International comparison

CCQM-K120.a

Carbon dioxide in Air at background level (380-480) µmol/mol

CCQM-K120.b

Carbon dioxide in Air at urban level (480-800) µmol/mol

(Final)

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Field: Amount of substance

Organizing Body: CCQM

Contents

1. Rationale for comparison

CCQM-K120.a comparison involves preparing standards of carbon dioxide in air which are fit for purpose for the atmospheric monitoring community, with stringent requirements on matrix composition and measurement uncertainty of the CO_2 mole fraction. This represents an analytical challenge and is therefore considered as a Track C comparison. The comparison will underpin CMC claims for CO_2 in air for standards and calibrations services for the atmospheric monitoring community, matrix matched to real air, over the mole fraction range of 250 µmol/mol to 520 µmol/mol.

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 mole 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

This study has involved a comparison at the BIPM of a suite of 44 gas standards prepared by each of the participating laboratories. Fourteen laboratories took part in both comparisons (CCQM-K120.a, CCQM-K120.b) and just one solely in the CCQM-K120.b comparison.

The standards were sent to the BIPM where the comparison measurements were performed. Two measurement methods were used to compare the standards, to ensure no measurement method dependant bias: GC-FID and FTIR spectroscopic analysis corrected for isotopic variation in the CO_2 gases, measured at the BIPM using absorption laser spectroscopy. Following the advice of the CCQM Gas Analysis Working Group, results from the FTIR method were used to calculate the key comparison reference values.

2. Measurand, quantities and Units

The measurand is the mole fraction of carbon dioxide in air, with measurement results being expressed in mol/mol (or one of its multiples mmol/mol, µmol/mol or nmol/mol).

3. Participants

This study involved a simultaneous comparison of a suite of 44 gas standards prepared by each of the participating laboratories. Fourteen laboratories took part in both comparisons (CCQM-K120.a and CCQM-K120.b: BFKH, GUM, KRISS, LNE, NIM, NIST, NMIJ, NMISA, NOAA, NPL, NPLI, UME, VNIIM and VSL) and only one solely in the CCQM-K120.b comparison (INRIM).

4. Schedule

The revised schedule for the project was as follows:

April 2016 – October 2016	Mixture preparation, verification and stability tests by participants.
November 2016 – February 2017	Shipment of cylinders to the BIPM (to arrive by 1 of December)
February 2017 – April 2017	Analysis of mixtures by the BIPM (details below)
May 2017 – July 2017	Shipment of cylinders from the BIPM to participants
August 2017 – November 2017	2nd set of analysis of mixtures by participants
January 2018	Distribution of Draft A of this report
May 2018	Distribution of Draft B of this report

4.1 Measurement order

The forty four cylinders of the comparison were separated into batches and analyzed, in the sequence described in Table 1. Each batch was made up of the participants' cylinders, control cylinders for ratio calculations and additional cylinders for quality control.

The FTIR measurements were organized in fourteen batches comprised each of four participant's cylinders including two control cylinders for ratio calculation and one for quality control.

For GC-FID measurements the cylinders were divided into nine batches. Batches were composed of between four and six participants' cylinders, three control cylinders (A, B and C) for ratio quantification and additional cylinders if required to maintain the total batch size of nine standards. Table 1 lists in detail the schedule of the GC-FID and FTIR measurements.

The Delta Ray measurements were organized in 12 batches containing four cylinders each and two calibration cylinders. These measurements were performed during weeks 14, 15 and 16.

Week in 2017	Batch	GC-FID measurements			Batch	FTIR measurements		
6 (6-10 February)	GC1	NIST	FB04278	379.045				
		NOAA	CC310084	379.500				
		VSL	5604614	378.900				
		NPL	2179	380.270				
		NMIJ	CPC00486	386.617				
7 (13-17 February)	GC2	VNIIM	M365601	380.200				
		LNE	1029045	379.480				
		KRISS	D500642	378.900				
		NIM	FB03747	383.430				
8 (20-24 February)	GC3	GUM	D298392	380.100				
		BFKH	OMH54	379.840				
		UME	PSM298266	379.920				
		NPLI	JJ108891	375.720				
		NMISA	M51 8232	380.200				
9 (27 February- 3 March)	GC4	NIST	FB04300	472.662				
		NOAA	CC305198	479.260				
		VSL	5604880	480.480				
		NPL	2170	480.020				
		NMIJ	CPC00494	471.301				
10 (6-10 March)	GC5	VNIIM	M365664	480.180	FT-1	NIST	FB04278	379.045
		LNE	1029047	477.600		NOAA	CC310084	379.500
		KRISS	D500647	480.000		NPL	2179	380.270
		NIM	FB03744	489.150	FT-2	NMIJ	CPC00486	386.617
11 (13-17 March)	GC6	GUM	D298393	478.100		NMIJ	CPC00486	386.617
		BFKH	OMH44	479.890		VNIIM	M365601	380.200
		UME	PSM266468	480.420	FT-3	KRISS	D500642	378.900
		NPLI	JJ108862	480.520		NIM	FB03747	383.430
		NMISA	M51 8167	479.500		LNE	1029045	379.480
		INRIM	D247440	479.300				
12 (20-24 March)	GC7	NIST	FB04287	794.533	FT-4	GUM	D298392	380.100
		NOAA	CB11668	794.080		NMISA	M51 8232	380.200
		VSL	5604705	795.700	FT-5	BFKH	OMH54	379.840
		NPL	2181	799.700		UME	PSM298266	379.920
		NMIJ	CPC00558	803.658		NPLI	JJ108891	375.720
13 (27-31 March)	GC8	VNIIM	M365707	800.730	FT-6	NIST	FB04300	472.662
		LNE	1029048	802.200		NOAA	CC305198	479.260
		KRISS	D500672	800.800		VSL	5604880	480.480
		NIM	FB03748	809.820	FT-7	NPL	2170	480.020
		GUM	D298402	800.500		NMIJ	CPC00494	471.301
14 (3-7 April)	GC9	BFKH	OMH69	800.300		VNIIM	M365664	480.180
		UME	PSM298347	800.760	FT-8	LNE	1029047	477.600
		NPLI	JJ108854	796.380		KRISS	D500647	480.000
		NMISA	M51 8244	799.100	FT-9	NIM	FB03744	489.150
		INRIM	D247445	798.900		GUM	D298393	478.100
15 (10-14 April)						BFKH	OMH44	479.890
					FT-10	UME	PSM266468	480.420
						NPLI	JJ108862	480.520
						NMISA	M51 8167	479.500
						INRIM	D247440	479.300
					FT-11	NIST	FB04287	794.533
						NOAA	CB11668	794.080
						VSL	5604705	795.700
					FT-12	NPL	2181	799.700
						NMIJ	CPC00558	803.658
						VNIIM	M365707	800.730
						LNE	1029048	802.200
					FT-13	KRISS	D500672	800.800
						NIM	FB03748	809.820

				GUM	D298402	800.500
				BFKH	OMH69	800.300
16 (17-21 April)			FT-14	UME	PSM298347	800.760
				NPLI	JJ108854	796.380
				NMISA	M51 8244	799.100
				INRIM	D247445	798.900

Table 1: Schedule of the CCQM-K120.a and CCQM-K120.b measurements.

5. Measurement standards

Each laboratory taking part in the CCQM-K120.a comparison was requested to produce one standard at the nominal mole fraction of 380 µmol/mol and another at the mole fraction 480 µmol/mol. For those taking part in the CCQM-K120.b comparison the standards were requested at the nominal mole fractions of 480 µmol/mol and 800 µmol/mol. The mole fraction of carbon dioxide was requested to be within ± 10 µmol/mol of the nominal mole 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:

Species	'Ambient' level mole fraction	Unit	Min mole fraction	Unit	Max mole fraction	Unit
N_2	0.780876	mol/mol	0.7804	mol/mol	0.7814	mol/mol
O_2	0.2093335	mol/mol	0.2088	mol/mol	0.2098	mol/mol
Ar	0.0093332	mol/mol	0.0089	mol/mol	0.0097	mol/mol
CH_4	1900	nmol/mol	0	nmol/mol	1900	nmol/mol
N_2O	330	nmol/mol	0	nmol/mol	330	nmol/mol

Table 2: CCQM-K120.a matrix composition limit values(380 µmol /mol and 480 µmol/mol CO_2 in air†). †Each participating laboratory was required to submit two standards, one with nominal CO_2 mole fraction of (370 to 390) µmol/mol and the second with (470 to 490) µmol/mol.

Species	'Ambient' level mole fraction	Unit	Min mole fraction	Unit	Max mole 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

Table 3: CCQM-K120.b matrix composition limits values(480 µmol /mol and 800 µmol/mol CO_2 in air‡)‡Each participating laboratory was required to submit two standards, one with nominal CO_2 mole fraction of (470 to 490) µmol/mol and the second with (790 to 810) µmol/mol. (A laboratory participating in both CCQM-K120.a and CCQM-K120.b need only submit 3 standards in total).

Aditionally the following information was requested from each participant:

In the case of standards produced with synthetic air:

- a purity table with uncertainties for the nominally pure CO_2 parent gas;
- a purity table with uncertainties for the nominally pure N_2, O_2, Ar, N_2O and CH_4 parent gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- 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.

In the case of standards produced with scrubbed ‘real’ air:

- a purity table with uncertainties for the nominally pure CO_2 parent gas;
- results of the analysis and mole fractions and uncertainties of N_2, O_2, Ar, N_2O and CH_4 in the scrubbed real air;
- a brief outline of the preparation procedure of the final mixtures;
- a composition table for each of the final mixtures, including gravimetric uncertainties when relevant;
- a brief outline of the verification procedure applied to the final mixtures;
- 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.

6. Preparation, values submitted and stability measurements by participants

Information on mixtures submitted by participating laboratories via the comparison submission forms on initial submission and after stability testing of cylinders is included in ANNEX V.

The CO_2 mole fractions submitted by participants are listed in Table 5 where:

x_{NMI}	is the value assigned by the participating NMIs;
$U(x_{\text{NMI}})$	is the expanded uncertainty including contributions from verification associated with the assigned value x_{NMI};

The comparison protocol permitted stability testing to be performed by laboratories after standards had been returned to them by the BIPM, and before the comparison results were known. As a result three laboratories provided new values and uncertainties, namely NIST, NPLI, and BFKH. In addition, UME modified the uncertainty budget only and resubmitted this to the comparison organizers. This subject was discussed during the 38th meeting of the CCQM GAWG (16-17 April 2018) and it was agreed that only the uncertainties resubmitted by UME (Table 15) will replace the original uncertainties. NIST, NPLI, BFKH resubmitted values and uncertainties will only be reported in an annex (see ANNEX II-) (Table 15) with no influence on the KCRV and the degree of equivalence (DOE) of the comparison.

Figure 1 plots the CO_2 mole fraction reported by the participants for each gas standard. In this figure the error bars represent the standard uncertainty associated with the reported value.

It can be observed that participants prepared all mixtures with a CO_2 mole fraction within 10 µmol mol^{-1} of the nominal values, as requested. At 380 µmol/mol, NPLI submitted the mixture with the smallest CO_2 mole fraction, 375.72±3.22 µmol/mol, and NIMJ with the highest, 386.62±0.05 µmol/mol. At 480 µmol/mol, NIMJ produced the lowest mole fraction, 471.30±0.05 µmol/mol, and NIM the highest, 489.15±0.22 µmol/mol. At 800 µmol/mol, NOAA produced the lowest mole fraction, 794.08±0.48 µmol/mol, and NIM the highest, 809.82±0.26 µmol/mol. The expanded uncertainties reported by the participants are plotted in Figure 2.

Regarding the gas matrix composition, thirty-five standards were produced in synthetic air and nine in purified (scrubbed) real air (see Table 5). The compositions of the mixtures reported by participants are listed in Table 6. Seven standards out of forty-four mixtures were not within specifications (gas mixture composition) as requested in the comparison protocol[1].

7. Measurements at the BIPM

On receipt by the BIPM, 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.

Cylinders were analysed in batches of *n* cylinders, first by GC-FID, then by FTIR, and finally by the Delta Ray.

For FTIR measurements, each batch contained 4 cylinders from participants and 2 controls (at nominal mole fractions of 480 and 800 µmol/mol). Each cylinder was connected from the pressure reducer to one inlet of a 32-inlet automatic gas sampler. The procedure before starting measurements was identical as described below for GC-FID. The reported value is the drift corrected ratio between the FTIR response and one control cylinder (at ~ 800 µmol mol^{-1}), with a further correction required to take into account the isotopic composition of each mixtures. Due to depletion of the control cylinder at nominally 480 µmol/mol before completion of all measurements, only ratios against the 800 µmol/mol cylinder could be calculated for all standards. Further details regarding the FTIR measurements are described in ANNEX IV- BIPM Value assignment procedure: FTIR.

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[1] *This nominal fraction limits were given in order to avoid possible biases that could be introduced into the spectroscopic comparison method (FTIR) due to variation in the composition of the air matrix in different standards. For those standards that did not meet the tolerances specified in the protocol, the BIPM included an additional uncertainty component in its FTIR analytical uncertainty to account for the impact of this.*

When the cylinders were analysed by GC-FID, batches were composed of between four and six participants' cylinders, three control cylinders (A, B and C, at nominal mole fractions of 380, 480 and 800 µmol/mol respectively) for ratio quantification and additional cylinders if required to maintain the total batch size of nine standards. Each cylinder was connected from the pressure reducer to one inlet of a 16-inlet automatic gas sampler. The sampler was connected to a gas chromatograph (GC-FID). 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 reported value was the drift corrected ratio between the GC-FID response and one control cylinder (at ~ 480 µmol mol^{-1}). These measurements were performed under intermediate precision conditions (over ten weeks). Ratios against the other control cylinders were calculated, but no substantial difference was observed with the ratio against the control cylinder at 480 µmol/mol. Further details regarding GC-FID measurements are described in ANNEX IV- BIPM Value assignment procedure: GC-FID.

When the cylinders were analyzed by the Delta Ray, each batch contained 4 cylinders from participants and 2 calibration standards. Each cylinder was connected from the pressure reducer to one inlet of a 16-inlet automatic gas sampler. The same procedure was again applied for flushing the gas lines. Further details are described in ANNEX IV- BIPM Value assignment procedure: Delta Ray.

The measurements performed by the Delta Ray analyser were only used to measure the isotopic ratios in each cylinder and further correct the FTIR responses due isotopic differences between the control cylinders and the samples as described in ANNEX IV- BIPM Value assignment procedure: FTIR. In this manner the FTIR reported values for each cylinder were corrected for the isotopic composition and further ratioed to the response to a control cylinder (also corrected for the isotopic composition).

7.1Measurements results

Measurements were performed at the BIPM from February to April 2017. Table 7 lists the inlet pressure before and after the standards were analyzed by the BIPM.

Each cylinder was value assigned using the methods described in section 7 (details in ANNEX IV- BIPM Value assignment procedure).

Results of these series of measurements are listed in Table 8 where:

$\overline{R}_{FT}$	is the (mean) ratio between the FTIR response to the mixture under analysis and the control cylinder, both corrected for the isotopic composition;
$u\left(\overline{R}_{FT}\right)$	is the standard uncertainty of the reported ratio based on FTIR measurements (described in ANNEX IV- BIPM Value assignment procedure: FTIR);
$\overline{R}_{wGC}$	is the reported value based on GC-FID measurements;

$u\left(\overline{R}_{GC}\right)$ the standard uncertainty of the reported value based on GC-FID (described in ANNEX IV- BIPM Value assignment procedure: GC-FID).

The $\delta^{13}C$ and $\delta^{18}O$ measurements on the VPDB-CO_2 scale performed by Delta Ray are listed in Table 11. The typical uncertainties for each of the methods used by the BIPM are listed in Table 4.

Comparison method name	Measurement quantity	Symbol	unit	Typical relative standard uncertainty (%)
FTIR	Ratio to control cylinder under intermediate precision condition	$\overline{R}_{FT}$	1	0.009
GC-FID	Ratio to control cylinder under intermediate precision conditions	$\overline{R}_{wGC}$	1	0.007

Table 4. Comparison methods used during the CCQM-K120 international comparison and typical uncertainties obtained by the BIPM.

Participant	Cylinder references	Gas Matrix	NMI's assigned CO_2 mole fraction x_{NMI} (µmol mol^{-1})	NMI's assigned CO_2 expanded uncertainty $U(x_{\mathrm{NMI}})$ $k = 2$ (µmol mol^{-1})
Before the return of cylinders				
BFKH	OMH54	Synthetic Air	379.840	1.710
BFKH	OMH44	Synthetic Air	479.890	2.110
BFKH	OMH69	Synthetic Air	800.300	2.920
GUM	D298392	Synthetic Air	380.100	4.400
GUM	D298393	Synthetic Air	478.100	5.200
GUM	D298402	Synthetic Air	800.500	8.600
INRIM	D247440	Synthetic Air	479.300	1.600
INRIM	D247445	Synthetic Air	798.900	2.600
KRISS	D500642	Synthetic Air	378.900	0.200
KRISS	D500647	Synthetic Air	480.000	0.200
KRISS	D500672	Synthetic Air	800.800	0.400
LNE	1029045	Synthetic Air	379.480	0.790
LNE	1029047	Synthetic Air	477.600	1.000
LNE	1029048	Synthetic Air	802.200	1.700
NIM	FB03747	Synthetic Air	383.430	0.200
NIM	FB03744	Synthetic Air	489.150	0.220
NIM	FB03748	Synthetic Air	809.820	0.260
NIST	FB04278	Real Air	379.045	0.391
NIST	FB04300	Real Air	472.662	0.428
NIST	FB04287	Real Air	794.533	1.029
NMIJ	CPC00486	Real Air	386.617	0.050

NMIJ	CPC00494	Real Air	471.301	0.051
NMIJ	CPC00558	Real Air	803.658	0.078
NMISA	M51 8232	Synthetic Air	380.200	2.000
NMISA	M51 8167	Synthetic Air	479.500	1.600
NMISA	M51 8244	Synthetic Air	799.100	1.000
NOAA	CC310084	Real Air	379.500	0.210
NOAA	CC305198	Real Air	479.260	0.260
NOAA	CB11668	Real Air	794.080	0.480
NPL	2179	Synthetic Air	380.270	0.190
NPL	2170	Synthetic Air	480.020	0.240
NPL	2181	Synthetic Air	799.700	0.400
NPLI	JJ108891	Synthetic Air	375.720	3.220
NPLI	JJ108862	Synthetic Air	480.520	3.040
NPLI	JJ108854	Synthetic Air	796.380	5.030
UME	PSM298266	Synthetic Air	379.920	0.190*
UME	PSM266468	Synthetic Air	480.420	0.250*
UME	PSM298347	Synthetic Air	800.760	0.360*
VNIIM	M365601	Synthetic Air	380.200	0.110
VNIIM	M365664	Synthetic Air	480.180	0.130
VNIIM	M365707	Synthetic Air	800.730	0.190
VSL	5604614	Synthetic Air	378.900	0.280
VSL	5604880	Synthetic Air	480.480	0.360
VSL	5604705	Synthetic Air	795.700	0.600

*Table 5. Standards and reported values provided by participants. *Re-submitted values following stability testing which were included following the decision of the CCQM GAWG, see ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018).*

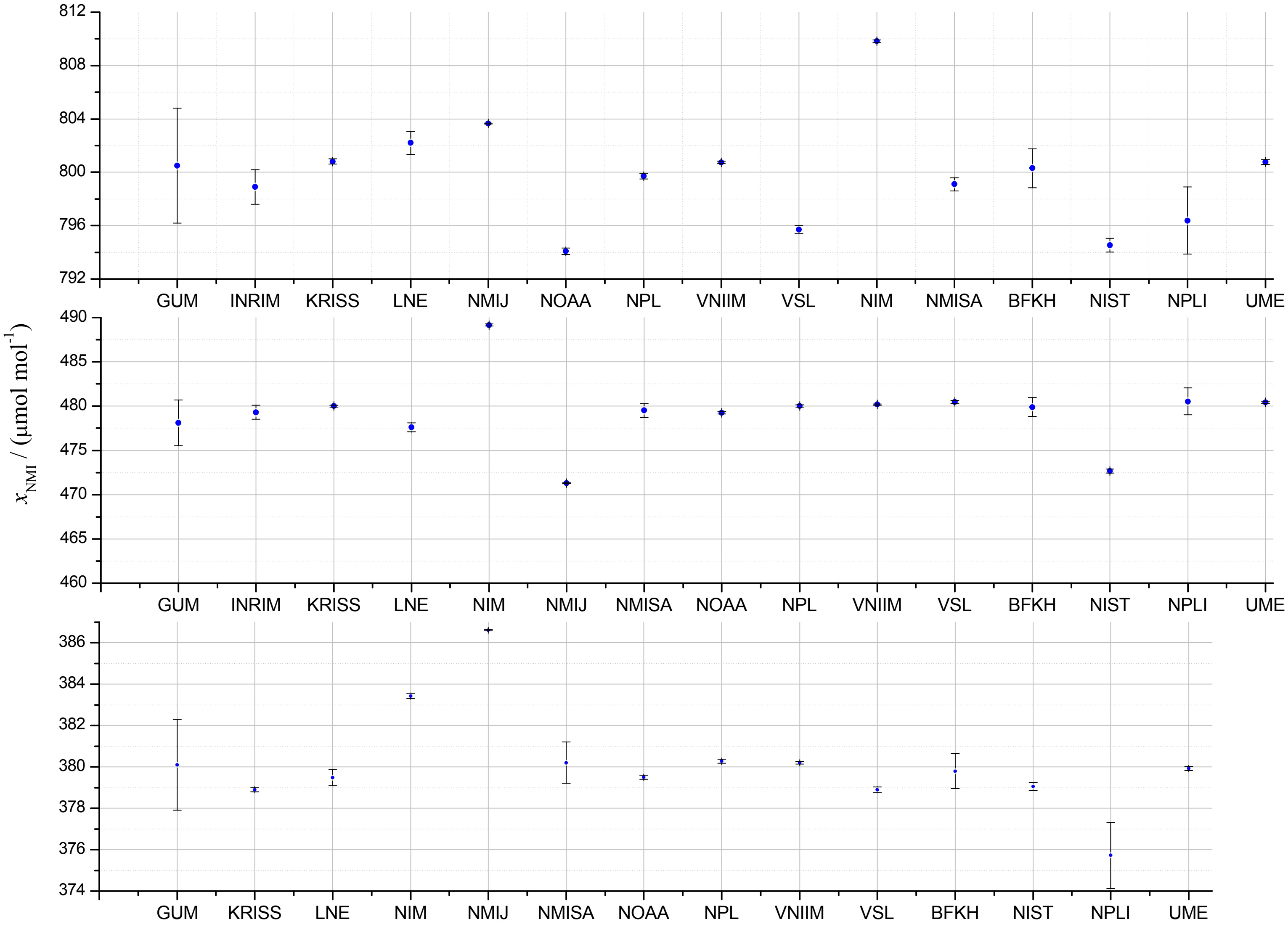

Figure 1. CO_2 mole fractions x_{NMI} reported by participants. The error bars represents the standard uncertainty (k=1) associated with the submitted values.

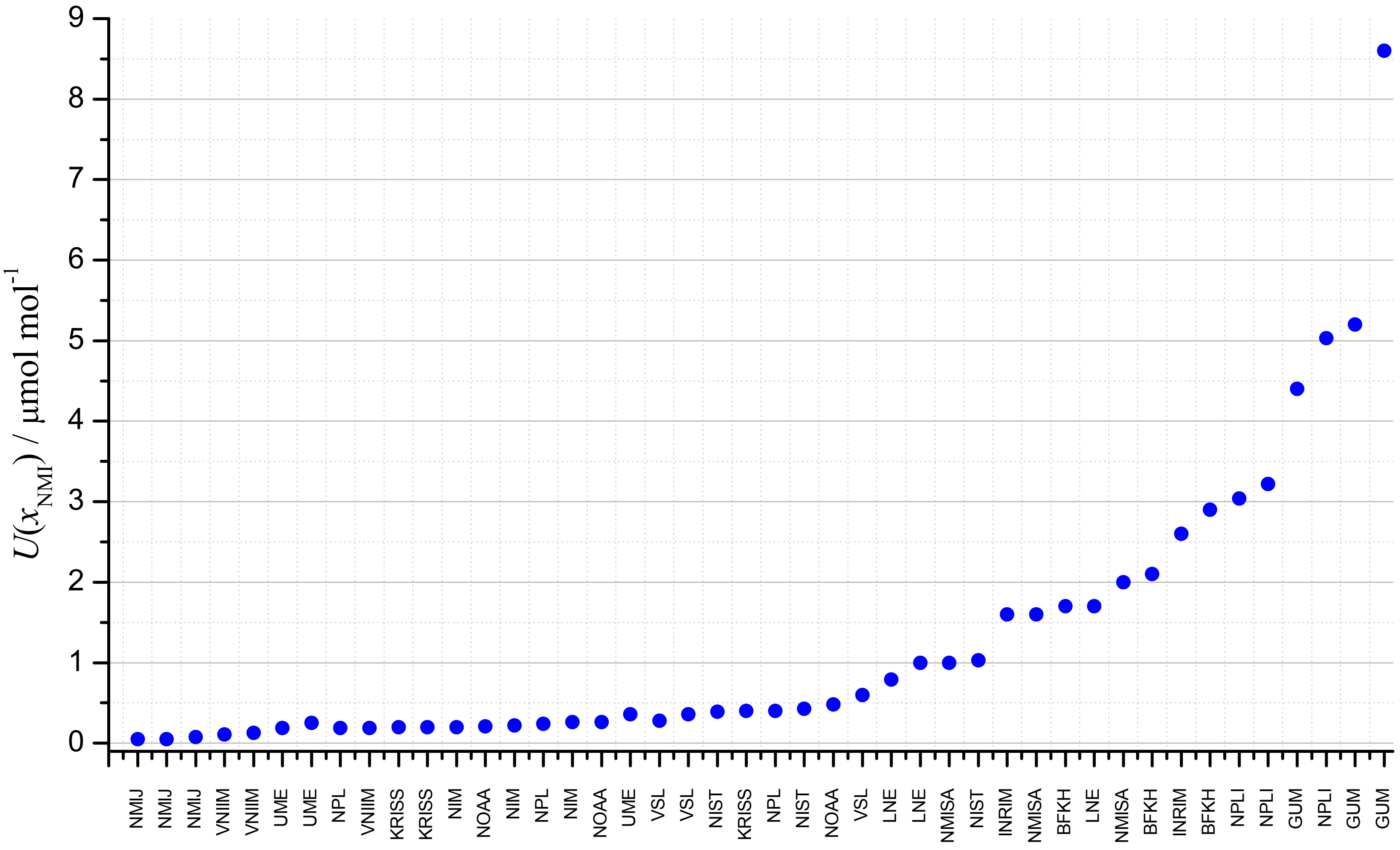

Figure 2. Participants' assigned CO_2 expanded uncertainties $U(x_{\mathrm{NMI}})$.

Participant	Number of Cylinder	NMI's assigned N_2 mole fraction x_{N2} (mol/mol)	NMI's assigned expanded uncertainty k =2 $U(x_{N2})$ (mol/mol)	NMI's assigned O_2 mole fraction x_{O2} (mol/mol)	NMI's assigned expanded uncertainty k=2 $U(x_{O2})$ (mol/mol)	NMI's assigned Ar mole fraction x_{Ar} (mol/mol)	NMI's assigned expanded uncertainty k =2 $U(x_{Ar})$ (mol/mol)	NMI's assigned CH_4 mole fraction x_{NMI} (nmol/mol)	NMI's assigned expanded uncertainty k=2 $U(x_{NMI})$ (nmol/mol)	NMI's assigned N_2O mole fraction x_{NMI} (nmol/mol)	NMI's assigned expanded uncertainty k=2 $U(x_{NMI})$ (nmol/mol)
BFKH	OMH54	0.780390	0.000160	0.209615	0.000048	0.009607	0.000017	1030	1200	*	*
BFKH	OMH44	0.780640	0.000160	0.209514	0.000048	0.009360	0.000017	1030	1200	*	*
BFKH	OMH69	0.780720	0.000160	0.209161	0.000048	0.009314	0.000017	1030	1200	*	*
GUM	D298392	0.780800	0.000200	0.209500	0.000100	0.009250	0.000010	*	*	*	*
GUM	D298393	0.780700	0.000200	0.209600	0.000100	0.009190	0.000010	*	*	*	*
GUM	D298402	0.780200	0.000200	0.209700	0.000100	0.009380	0.000010	*	*	*	*
INRIM	D247440	0.781132	0.000006	0.209063	0.000006	0.009326	0.000004	*	*	*	*
INRIM	D247445	0.782389	0.000006	0.207553	0.000005	0.009259	0.000004	*	*	*	*
KRISS	D500642	0.781139	0.000005	0.209256	0.000004	0.009226	0.000001	9	2	0.200	0.000
KRISS	D500647	0.780915	0.000004	0.209152	0.000004	0.009452	0.000001	10	3	0.200	0.000
KRISS	D500672	0.780407	0.000004	0.209452	0.000004	0.009339	0.000001	15	3	0.200	0.000
LNE	1029045	0.780686	0.000025	0.209528	0.000019	0.009407	0.000022	*	*	*	*
LNE	1029047	0.781355	0.000025	0.208794	0.000018	0.009374	0.000022	*	*	*	*
LNE	1029048	0.782710	0.000027	0.207187	0.000021	0.009301	0.000021	*	*	*	*
NIM	FB03747	0.782000	0.000029	0.209000	0.000028	0.009220	0.000010	1	0	0.791	0.607
NIM	FB03744	0.781000	0.000028	0.210000	0.000026	0.009040	0.000010	1	0	0.790	0.601
NIM	FB03748	0.781000	0.000027	0.210000	0.000026	0.007940	0.000010	1	0	0.790	0.586
NIST	FB04278	0.780812	0.000118	0.209470	0.000710	0.009339	0.000370	*	*	*	*
NIST	FB04300	0.780771	0.000128	0.209422	0.000081	0.009334	0.000034	*	*	*	*

NIST	FB04287	0.780499	0.000114	0.209370	0.000067	0.009336	0.000040	*	*	*	*
NMIJ	CPC00486	0.780915	0.000025	0.209365	0.000007	0.009334	0.000024	2	2	0.900	0.900
NMIJ	CPC00494	0.780937	0.000024	0.209259	0.000007	0.009333	0.000024	3	2	0.900	0.900
NMIJ	CPC00558	0.780602	0.000022	0.209270	0.000006	0.009325	0.000021	3	2	0.900	0.900
NMISA	M51 8232	0.780700	0.000048	0.209600	0.000015	0.009400	0.000005	7	4	0.000	0.000
NMISA	M51 8167	0.780900	0.000028	0.209600	0.000011	0.008900	0.000005	9	6	0.000	0.000
NMISA	M51 8244	0.779300	0.000031	0.210600	0.000016	0.009300	0.000005	10	6	0.000	0.000
NOAA	CC310084	*	*	0.209500	0.000200	*	*	1762	3	317.200	0.500
NOAA	CC305198	*	*	0.209500	0.000200	*	*	1887	4	328.600	0.500
NOAA	CB11668	*	*	0.209500	0.000200	*	*	1889	4	328.800	0.500
NPL	2179	0.780790	0.000470	0.209600	0.000130	0.009232	0.000018	<10	-	<10	0.000
NPL	2170	0.780690	0.780690	0.209500	0.209500	0.009334	0.009334	<10	-	<10	0.000
NPL	2181	0.780550	0.000470	0.209280	0.000130	0.009367	0.000019	<10	-	<10	0.000
NPLI	JJ108891	0.781273	0.002210	0.209688	0.000590	0.009040	0.000030	*	*	*	*
NPLI	JJ108862	0.781989	0.002210	0.208853	0.000590	0.009158	0.000030	*	*	*	*
NPLI	JJ108854	0.781363	0.002210	0.209789	0.000594	0.008847	0.000030	*	*	*	*
UME	PSM298266	0.780339	0.000017	0.209966	0.000017	0.009314	0.000002	*	*	*	*
UME	PSM266468	0.779968	0.000017	0.210229	0.000017	0.009322	0.000002	*	*	*	*
UME	PSM298347	0.779552	0.000016	0.210352	0.000016	0.009295	0.000002	*	*	*	*
VNIIM	M365601	0.781015	0.000013	0.209188	0.000013	0.009416	0.000005	9	2	*	*
VNIIM	M365664	0.780928	0.000011	0.209270	0.000012	0.009322	0.000005	10	2	*	*
VNIIM	M365707	0.781000	0.000011	0.209199	0.000012	0.009000	0.000005	10	2	*	*
VSL	5604614	0.781177	0.000017	0.209152	0.000016	0.009292	0.000006	16	7	0.021	0.024
VSL	5604880	0.781092	0.000017	0.209146	0.000016	0.009281	0.000006	16	7	0.021	0.024
VSL	5604705	0.780708	0.000017	0.209246	0.000015	0.009251	0.000006	16	7	0.021	0.024

Table 6. Matrix composition of the submitted gas mixtures according to participants' reports in ANNEX V. Synthetic Air is identified as S. A. and Purified real air as R. A. No data given.*

Lab	Number of Cylinder	Date of arrival	pressure on arrival Mpa	pressure on departure Mpa
BFKH	OMH54	12/9/2016	9.95	7.76
BFKH	OMH44	12/9/2016	9.59	7.84
BFKH	OMH69	12/9/2016	9.84	7.55
GUM	D298392	28/09/2016	14.46	11.03
GUM	D298393	28/09/2016	15.23	11.6
GUM	D298402	28/09/2016	15.05	10.8
INRIM	D247440	13/01/2017	8.97	5.34
INRIM	D247445	13/01/2017	9.22	5.44
KRISS	D500642	20/12/2016	9.27	7.39
KRISS	D500647	20/12/2016	8.84	7.11
KRISS	D500672	20/12/2016	9.05	7.03
LNE	1029045	28/11/2016	13.11	11.13
LNE	1029047	28/11/2016	12.87	11.13
LNE	1029048	28/11/2016	13.22	11.41
NIM	FB03747	14/12/2016	8.2	5.27
NIM	FB03744	14/12/2016	8.65	5.93
NIM	FB03748	14/12/2016	8.02	4.73
NIST	FB04278	3/1/2017	10.03	7.25
NIST	FB04300	3/1/2017	10.23	7.46
NIST	FB04287	3/1/2017	10.05	7.21
NMIJ	CPC00486	9/2/2017	9.57	7.53
NMIJ	CPC00494	9/2/2017	9.28	7.52
NMIJ	CPC00558	9/2/2017	8.4	6.77
NMISA	M51 8232	19/12/2016	12.97	9.52
NMISA	M51 8167	19/12/2016	9.6	7.09
NMISA	M51 8244	19/12/2016	10.61	5.72
NOAA	CC310084	3/2/2017	13.48	12.82
NOAA	CC305198	3/2/2017	13.42	12.84
NOAA	CB11668	3/2/2017	11.94	11.38
NPL	2179	9/12/2016	10.46	8.55
NPL	2170	9/12/2016	11.19	9.4
NPL	2181	9/12/2016	11.12	9.35
NPLI	JJ108891	9/2/2017	10	8.36
NPLI	JJ108862	9/2/2017	10.5	8.97
NPLI	JJ108854	9/2/2017	9.82	8.11
UME	PSM298266	23/11/2016	9.03	5.82
UME	PSM266468	23/11/2016	9.08	5.46
UME	PSM298347	23/11/2016	9.18	5.42
VNIIM	M365601	5/1/2017	8.4	4.3
VNIIM	M365664	5/1/2017	8.66	5.37
VNIIM	M365707	5/1/2017	8.53	5.27
VSL	5604614	15/11/2016	10.49	6.34
VSL	5604880	15/11/2016	10.12	6.8
VSL	5604705	15/11/2016	10.45	7.07

Table 7. Pressure of the gas standards on arrival and departure from the BIPM.

Participant	Number of Cylinder	x_{NMI} Assigned NMI's CO_2 mole fraction in (µmol/mol)	$u(x_{\text{NMI}})$ Assigned NMI's Standard uncertainty (k=1) (µmol/mol)	$\overline{R}_{FT}$ FTIR (Under intermediate precision conditions) Ratio to control cylinder	$u\left(\overline{R}_{FT}\right)$ Standard uncertainty in the Ratio to control cylinder	$\overline{R}_{wGC}$ GC-FID (Under intermediate precision conditions) Ratio to control cylinder	$u\left(\overline{R}_{GC}\right)$ Standard uncertainty in the Ratio to control cylinder
BFKH	OMH54	379.800	0.855	0.435893607	0.000026077	0.787699648	0.000056828
BFKH	OMH44	479.900	1.055	0.539981600	0.000030887	0.976036480	0.000059163
BFKH	OMH69	800.300	1.460	0.930134790	0.000079551	1.681896740	0.000095864
GUM	D298392	380.100	2.200	0.441372447	0.000014142	0.797442344	0.000052495
GUM	D298393	478.100	2.600	0.555225000	0.000027459	1.003704868	0.000094363
GUM	D298402	800.500	4.300	0.929933927	0.000085245	1.681786329	0.000104750
INRIM	D247440	479.300	0.800	0.556774608	0.000200000	1.006168965	0.000071077
INRIM	D247445	798.900	1.300	0.927989884	0.000059393	1.677871699	0.000087418
KRISS	D500642	378.900	0.100	0.440414238	0.000026926	0.795445471	0.000074696
KRISS	D500647	480.000	0.100	0.557780245	0.000035341	1.008228786	0.000056189
KRISS	D500672	800.800	0.200	0.930402740	0.000108930	1.682410057	0.000106300
LNE	1029045	379.480	0.395	0.440901535	0.000025239	0.796419628	0.000056088
LNE	1029047	477.600	0.500	0.554855777	0.000046174	1.002959828	0.000101902
LNE	1029048	802.200	0.850	0.932191570	0.000046232	1.685756190	0.000102865
NIM	FB03747	383.430	0.100	0.445715112	0.000021260	0.804945901	0.000057626
NIM	FB03744	489.150	0.110	0.568919872	0.000044283	1.028323070	0.000061887
NIM	FB03748	809.820	0.130	0.941620390	0.000127224	1.702705250	0.000084949
NIST	FB04278	379.045	0.195	0.441858957	0.000014036	0.798159371	0.000076697
NIST	FB04300	472.662	0.214	0.550247743	0.000021932	0.994649947	0.000056864
NIST	FB04287	794.530	0.514	0.924730373	0.000047693	1.672406610	0.000052361
NMIJ	CPC00486	386.617	0.025	0.449318716	0.000022804	0.811714164	0.000057115
NMIJ	CPC00494	471.301	0.026	0.547653232	0.000049336	0.989730987	0.000128859
NMIJ	CPC00558	803.658	0.039	0.933998556	0.000062657	1.689072068	0.000061122
NMISA	M51 8232	380.200	1.000	0.441463446	0.000030414	0.797746449	0.000071374
NMISA	M51 8167	479.500	0.800	0.556816358	0.000063789	1.006620384	0.000139031
NMISA	M51 8244	799.100	0.500	0.927761085	0.000058032	1.678197948	0.000120968
NOAA	CC310084	379.500	0.105	0.441196927	0.000016125	0.796836602	0.000097427
NOAA	CC305198	479.260	0.130	0.557198873	0.000046487	1.007173065	0.000061590
NOAA	CB11668	794.080	0.240	0.923707672	0.000052071	1.670538345	0.000102943
NPL	2179	380.270	0.095	0.442066316	0.000015232	0.798660385	0.000055036
NPL	2170	480.020	0.120	0.557939086	0.000029155	1.008480431	0.000075981
NPL	2181	799.700	0.200	0.929525453	0.000066014	1.680929399	0.000081883
NPLI	JJ108891	375.720	1.610	0.435541280	0.000044283	0.786899117	0.000051131
NPLI	JJ108862	480.520	1.520	0.558985244	0.000078492	1.010295612	0.000070031
NPLI	JJ108854	796.380	2.515	0.923587308	0.000048435	1.670046415	0.000092977
UME	PSM298266	379.92	0.095*	0.441777548	0.000066603	0.798242598	0.000076656
UME	PSM266468	480.42	0.125*	0.558597569	0.000077666	1.009847197	0.000062025
UME	PSM298347	800.760	0.180*	0.930853610	0.000059811	1.683852629	0.000186416

VNIIM	M365601	380.200	0.055	0.441966430	0.000016643	0.798479627	0.000066343
VNIIM	M365664	480.180	0.065	0.558130273	0.000048384	1.008861333	0.000059090
VNIIM	M365707	800.730	0.095	0.930604477	0.000058131	1.683192751	0.000075295
VSL	5604614	378.900	0.140	0.440539300	0.000017205	0.795901702	0.000077266
VSL	5604880	480.480	0.180	0.558580000	0.000018028	1.009802467	0.000054009
VSL	5604705	795.700	0.300	0.925375760	0.000052705	1.673272267	0.000122172

*Table 8. Results of BIPM CO_2 comparison measurements. *Re-submitted values following stability testing which were included following the decision of the CCQM GAWG (see ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018)).*

7.2 Graphical representation of measurement results

Table 9 summarizes the figures showing the measurements results obtained by different methods at the BIPM.

Comparison method	CO_2 mole fraction	Plot
FTIR (Ratio to control cylinder under intermediate precision conditions)		
	380 µmol/mol	Figure *3*
	480 µmol/mol	Figure *4*
	800 µmol/mol	Figure *5*
GC-FID (Ratio to control cylinder under intermediate precision conditions)		
	380 µmol/mol	Figure *6*
	480 µmol/mol	Figure *7*
	800 µmol/mol	Figure *8*

Table 9. List of figures corresponding to results obtained from FTIR and GC-FID at the BIPM

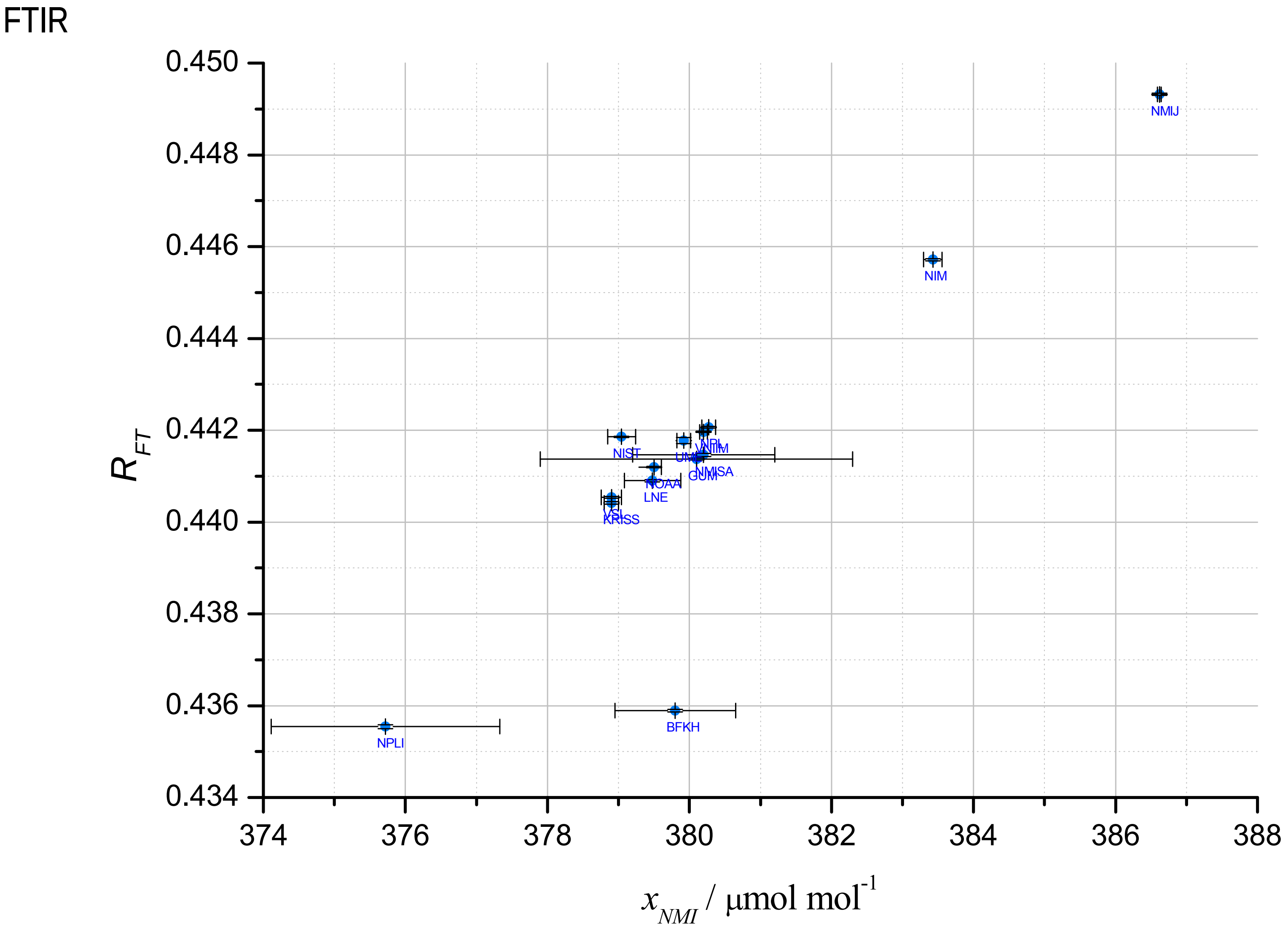

Figure 3. FTIR ratios to control standard for the cylinders at nominally 380 µmol mol^{-1}. The error bars represent the standard uncertainty (*k*=1) associated with the BIPM measurement results (*y*- axis) and the NMI reported values (*x*-axis).

