Key Comparison COOMET.QM-K120
“Carbon dioxide in Air at urban level (480- 800) µmol/mol”

Final report

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Field
Amount of substance

Subject
Comparison of carbon dioxide in air urban level (track A – core competences)

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1 Introduction

COOMET key comparison COOMET.QM-K120 is designed as linking to the appropriate CCQM comparison - CCQM-K120.b (2016-2018, Flores et al. 2018, [1]) and is intended to support CMCs of National Metrological Institutes of the countries – mainly members of COOMET.
The CCQM-K120.b was a gravimetric comparison which evaluated the level of compatibility of NMI preparative capabilities for carbon dioxide in air primary reference mixtures in the range (480-800) μmol/mol.
CCQM-K120.b is considered as a Track A comparison and tests core skills and competencies required in gravimetric preparation, analytical certification and purity analysis. Participants successful in CCQM-K120.b and the linked COOMET.QM-K120 comparison may use their results in the flexible scheme and underpin claims for all core mixtures in accordance with the GAWG strategy document [2].

2 Design and organization of comparison

2.1 Participants

Table 1 lists the participants of the comparison.

Table 1: List ofparticipants

Acronym	Country	Institute
VNIIM (Pilot lab.)	RU	D.I.Mendeleyev Institute for Metrology, St-Petersburg, Russia
Ukrmetrt-eststandart	UA	All-Ukrainian State Research and Production Center of Standard-ization, Metrology, Certification and Consumers Rights Protec-tion, Kiev, Ukraine
BelGIM	BY	Belorussian State Institute for Metrology, Minsk, Belarus
KAZINMETR	KZ	Karaganda branch of the RSE "Kazakhstan Institute for metrology"
NMC, A*STAR	SG	National Metrology Centre, Agency for Science, Technology and Research, Singapore

2.2 Measurement standards

Each laboratory taking part in the comparison was requested to produce one standard at the nominal amount fraction of 480 μmol/mol and another at the amount fraction 800 μmol/mol. The standards were to be prepared and verified by the participants using their usual procedures. The amount fraction of carbon dioxide was requested to be within ± 10 μmol/mol of the nominal amount fractions of the cylinders. The carbon dioxide was requested to be produced in a dry air matrix, produced from scrubbed real air or synthetic air that has been blended from pure gases that are the main constituents of air (nitrogen, oxygen, argon) and two other constituents (nitrous oxide and methane).The table below describes the limits of the gas matrix composition of the scrubbed dry real air and synthetic air, which were to be met by participants:

Table 2: Matrix composition limits

Species	'Ambient' level mole fraction	Unit	Min amount fraction	Unit	Max amount fraction	Unit
N_2	0.780876	mol/mol	0.7789	mol/mol	0.7829	mol/mol
O_2	0.2093335	mol/mol	0.2073	mol/mol	0.2113	mol/mol
Ar	0.0093332	mol/mol	0.0078	mol/mol	0.0108	mol/mol
CH_4	1900	nmol/mol	0	nmol/mol	1900	nmol/mol
N_2O	330	nmol/mol	0	nmol/mol	330	nmol/mol

Tables 3 and 4 show the reported amount fractions of CO_2 in the mixtures prepared by the participants, expanded uncertainties, pressure and information about cylinders. All participants submitted mixtures with CO_2 amount fraction within10 µmol mol^{-1}of the nominal values, as requested.

Table 3: Initially submitted values of CO_2 amount fraction, expanded uncertainties, pressure and information about cylinders for 480 µmol/mol level

Cylinder №	Pressure before measurements, bar	Pressure after measurements, bar	Reported values		*V*, L	Cylinder	NMI
			CO_2 amount fraction, µmol mol^{-1}	*U (k=2)* µmol mol^{-1}			
D914327	95	83	482.43	0.6	10	Luxfer	BelGIM
81205102	123	116	480.27	0.45	10	Al cyl.	Ukrmetrteststandart
K772-5	80	75	486.8	2.4	4	Al cyl.	KAZINMETR
D248767	100	86	479.87	0.51	5	Luxfer	NMC, A*STAR
M365664	90	85	480.18	0.13	5	Luxfer	VNIIM

Table 4: Initially submitted values of CO_2 amount fractions, expanded uncertainties, pressure and information about cylinders for 800 µmol/mol level

Cylinder №	Pressure before measurements, bar	Pressure after measurements, bar	Reported values		*V*, L	Cylinder	NMI
			CO_2 amount fraction, µmol mol^{-1}	*U (k=2)* µmol mol^{-1}			
5705631	94	93	802.59	1.2	10	Luxfer	BelGIM
81205166	122	121	799.99	0.83	10	Al cyl.	Ukrmetrteststandart
K772-7	90	88	799.4	4	4	Al cyl.	KAZINMETR
D248763	102	101	799.37	0.76	5	Luxfer	NMC, A*STAR
M365707	93	88	800.73	0.19	5	Luxfer	VNIIM

All the participants prepared their standards in accordance with [3] using as a matrix synthetic air that has been blended from pure gases - nitrogen, oxygen, argon, which were within specifications (matrix composition) for all participants as requested in the protocol.
The participants had opportunity to perform stability testing after standards had been returned to them from VNIIM, and before the comparison results were known. This was especially important, since the comparison schedule was significantly disrupted due to the partial closure of NMIs during the pandemic of COVID-19 and delays in the shipment of cylinders.

None of the participants except VNIIM presented isotope ratios of the CO_2 used (it was optional).

A more detailed information on the participants samples, including purity tables and uncertainty budgets can be find in the participant reports (see Appendix A).

2.3 The schedule

The actual schedule for the project was as follows:

Date	Action
June-August 2019	Preparation of the mixtures by participants
February 2020	Shipment of cylinders to the Pilot (to arrive by 1 of November) In fact the last cylinder was received in VNIIM in February 2020
August-September 2020	Analysis of mixtures by VNIIM Due to pandemic of COVID-19 measurements in VNIIM were carried out in August-September 2020
October 2020 - January 2021	Return of cylinders to participants
February 2021 – June 2021	2nd set of analysis of mixtures by participants
September 2021	Distribution of Draft A report

3 Comparison measurements

3.1 Control mixtures

VNIIM prepared 2 fresh standards at the nominal amount fraction of 480 µmol/mol and 2 standards at 800 µmol/mol. The cylinders were verified and one cylinder from each group was used as the reference for COOMET.QM-K120.

In order to provide link to CCQM-K120b and to check trueness these standards were used as reference in the analysis of the appropriate standards, that were prepared for CCQM-K120b.The results confirmed that the difference between the measured (against fresh cylinders) and the assigned value for CCQM-K120b cylinders is within the uncertainty of measurements. The testing was repeated twice in the period of comparison measurements. The results are shown in the Table 5.

Table 5: The results of measurements of the CCQM-K120b standards against new standards

Cylinder №	Date of preparation, DD.MM.YYYY	Date of measurements, DD.MM.YYYY	Gravimetric value, µmol mol^{-1}	Measured value, µmol mol^{-1}	Difference between the measured and gravimetric values, µmol mol^{-1}	Expanded uncertainty (k=2) of the difference, µmol mol^{-1}
M365686	10.10.2016	09.09.2020	480.26	480.42	0.16	0.24
		22.09.2020		480.43	0.17	
M365711	11.10.2016	09.09.2020	798.9	798.50	-0.40	0.43
		22.09.2020		798.54	-0.36	

3.2 Instrumentation and measurement procedure

All the measurements at the Pilot laboratory were carried out by Cavity ring-down spectroscopy in August-September 2020.

Instrument: Picarro G2131i + combustion module Picarro

Measurement cell temperature: 45°C

Measurement cell absolute pressure: 18.665 kPa
Data collection: by "Picarro Inc." software

The 10 cylinders of the comparison were separated into small batches and were analyzed mainly in two cylinders per day with i=3 sub-measurements for each.
All cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders were rolled for at least 1 hour to ensure homogeneity of the mixture. The pressure reducer of each cylinder was flushed nine times with the mixture. The cylinder valve was then closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa (abs). The cylinders were left stand at least 24 hours, to allow conditioning of the pressure reducers.

The sequence for measurements was as follows:
{nitrogen – analyzed mixture} –[nitrogen – reference standard – nitrogen – analyzed mixture – nitrogen – reference standard – nitrogen]$_{i=3}$
First part of the sequence indicated by braces {} was used for flushing the instrument and preparing for the measurements. The readings of the instrument at this stage were not used in the further calculation.
The measurements of $^{12}CO_2$ amount fractions were performed at the second part of the sequence indicated by square brackets [].
Subtraction of zero readings (N_2 readings) from the readings of reference and analyzed mixtures is performed in accordance with the following formula

$$A_{sti} = X_{sti} - \left(\frac{N_i+N_{i+1}}{2}\right) \qquad (0)$$

where A_{sti} is the corrected reading for ith-input of reference standard,
X_{sti} is the uncorrected reading for ith-input of reference standard,
N_i and N_{i+1} are the uncorrected readings for ith-input and ($i+1$)th-input of nitrogen appropriately.
Similar formulas are used to obtain $A_{st(i+1)}$ which is the corrected reading for ($i+1$)th-input of reference standard and A_{ai} which is the corrected reading for ith-input of analyzed mixture.

