International comparison

Report of the Pilot study CCQM-P188

(in parallel with CCQM-K120.a and b)

Carbon dioxide in Air (380-800) µmol/mol

(Final)

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Field: Amount of substance

Organizing Body: CCQM

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1. Rationale for comparison

The Pilot Study CCQM-P188 was conducted in parallel of the Key Comparisons CCQM-K120.a and CCQM-K120.b, which were designed to evaluate the level of compatibility of participants capabilities for value assigning carbon dioxide in air reference gas mixtures in the range (380-800) µmol/mol. It included two participants which did not take part in the Key Comparisons for the following reasons:

The Central Analytical Laboratory (CAL) of ICOS (Integrated Carbon Observation System) participated as an expert guest laboratory. The ICOS-CAL aims to ensure the accuracy of ICOS atmospheric measurement data as well as their traceability to the WMO scale. It provides reference gases for calibration of continuous in-situ measurements performed at monitoring stations, including real air reference gas with a certified value of carbon dioxide in air. It was agreed by the GAWG that its participation in this comparison would be of value to participating NMISs/DIs and bring a second link to the WMO scale as maintained by NOAA, which is itself a participant of the comparison as a designated institute by WMO.

The second participant was the BIPM, which took part as a participant with its PVT-CO_2 facility, which was still under development at the time of the comparison. It was the occasion for the BIPM to benchmark the performance of its system at its current state of development, based on accurate pressure measurements, using a method similar to that employed by NOAA[1].

This study involved the simultaneous comparison of a suite of 2 gas standards prepared by ICOS and 3 gas standards value assigned by the BIPM against cylinders prepared by laboratories that took part in the Key Comparison CCQM-K120, using exactly the same protocol.

The same two measurement methods that were described in the CCQM-K120 comparison report [see Flores et al. 2018] were used to compare standards in CCQM-P188, notably GC-FID, and FTIR spectroscopic analysis (corrected for isotopic variation in the CO_2 gases measured at the BIPM using absorption laser spectroscopy).

The reference value for a given gas standard in this Pilot Study was the predicted value and uncertainty from a calibration line derived from the self-consistent sets of standards used to calculate the Key Comparison reference values for CCQM-K120, to the extent possible with any deviations recorded and explained. Following the advice of the CCQM Gas Analysis Working Group, results from the FTIR method were used to calculate the Key Comparison reference values in CCQM-K120, and the reference values in this Pilot Study. Results obtained from the GC-FID are presented for information, except for the BIPM standard at 800 µmol mol^{-1} which was not measured by FTIR, so that a reference value calculated using GC-FID measurements had to be used.

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. 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
February 2018	Distribution of Draft A of this report
June 2018	Distribution of Draft B of this report

3.1 Measurement order

The cylinders of this comparison, together with the cylinders of the comparison CCQM-K120, were separated in batches and analyzed, when possible, in parallel by GC-FID, FTIR and Delta Ray in order to optimize the measurement time. Each batch was comprised by the participant's cylinders, control cylinders for ratio calculations and additional cylinders for quality control.

For GC-FID measurements the cylinders were divided in nine batches, each of them comprised by five participant's cylinders, three control cylinders (A, B and C) for ratio quantification and one cylinder 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. Table 1 lists with detail the schedule of the GC-FID and FTIR measurements.

ICOS cylinders were measured within batches 2 and 5 by GC-FID and batches 4 and 8 by FTIR. The BIPM value assigned cylinders, NPL 2215 and NPL 2219, were measured in batches 10 by GC-FID and 15 by FTIR, together with three other cylinders belonging to the BIPM (results not reported here).

The third BIPM cylinder, Scott CB10422, was used as control C during the GC-FID measurements of the CCQM-K120 comparison and for this reason only measured by GC-FID, but with more repeats than other cylinders. Results obtained during the analysis of batch 13 were used as they were the median of all results and ensured data treatment was the same as for other standards.

The Delta Ray measurements were organized in 12 batches containing four cylinders each and two calibration cylinders. These measurements were done during weeks 14, 15 and 16. For practical reasons the schedule of the measurements is not listed here.

Week	Batch	GC-FID measurements			Batch	FTIR measurements		
6 (6-10 April)	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				
		ICOS	D487652	379.900				
		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	FT-1	NIST	FB04278	379.045
10 (6-10 March)	GC5	VNIIM	M365664	480.180		NOAA	CC310084	379.500
		LNE	1029047	477.600		NPL	2179	380.270
		ICOS	D399085	449.100	FT-2	NMIJ	CPC00486	386.617
		KRISS	D500647	480.000		NMIJ	CPC00486	386.617
		NIM	FB03744	489.150		VNIIM	M365601	380.200
11 (13-17 March)	GC6	GUM	D298393	478.100	FT-3	KRISS	D500642	378.900
		BFKH	OMH44	479.890		NIM	FB03747	383.430
		UME	PSM266468	480.420		LNE	1029045	379.480
		NPLI	JJ108862	480.520	FT-4	GUM	D298392	380.100
		NMISA	M51 8167	479.500		ICOS	D487652	379.9
		INRIM	D247440	479.300		NMISA	M51 8232	380.200
12 (20-24 March)	GC7	NIST	FB04287	794.533	FT-5	BFKH	OMH54	379.840
		NOAA	CB11668	794.080		UME	PSM298266	379.920
		VSL	5604705	795.700		NPLI	JJ108891	375.720
		NPL	2181	799.700	FT-6	NIST	FB04300	472.662
		NMIJ	CPC00558	803.658		NOAA	CC305198	479.260
13 (27-31 March)	GC8	VNIIM	M365707	800.730		VSL	5604880	480.480
		LNE	1029048	802.200	FT-7	NPL	2170	480.020
		KRISS	D500672	800.800		NMIJ	CPC00494	471.301
		NIM	FB03748	809.820		VNIIM	M365664	480.180
		GUM	D298402	800.500	FT-8	LNE	1029047	477.600
14 (3-7 April)	GC9	BFKH	OMH69	800.300		ICOS	D399085	449.1
		UME	PSM298347	800.760		KRISS	D500647	480.000
		NPLI	JJ108854	796.380	FT-9	NIM	FB03744	489.150
		NMISA	M51 8244	799.100		GUM	D298393	478.100
		INRIM	D247445	798.900		BFKH	OMH44	479.890
						UME	PSM266468	480.420

