

5.1 Nominal CO_2 amount fractions

The participant is required to provide a standard at one or all of the nominal amount fractions summarized in Table 1, and in the matrix for the part (a - air or b - nitrogen) of the comparison they participate in.

Table 1: 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

5.2 Matrix Composition for Standards prepared in air (Part a)

Standards shall have a dry air matrix, which can be either *scrubbed real air* or *synthetic air* (blended from pure gases). The matrix shall contain the major constituents of air (nitrogen, oxygen, argon) and may contain nitrous oxide and methane at up to ambient amount fractions. The BIPM reference facility results are influenced by the nitrous oxide amount fraction but only weakly influenced by changes in the amount fractions of the major constituents of air (nitrogen, oxygen, argon). Participants are required to report the nitrous oxide amount fraction in their standards if present, with a standard measurement uncertainty of 5 nmol/mol or better. If the standards do not contain nitrous oxide, participants should state this in their report and describe the technical evidence supporting their statement. In the case that participants are preparing standards for calibration of precise atmospheric measurements using spectroscopic instruments, then these are affected by minor changes in matrix composition, and guidelines for acceptable limits of the amount fraction of the major constituents for such applications are listed in Table 1 and 3. Participants shall report the amount fractions of the major air constituents in their standards.

Table 1: Guideline for matrix composition limits for standards with CO_2 amount fractions below 530 µmol/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 2: Guideline for matrix composition limits for standards with CO_2 amount fractions above 530 µmol/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 shall be prepared following the requirements of ISO 6142 and ISO 19229 for preparation of gravimetric standards and purity respectively. A matrix composition table shall be supplied with each cylinder submitted. In particular, attention shall be paid to nitrous oxide amount fractions, that shall be reported and should be below 10 nmol mol, and reported with a standard uncertainty of 5 nmol mol^{-1} or better.

5.4 Cylinder characteristics and volume of gas used

Mixtures are to be prepared in cylinders with a volume equal or greater than 5 L, with total pressure in the range 100 bar to 150 bar and preferably fitted with a cylinder valve which conforms to one of the standards DIN, BS, AFNOR, CGA or JIS. Participants will be asked to provide this information to the BIPM upon registration. The BIPM measurements will use a minimum of 30 L of gas (at room temperature and pressure) and exceptionally 60 L of gas in case of a problem with one of the measurements runs on the standard.

6 Verification of mixtures

Participants may perform a verification of their mixtures before and after shipment, according to the principles listed below. The mixtures sent for the comparison are expected to be stable over the time period of the comparison, and any allowance for standard instability should be included as a component of the uncertainty submitted by the participants with their value at the start of the comparison. Verification by participants of their standards after completion of measurements at the BIPM, will allow the participant to confirm their uncertainty budget or increase the component accounting for stability.

6.1 Before shipment

Typically, the verification of the mixtures will have be performed within a year prior to their shipment, and participants should use this information for the uncertainty evaluation.

6.2 After shipment

After measurements at the BIPM and prior to the preparation of the Draft A the laboratories will have the opportunity to perform another verification of their standards.

The final results shall then be submitted to the BIPM within 4 months after the comparison measurements at the BIPM. No report will be written until the coordinator is informed of the final values.

7 Transport of cylinders to and from the BIPM

Cylinders shall be shipped to the BIPM no later than one week before the comparison date. The participating laboratory shall cover the cost and organise transport of their cylinders to the BIPM (door to door delivery), and to ensure that proper arrangements are made for local customs formalities. There are three likely scenarios depending on the location of the participating laboratory:

- countries within the E.U.;
- countries outside the E.U. and where the ATA carnet system is recognised;
- countries outside the E.U. but where the ATA is not recognised.

Laboratories are invited to consult the BIPM administrative document ADM-DOU-T-02 – *Information for laboratories shipping equipment to the BIPM for comparisons* - for additional information regarding the steps to be taken in each of the three cases above.