After subtracting the zero readings (N_2 readings) from the readings of reference and analyzed mixtures according to the formula (0) the following values were obtained: $-\left[A_{sti}- \; A_{ai}- \; A_{st(i+1)}\right]_{i=3} -$. In the sequence, A_{sti} and A_{ai} are the corrected readings for ith-input of reference standard and analyzed mixture appropriately.
Each reading is the average reading for 5 minutes of every-second measurements.
The instrument was pre-calibrated by reference materials of carbon isotopic composition IAEA-CO-8, IAEA-CH-7 to get $\delta^{13}C_{VPDB}$ values. The corresponding readings of the instrument relative to the VPDB are indicated as follows: $-\left[\delta_{sti}- \; \delta_{ai}- \; \delta_{st(i+1)}\right] -$.
The following formula was used to calculate $^{13}CO_2$ amount fractions B_{sti}, B_{ai} and $B_{st(i+1)}$

$$B_{sti} = \left(\frac{\delta_{sti}}{1000} + 1\right) * 0.01118^{(*)} * A_{sti} \qquad (1)$$

(*) – according to Werner R.A., Brand W.A. Referencing strategies and techniques in stable isotope ratio analysis. Rapid Commun Mass Spectrom. 2001;15(7):501-519

The measured $\delta^{13}C_{VPDB}$ in the mixtures prepared by the participants are shown in the Table 6.

Table 6: The results of measurements of the $\delta^{13}C_{VPDB}$ in the mixtures prepared by the participants

Cylinder №	Measured values		*V*, l	Cylinder	NMI
	$\delta^{13}C_{VPDB}$, ‰	*U (k=2) %*			
D914327	-47.8	0.5	10	Luxfer	BelGIM
81205102	-43.5	0.5	10	Al cyl.	Ukrmetrteststandart
K772-5	-30.4	0.5	4	Al cyl.	KAZINMETR
D248767	-28.3	0.5	5	Luxfer	NMC, A*STAR
D804726	-51.5	0.5	5	Luxfer	VNIIM
5705631	-47.8	0.5	10	Luxfer	BelGIM
81205166	-43.6	0.5	10	Al cyl.	Ukrmetrteststandart
K772-7	-30.3	0.5	4	Al cyl.	KAZINMETR
D248763	-28.5	0.5	5	Luxfer	NMC. A*STAR
D804728	-51.5	0.5	5	Luxfer	VNIIM

The total amount fraction of CO_2, taking into account the isotopic composition of the mixture, is calculated in accordance with (2)

$$x_{sti} = A_{sti} + B_{sti} \tag{2}$$

Similar formulas are used to obtain x_{ai} and $x_{st(i+1)}$.
The final amount fraction for the *i*th-measurement x_i which takes into account drift, is calculated in accordance with (3)

$$x_i = x_{ai}\frac{2\times G_{st}}{x_{sti} + x_{st(i+1)}} \tag{3}$$

where G_{st} is gravimetric value of CO_2 amount fraction for the reference standard.
Three measurements of x_i were performed each day. Such measurement cycle was repeated for each standard in 3 different days and the average was taken as a result x.

The results of A, B, δ and x for reference materials and participants' samples including their uncertainties are shown in the table 7. $u_{i,meas}$ is the uncertainty of measurements of cylinder *i* (µmol/mol) (*k*=1).

Table 7. Intermediate measurement results of COOMET.QM-K120

Cylinder №	**Type of cylinder**	**A, arbitrary units**	**B, arbitrary units**	**δ, ‰**	**x, µmol mol^{-1}**	**$u_{i,meas,}$, µmol mol^{-1}**
D914327	participants' sample	497.61	5.30	-47.6	482.20	0.05
81205102	participants' sample	493.63	5.28	-43.3	478.39	0.05
K772-5	participants' sample	502.26	5.45	-30.0	486.78	0.05
D248767	participants' sample	495.38	5.38	-28.0	480.19	0.05
D804726	participants' sample	495.52	5.26	-51.2	480.08	0.05
5705631	participants' sample	829.04	8.82	-48.2	803.14	0.14
81205166	participants'	823.10	8.80	-44.0	797.81	0.14

	sample					
K772-7	participants' sample	825.22	8.94	-30.8	799.03	0.14
D248763	participants' sample	825.16	8.96	-28.9	799.33	0.14
D804728	participants' sample	825.64	8.75	-52.2	800.04	0.14
D804731	reference material	495.41	5.25	-51.2	-	-
D804747	reference material	825.62	8.75	-51.9	-	-

The uncertainty of measurements $u_{i,meas}$ is calculated according to the following formula

$$u_{i,meas} = \sqrt{(u_x)^2 + (u_\delta)^2} \tag{4}$$

where u_x - standard uncertainty of CO_2 amount fraction, u_δ - standard uncertainty of $\delta^{13}C_{VPDB}$.

3.3 Stability measurements by participants

All the participants (except KASINMETR, who assigned to their results substantially larger uncertainties than the other participants) performed stability testing after standards had been returned from VNIIM, and before the comparison results were known. VNIIM (as a participant) and BelGIM confirmed their results, NMC, A*STAR and Ukrmetrteststandart also confirmed the initially presented gravimetric values but provided updated uncertainties.
The results received by NMC, A*STAR and Ukrmetrteststandart before and after measurements at the Pilot laboratory are shown in the table 8.

Table 8 Stability measurements by NMC, A*STAR and Ukrmetrteststandart

Participant/ Cylinder №	**Before measurements at the Pilot lab**		**After measurements at the Pilot lab.**		**Drift µmol mol^{-1}**	**Presented lab. values**	
	Value, µmol mol^{-1}	***U* (*k*=2), µmol mol^{-1}**	**Value, µmol mol^{-1}**	***U* (*k*=2), µmol mol^{-1}**		**Value, µmol mol^{-1}**	***U* (*k*=2), µmol mol^{-1}**
NMC, A*STAR D248767	480.09	0.51	480.49	0.69	0.39	479.87	0.69
D248763	798.94	0.76	799.34	0.90	0.40	799.37	0.90
Ukrmetrteststandart 81205102	480.27	0.45	481.03	0.76	0.76	480.3	0.9
81205166	799.99	0.83	801.00	0.74	1.01	800.0	1.3

The detected drift (less than 0,1 % for NMC, A*STAR and less than 0,16 % for Ukrmetrteststandart) and the stability uncertainty contribution are the reason for the participants to update the measurement uncertainty.

3.4 Degrees of equivalence

A unilateral degree of equivalence d_i in key comparisons is defined as

$$d_i = x_{i,lab} - x_{i,KCRV}, \tag{5}$$

and the uncertainty of the difference d_i at 95% level of confidence. Here $x_{i,KCRV}$ denotes the key comparison reference value, and $x_{i,lab}$ the result of laboratory *i*.

The 40-th meeting of GAWG CCQM [4] recommended not to use the regression analysis of the participants results for assignment of KCRV, but to use direct result of measurements against VNIIM standard.

The standard uncertainty of $x_{i,KCRV}$ can be expressed as

$$u^2(x_{i,KCRV}) = u^2_{st,prep} + u^2_{meas} + u^2_{d(VNIIM/CCQM-K120)} + u^2_{\Delta} \quad (6)$$

where $u_{st.prep}$ is the standard uncertainty of the VNIIM reference standard, u_{meas}. – the standard uncertainty of measurements, $u_{d(VNIIM/CCQM-K120)}$ is the standard uncertainty of VNIIM degree of equivalence in CCQM-K120, u_{Δ} – the standard uncertainty of the difference between the measured (against fresh cylinders) and assigned value for CCQM-K120 cylinders

In this case the standard uncertainty of d_i can be expressed as

$$u^2(d_i) = u^2_{i,lab} + u^2_{st,prep} + u^2_{meas} + u^2_{d(VNIIM/CCQM-K120)} + u^2_{\Delta} \quad (7)$$

4 Results

In this section, the results of the key comparison are summarised. In the tables 9 and 10, the following data is presented

$x_{i,lab}$- result of laboratory *i*, μmol/mol

$u_{i,lab}$- standard uncertainty of laboratory result[1], μmol/mol (*k*=1)

$x_{i,KCRV}$- reference value for cylinder of laboratory *i*, μmol/mol

$u_{st,prep}$- standard uncertainty of the reference standard used in the measurements of $x_{i,lab}$, μmol/mol (*k*=1)

$u_{i,meas}$- standard uncertainty of measurements of cylinder *i*, μmol/mol (*k*=1)

$u_{d(VNIIM/CCQM-K120)}$ - standard uncertainty of VNIIM degree of equivalence in CCQM-K120b, μmol/mol

u_{Δ} – standard uncertainty of the difference between the measured and assigned values for CCQM-K120b cylinders, μmol/mol

d_i - difference between laboratory result and reference value (degree of equivalence), μmol/mol

k - assigned coverage factor for degree of equivalence,

U (d_i)- expanded uncertainty of difference d_i, at 95 % level of confidence[2], μmol/mol

The results in graphical form are presented in the figures 1 and 2.