15 (10-14 April)					FT-10	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)	GC10	BIPM	NPL2215	380.250	FT-14	UME	PSM298347	800.760
		BIPM	NPL2219	483.560		NPLI	JJ108854	796.380
		BIPM				NMISA	M51 8244	799.100
		BIPM				INRIM	D247445	798.900
17 (24-28 April)					FT-15	BIPM	NPL2215	380.250
						BIPM	NPL2219	483.560
						BIPM		
						BIPM		

Table 1: Schedule of the CCQM-P188 Pilot Study measurements (in parallel with the CCQM-K120 comparisons). ICOS cylinders were measured within batches 2 and 5 by GC-FID and batches 4 and 8 by FTIR. BIPM value assigned cylinders, NPL 2215 and NPL 2219, were measured in batches 10 by GC-FID and 15 by FTIR. BIPM cylinder, Scott CB10422, was used as control C during the GC-FID measurements of the CCQM-K120 comparison.

4. Measurement standards

Each laboratory taking part in this Pilot Study was requested to produce and/or value assign at least two standards at the nominal mole fractions defined in the Key Comparisons CCQM-K120.a (380 µmol/mol and 480 µmol/mol) and CCQM-K120.b (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 in CCQM-K120 comparisons and in this parallel Pilot Study:

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.

5. Preparation and values submitted 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 I - Measurement reports of participants.

The CO_2 mole fractions submitted by participants are listed in Table 4 where:

x_{NMI} is the value assigned by the participant;

$U(x_{NMI})$ is the expanded uncertainty associated with the assigned value x_{NMI};

The standard prepared by ICOS at the nominal CO_2 mole fraction of 480 µmol mol^{-1} was reported with a value of 449.14 µmol mol^{-1}, which is outside the requested range (± 10 µmol/mol from the nominal value). As a consequence a different treatment was chosen to calculate its reference value, as explained later in section 8.

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. Participants in this Pilot Study did not report modified values after cylinders came back in their laboratories. The compositions of the mixtures submitted by the participants are listed in Table 5.

Participant	Cylinder references	Gas Matrix	NMI's assigned CO_2 mole fraction x_{NMI} (µmol mol^{-1})	NMI's assigned CO_2 expanded uncertainty $U(x_{NMI})$ $k = 2$ (µmol mol^{-1})
		Before the return of cylinders		
ICOS	D487652	Real Air	379.94	0.22
ICOS	D399085	Real Air	449.14	0.25
BIPM	NPL 2215	Synthetic air	380.14	0.29
BIPM	NPL 2219	Synthetic air	483.41	0.38
BIPM	CB10422	Real Air	791.06	0.53

Table 4. Mole fraction of CO_2 in air reported by participants.

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_{CH4} (nmol/mol)	NMI's assigned expanded uncertainty *k* =2 $U(x_{CH4})$ (nmol/mol)	NMI's assigned N_2O mole fraction x_{N2O} (nmol/mol)	NMI's assigned expanded uncertaint *k* =2 $U(x_{N2O})$ (nmol/mol)
ICOS	D487652	*	*	*	*	*	*	1914	1.1	324.2	0.45
ICOS	D399085	*	*	*	*	*	*	2104	1	339.8	0.45
BIPM	NPL 2215	0.781	0.008	0.2093	0.0021	0.00934	0.00009	1857	19	325.5	3.3
BIPM	NPL 2219	0.781	0.008	0.2095	0.0021	0.00925	0.00009	1856	19	324.7	3.2
BIPM	CB10422	*	*	*	*	*	*	1835.63	0.74	<1	*

*Table 5. Purity table of the submitted gas mixtures. * No data given.*

6. 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 analyzed in batches of *n* cylinders, first by GC-FID, then by FTIR, and finally by the Delta Ray (see section 3.1).

As described in the Comparison report CCQM-K120 when the cylinders were analyzed 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 was 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 (at ~ 380 µmol mol^{-1} and ~ 800 µmol mol^{-1}) 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 the report of the international comparison CCQM-K120.a and CCQM-K120.b ANNEX IV- BIPM Value assignment procedure: GC-FID.

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 above 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 in the report of the international comparison CCQM-K120.a and CCQM-K120.b ANNEX IV- BIPM Value assignment procedure: FTIR.

