CIPM MRA
Comparison reports

BIPM.QM-K2.b (SMU 2025)

Carbon dioxide in nitrogen

KEY COMPARISON

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Report of the comparison BIPM.QM-K2.b, on Carbon Dioxide in nitrogen at ambient levels, with SMU (2025)

Final Report

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Abstract

As part of the ongoing key comparison BIPM.QM-K2.b, a comparison has been performed on the amount fraction of carbon dioxide (CO_2) in nitrogen, in gaseous reference materials value assigned by the National Metrology Institute of Slovakia, Slovak Institute of Metrology (SMU), with the Key Comparison Reference Value based on measurements performed with the comparison reference facility maintained at the Bureau International des Poids et Mesures Headquarters (BIPM). One standard was used for the comparison that covers a CO_2 amount fraction range of 350 µmol mol^{-1} to 800 µmol mol^{-1}.

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1 Purpose and scope

The on-going Key Comparison BIPM.QM-K2 was launched in October 2024. The aim of BIPM.QM-K2 is the evaluation of participants' capabilities to accurately produce and/or value assign gas standards of CO_2 in air (part a) and in nitrogen (part b), at amount fractions covering a range between 350 µmol mol^{-1} and 800 µmol mol^{-1}.

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 PVT−CO_2 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 the samples by cryogenic trapping. The PVT−CO_2 facility performance has been validated during the Pilot Study CCQM-P225 [1], and described in detail in a publication [2].

SMU took part in BIPM.QM-K2.b, meaning that the matrix of the gaseous reference materials sent for the comparison was nitrogen.

2 Participants and coordinator

BIPM.QM-K2.b is an ongoing key comparison coordinated by the *Bureau International des Poids et Mesures* Headquarters, BIPM HQ, (abbreviated to BIPM in the rest of this report), which is structured as an ongoing series of bilateral comparisons. A full version of the protocol and the associated forms is available online at https://www.bipm.org/en/gas-metrology/ozone/bipm.qm-k2.

The results of the comparison with the Slovak Institute of Metrology (SMU, Slovakia) are reported here.

3 Measurand, quantities and Units

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

4 Measurements schedule

The BIPM.QM-K2.b protocol comprises three measurement periods: one conducted at the BIPM, and two by the participant—one before and one after the BIPM measurement. The measurements reported here were carried out at SMU in June and November 2025, and at the BIPM in September 2025.

5 Standards and values submitted by SMU

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

5.1 Nominal CO_2 amount fractions

The participant was required to provide a standard at one or all of the nominal amount fractions summarized in Table 1. SMU provided one standard with a CO_2 amount fraction close to 800 μmol mol^{-1}. The value reported by SMU was in accordance with the acceptable range defined in the protocol.

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 (μmol mol^{-1})	CO_2 amount fraction acceptable range (μmol mol^{-1})
0	380	350 to 430
0	480	430 to 530
1	800	530 to 800

5.2 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 and ISO 19229 for preparation of gravimetric standards and purity respectively. A matrix composition table was asked for 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 maximum standard uncertainty of 5 nmol mol^{-1}.

SMU reported that the mixture was prepared by themselves using the static gravimetric method for Class I mixtures according to ISO 6142-1:2015, by mixing nitrogen of BIP Plus quality and carbon dioxide of known purity. They reported the purity tables for both source gases, known from purity measurements and manufacturer specifications, showing the absence of N_2O in the source gases and in the mixture.

5.3 Mixtures preparation

The participant was asked to prepare and/or value assign their standards using their usual approaches. SMU reported that the mixtures were prepared in their laboratory using the static gravimetric method for Class I mixtures according to ISO 6142-1:2015.