Notes:

[1]*For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.*

[2] *In the figures1 and 2 the degrees of equivalence for all participating laboratories are given. The uncertainties are given as 95% confidence intervals as required by the MRA [5]. For the evaluation f uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor k = 2 was used.*

Table 9 : Results of COOMET.QM-K120 – level 480 µmol/mol

Laboratory	**Cylinder**	$x_{i,lab}$	$u_{i,lab}$	$x_{i,KCRV}$	$u_{st,prep}$	$u_{i,meas}$	$u_{d(VNIIM\ /\ CCQM-K120)}$	u_{Δ}	d_i	k	$U(d_i)$
BelGIM	D914327	482.40	0.3	482.20	0.09	0.05	0.088	0.12	0.20	2	0.70
KAZINMETR	K772-5	486.80	1.2	486.78	0.09	0.05	0.088	0.12	0.02	2	2.43
NMC, A*STAR	D248767	479.87	0.34	480.19	0.09	0.05	0.088	0.12	-0.32	2	0.77
Ukrmetrtest-standart	81205102	480.30	0.45	478.39	0.09	0.05	0.088	0.12	1.91	2	0.97
VNIIM	M365664	480.18	0.065	480.145	0.059 - u($x_{i\ KCRV}$)		-	-	0.035	2	0.175

Table 10: Results of COOMET.QM-K120 – level 800 µmol/mol

Laboratory	**Cylinder**	$x_{i,lab}$	$u_{i,lab}$	$x_{i,KCRV}$	$u_{st,prep}$	$u_{i,meas}$	$u_{d(VNIIM\ /\ CCQM-K120)}$	u_{Δ}	d_i	k	$U(d_i)$
BelGIM	5705631	802.60	0.6	803.14	0.13	0.14	0.127	0.215	-0.54	2	1.35
KAZINMETR	K772-7	799.40	2.0	799.38	0.13	0.14	0.127	0.215	0.02	2	4.05
NMC, A*STAR	D248763	799.37	0.45	799.33	0.13	0.14	0.127	0.215	0.04	2	1.10
Ukrmetrtest-standart	81205166	800.0	0.65	797.81	0.13	0.14	0.127	0.215	2.19	2	1.44
VNIIM	M365707	800.730	0.095	800.697	0.084- u($x_{i\ KCRV}$)		-	-	0.033	2	0.253

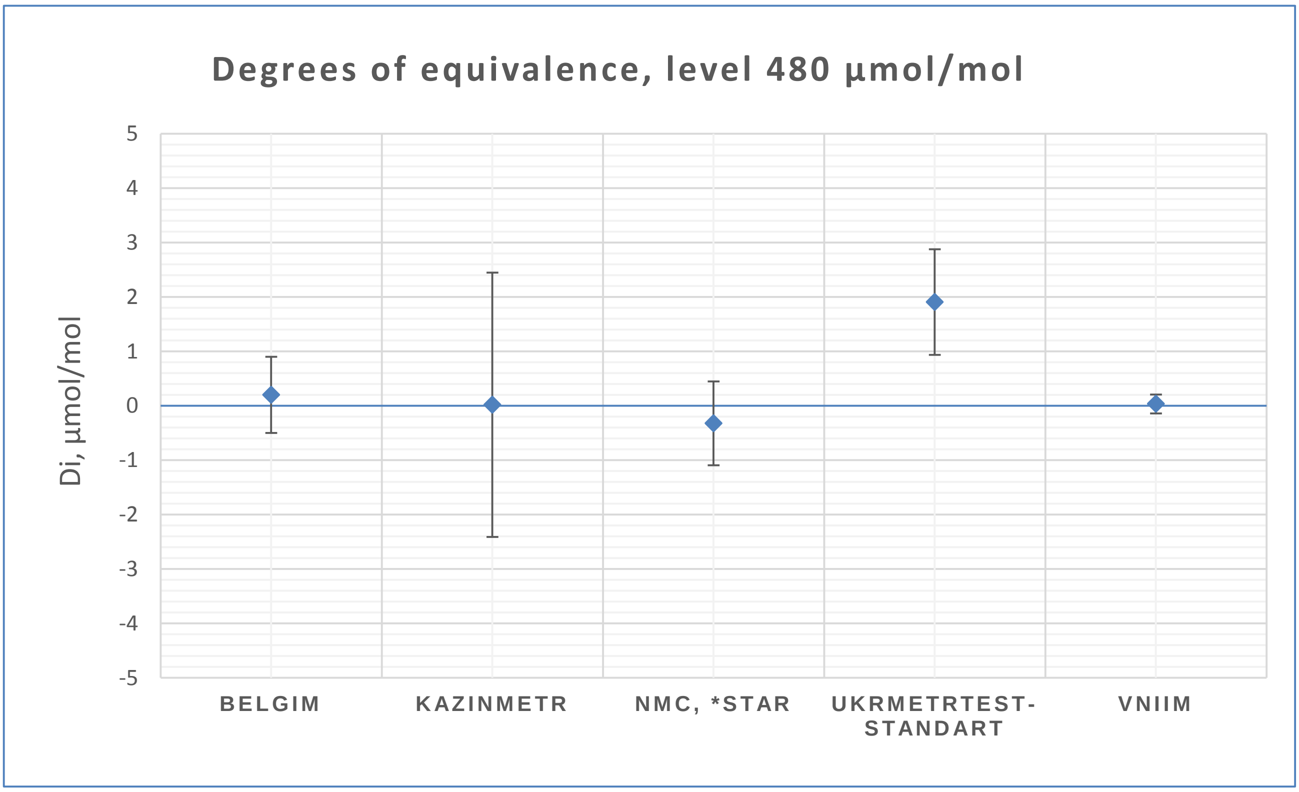

Figure 1 - Degrees of equivalence for level 480 µmol/mol

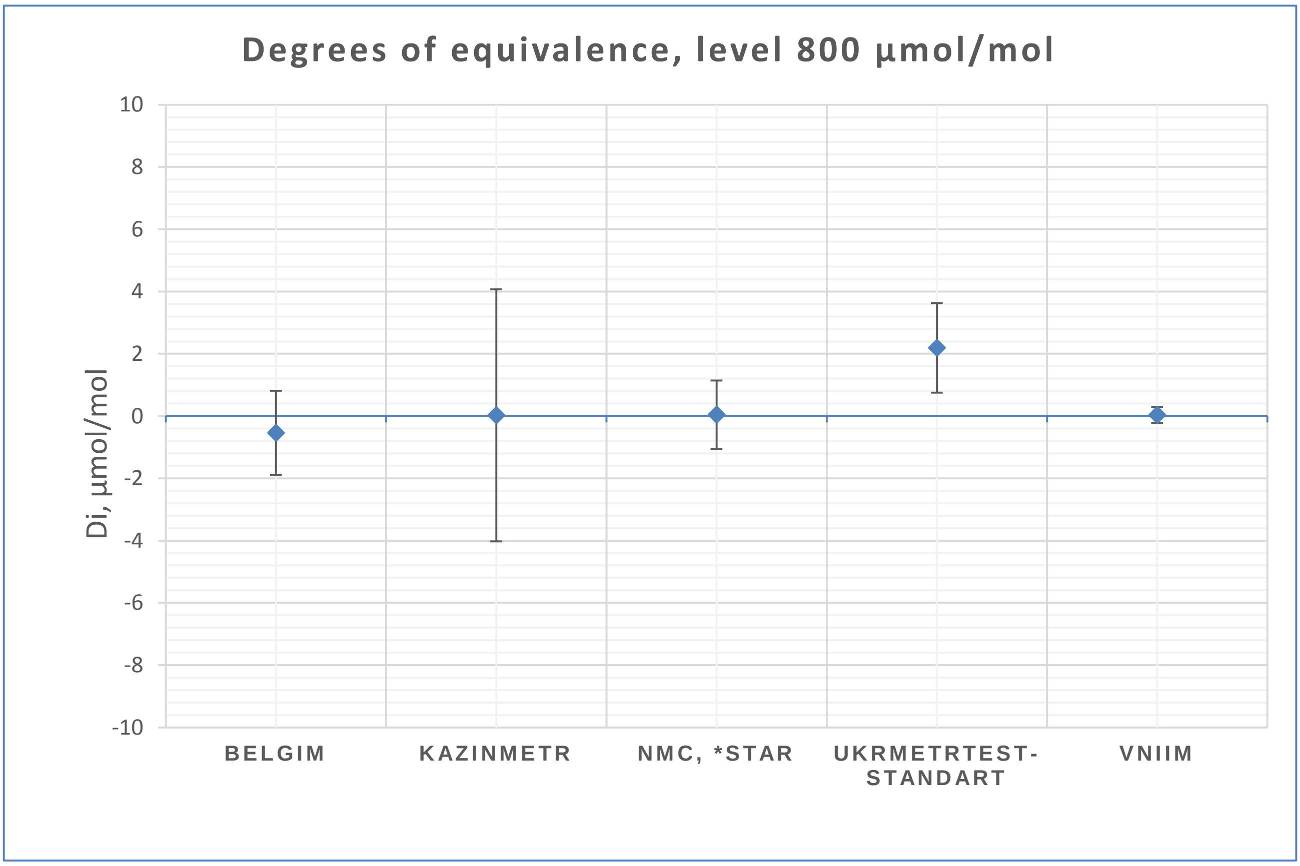

Figure 2 - Degrees of equivalence for level 800 µmol/mol

5 Supported CMC claims

The results of this key comparison can be used to support CMCs as described in the final report of CCQM-K120 in the section concerning CCQM-K120.b [1].

CCQM-K120.b comparison tests core skills and competencies required in gravimetric preparation, analytical certification and purity analysis. It is considered as a Track A comparison. It will underpin CO_2 in air and nitrogen claims in a amount fraction range starting at the smallest participant's reported expanded uncertainty and ending at 500 mmol/mol. Participants successful in this comparison may use their result in the flexible scheme and underpin claims for all core mixtures.

6 Discussion and conclusions

The results of this Track A key comparison are satisfactory. All the results except results of one NMI are consistent with the reference values All the results are within ± 0.4 % of the KCRV.

7 References

[1] Edgar Flores, Joële Viallon et al.CCQM-K120 (Carbon dioxide at background and urban level). Metrologia, V 56, N 1A.