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 the report of the international comparison CCQM-K120.a and CCQM-K120.b ANNEX IV - BIPM Value assignment procedure: Delta Ray. FTIR and GC-FID measurements were both used to derive the CO_2 mole fractions in each cylinder (except BIPM cylinder CB10422 which was analyzed by GC-FID only). The measurements performed by the Delta Ray analyzer 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 the report of CCQM-K120. 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).

6.1 Measurement results

Measurements were performed at the BIPM from February to April 2017. Results of these series of measurements are listed in Table 7 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 in the report of the international comparison CCQM-K120.a and CCQM-K120.b 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 the report of the international comparison CCQM-K120.a and CCQM-K120.b 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 10. The typical uncertainties for each of the methods used by the BIPM are listed in Table 6.

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 6. Summary of methods used during the CCQM-K120/ P-188 international comparison and typical uncertainties obtained by the BIPM.

Participant	Number of Cylinder	$\overline{R}_{FT}$ 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
ICOS	D487652	0.441783640	0.000015430	0.798112575	0.000071597
ICOS	D399085	0.522236759	0.000022824	0.943934314	0.000049441
BIPM	NPL 2215	0.441987560	0.000027200	0.798530146	0.000050782
BIPM	NPL 2219	0.561831519	0.000020200	1.015457235	0.000072362
BIPM	CB10422	*	*	1.663005900	0.000110260

Table 7. Results of measurements performed at the BIPM.

7. Results

Table 8 summarizes the figures showing the measurements results obtained by different methods at the BIPM. The results of this Pilot Study are displayed with the results in the parallel Key Comparison CCQM-K120.

Comparison method	CO_2 mole fraction	Plot
FTIR (Ratio to control cylinder under intermediate precision conditions)		
	380 µmol/mol	*Figure 1*
	480 µmol/mol	Figure *2*
GC-FID (Ratio to control cylinder under intermediate precision conditions)		
	380 µmol/mol	*Figure 3*
	480 µmol/mol	*Figure 4*
	800 µmol/mol	*Figure 6*

Table 8. List of figures corresponding to results obtained from FTIR and GC-FID.