In more detail, several calibration standards and the travelling standard mixture 0069F_7 were prepared in aluminium cylinders of a volume $V = 5$ dm^3. The inner surface of the cylinders was Aculife IV type. Before preparation, the cylinders were evacuated at least 15 hours using dry evacuation system.
The mass of the added amount of parent mixture was determined by the difference of the cylinder masses before and after filling. Weighing of evacuated and filled cylinder was executed on an automatic SMU balance system including Sartorius CC 10000 mass comparator with 1 mg resolution. Filled cylinder mass was not determined absolutely, but as a difference (6 repetitions) between filled cylinder mass and reference cylinder mass. For the achievement of target composition of the travelling standard, one premixture was made with nominal composition of 0.02 mol mol^{-1} of CO_2 in nitrogen.

5.4 Mixtures certification and/or verification

The participant was asked to verify or to value assign their standards using their usual approaches. SMU reported that the value of the CO_2 amount fraction in their mixture was the gravimetric values based on the added masses of carbon dioxide and nitrogen, taking into account their purity. They performed a first verification of the value by comparison with a set of five other mixtures of CO_2 in nitrogen prepared with the same method and covering an amount fraction range of 500 µmol mol^{-1} to 2000 µmol mol^{-1}. The analytical method used for the verification was Gas Chromatography with a Thermal Conductivity Detector (GC-TCD), implemented in the instrument Agilent 7890A.

A full description of the method and the metrological traceability of the reported value was provided by SMU in the Information Sheet annexed to this report (see Annex 1 – Participant reports).

A second verification period was allocated in the protocol, after measurements be performed at the BIPM. SMU reported that the same procedure employed for the verification was followed in November 2025, compared with the same five other mixtures. The second analytical value was found in good agreement with the first one, and both showed consistency with the assigned value by gravimetry, within the uncertainties.

5.5 CO_2 amount fraction and uncertainties reported by the participant.

The value submitted by SMU for their standard is reported in Table 2, with the expanded uncertainties and coverage factor. The standard was tracked with its cylinder ID (unique identifier engraved on a cylinder), which is also indicated in the table.

Table 2: Cylinder ID, CO_2 amount fraction ($x_p(CO_2)$), expanded uncertainties ($U(x_p(CO_2))$) and coverage factor reported by SMU.

Standard #	Cylinder ID	$x_p(CO_2)$	$U(x_p(CO_2))$	k
		µmol/mol	µmol/mol	
1	0069F_7	779.24	2.57	2

A full description of the calculations and the uncertainty budget was provided by SMU in the Information Sheet annexed to this report (see Annex 1 – Participant reports).

6 Measurements at the BIPM

6.1 Preparation and quality control of the BIPM comparison facility

Before starting the analysis of mixtures, it was ensured that all necessary calibrations of the measuring instruments (pressure gauges and temperature sensors) were performed within the appropriate period and that all quality controls were 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 was monitored carefully and observed to be stable within the uncertainties.

The BIPM makes use of a minimum of two quality control mixtures of CO_2 in dry air or nitrogen which are regularly analysed with the facility to check its stability. The stability of the system since the Pilot Study CCQM−P225 was already demonstrated in the previous report [3] with measurements performed on the QC mixture CC17623 (named QC #2 in the report). Further measurements performed on this mixture are displayed on Figure 1, covering a period between July 2024 and November 2025. Figure 2 shows measurements performed in the QC mixture #3 (D404749), between March 2025 and November 2025. Both graphs show stable and reproducible measurements, with a standard deviation of 0.059 µmol mol^{-1} over 18 months and of 0.057 µmol mol^{-1} over 6 months, comparable with the typical repeatability of the facility.

6.2 Preparation and connection of the cylinders

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.

6.3 Analysis of mixtures

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 $n \geq 3$ separate measurements. 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.