Laboratories are invited to inform the BIPM of its transport and customs arrangements prior to the cylinders leaving their laboratory by completing and returning the BIPM administrative document ADM-DOU-F-02 – *Shipping instructions for comparisons*. Any additional cost associated with custom clearance process which may be applied in case no form has been received will be charged to the participant.

At the conclusion of the comparison period the participants are responsible for the arrangements and costs of shipping the cylinders from the BIPM back to their laboratories. Any cylinders still remaining at the BIPM 4 months after the comparison will be shipped by the BIPM back to the participants' expense.

8 Comparison measurement procedure

8.1 Preparation of the BIPM comparison facility

The BIPM comparison facility will be prepared for a series of analyses before starting the measurement procedure, meaning that all necessary calibrations of the measuring instruments (pressure gauges and temperature sensors) will have been performed within the appropriate period and that all quality controls will have been realised within one month prior to the measurements. In particular, the volume ratio between the vessels used to handle the CO_2 gas and the sample from which it is extracted will have been monitored carefully.

The BIPM makes use of two quality control mixtures of CO_2 in dry air or nitrogen which are frequently analysed with the facility to check its stability. The two mixtures will be analysed in the weeks before and after the comparison measurement to demonstrate the stability of the facility over the period of the comparison.

8.2 Preparation and connection of the cylinders

After receipt by the BIPM, all cylinders will be allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders will then be rolled for at least 1 hour to

ensure homogeneity of the mixture before being transferred to the BIPM PVT-CO_2 laboratory. The cylinder connector appropriate to the cylinder valve will be provided by the BIPM. If this connector requires a gasket, it will be of an appropriately inert material (typically PCTFE). A pressure reducer will be connected between the cylinder connector and the input tubing of the facility.

8.3 Analysis of mixtures

The BIPM PVT-CO_2 facility samples 6L (at RTP) of gas for each analysis. The first amount of gas sampled will be used for conditioning of the measurement system and not as a measurement result. Standards will then be sampled in successive analysis, until a series of 3 repeated analysis is compliant with the stability criteria, defined by a standard deviation of n measurements below 0.04 µmol mol^{-1}, with $n \geq 3$. Any issue arising during one analysis will set the value of n to zero.

8.4 Analysis of N_2O amount fractions in standards with air matrix

Nitrous oxide amount fractions in CO_2 in air mixtures shall be verified by the BIPM using a N_2O analyser calibrated with standards of N_2O in air which were directly included or calibrated with standards included in the comparison CCQM-K68.2019 [3], allowing measurement of N_2O amount fractions with standard uncertainties of less than 1 nmol mol^{-1}. N_2O amount fractions shall be used in the measurement equation of the PVT-CO_2 system to provide values of CO_2 amount fractions.

9 Uncertainty budgets

9.1 Uncertainty budgets for the participants standards

Participants shall submit the assigned values and uncertainties of their standards at the same time as sending them to the BIPM. A full uncertainty budget shall be submitted to justify the uncertainty submitted, and shall include at least the following components or explanation why they are not relevant:

a) Components arising from the reference method used for value assignment;

b) Contributions from additional verification measurements

c) Contributions from purity assessment

d) Contributions from correction for CO_2 adsorption in cylinders if any (in this case the size of the correction should also be described in the result submission form)

9.2 Uncertainty budget of the BIPM PVT-CO_2

A complete description of the uncertainty budget of the BIPM facility can be found in [2]. The standard uncertainty $u(x)$ of the CO_2 amount fraction x measured with the PVT-CO_2 can be summarised in one equation:

$$u(x) = \sqrt{(u_1 x)^2 + u_2^2 + \sigma^2} \qquad (1)$$

Where u_1 is the relative part of the uncertainty (typical value 2.3×10^{-4}), u_2 is the combination of the uncertainties on the additive corrections without the repeatability (typical value 0.023 µmol mol^{-1}), and σ is the standard deviation of the mean over the

repeated measurements, which takes a typical value of 0.02 µmol mol^{-1} for five successive repeats.

The values of u_1 and u_2 are expected to be constant over time, unless changes are made to the facility. The value of σ is measured during each comparison. These values and any update of the uncertainty budget compared to the publication of 2023 [2] will be reported in the comparison report.