7.1 FTIR

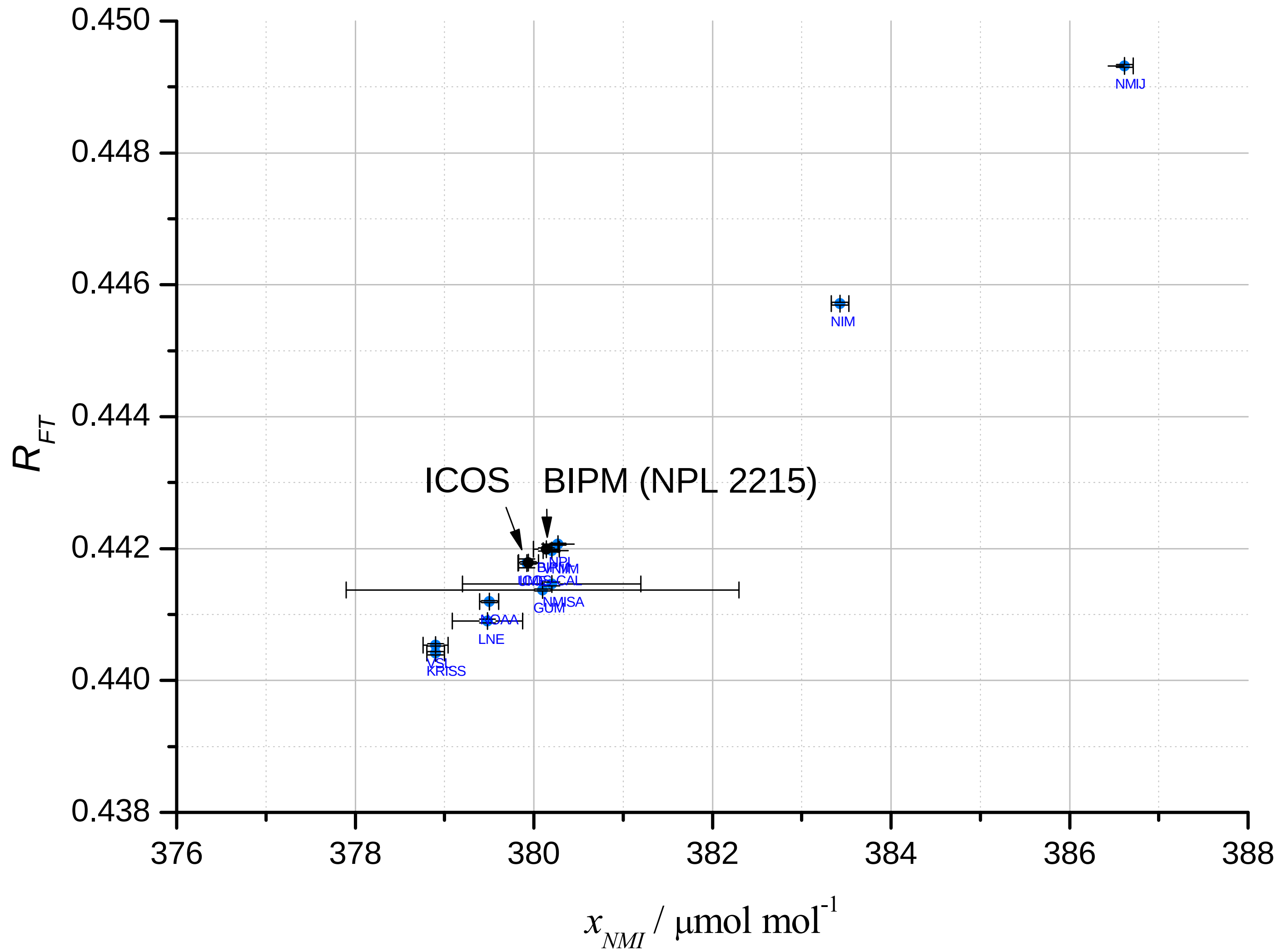

Figure 1. FTIR ratios to control standard for the cylinders at 380 µmol mol^{-1} from the international comparison CCQM-K120 and CCQM-P188: Blue dots: cylinder values used for the KCRV of the CCQM-K120 comparison. Black dots: ICOS and BIPM values. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

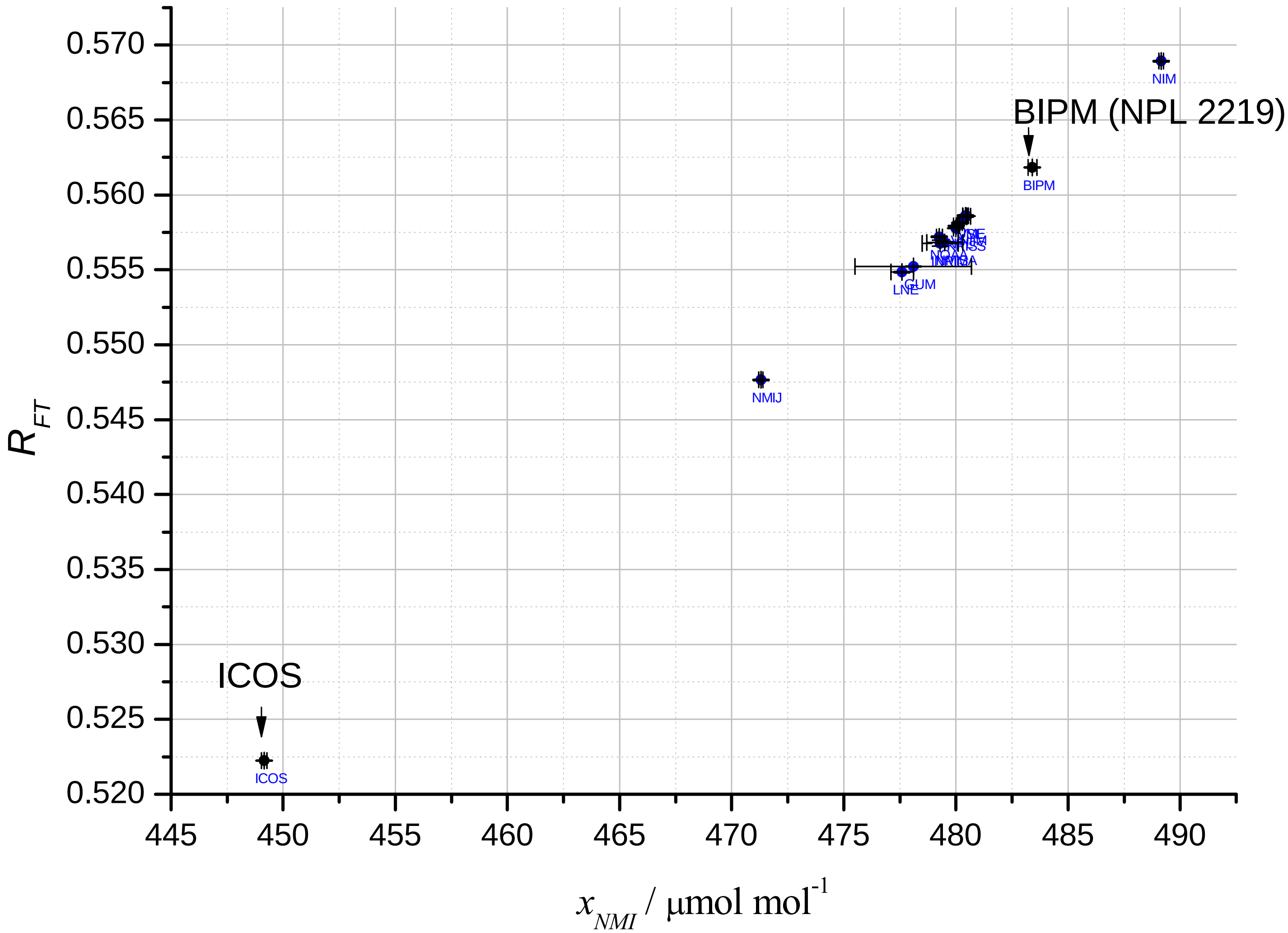

Figure 2. FTIR ratios to control standard for the cylinders at 480 µmol mol^{-1} from the international comparison CCQM-K120 and CCQM-P188 Blue dots: cylinder values used for the KCRV of the CCQM-K120 comparison. Black dots: ICOS and BIPM values. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