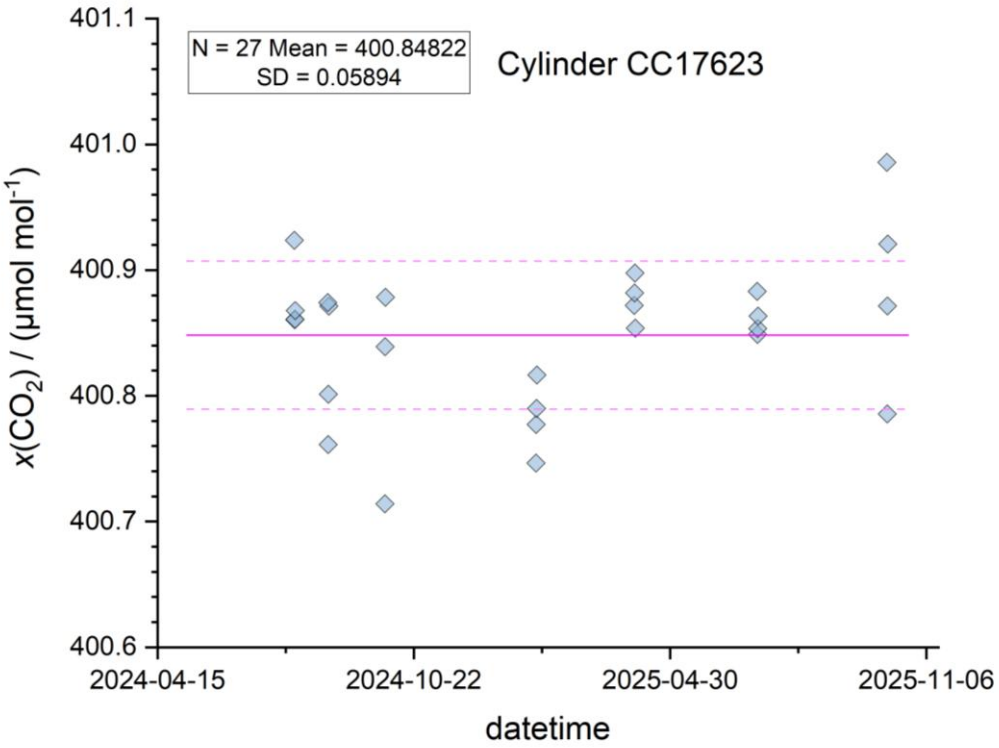

Figure 1: amount fraction of CO_2 in air, as measured by the BIPM PVT-CO_2 facility in the quality control mixture CC17623 since April 2024.

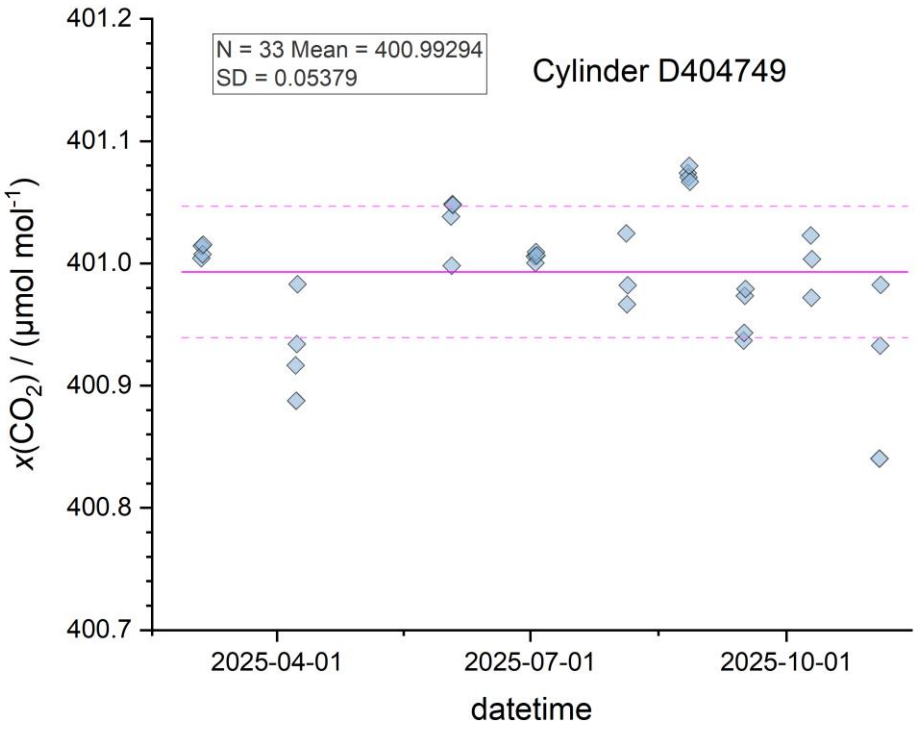

Figure 2: amount fraction of CO_2 in air, as measured by the BIPM PVT-CO_2 facility in the quality control mixture D404749 since March 2025.