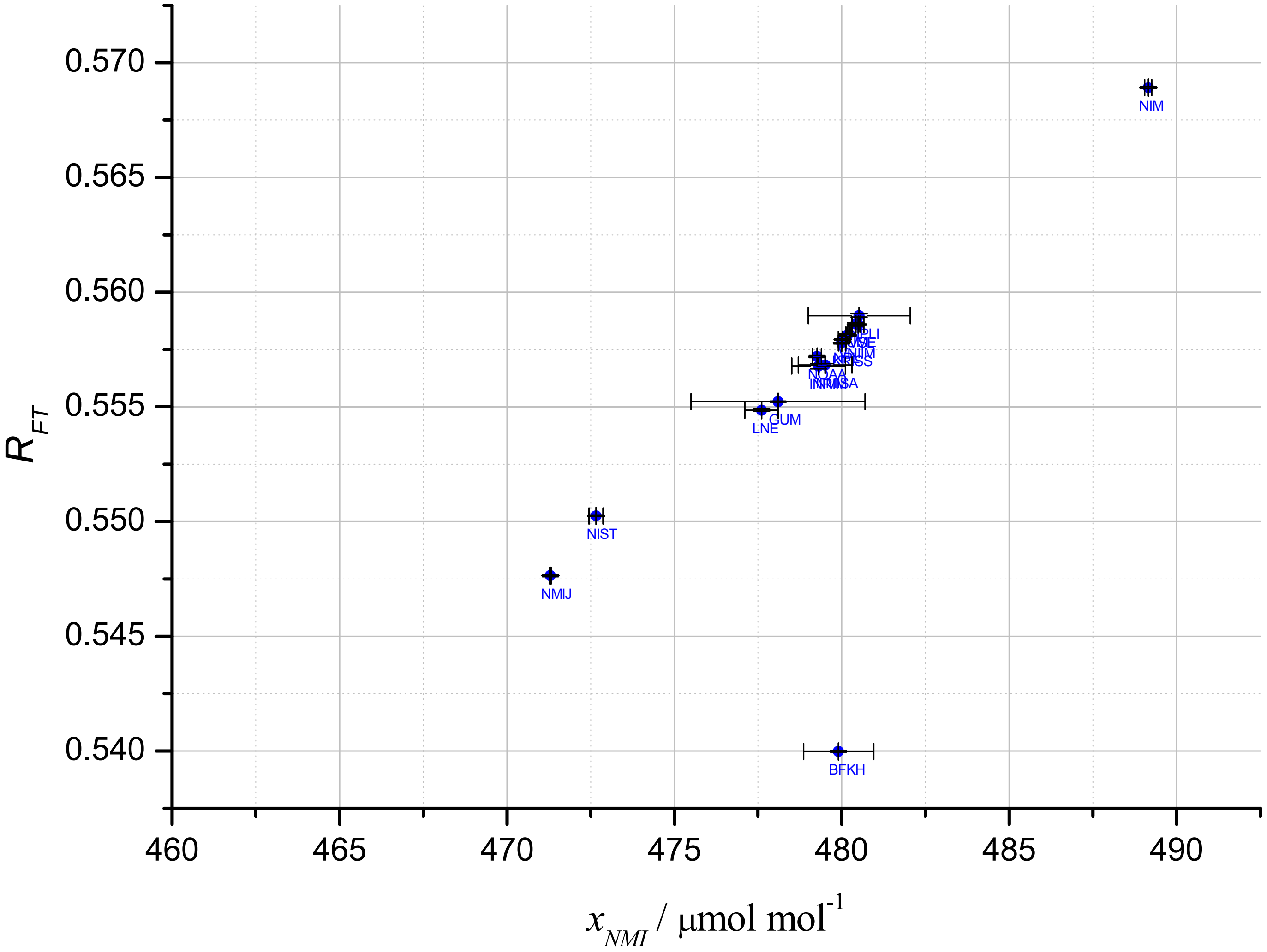

Figure 4. FTIR ratios to control standard for the cylinders at nominally 480 µmol mol^{-1}. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

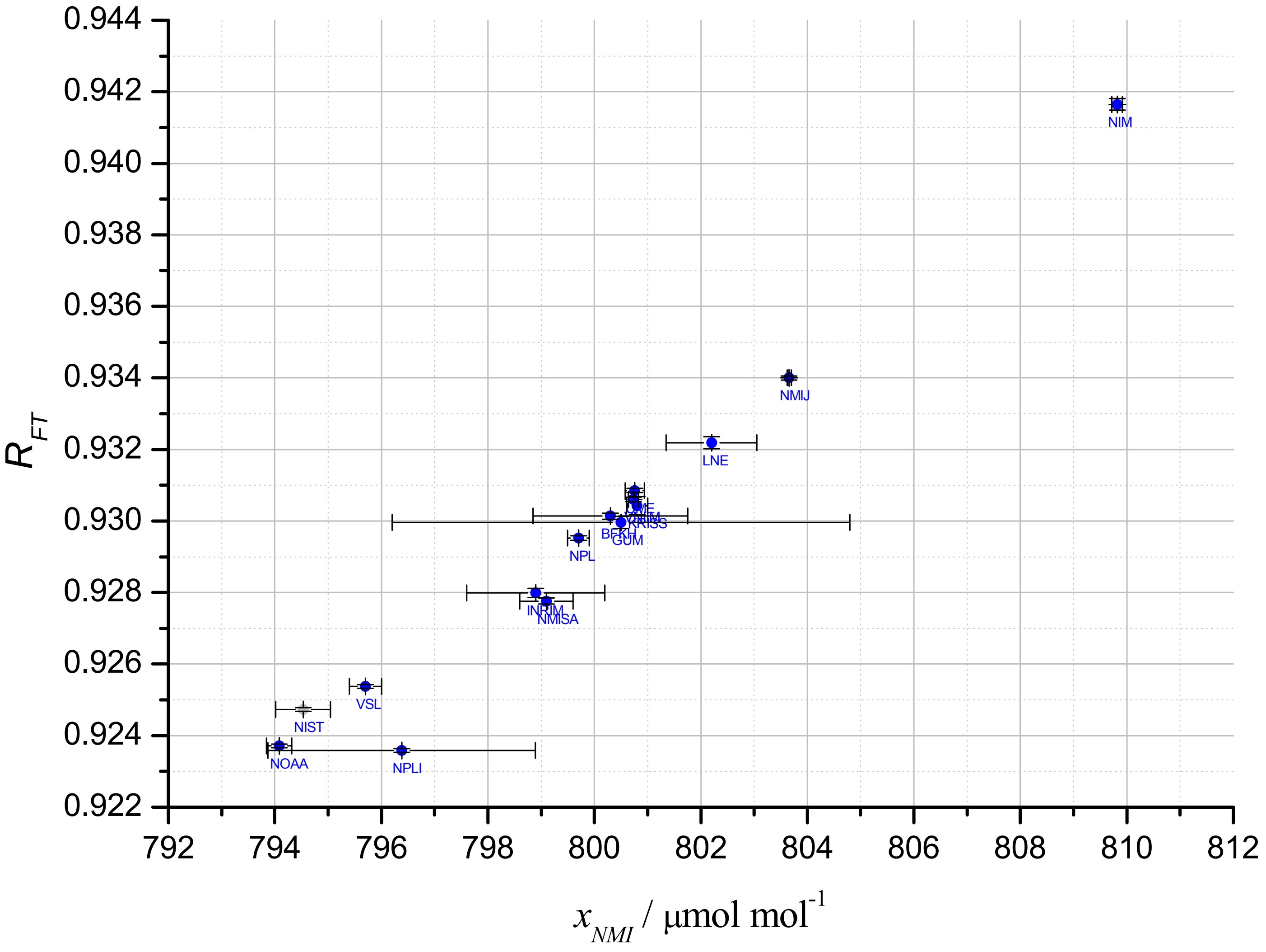

Figure 5. FTIR ratios to control standard for the cylinders at 800 µmol mol^{-1}. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

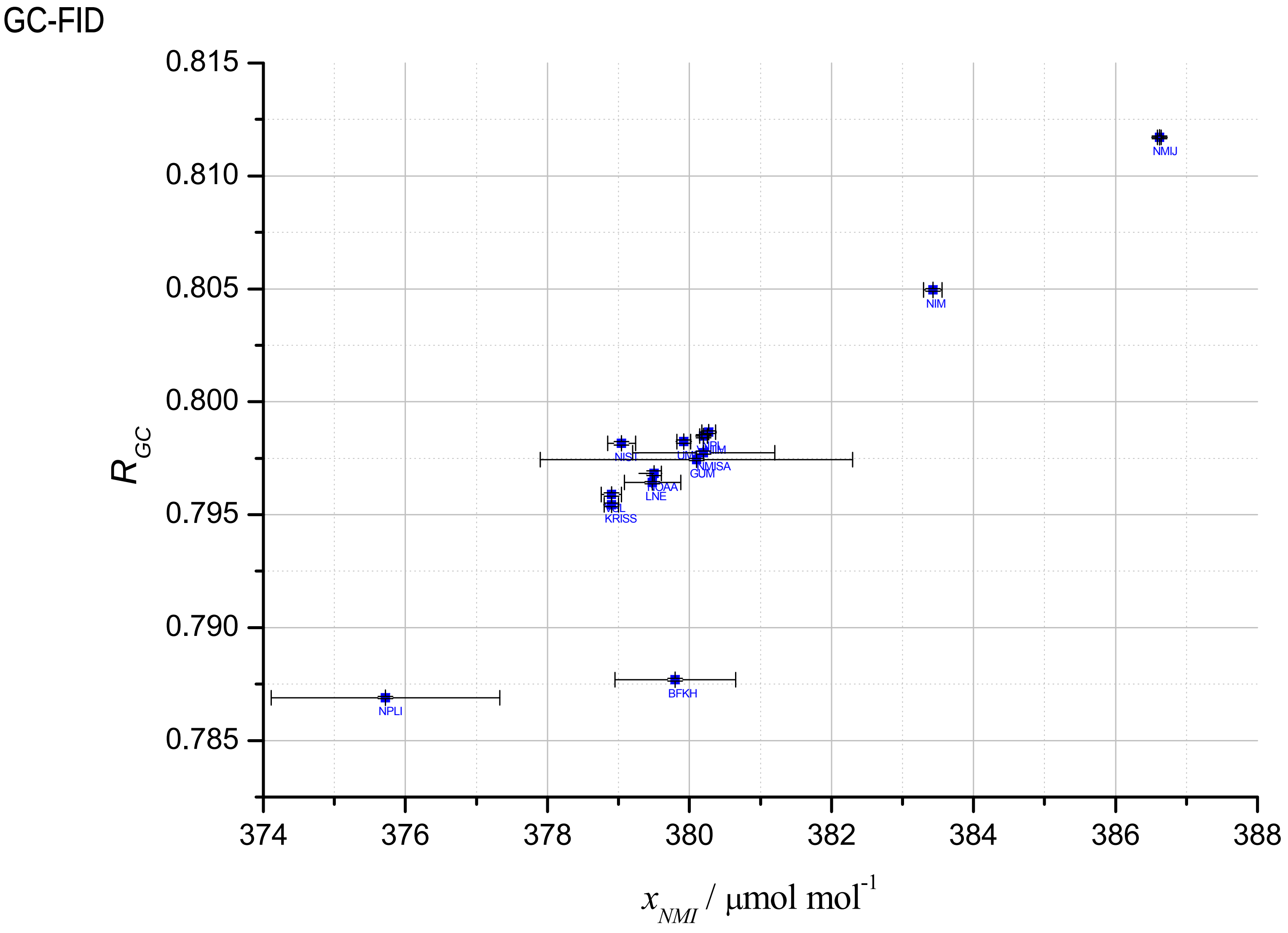

Figure 6. GC-FID ratios to control standard for the cylinders at nominally 380 µmol mol^{-1}. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

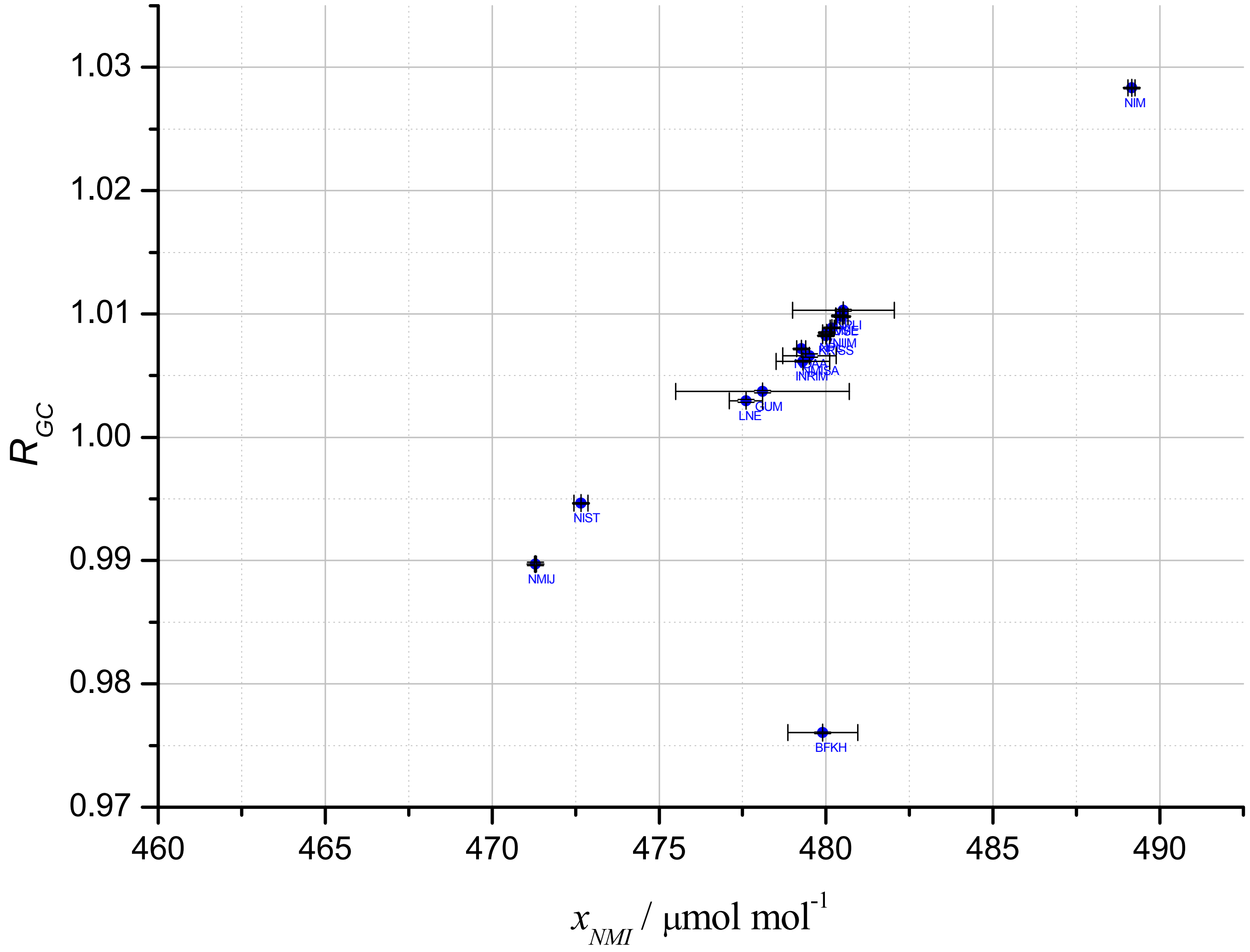

Figure 7. GC-FID ratios to control standard for the cylinders at 480 µmol mol^{-1}. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

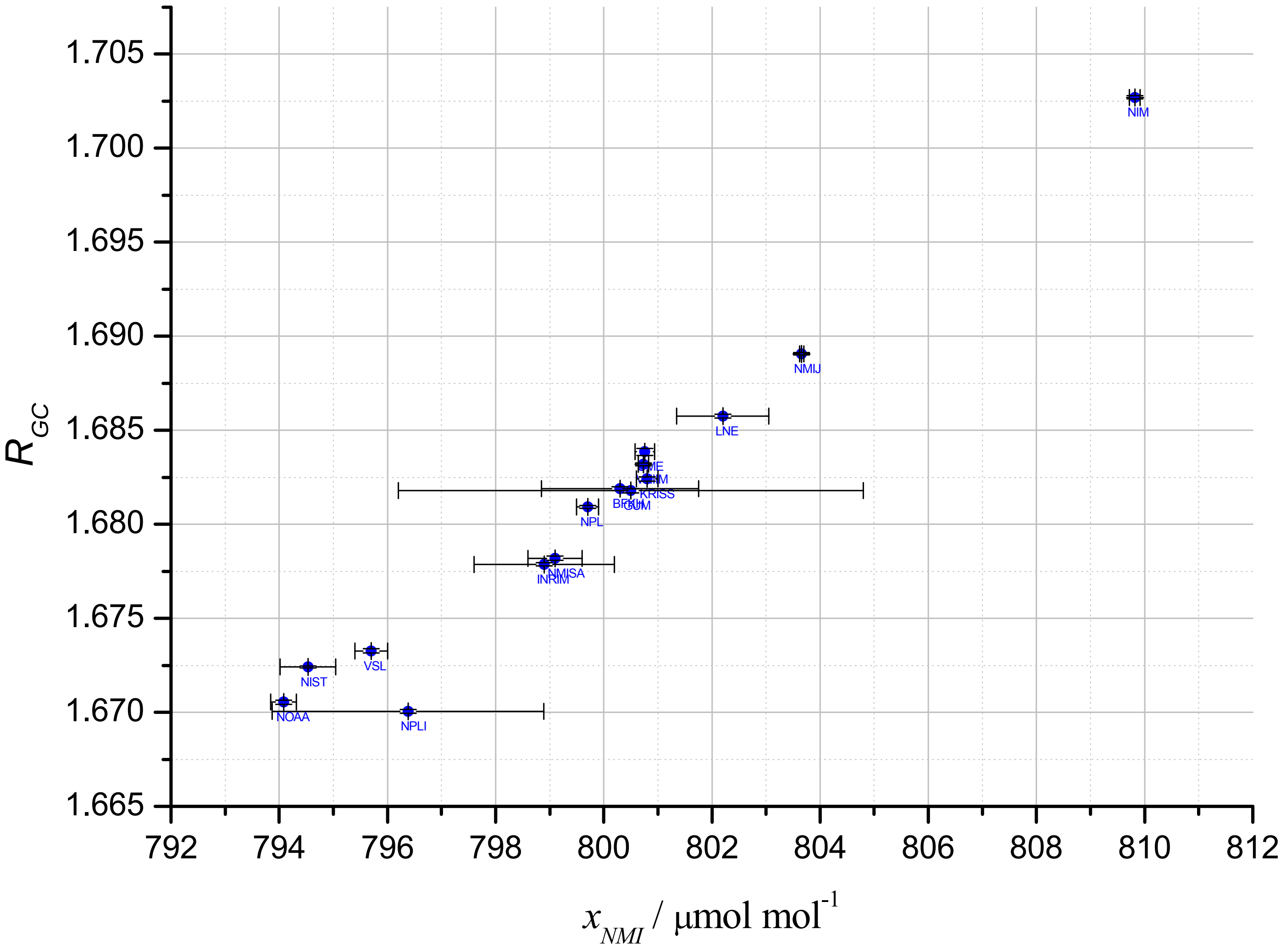

Figure 8. GC-FID ratios to control standard for the cylinders at 800 µmol mol^{-1}. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

7.3 Isotope ratios of CCQM-K120 standards

The $\delta^{13}C$ and $\delta^{18}O$ values reported by participants are listed in Table 10. The delta values of the complete set of cylinders, on the VPDB-CO_2 scale, were also measured by the BIPM using the Delta Ray analyser to correct the FTIR response. The measured isotope ratio values are listed Table 11. The method for measuring and calibrating the Delta Ray is fully described in ANNEX IV- BIPM Value assignment procedure: Delta Ray. The method used by the BIPM for measuring isotope ratios is described in a recent publication[5] and was validated with CO_2 in air standards that had been value assigned for their isotopic composition by the WMO-CCL laboratory for isotope ratios, MPI-BGC Jena, with traceability of the standards used to the VPDB-CO_2 scale realized with the JENA air standards reference set. The measurements made by the BIPM have been used for all corrections made in the FTIR comparison method, and were considered fit for purpose, noting that a 1 ‰ difference in $\delta^{13}C$ measurements can lead to a bias of 0.004 µmol/mol in CO_2 mole fraction measurements in instruments based on a spectroscopic technique; and similarly a 0.002 µmol/mol bias from a 1 ‰ difference in $\delta^{18}O$ measurements. Reported values for isotopic composition by participants were for information only. The agreement between reported values and BIPM measured values is variable. For $\delta^{13}C$ values the difference between BIPM measured values and those reported by participants was: smaller than 0.4 ‰, for NMIJ, NPL and NOAA; smaller than 2 ‰ for UME and VNIIM; and almost 12 ‰ for NIST (noting that the NIST reported at the 38th meeting of the CCQM GAWG, that this had been a typographical error on their part and the NIST and BIPM values were actually in full agreement). For $\delta^{18}O$ values the difference between BIPM measured values and those reported by participants is: smaller than 3 ‰, for NMIJ and NOAA; and almost 10 ‰ for NPL. The compatibility of CO_2 isotope ratio measurements will be the focus of a future CCQM GAWG comparison, enabling sources for differences to be studied in greater detail.

Lab	Number of Cylinder	$\delta^{13}C$ on VPDB-CO_2 scale	$u(\delta^{13}C)$ Standard uncertainty (k=1)	$\delta^{18}O$ on VPDB-CO_2 scale	$u(\delta^{18}O)$ Standard uncertainty (k=1)	Comments
		(‰)	(‰)	(‰)	(‰)	
NIST	FB04278	-28	2	-	-	
NIST	FB04300	-28	2	-	-	
NIST	FB04287	-28	2	-	-	
NMIJ	3BIS85282	-8.92**	-	-9.91	-	CO_2 pure
NOAA	CC310084	-8.7	0.2	-0.3	0.2	
NOAA	CC305198	-8.8	0.2	-6.4	0.2	
NOAA	CB11668	-8.5	0.4	-19.7	0.4	
NPL	2179	-5.5	0.5	-22.5	0.5	
NPL	2170	-5.5	0.5	-22.5	0.5	
NPL	2181	-5.5	0.5	-22.5	0.5	
UME	PSM298266	-1.65	0.05	-	-	CO_2 pure
VNIIM	M365601	-48	0.45	-	-	
VNIIM	M365664	-48	0.45	-	-	
VNIIM	M365707	-48	0.45	-	-	

*Table 10. $\delta^{13}C$ and $\delta^{18}O$ values reported by participants.** value measured by the gas supplier according to the participant.*

Lab	Number of Cylinder	$\delta^{13}C$ on VPDB-CO_2 scale (‰)	$u(\delta^{13}C)$ Standard uncertainty (k=1) (‰)	$\delta^{18}O$ on VPDB-CO_2 scale (‰)	$u(\delta^{18}O)$ Standard uncertainty (k=1) (‰)
BFKH	OMH54	-66.76	0.18	-17.23	0.48
BFKH	OMH44	-66.53	0.18	-17.34	0.48
BFKH	OMH69	-66.91	0.18	-26.15	0.48
GUM	D298392	-44.31	0.18	-28.77	0.48
GUM	D298393	-44.32	0.18	-28.65	0.48
GUM	D298402	-44.18	0.18	-28.47	0.48
INRIM	D247440	-49.27	0.18	-34.36	0.48
INRIM	D247445	-49.52	0.18	-34.49	0.48
KRISS	D500642	-23.38	0.18	-17.49	0.48
KRISS	D500647	-23.41	0.18	-19.03	0.48
KRISS	D500672	-23.34	0.18	-18.84	0.48
LNE	1029045	-37.81	0.18	-28.61	0.48
LNE	1029047	-37.86	0.18	-27.75	0.48
LNE	1029048	-38.11	0.18	-28.04	0.48
NIM	FB03747	-20.55	0.18	-30.07	0.48
NIM	FB03744	-20.52	0.18	-29.78	0.48
NIM	FB03748	-20.62	0.18	-29.95	0.48
NIST	FB04278	-39.83	0.18	-30.92	0.48
NIST	FB04300	-39.85	0.18	-30.48	0.48
NIST	FB04287	-39.83	0.18	-30.53	0.48
NMIJ	CPC00486	-8.91	0.18	-9.87	0.48
NMIJ	CPC00494	-9.03	0.18	-11.84	0.48
NMIJ	CPC00558	-8.97	0.18	-11.66	0.48
NMISA	M51 8232	-32.1	0.18	-26.61	0.48
NMISA	M51 8167	-32.09	0.18	-26.55	0.48
NMISA	M51 8244	-31.89	0.18	-26.46	0.48
NOAA	CC310084	-8.86	0.18	-0.32	0.48
NOAA	CC305198	-8.91	0.18	-9.06	0.48
NOAA	CB11668	-8.88	0.18	-21.28	0.48
NPL	2179	-5.22	0.18	-32.31	0.48
NPL	2170	-5.21	0.18	-31.7	0.48
NPL	2181	-5.25	0.18	-31.74	0.48
NPLI	JJ108891	-8.87	0.18	-10.87	0.48
NPLI	JJ108862	-9.17	0.18	-11.31	0.48
NPLI	JJ108854	-9.15	0.18	-11.49	0.48
UME	PSM298266	-0.07	0.18	-24.81	0.48
UME	PSM266468	-0.05	0.18	-24.53	0.48
UME	PSM298347	0.16	0.18	-24.46	0.48
VNIIM	M365601	-46.43	0.18	-26.61	0.48
VNIIM	M365664	-46.35	0.18	-25.84	0.48
VNIIM	M365707	-46.47	0.18	-25.94	0.48
VSL	5604614	-39.57	0.18	-32.88	0.48
VSL	5604880	-39.69	0.18	-32.24	0.48
VSL	5604705	-35.74	0.18	-30.64	0.48

Table 11. $\delta^{13}C$ and $\delta^{18}O$ value assignment, vs VPDB-CO_2, for each CO_2 in air standard.

In the case of the CCQM-K120.a comparison, it should be noted that the isotopic composition of CO_2 at background levels in the atmosphere would be expected to have values close to the nominal values of -8.5 ‰ for $\delta^{13}C$ and of 0 ‰ for $\delta^{18}O$ when expressed on the VPDB-CO_2 scale. The standards submitted for the CCQM-K120.a comparison had $\delta^{13}C$ values that varied between -67 ‰ to 0 ‰, and $\delta^{18}O$ values that varied between -35 ‰ to 0 ‰. This range of isotopic composition could result in measurement biases of up to 0.3 µmol/mol in spectroscopic instruments for which isotopic composition had not been taken into account.

8 Key Comparison Reference Value (KCRV)

During the 38th meeting of the CCQM GAWG it was agreed that the key comparison reference values for CCQM-K120.a and CCQM-K120.b were to be calculated using the measurement results of the FTIR spectrometer.

Several statistical approaches, all based on least-square regressions of measurement results obtained at the same nominal mole fraction, were presented during 38th meeting of the CCQM GAWG (GAWG/18-32). From this analysis, it was agreed to fit the FTIR results versus the participant' s submitted values with a line, using the Generalised Least Square approach defined in the standard ISO 6143:2001[9] (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures). It was also agreed to select the largest subset of cylinders contributing to the regression line so as to obtain a consistent set with regard to the regression, i.e. a set that allows the goodness-of-fit parameter Γ to be less than 2. The measure of goodness-of-fit Γ is defined as the maximum value of the weighted differences between the coordinates of measured and adjusted points (both on the x and the y axes). For all regressions, the normalized sum of the squared weighted deviations $\chi^2/(n-p)$, where n is the number of points and $p = 2$ the number of parameters of the fit, is also provided for indication. Both values are expected to be lower than 2, with the condition on Γ being stricter as it imposes all points to comply with the fit.

Notation

The degree of equivalence is defined as:

$$D = x_{NMI} - x_{KCRV} \tag{1}$$

where

x_{KCRV} is the amount of substance fraction in the cylinder predicted by the linear analysis function for the corresponding analyzer response (ratio to the control cylinder by FTIR);

$u(x_{\mathrm{KCRV}})$ is the standard uncertainty of the KCRV value;

x_{NMI} is the amount of substance fraction reported by the participating laboratory;

$u(x_{\mathrm{NMI}})$ is the standard uncertainty associated with the reported value x_{NMI};

D is difference in amount of substance fraction as measured by the laboratory and the reference value x; and

$u(D)$ is the standard uncertainty of this difference expressed as:

$$u(D) = \sqrt{u(x_{NMI})^2 - u(x_{KCRV})^2} \qquad (2)$$

and the expanded uncertainty, at 95 % confidence level

$$U(D) = k \cdot u(D) \qquad (3)$$

where k denotes the coverage factor, taken as $k = 2$ (normal distribution, approximately 95 % level of confidence).

8.1 Degrees of equivalence and graph of equivalence

The analysis of the data from the comparison was performed following the process outlined in ISO 6143:2001. The regression analysis was performed with XLGenlinev1.1, a computer programme developed by NPL which implements this methodology by taking into consideration uncertainties in both axes.

During the 38th meeting of the GAWG it was decided that due the potential adsorption of a proportion of CO_2 molecules onto the internal surface of a cylinder and valve (that can cause a deviation from the gravimetric amount fraction by as much as 100 nmol mol^{-1} demonstrated by Brewer et al.^{2}) a lower limit for uncertainties that could be used in the calculation of the KCRV was to be fixed. It was decided that any standard uncertainty value lower than 0.095 µmol mol^{-1} submitted by a participant was to be replaced by this value for the calculation of the KCRV. The limit value was chosen based on the lowest uncertainty that had been reported by a participant, for which adsorption effects had been considered (in this case NPL, with cylinder 2179). In this manner the original uncertainties for the KCRV calculation of standards CPC00486 (NMIJ, original uncertainty 0.025 µmol mol^{-1}), CPC00494 (NMIJ, original uncertainty 0.025 µmol mol^{-1}), CPC00558 (NMIJ, original uncertainty 0.039 µmol mol^{-1}), 0.0255, M365601 (VNIIM, original uncertainty 0.055 µmol mol^{-1}) and M365664 (VNIIM, original uncertainty 0.065 µmol mol^{-1}) were replaced by 0.095 µmol mol^{-1}. This cutoff was only applied to calculate the KCRVs. The degree of equivalences were calculated using the uncertainties submitted by participants (equation 1).

KCRV calculations for standards at a nominal mole fraction of 380 µmol mol^{-1}

With the FTIR measurement data set the set of self-consistent standards identified included eleven standards. Three standards were excluded, namely OMH54 (BFKH), FB04278 (NIST) and JJ108891 (NPLI), as these laboratories had reported changes in their reported values following stability testing.

The goodness-of-fit parameter obtained from the regression performed with this data set was 0.74, and the normalized sum of the squared weighted deviations $\chi^2/\,(11-2)=0.227$. Key comparison reference values and degrees of equivalence are listed in Table 12. Degrees of equivalence are plotted in Figure 9.

KCRV calculations for standards at a nominal mole fraction of 480 µmol mol^{-1}

With the FTIR measurement data set the set of self-consistent standards identified included twelve standards. Three standards were excluded, namely OMH44 (BFKH), FB03744 (NIST) and JJ108862 (NPLI) as these laboratories had reported changes in their reported values following stability testing.

The goodness-of-fit parameter obtained from the regression performed with this data set was 1.36, and the normalized sum of the squared weighted deviations $\chi^2/\,(12-2)=0.463$. The resulting key comparison reference values and degrees of equivalence are listed in Table 13. Degrees of equivalence are plotted in Figure 10.

KCRV calculations for standards at a nominal mole fraction of 800 µmol mol^{-1}

Several statistical approaches were presented during the 38th meeting of the CCQM GAWG (GAWG/18-32, see ANNEX II-) comprising different alternatives of sets of self-consistent standards. From those the GAWG selected a solution where the two extreme mole fractions at this nominal mole fraction, FB03748 (NIM, 810.424 µmol mol^{-1}) and CB11668 (NOAA, 794.608 µmol mol^{-1}) were removed from the set of self-consistent standards.

The solution involved then including ten cylinders for KCRV calculations. Five were excluded, namely: FB03748 (NIM), CB11668 (NOAA), OMH69 (BFKH), FB04287 (NIST) and JJ108854 (NPLI).

The goodness-of-fit parameter obtained from the regression performed with this data set was 1.80, and the normalized sum of the squared weighted deviations $\chi^2/\,(10-2)=0.950$. Key comparison reference values and degrees of equivalence are listed in Table 14. Degrees of equivalence are plotted in Figure 11.

Participant	Cylinder	x_{KCRV} (XLGENLINE predictied value from FTIR) (µmol/mol)	$u(x_{KCRV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{\mathrm{NMI}})$ (µmol/mol)	$D_1(x_{\mathrm{NMI}}$- $x_{\mathrm{KCRV}})$ (µmol/mol)	$u(D_1)$ (µmol/mol)	$U(D_1)$ (k=2) (µmol/mol)
GUM	**D298392**	**379.664**	**0.044**	**380.100**	**2.200**	**0.436**	**2.200**	**4.401**
KRISS	**D500642**	**378.828**	**0.055**	**378.900**	**0.100**	**0.072**	**0.114**	**0.228**
LNE	**1029045**	**379.253**	**0.051**	**379.480**	**0.395**	**0.227**	**0.398**	**0.796**
NIM	**FB03747**	**383.453**	**0.052**	**383.430**	**0.100**	**-0.023**	**0.113**	**0.226**
NMIJ	**CPC00486**	**386.597**	**0.088**	**386.617**	**0.025****	**0.020**	**0.091**	**0.182**
NMISA	**M51 8232**	**379.743**	**0.050**	**380.200**	**1.000**	**0.457**	**1.001**	**2.002**
NOAA	**CC310084**	**379.511**	**0.046**	**379.500**	**0.105**	**-0.011**	**0.115**	**0.229**
NPL	**2179**	**380.269**	**0.041**	**380.270**	**0.095**	**0.001**	**0.103**	**0.207**
VNIIM	**M365601**	**380.182**	**0.042**	**380.200**	**0.055****	**0.018**	**0.069**	**0.138**
VSL	**5604614**	**378.937**	**0.051**	**378.900**	**0.140**	**-0.037**	**0.149**	**0.298**
UME	**PSM298266**	**380.017**	**0.071**	**379.920**	**0.095***	**-0.097**	**0.118**	**0.237**
BFKH	OMH54	374.884	0.099	379.800	0.850	4.916	0.856	1.711
NIST	FB04278	380.088	0.042	379.045	0.195	-1.044	0.200	0.400
NPLI	JJ108891	374.576	0.108	375.720	1.610	1.144	1.614	3.227

*Table 12. Degrees of Equivalence using FTIR measurement results at the nominal mole fraction of 380 µmol mol^{-1}. Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** Uncertainties below the cutoff value of 0.095 µmol mol^{-1}.*

Participant	Cylinder	x_{KCRV} (XLGENLINE predictied value from FTIR) (µmol/mol)	$u(x_{KCRV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{\mathrm{NMI}})$ (µmol/mol)	$D_2(x_{\mathrm{NMI}}$- $x_{\mathrm{KCRV}})$ (µmol/mol)	$u(D_2)$ (µmol/mol)	$U(D_2)$ (k=2) (µmol/mol)
GUM	**D298393**	**477.706**	**0.051**	**478.100**	**2.600**	**0.394**	**2.601**	**5.201**
INRIM	**D247440**	**479.007**	**0.173**	**479.300**	**0.800**	**0.293**	**0.819**	**1.637**
KRISS	**D500647**	**479.851**	**0.052**	**480.000**	**0.100**	**0.149**	**0.113**	**0.225**
LNE	**1029047**	**477.397**	**0.061**	**477.600**	**0.500**	**0.203**	**0.504**	**1.007**
NIM	**FB03744**	**489.202**	**0.099**	**489.150**	**0.110**	**-0.052**	**0.148**	**0.296**
NMIJ	**CPC00494**	**471.351**	**0.094**	**471.301**	**0.026****	**-0.050**	**0.097**	**0.195**
NMISA	**M51 8167**	**479.042**	**0.068**	**479.500**	**0.800**	**0.458**	**0.803**	**1.606**
NOAA	**CC305198**	**479.363**	**0.058**	**479.260**	**0.130**	**-0.103**	**0.142**	**0.284**

NPL	**2170**	**479.985**	**0.049**	**480.020**	**0.120**	**0.035**	**0.130**	**0.259**
VNIIM	**M365664**	**480.145**	**0.059**	**480.180**	**0.065****	**0.035**	**0.088**	**0.175**
VSL	**5604880**	**480.523**	**0.045**	**480.480**	**0.180**	**-0.043**	**0.186**	**0.371**
UME	**PSM266468**	**480.537**	**0.078**	**480.420**	**0.125***	**-0.117**	**0.147**	**0.295**
BFKH	OMH44	464.911	0.138	479.900	1.050	14.989	1.059	2.118
NIST	FB04300	473.529	0.071	472.662	0.214	-0.867	0.225	0.451
NPLI	JJ108862	480.863	0.079	480.520	1.520	-0.343	1.522	3.044

*Table 13. Degrees of Equivalence using FTIR measurement results at the nominal mole fraction of 480 μmol mol^{-1}. Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** Uncertainties below the cutoff value of 0.095 μmol mol^{-1}.*

Participant	Cylinder	x_{KCRV} (XLGENLINE predictied value from FTIR) (µmol/mol)	$u(x_{KCRV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{\text{NMI}})$ (µmol/mol)	$D_3(x_{\text{NMI}}-x_{\text{KCRV}})$ (µmol/mol)	$u(D_3)$ (µmol/mol)	$U(D_3)$ (k=2) (µmol/mol)
GUM	**D298402**	**800.105**	**0.106**	**800.500**	**4.300**	**0.395**	**4.301**	**8.603**
INRIM	**D247445**	**798.389**	**0.128**	**798.900**	**1.300**	**0.511**	**1.306**	**2.613**
KRISS	**D500672**	**800.519**	**0.118**	**800.800**	**0.200**	**0.281**	**0.232**	**0.464**
LNE	**1029048**	**802.099**	**0.078**	**802.200**	**0.850**	**0.101**	**0.854**	**1.707**
NMIJ	**CPC00558**	**803.694**	**0.114**	**803.658**	**0.039****	**-0.036**	**0.120**	**0.240**
NPL	**2181**	**799.744**	**0.101**	**799.700**	**0.200**	**-0.044**	**0.224**	**0.448**
NMISA	**M518244**	**798.187**	**0.132**	**799.100**	**0.500**	**0.913**	**0.517**	**1.034**
VNIIM	**M365707**	**800.697**	**0.084**	**800.730**	**0.095**	**0.033**	**0.127**	**0.253**
VSL	**5604705**	**796.080**	**0.191**	**795.700**	**0.300**	**-0.380**	**0.356**	**0.712**
UME	**PSM298347**	**800.917**	**0.083**	**800.760**	**0.180***	**-0.157**	**0.198**	**0.396**
NIM	FB03748	810.424	0.327	809.820	0.130	-0.604	0.351	0.703
NOAA	CB11668	794.608	0.237	794.080	0.240	-0.528	0.337	0.674
BFKH	OMH69	800.282	0.100	800.300	1.450	0.018	1.453	2.907
NIST	FB04287	795.511	0.208	794.530	0.514	-0.981	0.555	1.109
NPLI	JJ108854	794.501	0.239	796.380	2.515	1.879	2.526	5.053

*Table 14. Degrees of Equivalence using FTIR measurement results at the nominal mole fraction of 800 μmol mol^{-1}. Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** Uncertainties below the cutoff value of 0.095 μmol mol^{-1}.*

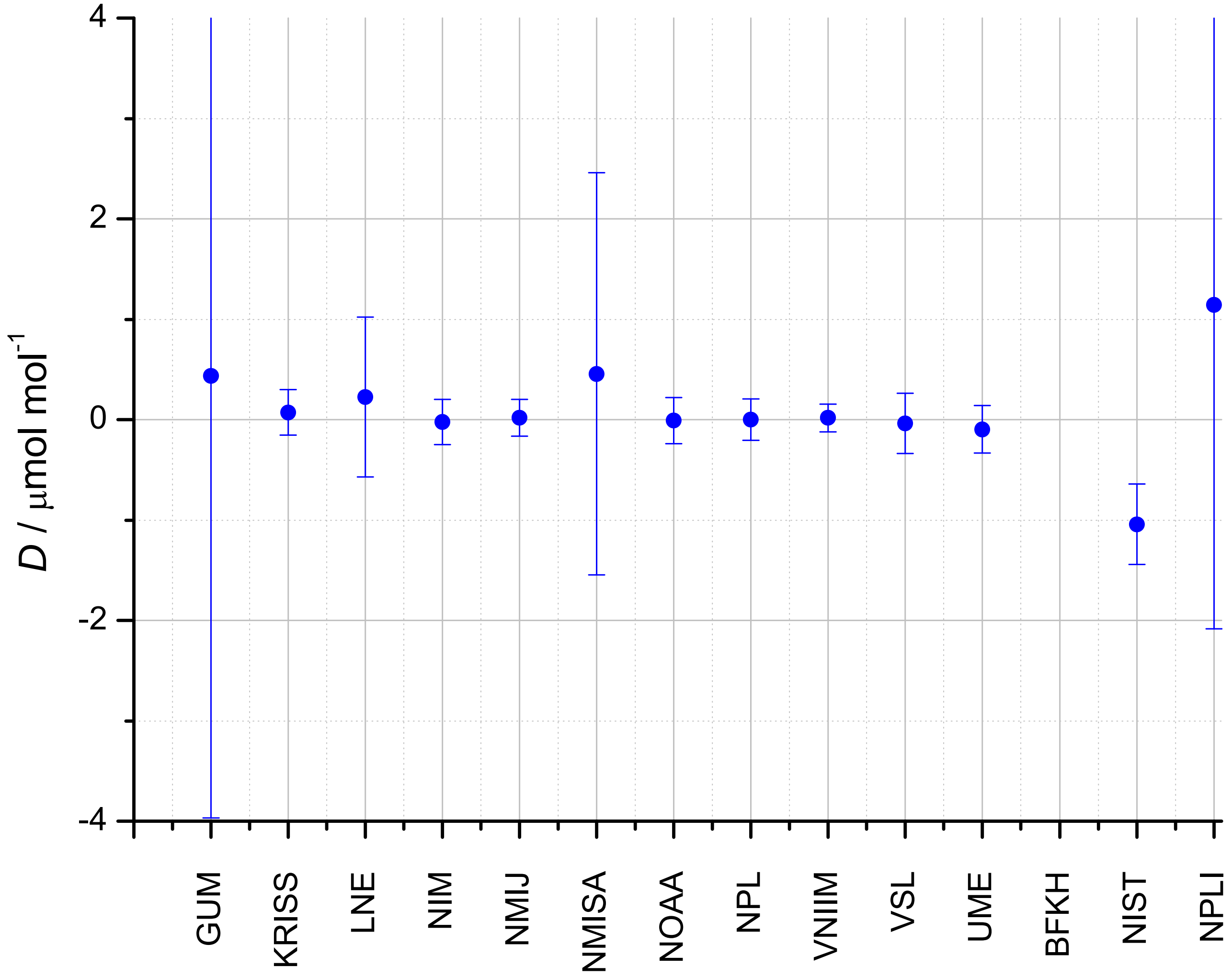

Figure 9**.** Degrees of Equivalence at a nominal value of 380 µmol/mol for CO_2 mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

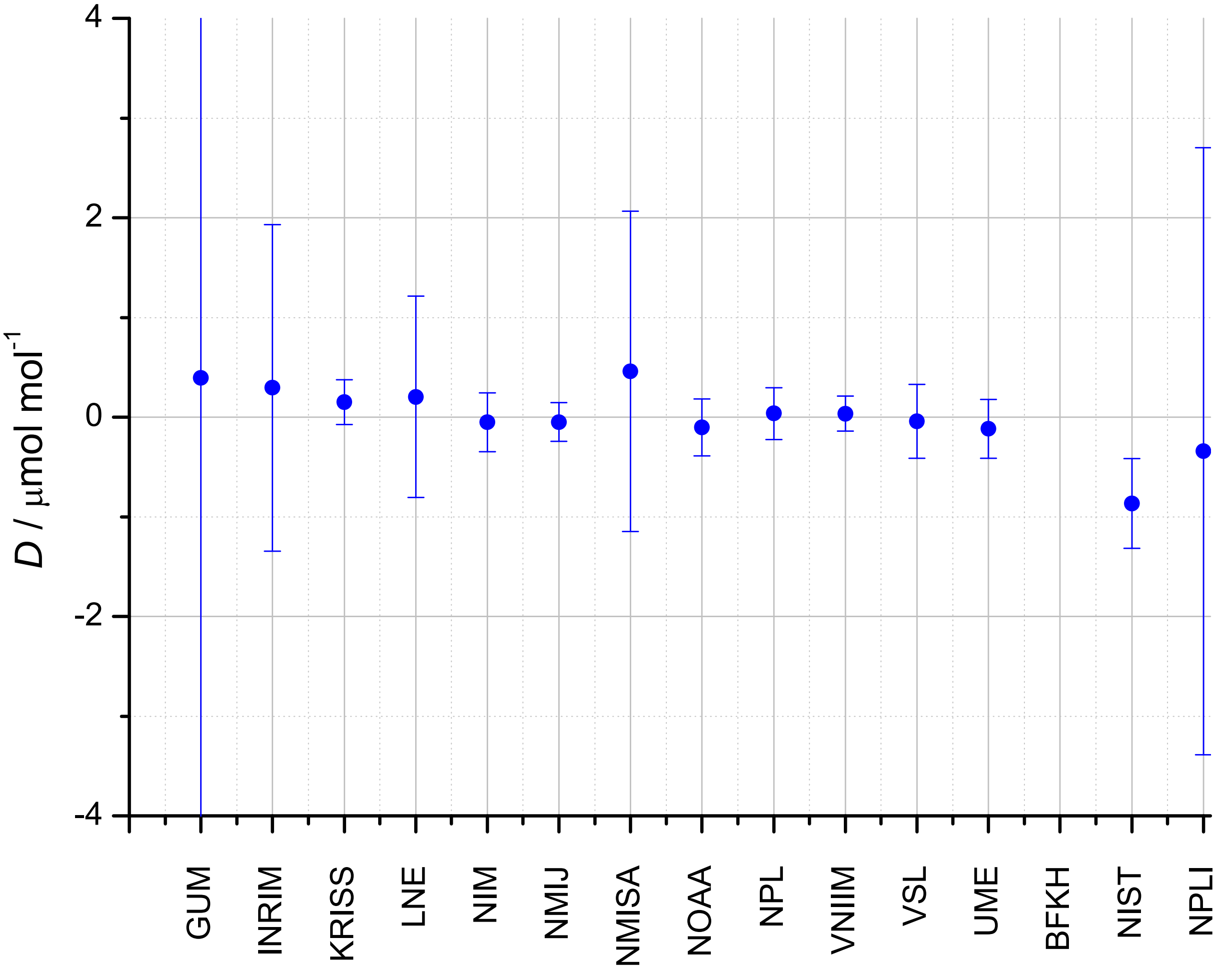

Figure 10. Degrees of Equivalence at a nominal value of 480 µmol/mol for CO_2 mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence..