7.2 GC-FID

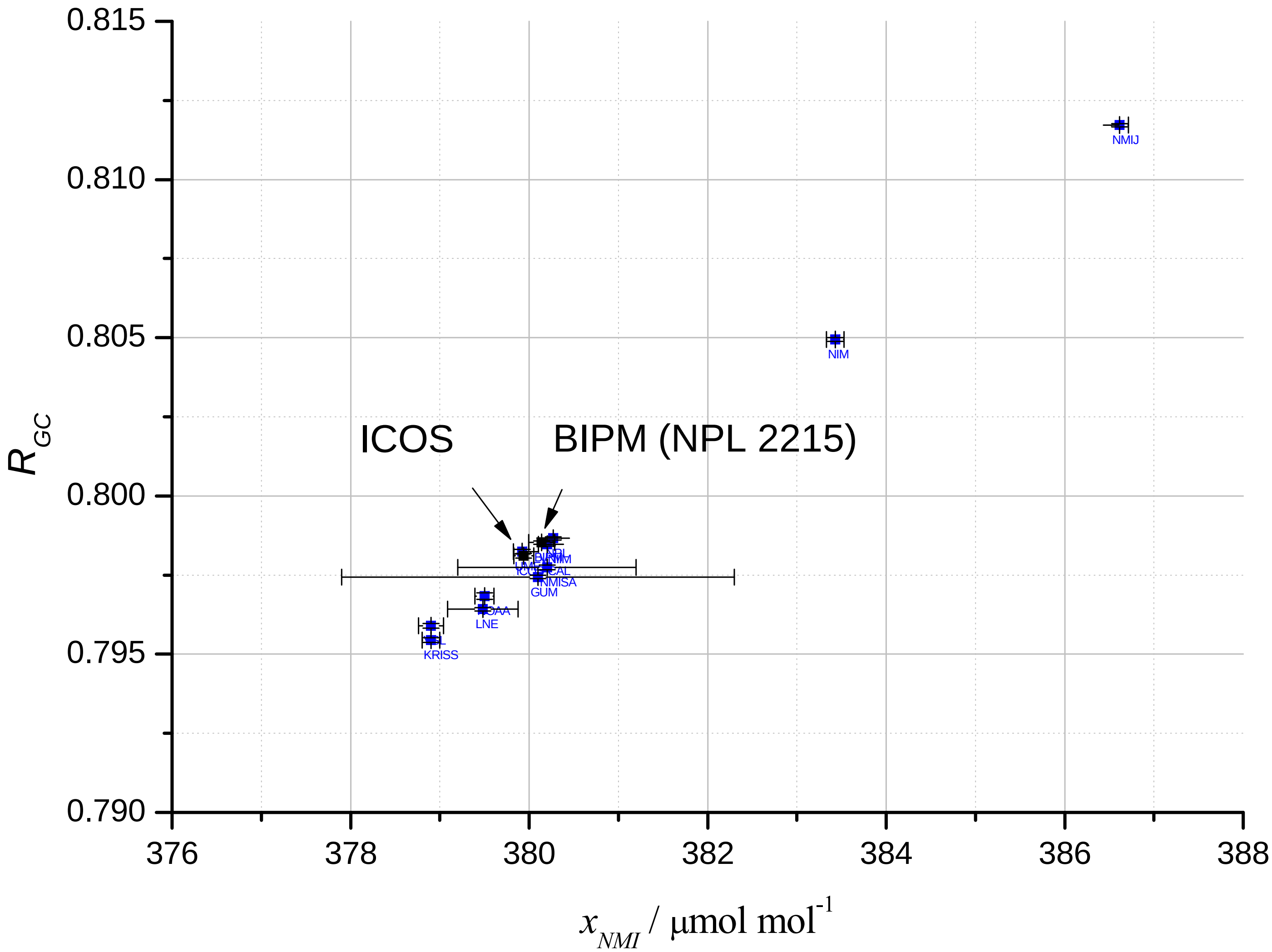

Figure 3. GC-FID ratios to control standard for the cylinders at 380 µmol mol^{-1} from the international comparison CCQM-K120 and CCQM-P188. Blue dots: cylinder values used for the KCRV of the CCQM-K120 comparison. Black dots: ICOS and BIPM values. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