[2] Brewer P.J., Van der Veen A.M.H., "GAWG strategy for comparisons and CMC claims", CCQM Gas Analysis Working Group, April 2016

[3] ISO 6142-1:2015. Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method
for Class I mixtures

[4] Minutes of the 40-meeting of the CCQM GAWG 8-9 APRIL 2019
https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg/2019-10-08

[5] CIPM, "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes", Sèvres (F), October 1999

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Annex A

Reports submitted by participating laboratories

Technical Committee TC 1.8 COOMET
«Physics-chemistry»

Report on results for the Key Comparison
COOMET.QM-K120.b(COOMET project № 772/RU/18)
"Carbon dioxide in air urban level (480-800) µmol/mol"

The general information

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Carbon dioxide mole fraction in standarts for comparison

No	Cylinder No (date of preparation)	Mole fraction $x_{CO_2.cert}$, µmol/mol	Expandeduncertainty, $U(x_{CO_2.cert})$, µmol/mol	Coverage factor, *k*
1	5705631 (02.08.2019)	802,6	1,2	2
2	D914327 (02.08.2019)	482,4	0,6	2

Matrix compositions for each standard

Standart № 1:<u>cylinder identification number 5705631</u>

Component	Mole fraction	Unit	Expandeduncertainty	Unit	Coverage factor, *k*
N_2	0,7789302	mol/mol	0,0000084	mol/mol	2
O_2	0,2109324	mol/mol	0,0000082	mol/mol	2
Ar	0,0093335	mol/mol	0,0000024	mol/mol	2
CH_4	15,1	ηmol/mol	13,4	ηmol/mol	2
H_2O	1070	ηmol/mol	1040	ηmol/mol	2
CO	88,9	ηmol/mol	90	ηmol/mol	2
H_2	4,1	ηmol/mol	4,4	ηmol/mol	2

Standart № 2: cylinder identification number D914327

Component	Mole fraction	Unit	Expanded uncertainty	Unit	Coverage factor, *k*
N_2	0,7803529	mol/mol	0,0000082	mol/mol	2
O_2	0,2097935	mol/mol	0,0000080	mol/mol	2
Ar	0,0093700	mol/mol	0,0000024	mol/mol	2
CH_4	14,9	ηmol/mol	13,4	ηmol/mol	2
H_2O	1070	ηmol/mol	1060	ηmol/mol	2
CO	88,9	ηmol/mol	92	ηmol/mol	2
H_2	4,1	ηmol/mol	4,6	ηmol/mol	2

Purity tables with uncertainties for the nominally pure parent gases

Purity table with uncertainties for the nominally pure CO_2parent gas

For a standarts preparation was used nominally pure CO_2(purity extent 5.3).Composition provided by the supplier certificate and composition taken over to calculation in accordance ISO/DIS 19229 are resulted in tables below.

Composition provided by the supplier certificate

Component	Value	Unit
CO_2	≥ 99,9993	mol/mol $\cdot 10^{-2}$
O_2	≤ 0,0002	mol/mol $\cdot 10^{-2}$
N_2	≤ 0,0003	mol/mol $\cdot 10^{-2}$
CH_4	≤ 0,0001	mol/mol $\cdot 10^{-2}$
CO	≤ 0,00005	mol/mol $\cdot 10^{-2}$
H_2O	≤ 0,0001	mol/mol $\cdot 10^{-2}$

Composition taken over to calculation in accordance ISO/DIS 19229

Component	Mole fraction	Unit	Standart uncertainty	Unit
CO_2	0,99999625	mol/mol	0,00000117	mol/mol
O_2	1000	ηmol/mol	600	ηmol/mol
N_2	1500	ηmol/mol	900	ηmol/mol
CH_4	500	ηmol/mol	300	ηmol/mol
CO	250	ηmol/mol	140	ηmol/mol
H_2O	500	ηmol/mol	300	ηmol/mol

Purity table with uncertainties for the nominally pure O_2parent gas

For a standarts preparation was used nominally pure HiQ O_2(purity extent 6.0).Composition provided by the supplier certificate and composition taken over to calculation in accordance ISO/DIS 19229 are resulted in tables below.

Composition provided by the supplier certificate

Component	Value	Unit
O_2	≥ 99,9999	mol/mol ·10^{-2}
N_2	≤ 0,00005	mol/mol ·10^{-2}
CO_2	≤ 0,00001	mol/mol ·10^{-2}
CH_4	≤ 0,00001	mol/mol ·10^{-2}
CO	≤ 0,00001	mol/mol ·10^{-2}
H_2O	≤ 0,00005	mol/mol ·10^{-2}
Ar	≤ 0,0001	mol/mol ·10^{-2}

Composition taken over to calculation in accordance ISO/DIS 19229

Component	Mole fraction	Unit	Standart uncertainty	Unit
O_2	0,99999885	mol/mol	0,00000036	mol/mol
N_2	250	ηmol/mol	140	ηmol/mol
CO_2	50	ηmol/mol	30	ηmol/mol
CH_4	50	ηmol/mol	30	ηmol/mol
CO	50	ηmol/mol	30	ηmol/mol
H_2O	250	ηmol/mol	140	ηmol/mol
Ar	500	ηmol/mol	300	ηmol/mol

Purity table with uncertainties for the nominally pure N_2parent gas

For a standarts preparation was used nominally pure N_2(purity extent 6.0).Composition provided by the supplier certificate and composition taken over to calculation in accordance ISO/DIS 19229 are resulted in tables below.

Composition provided by the supplier certificate

Component	Value	Unit
N_2	≥ 99,9999	mol/mol ·10^{-2}
O_2	≤ 0,000055	mol/mol ·10^{-2}
CO_2	≤ 0,00002	mol/mol ·10^{-2}
CH_4	≤ 0,000001	mol/mol ·10^{-2}
CO	≤ 0,00002	mol/mol ·10^{-2}
H_2O	≤ 0,00025	mol/mol ·10^{-2}
H_2	≤ 0,000001	mol/mol ·10^{-2}

Composition taken over to calculation in accordance ISO/DIS 19229

Component	Mole fraction	Unit	Standart uncertainty	Unit
N_2	0,99999821	mol/mol	0,00000072	mol/mol
O_2	280	ηmol/mol	160	ηmol/mol
CO_2	100	ηmol/mol	60	ηmol/mol
CH_4	5	ηmol/mol	3	ηmol/mol
CO	100	ηmol/mol	60	ηmol/mol
H_2O	1300	ηmol/mol	700	ηmol/mol
H_2	5	ηmol/mol	3	ηmol/mol

Purity table with uncertainties for the nominally pure Ar parent gas

For a standards preparation was used nominally pure Ar(purity extent 6.0).Composition provided by the supplier certificate and composition taken over to calculation in accordance ISO/DIS 19229 are resulted in tables below

Composition provided by the supplier certificate

Component	Value	Unit
Ar	≥ 99,9999	mol/mol $\cdot 10^{-2}$
N_2	≤ 0,000045	mol/mol $\cdot 10^{-2}$
O_2	≤ 0,00003	mol/mol $\cdot 10^{-2}$
CO_2	≤ 0,00001	mol/mol $\cdot 10^{-2}$
CH_4	≤ 0,000005	mol/mol $\cdot 10^{-2}$
CO	≤ 0,000005	mol/mol $\cdot 10^{-2}$
H_2O	≤ 0,00005	mol/mol $\cdot 10^{-2}$
H_2	≤ 0,000005	mol/mol $\cdot 10^{-2}$

Composition taken over to calculation in accordance ISO/DIS 19229

Component	Mole fraction	Unit	Standart uncertainty	Unit
Ar	0,999999245	mol/mol	0,000000215	mol/mol
N_2	230	ηmol/mol	130	ηmol/mol
O_2	150	ηmol/mol	90	ηmol/mol
CO_2	50	ηmol/mol	30	ηmol/mol
CH_4	25	ηmol/mol	14	ηmol/mol
CO	25	ηmol/mol	14	ηmol/mol
H_2O	250	ηmol/mol	140	ηmol/mol
H_2	25	ηmol/mol	14	ηmol/mol

A brief outline of the dilution series undertaken to produce the final mixtures

Final mixtures are obtained by using 2-time dilution: 100 % → 2 % → final mixtures.

Intermediate mixture was determined by a gravimetric method according to ISO 6142. Molar masses of components and their associated uncertainties are derived from ISO 14912:2003 (E). Intermediate mixture composition resulted in table below.

Intermediate mixture composition 2 % CO_2-N_2

Component	Mole fraction	Unit	Standart uncertainty	Unit

N_2	0,9791762818	mol/mol	0,00030852	mol/mol
CO_2	0,020822	mol/mol	0,000003	mol/mol
O_2	295	ηmol/mol	157	ηmol/mol
CO	103	ηmol/mol	59	ηmol/mol
CH_4	15,3	ηmol/mol	6,9	ηmol/mol
H_2O	1300	ηmol/mol	700	ηmol/mol
H_2	4,9	ηmol/mol	2,94	ηmol/mol

Verification procedure applied to the final mixtures

Verification of compositon was performed on a gas chromatographer (GC) "Crystal 5000" fitted with TCD in accordance with ISO 6142, ISO 6143. Gas-carrier is helium.

Verification was made to two stages with use of four CO_2-Air gas mixtures, one of which was the standar for comparison, within the linear range of an analytical method.