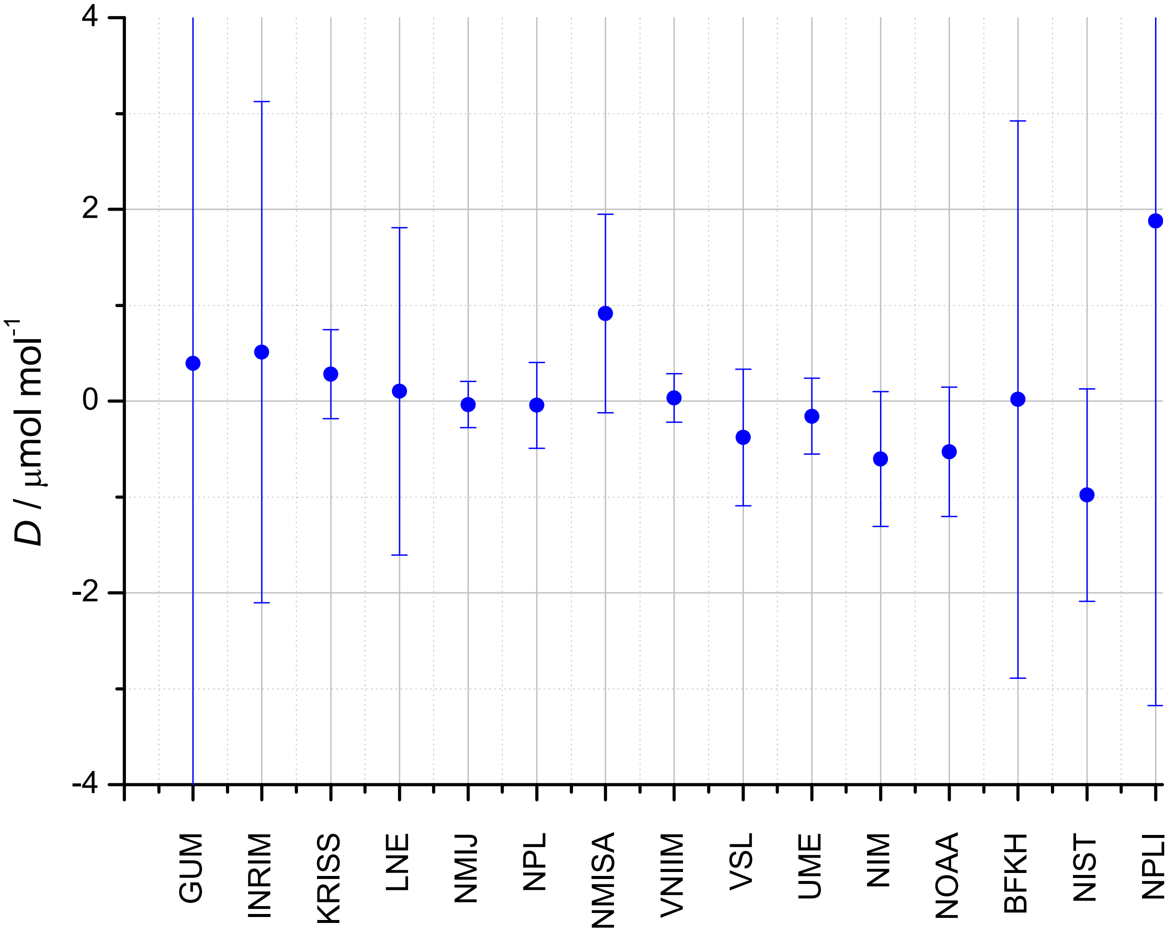

Figure 11. Degrees of Equivalence at a nominal value of 800 µmol/mol for CO_2 mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

9 Conclusions

The comparison have been successful in demonstrating the degrees of equivalence of CO_2 in air standards amongst participating NMIs at nominal mole fractions of 380 µmol/mol, 480 µmol/mol and 800 µmol/mol.

In addition, the results can be compared to those of CCQM-K52 (organized in 2006), allowing the following conclusions to be drawn:

a) the uncertainy of the key comparison reference value has been reduced by a factor of at least 4, with a standard uncertainty of 0.05 µmol/mol for CCQM-K120.a (compared to 0.2 µmol/mol for CCQM-K52);

b) methods based on spectroscopy (FTIR, with corrections for isotope ratios) and GC-FID for comparing CO_2 in air standards have demonstrated excellent agreement, with the standard deviation of the difference in reference values found by the two methods being 0.07 µmol/mol at 380 µmol/mol and 0.05 µmol/mol at 480 µmol/mol;

c) the uncertainties are now at the level where adsorption effects within cylinders and on surfaces needs to be considered, and this has led to a mnimium value of 0.095 µmol/mol being used as the standard uncertainty for standards for key comparison reference value calculation;

d) providing standards to communities measuring atmospheric CO_2 with spectroscopic methods produced with CO_2 originating from combustion sources can lead to isotope ratios in the CO_2 which will produce biases in mole fractions measurements of up to 0.3 µmol/mol. These biases can be corrected by either measuring isotope ratios of the gas standard and appropriate processing by the user, or by using CO_2 which has been closely matched to atmospheric isotope ratio values in the production of the standard.

10 'How far the light shines' statement

The following 'How far the light shines' statement agreed during the 38th meeting of the CCQM GAWG, was:

CCQM-K120.a comparison involves preparing standards of carbon dioxide in air which are fit for purpose for the atmospheric monitoring community, with stringent requirements on matrix composition and measurement uncertainty of the CO_2 mole fraction. This represents an analytical challenge and is therefore considered as a Track C comparison. The comparison will underpin CMC claims for CO_2 in air for standards and calibrations services for the atmospheric monitoring community, matrix matched to real air, over the mole fraction range of 250 µmol/mol to 520 µmol/mol.

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 mole 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

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ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018)

As results of the discussion of the key points of the *Draft A* report of the CCQM-K120 comparison during the 38th meeting of the CCQM GAWG the following decisions were taken:

a) the key comparison reference value for CCQM-K120.a and CCQM-K120.b are to be based on the measurement results of the FTIR spectrometer;

b) the re-submitted uncertainties by UME replace the original uncertainty values used in *Draft A* report (see Table 15) and are to be used for the calculation of the KCRV;

c) NIST, NPLI, and BFKH submitted new measurement results as well as uncertainties after the measurements performed on return of the standards in their laboratoires. This was not expected in the protocol of the comparison. Therefore their values have not been used in the KCRV calucltaions. The original values are used for DOE calculations, the modified values have been included in AnnexII;

d) considering that NPL was the only participant that considered a potential effect of adsorption of a proportion of the molecules onto the internal surface of a cylinder and valve (for more information see GAWG/18-00) a limit on the uncertainties claimed by participants contributing to the KCRV is fixed to 0.095 µmol mol^{-1} meaning that any uncertainty value smaller to this value will be replaced by 0.095 µmol mol^{-1} to calculate KCRVs;

e) The KCRV for the standatds at the nominal mole fraction of 800 µmol mol^{-1} are to be calculated including standards with mole fractions within ± 5 µmol mol^{-1} of the nominal value (795 µmol mol^{-1} to 805 µmol mol^{-1}).

ANNEX II- Stability studies by participants

After the return of cylinder to the participants and before results of the comparison were known, four participants reported modified uncertainties and also values and uncertainties compared to their originally reported values, see Table 15.

The participants that reported changes to their originally submitted values were:

- BFKH: submitted the same values but with less decimals for cylinders OMH54 and OMH69 and proposed a new value for cylinder OMH44. The new value changed from 479.89±2.11 µmol/mol to 464.4±2.11 µmol/mol.
- NIST: submitted new values and uncertainties for cylinders FB04278, FB04300 and FB04287.
- NPLI: submitted new values for cylinders JJ108891, JJ108862 and JJ108854. The mole fractions for cylinders JJ108891 and JJ108854 were increased by 2.52 µmol/mol and 2.42 µmol/mol, respectively, and reduced for cylinder JJ108862 by 1.95 µmol/mol. The uncertainties for cylinders JJ108891 and JJ108862 were also increased by 22 % and 72 % but reduced for cylinder JJ108854 by 33 %.
- UME: The uncertainties of cylinders PSM298266, PSM266468 and PSM298347 were increased by 19%, 47% and 33 %, respectively.

Participant	Cylinder references	Gas Matrix	NMI's assigned CO2 mole fraction x_{NMI} (µmol mol^{-1})	NMI's assigned CO_2 expanded uncertainty $U(x_{\text{NMI}})$ $k = 2$ (µmol mol^{-1})
		Before the return of cylinders		
BFKH	OMH54	Synthetic Air	379.840	1.710
BFKH	OMH44	Synthetic Air	479.890	2.110
BFKH	OMH69	Synthetic Air	800.300	2.920
GUM	D298392	Synthetic Air	380.100	4.400
GUM	D298393	Synthetic Air	478.100	5.200
GUM	D298402	Synthetic Air	800.500	8.600
INRIM	D247440	Synthetic Air	479.300	1.600
INRIM	D247445	Synthetic Air	798.900	2.600
KRISS	D500642	Synthetic Air	378.900	0.200
KRISS	D500647	Synthetic Air	480.000	0.200
KRISS	D500672	Synthetic Air	800.800	0.400
LNE	1029045	Synthetic Air	379.480	0.790
LNE	1029047	Synthetic Air	477.600	1.000
LNE	1029048	Synthetic Air	802.200	1.700
NIM	FB03747	Synthetic Air	383.430	0.200
NIM	FB03744	Synthetic Air	489.150	0.220

NIM	FB03748	Synthetic Air	809.820	0.260
NIST	FB04278	Real Air	379.045	0.391
NIST	FB04300	Real Air	472.662	0.428
NIST	FB04287	Real Air	794.533	1.029
NMIJ	CPC00486	Real Air	386.617	0.050
NMIJ	CPC00494	Real Air	471.301	0.051
NMIJ	CPC00558	Real Air	803.658	0.078
NMISA	M51 8232	Synthetic Air	380.200	2.000
NMISA	M51 8167	Synthetic Air	479.500	1.600
NMISA	M51 8244	Synthetic Air	799.100	1.000
NOAA	CC310084	Real Air	379.500	0.210
NOAA	CC305198	Real Air	479.260	0.260
NOAA	CB11668	Real Air	794.080	0.480
NPL	2179	Synthetic Air	380.270	0.190
NPL	2170	Synthetic Air	480.020	0.240
NPL	2181	Synthetic Air	799.700	0.400
NPLI	JJ108891	Synthetic Air	375.720	3.220
NPLI	JJ108862	Synthetic Air	480.520	3.040
NPLI	JJ108854	Synthetic Air	796.380	5.030
UME	PSM298266	Synthetic Air	379.920	0.160
UME	PSM266468	Synthetic Air	480.420	0.170
UME	PSM298347	Synthetic Air	800.760	0.270
VNIIM	M365601	Synthetic Air	380.200	0.110
VNIIM	M365664	Synthetic Air	480.180	0.130
VNIIM	M365707	Synthetic Air	800.730	0.190
VSL	5604614	Synthetic Air	378.900	0.280
VSL	5604880	Synthetic Air	480.480	0.360
VSL	5604705	Synthetic Air	795.700	0.600

Additional data received following stability testing

BFKH-2nd value	OMH54	Synthetic Air	379.8	1.7
BFKH-2nd value	OMH44	Synthetic Air	464.4	2.8
BFKH-2nd value	OMH69	Synthetic Air	800.3	2.9
NIST-2nd value	FB04278	Real Air	380.30	0.28
NIST-2nd value	FB04300	Real Air	473.40	0.34
NIST-2nd value	FB04287	Real Air	795.12	0.58
NIST-3th value	FB04278	Real Air	380.07	0.30
NIST-3th value	FB04300	Real Air	473.37	0.52
NIST-3th value	FB04287	Real Air	794.77	0.38
NPLI-2nd value	JJ108891	Synthetic Air	378.24	3.95
NPLI-2nd value	JJ108862	Synthetic Air	478.57	5.23
NPLI-2nd value	JJ108854	Synthetic Air	798.80	3.35
UME-2nd value	PSM298266	Synthetic Air	379.920	0.19

UME-2nd value	PSM266468	Synthetic Air	480.420	0.25
UME-2nd value	PSM298347	Synthetic Air	800.760	0.36

Table 15. Standards and reported values provided by participants in Draft A report.

ANNEX III- GC-FID results

GC-FID based candidate reference values for standards at a nominal mole fraction of 380 μmol mol^{-1}

With the GC-FID measurement data set the set of self-consistent standards identified was the same as with FTIR, including eleven standards with three excluded, namely OMH54 (BFKH, neither original nor newly submitted results included), FB04278 (NIST, neither original nor newly submitted results included) and JJ108891 (NPLI, neither original and newly submitted results included).

The goodness-of-fit parameter obtained from the regression performed with this data set was 1.69 (< 2 required to demonstrate consistency of the ensemble). Reference values and differences from these are listed in
Table 16.

The difference between the KCRV calculated with FTIR measurement data (x_{KCRV_FTIR}) and GC-FID based candidate reference values (x_{RV_FTIR}) measurements for this batch of cylinders is plotted in Figure 12, showing negligible difference between the methods.

GC-FID based candidate reference values for standards at a nominal mole fraction of 480 μmol mol^{-1}

With the GC-FID measurement data set the set of self-consistent standards identified was the same as with FTIR. The data set of self-consistent standards identified included twelve standards with three excluded, namely OMH44 (BFKH, neither original nor newly submitted results included), FB03744 (NIST, neither original nor newly submitted results included) and JJ108862 (NPLI, neither original nor newly submitted results included). The goodness-of-fit parameter obtained from the regression performed with this data set was 1.41 (< 2 required to demonstrate consistency of the ensemble). Reference values and differences from these are listed in
Table 17.

The difference between the KCRV calculated with FTIR measurement data (x_{KCRV_FTIR}) and GC-FID based candidate reference values (x_{RV_FTIR}) measurements for this batch of cylinders is plotted in Figure 13, showing negligible difference between the methods.

GC-FID based candidate reference values for standards at a nominal mole fraction of 800 µmol mol^{-1}

Including ten cylinders with five excluded, namely FB03748 (NIM), CB11668 (NOAA), OMH69 (BFKH, neither original and newly submitted results included), FB04287 (NIST, neither original nor newly submitted results included) and JJ108854 (NPLI, neither original nor newly submitted results included), the goodness-of-fit parameter obtained from the regression performed with this data set was 1.91(< 2 required to demonstrate consistency of the ensemble). Reference values and differences from these are listed in Table 18.

The difference between the KCRV calculated with FTIR measurement data (x_{KCRV_FTIR}) and GC-FID based candidate reference values (x_{RV_FTIR}) measurements for this batch of cylinders is plotted in Figure 14, showing negligible difference between the methods.

Participant	Cylinder	x_{RV} (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{RV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{NMI})$ (µmol/mol)	$D_I(x_{NMI}-x_{KCRV})$ (µmol/mol)	$u(D_I)$ (µmol/mol)	$U(D_I)$ (k=2) (µmol/mol)
GUM	**D298392**	**379.719**	**0.050**	**380.100**	**2.200**	**0.381**	**2.201**	**4.401**
KRISS	**D500642**	**378.753**	**0.063**	**378.900**	**0.100**	**0.147**	**0.118**	**0.236**
LNE	**1029045**	**379.224**	**0.054**	**379.480**	**0.395**	**0.256**	**0.399**	**0.797**
NIM	**FB03747**	**383.350**	**0.056**	**383.430**	**0.100**	**0.080**	**0.115**	**0.229**
NMIJ	**CPC00486**	**386.624**	**0.092**	**386.617**	**0.025****	**-0.007**	**0.095**	**0.190**
NMISA	**M51 8232**	**379.866**	**0.054**	**380.200**	**1.000**	**0.334**	**1.001**	**2.003**
NOAA	**CC310084**	**379.426**	**0.065**	**379.500**	**0.105**	**0.074**	**0.124**	**0.247**
NPL	**2179**	**380.308**	**0.048**	**380.270**	**0.095**	**-0.038**	**0.106**	**0.213**
VNIIM	**M365601**	**380.221**	**0.051**	**380.200**	**0.055****	**-0.021**	**0.075**	**0.150**
VSL	**5604614**	**378.973**	**0.062**	**378.900**	**0.140**	**-0.073**	**0.153**	**0.306**
UME	**PSM298266**	**380.106**	**0.055**	**379.920**	**0.095***	**-0.186**	**0.110**	**0.220**
BFKH	OMH54	375.005	0.101	379.800	0.850	4.795	0.856	1.712
NIST	FB04278	380.066	0.055	379.045	0.195	-1.021	0.203	0.406
NPLI	JJ108891	374.617	0.105	375.720	1.610	1.103	1.613	3.227

*Table 16. Difference from candidate reference value using GC-FID measurements at the nominal mole fraction of 380 µmol mol^{-1}. * Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** First uncertainty submitted by the participant (< 0.095 µmol mol^{-1}, see ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018).*

Participant	Cylinder	x_{RV} (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{RV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{\mathrm{NMI}})$ (µmol/mol)	$D_2(x_{\mathrm{NMI}} - x_{\mathrm{KCRV}})$ (µmol/mol)	$u(D_2)$ (µmol/mol)	$U(D_2)$ (k=2) (µmol/mol)
GUM	**D298393**	**477.789**	**0.065**	**478.100**	**2.600**	**0.311**	**2.601**	**5.202**
INRIM	**D247440**	**478.928**	**0.056**	**479.300**	**0.800**	**0.372**	**0.802**	**1.604**
KRISS	**D500647**	**479.881**	**0.051**	**480.000**	**0.100**	**0.119**	**0.112**	**0.225**
LNE	**1029047**	**477.444**	**0.069**	**477.600**	**0.500**	**0.156**	**0.505**	**1.009**
NIM	**FB03744**	**489.173**	**0.097**	**489.150**	**0.110**	**-0.023**	**0.147**	**0.294**
NMIJ	**CPC00494**	**471.327**	**0.107**	**471.301**	**0.026****	**-0.026**	**0.110**	**0.220**
NMISA	**M51 8167**	**479.137**	**0.078**	**479.500**	**0.800**	**0.363**	**0.804**	**1.608**
NOAA	**CC305198**	**479.392**	**0.053**	**479.260**	**0.130**	**-0.132**	**0.140**	**0.281**
NPL	**2170**	**479.997**	**0.056**	**480.020**	**0.120**	**0.023**	**0.133**	**0.265**
VNIIM	**M365664**	**480.173**	**0.052**	**480.180**	**0.065****	**0.007**	**0.083**	**0.167**
VSL	**5604880**	**480.608**	**0.051**	**480.480**	**0.180**	**-0.128**	**0.187**	**0.374**
UME	**PSM266468**	**480.629**	**0.053**	**480.420**	**0.125***	**-0.209**	**0.136**	**0.272**
BFKH	OMH44	464.994	0.144	479.900	1.050	14.906	1.060	2.120
NIST	FB04300	473.601	0.077	472.662	0.214	-0.940	0.227	0.455
NPLI	JJ108862	480.836	0.055	480.520	1.520	-0.316	1.521	3.042

*Table 17. Difference from candidate reference value using GC-FID measurements at the nominal mole fraction of 480 µmol mol^{-1}. Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** First uncertainty submitted by the participant (< 0.095 µmol mol^{-1}, see ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018).*

Participant	Cylinder	x_{RV} (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{RV})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{\mathrm{NMI}})$ (µmol/mol)	$D_3(x_{\mathrm{NMI}} - x_{\mathrm{KCRV}})$ (µmol/mol)	$u(D_3)$ (µmol/mol)	$U(D_3)$ (k=2) (µmol/mol)
GUM	**D298402**	**800.002**	**0.083**	**800.500**	**4.300**	**0.498**	**4.301**	**8.602**
INRIM	**D247445**	**798.031**	**0.105**	**798.900**	**1.300**	**0.869**	**1.304**	**2.608**
KRISS	**D500672**	**800.316**	**0.080**	**800.800**	**0.200**	**0.484**	**0.215**	**0.431**
LNE	**1029048**	**802.001**	**0.068**	**802.200**	**0.850**	**0.199**	**0.853**	**1.705**
NMIJ	**CPC00558**	**803.670**	**0.057**	**803.658**	**0.039****	**-0.012**	**0.069**	**0.138**
NPL	**2181**	**799.570**	**0.081**	**799.700**	**0.200**	**0.130**	**0.216**	**0.432**
NMISA	**M51 8244**	**798.195**	**0.111**	**799.100**	**0.500**	**0.905**	**0.512**	**1.024**
VNIIM	**M365707**	**800.710**	**0.066**	**800.730**	**0.095**	**0.020**	**0.116**	**0.232**
VSL	**5604705**	**795.715**	**0.150**	**795.700**	**0.300**	**-0.015**	**0.335**	**0.670**
UME	**PSM298347**	**801.042**	**0.180**	**800.760**	**0.135***	**-0.282**	**0.172**	**0.344**
NIM	FB03748	810.535	0.165	809.820	0.130	-0.715	0.210	0.420
NOAA	CB11668	794.338	0.170	794.080	0.240	-0.258	0.294	0.588
BFKH	OMH69	800.057	0.079	800.300	1.450	0.243	1.452	2.904

NIST	FB04287	795.279	0.147	794.530	0.514	-0.749	0.535	1.070
NPLI	JJ108854	794.091	0.173	796.380	2.515	2.289	2.521	5.042

*Table 18. Difference from candidate reference value using GC-FID measurement results at the nominal mole fraction of 800 µmol mol^{-1}. Bold: Data points included in the self-consistent set. *Re-submitted value following the decision of the the CCQM GAWG. ** First uncertainty submitted by the participant (< 0.095 µmol mol^{-1}, see ANNEX I- Decisions of the 38th meeting of the CCQM GAWG (16-17 April 2018).*

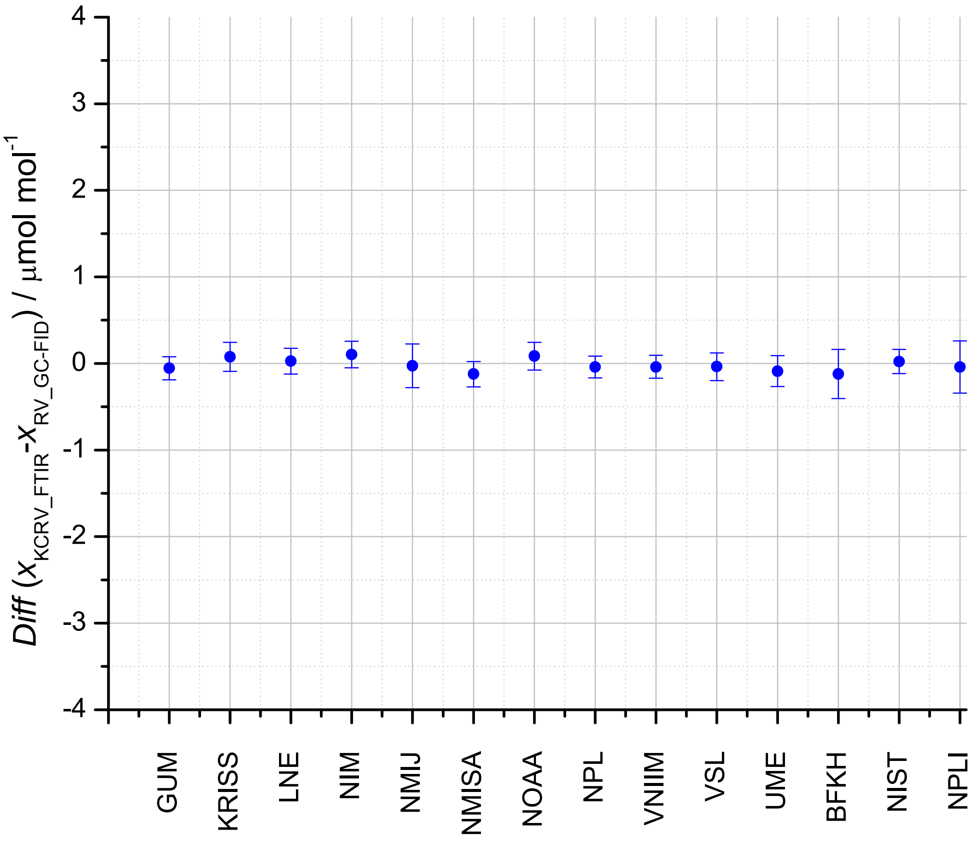

Figure 12. Difference between the KCRV values obtained using FTIR and GC-FID reference values at 380 µmol/mol. The error bar represents the expanded uncertainty at a 95 % level of confidence..

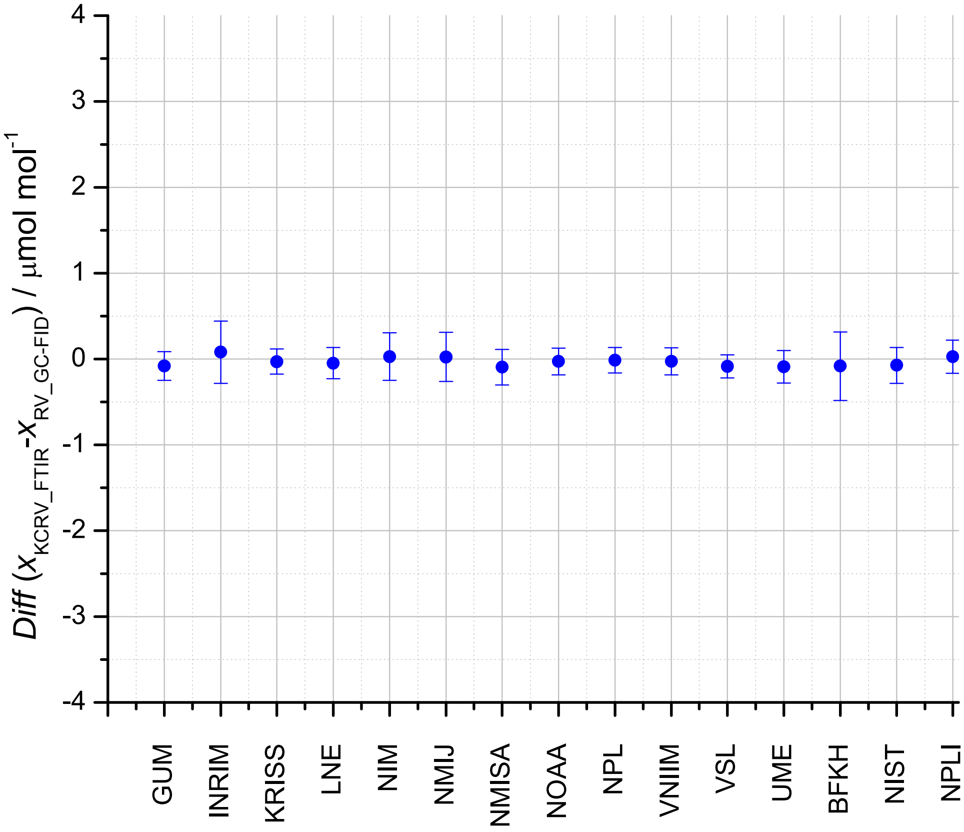

Figure 13. Difference between the KCRV values obtained using FTIR and GC-FID reference values at 480 µmol/mol. The error bar represents the expanded uncertainty at a 95 % level of confidence..

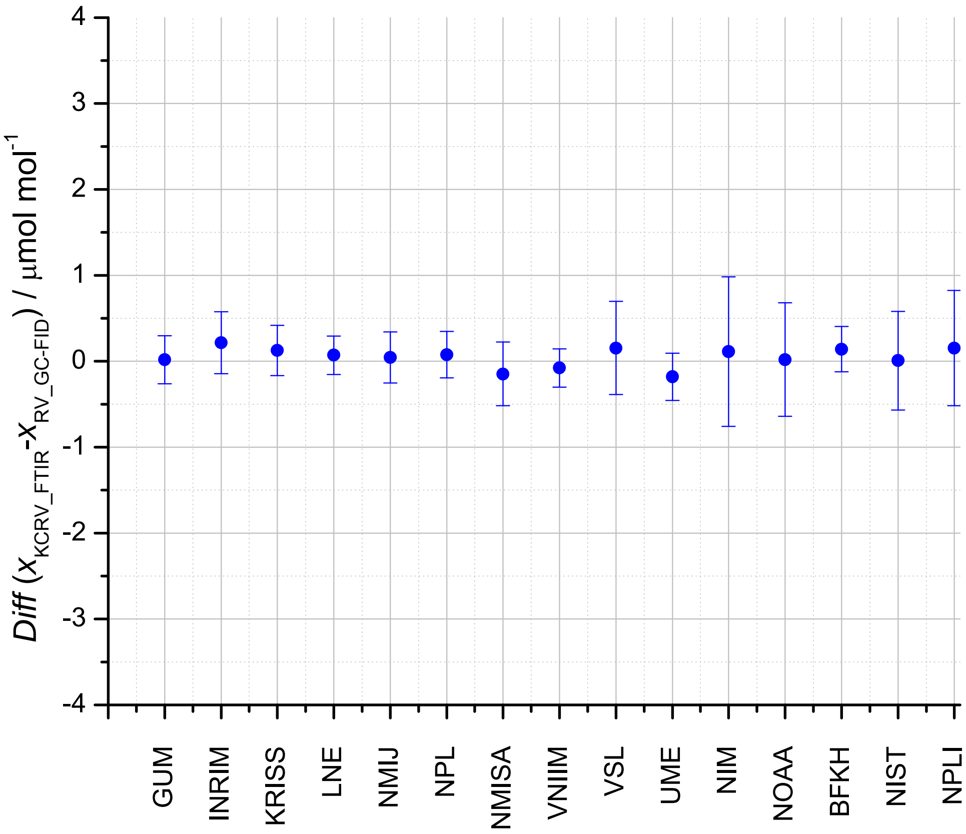

Figure 14 Difference between the KCRV values obtained using FTIR and GC-FID reference values at 800 µmol/mol. The error bar represents the expanded uncertainty at a 95 % level of confidence.

In summary the measurement performance obtained with GC-FID and FTIR, at the BIPM were rather similar with standard measurement uncertainties of the reference values having a range of:

- 0.04 µmol/mol to 0.11 µmol/mol at 380 µmol/mol nominal mole fraction CO_2 for FTIR;
- 0.05 µmol/mol to 0.11 µmol/mol at 380 µmol/mol nominal mole fraction CO_2 for GC-FID;
- 0.05 µmol/mol to 0.17 µmol/mol at 480 µmol/mol nominal mole fraction CO_2 for FTIR;
- 0.05 µmol/mol to 0.14 µmol/mol at 480 µmol/mol nominal mole fraction CO_2 for GC-FID;
- 0.08 µmol/mol to 0.33 µmol/mol at 800 µmol/mol nominal mole fraction CO_2 for FTIR;
- 0.06 µmol/mol to 0.18 µmol/mol at 800 µmol/mol nominal mole fraction CO_2 for GC-FID;

The reference values calculated from the two measurement techniques agree with each other within their stated uncertainties for: all measurement results at the nominal mole fraction of 380 µmol/mol; all measurement results at the nominal mole fraction of 480 µmol/mol; all measurement results at the nominal mole fraction of 800 µmol/mol.

The magnitude of the proposed reference values can be compared to the laboratories reported standard measurement uncertainties for their standards which range from 0.025 µmol/mol to 4.3 µmol/mol.

ANNEX IV- BIPM Value assignment procedure

The cylinders were analysed in batches, first by GC-FID, then by FTIR, and finally by the Delta Ray.

GC-FID

The GC-FID is a modified Agilent system series 7890A acquired from the SRA Instruments 'France. It is equipped with a flame ionization detector (FID), a Haysep Q (12 feet) column, a methanizer and the FID detector is supplied with pure oxygen and hydrogen (see Figure 15).

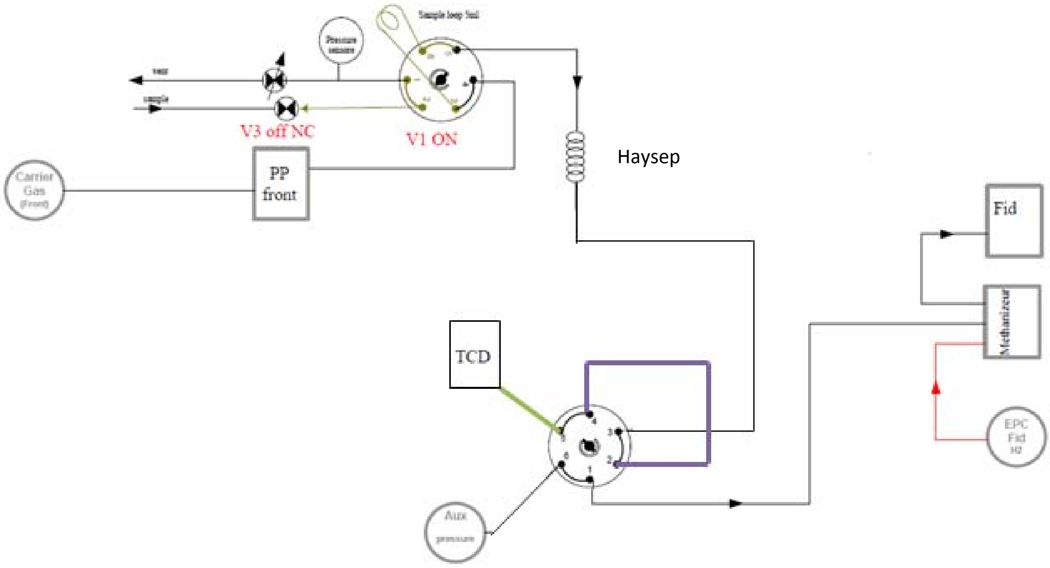

Figure 15 : Internal schematics of the BIPM system for Gas Chromatography with Flame Ionization Detector (GC-FID) comprised by a Haysep (12 feet) column, a Sample loop of 1 mL, two Valco six port valves and a FID detector.

The GC-FID is equipped with:

- two 6 port valve V1 (Vici-valco);
- one 1 mL stainless steel injection loop;
- one one-way valve;
- one Haysep Q (80-100 Mesh 12ftx1/8x2.0mm)
- one flame ionization detector (FID);
- one methanizer;
- one hydrogen generator;
- one helium purifier;
- one control computer for the GC-FID equipped with:
    - ChemStation version Rev. B.04.02 (118)
    - ProChem Set-up version 2.5.7
    - ProChem software version 2.0.1.
- one barometer (Sensor Technique DC 25/10)

The gas mixtures used for operating the facility were:

- one helium 6.0 gas cylinder, quality 99.9999%
- one oxygen 5.5 in gas cylinder, quality 99.9995 %.
- source of air with pressure of 7 bars.
- one 50 L CO_2/air commercial secondary gas standards (control standard *A*), produced by Messer, with an initial internal pressure of 150 bar with the composition specified to be within the following ranges:
  CH_4: 1.85 ppm;
  CO_2: 386 ppm;
  Ar: 9410 ppm;
  O_2: 20.7 %;
  N_2: Matrix gas.
- one 50 L CO_2/air commercial secondary gas standards (control standard *B*), produced by Messer, with an initial internal pressure of 150 bar with the composition specified to be within the following ranges:
  CH_4: 1.84 ppm;
  CO_2: 476 ppm;
  Ar: 9415 ppm;
  O_2: 21.0 %;
  N_2: Matrix gas.
- one 40 L CO_2/air standard (control standard *C*), produced by Scott Marrin (cylinder CB 10422), with an initial internal pressure of 100 bar with the composition specified to be within the following ranges:
  CO_2: 791.12 ppm;
  CH_4: 1.84 ppm;

GC-FID separation and quantification method

The GC-FID was operated at 30 °C. A Haysep Q (80-100 Mesh 12ftx1/8x2.0mm) column was used at a temperature of 30 °C for the analysis. Helium column carrier[2], gas passed through a heated gas purifier, was used at a flow rate of 40 ml min^{-1}. The FID was supplied with 320 ml min^{-1} of pure oxygen[3] and 40 ml min^{-1} of hydrogen[4]. A 1 ml stainless steel sample loop was used to introduce the CO_2/air sample onto the column. The pressure in the sample loop was measured by a calibrated pressure sensor having a resolution of 0.2 hPa and recorded at each injection. Finally the peak areas were estimated with an on-line computing integrator.

Sampling sequence

Table 19 displays a typical sampling sequence. The sampling sequence was setup so as to analyse six unkown CO_2/Air gas mixtures together with three control standards (*A*, *B*, *C*). Three unknown were bracketed by control standards *A* and *B*, followed by the other three bracketed by

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[2] The Carrier Gas is He grade 6.0 passing through a SAES getters® PS2-GC50-R-2 for extra purification.

[3] The Flame is produced from Oxygen grade 5.5.

[4] Hydrogen is produced on site by a commercial H_2 generator CG2200 (Claind). It produces grade 6.0 H_2 at a maximum flow rate of 200 ml/min with a purity higher than 99,99999%.

control standards *B* and *C*. Each individual cylinders analysis (unkowns and controls) consisted in three successive measurements of the GC-FID response (CO_2 peak area).

Control Cylinder *A*	A_1, A_2, A_3
Control Cylinder *B*	B_1, B_2, B_3
Cylinder 1	$Cyl_{1,1}, Cyl_{1,2}, Cyl_{1,3}$
Cylinder 2	$Cyl_{2,1}, Cyl_{2,2}, Cyl_{2,3}$
Cylinder 3	$Cyl_{3,1}, Cyl_{3,2}, Cyl_{3,3}$
Control Cylinder *A*	A_4, A_5, A_6
Control Cylinder *B*	B_4, B_5, B_6
Control Cylinder *B*	B_7, B_8, B_9
Control Cylinder *C*	C_1, C_2, C_3
Cylinder 4	$Cyl_{4,1}, Cyl_{4,2}, Cyl_{4,3}$
Cylinder 5	$Cyl_{5,1}, Cyl_{5,2}, Cyl_{5,3}$
Cylinder 6	$Cyl_{6,1}, Cyl_{6,2}, Cyl_{6,3}$
Control Cylinder *B*	B_{10}, B_{11}, B_{12}
Control Cylinder *C*	C_4, C_5, C_6

Table 19. Typical GC-FID sampling sequence.

Considering that the analysis of each CO_2/Air gas mixture took 10 minutes, this measuring sequence took about 390 minutes to be completed. This sequence was repeated four times, with the first one not used in the calculation. Adding flushing and conditioning, about three days were necessary to complete the analysis of six unkown cylinders.

Participant's cylinders were divided in batches of four to six and additional cylinders of the BIPM were added if required to obtain batches of equal size.

It was checked that the results obtained using controls *A, B* and *C* were consistent, but only the ratios to the control cylinder *B* were used as GC-FID results and listed in Table 8.

Ratios to the control standard

The ratios to the control cylinder were calculated determining first the average responses of three successive measurements performed on the CO_2/Air standard gas mixtures as well as on the control cylinders (*A, B* and *C*). The drift corrected response to the control cylinder as any time was calculated by interpolation in between two control measurements. The average response to the CO_2/air standards mixtures was then divided by the drift corrected response of the control cylinder to obtain $\overline{R}_{GC}$, the ratio for one cylinder in one sequence.

The last three sequences were then combined with the calculation of the weighted mean $\overline{R}_{wGC}$ defined as

$$\overline{R}_{wGC} = \sum_{l=1}^{3} w_l \overline{R}_{wGC\_l} \tag{1}$$

Where the weigth w_l for the series l is defined as

$$w_l = \frac{1/u\left(\overline{R}_{GC\_l}\right)^2}{\sum_{j=1}^{3} 1/u\left(\overline{R}_{GC\_l}\right)^2} \tag{2}$$

and $u\left(\overline{R}_{GC\_l}\right)$ is the standard deviation of the mean of the three repeats.

The uncertainty of the weighted mean, $(\overline{R}_{wGC})$, is defined as:

$$u\left(\overline{R}_{wGC}\right)^2 = \frac{1}{\sum_{l=1}^{3} 1/u\left(\overline{R}_{GC\_l}\right)^2} \tag{3}$$

In addition to this component, the intermediate precision, or stability of the instrument response during the full measuring period, was evaluated by the standard deviation of the mean of the drift corrected ratio to the control cylinder of one standard exclusively used for this purpose, giving $u_{\mathrm{Intpre}} = 0.000046$. This component was further combined with the weighted mean uncertainty to provide the combined standard uncertainty associated with measurements performed with GC-FID, resulting in a typical relative standard uncertainty of 0.007 %.

FTIR

A vacuum Bruker Vertex 70v FTIR Spectrometer equipped with a RockSolid interferometer (vacuum better than 0.2 hPa), with 1 cm^{-1} resolution (0.16 optional), a 40 mm beam diameter, a globar source and CaF_2 beam splitter was used for the study. The spectrometer was configured with a liquid N_2-cooled mid-infrared Indium Antimonide (InSb) detector and a 10.01 m multi-pass White-type gas cell of volume 0.75 L (Gemini Scientific Instruments, USA). The wetted surfaces of the gas cell were electro-polished stainless steel treated with silconert 2000 (Silcotek) and gold (mirror coatings) to minimize surface adsorption and desorption effects for CO_2. The interferometer was scanned at 64 scans min^{-1} and spectra co-added for five minutes to obtain an acceptable signal-to-noise ratio. The transmission spectra of gas reference standards obtained following this procedure had a very high signal to noise ratio of typically ~1 x 10^4 peak-peak from (2240–3380) cm^{-1}. In order to prevent nonlinear responses produced by excess photon flux reaching the InSb detector special care was put into adjusting the instrument parameters of the software to ensure that the apparent intensity from the InSb detector was zero at 1850 cm^{-1}.

The spectrometer user interface was controlled using a BIPM developed software named B-FOS, that allowed the automatic setting of all instrument parameters into Bruker's proprietary OPUS software for control, spectral acquisition and on-line analysis through the use of MALT (Multiple Atmospheric Layer Transmission)[3, 4, 6] spectrum analysis software, version 5.56.

MALT retrieves concentrations of each trace gas in the sample from a least-squares fit to the measured spectrum based on a model calculation and Hitran line parameters[12]. This code is the basis for quantitative analysis of open and closed path FTIR trace gas measurements and has been compared with other codes such as SFIT[1] for ground based solar FT-IR measurements with agreement of better than 0.7 % (Griffith et al.[8]).

The spectra were constructed by co-adding up to 320 scans recorded in about 5 minutes to provide a single spectrum of a sample. This single spectrum was ratioed with a similar spectrum of ultra-pure N_2 collected under similar conditions to provide an absorbance or transmission spectrum of the gas sample (relative to ultra-pure N_2) in the gas cell. The sample flow rates were kept at ~400 mL min^{-1}. Assuming perfect mixing in the cell it was estimated that 99.9 % of the sample was replaced after 10 min of flow, and 99.998 % replaced after 20 min[10]. In order to ensure the complete exchange of samples, only the measured spectra obtained after flowing the sample through the White-type cell for 40 min (99.99999 % gas replacement) were used for mole fraction determinations. The sample pressure was measured by means of the calibrated barometer Mensor Series 6000. The relative uncertainty of this pressure sensor was $u(P)$ = 0.02 %. The sample temperature was measured with a calibrated 100 Ω RTD temperature probe introduced into the outlet gas of the White-type gas cell with a standard uncertainty $u(T)$=0.02 K.