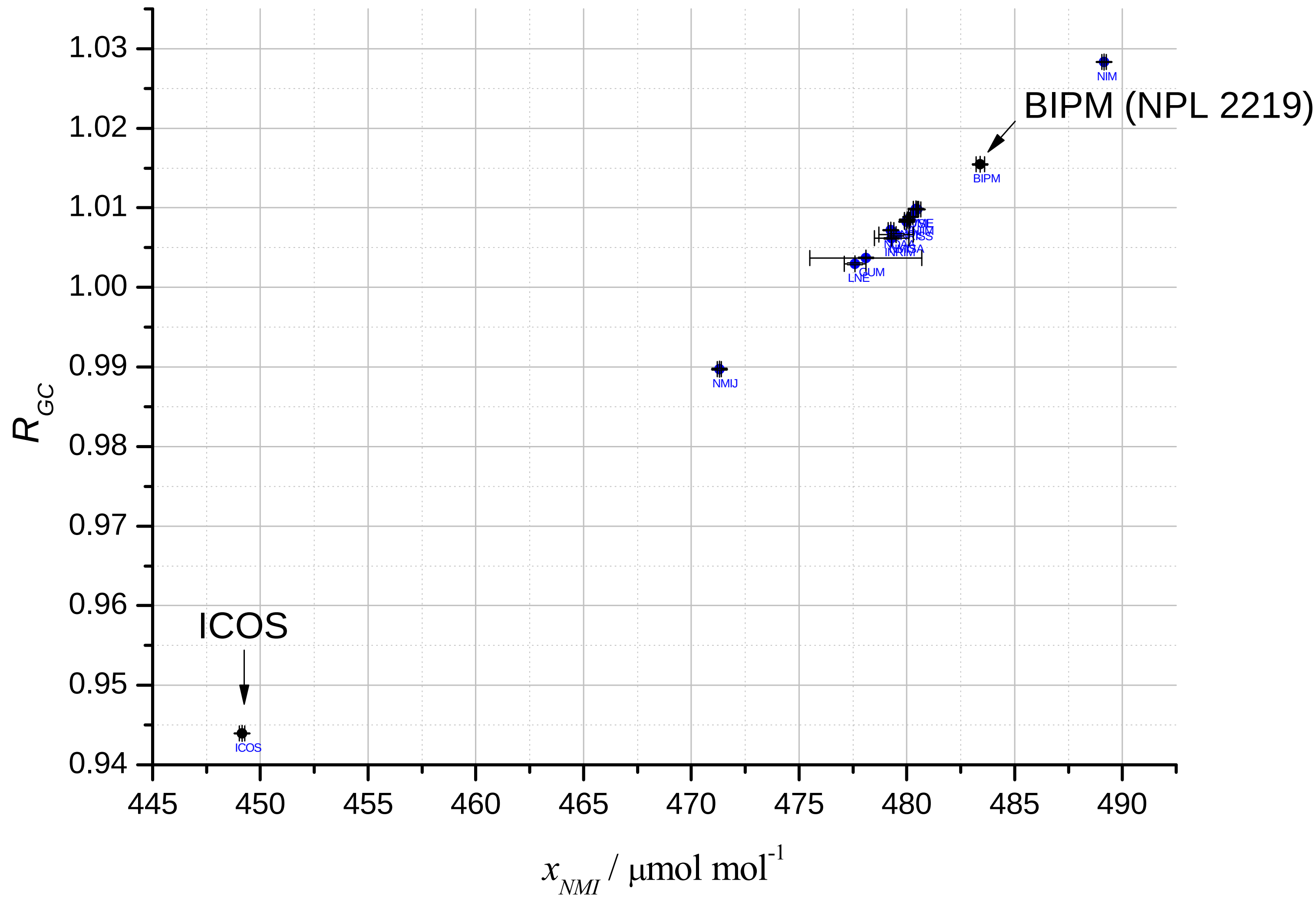

Figure 4. GC-FID ratios to control standard for the cylinders at 480 µmol mol^{-1} from the international comparison CCQM-K120 and CCQM-P188. Blue dots: cylinder values used for the KCRV of the CCQM-K120 comparison. Black dots: ICOS and BIPM values. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