6.4 Measurement results

The results of measurements performed with the PVT−CO_2 facility are summarised in Table 3. The number of measurements per series is indicated for information, as well as the value of the standard deviation of the mean, equal to 0.022 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.

Table 3: cylinder reference (ID), amount fraction of CO_2 measured by the BIPM ($x_R(CO_2)$), associated standard uncertainty ($u(x_R(CO_2))$), standard deviation of the mean (σ), number of repeats (n).

Standard #	Cylinder ID	$x_R(CO_2)$	$u(x_R(CO_2)$	σ	n
		µmol/mol	µmol/mol	µmol/mol	
1	0069F7	778.34	0.19	0.02	4

7 Key comparison reference value and uncertainty

There is one reference value for each mixture sent by the participant, defined by the results of measurements performed at the BIPM $x_R(CO_2)$, displayed in Table 3, with their standard uncertainties $u(x_R(CO_2)$.

The uncertainty budget for the PVT–CO_2 facility is described in [2]. It can be summarized in one equation expressing the standard uncertainty as a function of the CO_2 amount fraction x as follows:

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

Where $u_1 = 2.35 \times 10^{-4}$ is the relative part of the uncertainty, $u_2 = 0.023$ µmol mol^{-1} is the combination of the uncertainties on the additive corrections without the repeatability, and σ is the standard deviation of the mean over the repeated measurements, which takes the values displayed in Table 3.

8 Degrees of equivalence

There is one degree of equivalence defined in this comparison, expressed as:

$$\boldsymbol{D = x_P - x_{KCRV}} \qquad (1)$$

Where $x_P = x_P(CO_2)$ is the measurement results of the participants, and $x_{KCRV} = x_R(CO_2)$ is the KCRV for the same standard as defined in section 7. Its associated standard uncertainty is:

$$\boldsymbol{u(D) = \sqrt{u(x_P)^2 + u(x_{KCRV})^2}} \qquad (2)$$

where $u(x_P) = u(x_P(CO_2))$ and $u(x_{KCRV}) = u(x_R(CO_2))$ are the measurement uncertainties of the participant and of the BIPM respectively for the same standard.

The values are reported in Table 4 and plotted in Figure 3.

Table 4: Degrees of equivalence of SMU at the one CO_2 amount fractions in nitrogen measured in this comparison

Standard #	x_P / (µmol mol^{-1})	$u(x_P)$ / (µmol mol^{-1})	x_{KCRV} / (µmol mol^{-1})	u_{KCRV} / (µmol mol^{-1})	D / µmol mol^{-1})	$U(D)$ / (µmol mol^{-1})
1	779.24	1.29	778.34	0.19	0.90	2.60