Gas mixture compositions used for verification

No	Cylinder identification number	CO_2 mole fraction, μmol/mol	Standartuncertainty, according to gravimetric calculation, μmol/mol
1	5145	851,30	0,16
2	5335	452,11	0,14
3	5142	652,02	0,17
4	D914327	482,43	0,09
5	5705631	802,59	0,13

Measure of verification is requirement performance:

$$\left|X_{CO2} - X_{CO2,ver}\right| \le 2\sqrt{u^2(X_{CO2,prep}) + u^2(X_{CO2,ver})}, \qquad (1)$$

$X_{CO2,ver}$ и $u(X_{CO2,ver})$ - measured value of molar fraction CO_2in the standartsfor comparison and standartuncertainty of measuring accordingly, counted according to ISO 6143;

$u(X_{CO2,prep})$ - standartuncertainty of gravimetric preparation taking into account uncertainty of the instability, evaluated byformula

$$u(X_{CO2,prep}) = \sqrt{u^2(X_{CO2}) + u^2(X_{CO2,stab})}, \qquad (2)$$

где$u(X_{CO2})$ - standartuncertainty of gravimetric preparation;

$u(X_{CO2,stab})$ - standastuncertainty of the instability, evaluated during stability researches for such type mixtures; $u(X_{CO2,stab})$=0,1%rel.

TotalstandartuncertaintyofmolarfractionCO_2evaluated by following formula:

$$u_c(X_{CO2}) = \frac{1}{2}\sqrt{u^2(X_{CO2,prep}) + u^2(X_{CO2,ver}) + (X_{CO2} - X_{CO2,ver})^2}. \qquad (3)$$

Results of verification (date of verification – 11.08.2019)

Cylinder identification number	X_{CO2}, μmol/mol	$u^2(X_{CO2})$, μmol/mol	$X_{CO2,ver}$, μmol/mol	$u(X_{CO2,ver})$, μmol/mol	$\left\|X_{CO2} - X_{CO2,ver}\right\|$ μmol/mol	$u_c(X_{CO2})$, μmol/mol

D914327	482,43	0,09	482,37	0,26	0,06	0,28
5705631	802,59	0,13	801,88	0,32	0,71	0,56

Cylinder pressure before shipment to VNIIM – 9,9 MPa.

Checking the stability of the CO_2 content in the comparison samples

Upon returning the cylinders from the coordinator, the stability of the composition of the samples was checked. The stabilitychecking was performed on a gas chromatographer (GC) "Crystal 5000" fitted with TCD in accordance with ISO 6143 using 5 samples, two of which are samples for comparisons, within the linear range of the analytical method.

The criterion for confirming the stability of the composition is the fulfillment of condition (1)were $u(X_{CO2,prep})$ - standartuncertaintyof gravimetric preparation.

Date of checking stability – 18.02.2021.

The test results are listed in the table below.

Cylinder identifica-tion number	$X_{CO2,prep}$, µmol/mol	$u(X_{CO2,prep})$, µmol/mol	$X_{CO2,ver}$, µmol/mol	$u(X_{CO2,ver})$, µmol/mol	$\lvert X_{CO2,prep} - X_{CO2,ver} \rvert$ µmol/mol	$2\sqrt{u^2(X_{CO2,prep}) + u^2(X_{CO2,ver})}$ µmol/mol
5335	453,55	0,17	453,8	0,4	0,33	0,82
D914327	**482,43**	**0,09**	**482,1**	**0,4**	**0,11**	**0,72**
5142	651,23	0,22	651,12	0,28	0,51	0,66
5705631	**802,59**	**0,13**	**803,1**	**0,3**	**0,58**	**0,76**
5145	855,30	0,25	854,72	0,28	0,33	0,82

Conclusion

The declared gravimetric value of the mole fractionof CO_2 is confirmed within the dclared uncertainty.

Report COOMET.QM-K120

General information

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Values provided by NMI. Carbon dioxide content.

№	Cylinder identification number	Molar fraction of carbon dioxide, $X_{CO_{2,cert}}$ μmol /mol	Expanded uncertainty $U(X_{CO_{2,cert}})$ μmol /mol	Coverage ratio
1	K772-5	486,8	2,4	2
2	K772-7	799,4	4,0	2

Values provided by NMI. Matrix composition.

Cylinder No. K772-5

Component	**Molar fraction**	**Unit of measurement**	**Expanded uncertainty**	**Coverage ratio**
N_2	0,780935	mol/mol	0,004	2
O_2	0,209214	mol/mol	0,001	2
Ar	0,009362	mol/mol	0,00009	2
CH_4	1,4	μmol /mol	0,3	2
N_2O	-	-	-	-

Cylinder No. K772-7

Component	**Molar fraction**	**Unit of measurement**	**Expanded uncertainty**	**Coverage ratio**
N_2	0,780402	mol/mol	0,004	2
O_2	0,209405	mol/mol	0,001	2
Ar	0,009392	mol/mol	0,00009	2
CH_4	1,4	μmol /mol	0,3	2
N_2O	-	-	-	-

Additional Information

Purity table for nominally pure CO2 feed gas

Impurity	Method of measurement	Molar fraction, µmol / mol	Standard uncertainty of molar fraction, µmol / mol
N_2	GC-TCD	24,2	4,8
CO	GC-FID	1,0	0,3
O_2	GC –thermo-chemical detector	6,0	1,0
H_2	GC –thermo-chemical detector	0,5	0,2
CH_4	GC-FID	0,3	0,1
CO_2	Calculation	999 968	5,0

Purity table for nominally pure N2 feed gas

Impurity	Method of measurement	Molar fraction, µmol / mol	Standard uncertainty of molar fraction, µmol / mol
O_2	GC –thermo-chemical detector	10,1	3,0
H_2	GC –thermo-chemical detector	0,2	0,1
CH_4	GC-FID	0,2	0,1
CO	GC-FID	0,3	0,1
CO_2	GC-FID	0,2	0,1
N_2	Calculation	999 989	3,0

Purity table for nominally pure O2 feed gas

Impurity	Method of measurement	Molar fraction, µmol / mol	Standard uncertainty of molar fraction, µmol / mol
N_2	GC-TCD	367	37,0
CH_4	GC-FID	6,1	0,6
CO_2	GC-FID	2,0	0,4
O_2	Calculation	999 625	37,0

Purity table for nominally pure Ar feed gas

Impurity	Method of measurement	Molar fraction, µmol / mol	Standard uncertainty of molar fraction, µmol / mol
CO_2	GC-FID	0,2	0,1
N_2	GC-TCD	15,0	7,5

O_2	GC –thermo-chemical detector	3,5	1,7
H_2	GC –thermo-chemical detector	0,7	0,4
CH_4	GC-FID	0,2	0,1
CO	GC-FID	1,1	0,4
Ar	Calculation	999 979	7,7

The following series of dilutions were used to prepare the target mixtures:
- К772-1(CO2-Ar) >К772-3 (CO2-Ar-N2) >К772-5 (CO2-Ar-O2-N2)and*К772-8 (CO2-Ar-O2-N2) (for verification)*
- К772-2 (CO2-Ar) >К772-4 (CO2-Ar-N2) >К772-7 (CO2-Ar-O2-N2)and*К772-6 (CO2-Ar-O2-N2) (for verification)*

The nominal values of the molar fraction of components in intermediate gas mixtures are presented in tables 1 and 2.

Table 1

Cylinder No.	Molar fraction, mol/mol	
	CO_2	Ar
К772-1	0,049	0,951
К772-2	0,078	0,922

Table 2

Cylinder No.	Molar fraction, mol/mol		
	CO_2	Ar	N_2
К772-3	0,006	0,112	0,882
К772-4	0,012	0,134	0,854

The pressure in the cylinders before being sent to the coordinating laboratory was 10.0 MPa.

Report form COOMET.QM-K120 (1)

(submitted 12/02/2020)

A1. Generalinformation

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A2. NMI submittedvalues. Carbon dioxide mole fraction

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ μmol/mol	Expanded uncertainty $U(x_{CO2,cert})$ μmol/mol	Coverage factor
1	D248767	479.87	0.51	2
2	D248763	799.37	0.76	2

A3. NMI submittedvalues

Matrix compositions (for each standard submitted):

(Standard 1) Cylinder Identification Number:D248767

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780894	mol/mol	0.000016	mol/mol	2
O_2	0.209233	mol/mol	0.000015	mol/mol	2
Ar	0.009393	mol/mol	0.000003	mol/mol	2
CH_4	0.050	μmol/mol	0.044	μmol/mol	2

(Standard2)CylinderIdentificationNumber: D248763

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780338	mol/mol	0.000016	mol/mol	2
O_2	0.209459	mol/mol	0.000015	mol/mol	2
Ar	0.009403	mol/mol	0.000003	mol/mol	2
CH_4	0.050	μmol/mol	0.042	μmol/mol	2

A4. Uncertainty Budget

Uncertainty budgets for the CO2 mole fraction values reported

Cylinder Identification Number	Gravimetric preparation uncertainty, μmol/mol	Verification uncertainty, μmol/mol	Combined uncertainty, μmol/mol	Expanded uncertainty, μmol/mol	Coverage factor
D248767	0.11	0.23	0.26	0.51	k=2
D248763	0.13	0.36	0.38	0.76	k=2

5. Additional information

Purity table for Pure CO2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	2.000E-07	Normal	3.325E-09
Impurity	O_2	6.000E-08	Normal	3.139E-09
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	C_2H_4	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	2.500E-06	Rectangular	1.443E-06
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	H_2	1.200E-07	Normal	6.928E-08
Impurity	Ar	9.000E-08	Normal	6.213E-09
Balance gas	CO_2	0.99999691		1.446E-06

Purity table for Pure N_2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	O_2	2.500E-08	Rectangular	1.443E-08
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	H_2	2.500E-08	Rectangular	1.443E-08