The recorded spectra were analysed online by non-linear least squares fitting in the spectra region 3500–3800 cm^{-1} (plotted in Figure 16) with modelled spectra calculated by MALT 5.5 using absorption line parameters from the HITRAN database version 2012. As previously described by Griffith et al.[7], this region shows peaks that are due to the major isotopologue $^{12}C^{16}O^{16}O$ (written 626 using the Hitran/Air Force Geophysics Laboratory (AFGL) shorthand notation [11]). Since all standards used during this work were ultra-dry CO_2/air gas mixtures the cross sensitivity with H_2O was not considered.

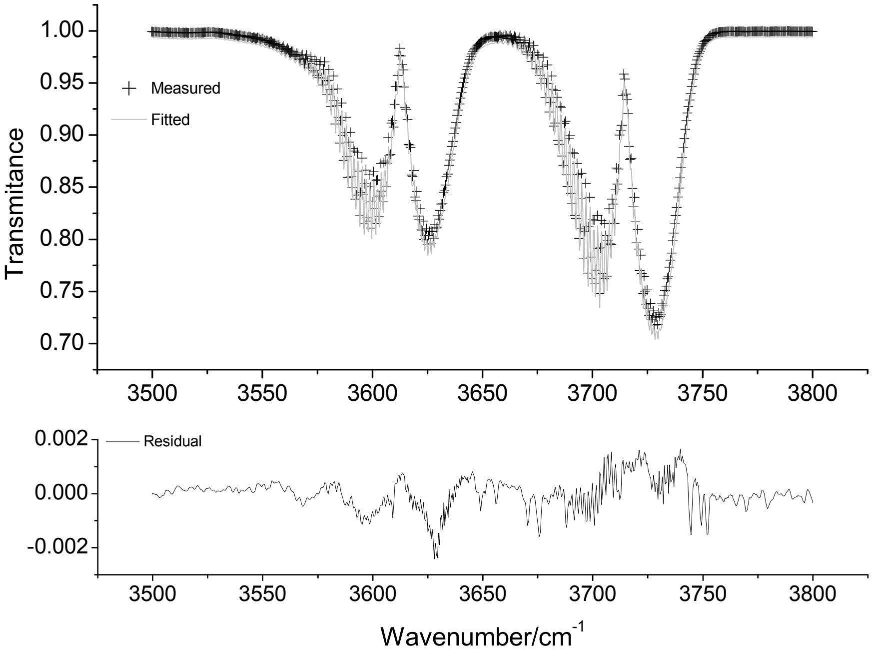


Figure 16. Typical measured and fitted spectra (upper part), and residual signal (lower part) in the region 3500–3800 cm^{-1} obtained on a standard of CO_2 in air at 384.33 µmol mol^{-1}. The absorption feature is due to the major isotopologue 626.

Ratios to the control standard

The ratios to the control cylinder were calculated between the FTIR responses measured at the 626 isotopologue band of the sample *i* (*Cyl_i*) and of the control cylinder.

The measurements were performed following a sequence which included the analysis of four cylinders bracketed by the analysis of the two control cylinders (*A*, *B*) repeated three times. Control A was the Scott Marrin cylinder CB 10326 value assigned by NIST with a mole fraction of 378.90±0.09 µmol mol^{-1} and as control B was used the commercial mixture Messer 400309 with a mole fraction of 850.00±17 µmol mol^{-1}.

Since the analysis of each CO_2/Air gas mixture takes 40 minutes (35 minutes of flush and 5 minutes of acquisition), fifteen hours of continuous measurements were necessary to accomplish the measurement of four cylinders.

The drift corrected response to the control cylinder *B* during the analysis of a sample, B_{cor} was estimated by interpolation in between two measurements of *B*. The ratio R_{FT} between the response to a sample *Cyl* and the drift corrected control B_{cor} was then calculated. Finally, the measurement results for one cylinder was the average of the three ratios obtained during a full sequence, named $R_{\text{FT},i}$ for cylinder Cyl_i.

The control cylinder *A* suffered from a leak in the gas line to the autosampler and was emptied before the end of all measurements. It was however checked that measurements performed with this control cylinder *A* with sufficient pressure were equivalent to those obtained with the control cylinder *B*.

Uncertainty determination

The uncertainty assigned to each ratio to the control cylinder, u_{FT_R}, was the combination of three components combined according to the Guide for Uncertainty in Measurements using the software GUM workbench (see Table 21):

- u_{Stab}, the short term stability of the 626 response to the sample. This term was estimated from the typical Allan deviation at an averaging time of five minutes of the FTIR response measured on the 626 peak, resulting in the value u_{stab} = 6 nmol mol^{-1}, independent of the mole fraction. This same term applies to the control cylinder measurements.
- u_{IsoCorr}, the uncertainty contribution due to the correction of the 626 response arising from the sample isotopic composition (also valid for the control cylinder), as measured by the Delta Ray. All responses of the FTIR calculated at the 626 peak had to be corrected to account for the fact that samples had a different isotopic composition than natural air. The correction was calculated with the Delta Ray, so that the uncertainty contribution due to the isotopic composition correction was estimated from the uncertainty of the Delta Ray measurements: $u_{\delta 13\text{C}}$=0.18 ‰ and $u_{\delta 18\text{O}}$=0.48 ‰ (see further information in Flores et al.[5]). It can be calculated that a 1 ‰ bias in δ^{13}C results in a bias equal to 4.1 nmol mol^{-1} in the CO_2 mole fraction. Similarly, a 1 ‰ bias in δ^{18}O results in a bias equal to 1.7 nmol mol^{-1}. Therefore assuming maximum biases in the delta values equal to the Delta Ray standard uncertainty, the maximum biases in the CO_2 mole fraction were estimated to be 0.72 nmol mol^{-1} (from δ^{13}C) and 0.82 nmol mol^{-1} (from δ^{18}O). Being conservative, the two terms were added in a maximum bias of 1.54 nmol mol^{-1}. Considering a

rectangular distribution of the uncertainty, the standard uncertainty takes the value $u_{isocorr} = 1.54/\sqrt{3} = 0.89$ nmol mol^{-1}. This is negligible compared to other components.

- u_{PBEs}, the uncertainty contribution due Pressure Broadening Effects was calculated through a sensitivity study of MALT. Using one primary version of MALT in 1982 D. Griffith looked at the carrier gas effect in NDIR analyzers for CO_2. MALT by default uses either the amount-weighted self/air broadened widths or the air only widths provided by HITRAN and allows some degree of fiddling for fitting spectra contained in different gas matrices since it allows to the users to scale the input parameter *broad* by any arbitrary factor. Different line broadening factor can be calculated then for air using Griffth et. al. 1982 equation:

$$F_{AIR} = x_{N2}F_{N2} + x_{O2}F_{O2} + x_{Ar}F_{Ar} \tag{7}$$

Where x_{N2}, x_{O2} and x_{Ar} are the mole fractions of nitrogen, oxygen and argon in air, $F_{N2} = 1$ by definition, $F_{O2} = 0.81$ and $F_{Ar} = 0.78$ are the line broadening factors for oxygen and argon (in average). Assuming $x_{N2} = 0.780876$ mol mol^{-1}, $x_{O2} = 0.2093335$ mol mol^{-1} and $x_{Ar} = 0.0093332$ mol mol^{-1}, then the line broadening factor of air F_{AIR} should be equal to 0.95771603. The broadening parameter in MALT for air is *broad* = 1 by convention. It can be scaled by F_{AIR} to obtain a *broad* value for any "air like" matrix, using the equation:

$$broad = \frac{1}{F_{AIR}}(x_{N2} + x_{O2}F_{O2} + x_{Ar}F_{Ar}) \tag{8}$$

In order to estimate the amount of the change in the CO_2 response, one absorbance spectrum was fitted using standard input parameters, varying the factor *broad* according to the two possible extremes composition of the matrix as stated in the protocol of the CCQM-K120a and CCQM-K120b comparisons.

In the case of the CCQM-K120a comparison, two values of the factor *broad* were determined using equation 8, modelling cylinders containing the minimum and the maximum allowed mole fractions of oxygen and assuming nitrogen and argon were impacted to keep a sum of the three equals to 1. The mole fractions and the corresponding values of *broad* are summarized in the table below:

	K120a min	*K120a max*
Compound	**x_i / (mol mol^{-1})**	**x_i / (mol mol^{-1})**
Nitrogen	0.78140	0.78042
Oxygen	0.20880	0.20980
Argon	0.00934	0.00933
broad	1.000105801	0.999907486

Table 20. Extermes of air matrix compositions in the comparison CCQM-K120a and the corresponding values of broad

As result a ΔCO_2 equal to 0.031 µmol mol^{-1} was observed between both fittings. Considering this difference as a rectangular distribution, then a $u_{PBEs\_\Delta O2\_\ K120.a}$= (0.0.031)/(2√3) = 0.009 µmol mol^{-1} is obtained. The same procedure was used with the the limits stated for the CCQM-K120.b and a ΔCO_2 of 0.467 µmol mol^{-1} was obtained with factors $F_{AIR\_CCQM\text{-}K120.b\_min}$= 1.000403273 and $F_{AIR\_CCQM\text{-}K120.b\_max}$= 0.999610014. If this difference is considered again as a rectangular distribution then $u_{PBEs\_\Delta O2\_\ K120.b}$= (0.125)/(2√3) = 0.036 µmol mol^{-1}.

Quantity	Value	Standard Uncertainty	Sensitivity Coefficient	Uncertainty contribution	Index
Cly	$480.00\cdot10^{-6}$ mol mol^{-1}	$0.0108\cdot10^{-6}$ mol mol^{-1}	$1.2\cdot10^{-3}$	$13\cdot10^{-6}$ (Ratio)	74.7 %
Ctl_{B1}	$846.05\cdot10^{-6}$ mol mol^{-1}	$0.0150\cdot10^{-6}$ mol mol^{-1}	$-450\cdot10^{-6}$	$-6.7\cdot10^{-6}$ (Ratio)	20.5 %
Ctl_{B2}	$846.95\cdot10^{-6}$ mol mol^{-1}	$0.0150\cdot10^{-6}$ mol mol^{-1}	$-220\cdot10^{-6}$	$-3.4\cdot10^{-6}$ (Ratio)	5.1 %
				Value	Standard Uncertainty
				0.567141 (Ratio)	$15\cdot10^{-6}$ (Ratio)

Table 21. Uncertainty budget for the calculation of the FTIR ratios to the control cylinder.

The final uncertainty for the ratios of the cylinders that had a gas matrix within the limits of the CCQM-K120a were at 380 µmol mol^{-1} $u_{FT\_R\_380.A}$=14 ×10^{-6} and at 480 µmol mol^{-1} $u_{FT\_R\_480.A}$ =15 ×10^{-6}. The uncertainty for the ratios of the cylinders that had a gas matrix within the limits of the CCQM-K120b were at 480 µmol mol^{-1} $u_{FT\_R\_480.A}$ =44 ×10^{-6} at 800 µmol mol^{-1} $u_{FT\_R\_480.A}$ =45 ×10^{-6}. Combined with the standard deviations on three ratios, this resulted in standard relative uncertainties on the averaged ratio between 1.4×10^{-5} and 2.5×10^{-4}. All the combined standard uncertainties are listed in Table 8.

Delta Ray

Since MALT measurements (FTIR) are done using linestrengths from the HITRAN database, that are scaled by the natural abundance for each isotopologue, the $^{12}CO_2$ measurement of each cylinder needed to be corrected according their own isotopic composition. The isotopic composition of each cylinder was measured using the Delta Ray. Delta Ray is based on direct absorption laser spectroscopy. It uses a tunable diode laser which scans over the spectral region that covers ^{18}O and ^{13}C isotopologues of CO_2.

For this comparison Delta Ray measurements were performed after calibrating the instrument following the manufacturer's recommendations that consist in using two pure CO_2 references gases, with high and low isotope values, two CO_2 in air reference standards with high and low concentration and one dry CO_2 scrubbed whole air (Scott Marrin, Inc.). The instrument was calibrated using cylinder 401557 (pure CO_2, source: gas well, $\delta^{13}C$ = - 1.38 ‰ and $\delta^{18}O$ = - 7.14 ‰ VPDB/j-RAS06 scale), cylinder C11375KO (pure CO_2, source combustion, $\delta^{13}C$ = - 42.13 ‰ and $\delta^{18}O$ = -27.7 ‰, VPDB/j-RAS06 scale); standard NPL 1788 (NPL, CO_2 in air, mole fraction: 380.0±0.19 µmol mol^{-1}, $\delta^{13}C$ = - 1.38 ‰ and $\delta^{18}O$ = - 7.14 ‰ VPDB/j-RAS06 scale), standard NPL 1907 (NPL, CO_2 in air, mole fraction: 791.0±0.4 μmol mol^{-1}, $\delta^{13}C$ = - 42.13 ‰ and $\delta^{18}O$ = -27.7 ‰, VPDB/j-RAS06 scale) and dry CO_2 scrubbed whole air (Scott Marrin).

As reported by Flores et al. 2018[5] a residual bias in the $\delta^{13}C$ and $\delta^{18}O$ measurements, which remained following the implementation of the manufacturer's calibration procedure, was removed by the application of an additional two point calibration (two CO_2 in air standards with known but differing isotopic composition). Standards NPL 1788 ($\delta^{13}C$ = - 1.38 ‰ and $\delta^{18}O$ = - 7.14 ‰) and NPL 1907 ($\delta^{13}C$ = - 42.13 ‰ and $\delta^{18}O$ = -27.7 ‰) were used as two point calibration mixtures.

Sampling sequence

The measurement procedure for analyzing a set of CO_2/Air gas standards by Delta Ray is based on the analysis of four CO_2/Air gas mixtures between two CO_2/Air gas mixture used as the two-point calibration standards (*A, B*). The measurement sequence starts by measuring the $\delta^{13}C$ and $\delta^{18}O$ response of calibration cylinder (*A*) and (*B*) then of four CO_2/Air standards for finalizing again with the calibration standars. Since the analysis of each CO_2/Air gas mixture takes 40 minutes, sixteen hours of continuous measurements were necessary to accomplish the measurement of four cylinders three times.

The measured $\delta^{13}C$ and $\delta^{18}O$ responses of the control cylinders were drift corrected. Then used together with the $\delta^{13}C$ and $\delta^{18}O$ measured by *MPI-Jena* in XLGenlinev1.1 for predicting the $\delta^{13}C$ and $\delta^{18}O$ of the unknown cylinders traceable to the VPDB-CO_2 scale.

Uncertainty determination

Times series analysis were performed with the Delta Ray during the validation work, resulting in Allan deviations of 0.03 ‰ for $\delta^{13}C$ and 0.05 ‰ for $\delta^{18}O$ at the optimum averaging time of 300 s. In addition, it was further noted that the noise of the instrument was significantly higher when measuring during two hours, which is the time period of a typical calibration. Using a rectangular distribution the standard uncertainty of 0.31 ‰ for $\delta^{13}C$ and 0.35 ‰ for $\delta^{18}O$ was observed. This component was further combined with the Allan deviations and taken as the stability uncertainty associated with the instrument response.

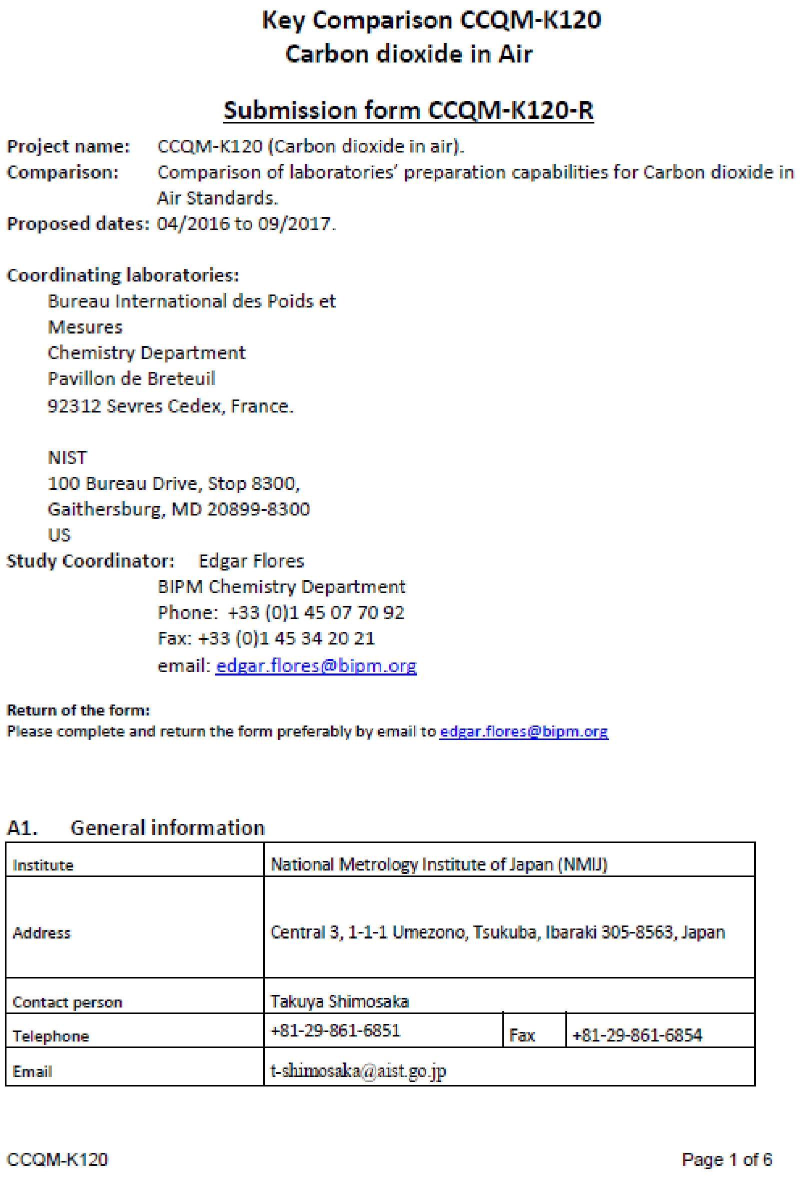
The two-point calibration of the delta value requires the knowledge of the uncertainty associated with them, which was in this case taken as the uncertainties deduced from MPI-Jena measurements equal to 0.015‰ for $\delta^{13}C$ and 0.328‰ for $\delta^{18}O$.

After calibration with the two additional CO_2 in air standards, the standard uncertainties associated with the instrument measurement were finally equal to 0.18 ‰ for $\delta^{13}C$ and 0.48 ‰ for $\delta^{18}O$.

ANNEX V - Measurement reports of participants

NMIJ

Measurements before return of cylinders



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: 04/2016 to 09/2017.

Coordinating laboratories:
Bureau International des Poids et
Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300,
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Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
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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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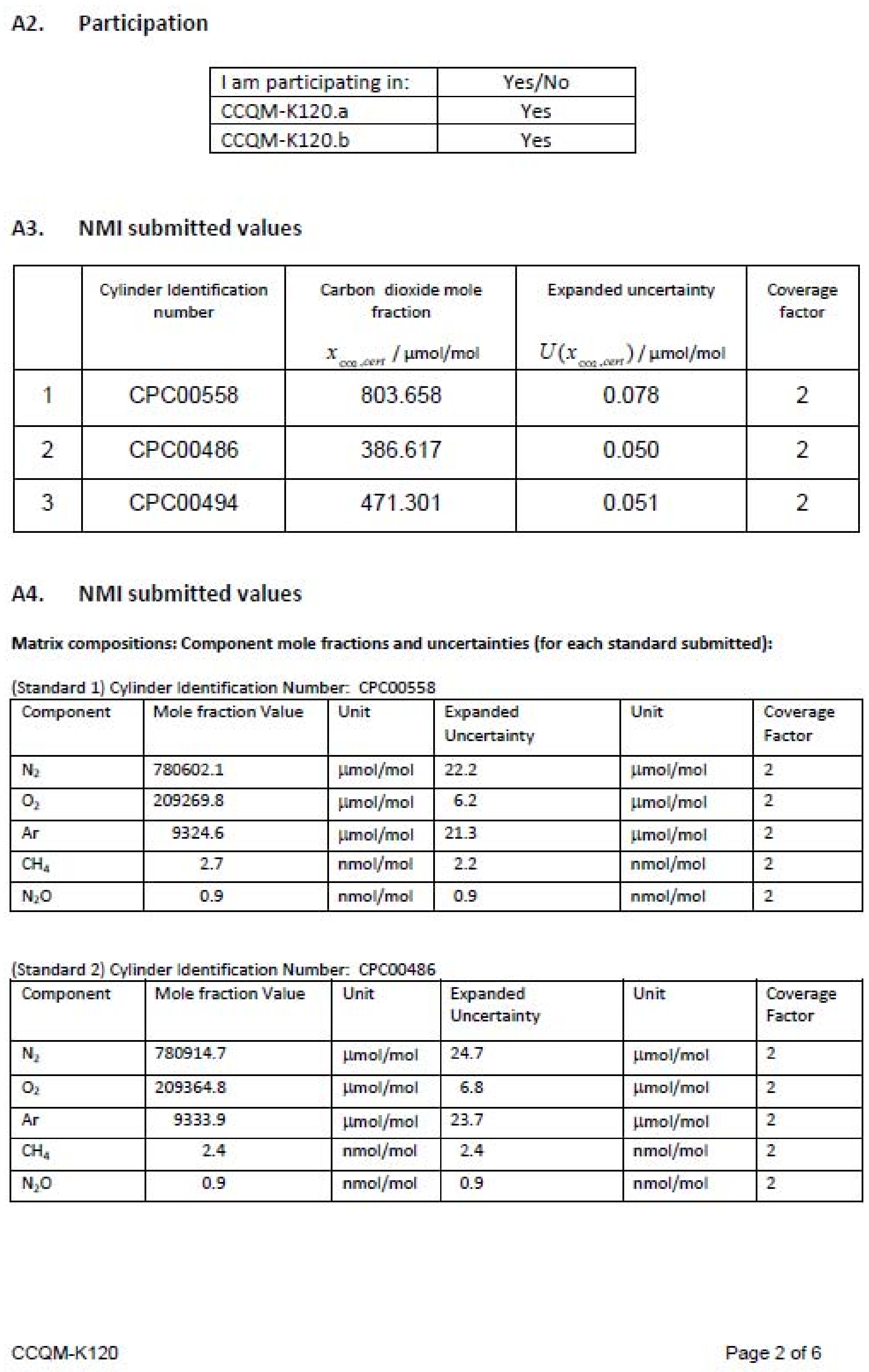

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO_2},\mathrm{cert}}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO_2},\mathrm{cert}})$ / µmol/mol	Coverage factor
1	CPC00558	803.658	0.078	2
2	CPC00486	386.617	0.050	2
3	CPC00494	471.301	0.051	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: CPC00558

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	780602.1	µmol/mol	22.2	µmol/mol	2
O_2	209269.8	µmol/mol	6.2	µmol/mol	2
Ar	9324.6	µmol/mol	21.3	µmol/mol	2
CH_4	2.7	nmol/mol	2.2	nmol/mol	2
N_2O	0.9	nmol/mol	0.9	nmol/mol	2

(Standard 2) Cylinder Identification Number: CPC00486

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	780914.7	µmol/mol	24.7	µmol/mol	2
O_2	209364.8	µmol/mol	6.8	µmol/mol	2
Ar	9333.9	µmol/mol	23.7	µmol/mol	2
CH_4	2.4	nmol/mol	2.4	nmol/mol	2
N_2O	0.9	nmol/mol	0.9	nmol/mol	2

(Standard 3) Cylinder Identification Number: CPC00494

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	780936.9	µmol/mol	24.4	µmol/mol	2
O_2	209258.7	µmol/mol	6.7	µmol/mol	2
Ar	9333.2	µmol/mol	23.5	µmol/mol	2
CH_4	2.5	nmol/mol	2.3	nmol/mol	2
N_2O	0.9	nmol/mol	0.9	nmol/mol	2

A4. Uncertainty Budget

The combined standard uncertainty of the CO_2 mole fraction in the final mixtures was calculated as follows:

$$u(x_{CO_2}) = \sqrt{u^2(x_{CO_2,\mathrm{grav}}) + u^2(x_{CO_2,\mathrm{ver}})}\,, \tag{1}$$

where $u(x_{CO_2,\mathrm{grav}})$ is the standard uncertainty for the gravimetric method [1], $u(x_{CO_2,\mathrm{ver}})$ is the standard uncertainty for verification. Table 1 shows the uncertainty budget table of three final mixtures.

Table 1. Uncertainty budget table for the three final mixtures (unit : µmol/mol)

	Cylinder number		
	CPC00558	CPC00494	CPC00486
standard uncertainty of the amount fraction, $u(x_{CO_2,\mathrm{grav}})$	0.038	0.022	0.020
uncertainty of verification, $u(x_{CO_2,\mathrm{ver}})$	0.011	0.013	0.015
Total standard uncertainty	0.039	0.025	0.025

A5. Additional information

a) a purity table with uncertainties for the nominally pure CO_2 parent gas;

Components	Cylinder number : 3BIS85282			
	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	Analytical method
H_2	2.2	1.25	Rectangular	GC-TCD
O_2	0.3	0.1	Normal	GC-TCD
N_2	0.9	0.5	Normal	GC-TCD
H_2O	4.8	2.7	Normal	Capacitance-type moisture meter
CH_4	0.6	0.3	Rectangular	GC-TCD
C_3H_8	0.9	0.5	Rectangular	GC-TCD
Purity	99.9990 cmol/mol			

b) results of the analysis and mole fractions and uncertainties of CO_2, N_2, O_2, Ar, H_2O, N_2O and CH_4 in the scrubbed real air;

Table 2 Mole fractions and uncertainties for CO_2, N_2, O_2, Ar, H_2O, N_2O and CH_4 in the scrubbed real air (TLB 83648)

Components	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	Analytical method
N_2	78213.8	13.4	Rectangular	-
O_2	209446.6	3.7	Normal	Paramagnetic oxygen analyser
Ar	9339.6	12.9	Normal	GC-TCD
H_2O	0.44	0.25	Rectangular	Capacitance-type moisture meter
CO_2	0.0187	0.0004	Normal	FT-IR
CH_4	0.0022	0.0013	Rectangular	FT-IR
N_2O	0.00088	0.0005	Rectangular	FT-IR

Table 3 Mole fractions and uncertainties for CO_2, N_2, O_2, Ar, H_2O, N_2O and CH_4 in the scrubbed real air (NSY 55-49)

Components	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Distribution	Analytical method
N_2	78311.5	13.4	Rectangular	-
O_2	209351.2	3.7	Normal	Paramagnetic oxygen analyser
Ar	9337.4	12.9	Normal	GC-TCD
H_2O	0.44	0.25	Rectangular	Capacitance-type moisture meter
CO_2	0.0266	0.0004	Normal	FT-IR
CH_4	0.0022	0.0013	Rectangular	FT-IR
N_2O	0.00088	0.0005	Rectangular	FT-IR

c) a brief outline of the preparation procedure of the final mixtures;

The standards were prepared from pure CO_2 and the scrubbed real air by three step dilution as shown in Figure 1.

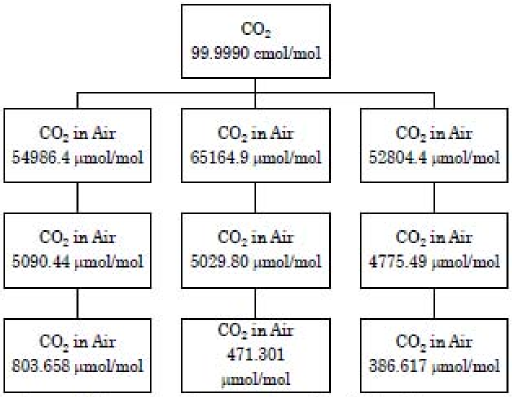

Figure 1. The preparation procedure of the final mixtures

Mole fractions ($x_{\mathrm{CO_2,grav}}$)and their uncertainties ($u\left(x_{\mathrm{CO_2,grav}}\right)$) of CO_2 in air were determined according to ISO 6142:2015 (4). The mole fractions were calculated using the following equation:

$$x_{\mathrm{CO_2,grav}} = \frac{\sum_{j=1}^{r}\left(\frac{x_{\mathrm{CO_2},j} \times m_j}{M_j}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{M_j}\right)}. \tag{2}$$

$u\left(x_{\mathrm{CO_2,grav}}\right)$ were calculated by the application of the law of uncertainty propagation:

$$u^2\left(x_{\mathrm{CO_2,grav}}\right) = \sum_{j=1}^{r}\left(\frac{\partial x_{CO_2}}{\partial \bar{M}_j}\right)^2 \times u^2\left(\bar{M}_j\right) + \sum_{j=1}^{r}\left(\frac{\partial x_{CO_2}}{\partial m_j}\right)^2 \times u^2\left(m_j\right) + \sum_{j=1}^{r}\left(\frac{\partial x_{CO_2}}{\partial x_{CO_2,j}}\right)^2 \times u^2\left(x_{CO_2,j}\right) \tag{3}$$

where *j* expresses the parent gas and dilution gas which are filled into a cylinder, $x_{\mathrm{CO_2},j}$ mole fraction of CO_2 in gas *j*, m_j mass of the gas *j*, $\bar{M}_j$ average molar mass of the gas *j*. $u\left(x_{CO_2,j}\right)$, $u\left(m_j\right)$, and $u\left(\bar{M}_j\right)$ the uncertainty of $x_{\mathrm{CO_2},j}$, m_j, and $\bar{M}_j$. Tables 4, 5 and 6 show the uncertainty budget tables according to eq(3) for the mole fraction of CO_2 in the final mixtures.

Table 4. Uncertainty budget for the preparation value of CO_2 mole fraction of in the cylinder CPC00558

Uncertainty Components	Estimate	Standard uncertainty	Distribution	Sensitivity coefficient	Contribution
Mass of the parent gas (CO2 in Air)	171478.26 mg	1.163 mg	Normal	0.00395 μmol/mol/mg	0.0046 μmol/mol
Mass of the dilution gas (Air)	912377.96 mg	1.171 mg	Normal	-0.000742μmol/mol/mg	0.0009 μmol/mol
Average molar mass of the parent gas	29036.098 mg	0.509 mg	Normal	-23.3 μmol/mol/mg	0.0119 μmol/mol
Average molar mass of the dilution gas	28959.766 mg	0.746 mg	Normal	23.4 μmol/mol/mg	0.0174 μmol/mol
Mole fraction of CO_2 in the parent gas	5090.437 μmol/mol	0.195 μmol/mol	Rectangular	158000	0.0308 μmol/mol
Mole fraction of CO_2 in dilution gas	0.092 μmol/mol	0.004 μmol/mol	Rectangular	842000	0.0037 μmol/mol

Table 5. Uncertainty budget for the mole fraction of CO_2 in the cylinder CPC00486

Uncertainty Components	Estimate	Standard uncertainty	Distribution	Sensitivity coefficient	Contribution
Mass of the parent gas (CO2 in Air)	97311.554 mg	1.163 mg	Normal	0.00365 μmol/mg mol	0.0042 μmol/mol
Mass of the dilution gas (Air)	1102002.070 mg	1.178 mg	Normal	-0.000322 μmol/mol/mg	0.0004 μmol/mol
Average molar mass of the parent gas	29031.362 mg	0.518 mg	Normal	-12.2 μmol/mol/mg	0.0063 μmol/mol
Average molar mass of the dilution gas	28959.4844 mg	0.759 mg	Normal	12.3 μmol/mol/mg	0.0093 μmol/mol
Mole fraction of CO_2 in the parent gas	4775.494 μmol/mol	0.190 μmol/mol	Rectangular	81000	0.0154 μmol/mol
Mole fraction of CO_2 in dilution gas	0.015 μmol/mol	0.002 μmol/mol	Rectangular	919000	0.0017 μmol/mol

Table 6. Uncertainty budget for the mole fraction of CO_2 in the cylinder CPC00494

Uncertainty Components	Estimate	Standard uncertainty	Distribution	Sensitivity coefficient	Contribution
Mass of the parent gas (CO2 in Air)	109385.566 mg	1.163 mg	Normal	0.00390 μmol/mol/mg	0.0045 μmol/mol
Mass of the dilution gas (Air)	1055286.871 mg	1.176 mg	Normal	-0.000405 μmol/mol/mg	0.0005 μmol/mol
Average molar mass of the parent gas	29035.429 mg	0.570 mg	Normal	-14.7 μmol/mol/mg	0.0084 μmol/mol
Average molar mass of the dilution gas	28959.437 mg	0.759 mg	Normal	14.7 μmol/mol/mg	0.0112 μmol/mol
Mole fraction of CO_2 in the parent gas	5029.803 μmol/mol	0.179 μmol/mol	Rectangular	93000	0.0166 μmol/mol
Mole fraction of CO_2 in dilution gas	0.027 μmol/mol	0.001 μmol/mol	Rectangular	906000	0.0006 μmol/mol

d) the verification procedure

Verification of CO_2 amount fraction in the final mixtures was performed by measuring the three final mixtures and another reference mixture using a CRDS. The data were then analyzed using a generalized least squares regression.

If all mixtures satisfies the following criterion, we consider that the final mixtures are correctly prepared.

$$|x_{CO_2,grav} - x_{CO_2,ver}| \le 2\sqrt{u^2(x_{CO_2,grav}) + u^2(x_{CO_2,ver})}, \qquad (4)$$

where $x_{CO_2,ver}$ is the amount fration of CO_2 estimated from the regression, and $u(x_{CO_2,ver})$ is the standard uncertainty of $x_{CO_2,ver}$.

e) Stability test of the mixtures between the time they are prepared and the time they are shipped to the BIPM

We tested stability of the final mixtures twice before shipping to BIPM. The stability tests were performed in Nov. and Dec. by determining the CO_2 mole fraction in the three final mixtures with reference mixtures prepared just before the determination. All of the final mixtures satisfied the criterion of eq (4) in both of the stability tests.

f) Cylinder pressure before shipment to the BIPM

	Cylinder number	Pressure
1	CPC00558	8.5 MPa
2	CPC00486	9.5 MPa
3	CPC00494	9.5 MPa

Remarks

$\delta^{13}C$ and $\delta^{18}O$ isotope ratios in pure CO_2 (3BIS85282) were determined based on the Vienna Pee Dee Belemnite (VPDB) scale by the manufacture. Table 5 shows the isotope ratio.

Table 7 $\delta^{13}C$ and $\delta^{18}O$ Isotope ratios in the pure CO_2 which is a source gas of the final mixtures.

	Cylinder Identification Number	$\delta^{13}C$	$U(\delta^{13}C)$	Coverage Factor	$\delta^{18}O$	$U(\delta^{18}O)$	Coverage Factor
1	3BIS85282	-8.92 ‰	–	–	-9.91 ‰	–	–

References

1. ISO 6142-1:2015, "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method for Class I mixtures".

Authors

Nobuyuki Aoki, Takuya Shimosaka

GUM

Measurements before return of cylinders

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: 04/2016 to 09/2017.

Coordinating laboratories:

Bureau International des Poids et Mesures
Chemistry Department
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NIST
100 Bureau Drive, Stop 8300,
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Study Coordinator: Edgar Flores
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A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	D298392	380,1	4,4	2
2	D298393	478,1	5,2	2
3	D298402	800,5	8,6	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: D298392

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7808	mol/mol	0,0002	mol/mol	2
O_2	0,2095	mol/mol	0,0001	mol/mol	2
Ar	0,00925	mol/mol	0,00001	mol/mol	2
CH_4	0	nmol/mol	-	nmol/mol	-
N_2O	0	nmol/mol	-	nmol/mol	-

(Standard 2) Cylinder Identification Number: D298393

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7807	mol/mol	0,0002	mol/mol	2
O_2	0,2096	mol/mol	0,0001	mol/mol	2
Ar	0,00919	mol/mol	0,00001	mol/mol	2
CH_4	0	nmol/mol	-	nmol/mol	-
N_2O	0	nmol/mol	-	nmol/mol	-

(Standard 3) Cylinder Identification Number: D298402

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7802	mol/mol	0,0002	mol/mol	2
O_2	0,2097	mol/mol	0,0001	mol/mol	2
Ar	0,00938	mol/mol	0,00001	mol/mol	2
CH_4	0	nmol/mol	-	nmol/mol	-
N_2O	0	nmol/mol	-	nmol/mol	-

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	D298392	-	-	-	-	-	-
2	D298393	-	-	-	-	-	-
3	D298402	-	-	-	-	-	-

A4. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO_2 mole fraction values reported

Uncertainty budget for the cylinder no. D298392

Uncertainty source	Estimate (µmol/mol)	Standard uncertainty (µmol/mol)	Distribution	Sensitivity coefficient	Contribution (µmol/mol)
gravimetric	380,1	0,42	normal	1	0,42
verification	-	1,12	normal	1	1,12
systematic error	-	1,87	rectangular	1	1,87

Uncertainty budget for the cylinder no. D298393

Uncertainty source	Estimate (µmol/mol)	Standard uncertainty (µmol/mol)	Distribution	Sensitivity coefficient	Contribution (µmol/mol)
gravimetric	478,1	0,48	normal	1	0,48

verification	-	0,98	normal	1	0,98
systematic error	-	2,35	rectangular	1	2,35

Uncertainty budget for the cylinder no. D298402

Uncertainty source	Estimate (µmol/mol)	Standard uncertainty (µmol/mol)	Distribution	Sensitivity coefficient	Contribution (µmol/mol)
gravimetric	800,5	0,68	normal	1	0,68
verification	-	1,60	normal	1	1,60
systematic error	-	3,93	rectangular	1	3,93

A5. Additional information

The final mixtures were prepared according ISO 6142: the cylinders evacuated on turbo molecular pump, filled up an weighted on the verification balance. The mixtures were prepared in aluminium (with coated layers) cylinders. The mixtures were prepared with used pure nitrogen and oxygen and one step premixture of argon and two steps premixture of carbon dioxide.

The verification according to ISO 6143. The measurements were repeated 10 times for the standards and the sample. The curve was calculated from ratios by the software B_least.exe (linear case).

The standards were prepared by gravimetric method according to ISO 6142. The standards were prepared from separate premixtures and were diluted according ISO 6145-9.

The purity of pure gases used for preparation was taken from the certificates of producer.
Cylinder pressure before shipment to the BIPM:
- cylinder D298392: 139 bar
- cylinder D298393: 147 bar
- cylinder D298402: 147 bar.

INRIM

Measurements before return of cylinders

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: 04/2016 to 09/2017.

Coordinating laboratories:

Bureau International des Poids et
Mesures
Chemistry Department
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A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	D247440	479.3	1.6	2
2	D247445	798.9	2.6	2
3				

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **D247440**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.781132	mol/mol	0.000006	mol/mol	2
O_2	0.2090627	mol/mol	0.0000055	mol/mol	2
Ar	0.0093259	mol/mol	0.0000037	mol/mol	2
CH_4	-	nmol/mol		nmol/mol	
N_2O	-	nmol/mol		nmol/mol	

(Standard 2) Cylinder Identification Number: **D247445**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.782389	mol/mol	0.000006	mol/mol	
O_2	0.2075526	mol/mol	0.0000054	mol/mol	
Ar	0.0092586	mol/mol	0.0000036	mol/mol	
CH_4		nmol/mol		nmol/mol	
N_2O		nmol/mol		nmol/mol	

A4. Uncertainty Budget

The model equation used to calculate the mole fraction of CO_2 in the final mixtures is taken from the International Standard ISO 6142-1:2015:

$$x_{\mathrm{CO_2,prep}} = \frac{\sum_{j=1}^{r}\left(\frac{x_{\mathrm{CO_2},j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}$$

where the index *i* refers to the various components, while *j* refers to the different parent mixtures.

The uncertainty budget was evaluated according to the guidelines prescribed in ISO 6142-1:2015.
The uncertainty budget for the gravimetric preparation of the mixture at 479.3 µmol/mol of CO_2, which takes into account the weighted masses of the parent mixtures, the molar masses of gases and their purity, is reported in the following table:

Uncertainty component **$u(x_i)$**	**Uncertainty source**	**Standard uncertainty,** **$u(x_i)$**	**$\delta x_{CO2,prep}/\delta x_i$**	**Contribution to** **$u(x_{CO2,\ prep})$** **$\lvert\delta x_{CO2,prep}/\delta x_i\rvert\cdot u(x_i)$**
$u(m_{CO2})$	Weighed mass of the parent mixture of CO_2	$8.2\cdot10^{-4}$ g	$7.20\cdot10^{-6}$ $mol\cdot mol^{-1}\cdot g^{-1}$	$5.9\cdot10^{-9}$ $mol\cdot mol^{-1}$
$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2\cdot10^{-4}$ g	$-7.64\cdot10^{-7}$ $mol\cdot mol^{-1}\cdot g^{-1}$	$6.3\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(m_{Ar\_O2})$	Weighed mass of the parent mixture of Ar in O_2	$8.2\cdot10^{-4}$ g	$-6.62\cdot10^{-7}$ $mol\cdot mol^{-1}\cdot g^{-1}$	$5.4\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(M_{CO2})$	Molar mass of CO_2	$1.0\cdot10^{-3}$ $g\cdot mol^{-1}$	$-7.72\cdot10^{-8}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$7.7\cdot10^{-11}$ $mol\cdot mol^{-1}$
$u(M_{N2})$	Molar mass of N_2	$2.0\cdot10^{-4}$ $g\cdot mol^{-1}$	$-3.61\cdot10^{-6}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$7.2\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(M_{Ar})$	Molar mass of Ar	$5.8\cdot10^{-4}$ $g\cdot mol^{-1}$	$1.38\cdot10^{-7}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$8.0\cdot10^{-11}$ $mol\cdot mol^{-1}$
$u(M_{O2})$	Molar mass of O_2	$2.8\cdot10^{-4}$ $g\cdot mol^{-1}$	$3.10\cdot10^{-6}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$8.7\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(x_{N2inCO2})$	Mole fraction of N_2 in the parent mixture of CO_2	$1.0\cdot10^{-6}$ $mol\cdot mol^{-1}$	$-4.32\cdot10^{-4}$	$4.3\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7\cdot10^{-7}$ $mol\cdot mol^{-1}$	$3.29\cdot10^{-4}$	$2.9\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(x_{ArinAr\_O2})$	Mole fraction of Ar in the parent mixture of Ar in O_2	$8.7\cdot10^{-6}$ $mol\cdot mol^{-1}$	$1.29\cdot10^{-4}$	$1.1\cdot10^{-9}$ $mol\cdot mol^{-1}$
$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4\cdot10^{-7}$ $mol\cdot mol^{-1}$	$3.75\cdot10^{-4}$	$5.3\cdot10^{-11}$ $mol\cdot mol^{-1}$
$u(x_{O2inAr\_O2})$	Mole fraction of O_2 in the parent mixture of Ar in O_2	$8.7\cdot10^{-6}$ $mol\cdot mol^{-1}$	$1.04\cdot10^{-4}$	$9.0\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(x_{CO2inCO2})$	Mole fraction of CO_2 in the parent mixture of CO_2	$1.0\cdot10^{-6}$ $mol\cdot mol^{-1}$	$9.51\cdot10^{-2}$	$9.5\cdot10^{-8}$ $mol\cdot mol^{-1}$
$u(x_{CO2inN2})$	Mole fraction of CO_2 in balance gas (impurity)	$2.9\cdot10^{-8}$ $mol\cdot mol^{-1}$	$6.86\cdot10^{-1}$	$2.0\cdot10^{-8}$ $mol\cdot mol^{-1}$
$u(x_{CO2inAr\_O2})$	Mole fraction of CO_2 in the parent mixture of Ar in O_2	$8.7\cdot10^{-8}$ $mol\cdot mol^{-1}$	$2.19\cdot10^{-1}$	$1.9\cdot10^{-8}$ $mol\cdot mol^{-1}$

Uncertainty budget for the gravimetric preparation of the mixture at 479.3 µmol/mol of CO_2

The following table reports the uncertainty budget for the gravimetric preparation of the mixture at 798.9 µmol/mol of CO_2.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**	**$\delta x_{CO2,prep}/\delta x_i$**	**Contribution to $u(x_{CO2,\ prep})$ $\lvert\delta x_{CO2,prep}/\delta x_i\rvert \cdot u(x_i)$**
$u(m_{CO2})$	Weighed mass of the parent mixture of CO_2	$8.2 \cdot 10^{-4}$ g	$6.71 \cdot 10^{-6}$ $mol \cdot mol^{-1} \cdot g^{-1}$	$5.5 \cdot 10^{-9}$ $mol \cdot mol^{-1}$
$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2 \cdot 10^{-4}$ g	$-1.28 \cdot 10^{-6}$ $mol \cdot mol^{-1} \cdot g^{-1}$	$1.0 \cdot 10^{-9}$ $mol \cdot mol^{-1}$
$u(m_{Ar\_O2})$	Weighed mass of the parent mixture of Ar in O_2	$8.2 \cdot 10^{-4}$ g	$-1.11 \cdot 10^{-6}$ $mol \cdot mol^{-1} \cdot g^{-1}$	$9.1 \cdot 10^{-10}$ $mol \cdot mol^{-1}$
$u(M_{CO2})$	Molar mass of CO_2	$1.0 \cdot 10^{-3}$ $g \cdot mol^{-1}$	$3.65 \cdot 10^{-7}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$3.6 \cdot 10^{-10}$ $mol \cdot mol^{-1}$
$u(M_{N2})$	Molar mass of N_2	$2.0 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$4.69 \cdot 10^{-4}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$9.4 \cdot 10^{-8}$ $mol \cdot mol^{-1}$
$u(M_{Ar})$	Molar mass of Ar	$5.8 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$5.10 \cdot 10^{-6}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$3.0 \cdot 10^{-9}$ $mol \cdot mol^{-1}$
$u(M_{O2})$	Molar mass of O_2	$2.8 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$1.14 \cdot 10^{-4}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$3.2 \cdot 10^{-8}$ $mol \cdot mol^{-1}$
$u(x_{N2inCO2})$	Mole fraction of N_2 in the parent mixture of CO_2	$1.0 \cdot 10^{-6}$ $mol \cdot mol^{-1}$	$-6.69 \cdot 10^{-4}$	$6.7 \cdot 10^{-10}$ $mol \cdot mol^{-1}$
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$4.98 \cdot 10^{-4}$	$4.3 \cdot 10^{-10}$ $mol \cdot mol^{-1}$
$u(x_{ArinAr\_O2})$	Mole fraction of Ar in the parent mixture of Ar in O_2	$8.7 \cdot 10^{-6}$ $mol \cdot mol^{-1}$	$2.14 \cdot 10^{-4}$	$1.9 \cdot 10^{-9}$ $mol \cdot mol^{-1}$
$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$5.69 \cdot 10^{-4}$	$8.0 \cdot 10^{-11}$ $mol \cdot mol^{-1}$
$u(x_{O2inAr\_O2})$	Mole fraction of O_2 in the parent mixture of Ar in O_2	$8.7 \cdot 10^{-6}$ $mol \cdot mol^{-1}$	$1.71 \cdot 10^{-4}$	$1.5 \cdot 10^{-9}$ $mol \cdot mol^{-1}$
$u(x_{CO2inCO2})$	Mole fraction of CO_2 in the parent mixture of CO_2	$1.0 \cdot 10^{-6}$ $mol \cdot mol^{-1}$	$1.59 \cdot 10^{-1}$	$1.6 \cdot 10^{-7}$ $mol \cdot mol^{-1}$
$u(x_{CO2inN2})$	Mole fraction of CO_2 in balance gas (impurity)	$2.9 \cdot 10^{-8}$ $mol \cdot mol^{-1}$	$6.24 \cdot 10^{-1}$	$1.8 \cdot 10^{-8}$ $mol \cdot mol^{-1}$
$u(x_{CO2inAr\_O2})$	Mole fraction of CO_2 in the parent mixture of Ar in O_2	$8.7 \cdot 10^{-8}$ $mol \cdot mol^{-1}$	$2.17 \cdot 10^{-1}$	$1.9 \cdot 10^{-8}$ $mol \cdot mol^{-1}$

Uncertainty budget for the gravimetric preparation of the mixture at 798.9 µmol/mol of CO_2

The additional contribution derived from the analytical verification was taken into account in accordance to the prescription of ISO 6142-1:2015:

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

The following table reports the mole fractions with the associated uncertainties of the preparation and verification for the two prepared mixtures.