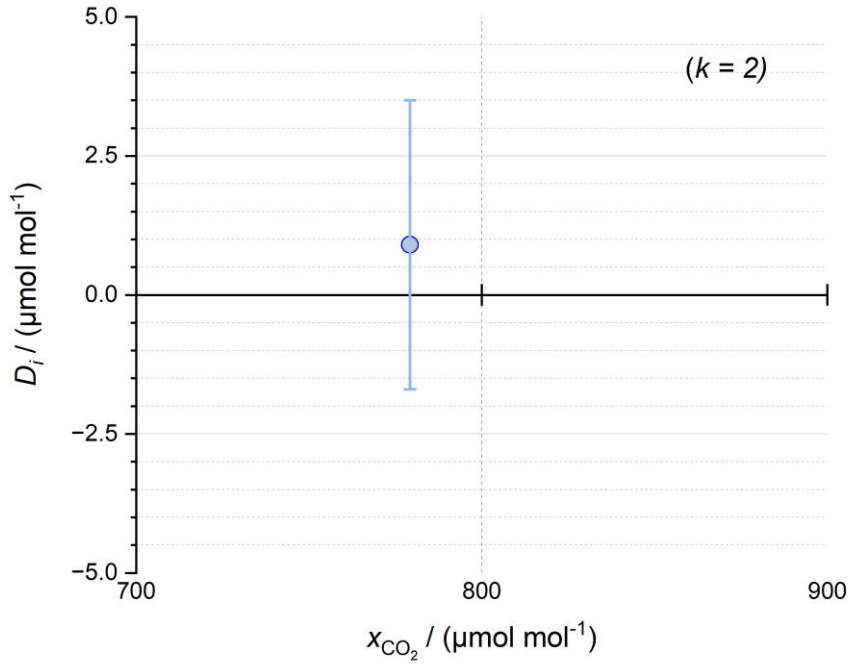

Figure 3: Graph of equivalence

The results show good agreement between the values assigned by SMU and by the BIPM PVT-CO_2 facility.

9 Conclusion

For the first time since the launch of the ongoing key comparison BIPM.QM-K2, a comparison has been performed between the CO_2 amount fraction value assigned by SMU, NMI of Slovakia, in reference material prepared by them, and the value assigned by the common reference facility of the key comparison, maintained by the BIPM. one One mixture of CO_2 in nitrogen at an amount fraction close to 780 µmol mol^{-1} was sent by the participant for this comparison, within the range of the comparison (350 µmol mol^{-1} to 800 µmol mol^{-1}). The degree of equivalence of this comparison indicated good agreement.

10 Annex 1 – Participant reports

Two reports are displayed entirely in the following pages (PDF version only): the result form (Excel Spreadsheet) and the Information Sheet. Both were completed by the participant.

11 References

[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., 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

[3] Viallon J., Moussay P., Wielgosz R. and Pachinger D., 2025, Report of the comparison BIPM.QM-K2.b, on carbon dioxide in nitrogen at ambient levels, with E+ E Elektronik (2025), *Metrologia*, **62**, 08022, 10.1088/0026-1394/62/1A/08022

Result Form for the comparison

BIPM.QM-K2.a and b, Carbon Dioxide in air (a) or nitrogen (b)

Participating institute information	
Institute	**Slovak Institute of Metrology**
Address	**Karloveska 63, SK- 841 04 Bratislava, Slovakia**
Contact	**Dr. Miroslava Valkova**
Email	valkova@smu.gov.sk
Telephone	**+421 260294211**

Comparison part (a/b)	**b**

Transfer Standards (cylinders) Information		
Number of standards	1	

Standard #	ID (Serial Number)	Date of preparation	Pressure	(unit)
1	0069F_7	2025-06-05	110	bar
2	***	***		
3	***	***		

Content of the form

page 1	General information
page 2	Standards composition

This result form is to be completed by participants in BIPM.QM-K2

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	0069F_7	779.24	2.57	2
2	***			
3	***			

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	0069F_7	none		
2	***			
3	***			

BIPM.QM-K2.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						

Information Sheet BIPM.QM-K2-R3
Key Comparison BIPM.QM-K2.a and .b

Please complete this information sheet, 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 BIPM.QM-K2-R2 (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:

SMU BIPM.Q M-K2-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.

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

Participating institute information	
Institute	**SMU/Slovak Institute of Metrology**
Contact	**Dr. Miroslava Valkova**
Email	**valkova@smu.gov.sk**

Transfer Standards (cylinders) Information		
Number of standards	1	

Standard #	ID (Serial Number)
1	0069F _7
2	
3	

Mandatory information

1) Traceability of the measurement results

[Instructions below may be removed]

The Key Comparisons BIPM.QM-K2.a and b are aimed at underpinning the capabilities of the participants to measure the amount fraction of CO_2 in air (part a) or in nitrogen (part b) 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. Explain here how the measurement results reported in the result form are traceable to the SI, including information on:

- The reference method used for value assignment;
- Additional verification measurements;
- Purity assessment of the different gases if applicable;
- Evaluation of CO_2 adsorption in cylinders if any.