Impurity	CO_2	5.000E-08	Rectangular	2.887E-08
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	1.000E-08	Rectangular	5.774E-09
Balance gas	N_2	0.99999982		4.822E-08

Purity table for pure O2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	5.000E-07	Rectangular	2.887E-07
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	CO_2	2.500E-08	Rectangular	1.443E-08
Impurity	H_2	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	2.500E-07	Rectangular	1.443E-07
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	Ar	5.000E-08	Rectangular	2.887E-08
Balance gas	O_2	0.99999905		3.272E-07

Purity table for pure Ar

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	1.000E-06	Rectangular	5.774E-07
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	CO_2	2.500E-08	Rectangular	1.443E-08
Impurity	H_2O	5.000E-07	Rectangular	2.887E-07
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	O_2	5.000E-07	Rectangular	2.887E-07
Balance gas	Ar	0.99999790		7.080E-07

Gas mixture verification

The carbon dioxide in air mixtures were analyzed on a cavity ring-down spectroscopy(CRDS) instrument, i.e., Picarro G2401 Analyzer. Verification of the mixtures was carried out using our freshly prepared standards. Cylinders were equipped with pressure reducers and they were flushed three times before measurement. Cylinders were then connected to a mass flow controller (MFC) and the flow rate was fixed at 500 sccm. In the sample line between MFC and CRDS, there was a bypass to allow excessive gas to be vented out. Each cylinder was measured and data recorded for 15 minutes. The readings from 13 to 14 minutes were selected for the determination of average values for each cylinder at each measurement.

Measurements of all gas mixtures have been repeated for 3 days. The deviation between the measured value and gravimetric value for the prepared gas mixtures are below the verification uncertainty.

Total uncertainty estimation

The uncertainties of the gas mixture has been estimated by combining the gravimetic preparation uncertainty and the verification uncertainty. The gravimetic preparation uncertainty includes contribution from impurity of source gas (CO_2, Ar, O_2, N_2) and premix, molar mass and cylinder weighing process. The verification uncertainty includes contribution from the day-to-day variation, measurement repeatability, consistency check error and regression analysis residual error.

Uncertainty budgets for the CO2 mole fraction values reported

Cylinder Identification Number	Gravimetric preparation uncertainty, µmol/mol	Verification uncertainty, µmol/mol	Combined uncertainty, µmol/mol	Expanded uncertainty, µmol/mol	Coverage factor
D248767	0.11	0.23	0.26	0.51	k=2
D248763	0.13	0.36	0.38	0.76	k=2

Report form COOMET.QM-K120 (2)

(submitted 28/07/2021)

A1. General information

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A2. NMI submittedvalues. Carbon dioxide mole fraction

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ µmol/mol	Expanded uncertainty $U(x_{CO2,cert})$ µmol/mol	Coverage factor
1	D248767	479.87	0.69	2
2	D248763	799.37	0.90	2

A3. NMI submittedvalues

Matrix compositions (for each standard submitted):

(Standard 1) Cylinder Identification Number: D248767

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780894	mol/mol	0.000016	mol/mol	2
O_2	0.209233	mol/mol	0.000015	mol/mol	2
Ar	0.009393	mol/mol	0.000003	mol/mol	2
CH_4	0.050	µmol/mol	0.044	µmol/mol	2

(Standard2)CylinderIdentificationNumber: D248763

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780338	mol/mol	0.000016	mol/mol	2
O_2	0.209459	mol/mol	0.000015	mol/mol	2
Ar	0.009403	mol/mol	0.000003	mol/mol	2
CH_4	0.050	μmol/mol	0.042	μmol/mol	2

A4. Uncertainty Budget

Uncertainty budgets for the reported CO_2 mole fraction values

Cylinder Identification Number	Gravimetric preparation uncertainty, μmol/mol	Verification uncertainty, μmol/mol	Stability uncertainty, μmol/mol	Combined uncertainty, μmol/mol	Expanded uncertainty, μmol/mol	Coverage factor
D248767	0.11	0.23	0.23	0.34	**0.69**	k=2
D248763	0.13	0.36	0.23	0.45	**0.90**	k=2

A5. Additional information

Purity table for Pure CO2

Components		**Concentration (mol/mol)**	**Distribution**	**Standard Uncertainty (mol/mol)**
Impurity	N_2	2.000E-07	Normal	3.325E-09
Impurity	O_2	6.000E-08	Normal	3.139E-09
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	C_2H_4	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	2.500E-06	Rectangular	1.443E-06
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	H_2	1.200E-07	Normal	6.928E-08
Impurity	Ar	9.000E-08	Normal	6.213E-09
Balance gas	CO_2	0.99999691		1.446E-06

Purity table for Pure N_2

Components		**Concentration (mol/mol)**	**Distribution**	**Standard Uncertainty (mol/mol)**
Impurity	O_2	2.500E-08	Rectangular	1.443E-08
Impurity	CO	2.500E-08	Rectangular	1.443E-08

Impurity	H_2	2.500E-08	Rectangular	1.443E-08
Impurity	CO_2	5.000E-08	Rectangular	2.887E-08
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	1.000E-08	Rectangular	5.774E-09
Balance gas	N_2	0.99999982		4.822E-08

Purity table for pure O2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	5.000E-07	Rectangular	2.887E-07
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	CO_2	2.500E-08	Rectangular	1.443E-08
Impurity	H_2	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	2.500E-07	Rectangular	1.443E-07
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	Ar	5.000E-08	Rectangular	2.887E-08
Balance gas	O_2	0.99999905		3.272E-07

Purity table for pure Ar

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	1.000E-06	Rectangular	5.774E-07
Impurity	CO	2.500E-08	Rectangular	1.443E-08
Impurity	CO_2	2.500E-08	Rectangular	1.443E-08
Impurity	H_2O	5.000E-07	Rectangular	2.887E-07
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	O_2	5.000E-07	Rectangular	2.887E-07
Balance gas	Ar	0.99999790		7.080E-07

Gas mixture verification

The carbon dioxide in air mixtures were analyzed on a cavity ring-down spectroscopy (CRDS) instrument, i.e., Picarro G2401 Analyzer. Verification of the mixtures was carried out using our freshly prepared standards. Cylinders were equipped with pressure reducers and they were flushed three times before measurement. Cylinders were then connected to a mass flow controller (MFC) and the flow rate was fixed at 500 sccm. In the sample line between MFC and CRDS, there was a bypass to allow excessive gas to be vented out. Each cylinder was measured and data recorded for 15 minutes. The readings from 13 to 14 minutes were selected for the determination of average values for each cylinder at each measurement.

Measurements of all gas mixtures have been repeated for 3 days. The deviation between the measured value and gravimetric value for the prepared gas mixtures are below the verification uncertainty.

Gas mixture stability check

The carbon dioxide in air mixtures (D248767, D248763) were returned to NMC and analyzed again in Mar 2021 using a CRDS instrument, i.e., Picarro G2401 Analyzer. Cylinders were equipped with pressure reducers and they were flushed three times before measurement. Cylinders were then connected to a MFC and the flow rate was fixed at 500 sccm. The analyser's readings of 1 minute were used for the determination of average concentration values for each cylinder. Measurements for the two cylinders have been repeated in 2 days.

The deviation between the measured value in Jul 2019 and Mar 2021 (Δx) are shown in the table below. The standard uncertainty due to stability (k=1) was derived as $u_s = \Delta x/\sqrt{3}$.

Stability check for the two gas mixtures (D248767, D248763)

Cylinder Identification Number	GSM mixture std	measured value in Jul 2019, ppm	measured value in Mar 2021, ppm	Deviation between two measurements (Δx), ppm	uncertainty due to stability (k=1), ppm
D248767	PSM118767	480.09	480.49	0.39	0.23
D248763	PSM118763	798.94	799.34	0.40	0.23

Total uncertainty estimation

The uncertainties of the gas mixture has been estimated by combining the gravimetic preparation uncertainty, the verification uncertainty and the stability uncertainty. The gravimetic preparation uncertainty includes contribution from impurity of source gas (CO_2, Ar, O_2, N_2) and premix, molar mass and cylinder weighing process. The verification uncertainty includes contribution from the day-to-day variation, measurement repeatability, consistency check error and regression analysis residual error.