Cylinder number	**$x_{\mathrm{CO2,\ prep}}$ /µmol/mol**	**$u(x_{\mathrm{CO2,prep}})$ /µmol/mol**	**$x_{\mathrm{CO2,\ ver}}$ /µmol/mol**	**$u(x_{\mathrm{CO2,ver}})$ /µmol/mol**
D247440	479.3	0.1	478.3	1.2
D247445	798.9	0.2	796.5	1.2

A5. Additional information

a) **Purity table with uncertainties for the nominally pure CO_2 parent gas:**

Component	**Mole Fraction, *x***	***u*(*x*)**
CO_2	>0.99998 mol/mol	5.8 µmol/mol
CO	≤0.1 µmol/mol	0.03 µmol/mol
H_2	≤0.1 µmol/mol	0.03 µmol/mol
N_2	≤10 µmol/mol	3 µmol/mol
O_2	≤3 µmol/mol	0.9 µmol/mol
H_2O	≤5 µmol/mol	1.4 µmol/mol
C_nH_m	≤3 µmol/mol	0.9 µmol/mol

Purity table for CO_2

b) **Purity table with uncertainties for the nominally pure N_2, O_2, Ar parent gases**:

Component	**Mole Fraction, *x***	***u*(*x*)**
N_2	>0.999999 mol/mol	0.3 µmol/mol
CO_2	<0.1 µmol/mol	0.03 µmol/mol
H_2	<0.1 µmol/mol	0.03 µmol/mol
O_2	<0.5 µmol/mol	0.14 µmol/mol
H_2O	<0.5 µmol/mol	0.14 µmol/mol
C_nH_m	<0.1 µmol/mol	0.03 µmol/mol

Purity table for N_2

Component	**Mole Fraction, *x***	***u*(*x*)**
O_2	>0.999999 mol/mol	0.3 µmol/mol
CO	<0.1 µmol/mol	0.03 µmol/mol
CO_2	<0.1 µmol/mol	0.03 µmol/mol
H_2	<0.1 µmol/mol	0.03 µmol/mol
H_2O	<0.5 µmol/mol	0.14 µmol/mol
C_nH_m	<0.1 µmol/mol	0.03 µmol/mol

Purity table for O_2

Component	Mole Fraction, *x*	*u*(*x*)
Ar	>0.99999 mol/mol	2.9 µmol/mol
O_2	<2 µmol/mol	0.6 µmol/mol
H_2O	<3 µmol/mol	0.9 µmol/mol
C_nH_m	<0.5 µmol/mol	0.14 µmol/mol

Purity table for Ar

c) Brief outline of the dilution series undertaken to produce the final mixtures.

In order to produce the final mixtures, the following premixtures were prepared:

1) Premixture of CO_2 in N_2 at 0.080122 mol/mol (U=0.000025 mol/mol) gravimetrically prepared (double substitution scheme A-B-B-A) from pure CO_2 (4.8) and N_2 (6.0)
2) Premixture of CO_2 in N_2 at 5005.4 µmol/mol (U=2.1 µmol/mol) gravimetrically prepared (double substitution scheme A-B-B-A) from the above mentioned mixture n. 1 of CO_2 in N_2 (0.080122 mol/mol) diluted with N_2 (6.0)
3) Premixture of Ar in O_2 (Ar: 0.042703 mol/mol, O_2: 0.957297 mol/mol) gravimetrically prepared (double substitution scheme A-B-B-A) from pure Ar (5.0) and O_2 (6.0)

The final mixtures were gravimetrically prepared (double substitution scheme A-B-B-A) by using premixtures n. 2 and n. 3 as parent mixtures and using N_2 6.0 as balance gas to obtain the target CO_2 mole fractions.

Concerning premixture n. 3, an additional determination of the mole fraction of CO_2 in the mixture was carried out by NDIR spectroscopy. The instrument was calibrated in the range (0.1-1) µmol/mol using dynamic dilution. The obtained value is 0.3 µmol/mol of CO_2 (u=0.09 µmol/mol, calculated assuming a rectangular distribution), which was taken into account for assigning the mole fraction of the final mixtures (CO_2: 479.3 and 798.9 µmol/mol, respectively) and evaluating the associated uncertainty.

d) Brief outline of the verification procedure applied to the final mixtures.

After preparation, the mixtures were rolled for 24 h to be homogenized. An analytical verification was carried out by NDIR spectroscopy, using for each mixture a 3-point calibration curve based on WTLS in the range (330-520) µmol/mol and (690-900) µmol/mol, respectively. The calibration standards were prepared starting from a mixture of CO_2 in synthetic air at a nominal mole fraction of 4800 µmol/mol, diluted with synthetic air by means of Mass Flow Controllers calibrated at INRiM. Each calibration point was repeated 5 times. Each calibration curve was validated by using an independent mixture of CO_2 in synthetic air having a the mole fraction within the calibration range.

e) 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 mixtures were tested for their stability on a weekly basis following the same procedure as described in d). No trends in the analytical response were observed within 3 weeks and the mixtures could be considered stable.

f) Cylinder pressure before shipment to the BIPM: 90 bar for each cylinder.

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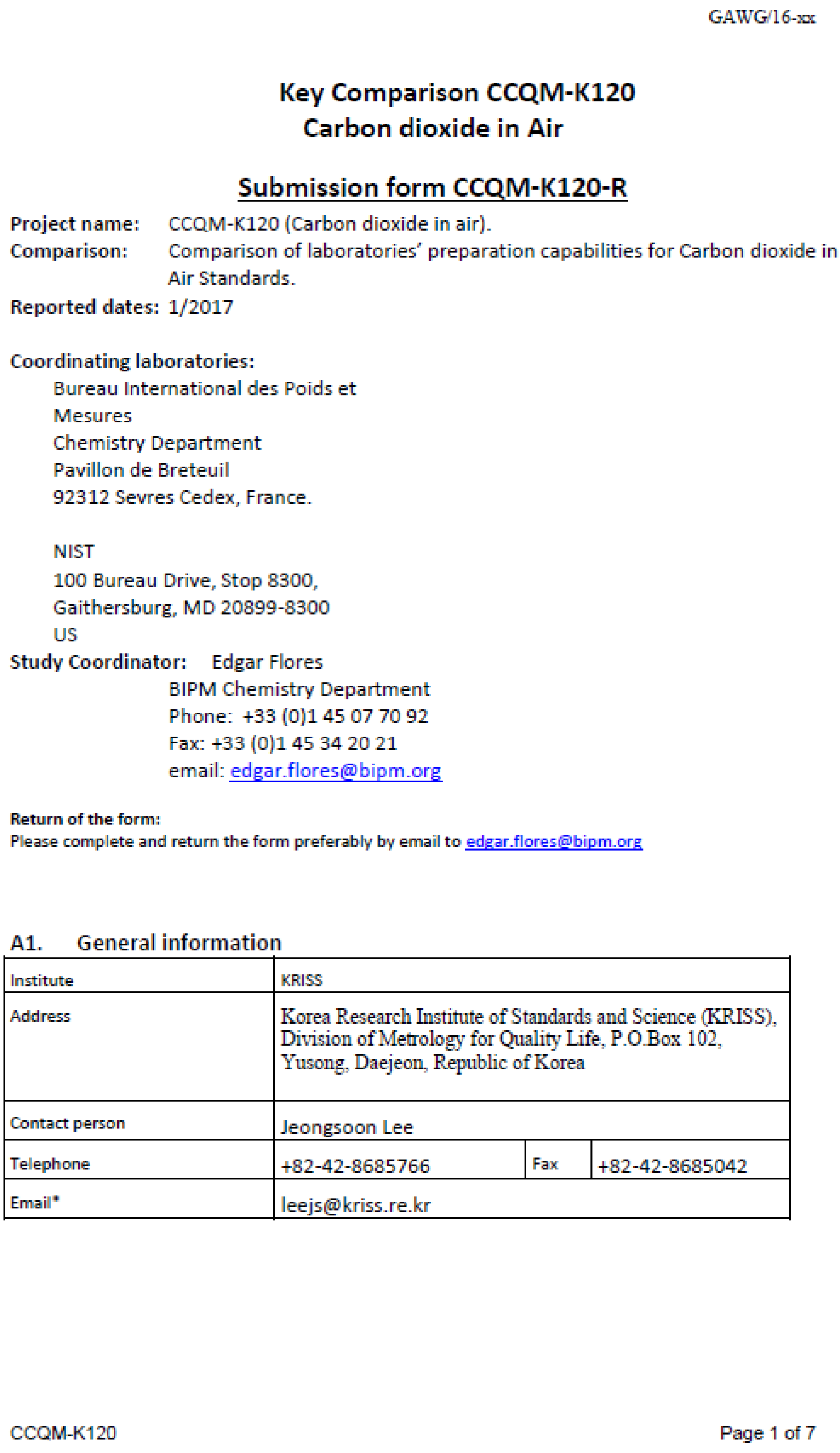
Measurements before return of cylinders



GAWG/16-xx

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.
Reported dates: 1/2017

Coordinating laboratories:
Bureau International des Poids et
Mesures
Chemistry Department
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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	y
CCQM-K120.b	y

A3. 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	**D500642**	378.9	0.2	*k* = 2
2	**D500647**	480.0	0.2	*k* = 2
3	**D500672**	800.8	0.4	*k* = 2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **D500642**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.781139	mol/mol	5	10^{-6}mol/mol	***k* = 2**
O_2	0.209256	mol/mol	4	10^{-6}mol/mol	***k* = 2**
Ar	0.0092255	mol/mol	1.0	10^{-6}mol/mol	***k* = 2**
CH_4	9.0	nmol/mol	2.0	nmol/mol	***k* = 2**
N_2O	0.2	nmol/mol	0.1	nmol/mol	***k* = 2**

(Standard 2) Cylinder Identification Number: **D500647**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780915	mol/mol	4	10^{-6}mol/mol	*k*=2
O_2	0.209152	mol/mol	4	10^{-6}mol/mol	*k*=2
Ar	0.0094520	mol/mol	1.0	10^{-6}mol/mol	*k*=2
CH_4	10.2	nmol/mol	3.0	nmol/mol	*k*=2
N_2O	0.2	nmol/mol	0.1	nmol/mol	*k*=2

(Standard 3) Cylinder Identification Number: **D500672**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780407	mol/mol	4	10^{-6}mol/mol	*k*=2
O_2	0.209452	mol/mol	4	10^{-6}mol/mol	*k*=2
Ar	0.0093394	mol/mol	1.0	10^{-6}mol/mol	*k*=2
CH_4	15.0	nmol/mol	3.0	nmol/mol	*k*=2
N_2O	0.2	nmol/mol	0.1	nmol/mol	*k*=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							
2							
3							

A4. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO_2 mole fraction values reported

- CO_2 amount-of-substances mole fraction calculated from gravimetry, and purity analysis of parent gases, were used as reference values.

	Cylinder Identification Number	Preparation U_{prep} [µmol/mol]	Purity U_{pur} [µmol/mol]	Verification U_{ver} [µmol/mol]	Stability U_{sta} [µmol/mol]	Total U_{comb} [µmol/mol]	Coverage Factor
1	D500642	0.01	0.02	0.2	-	0.2	*k* = 2
2	D500647	0.01	0.02	0.2	-	0.2	*k* = 2
3	D500672	0.02	0.04	0.4	-	0.4	*k* = 2

A5. Additional information

Please include in this section in the case of standards produced with synthetic air:

a) a purity table with uncertainties for the nominally pure CO_2 parent gas;

- **CO_2**

cylinder number : NB16027 (Dukyang gas)

component	value (μmol/mol)	detector	Distribution	Applied value (μmol/mol)	standard uncertainty (μmol/mol)
H_2	6.4	GC/TCD	Normal	6.4	0.6*
O_2	79.5	GC/TCD	Normal	79.5	4.8*
Ar	3.5	GC/TCD	Normal	3.5	0.4*
N_2	214.8	GC/TCD	Normal	214.8*	10.8*
CO	39.6	GC/TCD	Normal	39.6	2.0*
CH_4	15.2	GC/TCD	Normal	15.2	0.8*
H_2O	0.54	dew point meter	Normal	0.54	0.05
THC	<0.2	GC/AED	Rectangular	0.1	0.06
Total Sulfur	<0.01	GC/AED	Rectangular	0.01	0.003
			impurities	359.67	12.0
			CO_2 purity	**999,640.4**	24.0 (k = 2)

*because of matrix difference between standard(He) and sample(CO_2), it shows relatively large uncertainty.

b) a purity table with uncertainties for the nominally pure N_2, O_2, Ar, NO_2 and CH_4 parent gas;

- **N_2**

cylinder number : HP07725 (Daesung gas)

component	value (μmol/mol)	detector	Distribution	Applied value (μmol/mol)	standard uncertainty (μmol/mol)
H_2	< 0.1	GC/PDD	Rectangular	0.05	0.033
O_2	0.125	Galvanic Sensor oxygen analyzer	Normal	0.11	0.011
Ar	4.51	GC/TCD	Normal	4.48	0.448
CO	< 0.003	GC/FID	Rectangular	0.002	0.001
CO_2	0.01	GC/FID	Normal	0.011	0.001
CH_4	< 0.002	GC/FID	Rectangular	0.001	0.001

H_2O	0.55	dew point meter	Normal	0.55	0.055
N_2O	0.00014	GC/µECD	Normal	0.00014	0.00001
THC	< 0.5	GC/FID	Rectangular	0.25	0.144
			impurities	5.45	0.47
——			**N_2 purity**	**999,994.55**	0.94 (*k*=2)

- **O_2**

cylinder number : 406371 (MS gas)

component	value (µmol/mol)	detector	Distribution	Applied value (µmol/mol)	standard uncertainty (µmol/mol)
H_2	< 0.1	GC/PDD	Rectangular	0.05	0.029
Ar	< 1.00	GC/TCD	Rectangular	0.50	0.289
N_2	1.64	GC/PDD	Normal	1.64	0.164
CO	< 0.02	GC/FID	Rectangular	0.01	0.006
CO_2	0.13	GC/FID	Normal	0.127	0.013
CH_4	< 0.02	GC/FID	Rectangular	0.01	0.006
H_2O	0.42	dew point meter	Normal	0.42	0.042
N_2O	0.00033	GC/µECD	Normal	0.00033	0.00003
THC	< 0.5	GC/FID	Rectangular	0.25	0.144
			impurities	3.01	0.37
			O_2 purity	**999,996.99**	0.74 (*k*=2)

k=

- **Ar**

cylinder number : 566303 (Dukyang gas)

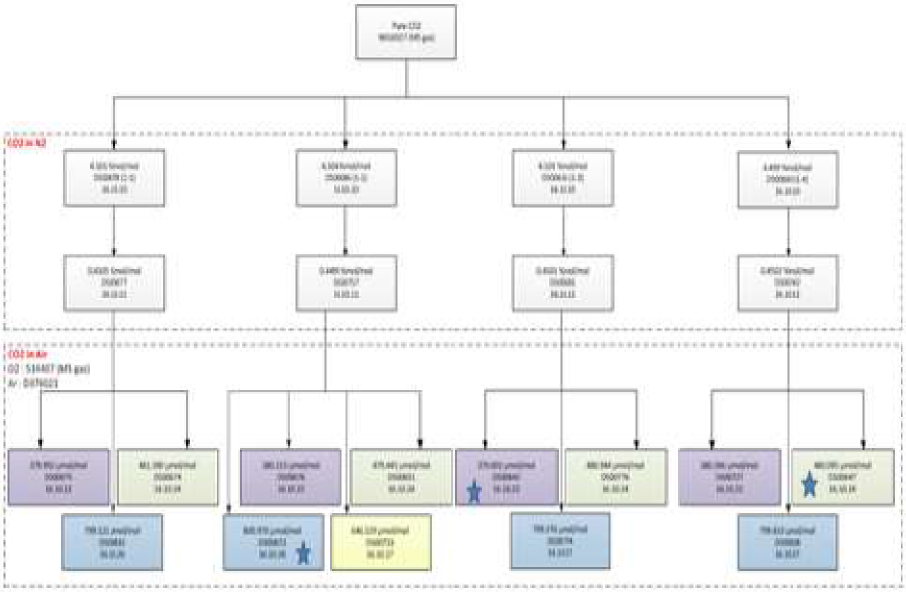
component	value (µmol/mol)	detector	Distribution	Applied value (µmol/mol)	standard uncertainty (µmol/mol)
H_2	< 0.1	GC/PDD	Rectangular	0.05	0.029
O_2	0.055	Galvanic Sensor oxygen analyzer	Normal	0.055	0.006
N_2	0.56	GC/PDD	Normal	0.560	0.056
CO	< 0.003	GC/FID	Rectangular	0.002	0.001
CO_2	0.025	GC/FID	Normal	0.025	0.003

CH_4	< 0.002	GC/FID	Rectangular	0.001	0.001	
H_2O	0.27	dew point meter	Normal	0.270	0.027	
N_2O	0.00020	GC/μECD	Normal	0.0002	0.00002	
THC	< 0.5	GC/FID	Rectangular	0.25	0.144	
			impurities	1.21	0.16	
			Ar purity	**999,998.79**	0.32 (*k*=2)	*k*

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

- Three set of mixtures of carbon dioxide in synthetic air, were gravimetrically(ISO G 6142) prepared through 3 step dilutions by the coordinating laboratory of KRISS.

Cylinder tree – CO2

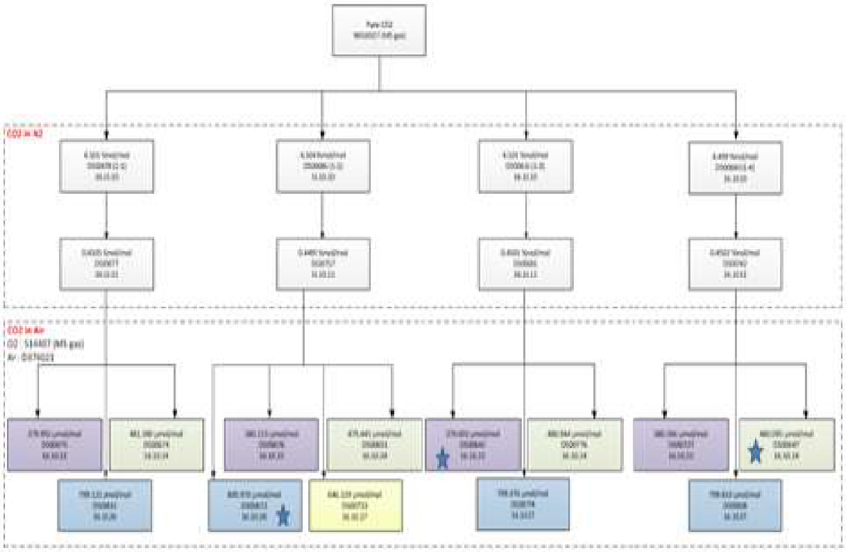


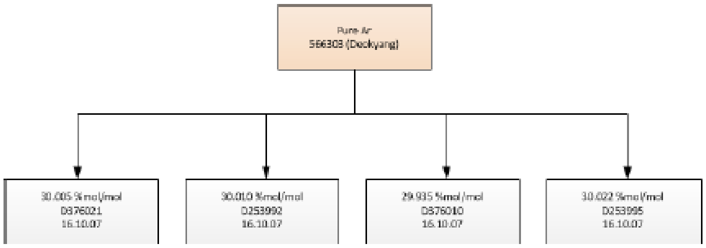
CH_4	< 0.002	GC/FID	Rectangular	0.001	0.001	
H_2O	0.27	dew point meter	Normal	0.270	0.027	
N_2O	0.00020	GC/μECD	Normal	0.0002	0.00002	
THC	< 0.5	GC/FID	Rectangular	0.25	0.144	
			impurities	1.21	0.16	
			Ar purity	**999,998.79**	0.32 (k=2)	k=2

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

- Three set of mixtures of carbon dioxide in synthetic air, were gravimetrically$^{(ISO\ G\ 6142)}$ prepared through 3 step dilutions by the coordinating laboratory of KRISS.

Cylinder tree – CO2





d) a brief outline of the verification procedure applied to the final mixtures;

- Each set of mixtures (with nominal value of 380, 480, 800 μmol/mol) was then verified by means of a GC/FID or GC/TCD analyzer, against one of them prepared in a set.
- Configuration of analysis system: gas cylinder → regulator → MFC → GC-TDC or GC-FID → response comparison → results

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;

- A comparison results show that there is around -0.1 % difference between the k120 mixture (prepared in 2016) and the K52 mixture (prepared in 2006). It is because that the purity analysis for the K120 was conducted very thoroughly and applied to the value assignment. By the way, there is also 0.1 % difference between the k52 mixtures (prepared in 2006).

	Cylinder Identification Number	Preparation [μmol/mol]	Difference (D500676$_{K120}$-ME5590$_{K52}$) %	Difference (D500676$_{K120}$-ME5672$_{K52}$) %	Difference (ME5590$_{K52}$-ME5672$_{K52}$) %
K120	D500676	380.16	- 0.1	- 0.1	
K52	ME5590	387.05			
K52	ME5672	369.93			0.1

f) cylinder pressure before shipment to the BIPM

	Cylinder ID #	Pressure MPa
1	D500642	9.4
2	D500647	9.1
3	D500672	9.1

LNE

Measurements before return of cylinders

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: 04/2016 to 09/2017.

Coordinating laboratories:

Bureau International des Poids et
Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sevres Cedex, France.

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Return of the form:

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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

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	1029045-CO_2/air 0028	379,48	0,79	2
2	1029047-CO_2/AIR 0029	477,6	1,0	2
3	1029048-CO_2/AIR 0030	802,2	1,7	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: CO_2/AIR 0028

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,780686	mol/mol	0,000025	mol/mol	2
O_2	0,209528	mol/mol	0,000019	mol/mol	2
Ar	0,009407	mol/mol	0,000022	mol/mol	2

(Standard 2) Cylinder Identification Number: CO_2/AIR 0029

Component	Mole fraction Value	Unit	Expanded	Unit	Coverage

			Uncertainty		Factor
N_2	0,781355	mol/mol	0,000025	mol/mol	2
O_2	0,208794	mol/mol	0,000018	mol/mol	2
Ar	0,009374	mol/mol	0,000022	mol/mol	2

(Standard 3) Cylinder Identification Number: CO_2/AIR 0030

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,782710	mol/mol	0,000027	mol/mol	2
O_2	0,207187	mol/mol	0,000021	mol/mol	2
Ar	0,009301	mol/mol	0,000021	mol/mol	2

A4. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO_2 mole fraction values reported

CO_2/Air 0028	379,48 ± 0,79 µmol/mol (k=2)

Xi	Unit	Value	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	poids
Mass CO_2 Premix	g	60,21896	0,017	6,06175153	0,10304978	6,79%
CO_2 molar mass	g/mol	44,0095	0,00091	-0,12936318	-0,00011772	0,00%
CO_2 concentration (premix)	mol/mol	0,00998425	0,00000097	37797,9757	0,03666404	0,86%
N_2 molar mass	g/mol	28,01348	0,000099	-2,76210444	-0,00027345	0,00%
Mass Arg/O_2 Premix	g	398,1732	0,017	-0,20862621	-0,00354665	0,01%
Arg concentration (premix)	mol/mol	0,04288429	0,0000048	20,4187142	9,801E-05	0,00%
Arg molar mass	g/mol	39,948	0,001	0,11015474	0,00011015	0,00%
O_2 molar mass	g/mol	31,9988	0,00042	2,45849547	0,00103257	0,00%
N_2 purity	mol/mol	0,99997493	0,0000144	-281,970074	-0,00406037	0,01%
Mass N_2	g	1170,753	0,02	-0,24083902	-0,00481678	0,01%
Stability	%	0	0,38	1	0,38	92,32%

CO_2/Air 0029	477,6 ± 1,0 µmol/mol (k=2)

Xi	Unit	Value	u(Xi)	Sensib. C(Xi)	C(Xi).u(Xi)	Weight
Mass CO_2 Premix	g	76,35147	0,017	5,95567319	0,10124644	3,91%
CO_2 molar mass	g/mol	44,0095	0,00091	-0,16114898	-0,00014665	0,00%
CO_2 concentration (premix)	mol/mol	0,00998425	0,00000097	47573,918	0,0461467	0,81%
N_2 molar mass	g/mol	28,01348	0,000099	-3,46583037	-0,00034312	0,00%

Mass Arg/O_2 Premix	g	399,7202	0,017	-0,26063746	-0,00443084	0,01%
Arg concentration (premix)	mol/mol	0,04288429	0,0000048	25,6082804	0,00012292	0,00%
Arg molar mass	g/mol	39,948	0,001	0,13815138	0,00013815	0,00%
O_2 molar mass	g/mol	31,9988	0,00042	3,08334014	0,001295	0,00%
N_2 purity	mol/mol	0,99997494	0,0000144	-350,551134	-0,00504794	0,01%
Mass N_2	g	1165,053	0,02	-0,30088103	-0,00601762	0,01%
Stability	%	0	0,5	1	0,5	95,25%

CO_2/Air 0030	802,2 ± 1,7 µmol/mol (k=2)

Uncertainty source	Unit	Value Xi	u(Xi)	Sensitivity coefficient. C(Xi)	C(Xi).u(Xi)	Contribution to the uncertainty
Mass CO_2 Premix	g	128,097	0,020	5,75918809	0,11518376	2,01%
CO_2 molar mass	g/mol	44,0095	0,00091	-0,2614445	-0,00023791	0,00%
CO_2 concentration (premix)	mol/mol	0,00998425	0,00000097	79926,3648	0,07752857	0,91%
N_2 molar mass	g/mol	28,01348	0,000099	-5,78813182	-0,00057303	0,00%
Mass Arg/O_2 Premix	g	396,1709	0,021	-0,43832537	-0,00920483	0,01%
Arg concentration (premix)	mol/mol	0,04288429	0,0000048	42,6841537	0,00020488	0,00%
Arg molar mass	g/mol	39,948	0,001	0,23027218	0,00023027	0,00%
O_2 molar mass	g/mol	31,9988	0,00042	5,13934409	0,00215852	0,00%
N_2 purity	mol/mol	0,99997493	0,0000144	-564,097099	-0,008123	0,01%
Mass N_2	g	1114,778	0,023	-0,50600475	-0,01163811	0,02%
Stability	%	0	0,8	1	0,8	97,04%

A5. Additional information

Please include in this section in the case of standards produced with synthetic air:

a) a purity table with uncertainties for the nominally pure CO_2 parent gas;

°°°°°°°°°°°°° Pur\CO2pur007.txt °°°°°°°°°°°°°°

```
Component      mol/mol          uncertainty
-----------------------------------------------
CO2         0,9999922500      0,0000026021
H2O         0,0000015000      0,0000008660
O2          0,0000010000      0,0000005774
Methane     0,0000010000      0,0000005774
H2          0,0000002500      0,0000001443
N2          0,0000040000      0,0000023094
```

b) a purity table with uncertainties for the nominally pure N_2, O_2, Ar parent gas

  a. Pure Argon

```
°°°°°°°°°°°°°° Pur\Ar_A106273.txt °°°°°°°°°°°°°°

Component      mol/mol          uncertainty
-----------------------------------------------
Ar          0.9999998100      0.0000000880
O2          0.0000000050      0.0000000029
H2O         0.0000000100      0.0000000058
CO2         0.0000000005      0.0000000003
CnHm        0.0000000250      0.0000000144
N2          0.0000001500      0.0000000866
```

  b. Pure Oxygen

```
°°°°°°°°°°°°°° Pur\O2_207494H.txt °°°°°°°°°°°°°°

Component      mol/mol          uncertainty
-----------------------------------------------
O2          0.9999974360      0.0000011650
CO2         0.0000001640      0.0000000082
CO          0.0000000500      0.0000000289
CnHm        0.0000000500      0.0000000289
N2          0.0000020000      0.0000011547
H2O         0.0000002500      0.0000001443
H2          0.0000000500      0.0000000289
```

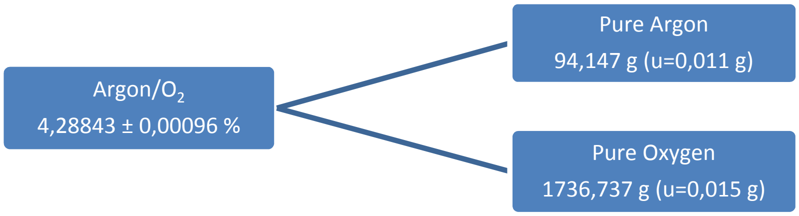
  c. Pure Nitrogen

```
°°°°°°°°°° Pur\azote_bip_GQ88DUI.txt °°°°°°°°°°°
```

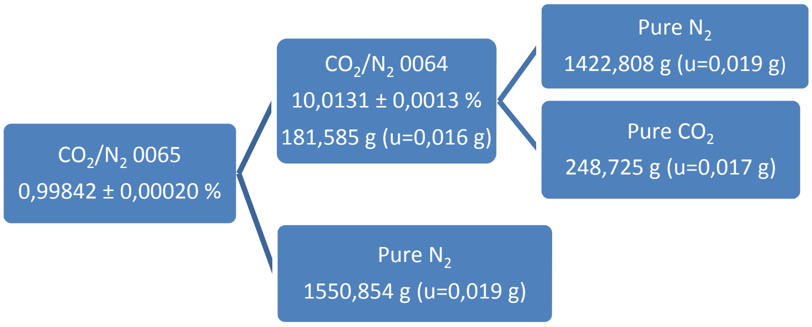
Component	mol/mol	uncertainty
N2	0.9999749345	0.0000144338
CO2	0.0000000005	0.0000000003
H2O	0.0000000100	0.0000000058
Ar	0.0000250000	0.0000144338
O2	0.0000000050	0.0000000029
H2	0.0000000250	0.0000000144
CnHm	0.0000000250	0.0000000144

c) Dilution series undertaken to produce the final mixtures

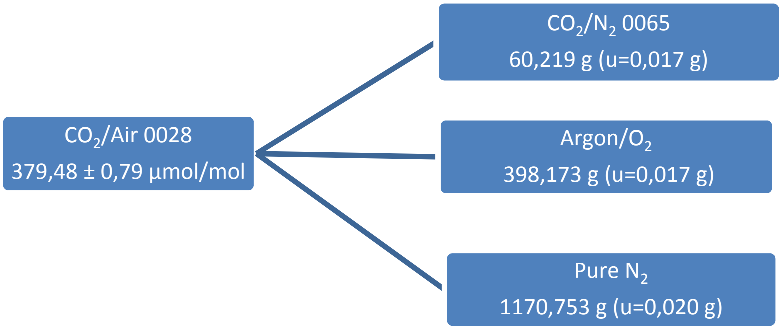
a. Argon/oxygen premix

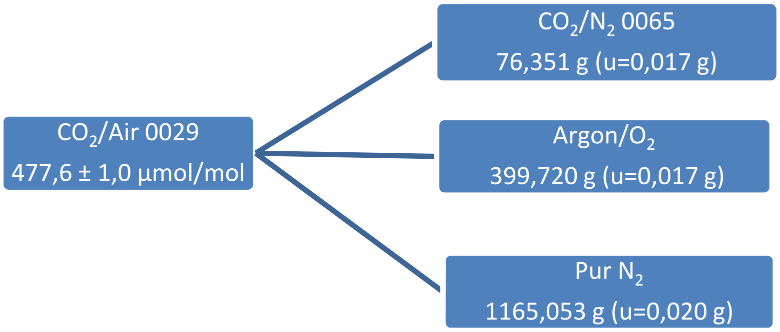


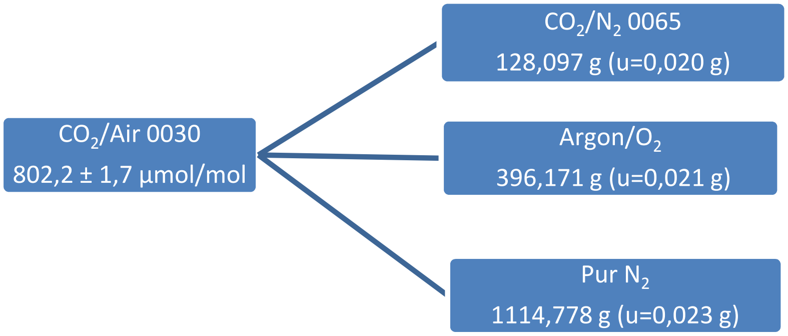
b. CO_2/N_2 premix



c. Final mixtures of CO_2 in air







d) a brief outline of the verification procedure applied to the final mixtures

The gravimetric concentrations of the CO_2 gas mixtures in air have been verified with a micro gas chromatograph (chrompack CP2003). The components are separated by a HayeSep A column at 70°C with an hydrogen pressure at 200 kPa. The injection is performed at a pressure of 1.5 bar during 100 ms.

Each CO_2 gas mixture in air is compared by chromatography to a reference gas mixture of CO_2 in air generated by dilution of a high concentration gravimetric gas mixture (CO_2 in nitrogen) with a Molbloc flowmeter.

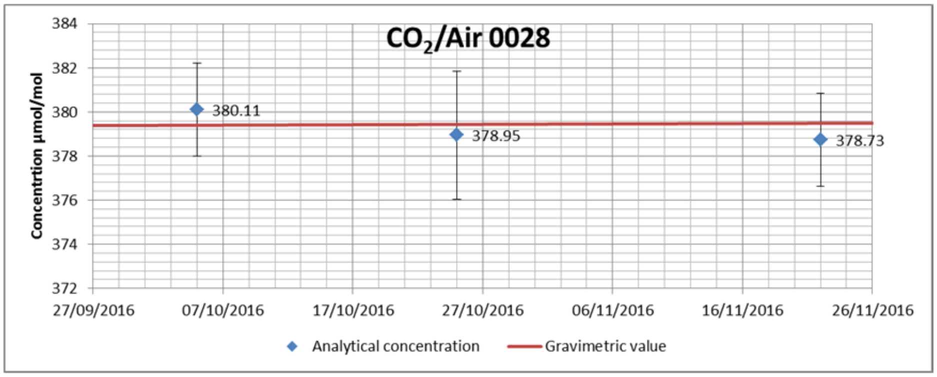
30 runs are performed with the reference gas mixture, 30 runs are performed with the gas mixture to be verified and 30 runs are performed again with the reference gas mixture.

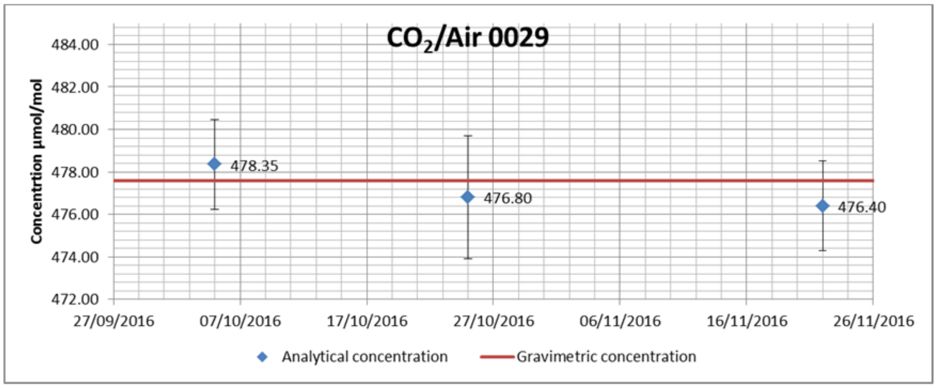
The 10 previous runs are used to calculate the analytical concentration.

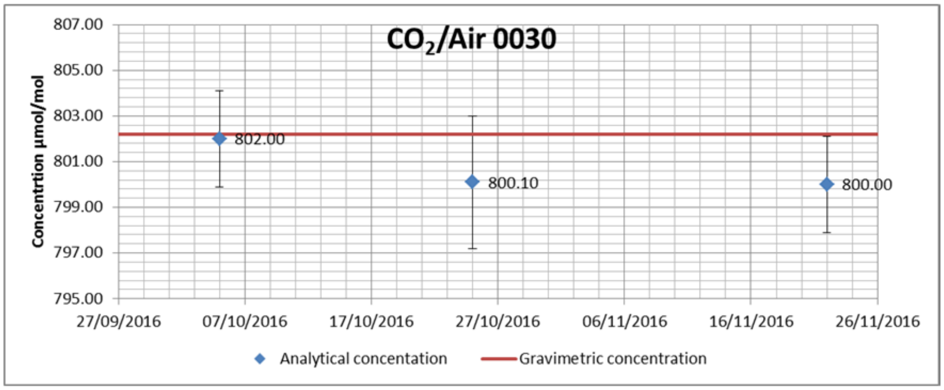
The gas mixture is validated if the difference between the analytical and gravimetric concentrations is lower than the quadratic sum of the variances.

e) Stability of the gas mixtures between the time they were prepared and the time they were shipped to the BIPM

The CO_2 gases mixtures in air have been analysed 3 times during a period of 2 months before being sent to BIPM.






CO$_2$/Air 0030
Concentrtion µmol/mol
807.00
805.00
803.00
801.00
799.00
797.00
795.00
27/09/2016
07/10/2016
17/10/2016
27/10/2016
06/11/2016
16/11/2016
26/11/2016
802.00
800.10
800.00
Analytical concentation
Gravimetric concentration

BFKH

Measurements before return of cylinders

Key Comparison CCQM-K120
Carbon dioxide in Air

Comparison of laboratories' preparation capabilities for carbon dioxide in air standards in the range (380-480) µmol/mol and (480-800) µmol/mol

A1. General information

Institute	Hungarian Trade Licensing Office, MKEH		
Address	Németvölgyi út 37-39. Budapest 1124 Hungary		
Contact person	Judit Fükő, Zsófia Nagyné Szilágyi, Tamás Büki		
Telephone	+36 1 4585988, +36 1 4585800	Fax	+ 36 1 4585 937
Email*	tothnefj@mkeh.hu		

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	OMH54	379.84	1.71	2
2	OMH44	479.89	2.11	2
3	OMH69	800.30	2.92	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **OMH54**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78039	mol/mol	0.00016	mol/mol	2
O_2	0.209615	mol/mol	0.000048	mol/mol	2
Ar	0.009607	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5130	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

(Standard 2) Cylinder Identification Number: OMH44

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor

N_2	0.78064	mol/mol	0.00016	mol/mol	2
O_2	0.209514	mol/mol	0.000048	mol/mol	2
Ar	0.009360	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5130	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

(Standard 3) Cylinder Identification Number: OMH69

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78072	mol/mol	0.00016	mol/mol	2
O_2	0.209161	mol/mol	0.000048	mol/mol	2
Ar	0.009314	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5130	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

A4. Uncertainty Budget

Uncertainty budget of preparation of CO_2 standard by gravimetry:

OMH69	800ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	1,38729	g	Normal	0,00046	g	1	3,3158E-04
martix mass	1139,7986	g	Normal	0,026	g	1	2,2811E-05

Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000333

ppm: 0,27

OMH44	480ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	0,81399	g	Normal	0,00034	g	1	4,1770E-04
martix mass	1115,78	g	Normal	0,026	g	1	2,3302E-05
Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000419

ppm: 0,20

OMH54	380ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	0,64422	g	Normal	0,00032	g	1	4,9672E-04
martix mass	1115,9357	g	Normal	0,026	g	1	2,3299E-05
Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000498

ppm: 0,19

The standard uncertainty of x_i can be expressed as

$$u^2(x_i) = u^2(x_{i,prep}) + u^2(x_{i,ver}) + u^2(\Delta x_{i,ver}) + u^2(x_{i,st}), \qquad (1)$$

x_{prep}	amount-of-substance fraction, from preparation (µmol/mol)
u_{prep}	uncertainty of x_{prep} (µmol/mol)
u_{ver}	uncertainty from verification (µmol/mol)
u_{st}	uncertainty of calibration standard (µmol/mol)
$\Delta x_{i,ver}$	diffenece between the gravimetric preparation value and the result of verification measurement (µmol/mol)
U_x	stated uncertainty of laboratory, at 95 % level of confidence (µmol/mol)
k	assigned coverage factor for degree of equivalence

Laboratory Code	Cylinder	xprep	uprep	uver	ust	$\Delta x_{i,ver}$	k	U(xi)	U(xi)
		ppm						ppm	rel%
MKEH	OMH54	379.84	0.19	0.8	0.19	0.14	2	1.71	0.45
	OMH44	479.89	0.20	1.0	0.20	0.18	2	2.11	0.44
	OMH69	800.30	0.27	1.4	0.28	0.15	2	2.92	0.36

A5. Additional information

A5.1 SOURCE OF CO$_2$, NITROGEN, OXIGEN, ARGON,:

CO_2	4.8 from SIAD Italy
N_2	4.5 from Messer Hungary
O_2	5.0 from Messer Hungary
Ar	4.6 from Messer Hungary

A5.2 PURITY TABLE OF PURE CO$_2$: (38458)

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
CO_2	specifications	0.9999885	0.0000133
N_2	specifications	0.0000050	0.0000058
H_2O	specifications	0.0000025	0.0000029

CH_4	specifications	0.0000025	0.0000029
O_2	specifications	0.0000015	0.0000017

A5.3 PURITY TABLE OF PURE NITROGEN:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
N_2	specifications	0.9999870	0.0000150
O_2	specifications	0.0000050	0.0000058
H_2O	specifications	0.0000050	0.0000058
CH_4	specifications	0.0000025	0.0000029
CO	specifications	0.0000005	0.0000006

A5.4 PURITY TABLE OF PURE OXIGEN:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
O_2	specifications	0.9999866	0.0000155
N_2	specifications	0.0000100	0.0000115
H_2O	specifications	0.0000025	0.0000029
CH_4	specifications	0.00000003	0.0000004
CO	specifications	0.00000003	0.0000004
CO_2	specifications	0.00000003	0.0000004

A5.5 PURITY TABLE OF PURE ARGON:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
Ar	specifications	0.9999822	0.0000206

O_2	specifications	0.0000025	0.0000029
H_2O	specifications	0.0000050	0.0000058
N_2	specifications	0.0000100	0.0000116
CO_2	specifications	0.0000003	0.0000004

A5.6 PREPARATION OF THE MIXTURES:

We used 9.4 L aluminum cylinder (Luxfer) with brass valves DIN10.
All the three mixtures were prepared without dilution series.
First the pure CO2 was filled with using loop into the properly prepared cylinder, the mass measurement of the loop was carried out by an analytical balance – Mettler Toledo AE240-S. After the pure gases were filled directly gravimetrically after each other, and the measurement of the gas mass was carried out by a topload balance – Mettler Toledo XP26003L.