Static gravimetric method for Class I mixtures according to ISO 6142-1:2015 for Carbon dioxide amount-of-substance fraction value assignment was used in this comparison as a source of traceability. Calibration standard values are true gravimetric values based on the added masses and purities of Carbon dioxide and Nitrogen.
For the verification of travelling standard mixture 0069F_7 in accordance to ISO 6143:2025 calibration was used with SMU primary standards. Neither stability changes were assumed. Travelling standard mixture was validated on GC Agilent 7890A using TCD detector.

Analytical method GC

GC method parameters for Carbon dioxide analysis are shown in the following table.

Table 1 *GC Settings*

GC	L; cm^3	Oven temperature; °C	Total time; min	Inlet flow He; cm^3/min	TCD temperature; °C	TCD flow He; cm^3/min	TCD Make Up flow; cm^3/min
Agilent 7890A	1.0	40-220	13.83	20.4	250	10	5

All measurements were done in automatic way using selector gas valve. Before entering sample loops all gas mixtures went through a mass flow controller for regulation. Measurement method with 5 automated runs was used. From each run was made one calibration curve linear and quadratic model with sample signals. Data were subjected to the B_least program (weighted least square regression). The inputs were: mole fractions and uncertainties of calibration standards, signals from the chromatograph with associated uncertainties. The result of the measurement sequence x_{an} was the average of amount-of-substance fractions from five results. Validation

criterion of travelling standard was tested. Calibration standards data prepared in SMU and results of the second run are shown in following table.

Table 2 *Calibration standards - measurement data of the second run*

Cylinder number	**Component**	**x_{cert} (µmol/mol)**	**u_{xcert} (µmol/mol)**	**signal**	**u_{signal}**
0098F_7	CO_2	517.21	0.78	16.04	0.04
0088F_5	CO_2	785.53	1.37	24.45	0.02
0083F_7	CO_2	796.51	1.27	24.72	0.02
0078F_5	CO_2	1013.89	1.52	31.51	0.12
0717E_11	CO_2	2058.24	3.09	64.19	0.12

Results of travelling standard verification measurement are shown in following table.

Table 3 *Quadratic calibration results verification measurement date 16.-17.06.2025*

Cylinder number	**x(an) (mol/mol)**	**$u(x_{an})(k=1)$ (mol/mol)**	**$u(x_{an})$ (%)**	**$x(_{grav})$ (mol/mol)**	**$u(x_{gr})k=1$ (mol/mol)**	**$\|x(_{an})-x(_{grav})\|$**	**criterion 2*odm(u(an)^2 +u(gr)^2)**
0098F_7	0.00051682	0.00000084	0.16%				
0088F_5	0.0007883	0.0000013	0.16%				
0083F_7	0.0007972	0.0000019	0.24%				
0069F_7	**0.0007811**	**0.0000018**	**0.23%**	**0.00077924**	**0.00000012**	**1.86E-06**	**3.60799E-06 OK**
0078F_5	0.0010103	0.0000025	0.25%				
0717E_11	0.0020588	0.0000032	0.16%				

Table 4 *Quadratic calibration curve parameters of the second run*

b_0	**$u(b_0)$**	**b_1**	**$u(b_1)$**	**b_2**	**$u(b_2)$**
5.67E-07	6.55E-06	3.23E-05	4.21E-07	-3.43E-09	5.49E-09