Uncertainty budgets for the reported CO_2 mole fraction values

Cylinder Identification Number	Gravimetric preparation uncertainty, μmol/mol	Verification uncertainty, μmol/mol	Stability uncertainty, μmol/mol	Combined uncertainty, μmol/mol	Expanded uncertainty, μmol/mol	Coverage factor
D248767	0.11	0.23	0.23	0.34	**0.69**	k=2
D248763	0.13	0.36	0.23	0.45	**0.90**	k=2

Key Comparison COOMET.QM-K120.b
Carbon dioxide in Air

A1. General information

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Contact person	OvsiyLevbarg		
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Email*	molar@ukrcsm.kiev.ua		

A2. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ / µmol/mol	Expanded uncertainty $U(x_{CO2,cert})$ / µmol/mol	Coverage factor
1	81205102	480,27	0,45	2
2	81205166	799,99	0,83	2

A3. NMI submitted values

Matrix compositions: Component mole fractions and uncertainties (for each standard submitted):

(Standard 1) Cylinder Identification Number: **81205102**

Component	Mole fraction value	Unit	Expanded uncer-tainty	Unit	Coverage factor
N_2	0,782774	mol/mol	0,000012	mol/mol	2
O_2	0,207361	mol/mol	0,000011	mol/mol	2
Ar	0,009382	mol/mol	0,000005	mol/mol	2
CH_4	91	nmol/mol	3	nmol/mol	2
N_2O	not measured	nmol/mol	-	nmol/mol	-
CO	77	nmol/mol	3	nmol/mol	2
H_2O	2,03	µmol/mol	0,12	µmol/mol	2

(Standard 2) Cylinder Identification Number: **81205166**

Component	Mole fraction value	Unit	Expanded uncertainty	Unit	Coverage factor
N_2	0,781565	mol/mol	0,000011	mol/mol	2
O_2	0,208084	mol/mol	0,000011	mol/mol	2
Ar	0,009548	mol/mol	0,000004	mol/mol	2
CH_4	93	nmol/mol	3	nmol/mol	2
N_2O	not measured	nmol/mol	-	nmol/mol	-
CO	88	nmol/mol	3	nmol/mol	2
H_2O	2,26	µmol/mol	0,10	µmol/mol	2

CO_2 isotope ratio (vs. VPDB) for each standard submitted (Optional):

	Cylinder Identification Number	$\delta^{13}C$	$U(\delta^{13}C)$	Coverage Factor	$\delta^{18}O$	$U(\delta^{18}O)$	Coverage Factor
1	not measured						
2	not measured						

A4. Uncertainty Budget

AcombinedstandarduncertaintyoftheamountfractionofCO_2,$u_c(y_k)$, inthefinalmixtures was calculated using formula from ISO 6142-1:2015

$$u_c(y_k)=\frac{1}{2}\sqrt{u^2(y_{k,\mathrm{prep}})+u^2(y_{k,\mathrm{ver}})+(y_{k,\mathrm{prep}}-y_{k,\mathrm{ver}})^2}$$

where $u(y_{k,\text{ prep}})$ is a gravimetric preparation standard uncertainty, $u(y_{k,\text{ ver}})$ is a verification standard uncertainty, $y_{k,\text{ prep}}$ and $y_{k,\text{ ver}}$ are amount fraction values obtained by gravimetric procedure and by verification, respectively.

$y_{k,\text{ prep}}$ and $u(y_{k,\text{ prep}})$ were calculated according to the ISO 6142-1:2015 based on the transferred parent-gas masses with their uncertainties, as well as purity tables for parent gases and pre-mixture composition that are given below in A.5.

$y_{k,\text{ ver}}$ and $u(y_{k,\text{ ver}})$ were calculated according to ISO 6143:2001.

An expanded uncertainty, $U_c(y_k)$, was calculated as $U_c(y_k) = k \times u_c(y_k)$, where k= 2.

Uncertainty budget is given in the table:

Cylinder Identification Number	$u(y_{k,\text{ prep}})$, µmol/mol	$u(y_{k,\text{ ver}})$, µmol/mol	$\lvert y_{k,\text{ prep}} - y_{k,\text{ ver}}\rvert$, µmol/mol	$u_c(y_k)$, µmol/mol	$U_c(y_k)$, µmol/mol
81205102	0,133	0,292	0,311	0,223	0,45
81205166	0,149	0,497	0,651	0,416	0,83

A5. Additional information

a) Purity table for CO_2

Purity table for CO_2

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
CO_2	99,9885	0,0005	2
N_2	0,0082	0,0004	2
O_2	0,00020	0,00006	2
CH_4	0,00044	0,00002	2
C_2H_6	0,00045	0,00002	2
H_2O	0,0022	0,0001	2

b) Purity tablesfor other parent gases and pre-mixture composition

Purity table for N_2 (used to prepare pre-mixture)

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
N_2	99,9857	0,0008	2
CO_2	0,00047	0,00004	2
O_2	0,000019	0,000002	2
CH_4	0,000012	0,000001	2
Ar	0,0134	0,0007	2
H_2O	0,00037	0,00003	2

Purity table for N_2 (used to prepare Standard 1)

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
N_2	99,9866	0,0008	2
CO	0,000010	0,000001	2
O_2	0,000050	0,000005	2
CH_4	0,000010	0,000001	2
Ar	0,0133	0,0007	2
H_2O	0,00005	0,00001	2

Purity table for N_2 (used to prepare Standard 2)

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
N_2	99,9930	0,0005	2
CO	0,000011	0,000001	2
O_2	0,000122	0,000006	2
CH_4	0,0000017	0,0000002	2
Ar	0,0068	0,0004	2

H_2O	0,00007	0,00001	2

Purity table for O_2

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
O_2	99,9992	0,0001	2
CO_2	0,0000093	0,0000005	2
CH_4	0,000005	0,000001	2
H_2O	0,00076	0,00004	2

Purity table for Ar

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
Ar	99,9995	0,0001	2
N_2	0,000105	0,000005	2
CO_2	0,000092	0,000004	2
O_2	0,000044	0,000002	2
CH_4	0,000001	0,000001	2
H_2O	0,000242	0,000006	2

Pre-mixture composition

Component	Mole fraction, 10^{-2} mol/mol	Expanded uncer-tainty, 10^{-2} mol/mol	Coverage Factor
CO_2	5,019	0,001	2
N_2	94,9676	0,001	2
O_2	0,000028	0,000003	2
CH_4	0,000033	0,000003	2
Ar	0,0127	0,0007	2
H_2O	0,00046	0,00004	2

c) CO_2/N_2 pre-mixture of about 5 % CO_2 mole fraction was prepared. Detailed composition of the pre-mixture is given above. Then it was diluted with pure oxygen, argon and nitrogen to obtain Standard 1 and Standard 2.

Pure nitrogen from three different cylinders was used to prepare pre-mixture, Standard 1 and Standard 2.

d) The prepared mixtures were verified by comparison according to ISO 6143:2001. For this purpose two additional three-mixture sets, having the same matrix and CO_2 mole fraction close to Standard 1 and Standard 2, respectively, were prepared. The mixtures were compared using gas chromatograph with methanizer and FID detector. The calibration function was linear.

e) Cylinders pressure before shipment to VNIIM was 12,9 MPa in both cylinders.

Report of stability measurements after return of the cylinders

Cylinder Identification Number	Pressure before shipment to VNIIM, MPa	Pressure after return from VNIIM, MPa	Final analysis date before shipment to VNIIM	Final analysis date after return from VNIIM
81205102	12,9	11,0	29.05.2019	14.07.2021
81205166	12,9	11,0	06.06.2019	08.07.2021

Stability was evaluated by comparison with newly prepared primary gas mixtures of similar composition (one for each mole fraction level) in accordance with ISO 16664 and ISO 6142-1. Comparison procedure used was "Single-point through origin calibration" according to ISO 12963.

Stability evaluation results are given in the table below.

Cylinder Identification Number	Before shipment		After returnµmol/mol		Drift, µmol/mol
	CO_2 mole fraction,µmol/mol	$u_c(y_k)$, µmol/mol	CO_2 mole fraction,µmol/mol	$u_c(y_k)$, µmol/mol	
81205102	480,27	0,223	481,03	0,379	0,76
81205166	799,99	0,416	801,00	0,368	1,01

Acording to the criterion stated in ISO 16664 (D> 2, where D is given by Formula (A.1) of ISO 16664:

$$D=\frac{|x_0-x_1|}{\sqrt{u^2(x_0)+u^2(x_1)}}$$),

the drift is significant

The evaluated drift was treated as an uncertainty due to instability, $u(y_{k,\mathrm{stab}})$, and accounted for in the uncertainty budget by Formula (7) of ISO 6142-1:

$$u(y_{k,\mathrm{prep}})=\sqrt{u^2(y_{k,\mathrm{grav}})+u^2(y_{k,\mathrm{stab}})}$$

Uncertainty budget re-evaluated according to Formulae (7) and (9) of ISO 6142-1 is given in the table below.

Cylinder Identification number	$u(y_{k,\mathrm{grav}})$, µmol/mol	$u(y_{k,\mathrm{stab}})$, µmol/mol	$u(y_{k,\mathrm{prep}})$, µmol/mol	$u(y_{k,\mathrm{ver}})$, µmol/mol	$\lvert y_{k,\mathrm{prep}} - y_{k,\mathrm{ver}}\rvert$, µmol/mol	$u_c(y_k)$, µmol/mol	$U_c(y_k)$, µmol/mol
81205102	0,133	0,76	0,77	0,292	0,311	0,441	0,88
81205166	0,149	1,01	1,02	0,497	0,651	0,654	1,3

Thus, final submitted values are as following:

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ / µmol/mol	Expanded uncertainty $U(x_{CO2,cert})$ / µmol/mol	Coverage factor
1	81205102	480,3	0,9	2
2	81205166	800,0	1,3	2

Authors: S. Kisel, O. Levbarg, D. Melnyk, M. Rozhnov, S. Shpilnyi, S. Yakubov

Key Comparison CCQM- K120
Carbon dioxide in Air

Submission form CCQM- K120- R

Project name: CCQM- K120 (Carbon dioxide in air).
Comparison: Comparison of laboratories' preparation capabilities for Carbon dioxide in Air Standards.

Proposed dates: 09/2016 to 12/2017.