A5.7 VERIFICATION OF THE MIXTURES:

All the three mixtures measured using methaniser at Agilent GC-FID, and we used MKEH standard gases one by one for calibration this method to the purpose of confirm that the gravimetric value and uncertainty for the carbon dioxide mole fraction of its standards is valid and it is included in the calculation of the reference value.

A5.8 STABILITY OF THE MIXTURES:

All the three mixtures were measured using methaniser at Agilent GC-FID three times independently between the time they are prepared and the time they are shipped to the BIPM. There wasn’t significant difference between the certified values and the measured values.

A5.9 CYLINDER PRESSURE BEFORE SHIPMENT TO THE BIPM: 100 bar

Report of stability measurements after return of cylinders

Key Comparison CCQM-K120

Carbon dioxide in Air

Comparison of laboratories' preparation capabilities for carbon dioxide in air standards in the range (380-480) µmol/mol and (480-800) µmol/mol

A1. General information

Institute	Government Office of the Capital City Budapest, BFKH (former MKEH)		
Address	Németvölgyi út 37-39. Budapest 1124 Hungary		
Contact person	Judit Fükő, Tamás Büki, Zsófia Nagyné Szilágyi		
Telephone	+36 1 4585988, +36 1 4585800	Fax	+ 36 1 4585 937
Email*	fukojudit@bfkh.gov.hu		

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	**Carbon dioxide mole fraction** $x_{\mathrm{CO2},cert}$ **/ µmol/mol**	**Expanded uncertainty** $U(x_{\mathrm{CO2},cert})$ **/ µmol/mol**	**Coverage factor**
1	**OMH54**	**379.8**	**1.7**	**2**
2	**OMH44**	**464,4**	**2.8**	**2**

3	**OMH69**	**800.3**	**2.9**	**2**

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **OMH54**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78039	mol/mol	0.00016	mol/mol	2
O_2	0.209615	mol/mol	0.000048	mol/mol	2
Ar	0.009607	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5100	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

(Standard 2) Cylinder Identification Number: OMH44

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78064	mol/mol	0.00016	mol/mol	2
O_2	0.209514	mol/mol	0.000048	mol/mol	2
Ar	0.009360	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5100	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

(Standard 3) Cylinder Identification Number: OMH69

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78072	mol/mol	0.00016	mol/mol	2
O_2	0.209161	mol/mol	0.000048	mol/mol	2
Ar	0.009314	mol/mol	0.000017	mol/mol	2
CH_4	1030	nmol/mol	1200	nmol/mol	2
N_2O	-	nmol/mol	-	nmol/mol	-
H_2O	4480	nmol/mol	5100	nmol/mol	2
CO	440	nmol/mol	520	nmol/mol	2

A4. Uncertainty Budget

Uncertainty budget of preparation of CO_2 standard by gravimetry:

OMH69	800ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	1,38729	g	Normal	0,00046	g	1	3,3158E-04
martix mass	1139,7986	g	Normal	0,026	g	1	2,2811E-05
Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000333

ppm: 0,27

OMH44	480ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	0,81399	g	Normal	0,00034	g	1	4,1770E-04
martix mass	1115,78	g	Normal	0,026	g	1	2,3302E-05
Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000419

ppm: 0,20

OMH54	380ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
CO_2 purity	99,99885	%	Rectangular	13,3	ppm	1	1,3300E-07
CO_2 mass	0,64422	g	Normal	0,00032	g	1	4,9672E-04
martix mass	1115,9357	g	Normal	0,026	g	1	2,3299E-05
Stability	100	%		0,002	%	1	2,0000E-05
Variancia							0,000498
						ppm:	0,19

The standard uncertainty of x_i can be expressed as

$$u^2(x_i) = u^2(x_{i,prep}) + u^2(x_{i,ver}) + u^2(\Delta x_{i,ver}) + u^2(x_{i,st}), \qquad (1)$$

x_{prep}	amount-of-substance fraction, from preparation (µmol/mol)
u_{prep}	uncertainty of x_{prep} (µmol/mol)
u_{ver}	uncertainty from verification (µmol/mol)
u_{st}	uncertainty of calibration standard (µmol/mol)
$\Delta x_{i,ver}$	diffenece between the gravimetric preparation value and the result of verification measurement (µmol/mol)
U_x	stated uncertainty of laboratory, at 95 % level of confidence (µmol/mol)
k	assigned coverage factor for degree of equivalence

Laboratory Code	**Cylinder**	x_{prep}	u_{prep}	x_{meas}	u_m	u_{st}	$\Delta x_{i,ver}$	k	$U(x_i)$	$U(x_i)$
		ppm	*ppm*	*ppm*	*ppm*	*ppm*	ppm		*rel%*	
BFKH	OMH54	**379.84**	**0.19**		0.8	0.19	0.14	2	1.7	0.45
	OMH44	**479.89**	**0.20**	**464.44**	1.4	0.20		2	2.8	0.58
	OMH69	**800.30**	**0.27**		1.4	0.28	0.15	2	2.9	0.36

The stability measurements indicated some preparation mistake in case of the OMH44 cylinder. The certified value of this cylinder was calculated from the measurements and the uncertainty from the equation below:

$$u^2(x_i) = u^2(x_{i,prep}) + u^2(x_{i,meas}) + u^2(x_{i,st}),$$

A5. Additional information

A5.1 SOURCE OF CO_2, NITROGEN, OXIGEN, ARGON,:

CO_2	4.8 from SIAD Italy
N_2	4.5 from Messer Hungary
O_2	5.0 from Messer Hungary
Ar	4.6 from Messer Hungary

A5.2 PURITY TABLE OF PURE CO_2: (38458)

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
CO_2	Specifications	0.9999885	0.0000133
N_2	Specifications	0.0000050	0.0000058
H_2O	Specifications	0.0000025	0.0000029
CH_4	Specifications	0.0000025	0.0000029
O_2	Specifications	0.0000015	0.0000017

A5.3 PURITY TABLE OF PURE NITROGEN:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
N_2	Specifications	0.9999870	0.0000150
O_2	Specifications	0.0000050	0.0000058
H_2O	Specifications	0.0000050	0.0000058
CH_4	Specifications	0.0000025	0.0000029
CO	Specifications	0.0000005	0.0000006

A5.4 PURITY TABLE OF PURE OXIGEN:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
O_2	Specifications	0.9999866	0.000016
N_2	Specifications	0.0000100	0.000012
H_2O	Specifications	0.0000025	0.0000029
CH_4	Specifications	0.00000003	0.0000004
CO	Specifications	0.00000003	0.0000004
CO_2	Specifications	0.00000003	0.0000004

A5.5 PURITY TABLE OF PURE ARGON:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
Ar	Specifications	0.9999822	0.0000200
O_2	Specifications	0.0000025	0.0000029
H_2O	Specifications	0.0000050	0.0000058
N_2	Specifications	0.0000100	0.000012
CO_2	Specifications	0.0000003	0.0000004

A5.6 PREPARATION OF THE MIXTURES:

We used 9.4 L aluminum cylinder (Luxfer) with brass valves DIN10.

All the three mixtures were prepared without dilution series.
First the pure CO2 was filled with using loop into the properly prepared cylinder, the mass measurement of the loop was carried out by an analytical balance – Mettler Toledo AE240-S. After the pure gases were filled directly gravimetrically after each other, and the measurement of the gas mass was carried out by a topload balance – Mettler Toledo XP26003L.

A5.7 VERIFICATION OF THE MIXTURES:

All the three mixtures measured using methaniser at Agilent GC-FID, and we used MKEH standard gases one by one for calibration this method to the purpose of confirm that the gravimetric value and uncertainty for the carbon dioxide mole fraction of its standards is valid and it is included in the calculation of the reference value.

A5.8 STABILITY OF THE MIXTURES:

All the three mixtures were measured using methaniser at Agilent GC-FID three times independently between the time they are prepared and the time they are shipped to the BIPM.

A5.9 CYLINDER PRESSURE BEFORE SHIPMENT TO THE BIPM: 100 bar

NIM

Measurements before return of cylinders

Key Comparison CCQM-K120 Carbon dioxide in Air

Laboratory: National Institute of Metrology

Cylinders number: **FB03748; FB03744; FB03747**

Preparation report:

A1. General information

Institute	National Institute of Metrology, China		
Address	18, Bei San Huan Dong Lu; Chaoyang District; City: Bei Jing Building 17, Room 217		
Contact person	BI, Zhe, Zeyi Zhou		
Telephone	86-10-84232306	Fax	86-10-84232306
Email*	zhouzy@nim.ac.cn; bizh@nim.ac.cn		

A2. Participation

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

A3. Submitted values for carbon dioxide preparation results in each standard

	Cylinder Identification number	**Carbon dioxide mole fraction**	**Expanded uncertainty**	**Coverage factor**
		$x_{\text{CO2},cert}$ / µmol/mol	$U(x_{\text{CO2},cert})$ / µmol/mol	
1	FB03748	809.82	0.26	2
2	FB03744	489.15	0.22	2

3	FB03747	383.43	0.20	2

A4. Submitted values for each standard's matrix

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

(Standard 1) Cylinder Identification Number: FB03748

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
CH_4(Methane)	1.01×10^{-9}	mol/mol	2.03E-10	mol/mol	2
C_2H_4(Ethene)	1.46×10^{-10}	mol/mol	1.13E-10	mol/mol	2
C_3H_8(Propane)	5.18×10^{-10}	mol/mol	4.05E-10	mol/mol	2
N_2(Nitrogen)	0.781	mol/mol	2.71E-05	mol/mol	2
O_2(Oxygen)	0.210	mol/mol	2.60E-05	mol/mol	2
Ar(Argon)	7.94×10^{-3}	mol/mol	9.69E-06	mol/mol	2
H_2O(Water)	2.91×10^{-7}	mol/mol	1.39E-07	mol/mol	2
N_2O(Dinitrogen_oxide)	7.90×10^{-10}	mol/mol	5.86E-10	mol/mol	2
CO_2(Carbon_dioxide)	8.0982×10^{-4}	mol/mol	2.48E-07	mol/mol	2

(Standard 2) Cylinder Identification Number: **FB03744**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
CH_4(Methane)	1.01E-09	mol/mol	3.08E-10	mol/mol	2
C_2H_4(Ethene)	8.80E-11	mol/mol	6.85E-11	mol/mol	2
C_3H_8(Propane)	3.13E-10	mol/mol	2.45E-10	mol/mol	2
N_2(Nitrogen)	7.81E-01	mol/mol	2.75E-05	mol/mol	2
O_2(Oxygen)	2.10E-01	mol/mol	2.64E-05	mol/mol	2
Ar(Argon)	9.04E-03	mol/mol	9.90E-06	mol/mol	2
H_2O(Water)	2.90E-07	mol/mol	1.39E-07	mol/mol	2
N_2O(Dinitrogen_oxide)	7.90E-10	mol/mol	6.01E-10	mol/mol	2
CO_2(Carbon_dioxide)	4.8915E-04	mol/mol	1.91E-07	mol/mol	2

(Standard 3) Cylinder Identification Number: **FB03747**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
CH_4(Methane)	1.01E-09	mol/mol	4.08E-10	mol/mol	2
C_2H_4(Ethene)	6.90E-11	mol/mol	5.37E-11	mol/mol	2
C_3H_8(Propane)	2.45E-10	mol/mol	1.92E-10	mol/mol	2
N_2(Nitrogen)	7.82E-01	mol/mol	2.88E-05	mol/mol	2
O_2(Oxygen)	2.09E-01	mol/mol	2.76E-05	mol/mol	2
Ar(Argon)	9.22E-03	mol/mol	1.02E-05	mol/mol	2
H_2O(Water)	2.89E-07	mol/mol	1.39E-07	mol/mol	2
N_2O(Dinitrogen_oxide)	7.91E-10	mol/mol	6.07E-10	mol/mol	2
CO_2(Carbon_dioxide)	3.8343E-04	mol/mol	1.83E-07	mol/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	/	/	/	/	/	/	/
2	/	/	/	/	/	/	/
3	/	/	/	/	/	/	/

A5. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO_2 mole fraction values reported

Uncertainty budget

Cylinder	Gravimetric value/µmol/mol	Component	distribution	Standard uncertainty/µmol/mol
FB03748	809.82	Combined uncertainty of Purity, Molecular and Weighing	Normal	0.124
		Repeatability of the measurement	Normal	0.040
Combined standard uncertainty				0.13
FB03744	489.15	Combined uncertainty of Purity, Molecular and Weighing	Normal	0.096
		Repeatability of the measurement	Normal	0.030
Combined standard uncertainty				0.11
FB03747	383.43	Combined uncertainty of Purity, Molecular and Weighing	Normal	0.092
		Repeatability of the measurement	Normal	0.030
Combined standard uncertainty				0.10

A6. Additional information

Please include in this section in the case of standards produced with synthetic air:

- *g) a purity table with uncertainties for the nominally pure CO_2 parent gas;*
- *h) a purity table with uncertainties for the nominally pure N_2, O_2, Ar, NO_2 and CH_4 parent gas;*
- *i) a brief outline of the dilution series undertaken to produce the final mixtures;*
- *j) a brief outline of the verification procedure applied to the final mixtures;*
- *k) 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; and*
- *l) cylinder pressure before shipment to the BIPM*

a) purity table for the nominally pure CO_2: 0.9999924 mol/mol

Component	Amount fraction (10^{-6}mol/mol)	Standard uncertainty (10^{-6}mol/mol)	Assumed distribution
CH_4	1.13	0.45	Normal
C_2H_4	0.18	0.07	Normal
C_3H_8	0.64	0.25	Normal
O_2	0.52	0.21	Normal
Ar	0.10	0.04	Normal
N_2	2.51	1.00	Normal
H_2O	2.50	1.00	Normal
N_2O	0.001	0.0006	Rectangular
CO_2	999992.4	1.5	Normal

b) purity table for the nominally pure N_2: 0. 9999521 mol/mol

Component	Amount fraction (10^{-6}mol/mol)	Standard uncertainty (10^{-6}mol/mol)	Assumed distribution
CH_4	0.001	0.0005	Rectangular
Ar	48.3	4.8	Normal
O_2	0.02	0.006	Normal
CO_2	0.010	0.003	Normal
H_2O	0.10	0.04	Normal
N_2O	0.001	0.0004	Rectangular

N_2	999952.1	4.8	Normal

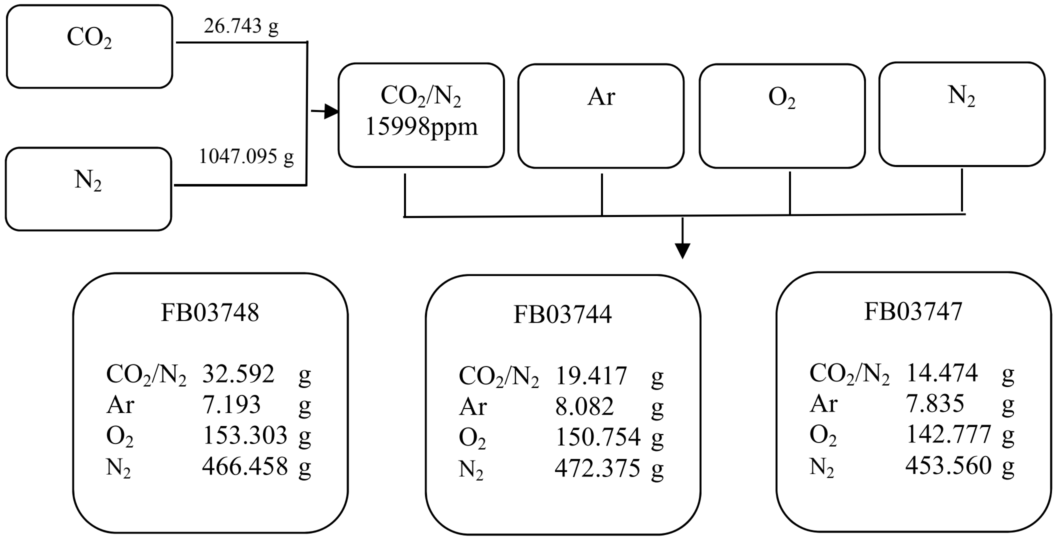
purity table for the nominally pure O_2: 0. 9999959 mol/mol

Component	Amount fraction (10^{-6}mol/mol)	Standard uncertainty (10^{-6}mol/mol)	Assumed distribution
CH_4	0.001	0.0003	Normal
Ar	2.0	0.5	Normal
N_2	1.1	0.3	Normal
CO_2	0.0012	0.0004	Rectangular
H_2O	1.2	0.4	Normal
N_2O	0.001	0.0004	Rectangular
O_2	999995.9	4.8	Normal

purity table for the nominally pure Ar: 0.9999998 mol/mol

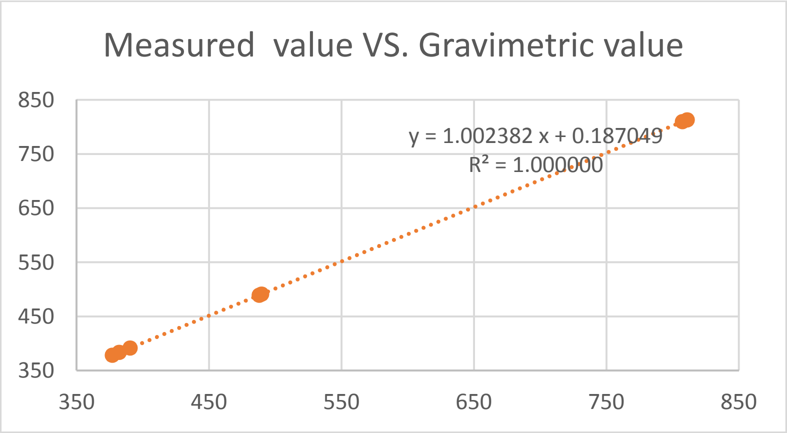
Component	Amount fraction (10^{-6}mol/mol)	Standard uncertainty (10^{-6}mol/mol)	Assumed distribution
CH_4	0.001	0.0003	Normal
O_2	0.020	0.005	Normal
N_2	0.010	0.001	Normal
CO_2	0.001	0.0004	Rectangular
H_2O	0.1	0.4	Normal
N_2O	0.001	0.0004	Rectangular
Ar	999999.8	4.8	Normal

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



d) a brief outline of the verification procedure applied to the final mixtures:

Seven primary standard cylinders of CO_2 in air mixture were measured by CRDs. A linearity regression was established based on these seven cylinders. For each point, an average of date recorded in 2 minutes were used. The verification wre done by the comparison of gravimetric values and the calculated values.



Gravimetric value	Fitted value	Relative deviation

µmol/mol	µmol/mol	%
809.82	809.65	-0.021%
813.07	813.19	0.015%
491.06	491.13	0.014%
489.15	489.28	0.025%
378.19	378.18	-0.003%
391.62	391.61	-0.004%
383.43	383.32	-0.030%

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**:

Three test gas mixtures were prepared 3 months before the comparison. After gas mixtures for the comparison were prepared, a liner regression was done by combining the test gas mixtures and the comparison cylinders. No significant drift of the values was observed between the time they were prepared and the time they were shipped to the BIPM.

f) cylinders pressure before shipment to the BIPM:

Cylinder No.	Pressure (bar)
FB03748	90
FB03744	90
FB03747	90

NIST

Measurements before return of cylinders

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: 04/2016 to 09/2017.

Coordinating laboratories:
Bureau International des Poids et
Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300,
Gaithersburg, MD 20899-8300
US

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

A1. General information

Institute	NIST		
Address	100 Bureau Drive Stop 8393 Gaithersburg, MD 20899-8393		
Contact person	George C. Rhoderick		
Telephone	301-975-3937	Fax	301-977-8392

Email*	George.Rhoderick@nist.gov

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	FB04278	379.0449	0.3908	2
2	FB04300	472.6617	0.4280	2
3	FB04287	794.5334	1.0287	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: FB04278

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780812	mol/mol	0.000118	mol/mol	2
O_2	0.209470	mol/mol	0.00071	mol/mol	2
Ar	0.009339	mol/mol	0.00037	mol/mol	2
CH_4		nmol/mol		nmol/mol	
N_2O		nmol/mol		nmol/mol	

(Standard 2) Cylinder Identification Number: FB04300

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780771	mol/mol	0.000128	mol/mol	2
O_2	0.209422	mol/mol	0.000081	mol/mol	2
Ar	0.009334	mol/mol	0.000034	mol/mol	2
CH_4		nmol/mol		nmol/mol	
N_2O		nmol/mol		nmol/mol	

(Standard 3) Cylinder Identification Number: FB04287

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.780499	mol/mol	0.000114	mol/mol	2
O_2	0.209370	mol/mol	0.000067	mol/mol	2
Ar	0.009336	mol/mol	0.000040	mol/mol	2
CH_4		nmol/mol		nmol/mol	
N_2O		nmol/mol		nmol/mol	

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	FB04278	-28	± 2	1			
2	FB04300	-28	± 2	1			
3	FB04287	-28	± 2	1			

A4. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO_2 mole fraction values reported

FB04278				
	Value	Standard Uncertainty	Relative Uncertainty	% Contribution to Uncertainty
Major Component MW	28.01340	0.00016	0.0000058	0.0020%
Minor Component MW	44.00950	0.00052	0.0000119	0.0041%
Mass Parent Gas	18.93585	0.00146	0.0000769	0.0264%
Mass Balance Gas	745.3878	0.0020	0.0000027	0.0009%
Minor Component Wt Fraction	0.023250750	0.000006755	0.0002905	0.0997%
Mass minor component - Parent	0.44027281	0.00013232	0.0003005	0.1031%
Mass minor component - Bal	0.00006695	0.00001936	0.2890953	99.1626%
Total mass minor component	0.44017935	0.00022556	0.0005124	0.1758%
Moles of minor component	0.01000192	0.00000513	0.0005126	0.1758%
Balance gas wt fraction (purity)	0.755569792	3.90976E-05	0.0000517	0.0177%
Mass balance gas - parent	13.97906371	0.00148549	0.0001063	0.0365%
Mass balance gas - balance	563.19253120	0.02918142	0.0000518	0.0178%
Total mass balance gas	577.17159491	0.02921920	0.0000506	0.0174%
Moles of balance gas	20.60341104	0.00104994	0.0000510	0.0175%
Moles impurities from parent	0.13966291020	0.00002524000	0.0001807	0.0620%
Moles impurities from balance	5.6340784	0.0010163	0.0001804	0.0619%
Total Moles of gas	26.3871542	0.0014615	0.0000554	0.0190%
Conc minor component (ppm)	379.0449	0.1954		
	Relative uncert	0.052%	0.292	100.000%

FB04300				
	Value	Standard Uncertainty	Relative Uncertainty	% Contribution to Uncertainty
Major Component MW	28.01340	0.00016	0.0000058	0.0025%
Minor Component MW	44.00950	0.00052	0.0000119	0.0050%
Mass Parent Gas	29.53886	0.00141	0.0000477	0.0201%
Mass Balance Gas	748.69117	0.00194	0.0000026	0.0011%
CO2 Component Wt Fraction	0.018926076	0.000006339	0.0003350	0.1414%
Mass CO2 component - Parent	0.55905476	0.00018915	0.0003383	0.1428%
Mass CO2 component - Balance Air	0.00003828	0.00000898	0.2345407	98.9951%
Total mass CO2 component	0.55885777	0.00025068	0.0004486	0.1893%
Moles of minor component	0.01269857	0.00000570	0.0004487	0.1894%
Balance gas wt fraction (purity)	0.7556035	0.00004300	0.0000569	0.0240%
Mass balance gas - parent	21.90310136	0.00191642	0.0000875	0.0369%
Mass balance gas - balance	565.71366688	0.03222901	0.0000570	0.0240%
Total mass balance gas	587.61676824	0.03228594	0.0000549	0.0232%
Moles of balance gas	20.97627451	0.00115899	0.0000553	0.0233%
Moles impurities from parent	0.21883087438	0.00003747112	0.0001712	0.0723%
Moles impurities from balance	5.6582830	0.0011276	0.0001993	0.0841%
Total Moles of gas	26.8660869	0.0016174	0.0000602	0.0254%
Conc minor component (ppm)	472.6617	0.2140		
	Relative uncert	0.045%	0.237	100.000%

FB04287				
	Value	Standard Uncertainty	Relative Uncertainty	% Contribution to Uncertainty
Major Component MW	28.01340	0.00016	0.0000058	0.0021%
Minor Component MW	44.00950	0.00052	0.0000119	0.0042%
Mass Parent Gas	39.57940	0.00137	0.0000346	0.0122%
Mass Balance Gas	722.7358	0.0020	0.0000028	0.0010%
Minor Component Wt Fraction	0.023250750	0.000006716	0.0002889	0.1017%
Mass minor component - Parent	0.92025076	0.00026773	0.0002909	0.1025%
Mass minor component - Bal	0.00005052	0.00001421	0.2813263	99.0842%
Total mass minor component	0.92005795	0.00059343	0.0006450	0.2272%
Moles of minor component	0.02090589	0.00001349	0.0006451	0.2272%
Balance gas wt fraction (purity)	0.755575527	3.89029E-05	0.0000515	0.0181%
Mass balance gas - parent	29.21880196	0.00218877	0.0000749	0.0264%
Mass balance gas - balance	546.08149036	0.02815892	0.0000516	0.0182%
Total mass balance gas	575.30029233	0.02824386	0.0000491	0.0173%
Moles of balance gas	20.53661078	0.00101531	0.0000494	0.0174%
Moles impurities from parent	0.29192104701	0.00004836046	0.0001657	0.0583%
Moles impurities from balance	5.4627264	0.0009803	0.0001795	0.0632%
Total Moles of gas	26.3121641	0.0014122	0.0000537	0.0189%
Conc minor component (ppm)	794.5334	0.5143		
	Relative uncert	0.065%	0.284	100.000%

A5. Additional information

Please include in this section in the case of standards produced with synthetic air:

- m) a purity table with uncertainties for the nominally pure CO_2 parent gas;
- n) a purity table with uncertainties for the nominally pure N_2, O_2, Ar, NO_2 and CH_4 parent gas;
- o) a brief outline of the dilution series undertaken to produce the final mixtures;
- p) a brief outline of the verification procedure applied to the final mixtures;
- q) 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; and
- r) cylinder pressure before shipment to the BIPM

Or, with real air:

- a) a purity table with uncertainties for the nominally pure CO_2 parent gas;

Compound	mol/mol	Uncertainty
CO_2	0.999994000	0.000002000
N_2	0.000002000	0.000001155
O2	0.000002000	0.000001155
Ar	0.000002000	0.000001155

- b) results of the analysis and mole fractions and uncertainties of CO_2, N_2, O_2, Ar, N_2O and CH_4 in the scrubbed real air (if performed);

Cylinder FB04300

Compound	mol/mol	Uncertainty
N_2	0.781133467	0.000043500
CO_2	0.000000151	0.000000036
O_2	0.209528241	0.000039865
Ar	0.009338142	0.000017407

Cylinder FB04278

Compound	mol/mol	Uncertainty
N2	0.781102830	0.000039359
CO_2	0.000000059	0.000000017
O_2	0.209554557	0.000034507
Ar	0.009342554	0.000018932

Cylinder FB04287

Compound	mol/mol	Uncertainty
N_2	0.781108354	0.000039152
CO_2	0.000000046	0.000000013
O_2	0.209548136	0.000033045
Ar	0.009343463	0.000020998

c) a brief outline of the preparation procedure of the final mixtures;

The three cylinders were evacuated to ~ 0.5 µ of Hg, filled to ~ 0.7 Mpa with UHP Air and vented to atmosphere (four times) and evacuated to ~ 0.5 µ Hg.
A calculated aliquot of the parent cylinder was added to each cylinder and then weighed.
A calculated aliquot of the matrix gas was added to each cylinder and then weighed.
The cylinders were rolled for ~ three hours to mix the component gases.

d) a composition table for each of the final mixtures, including gravimetric Uncertainties when relevant;

Cylinder FB04300

Compound	mol/mol	Uncertainty
CO_2	0.000472662	0.000000214
N_2	0.780771482	0.000063800
O_2	0.209421668	0.000040372
Ar	0.009334188	0.000016775

Cylinder FB04278

Compound	mol/mol	Uncertainty
CO_2	0.000379045	0.000000195
N_2	0.780812166	0.000058766
O2	0.209469584	0.000035657
Ar	0.009339205	0.000018480

Cylinder FB04287

Compound	mol/mol	Uncertainty
CO_2	0.000794533	0.000000514
N_2	0.780498735	0.000056955
O_2	0.209370336	0.000033285
Ar	0.009336395	0.000019945

e) a brief outline of the verification procedure applied to the final mixtures;

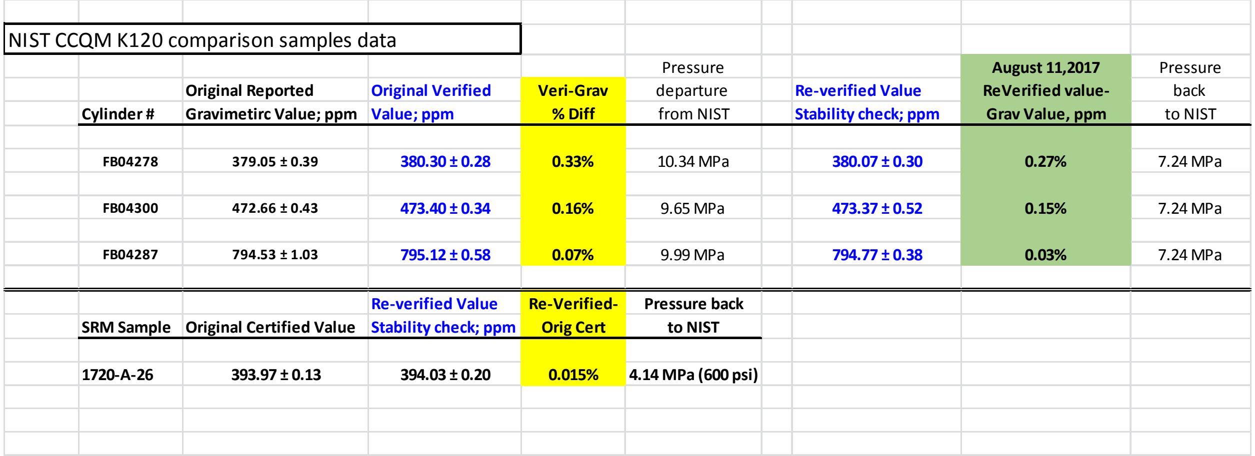
The cylinders were verified against five existing PSMs a minimum of six times using an Isotopic CO_2 Cavity Ringdown Spectrometer.

f) 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; and
g) cylinder pressure before shipment to the BIPM

Cylinder	MPa
FB04300	9.65
FB04278	10.34
FB04278	9.99

Report of stability measurements after return of cylinders

1st report:



NIST CCQM K120 comparison samples data

Cylinder #	Original Reported Gravimetirc Value; ppm	Original Verified Value; ppm	Veri-Grav % Diff	Pressure departure from NIST	Re-verified Value Stability check; ppm	August 11,2017 ReVerified value-Grav Value, ppm	Pressure back to NIST
FB04278	379.05 ± 0.39	380.30 ± 0.28	0.33%	10.34 MPa	380.07 ± 0.30	0.27%	7.24 MPa
FB04300	472.66 ± 0.43	473.40 ± 0.34	0.16%	9.65 MPa	473.37 ± 0.52	0.15%	7.24 MPa
FB04287	794.53 ± 1.03	795.12 ± 0.58	0.07%	9.99 MPa	794.77 ± 0.38	0.03%	7.24 MPa

SRM Sample	Original Certified Value	Re-verified Value Stability check; ppm	Re-Verified-Orig Cert	Pressure back to NIST
1720-A-26	393.97 ± 0.13	394.03 ± 0.20	0.015%	4.14 MPa (600 psi)

2nd report received on May 16, 2018.

Addendum to NIST Report for CCQM-K120a and b

1. Introduction

NIST agreed to participate in the CCQM-K120a and b Key Comparison (KC) with the understanding that this KC involved gravimetrically value-assigned samples. As stated in the protocol summary the comparison involved "… preparative capabilities for carbon dioxide in air primary reference mixtures." Based on this description of the KC as involving primary reference mixtures, NIST assumed that the participants' value assignments and reported data were restricted solely to those that derive from purity assessments and primary gravimetric measurements. However, prior to submission of the reported concentrations to GAWG, NIST discovered a significant discrepancy in the gravimetric values, which was caused by extenuating circumstances (discussed below) and which was quantified using supplementary measurements carried out at NIST. Nevertheless, to follow the KC protocol and to meet the imposed deadlines, NIST submitted only the gravimetric-based concentration values for the three required CO_2-in-air samples despite having assessed that the results were not expected to agree with the eventual calculated KCRV.

2. Background Studies on CO_2 adsorption/desorption issues

NIST performed and continues to investigate an adsorption/desorption phenomenon with CO_2 in air mixtures [1]. NIST has observed, in 5 and 6 L aluminum cylinders containing nominal 400 µmol/mol CO_2 in air mixtures, initial CO_2 adsorption to the cylinder walls of as little as 0.2 µmol/mol to more than 1 µmol/mol depending on the cylinder and internal treatment tested. It has been observed that CO_2 initially adsorbs on the cylinder walls when a mixture is prepared to high pressure (≈12 MPa; ≈1800 psi). NIST modeled some of that early data that shows an increase in CO_2 mole fraction (Δx) with reduced cylinder pressure from measurements of a CO_2 in air mixture contained in a 6 L aluminum cylinder using the Langmuir isotherm (Irving Langmuir, 1916, 1918) and is shown in Figure 1.

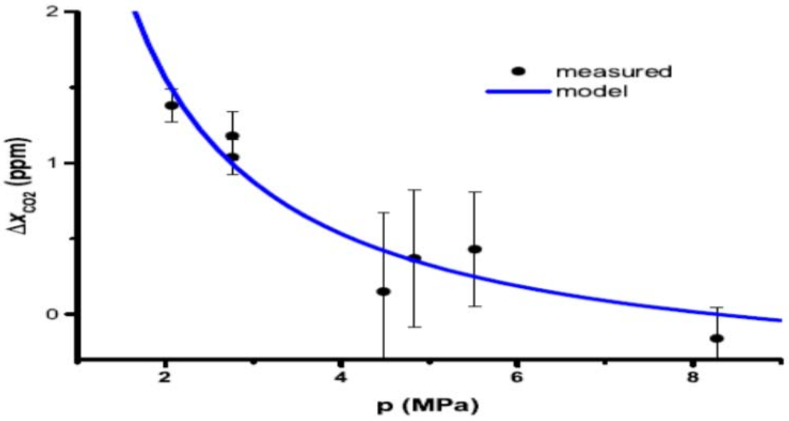


Figure 1. Measured CO_2 mole fraction increase versus pressure decrease in a 6 L aluminum cylinder. Solid black points represent actual measured mole fraction. Solid blue line represents applied Langmuir Isotherm model.

Using the actual measured CO_2 change in 5 L and 6 L cylinders and the Langmuir isotherm, NIST modeled for projected Δx CO_2 variation for 30 L and 47 L aluminum cylinders as shown in Figure 2. The models predict that the larger the cylinder volume the less change in the CO_2 mole fraction with pressure loss. NIST studies of CO_2 in air mixtures contained in 30 L cylinders indeed show less increase in the mole fraction of CO_2 as the pressure in the cylinder decreases. Therefore, the surface-to-volume ratio appears to play a major role: the larger the cylinder volume the less CO_2 increase. It is most likely that this phenomenon takes place not only at ambient CO_2 mole fractions but also at much higher levels including a few %mol/mol and higher.

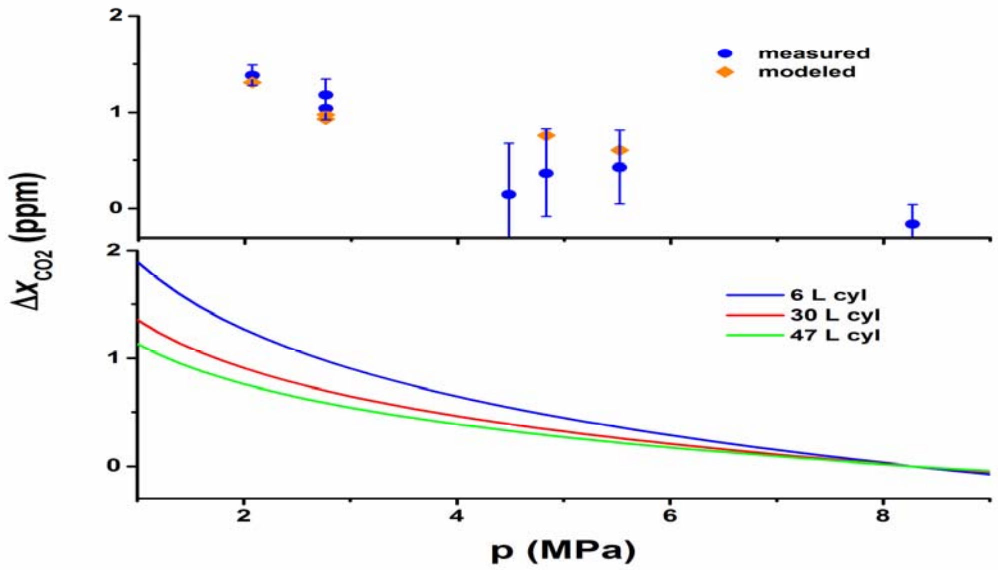


Figure 2. Projected variation in Δx for 6-L, 30-L and 47-L cylinders applying Langmuir Isotherm.

This background information was presented at the GAWG meeting in April 2017 as analyses of K120 a and b were underway. These results account for the discrepant NIST values in K120 a and b. More generally this study informed participants of the serious potential pitfalls associated with desorption of CO_2 from cylinder walls and the dependence of this process on total charge, cylinder dimensions etc., and revealed the possibility of unaccounted for Type B uncertainties caused by interactions of CO_2 with cylinder walls. Partly because of these findings and the occurrence of extremely low uncertainties reported by some NMIs, GAWG decided to put a lower limit on the expanded uncertainty equal to 0.19 µmol mol^{-1}, thus affecting the relative weighting of the results contributing to the KCRV.

3. Preparation of K120 Samples

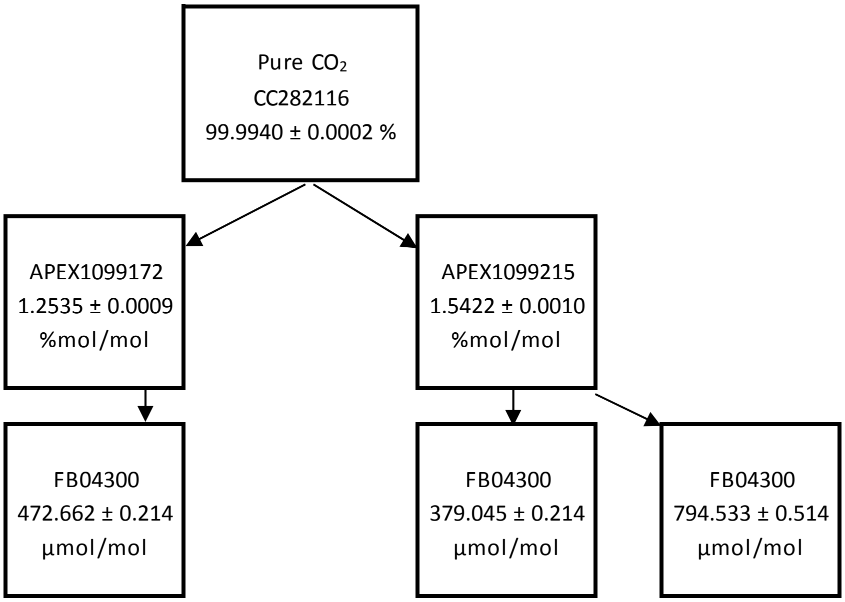
In conjunction with submitting freshly prepared gravimetric standards for the CCQM-K120 CO_2 in air key comparison, NIST also wanted to prepare a complete new suite of ambient level CO_2 in air primary standard mixtures (PSMs) starting with a pure natural isotopic CO_2 source. That new pure CO_2 source arrived at NIST in November 2016. Because there was a limited amount of pure CO_2 in the cylinder obtained, NIST started development by gravimetrically preparing four PSMs in the range of 1-3 % mol/mol in CO_2 and moisture scrubbed real air. Upon completion of those PSMs in early December 2016, they were analyzed by GC-TCD, along with the NIST 2012 CO_2 suite, with ratios calculated from peak area responses to a control. Generalized least squares regression was used to plot the ratios vs. gravimetric values of the 2012 PSMs. The new percent level PSMs were predicted from the regression line. The results of that comparison are shown in Table 1. Inspection of the residuals from the difference of the predicted $Y_{solution}$- Y_{Grav} value for the 2012 PSMs, reveals excellent agreement. However, the predicted Y_{eval} values for the new PSMs disagree with their gravimetric values by more than -2 %.

Table 1. New percent level PSMs predicted from linear regression of 2012 PSMs.

2012 PSM	X (Ratio)	Y (Grav; %mol/mol)	X-Solution	Y-Solution	uTest	% Residual (Y-Sol-Grav)
FA02584	2.44265	4.9500	2.44266	4.9490	Pass	-0.02%
FA02588	2.2877	4.6190	2.2877	4.6205	Pass	0.03%
APEX1099215	0.78272	1.5422	0.78272	1.5420	Pass	-0.01%
APEX1099172	0.63673	1.2535	0.63656	1.2538	Pass	0.02%
CAL016532	0.50028	0.9869	0.5003	0.9869	Pass	0.00%
*From New CO_2	Xin (Ratio)	uXin	Yeval (%mol/mol)	uYeval	**Grav Value**	**% difference Yeval-Grav**
FB03808	1.39347	0.00103	2.7669	0.0033	**2.8288**	**-2.19%**
APEX1099165	1.18456	0.00141	2.3442	0.0035	**2.4043**	**-2.50%**
APEX1099188	1.1708	0.00130	2.3164	0.0033	**2.3773**	**-2.56%**
APEX1099246	0.78483	0.00058	1.5462	0.0015	**1.5822**	**-2.28%**
					(± 0.0007)	

Based on these results, either the 2012 suite of PSMs had increased in mole fraction, because of desorption of CO_2 from the cylinder surface with pressure decrease, or the new source of pure CO_2 was contaminated. Indeed, the pure CO_2 was eventually analyzed in January of 2017 and found to be contaminated with 3.1 % mol/mol N_2. Because NIST had no time to obtain another source of pure CO_2 to make another set of PSMs (K120 samples needed to be shipped to BIPM by the end of December 2016), we had to assume that the 2012 percent level PSMs were stable. We made this assumption knowing that it most likely was not the case because the CO_2 mole fraction had increased as these standards were below ≈ 4.5 MPa (≈650 psi). Not having another source of CO_2 **(the original CO2 source used for the 2012 suite and the source for over three decades was spent)**, NIST could not prepare new percent-level standards to verify the 2012 percent level standards and determine if the CO_2 had indeed increased.

NIST moved forward and prepared the three K120 standards from the 2012 PSMs: cylinder number APEX1099215 at (1.5422 ± 0.0010) % mol/mol and APEX1099172 at (1.2535 ± 0.0009) % mol/mol (highlighted in green in Table 1). Figure 3 shows the preparation scheme.



*combined uncertainties, *k*=1

Figure 3. Preparation scheme for NIST K120 samples.

It is very important to state here that both cylinders were low in pressure when the three K120 standards were prepared from them: APEX1099215 at 520 psi and APEX1099172 at 390 psi. While NIST did not have stability data for percent-level CO_2 in air mixtures, we still suspected that the CO_2 also increases at this mole fraction level as the pressure decreases.

After preparation of the three K120 standards, they were compared to the 2012 ambient level PSMs and three SRM samples were also included. Figure 4 shows the generalized least squares regression plotted for the 2012 PSMs represented by the black circles. The blue circles represent the predicted value for the SRM 1720 samples from that regression and the red triangles represent the original SRM 1720 certified value. The green squares represent the predicted value for the K120 samples from that regression line while the yellow circle with red border represent the gravimetric values. From this plot the blue dotted linear regression line appears to cover all the data points.