All calibration standards and travelling standard mixture 0069F_7 were prepared in aluminium cylinders V= 5 dm^3in SMU. Inner surface of the cylinder was Aculife IV type. Before preparation. the cylinder was evacuated at least 15 hours using dry evacuation system.
The mass of added amount of parent mixture was determined by the difference of the cylinder masses before and after filling. Weighting of evacuated and filled cylinder was executed on automatic SMU balance system including Sartorius CC 10000 mass comparator with 1 mg resolution. Filled cylinder mass was not determined absolutely, but as a difference (6 repetitions) between filled cylinder mass and reference cylinder mass. For the achievement of target composition of travelling standard, one premixture was made with nominal composition 0.02 mol/mol CO_2 in Nitrogen.
For the calculations of the gravimetric composition with associated uncertainties from weighing. purity analysis and Molar masses, validated spreadsheet xlISO6142 v1.11 was used based on the models described in ISO 6142-1:2015 and ISO 19229.

Each component has its purity table with composition from purity measurements and manufacturer specifications. Gravimetric data of the pure gases, premixture 0055F_8 and final mixture 0069F_7 are shown in following tables.

Table 5 *Nitrogen Bip Plus Purity table*

Component	**amount-of-substance fraction (mol/mol)**	**uncertainty k=1) (mol/mol)**
CO	0.0000000044	0.000000000025
CO_2	0.00000064	0.00000010
H_2O	0.000000010	0.0000000058
O_2	0.0000000081	0.0000000011
H_2	0.000000025	0.00000014
CH_4	0.000000090	0.000000052
N_2	**0.99999922**	**0.00000012**

Table 6 *Carbon Dioxide Purity table*

Component	**amount-of-substance fraction (mol/mol)**	**uncertainty k=1) (mol/mol)**
CO	0.000000025	0.000000014
N_2	0.0000423	0.0000017
H_2O	0.0000020	0.0000012
O_2	0.00000829	0.00000077
Ar	0.000000910	0.000000044
CH_4	0.000000025	0.000000014
CO_2	**0.99994645**	**0.00000219**

Table 7 *Premixture 0055F_8 Gravimetric composition*

Component	**amount-of-substance fraction (mol/mol)**	**uncertainty k=1) (mol/mol)**
CO	0.00000000485	0.00000000029
N_2	0.9797124	0.0000012
H_2O	0.000000866	0.000000034
O_2	0.000000168	0.000000016
H_2	0.0000000245	0.0000000071
Ar	0.00000001846	0.00000000089
CH_4	0.000000089	0.000000025
CO_2	**0.0202864**	**0.0000012**

Table 8 *Travelling standard 0069F_7 Gravimetric composition*

Component	**amount-of-substance fraction (mol/mol)**	**uncertainty k=1) (mol/mol)**
CO	0.00000000444	0.000000000027
N_2	0.99922059	0.00000013
H_2O	0.0000000410	0.0000000017
O_2	0.00000000645	0.00000000060
H_2	0.0000000249	0.0000000069
Ar	0.000000000708	0.000000000034
CH_4	0.000000090	0.000000025
CO_2	**0.00077924**	**0.00000012**

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. Express clearly if uncertainties are reported with a confidence factor (k) and its value.

To the validated CRM´s used as the calibration standards were assigned values of amount-of-substance fraction of Carbon dioxide derived from the process of gravimetric preparation. Standard uncertainties of calibration standards are given in the Table 2. These combined standard uncertainties were calculated in accordance to the following formula (ISO 6142-1:2015):

$$u_{cert.x.i} = \frac{1}{2}\sqrt{u^2(x_{i.grav}) + u^2(x_{i.ver}) + (x_{i.grav} - x_{i.ver})^2} \quad (1)$$