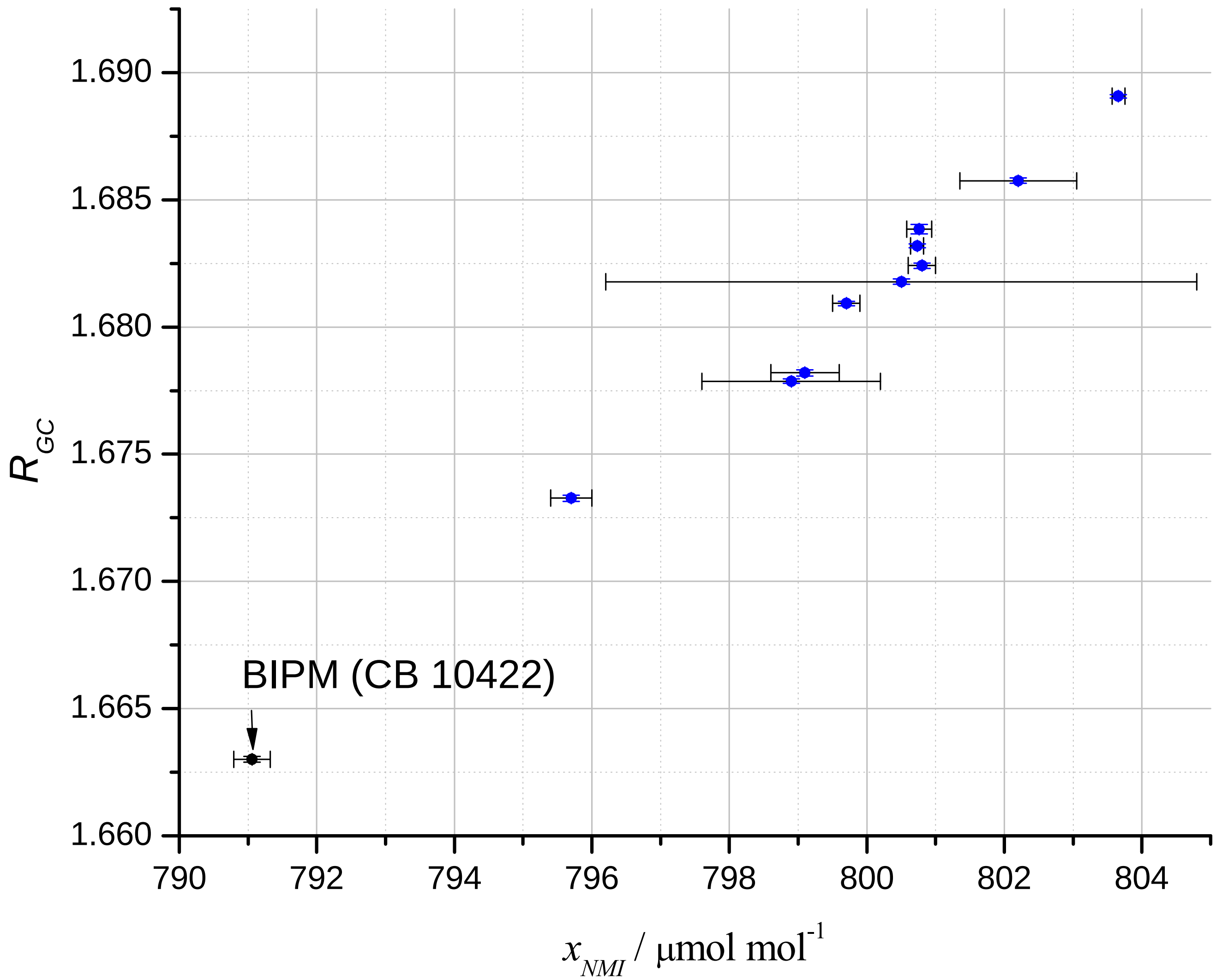

Figure 5. GC-FID ratios to control standard for the cylinders at 480 µmol mol^{-1} from the international comparison CCQM-K120 and CCQM-P188. Blue dots: cylinder values used for the KCRV of the CCQM-K120 comparison. Black dots: ICOS and BIPM values. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI reported values (x-axis).

7.3 Isotope ratios

The $\delta^{13}C$ and $\delta^{18}O$ values reported by participants are listed in Table 9. The values reported by the BIPM for the two standards NPL 2215 and NPL 2219 were the ones obtained during the series of measurement performed with the Delta Ray for this Pilot Study, as explained below, and are therefore only listed in Table 10. The values reported by the BIPM for the standard CB10422 were assumed to be the same as in a cylinder of the same batch, analyzed at MPI-Jena by IRMS. This standard was not analyzed by the Delta Ray and therefore no value is reported in Table 10.

The delta values of the cylinders, on the VPDB-CO_2 scale, were measured by the BIPM using the Delta Ray analyzer to correct the FTIR response. The measured isotope ratio values are listed Table 10. The method for measuring and calibrating the Delta Ray is fully described in the report of the international comparison CCQM-K120.a and CCQM-K120.b ANNEX IV- BIPM Value assignment procedure: Delta Ray. The method used by the BIPM for measuring isotope ratios is described in a recent publication[2] 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. In this case good agreement was observed between reported values by ICOS and BIPM measured values, noting that during measurements for the $\delta^{18}O$ value of cylinder D399085 the reference cylinder was emptied and replaced with a calibration standard out of range, resulting in an uncertainty one order of magnitude larger than usual (see Flores et al. 2018).

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	$\delta^{13}C$	$u(\delta^{13}C)$ Assigned NMI's Standard uncertainty (k=1)	$\delta^{18}O$	$u(\delta^{18}O)$ Assigned NMI's Standard uncertainty (k=1)
		(‰)	(‰)	(‰)	(‰)
ICOS	D487652	-7.962	0.024	-2.591	0.035
ICOS	D399085	-10.974	0.026	-2.692	0.038
BIPM	CB10422	-35.68	0.03	-34.48	0.66

Table 9. $\delta^{13}C$ and $\delta^{18}O$ reported by participants.

Lab	Number of Cylinder	$\delta^{13}C$	$u(\delta^{13}C)$ Standard uncertainty (k=1)	$\delta^{18}O$	$u(\delta^{18}O)$ Standard uncertainty (k=1)
		(‰)	(‰)	(‰)	(‰)
ICOS	D487652	-7.950	0.18	-2.290	0.48
ICOS	D399085	-11.101	0.18	-5.736	4.17
BIPM	NPL 2215	-8.211	0.18	-11.733	0.48
BIPM	NPL 2219	-8.121	0.18	-11.720	0.48

Table 10. $\delta^{13}C$ and $\delta^{18}O$ measured by the BIPM.

8. Reference Value Calculations

The reference values for individual cylinders were those calculated from the regression lines computed from the self-consistent sets of standards used to calculate the Key Comparison reference values for CCQM-K120, to the extent possible with any deviations recorded and explained here.

The analysis of the data from the comparison was done following the procedures outlined in ISO 6143:2001[3] (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures). 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.