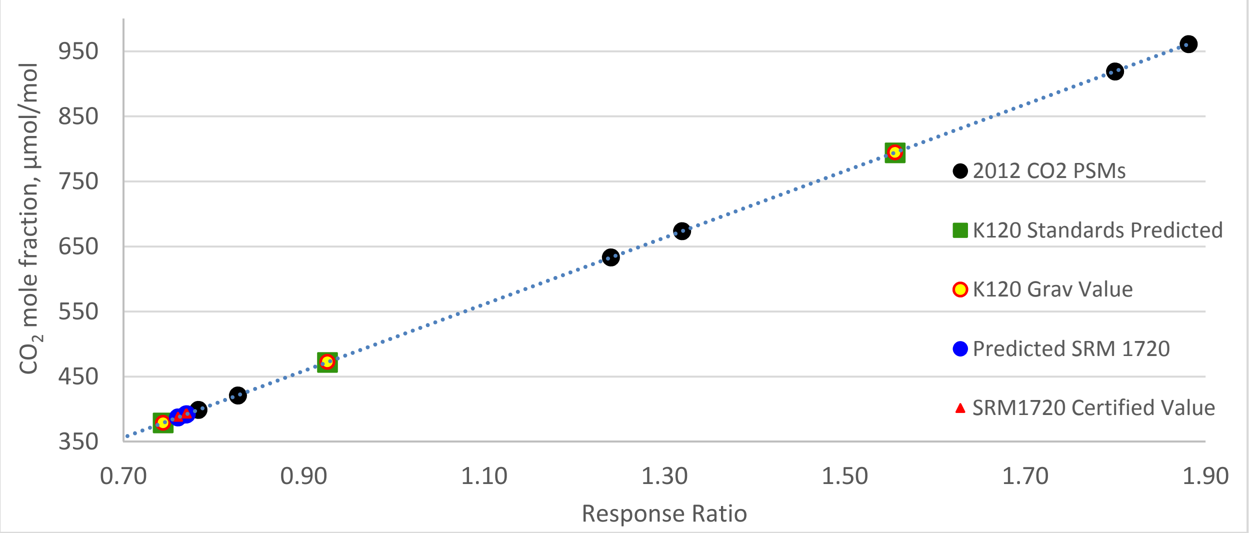


Figure 4. Generalized least squares regression through NIST 2012 ambient CO_2 PSM suite predicting SRM 1720 and K120 samples.

However, if we expand the lower portion of the regression from (350-400) µmol/mol we see disagreement between the new standards and SRM 1720 certified values as shown in Figure 5. While the predicted and gravimetric value for the 380 µmol/mol K120 standard are still on the regression line, the SRM 1720 certified values are off the regression line by around +1 µmol/ mol (0.3 % relative). However, the predicted and gravimetric value for the 380 µmol/mol K120 sample lie on the regression line. NIST has complete confidence that the SRM 1720 samples, contained in 30-L cylinders are stable since they were all at pressures of +11 MPa. Therefore, NIST suspected that the 2012 PSMs all had increased in concentration and hence would predict the SRM 1720 samples to have less CO_2. The fact that the K120 samples also lie on the line with the 2012 PSM regression, we can postulate that the 2012 percent level PSMs had also increased in CO_2 mole fraction as they had pressures less than 4.5 MPa (650 psi) when used to prepare the K120 samples.

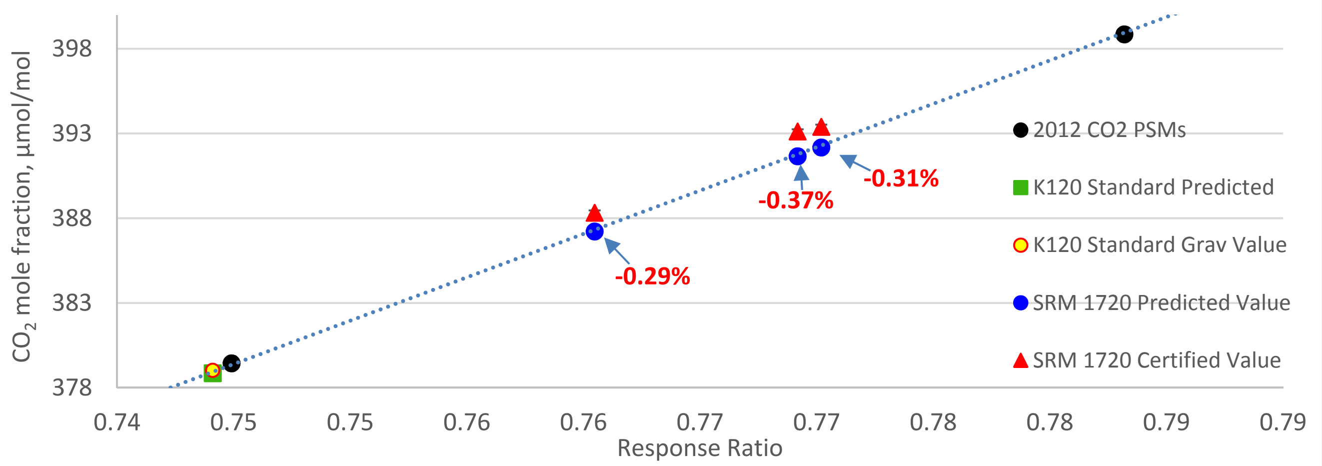


Figure 5. Expansion of Figure 4 illustrating that the SRM 1720 certified values lie off the regression line while K120 gravimetric and predicted values are still on the regression line. Expanded uncertainty error bars are present but too small to be observed except in the red triangle SRM 1720 Certified Value.

NIST took this data for the 2012 ambient level PSMs and determined values by comparison to SRM sample 1720-A-29 with a certified value of (393.12 ± 0.13) µmol/mol with and (*k* = 2) uncertainty value, at a pressure of +12 MPa. The values determined for the PSMs from the SRM 1720 sample are significantly different from their gravimetric values with reduced pressure as shown in Table 2.

Table 2. Ambient level 2012 PSMs determined from SRM sample 1720-A-29.

	Gravimetric	Concentration vs. SRM1720	Difference		Pressure
2012 PSM	Mole Fraction, µmol/mol	µmol/mol	µmol/mol	% Diff	psi (Mpa)
APEX1099211	961.07 ± 0.03	**960.91 ± 0.20**	0.160	0.02%	1200 (8.27)
APEX1099176	919.07 ± 0.46	**919.22 ± 0.25**	-0.150	-0.02%	650 (4.48)
APEX1099164	673.62 ± 0.35	**674.05 ± 0.15**	-0.430	-0.06%	800 (5.52)
APEX1099223	633.30 ± 0.42	**633.67 ± 0.17**	-0.370	-0.06%	700 (4.83)
APEX1005714	421.08 ± 0.06	**422.46 ± 0.09**	-1.380	**-0.33%**	300 (2.07)
APEX1005721	398.85 ± 0.06	**400.03 ± 0.15**	-1.180	**-0.30%**	400 (2.76)
APEX1005690	379.44 ± 0.06	**380.48 ± 0.10**	-1.040	**-0.27%**	400 (2.76)
	* uncertainty *k*=1				

4. Validity of SRM 1720 samples

The SRM 1720 sample used to verify these PSMs is contained in a 30-Liter aluminum cylinder. Other SRM 1720 samples have shown to be stable within uncertainty limits down to around 600 psi as shown in Table 3.

Table 3. Mole fractions showing increase in 30 Liter SRM 1720 samples with pressure loss.

30 -Liter SRM Sample	Original Certified Value; ppm		August 2017 Stability check value; ppm	Stability 2017 - Cert; ppm		
1720-A-26[a]	393.97 ± 0.13	(SRM used by BIPM for K120)	394.03 ± 0.20	+ 0.06	600 psi	4.14 Mpa
1720-AL-01	388.33 ± 0.13		388.67 ± 0.14	+ 0.34	325 psi	2.24 Mpa
1720-AL-27	393.39 ± 0.13		393.64 ± 0.15	+ 0.25	450 psi	3.1 Mpa

**All verified and stability check values determined against SRM 1720-A-29 (still at a pressure of 1500+ psi)

**All uncertainties reported as expanded; *k* = 2.

[a] SRM 1720-A-26 was sent to BIPM as part of their system validation for K120

SRM 1720 samples were originally certified by comparing to the 2012 suite of four PSMs when they were at full pressure (+11 MPa), three of which are given in Table 2: APEX1005714 (421.08 ± 0.06) µmol/mol, APEX1005721 (398.85 ± 0.06) µmol/mol and APEX1005690 (379.44 ± 0.06) µmol/mol. The SRM 1720 samples were also analyzed by NOAA with results showing agreement between NIST and NOAA [2]. Figure 6 shows that agreement for the 30 real air cylinder samples that comprised SRM 1720.

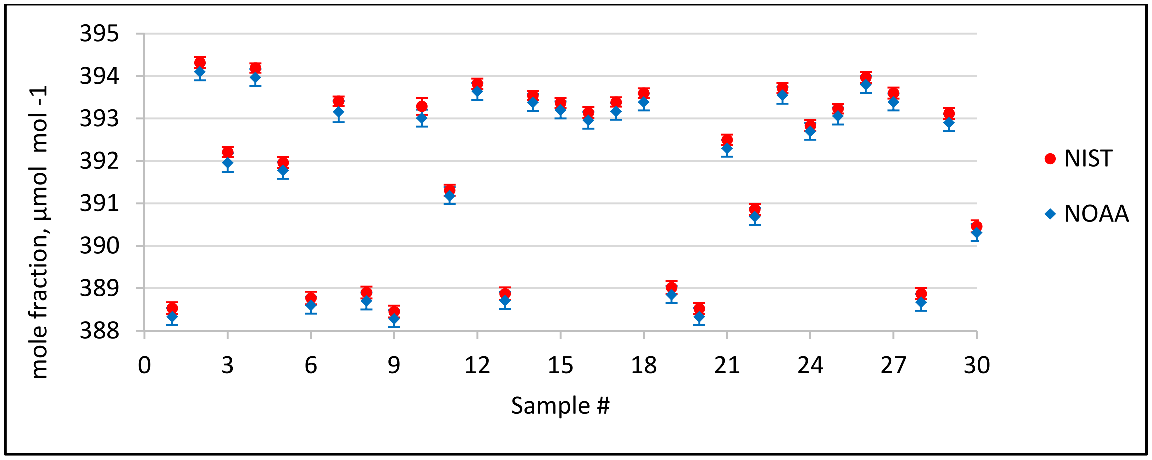


Figure 6. Comparison of NIST and NOAA CO_2 values for 30 SRM 1720 samples. Error bars are expanded uncertainties at approximate 95 % confidence interval.

5. Verifying the K120 Samples

Because all the original NIST 2012 PSMs at the 380 to 420 µmol/mol range were low in pressure, they could not be trusted to verify the new K120 PSMs. Therefore, in late December 2016 NIST used SRM sample 1720-A-29, then at 1700 psi, to verify the gravimetric mole fractions in the K120 standards using CRDS. Table 4 shows the gravimetric and verified values for the NIST K120 samples. The December 2016 verified value is significantly higher, by as much as 1 µmol/mol, than the gravimetric value for each of the three K120 standards. This provides strong evidence that even the %mol/mol 2012 PSMs have increased in mole fraction with the decrease in pressure.

Table 4. Gravimetric and verified values for NIST K120 samples.

Cylinder #	Original Reported Gravimetirc Value; ppm	December 2016 Verified Verified Value; µmol/mol	Verified-Grav Diff in µmol/mol	Verified-Grav % Diff	Pressure departure from NIST
FB04278	379.05 ± 0.39	380.08 ± 0.28	1.03	0.27%	10.34 MPa
FB04300	472.66 ± 0.43	473.40 ± 0.34	0.68	0.16%	9.65 MPa
FB04287	794.53 ± 1.03	795.12 ± 0.58	0.59	0.07%	9.99 MPa

*Uncertainties at 95 % confidence interval.

NIST was aware when they shipped their K120 samples to BIPM for the K120 comparison that their gravimetric values were not good. However, we followed the K120 protocol laid down for "preparative capabilities for carbon dioxide in air **primary** reference mixtures" and submitted the gravimetric values, knowing that the verified values were the correct molar fractions for these mixtures.

6. Stability check of K120 samples

NIST received the three K120 samples back from BIPM in August 2017 and proceeded to check them for stability. The three samples were once again compared to SRM 1720-A-29 and those results are shown in Table 5. The August 2017 stability check values agree with the December 2016 verified values and therefore have remained stable, as they should be since the pressures were well above those where increases in mole fraction have been observed.

Table 5. Stability check results for K120 samples.

Cylinder #	**December 2016 Verified Verified Value; µmol/mol**	**August 2017 Stability check; µmol/mol**	**August 2017 Stability check-Dec 2016 Verified Value, µmol/mol**	**August 2017 Stabiity check- Verified Value, % Diff**	Pressure back to NIST
FB04278	**380.08 ± 0.28**	**380.07 ± 0.30**	-0.01	**-0.003%**	7.24 MPa
FB04300	**473.40 ± 0.34**	**473.37 ± 0.52**	-0.03	**-0.006%**	7.24 MPa
FB04287	**795.12 ± 0.58**	**794.77 ± 0.38**	-0.35	**-0.044%**	7.24 MPa

*Uncertainties at 95 % confidence interval.

7. Isotopic Composition

The original value submitted by NIST for δ13C of -28 ± 2 ‰ was an error of data transcription. NIST had determined this value in 2014 for the pure source of CO_2 used to prepare the submitted standards to be $\delta^{13}C$ = -38 ± 2 ‰ as determined by FTIR. After receiveing the three standards back from BIPM, NIST measured the $\delta^{13}C$ to be -40.1 ± 0.1 ‰ as determined by GC-IRMS.

8. NIST Best-Estimate Value

If it had been explicitly stated that participants could report their "best-estimate value" for samples submitted for this CCQM-K120 key comparison for ambient CO2 in air, which would not necessarily be their true gravimetric value, then NIST would have submitted the values obtained from verification against the SRM sample. NIST "best-estimate values" are thus given in Table 6.

Table 6. NIST Best-Estimate (Verified) Values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	FB04278	380.08	0.28	2
2	FB04300	473.40	0.34	2
3	FB04287	795.12	0.58	2

9. Observations from this Comparison

NIST has the opinion that this key comparison was unnecessarily rushed to completion by the pilot laboratory. As co-pilot on this comparison, NIST should not have agreed to the arbitrary and premature deadline imposed by the pilot laboratory, knowing that an optimal level of sample control had not been demonstrated. Given that future key comparisons will continue to be co-piloted, both parties must agree that the preliminary studies and procedures are sufficiently well-established to set firm deadlines for sample submission by participating NMI's. Ideally, the mutual decision to set the timeline for the KC, and the readiness of other NMI's to participate, should be discussed formally by the GAWG at the Spring or Fall meeting.

NIST also recommends that the GAWG draft a formal policy document that unambiguously defines the terms such as, "gravimetric", "primary", "preparative", "analytical", "best-estimate", among others, which are used to describe the scope of key comparisons. For example, in the context of gas standards, we might propose that "primary" refers to mixtures prepared by gravimetry or manometry. On the other hand, "preparative" appears with "primary" in the K120 a and b protocol summary statement. What is the exact meaning of "preparative" in this context? Similarly, the term "best-estimate" was mentioned in discussions on K120 a and b during the April 2018 GAWG meeting when referring to acceptable reported values by NMIs, although the exact meaning of this term was not clarified. NIST's current position is that "best-estimate" falls outside the scope of K120a and b and is more consistent with an "analytical" comparison. These examples illustrate the need for a precise terminology to specify acceptable methods used for value assignment in future KCs. For transparency, this terminology should be formally defined by the GAWG for unambiguous use in subsequent KC protocols.

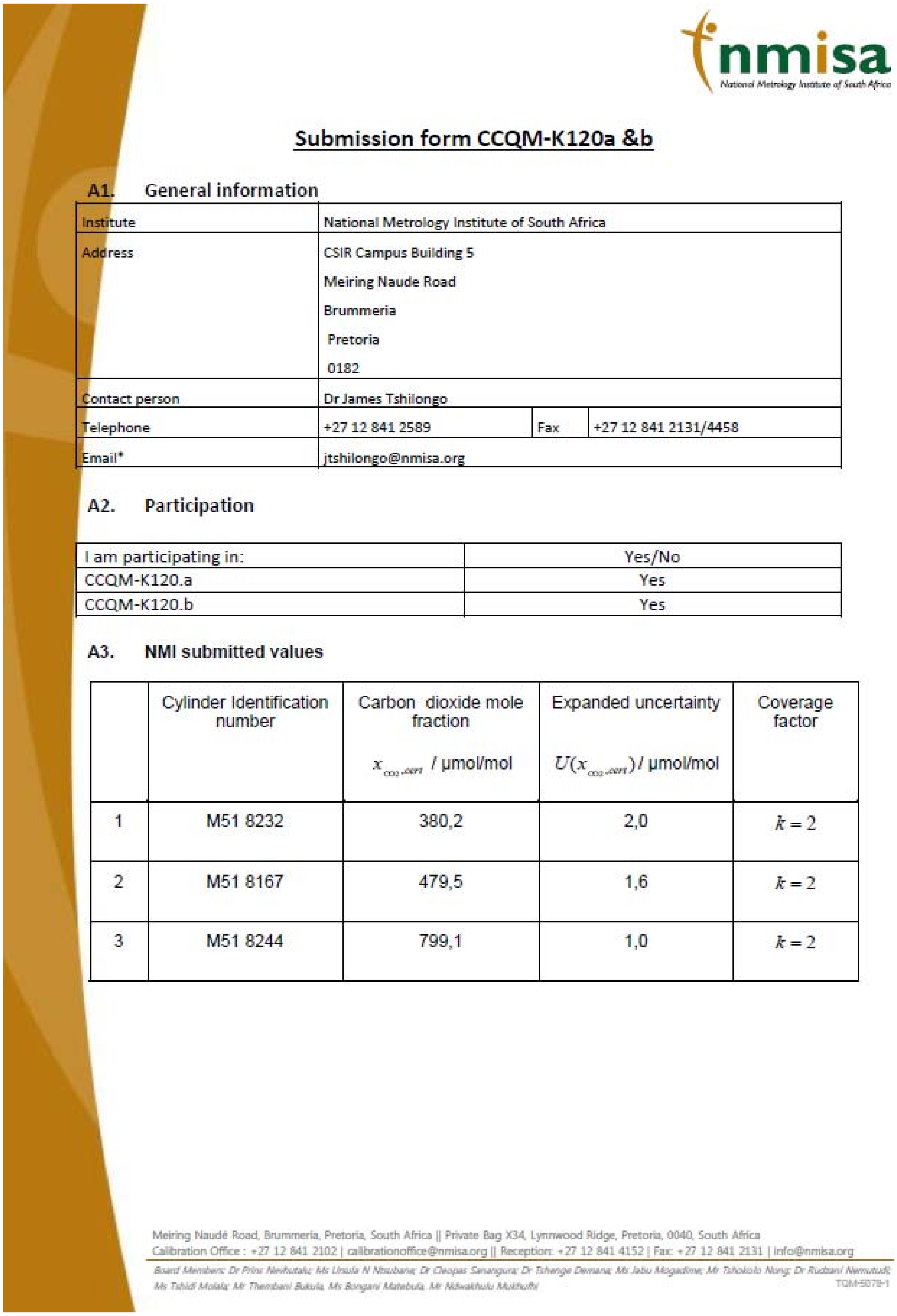
References

1. Miller, WR, Rhoderick, GC, Guenther, FR. Anal Chem, **2015**, 87(3), pp. 1957-1962**.**

2. Rhoderick, GR, Kitzis, DR, Kelley, ME, Miller, WR, Hall, BD, Dlugokencky, EJ, Tans, PP, Possolo, A, Carney, J, Anal Chem, **2016**, 88(6), 3376-3385 doi: 10.1021/acs.analchem.6b00123.

NMISA

Measurements before return of cylinders



Submission form CCQM-K120a &b

A1. General information

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Contact person	Dr James Tshilongo		
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Email*	jtshilongo@nmisa.org		

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO_2,cert}}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO_2,cert}})$ / µmol/mol	Coverage factor
1	M51 8232	380,2	2,0	$k = 2$
2	M51 8167	479,5	1,6	$k = 2$
3	M51 8244	799,1	1,0	$k = 2$

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TQM-5079-1

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: M51 8232

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7807	mol/mol	48×10^{-6}	mol/mol	$k = 2$
O_2	0,2096	mol/mol	15×10^{-6}	mol/mol	$k = 2$
Ar	0,0094	mol/mol	$4,6 \times 10^{-6}$	mol/mol	$k = 2$
CH_4	6,624	nmol/mol	4,3	nmol/mol	$k = 2$
N_2O	0	nmol/mol	0	nmol/mol	$k = 2$

(Standard 2) Cylinder Identification Number: M51 8167

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7809	mol/mol	28×10^{-6}	mol/mol	$k = 2$
O_2	0,2096	mol/mol	11×10^{-6}	mol/mol	$k = 2$
Ar	0,0089	mol/mol	$4,7 \times 10^{-6}$	mol/mol	$k = 2$
CH_4	8,869	nmol/mol	6,2	nmol/mol	$k = 2$
N_2O	0	nmol/mol	0	nmol/mol	$k = 2$

(Standard 3) Cylinder Identification Number: M51 8244

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,7793	mol/mol	31×10^{-6}	mol/mol	$k = 2$
O_2	0,2106	mol/mol	16×10^{-6}	mol/mol	$k = 2$
Ar	0,0093	mol/mol	$4,6 \times 10^{-6}$	mol/mol	$k = 2$
CH_4	10,09	nmol/mol	5,8	nmol/mol	$k = 2$
N_2O	0	nmol/mol	0	nmol/mol	$k = 2$

A4. Uncertainty Budget

The results for each day yielded an average concentration and a standard deviation. The average concentration and ESDM were obtained by the method of bracketing.

The predicted concentrations for the sample for the three days were averaged, and a standard deviation calculated for the three values. The uncertainties for the three different days and the verification uncertainty (ESDM) were combined as shown in Equation 1:

$$u_c^2 = \frac{u_{Day1}^2 + u_{Day2}^2 + u_{Day3}^2}{3} \ldots + (u_{ESDM})^2 + x_{grv}^2 \qquad \text{Equation 1}$$

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor k = 2 as in Equation 2.

$U = k \times u_c$, where k = 2 .... Equation 2

A5. Additional information

a) Purity table with uncertainties for the nominally pure CO_2 parent gas (cylinder# APL002961)

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
CO_2	0.9992	mol/mol	82×10^{-6}	mol/mol	$k=2$
N_2	$823,42\times10^{-6}$	mol/mol	$82,34\times10^{-6}$	mol/mol	$k=2$
Ar	$0,22\times10^{-6}$	mol/mol	$0,022\times10^{-6}$	mol/mol	$k=2$
CH_4	$4,268\times10^{-6}$	mol/mol	$1,3\times10^{-6}$	mol/mol	$k=2$
H_2O	$2,6\times10^{-7}$	mol/mol	$0,3\times10^{-6}$	mol/mol	$k=2$
H_2	20,00	nmol/mol	23	nmol/mol	$k=2$
CO	22,35	nmol/mol	26	nmol/mol	$k=2$
C_2H_6	6,00	nmol/mol	6,9	nmol/mol	$k=2$

All the three cylinders, M51 8232, M51 8167 and M51 8244 are traceable to the carbon dioxide purity table above.

b) Purity table with uncertainties for the nominally pure, O_2, N_2 and Ar, parent gas:

The two cylinders, M51 8232 and M51 8244 are traceable to the oxygen purity table below.

(Nominal pure O_2) Cylinder Identification Number: O_2UHP 333764

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	$2{,}000\times10^{-6}$	mol/mol	$2{,}3\times10^{-6}$	mol/mol	$k=2$
O_2	0,999995	mol/mol	$3{,}7\times10^{-6}$	mol/mol	$k=2$
Ar	$2{,}5\times10^{-6}$	mol/mol	$2{,}9\times10^{-6}$	mol/mol	$k=2$
CO	$0{,}26\ \times10^{-6}$	mol/mol	$0{,}078\times10^{-6}$	mol/mol	$k=2$
CO_2	$0{,}11\times10^{-6}$	mol/mol	$0{,}032\times10^{-6}$	mol/mol	$k=2$
CH_4	6,000	nmol/mol	6,9	nmol/mol	$k=2$
C_2H_6	6,000	nmol/mol	6,9	nmol/mol	$k=2$
H_2O	1,000	nmol/mol	1,2	nmol/mol	$k=2$

The cylinder, M51 8167 is traceable to the oxygen purity table below.

Nominal pure O_2) Cylinder Identification Number: O_2UHP 3348181

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	$2{,}000\times10^{-6}$	mol/mol	$2{,}3\times10^{-6}$	mol/mol	$k=2$
O_2	0,999995	mol/mol	$3{,}7\times10^{-6}$	mol/mol	$k=2$
Ar	$2{,}5\times10^{-6}$	mol/mol	$2{,}887\times10^{-6}$	mol/mol	$k=2$
CO	$0{,}28\ \times10^{-6}$	mol/mol	$0{,}085\times10^{-6}$	mol/mol	$k=2$
CO_2	$0{,}35\times10^{-6}$	mol/mol	$0{,}1\times10^{-6}$	mol/mol	$k=2$
CH_4	6	nmol/mol	6,9	nmol/mol	$k=2$
C_2H_6	6	nmol/mol	6,9	nmol/mol	$k=2$
H_2O	1	nmol/mol	1,2	nmol/mol	$k=2$

(Nominal pure N_2) Cylinder Identification Number: BIPN_2 3166101 used for standard 1 (M51 8232)

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,99994	mol/mol	$5{,}5\times10^{-6}$	mol/mol	$k=2$
Ar	$54{,}99\times10^{-6}$	mol/mol	$5{,}5\times10^{-6}$	mol/mol	$k=2$
O_2	1,165	nmol/mol	1,3	nmol/mol	$k=2$
CO	6,74	nmol/mol	7,8	nmol/mol	$k=2$
CO_2	11,40	nmol/mol	14	nmol/mol	$k=2$
CH_4	4,724	nmol/mol	5,5	nmol/mol	$k=2$
C_2H_6	7,070	nmol/mol	8,2	nmol/mol	$k=2$
H_2O	10,0	nmol/mol	12	nmol/mol	$k=2$
H_2	9,0	nmol/mol	11	nmol/mol	$k=2$

Nominal pure N_2) Cylinder Identification Number: BIPN_2 291441 used for standard 2 (M51 8167)

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,999944	mol/mol	$5{,}6\times10^{-6}$	mol/mol	$k=2$
Ar	$55{,}81\times10^{-6}$	mol/mol	$5{,}6\times10^{-6}$	mol/mol	$k=2$
O_2	1,165	nmol/mol	1,4	nmol/mol	$k=2$
CO	6,74	nmol/mol	7,8	nmol/mol	$k=2$
CO_2	67	nmol/mol	20	nmol/mol	$k=2$
CH_4	7,25	nmol/mol	8,4	nmol/mol	$k=2$
C_2H_6	8,0	nmol/mol	8,2	nmol/mol	$k=2$
H_2O	10,0	nmol/mol	12	nmol/mol	$k=2$
H_2	9,0	nmol/mol	11	nmol/mol	$k=2$

Nominal pure N_2) Cylinder Identification Number: BIPN_2 327042 used for standard 3 (M51 8244)

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0,999943	mol/mol	$5{,}7\times10^{-6}$	mol/mol	$k=2$
Ar	$56{,}67\times10^{-6}$	mol/mol	$5{,}7\times10^{-6}$	mol/mol	$k=2$
O_2	1,165	nmol/mol	1,4	nmol/mol	$k=2$
CO	6,74	nmol/mol	7,8	nmol/mol	$k=2$
CO_2	69	nmol/mol	21	nmol/mol	$k=2$
CH_4	7,25	nmol/mol	8,4	nmol/mol	$k=2$
C_2H_6	8,0	nmol/mol	8,2	nmol/mol	$k=2$
H_2O	10,0	nmol/mol	12	nmol/mol	$k=2$
H_2	9,0	nmol/mol	11	nmol/mol	$k=2$

(Nominal pure Argon) Cylinder Identification Number: Ar BIP 328877

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	7×10^{-6}	nmol/mol	$8{,}083\times10^{-6}$	nmol/mol	$k = 2$
Ar	0,999999	mol/mol	$0{,}0324\times10^{-6}$	mol/mol	$k = 2$
O_2	5×10^{-6}	nmol/mol	$5{,}774\times10^{-6}$	nmol/mol	$k = 2$
CO	$21{,}08\times10^{-6}$	nmol/mol	$24{,}34\times10^{-6}$	nmol/mol	$k = 2$
CO_2	$9{,}815\times10^{-6}$	nmol/mol	$11{,}33\times10^{-6}$	nmol/mol	$k = 2$
CH_4	5,835	nmol/mol	6,738	nmol/mol	$k = 2$
C_2H_6	6,095	nmol/mol	7,038	nmol/mol	$k = 2$
H_2O	10	nmol/mol	11,54	nmol/mol	$k = 2$

All the three cylinders, M51 8232, M51 8167 and M51 8244 are traceable to the argon purity table above.

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

The production diagram for the overall carbon dioxide standards is show in **figure 1**. The preparation was done in three dilution steps. The first step was to prepare 10 %mol/mol of CO2 in nitrogen. The second step was to prepare 2 %mol/mol and 1.0 %mol/mol of CO_2 in nitrogen. The last step was to prepare four (4) PSGMs of CO_2 in air with known mole fraction of 380 µmol/mol, 480 µmol/mol and 800 µmol/mol.

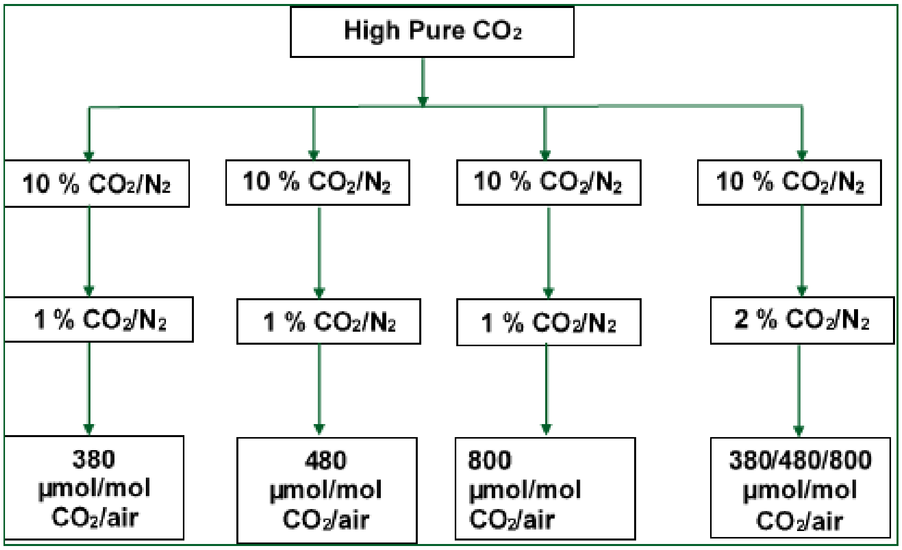


Figure 1 Production diagram for the carbon dioxide gas mixtures

d) A brief outline of the verification procedure applied to the final mixtures

Calibration standards:

The calibration standards consisted of a set of a total of twelve (12) PSGMs of CO_2 in air. Four (4) PSGMs of 380 µmol/mol, 480 µmol/mol and 800 µmol/mol were prepared from pre-mixtures in accordance with ISO 6142:2001 (Gas analysis - Preparation of calibration gas mixtures – Gravimetric method). The pre-mixtures were prepared from high pure CO_2 (3.2), BIP Nitrogen (4.4), Oxygen (5.5) and Argon (6.0) from Air Products, South Africa.

The prepared CO_2 PSGMs were analysed using substitution method (A-B-A method), where 'A' and 'B' represents the reference and sample respectively. One of the gas standards was chosen as a reference cylinder. The reference mixture was analysed before and after the sample, a typical sequence follows: A, B, A_1, C, A_2 until all four PSGMs from each mole fraction had been analysed. The analysis was performed under repeatable conditions.

Instruments:

The carbon dioxide (CO_2) in synthetic air was analysed using gas chromatography and cavity ring-down spectrometer techniques. The gas chromatography used was equipped with a methaniser-flame ionization detector and thermal conductivity detector (GC-meth-FID and GC-TCD). Table **1** and **2** below shows the conditions used to verify CO_2 in synthetic air using GC-meth-FID and GC-TCD.

Table 1: Analytical conditions for GC-methaniser-FID

Column oven temperature	100 °C
Column flow	5,4 mℓ/min
Column pressure	101,47 kPa
Carrier gas flow (N_2)	9 mℓ/min
Detector temperature	300 °C
Methaniser temperature	375 °C
Sample flow	40 mℓ/min
Sample loop	1 mℓ

Table 2: Analytical conditions for GC-TCD

Column oven temperature	65 °C
Column flow	6 mℓ/min
Column pressure	133 kPa
Carrier gas flow (H_2)	5 mℓ/min
Detector temperature	250 °C
Sample flow	30 mℓ/min
Sample loop	1 mℓ

The method of reference>>sample>>>reference was followed when determining the verification concentration of the prepared sample.

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 CCQM samples were prepared in June 2016 and analysed from June until November 2016.

f) Cylinder pressure before shipment to the BIPM

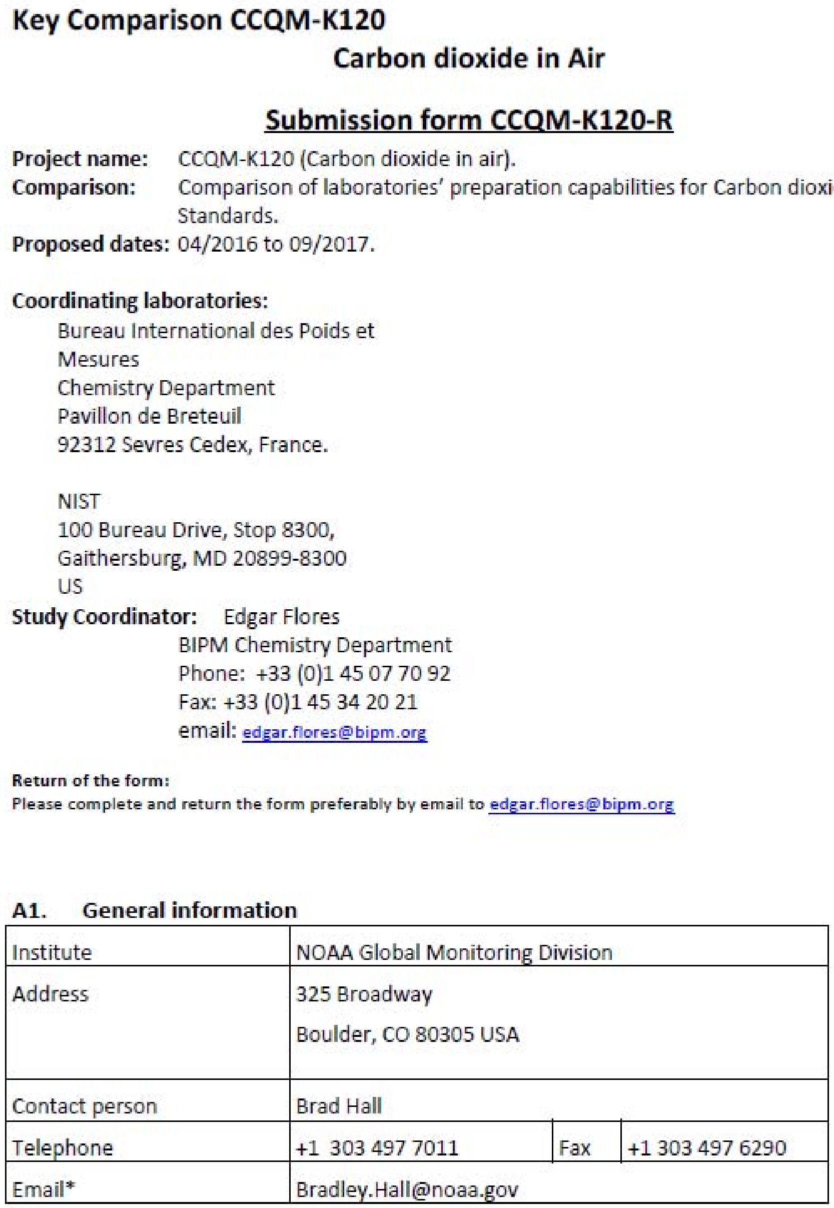
The cylinder pressure standard 1 (M51 8232) is **14 MPA**.

The cylinder pressure standard 2 (M51 8167) is **12 MPA**.

The cylinder pressure standard 3 (M51 8244) is **10 MPA**.

NOAA

Measurements before return of cylinders



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: 04/2016 to 09/2017.

Coordinating laboratories:

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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

	Cylinder Identification number	Carbon dioxide mole fraction $x_{CO2,cert}$ / µmol/mol	Expanded uncertainty $U(x_{CO2,cert})$ / µmol/mol	Coverage factor
1	CC310084	379.50	0.21	2
2	CC305198	479.26	0.26	2
3	CB11668	794.08	0.48	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **CC310084**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	Not measured	mol/mol		mol/mol	
O_2	0.2095	mol/mol	0.0002	mol/mol	2
Ar	Not measured	mol/mol		mol/mol	
CH_4	1762.2	nmol/mol	3.4	nmol/mol	2
N_2O	317.2	nmol/mol	0.5	nmol/mol	2

(Standard 2) Cylinder Identification Number: **CC305198**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	Not measured	mol/mol		mol/mol	
O_2	0.2095	mol/mol	0.0002	mol/mol	2
Ar	Not measured	mol/mol		mol/mol	
CH_4	1887.2	nmol/mol	3.6	nmol/mol	2
N_2O	328.6	nmol/mol	0.5	nmol/mol	2

(Standard 3) Cylinder Identification Number: **CB11668**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	Not measured	mol/mol		mol/mol	
O_2	0.2095	mol/mol	0.0002	mol/mol	2
Ar	Not measured	mol/mol		mol/mol	
CH_4	1888.5	nmol/mol	3.6	nmol/mol	2
N_2O	328.8	nmol/mol	0.5	nmol/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	CC310084	-8.7	0.2		-0.3	0.2	
2	CC305198	-8.8	0.2		-6.4	0.2	
3	CB11668	-8.5	0.4		-19.7	0.4	

*Uncertainties are approximate

A4. Uncertainty Budget

NOAA uses a manometric method to determine the mole fraction of CO_2 in dry air. The pressure and temperature of an air sample transferred to a large glass volume (~6 L) is compared to the pressure and temperature of CO_2 extracted from that air sample, and transferred to a small glass volume (~7 mL).

The measurement equation used to determine the mole fraction of CO_2 in dry air is:

$$X_{CO2} = (\phi^{-1})\frac{P_{CO2}T_{air}}{P_{air}T_{CO2}}(1 + A_1 - A_2) - X_{N2O} + X_{CO2\_loss}$$

Where $A_1 = \frac{P_{air}\beta_{air}}{RT_{air}}$, $A_2 = \frac{P_{CO2}\beta_{CO2}}{RT_{CO2}}$

Φ is the ratio of the large and small volumes, χ_{N2O} is the mole fraction of N_2O in the cylinder (measured separately), β_{air} and β_{CO2} are second Virial coefficients, R is the gas constant, and χ_{CO2_loss} is the amount of CO_2 lost during the measurement process (diffusion through o-rings, adsorption to surfaces, etc). χ_{CO2_loss} is determined from the rate of change of pressure and temperature during the experiment. Uncertainty budgets for nominal 400 and 800 µmol/mol CO_2 samples are shown in the Tables below.

We correct our manometric CO_2 result for N_2O because N_2O and CO_2 are inseparable in our system. We have analysed the purity of the CO_2 extract from one manometer experiment to demonstrate that N_2O is the only significant impurity. While we did not find any impurities present at levels that would warrant additional corrections (other than N_2O), we would like to repeat that experiment and will include those results here at a later time.

Uncertainty Budget at nominal 400 µmol/mol

Variable	Typical value	Standard uncertainty	unit	Contribution to uncertainty	Relative contribution to uncertainty
P_{air}	83	0.0025	kPa	1.198E-08	7%
P_{CO2}	30	0.0022	kPa	3.018E-08	17%
T_{air}	310	0.009	K	1.152E-08	6%
T_{CO2}	310	0.015	K	1.920E-08	11%
Φ (vol. ratio)	880.10	0.206	dimensionless	9.400E-08	53%
B_{air}	-5.87	0.2	cm^3/mol	8.940E-14	0%
B_{CO2}	-112.8	0.2	cm^3/mol	2.560E-13	0%
CO_2 loss	0.15	0.015	µmol/mol	1.406E-09	0.8%
X_{N2O}	0.325	0.0005	nmol/mol	2.441E-12	0%
repeatability, N=8		0.035	µmol/mol	7.813E-09	4%
analytical reproducibility		0.02	µmol/mol	2.500E-09	1%

Uncertainty Budget at nominal 800 µmol/mol

Variable	Typical value	Standard uncertainty	unit	Contribution to uncertainty	Relative contribution to uncertainty
P_{air}	83	0.0025	kPa	2.480E-08	7%
P_{CO2}	60	0.0022	kPa	3.014E-08	9%
T_{air}	310	0.009	K	2.385E-08	7%
T_{CO2}	310	0.015	K	4.005E-08	12%
Φ (vol. ratio)	880.10	0.206	dimensionless	1.928E-07	56%
B_{air}	-5.87	0.2	cm^3/mol	5.280E-13	0%
B_{CO2}	-112.8	0.2	cm^3/mol	3.820E-13	0%
CO_2 loss	0.3	0.03	µmol/mol	1.406E-09	0.4%
X_{N2O}	0.325	0.0005	nmol/mol	3.906E-13	0%
extrapolation		0.135	µmol/mol	2.983E-08	8.7%
analytical reproducibility		0.03	µmol/mol	1.406E-09	0.4%

A5. Additional information

Samples provided contain modified real air. CO_2 or scrubbed real air was added to achieve the target CO_2 mole fractions.

CO_2 mole fractions for CC310084 and CC305198 were determined by analysis using laser-spectroscopic methods as described in Tans et al. 2017. The laser spectroscopic system was calibrated against secondary standards over the nominal range 250-600 µmol/mol. Secondary standard value assignments were determined by comparison to primary standards on the laser spectroscopic system. Primary standard value assignments were determined by the NOAA manometric method.

The CO_2 mole fraction for CB11668 was also determined by analysis using laser spectroscopy using an extended set of primary and secondary standards for calibration. Standards used to extend the scale beyond the WMO scale range are not well-characterized, so we include additional uncertainty due to extrapolation.

Results are provided on scale WMO-CO2-X2017p, which represents a recent revision of scale WMO-CO2-X2007 (Hall et al, 2017). We define the scale as "provisional" because the update is not complete and has not yet been released to users.

Cylinder pressures at time of shipment

CC310084	1900 psi
CC305198	1950 psi
CB11668	1730 psi

Cylinders were analyzed over a period of 6 months. Initial results indicate stability to within 0.0075%. We will re-assess stability after they return.

Tans, P. P, A. M. Crotwell, K. W. Thoning, Abundances of isotopologues and calibration of CO_2 greenhouse gas measurements, Atmos. Meas. Tech. Discuss., 2017.

Hall, B. D., D. Kitzis, A. M. Crotwell, T. Mefford, and P. P. Tans, Revision of the WMO calibration scale for atmospheric carbon dioxide, *manuscript in preparation*, 2017.

NPL

Measurements before return of cylinders

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

A1. General information

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A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide amount fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	2179	380.27	0.19	2
2	2170	480.02	0.24	2
3	2181	799.70	0.40	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **2179**

Component	Amount fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78079	mol/mol	0.00047	mol/mol	2
O_2	0.20960	mol/mol	0.00013	mol/mol	2
Ar	0.009232	mol/mol	0.000018	mol/mol	2
CH_4	<10	nmol/mol	-	nmol/mol	-
N_2O	<10	nmol/mol	-	nmol/mol	-

Table 1 Composition of standard 1

(Standard 2) Cylinder Identification Number: **2170**

Component	Amount fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78069	mol/mol	0.00047	mol/mol	2
O_2	0.20950	mol/mol	0.00013	mol/mol	2
Ar	0.009334	mol/mol	0.000019	mol/mol	2
CH_4	<10	nmol/mol	-	nmol/mol	-
N_2O	<10	nmol/mol	-	nmol/mol	-

Table 2 Composition of standard 2

(Standard 3) Cylinder Identification Number: **2181**

Component	Amount fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.78055	mol/mol	0.00047	mol/mol	2
O_2	0.20928	mol/mol	0.00013	mol/mol	2
Ar	0.009367	mol/mol	0.000019	mol/mol	2
CH_4	<10	nmol/mol	-	nmol/mol	-
N_2O	<10	nmol/mol	-	nmol/mol	-

Table 3 Composition of standard 3

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	2179	-5.5 ‰	1.0 ‰	2	-22.5 ‰	1.0 ‰	2
2	2170	-5.5 ‰	1.0 ‰	2	-22.5 ‰	1.0 ‰	2
3	2181	-5.5 ‰	1.0 ‰	2	-22.5 ‰	1.0 ‰	2

Table 4 Isotopic composition of each submitted standard vs VPDB

A4. Uncertainty Budget

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of CO_2 and synthetic air
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analytical validation

Table 5 details the uncertainty analysis. The preparation component includes estimated uncertainty from purity analysis, weighing and atomic weights.