Coordinating laboratories:

Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
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Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

A1. General information

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A2. Participation

I am participating in:	Yes/No
CCQM- K120.a	Yes
CCQM- K120.b	Yes

A3. NMI submitted values

Table 1

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ / µmol/mol	Expanded uncertainty $U(x_{CO2,cert})$/ µmol/mol	Coverage factor
1	M365601	380.20	0.11	2
2	M365664	480.18	0.13	2
3	M365707	800.73	0.19	2

Matrix compositions: Component mole fractions and uncertainties (for each standard submitted):

Table 2: (Standard 1) Cylinder Identification NumberM365601

Component	Mole fraction Value	Unit	Expanded Un-certainty*	Unit	CoverageFactor
N_2	78.1015	10^{-2} mol/mol	0.0013	10^{-2} mol/mol	2
O_2	20.9188	10^{-2} mol/mol	0.0013	10^{-2} mol/mol	2
Ar	0.9416	10^{-2} mol/mol	0.0005	10^{-2} mol/mol	2
CH_4	0.00000094	10^{-2} mol/mol	0.00000022	10^{-2} mol/mol	2
N_2O	not measured				

Table 3:(Standard 2) Cylinder Identification NumberM365664

Component	Mole fraction Value	Unit	Expanded Un-certainty*	Unit	CoverageFactor
N_2	78.0928	10^{-2} mol/mol	0.0011	10^{-2} mol/mol	2
O_2	20.9270	10^{-2} mol/mol	0.0012	10^{-2} mol/mol	2
Ar	0.9322	10^{-2} mol/mol	0.0005	10^{-2} mol/mol	2
CH_4	0.00000096	10^{-2} mol/mol	0.00000022	10^{-2} mol/mol	2
N_2O	not measured				

Table 4:(Standard 3) Cylinder Identification NumberM365707

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	CoverageFactor
N_2	78.1000	10^{-2} mol/mol	0.0011	10^{-2} mol/mol	2
O_2	20.9199	10^{-2} mol/mol	0.0012	10^{-2} mol/mol	2
Ar	0.9000	10^{-2} mol/mol	0.0005	10^{-2} mol/mol	2
CH_4	0.00000097	10^{-2} mol/mol	0.00000022	10^{-2} mol/mol	2
N_2O	not measured				

*Uncertainty in the tables 2-4 includes only constituents related to gravimetry (weighing and purity)

Table 5:CO2 isotope ratio (vs. VPDB) for each standard submitted (Optional):

	Cylinder Identification Number	$\delta^{13}C$	$U(\delta^{13}C)$	Coverage Factor	$\delta^{18}O$	$U(\delta^{18}O)$	Coverage Factor
1	M365601	-48.0	0.9	2	-	-	-
2	M365664	-48.0	0.9	2	-	-	-
3	M365707	-48.0	0.9	2	-	-	-

A4. Uncertainty Budget

Table 6: Uncertainty budget (only gravimetry) for CO_2 mole fraction for the cylinder M365601

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.672µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.381µmol/mol	B	Rectangular	0.015µmol/mol	0.06733	0.00101
Purity of CO_2		999993.450µmol/mol	B	Rectangular	0.374µmol/mol	0.00016	0.00006
Purity of Ar		999998.209µmol/mol	B	Rectangular	0.030µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	20.15723g	A,B	Normal	0.00223g	-18.54106	-0.04140
Weighing** premixture	N_2	1153.59704g	A,B	Normal	0.01962 g	0.32397	0.00636
Weighing** final mixture	pre-mixture	20.48733 g	A,B	Normal	0.00203 g	-17.91563	-0.03630
Weighing** final mixture	Ar	7.90915 g	A,B	Normal	0.00200 g	0.45258	0.00091
Weighing** final mixture	O_2	140.75497 g	A,B	Normal	0.00353 g	0.56493	0.00200
Weighing** final mixture	N_2	439.93136 g	A,B	Normal	0.01021 g	0.64543	0.00659
Molar mass of CO_2 (component due to isotopic composition)		44.0100 g/mol	A	Normal	0.00035 g/mol	8.6286	0.00302
Combined standard uncertainty							**0.05596**

Expanded uncertainty k=2	**0.112**

Table 7: Uncertainty budget (only gravimetry) for CO_2 mole fraction for the cylinder M365664

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.672µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.390µmol/mol	B	Rectangular	0.011µmol/mol	0.06909	0.00076
Purity of CO_2		999993.450µmol/mol	B	Rectangular	0.374µmol/mol	0.00020	0.000075
Purity of Ar		999998.209µmol/mol	B	Rectangular	0.030µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	19.47854g	A,B	Normal	0.00224g	-24.23572	-0.05424
	N_2	1118.50932g	A,B	Normal	0.01950 g	0.42206	0.00823
Weighing** final mixture	pre-mixture	25.86420 g	A,B	Normal	0.00204 g	-17.75177	-0.03626
	Ar	7.80100 g	A,B	Normal	0.00200 g	0.57374	0.00115
	O_2	140.28618 g	A,B	Normal	0.00391 g	0.71611	0.00280
	N_2	432.88272 g	A,B	Normal	0.00915 g	0.81821	0.00749
Molar mass of CO_2 (component due to isotopic composition)		44.0100 g/mol	A	Normal	0.00035 g/mol	10.9066	0.00382
Combined standard uncertainty							0.066379
Expanded uncertainty k=2							**0.133**

Table 8: Uncertainty budget (only gravimetry) for CO_2 mole fraction for the cylinder M365707

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.672µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.390µmol/mol	B	Rectangular	0.011µmol/mol	0.06733	0.00076
Purity of CO_2		999993.450µmol/mol	B	Rectangular	0.374µmol/mol	0.00035	0.00013
Purity of Ar		999998.209µmol/mol	B	Rectangular	0.030 µmol/mol	0.00500	0.00015
Weighing** premixture	CO_2	20.15723 g	A,B	Normal	0.00223g	-39.05886	-0.08721
	N_2	1153.59704g	A,B	Normal	0.01962 g	0.68249	0.01339

Weighing** final mixture	pre-mixture	42.82195 g	A,B	Normal	0.00220 g	-17.33744	-0.03823
	Ar	7.50252 g	A,B	Normal	0.00202 g	0.96046	0.00194
	O_2	139.69676 g	A,B	Normal	0.00403 g	1.19851	0.00483
	N_2	414.48867 g	A,B	Normal	0.00834 g	1.36969	0.01143
Molar mass of CO_2 (component due to isotopic composition)		44.0100 g/mol	A	Normal	0.00035 g/mol	18.1777	0.006362
Combined standard uncertainty							**0.09719**
Expanded uncertainty k=2							**0.194**

**Uncertainty due to weighing includes constituents related to accuracy of balance, buoyancy effect resulting from change of cylinder volume during filling, mass pierces used, drift of balance, residual gas in cylinder.

A5. Additional information

Table 9: Purity table with uncertainties for the nominally pure CO_2 parent gas

Cylinder N 74318
Main component CO_2 Mole fraction 99.999345%

Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
N_2	0.25	0.14
CO	0.029	0.001
CH_4	0.149	0.002
He	0.5	0.29
H_2	3.22	0.07
O_2	0.25	0.14
H_2O	2.15	0.11

Purity tables with uncertainties for the nominally pure N_2, O_2, and Ar parentgases

Table 10: Purity table for N_2

Monoblock
Main component N_2 Mole fraction 99.9998672%

Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
Ar	0.916	0.011
O_2	0.0015	0.0009
CO_2	0.0025	0.0014
H_2	0.0025	0.0014
CH_4	0.0025	0.0014
CO	0.0025	0.0014
H_2O	0.40	0.20

Table 11: Purity table for O_2

Cylinder N 910281 Main component O_2 Mole fraction 99.9999381%		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
H_2	0.0025	0.0014
Ar	0.181	0.004
N_2	0.307	0.012
Kr	0.0025	0.0014
CO	0.0075	0.0043
CH_4	0.0347	0.0008
CO_2	0.081	0.005
Xe	0.0025	0.0014

Table 12: Purity tablefor Ar

Cylinder N 283162 Main component Ar Mole fraction 99.9998209%		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
O_2	0.0231	0.0013
N_2	1.188	0.015
CH_4	0.015	0.009
CO_2	0.030	0.017
H_2	0.025	0.014
CO	0.010	0.006
H2O	0.50	0.01

c) a brief outline of the dilution series undertaken to produce the final mixtures

Preparation of final mixtures (CO_2 in synthetic air) was carried out from pure substances in 2 stages:
1-st stage – 3 mixtures CO_2/N_2 –level 1.1 %,
2-nd stage – 3x3target mixtures CO_2/synthetic air.

All the mixtures were prepared in Luxfer cylinders (V=10 and 5 dm^3)

d) a brief outline of the verification procedure applied to the final mixtures;
CRDS analyzer was used for verification
4 measurement series were carried out within each verification procedure.
SD of a single measurement (reproducibility between series) was 0,003 % -0,006 %.

CRDS analyzer was used for verification
Instrument: Picarro G2401
Measurement cell temperature: 45°C
Measurement cell pressure: 18,665 kPa
Data collection: by “Picarro Inc.” software

CRDS analyzer was used for $\delta^{13}C$ measurements
Instrument: Picarro G2131i
Reference materials used for calibration: IAEA-CO-8, IAEA-CH-7
Measurement cell temperature: 45°C

Measurement cell pressure: 18,665 kPa
Data collection: by "Picarro Inc." software

e) a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM

The final mixtures were prepared 03.10 -13.10.2016.
First verification measurement was carried out 17.10 -21.10 2016.
Second verification measurement was carried out 26.10 -28.10.2016.
Verification measurements were performed by checking consistency within the group of the 3x3 prepared mixtures.
u_{ver} *=0,003 %*
Stability testing (short-term) did not show instability within the accuracy of the measurement method.
Long-term stability testing (measurements 21.08.-23.08.2017and 09.10-11.10.2017) did not show instability within the accuracy of the measurement method.

f) cylinder pressure before shipment to the BIPM

8.9 MPa for M365601
9.0 MPa for M365664
9.3 MPa for M365707