10 Key Comparison Reference Values (KCRVs)

For each standard of the participant, the KCRV is the CO_2 amount fraction measured by the BIPM PVT-CO_2, with its measurement uncertainty calculated following equation (1). The KCRVs will be calculated by the coordinator and reported in the result form of the comparison.

11 Degrees of equivalence

Each comparison will result in three degrees of equivalence, one for each standard, defined as:

$$D_i = x_{i,\mathrm{lab}} - x_{i,\mathrm{KCRV}} \quad (1)$$

Where $x_{i,\mathrm{lab}}$ (i = 1,2,3) is the measurement results of the participants for the standard i, and $x_{i,\mathrm{KCRV}}$ is the KCRV for the same standard as defined in section 10. Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_{i,\mathrm{lab}}^2 + u_{i,\mathrm{KCRV}}^2} \quad (2)$$

where $u_{i,\mathrm{lab}}$ and $u_{i,\mathrm{KCRV}}$ are the measurement uncertainties of the participant and of the BIPM respectively for the standard i.

12 Support of calibration and measurement capabilities

BIPM.QM-K2.a and BIPM.QM-K2.b are Track A comparisons for participating NMIs/DIs as they test core skills and competencies required in gravimetric preparation, analytical certification and purity analysis.

CMCs supported by BIPM.QM-K2 (parts a and b) are for CO_2 amount fractions in air or nitrogen, with minimum values to be clarified after each bilateral comparison with a participant. The GAWG guidance will be followed to calculate the range of CO_2 amount fraction, with a turning point of 10 µmol mol^{-1}, and

- a lower boundary equal to the smallest absolute expanded uncertainty that can be claimed based on the participant result in the comparison,
- an upper boundary equal to 500 mmol mol^{-1} for all participants.

13 Reporting and publication of Results

The participant reports its measurements results in a copy of the result form BIPM.QM-K2-R2 (Excel workbook) and sends it to the coordinator before the start of the measurements at the BIPM. If the participant decides to verify the mixtures after the comparison, a new version of the results form is created and sent to the coordinator.

Upon completion of the measurements with the BIPM facility, the coordinator analysis the data and verify the absence of anomalies. In case of suspicious results, the coordinator can contact the participant and suggest a verification of its results.

The coordinator is responsible for the preparation of the reports of the comparisons. The first draft, Draft A, can be completed once uncertainties of values that were submitted by participants with their standards are confirmed by participants on return of their standards to them. The draft A report includes the calculation of the KCRVs and the degrees of equivalence. The participant can make editorial changes to the report and suggest more important changes to the description of its standards and measurements techniques if relevant.

The second draft, Draft B, is prepared by the coordinator and reviewed by the CCQM/GAWG following their agreed process.

After consideration of comments received from the CCQM/GAWG by the coordinator, the final report is prepared and sent for submission in the technological supplement of Metrologia. The coordinator also communicates the results of the comparison to the BIPM KCDB.

In agreeing to participate in the comparison, the participant agrees for their result to be identified in the comparison's report. The participants are co-authors of the final report publication.

14 Bibliography

[1] Viallon J., Choteau T., Moussay P., Wielgosz R., Veen A.v.d., Bi Z., Crotwell A., Hall B., Webber E.M. and Hill− Pearce R., 2023, 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), *Metrologia*, **60**, 08029,

[2] Viallon J., Meyer C.W., Moussay P., Schmidt J., Maxwell S.E., Arrhen F. and Wielgosz R., 2023, A high accuracy reference facility for ongoing comparisons of CO2 in air standards, *Metrologia*,

[3] Viallon J., Choteau T., Flores E., Idrees F., Moussay P., Wielgosz R.I., Lim J.S., Lee J., Lee J., Moon D., et al., 2023, CCQM-K68.2019, nitrous oxide (N2O) in air, ambient level, final report, *Metrologia*, **60**, 08011, 10.1088/0026-1394/60/1A/08011