		Relative Uncertainty (%)		
Identifier	**Component**	**Preparation (k=1)**	**Validation (k=1)**	**Total (k=2)**
2179	CO_2	0.018	0.02	0.05
2170	CO_2	0.014	0.02	0.05
2181	CO_2	0.010	0.02	0.05

Table 5: Uncertainty contributors

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

A5. Additional information

Description of the procedure

Three gas mixtures were prepared for this comparison (2170, 2179 and 2181) at NPL in synthetic air from sources of CO_2 (BOC speciality gases), O_2 (BOC speciality gases, N 6.0), N_2 (Air Products, BIP$^+$) and Ar (Air Products, BIP$^+$). The pure industrial source of CO_2 was spiked with pure $^{13}CO_2$ to achieve an isotopic composition close to natural abundance. The mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. Two further sets of three reference standards was prepared and these were used to validate the comparison mixtures. The scheme below shows the gravimetric dilutions with nominal CO_2 amount fractions.

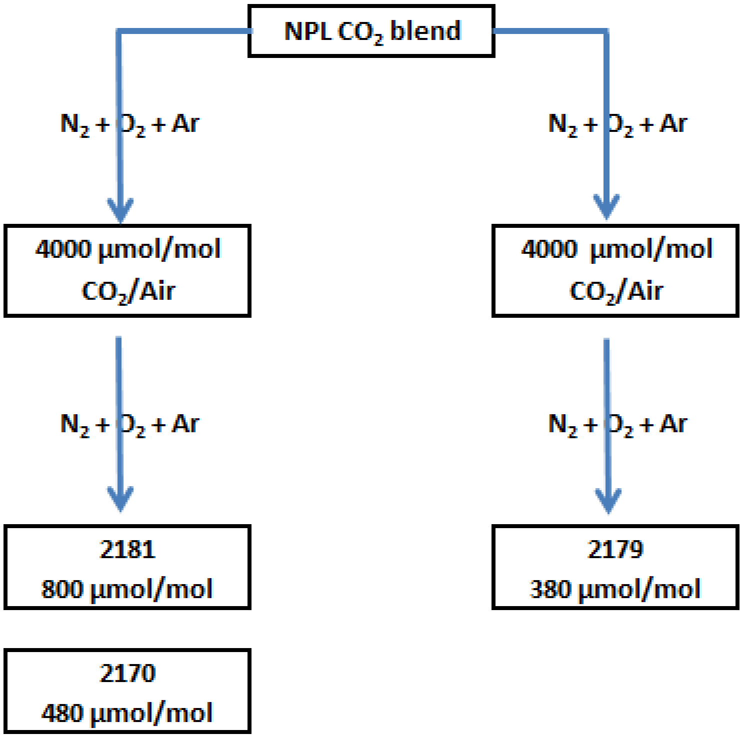

Figure 1 Dilution scheme for gravimetric preparation

A Picarro G2301 Cavity ring-down spectrometer was used to validate the amount fraction of CO_2 in mixtures 2170, 2179 and 2181. The analyser response to the matrix gas was recorded. The analyser response to a reference mixture was then recorded for a five minute period followed by either 2170, 2179 or 2181 for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of 2170, 2179 and 2181 were then determined by multiplying the ratio of the analyser response to each mixture and the reference mixture (both were corrected for the analyser response to matrix gas) with the amount fraction of the reference mixture. These measurements were used to validate the gravimetric amount fractions submitted.

Cylinders were maintained at a laboratory temperature of (20 ± 3) °C throughout the period of analysis. Samples were introduced into the analyser at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

Purity tables for the CO_2, Ar, N_2 and O_2 are provided below.

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
CO_2	999999.80	0.06
N_2	0.050	0.029
O_2	0.050	0.029
CO	0.050	0.029
Ar	0.050	0.029

Table 6: CO_2 purity table

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
Ar	999999.93	0.02
N_2	0.039	0.023
O_2	0.0050	0.0029
CO_2	0.007	0.004
CO	0.0018	0.0010
CH_4	0.00029	0.00017

Table 7: Ar purity table

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
N_2	999984.3	1.6
O_2	0.015	0.009
Ar	15.67	1.57
CO_2	0.00085	0.00049
CO	0.00058	0.00033
CH_4	0.00080	0.00046

Table 8: N_2 purity table

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
O_2	999999.1	0.3
N_2	0.50	0.29
Ar	0.050	0.029
CO_2	0.19	0.19
CH_4	0.0282	0.0048

Table 9: O_2 purity table

The mixtures were prepared on during the period 24th October to 8th November 2016. Measurements to study the stability of the mixtures were carried out over a 6 week period.
The cylinder pressure of mixtures 2170, 2179 and 2181 prior to shipping was > 10 MPa.

NPLI

Measurements before return of cylinders

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.
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A1. General information

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A2. Participation

I am participating in:	Yes/No
CCQM-K120.a (only)	yes
CCQM-K120.b (only)	Yes

A3. NMI submitted values

	Cylinder Identification Number	Carbon Dioxide mole fraction $X_{CO2cert}$/ µmol/mol	Expanded Uncertainties µmol/mol	Coverage factor
1	JJ108891	375.72	3.22	2
2	JJ108862	480.52	3.04	2
3	JJ108854	796.38	5.03	2

A4. NMI submitted values

Matrix composition: Component mol fraction and uncertainties (for each standard submitted):

Standard1: Cylinder Number: JJ108891

component	Mole fraction value	unit	Expanded Uncertainty	Unit	Coverage Factor
N2	0.781273	mol/mol	0.002210	mol/mol	2
O2	0.209688	mol/mol	0.000590	mol/mol	2
Ar	0.009040	mol/mol	0.000030	mol/mol	2

Standard 2: Cylinder Number: JJ108862

component	Mole fraction value	unit	Expanded Uncertainty	Unit	Coverage Factor
N2	0.781989	mol/mol	0.002210	mol/mol	2
O2	0.208853	mol/mol	0.000590	mol/mol	2
Ar	0.009158	mol/mol	0.000030	mol/mol	2

Standard 3: Cylinder Number: JJ108854

Component	Mole fraction value	unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.781363	mol/mol	0.002210	mol/mol	2
O_2	0.209789	mol/mol	0.000594	mol/mol	2
Ar	0.008847	mol/mol	0.000030	mol/mol	2

A4. Uncertainty Budget

The final uncertainty budget was estimated by combining two uncertainty components (i.e., preparation of PSGM and its analysis both).

(i) The Expanded Uncertainty estimation of all the prepared gas mixtures (PSGMs) has been calculated according to ISO 6142: Preparation of Calibration gas mixtures – Gravimetric method taking account of following factors:

1 Raymor Balance
1. Mass Pieces
2. Bouancy corrections for weights
3. Handling of cylinder
4. Residual gases in the cylinder
5. Expansion of the cylinder due to filling of gas at High pressure

(ii) Uncertainties in the analysis
These are calculated taking acount of

1. Standard deviation/ Repeatability
2. Reproducibility &
3. Instrument response

A5. Additional Information

b) A purity table with uncertainties for pure Ar, N_2 and O_2 parent gas

The purity of N_2, O_2 and Ar parent gases were determined using tiger optics CRDS analyzers model for the following H_2O, CH_4 and CO gas components. The moisture of the gases were determined using Tiger Optics moisture analyzer model LaserTrace. CH_4 was determined using Tiger Optics methan analyzer model MTO-1000-CH4 and CO gas was determined using Tiger Optics CO analyzer model HALO 3-CO.

Purity of Argon gas was found to be as given below

Name of gases	Concentration ppm	Expanded Uncertainties	Coverage factor
H_2O / moisture	1.45	0.23	2
CO gas	0.27	0.08	2
CH_4 gas	Not Detected (N.D) (<0.001)		

Purity of N_2 gas was found to be as given below

Name of gases	Concentration ppm	Expanded Uncertainties	Coverage factor
H_2O / moisture	0.83	0.05	2
CO gas	3.4	0.24	2
CH_4 gas	N.D (<0.001)		

Purity of O_2 gas was found to be as given below

Name of gases	Concentration ppm	Expanded Uncertainties	Coverage factor
H_2O / moisture	0.95	0.05	2
CH_4 gas	N.D (<0.001)		

c) A brief out line of the dilution series undertaken to produce the final mixtures

The preparation procedure involves following steps

1) **Preparation of gas mixtures of CO_2 in nitrogen gas**.

Al cylinders 10 litre were evacuated and purged with nitogen gas and again evacuated with heating of the cylinders at 60-70^{o}C. This process is repeated thrice before any preparation of gas mixture was carried out. The theoritical calculations were carried out for the desired concentrations.

Gas mixtures of CO_2 in nitrogen gas from pure gas were prepared in two series in the concentrations around 20544 and 20392 μmol/mol. These gas mixtures were diluted in the concentration ranges from (370~ 1000 μmol/mol). Total of 9 cylindres were prepared. All the preparation of Primary Standard Gas Mixtures (PSGM) were done in acordance to ISO 6142: Gas Analysis -Preparation of calibration gas mixtures - Gravimetric Method. These cylinders were validated in acordance to ISO 6143: Gas analysis - Comparision method for determining and checking the composition of calibration gas mixtures. Thus the prepared CO_2 gas mixtures were certified as CO_2 in Nitrogen gas Primary Standard Gas Mixtures (PSGM).

2) **Preparation of CO_2 in synthetic air:**

These mixtures were prepared from the two series of CO_2 premixtures prepared in nitrogen gas in the concentration around 20544 and 20392 μmol/mol as mentioned above. The empty cylinders were evacuated and purged with dry nitogen gas and again evacuated with heating. This process is repeated thrice for the pre-preparation of the cylinders. The thoeritical calculations were carried out similating the desired concentration range as given in CCQM K-120. The required amount of pre mixture of CO_2 in Nitrogen is transferred in the pre prepared evacuated cylinder. These mixtures were now added with desired amount of pure Argon gas, pure oxygen gas and finally top up has been done by nitrogen gas to simulate the synthetic air concentration. Total of 9 cylinders were prepared in the concentration ranges (370~800 μmol/mol). These cylinders were validated using above prepared binary mixtures of CO_2 in Nitrogen gas Primary Standard Gas Mixtures (PSGM).

d) a brief outline of the verification procedure applied to the final mixtures

Validation of Synthetic Air Mixtures

The prepared synthetic air gas mixture cylinders were validated using above prepared binary mixtures of CO_2 in Nitrogen gas Primary Standard Gas Mixtures (PSGM) as per ISO 6143.

The standard and sample gases were injected into eight-port gas sampling valves of the Agilent Gas Chromatograph with flame ionization detector (FID) Model 6890N/ US 10723001. The GC column used was Haysep D, length 12 ft dia 1/8” and mesh 100/120. Helium gas was used as a carrier gas. The measurement conditions were the sample loop of 0.5 ml, oven temperature of 80^oC, detector temperature of 250^oC, hydrogen and air flow rate of 20 ml/min and 300 ml/min, respectively. All the Synthetic air CO_2 gas mixtures were evaluated using a higher concentration CO_2 in Nitrogen gas Primary Standard Gas Mixtures (PSGM). The average response was calculated by using the six values rejecting first and last two values each time for each measurement series. The analysis of the cylinders were carried out three times. The collected data is analysed and the uncertainty budget was evaluated.

f) Cylider pressure before shipment to BIPM

Sl.No.	Cylinder No / Conc (Approx) μmol/mol	Pressure
1	JJ108891/ 380	110Bar/ 1596 psi
2	JJ108862/ 480	110Bar/ 1596 psi
3	JJ108854/ 800	110Bar/ 1596 psi

The Team members : Dr. Daya Soni, Dr. Khem Singh, Ms. S. Bhatt, Ms Joty Pokheryal, Dr. S.G. Aggarwal, Dr. P.Johri

Report of stability measurements after return of cylinders

Key Comparison CCQM-K120
Carbon dioxide in Air

Submission form CCQM-K120-R (Stability Studies)

Project name: CCQM-K120 (Carbon dioxide in air).
Comparison: Comparison of laboratories' preparation capabilities for Carbon dioxide in Air Standards.
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A1. General information

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A2. Participation

I am participating in:	Yes/No
CCQM-K120.a (only)	yes
CCQM-K120.b (only)	Yes

Stability Studies Result

A3. NMI stability analysis values with its analytical uncertainty budget only

	Cylinder Identification Number	Carbon Dioxide mole fraction $X_{CO2cert}$/ µmol/mol	Expanded Uncertainties µmol/mol	Coverage factor
1	JJ108891	378.24	3.95	2
2	JJ108862	478.57	5.23	2
3	JJ108854	798.80	3.35	2

A4. Uncertainty Budget

The stability uncertainty budget was estimated using analytical uncertainty components only
These are calculated taking account of

1. Standard deviation/ Repeatability
2. Calibration standard uncertainty
3. Instrument response

A5: A brief outline of the Stability Analysis Procedure applied to the Cylinders returned from BIPM France

The cylinders of the synthetic air gas mixtures arrived from BIPM France cylinders were analyzed using the prepared binary mixtures of CO_2 in Nitrogen gas Primary Standard Gas Mixtures (PSGM) as per ISO 6143. The cylinders returned from BIPM and the binary standards gas mixtures in nitrogen gas cylinders are put to rotation for over night before using for its stability studies.

The standard and sample gases were injected into eight-port gas sampling valves of the Agilent Gas Chromatograph with flame ionization detector (FID) Model 6890N/ US 10723001. The GC column used was Haysep D, length 12 ft dia 1/8" and mesh 100/120. Helium gas was used as a carrier gas. The measurement conditions were the sample loop of 0.5 ml, oven temperature of 80^{o}C, detector temperature of 250^{o}C, hydrogen and air flow rate of 20 ml/min and 300 ml/min, respectively. All the Synthetic air CO_2 gas mixtures were evaluated using a higher concentration CO_2 in Nitrogen gas Primary Reference Gas Mixtures (PRGM). The average response was calculated by using six values rejecting first and last two values each time for each measurement series. The analysis of the cylinders was carried out three times. The collected data is analyzed and the analytical uncertainty budget was evaluated and reported in the stability result.

The Team members : Dr. Daya Soni, Dr. Khem Singh, Ms. S. Bhatt, Dr. S.G. Aggarwal, Dr. P.Johri

UME

Measurements before return of cylinders

Key Comparison CCQM-K120
Carbon dioxide in Air
Submission form CCQM-K120-R

A1. General information

Institute	**UME**		
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Contact person	**Dr. Tanıl Tarhan**		
Telephone	**+ 90 262 679 5000 / 6401**	Fax	**+ 90 262 679 5001**
Email*	**tanil.tarhan@tubitak.gov.tr**		

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	PSM298266	379.92	0.16	2
2	PSM266468	480.42	0.17	2
3	PSM298347	800.76	0.27	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **PSM298266**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7803392	mol/mol	0.0000166	mol/mol	2
O_2	0.2099663	mol/mol	0.0000166	mol/mol	2
Ar	0.0093140	mol/mol	0.0000023	mol/mol	2

(Standard 2) Cylinder Identification Number: **PSM266468**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7799681	mol/mol	0.0000165	mol/mol	2
O_2	0.2102293	mol/mol	0.0000166	mol/mol	2
Ar	0.0093215	mol/mol	0.0000023	mol/mol	2

(Standard 3) Cylinder Identification Number: **PSM298347**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7795520	mol/mol	0.0000164	mol/mol	2
O_2	0.2103522	mol/mol	0.0000164	mol/mol	2
Ar	0.0092945	mol/mol	0.0000023	mol/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	**PSM298266**	-1.65	0.05	2	-	-	-

A4. Uncertainty Budget

The basis for the uncertainty budget is formed by the uncertainty evaluation from the gravimetric preparation and analytical measurements. Gravimetric preparation contains uncertainty sources from weighing and those from purity of the parent gases. Gravimetric preparation and uncertainty evaluation have performed according to ISO 6142 [1]. The measurement uncertainty of each mixture was determined according to ISO 6143 [2].

The combined standard uncertainty of each mixture was determined by the following equation:

$$\mathrm{u_c} = \sqrt{\mathrm{u_m^2} + \mathrm{u_g^2}}$$

where

u_m, standard uncertainty from measurements

u_g, standard uncertainty from gravimetric preparation

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

A5. Additional information

Mixtures were produced with synthetic air.

s) Purity table with uncertainties for the nominally pure CO_2 parent gas;

Main component	carbon dioxide	
Cylinder Code	LG7524	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
carbon dioxide	999977.50	9.24
water	2.50	1.44
nitrogen	15.00	8.66
oxygen	5.00	2.89

t) Purity tables with uncertainties for the nominally pure N_2, O_2, and Ar parent gas;

Main component	nitrogen	
Cylinder Code	LG1220 and LG1221	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
carbon monoxide	0.05	0.03
carbon dioxide	0.05	0.03
methane	0.05	0.03
water	0.25	0.14
nitrogen	999999.35	0.21
oxygen	0.25	0.14

Main component	oxygen

Cylinder Code	LG3367	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
argon	1.00	0.58
carbon dioxide	0.10	0.06
methane	0.10	0.06
water	1.50	0.87
nitrogen	2.50	1.44
oxygen	999994.80	1.78

Main component	argon	
Cylinder Code	LG1313	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
argon	999993.00	1.22
water	1.50	0.87
nitrogen	4.00	2.31
oxygen	1.50	0.87

u) Mixtures were prepared according to the scheme displayed in Figure 1. Two different types of the pre-mixtures were prepared. These are 10 % and 0.5 % carbon dioxide in nitrogen and 15 % argon in nitrogen. 0.5 % carbon dioxide in nitrogen and 15 % argon in nitrogen pre-mixtures were used together with pure nitrogen and pure oxygen for the final mixtures.

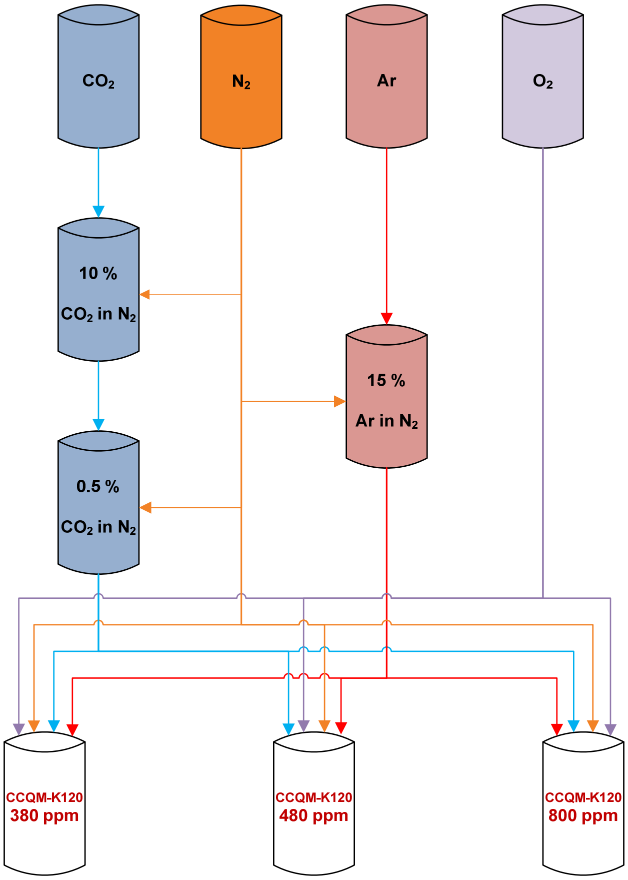

Figure 1. Preparation scheme for the mixtures.

v) Verification procedure applied to the final mixtures:

The carbon dioxide (CO_2) in air mixtures were analyzed on a cavity ring-down spectroscopy (CRDS) instrument, i.e., Picarro G2401 CO/CO2/CH4/H2O Analyzer equipped with 16-Port Distribution Manifold. Verification of the mixtures was carried out using own standards. Cylinders were equipped with pressure reducers and connected to 16-port distribution manifold. They were flushed three times before the first measurement. The analyzer operates vacuum pump to get the sample. Therefore, excess amount of gas than the amount of gas required by CRDS has been sent to the analyzer by adjusting the reducers. The excess gas has been sent to the atmosphere through a bypass connected to sample line in between distribution manifold and the analyzer. Each cylinder was measured for 15 minutes which is a sufficient time to obtain stable results. The measurement data was collected using CRDS software. Software takes about 2850 readings for 15 minutes. During the data evaluation, total number of 240 readings in between 10-14 minutes has been used for determination of average values and uncertainties for each cylinder at each measurement.

w) Stability testing of the mixtures:

Pre-mixtures and final mixtures were prepared in 01-17 April 2016. First verification was performed in 21-24 April 2016. Second verification was carried out in 22 September 2016. Final verification was performed 11-19 October 2016. Measurement results are shown in Figure 2. As can be seen from the figure, instrument response does not vary with time for each cylinder. Stability testing did not show any instability within the accuracy of the measurement method.

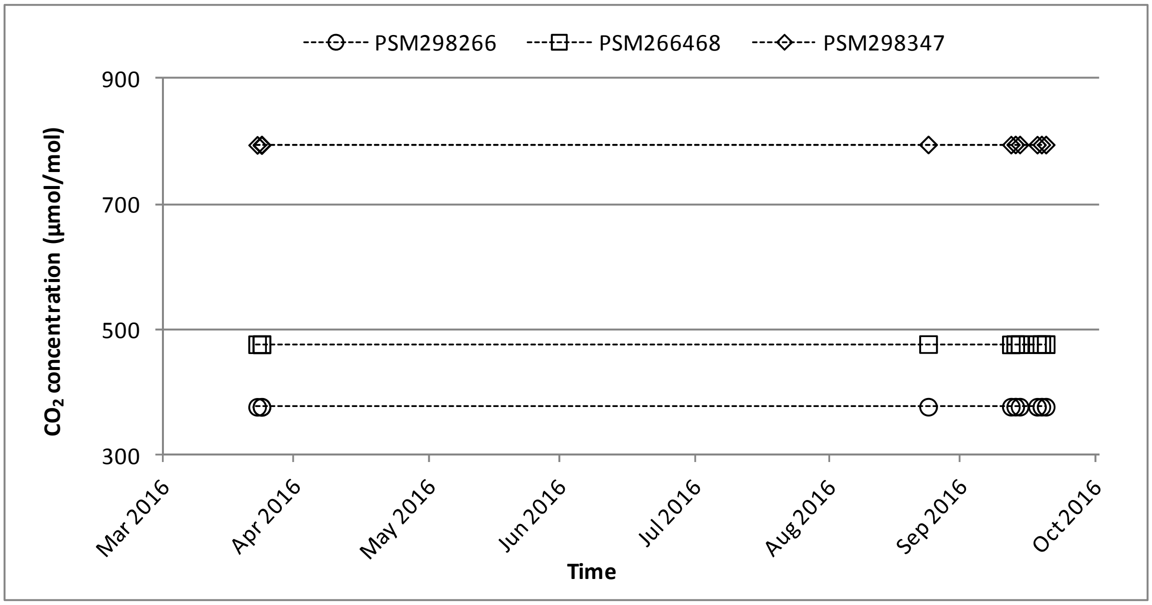

Figure 2. Stability measurements.

x) Cylinder pressures before shipment to the BIPM are given below.

Cylinder Code	Pressure, bar
PSM298266	86
PSM266468	86
PSM298347	90

References:

[1] International Organization for Standardization, “ISO 6142 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods”, ISO Geneva, 2001

[2] International Organization for Standardization, "ISO 6143 Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures ", ISO Geneva, 2001

Report of stability measurements after return of cylinders

Key Comparison CCQM-K120
Carbon dioxide in Air
Submission form CCQM-K120-R

A1. General information

Institute	**UME**		
Address	**TÜBİTAK UME - Gas Metrology Laboratory** **Baris Mah. Dr. Zeki Acar Cad. No:1** **41470 Gebze / Kocaeli TURKEY**		
Contact person	**Dr. Tanıl Tarhan**		
Telephone	**+ 90 262 679 5000 / 6401**	Fax	**+ 90 262 679 5001**
Email*	**tanil.tarhan@tubitak.gov.tr**		

A2. Participation

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

A3. NMI submitted values

	Cylinder Identification number	Carbon dioxide mole fraction $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / µmol/mol	Coverage factor
1	PSM298266	379.92	0.19	2
2	PSM266468	480.42	0.25	2
3	PSM298347	800.76	0.36	2

A4. NMI submitted values

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

(Standard 1) Cylinder Identification Number: **PSM298266**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7803392	mol/mol	0.0000166	mol/mol	2
O_2	0.2099663	mol/mol	0.0000166	mol/mol	2
Ar	0.0093140	mol/mol	0.0000023	mol/mol	2

(Standard 2) Cylinder Identification Number: **PSM266468**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7799681	mol/mol	0.0000165	mol/mol	2

O_2	0.2102293	mol/mol	0.0000166	mol/mol	2
Ar	0.0093215	mol/mol	0.0000023	mol/mol	2

(Standard 3) Cylinder Identification Number: **PSM298347**

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.7795520	mol/mol	0.0000164	mol/mol	2
O_2	0.2103522	mol/mol	0.0000164	mol/mol	2
Ar	0.0092945	mol/mol	0.0000023	mol/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	**PSM298266**	-1.65	0.05	2	-	-	-

A4. Uncertainty Budget

The basis for the uncertainty budget is formed by the uncertainty evaluation from the gravimetric preparation and analytical measurements. Gravimetric preparation contains uncertainty sources from weighing and those from purity of the parent gases. Gravimetric preparation and uncertainty evaluation have performed according to ISO 6142 [1]. The measurement uncertainty of each mixture was determined according to ISO 6143 [2]. The mixtures were analyzed for stability after receiving them back from BIPM.

The combined standard uncertainty of each mixture was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2 + u_s^2}$$

where

u_m, standard uncertainty from measurements

u_g, standard uncertainty from gravimetric preparation

u_s, standard uncertainty for stability

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

A5. Additional information

Mixtures were produced from pure components of CO_2, N_2, O_2, and Ar.

y) Purity table with uncertainties for the nominally pure CO_2 parent gas;

Main component	carbon dioxide	
Cylinder Code	LG7524	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
carbon dioxide	999977.50	9.24
water	2.50	1.44
nitrogen	15.00	8.66
oxygen	5.00	2.89

z) Purity tables with uncertainties for the nominally pure N_2, O_2, and Ar parent gas;

Main component	nitrogen	
Cylinder Code	LG1220 and LG1221	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
carbon monoxide	0.05	0.03
carbon dioxide	0.05	0.03
methane	0.05	0.03
water	0.25	0.14
nitrogen	999999.35	0.21
oxygen	0.25	0.14

Main component	oxygen	
Cylinder Code	LG3367	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
argon	1.00	0.58
carbon dioxide	0.10	0.06
methane	0.10	0.06
water	1.50	0.87
nitrogen	2.50	1.44
oxygen	999994.80	1.78

Main component	argon	
Cylinder Code	LG1313	
Component	**Mole fraction [µmol/mol]**	**Standard uncertainty [µmol/mol]**
argon	999993.00	1.22
water	1.50	0.87
nitrogen	4.00	2.31
oxygen	1.50	0.87

aa) Mixtures were prepared according to the scheme displayed in Figure 1. Two different types of the pre-mixtures were prepared. These are 10 % and 0.5 % carbon dioxide in nitrogen and 15 % argon in nitrogen. 0.5 % carbon dioxide in nitrogen and 15 % argon in nitrogen pre-mixtures were used together with pure nitrogen and pure oxygen for the final mixtures.

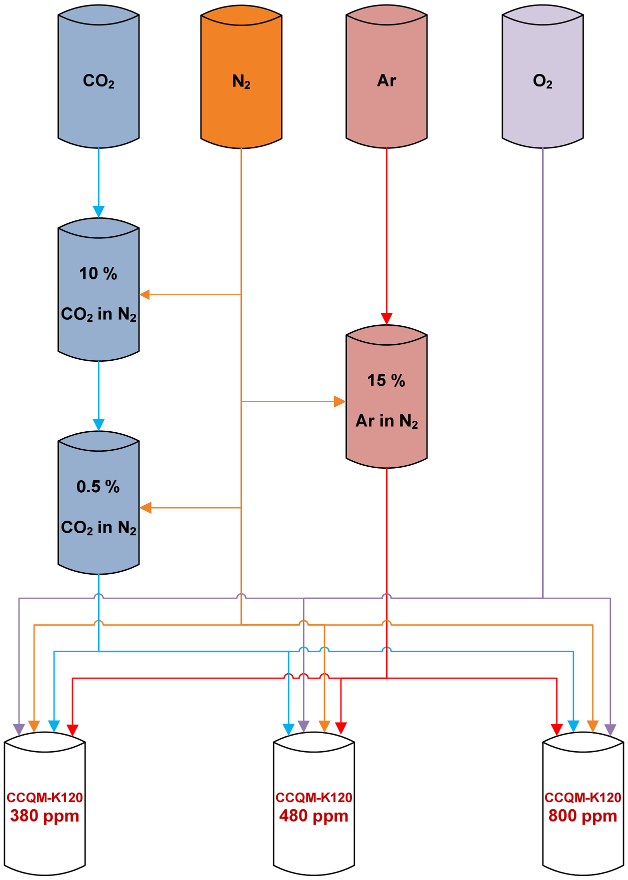

Figure 1. Preparation scheme for the mixtures.

bb) Verification procedure applied to the final mixtures:

The carbon dioxide (CO_2) in air mixtures were analyzed on a cavity ring-down spectroscopy (CRDS) instrument, i.e., Picarro G2401 CO/CO2/CH4/H2O Analyzer equipped with 16-Port Distribution Manifold. Verification of the mixtures was carried out using own standards. Cylinders were equipped with pressure reducers and connected to 16-port distribution manifold. They were flushed three times before the first measurement. The analyzer operates vacuum pump to get the sample. Therefore, excess amount of gas than the amount of gas required by CRDS has been sent to the analyzer by adjusting the reducers.

The excess gas has been sent to the atmosphere through a bypass connected to sample line in between distribution manifold and the analyzer. Each cylinder was measured for 15 minutes which is a sufficient time to obtain stable results. The measurement data was collected using CRDS software. Software takes about 2850 readings for 15 minutes. During the data evaluation, total number of 240 readings in between 10-14 minutes has been used for determination of average values and uncertainties for each cylinder at each measurement.

cc) Stability testing of the mixtures:

Pre-mixtures and final mixtures were prepared in 01-17 April 2016. First verification was performed in 21-24 April 2016. Second verification was carried out in 22 September 2016. Final verification was performed during 11-19 October 2016. Measurement results are shown in Figure 2. As can be seen from the figure, instrument response does not vary with time for each cylinder. Stability testing did not show any instability within the accuracy of the measurement method before sending the cylinders to BIPM.

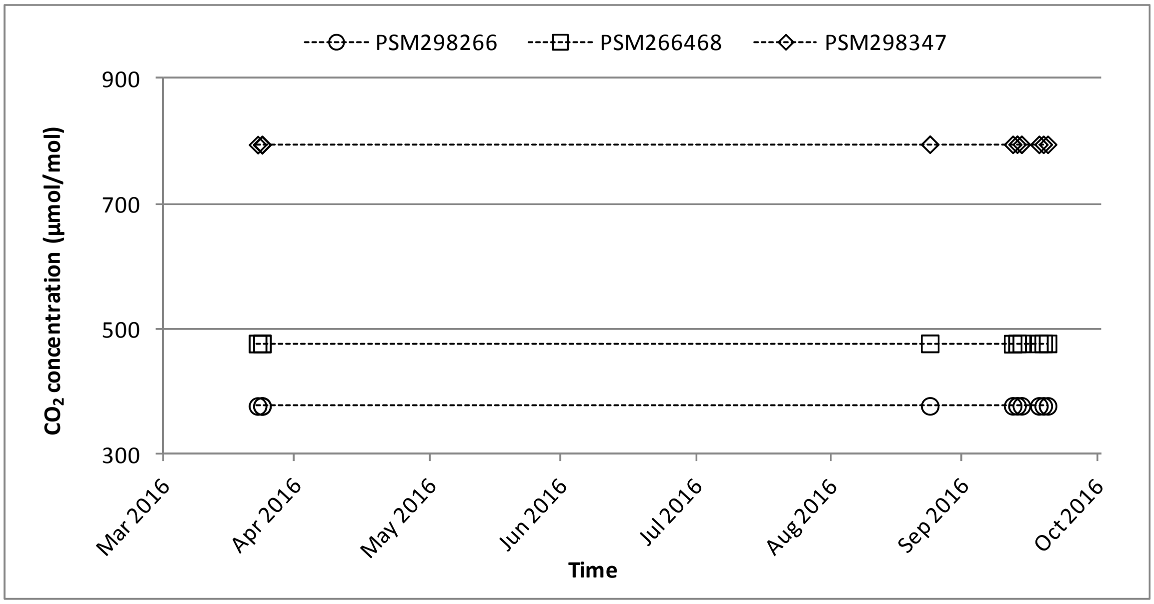

Figure 2. Stability measurements before sending the cylinders.

After receiving the cylinders, they have been analyzed for stability. Measurements were carried out during 23-24 August 2017 and 06-07 September 2017. Instrument responses were plotted against time as shown in Figure 3. The slope of the responses has been checked. Uncertainty for stability has been determined and has been included in the combined uncertainty.

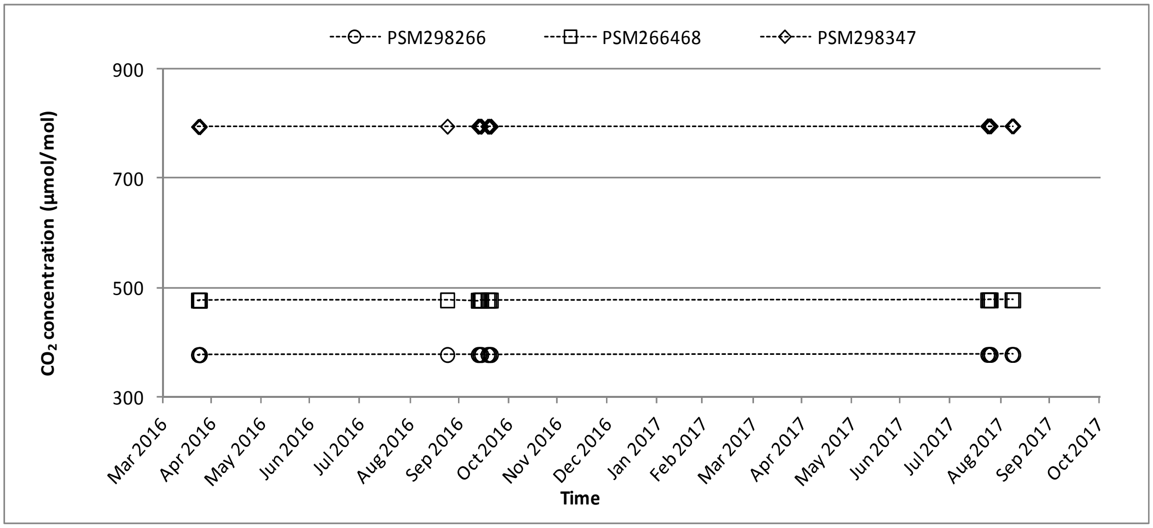

Figure 3. Stability measurements after receiving the cylinders.

dd) Cylinder pressures before shipment to the BIPM are given below.

Cylinder Code	Pressure, bar
PSM298266	86
PSM266468	86
PSM298347	90

References:

[1] International Organization for Standardization, “ISO 6142 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods”, ISO Geneva, 2001

[2] International Organization for Standardization, "ISO 6143 Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures ", ISO Geneva, 2001

VNIIM

Measurements before return of cylinders

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
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300,
Gaithersburg, MD 20899-8300
US

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
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email: edgar.flores@bipm.org

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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Email*	fhi@b10.vniim.ru		

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 $x_{\mathrm{CO2},cert}$ / 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 Number M365601

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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 Number M365664

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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 Number M365707

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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		999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.381 µmol/mol	B	Rectangular	0.015 µmol/mol	0.06733	0.00101
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00016	0.00006
Purity of Ar		999998.209 µmol/mol	B	Rectangular	0.030 µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	20.15723 g	A,B	Normal	0.00223g	-18.54106	-0.04140
	N_2	1153.59704 g	A,B	Normal	0.01962 g	0.32397	0.00636
Weighing**	pre-	20.48733 g	A,B	Normal	0.00203 g	-17.91563	-0.03630

final mixture	mixture						
	Ar	7.90915 g	A,B	Normal	0.00200 g	0.45258	0.00091
	O_2	140.75497 g	A,B	Normal	0.00353 g	0.56493	0.00200
	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		999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.390 µmol/mol	B	Rectangular	0.011 µmol/mol	0.06909	0.00076
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00020	0.000075
Purity of Ar		999998.209 µmol/mol	B	Rectangular	0.030 µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	19.47854 g	A,B	Normal	0.00224 g	-24.23572	-0.05424
	N_2	1118.50932 g	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		999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.390 µmol/mol	B	Rectangular	0.011µmol/mol	0.06733	0.00076
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00035	0.00013
Purity of Ar		999998.209 µmol/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	1153.59704 g	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 parent gases

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 table for 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 – 3x3 target 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.

f) cylinder pressure before shipment to the BIPM

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

Report of stability measurements after return of cylinders

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
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300,
Gaithersburg, MD 20899-8300
US

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

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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Telephone	+7 812 315 11 45	Fax	+7 812 315 15 17
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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 $x_{\mathrm{CO2},cert}$ / µmol/mol	Expanded uncertainty $U(x_{\mathrm{CO2},cert})$ / 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 Number M365601

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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 Number M365664

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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 Number M365707

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
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		999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.381 µmol/mol	B	Rectangular	0.015 µmol/mol	0.06733	0.00101
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00016	0.00006
Purity of Ar		999998.209 µmol/mol	B	Rectangular	0.030 µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	20.15723 g	A,B	Normal	0.00223g	-18.54106	-0.04140
	N_2	1153.59704 g	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
	Ar	7.90915 g	A,B	Normal	0.00200 g	0.45258	0.00091
	O_2	140.75497 g	A,B	Normal	0.00353 g	0.56493	0.00200

	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		999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109
Purity of O_2		999999.390 µmol/mol	B	Rectangular	0.011 µmol/mol	0.06909	0.00076
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00020	0.000075
Purity of Ar		999998.209 µmol/mol	B	Rectangular	0.030 µmol/mol	0.00534	0.00016
Weighing** premixture	CO_2	19.47854 g	A,B	Normal	0.00224 g	-24.23572	-0.05424
	N_2	1118.50932 g	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	999998.672 µmol/mol	B	Rectangular	0.200 µmol/mol	0.00545	0.00109

Purity of O_2		999999.390 µmol/mol	B	Rectangular	0.011µmol/mol	0.06733	0.00076
Purity of CO_2		999993.450 µmol/mol	B	Rectangular	0.374 µmol/mol	0.00035	0.00013
Purity of Ar		999998.209 µmol/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	1153.59704 g	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 parent gases

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 table for 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 – 3x3 target 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.-23.08.2017 and 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

VSL

Measurements before return of cylinders

Laboratory name: VSL, Dutch Metrology Institute

Authors: Ewelina T. Zalewska, Gerard Nieuwenkamp

VSL participates in:	
CCQM-K120.a	yes
CCQM-K120.b	yes

VSL 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	5604614	378.90	0.28	2
2	5604880	480.48	0.36	2
3	5604705	795.70	0.60	2

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

(Standard 1) Cylinder Identification Number: **5604614**

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)	Coverage Factor
Argon	0.0092917	0.0000029	1
Methane	0.0000000157	0.0000000036	1
Carbon monoxide	0.000000033	0.000000014	1
Carbon dioxide	0.000378900	0.000000083	1
Hydrogen	0.000000019	0.000000011	1
Water	0.000000113	0.000000060	1
Nitrogen	0.7811771	0.0000084	1
Oxygen	0.2091520	0.0000078	1
Nitrous oxide	0.000000000021	0.000000000012	1

(Standard 2) Cylinder Identification Number: **5604880**

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)	Coverage Factor
Argon	0.0092811	0.0000029	1
Methane	0.0000000157	0.0000000035	1
Carbon monoxide	0.000000033	0.000000014	1
Carbon dioxide	0.000480485	0.000000094	1
Hydrogen	0.000000019	0.000000010	1
Water	0.000000113	0.000000060	1
Nitrogen	0.7810919	0.0000084	1
Oxygen	0.2091463	0.0000078	1
Nitrous oxide	0.000000000021	0.000000000012	1

(Standard 3) Cylinder Identification Number: **5604705**

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)	Coverage Factor
Argon	0.0092506	0.0000029	1
Methane	0.0000000158	0.0000000036	1
Carbon monoxide	0.000000033	0.000000014	1
Carbon dioxide	0.00079571	0.00000023	1
Hydrogen	0.000000019	0.000000011	1
Water	0.000000114	0.000000061	1
Nitrogen	0.7807076	0.0000084	1
Oxygen	0.2092458	0.0000077	1
Nitrous oxide	0.000000000021	0.000000000012	1

Purity data of the parent gases

All raw materials have been checked for impurities in accordance with ISO 19229 [1]. The results of the purity analysis have been summarised in the tables in this section.

Table 1. Purity table of carbon dioxide

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Methane	0.00000010	0.00000006
Carbon monoxide	0.0000005	0.0000003
Carbon dioxide	0.9999868	0.0000040
Water	0.0000017	0.0000003
Nitrogen	0.0000061	0.0000031
Oxygen	0.0000048	0.0000024

Table 2. Purity table of argon

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Argon	0.999999385	0.000000500
Methane	0.000000050	0.000000029
Carbon monoxide	0.000000025	0.000000013
Carbon dioxide	0.000000025	0.000000013
Water	0.000000010	0.000000006
Nitrogen	0.00000050	0.00000029
Oxygen	0.000000005	0.000000003

Table 3. Purity table of nitrogen

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Argon	0.000005	0.000003
Methane	0.000000008	0.000000005
Carbon monoxide	0.000000015	0.000000009
Carbon dioxide	0.000000010	0.000000006

Hydrogen	0.000000025	0.000000015
Water	0.000000010	0.000000006
Nitrogen	0.999994927	0.000006000
Oxygen	0.000000005	0.000000003

Table 4. Purity table of oxygen

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Argon	0.00000100	0.00000058
Methane	0.0000000429	0.0000000014
Carbon monoxide	0.000000100	0.000000058
Carbon dioxide	0.0000000100	0.0000000058
Water	0.00000050	0.00000029
Nitrogen	0.00000050	0.00000029
Oxygen	0.999997856	0.000000709
Nitrous oxide	0.0000000010	0.0000000006

Mixture preparation

All mixtures were prepared in accordance with ISO 6142-1 [2]. The mixtures have been prepared using two different types of pre-mixtures: carbon dioxide in nitrogen and argon in nitrogen. Carbon dioxide in nitrogen was prepared with two dilution steps, argon in nitrogen with one dilution steps.

Verification procedure

The verification of carbon dioxide was carried out using an Agilent 6890N gas chromatograph with methanizer and flame ionisation detector (GC/NICAT-FID). The components were separated on a 10 ft, 1/8 inch, sulfinert packed PorapakT (80-100 mesh) column. A sample volume of 1 mL was injected on the column and helium was used as the carrier gas.

Three independent measurements were performed for carbon dioxide. Carbon dioxide was measured against set of primary standards containing carbon dioxide in synthetic air. A quadratic curve was used for the evaluation.

Due to instrument drift, an area correction was applied. A correction cylinder was injected before and after each cylinder. A corrected response for each cylinder was determined by dividing the area of measured cylinder of the sample by area of correction cylinder using the following equation [3]:

$$y_i = \frac{A_i}{A_{ref,i}}$$

Where y_i is the corrected response, A_i is the average of the areas of the sample (6 injections) and $A_{ref,i}$ is the area of the correction cylinder.

Uncertainty evaluation

The calibration curves were obtained in accordance with ISO 6143 [4]. As indicated, a parabola was used for the evaluation.
The value for amount of fraction was obtained by reverse use of the calibration curve [5]. The associated uncertainty was obtained using the law of propagation of uncertainty.

To come to the final result, the results of the three measurements were combined using meta-analysis. The "Der Simonian – Laird" model was used to calculate the mean of the three measurements and the associated standard error. The standard error of the mean was combined with the pooled uncertainty from evaluating the data according to ISO 6143. The expanded uncertainty was obtained by multiplying the standard uncertainty with a coverage factor of $k = 2$.

Stability testing

All the mixtures were prepared in June 2016. The verification measurements were performed within three months after preparation with an interval time around 3 – 4 weeks.
The pressures in the cylinders before shipment to BIPM were as follows:

- VSL144614 – 10.8 MPa
- VSL144880 – 10.5 MPa
- VSL144705 – 10.8 MPa

References

[1] International Organization for Standardization, "ISO 19229 Gas analysis – Purity analysis and the treatment of purity data", ISO, Geneva, 2015

[2] International Organization for Standardization, "ISO 6142-1 Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures", 3rd edition, ISO, Geneva, 2015

[3] Van der Veen A.M.H., Ziel P.R., Oudwater R., Quist Y.M., Alberti D., Zalewska E.T. (2012) Natural gas analysis - Development of a method for retaining the calibration status of a gas chromatograph, Delft VSL, rapportnummer: S-CH.09.34

[4] International Organization for Standardization, "ISO 6143 – Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures", 2nd edition, ISO, Geneva, 2001

[5] Van der Veen A.M.H., "Generalised distance regression in gas analysis", Report S-CH.10.28, VSL, Delft, the Netherlands, June 2010