Uncertainty of verification result was evaluated in accordance with ISO 6143:2025. Uncertainty $u(x_{ver})$ was calculated using B_least program. The inputs were: amount-of-substance fractions and uncertainties of calibration standards calculated by formula (1) and signals from the chromatograph with associated uncertainties. Example of the uncertainties is given in the Table 2. From five runs results average of amount-of-substance fractions standard deviations were found $u_1(\overline{x_i})$ and from runs results uncertainties the mean (through squares) was found $u_2(\overline{x_i})$. These 2 figures were combined to give standard uncertainty $u_{ver}(\overline{x_i})$. Following formulas were used for the uncertainty calculations of verification measurement:

$$u_1(\overline{x_i}) = 1.4 * \sqrt{\frac{\sum_{j=1}^{n}(x_j - \overline{x_i})^2}{n.(n-1)}} \quad (2)$$

$$u_2(\overline{x_i}) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}} \quad (3)$$

$$u_{\text{ver}}(\overline{x}_i) = \sqrt{u_1(\overline{x}_i)^2 + u_2(\overline{x}_i)^2} \quad (4)$$

$$\overline{x}_i = \frac{\sum_{j=1}^{n} x_j}{n} \quad (5)$$

Associated combined uncertainty of the verification result is given in the Table 9.

Table 9 *Combined standard uncertainty of the amount-of-substance fraction 0069F_7*

quantity	$u_1(\overline{x}_i)$ **(k=1) (mol/mol)**	$u_2(\overline{x}_i)$ **(k=1) (mol/mol)**	**combined uncertainty (k=1) (mol/mol)**
$\overline{x}_{,ver}$	0.00000151	0.00000092	**0.00000177**

Final uncertainty for travelling standard was calculated in accordance to formula (1).

quantity	$u(_{CO2,grav})$ **(k=1) (mol/mol)**	$u(x_{CO2,ver})$ **(k=1) (mol/mol)**	$(x_{CO2,grav} - x_{CO2,ver})$ **(k=1) (mol/mol)**	$u_{cert,CO2}$ **(k=1) (mol/mol)**
$x_{cert,\,CO2}$	0.00000012	0.00000177	0.00000186	**0.00000129**

Final result for the amount-of-substance fraction of Carbon dioxide derived from the gravimetric preparation and verification of the mixture 0069F_7 is:
(779.24 ± 2.57) µmol/mol U(k=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

[Instructions below may be removed]

Provide here any useful information on the gas mixture composition which is not already provided in the accompanying result form. If the mixtures contain N_2O. describe the source of the gas and measurements performed to estimate its amount fraction if applicable. If the mixtures do not contain N_2O. describe the supporting evidence of this statement.

Purity tables of travelling standard and pure gases are stated in Paragraph 1 in the Tables 5. 6. 7 and 8. Presence of N_2O was not detected.

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.

Calibration mixtures and travelling standard were prepared in SMU using static gravimetric method. Preparation method and instrumentation is introduced in Paragraph 1 of this report.

5) Second verification of mixtures

[Instructions below may be removed]

If the mixtures were verified after the measurements at the BIPM. 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.

Second measurement after shipment of the cylinder from BIPM to SMU was executed at 06.11.-07.11.2025. Measurement procedure and analytical instrument was the same as was described in Paragraph 1 of this report. Calibration standards and the results from the calibration are stated in the Table 10.

Result value from second verification measurement confirmed reported gravimetric value for CO_2 amount-of-substance fraction of the mixture 0069F_7 :

(779.24 ± 2.57) µmol/mol U(k=2).

Table 10 *Quadratic calibration results second verification measurement date 06.-07.11.2025*

Cylinder number	**x(an) (mol/mol)**	**$u(x_{an})(k=1)$ (mol/mol)**	**$u(x_{an})$ (%)**	**$x(_{grav})$ (mol/mol)**	**$u(x_{gr})k=1$ (mol/mol)**	**$\lvert x(_{an})-x(_{grav})\rvert$**	**criterion 2*odm(u(an)^2 +u(gr)^2)**
0098F_7	0.0005179	0.0000013	0.25%				
0059F_8	0.0007439	0.0000022	0.30%				
0069F_7	**0.0007788**	**0.0000010**	**0.13%**	**0.00077924**	**0.00000012**	**4.4E-07**	**2.01435E-06 OK**
0088F_5	0.0007881	0.0000013	0.16%				
0083F_7	0.0007958	0.0000021	0.26%				
0078F_6	0.0010181	0.0000018	0.18%				