The consistency between the participating laboratory's results and the reference values is presented in terms of a difference (D) defined as:

$$D = x_{NMI} - x_{K120} \quad (1)$$

where

x_{K120}	is the amount of substance fraction in the cylinder predicted by the linear analysis function of the CCQM-K120 for the corresponding analyzer response (ratio to the control cylinder with the FTIR or GC-FID);
$u(x_{K120})$	is the uncertainty of the predicted value;
x_{NMI}	is the amount of substance fraction submitted by the participating laboratory;
$u(x_{\text{NMI}})$	is the standard uncertainty associated with the submitted 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 expanded uncertainty of this difference expressed as:

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

and the expanded uncertainty, at 95 % confidence level

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

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

Differences from reference value for standards at a nominal mole fraction of 380 μmol mol^{-1}

The reference values for the ICOS cylinder D487652 and the BIPM value assigned cylinder NPL 2215 were calculated using the standards used to calculate KCRVs for CCQM-K120.a at 380 μmol mol^{-1} (see Flores et al. 2018).

For measurements performed by FTIR the difference (D) is listed in Table 11 and for GC-FID in Table 12, together with plots and comparison to the CCQM-K120.a degrees of equivalence in Figure 6.

Differences from refrence value for the BIPM value assigned cylinder NPL 2219 at a nominal mole fraction of 480 μmol mol^{-1}

The reference value for the BIPM value assigned cylinder NPL 2219 was calculated using the standards used to calculate KCRVs for CCQM-K120.a at 480 μmol mol^{-1} (see Flores et al. 2018).

The differences from the reference value (*D*) are listed in Table 13 and Table 14 and plotted together with the CCQM-K120.a degrees of equivalence in Figure 7.

Differences from reference value for ICOS standard D399085 in the nominal mole fraction range of 380 µmol mol-1 to 480 µmol mol^{-1}

The nominal value of the ICOS cylinder D399085 was 450 µmol mol^{-1}, lying between two nominal mole fractions requested for the comparison. In order to avoid potential extrapolation errors, a reference value was calculated from the regression line derived from the full set of standards that were used for KCRV calculations at 380 µmol mol^{-1} and 480 µmol mol^{-1} for CCQM-K120.a, excluding only cylinder FB3744 from NIM (which was at the extreme of the range and not consistent with the regression line calculated from the remaining standards). Table 15 shows the parameters of the straight-line model analysis function produced as output by the GLS algorithm for each instrument.

The differences from the reference value (*D*) are listed in Table 16 and Table 17 and plotted together with the CCQM-K120.a reference values in Figure 8.

Differences from reference value for the BIPM value assigned cylinder CB10422 at a nominal mole fraction of 800 µmol mol^{-1}

The BIPM cylinder CB10422 was used as control C cylinder during the CCQM-K120 measurements. The analysis of the CB10422 cylinder was performed exclusively by GC-FID.

The reference value for the cylinder was calculated using the standards used to calculate KCRVs for CCQM-K120.a CCQM-K120.b at 800 µmol mol^{-1} (see Flores et al. 2018).

The difference from the reference value (*D*) is listed in Table 18 and plotted together with the CCQM-K120.b degrees of equivalence in Figure 9.

Participant	Cylinder	x_{K120} (XLGENLINE predictied value from FTIR) (μmol/mol)	$u(x_{K120.})$ (μmol/mol)	x_{NMI} (μmol/mol)	$u(x_{NMI})$ (μmol/mol)	$D_1(x_{NMI-} \ x_{Ref})$ (μmol/mol)	$u(D_1)$ (μmol/mol)	$U(D_1)$ (k=2) (μmol/mol)
ICOS	D487652	380.023	0.042	379.940	0.110	-0.083	0.118	0.236
BIPM	NPL 2215	380.201	0.046	380.140	0.145	-0.061	0.152	0.304

Table 11. Difference from the reference value using FTIR measurement results at the nominal mole fraction of 380 μmol mol^{-1} using the data points included in the self-consistent set of the CCQM-K120a comparison report.

Participant	Cylinder	$x_{K120.a}$ (XLGENLINE predictied value from GC-FID) (μmol/mol)	$u(x_{K120.a})$ (μmol/mol)	x_{NMI} (μmol/mol)	$u(x_{NMI})$ (μmol/mol)	$D_1(x_{NMI-} \ x_{Ref})$ (μmol/mol)	$u(D_1)$ (μmol/mol)	$U(D_1)$ (k=2) (μmol/mol)
ICOS	D487652	380.043	0.054	379.940	0.110	-0.103	0.122	0.245
BIPM	NPL 2215	380.245	0.047	380.140	0.145	-0.105	0.152	0.305

Table 12. Difference from the reference value using GC-FID measurement results at the nominal mole fraction range 380 μmol mol^{-1} using the data points included in the self-consistent set of the CCQM-K120a comparison report.

Participant	Cylinder	$x_{K120.a}$ (XLGENLINE predictied value from FTIR) (μmol/mol)	$u(x_{K120.a})$ (μmol/mol)	x_{NMI} (μmol/mol)	$u(x_{NMI})$ (μmol/mol)	$D_1(x_{NMI-} \ x_{Ref})$ (μmol/mol)	$u(D_1)$ (μmol/mol)	$U(D_1)$ (k=2) (μmol/mol)
BIPM	NPL 2219	483.252	0.055	483.410	0.190	0.158	0.198	0.395

Table 13. Difference from the reference value using FTIR measurement results at the nominal mole fraction of 480 μmol mol^{-1} using the data points included in the self-consistent set of the CCQM-K120a comparison report.

Participant	Cylinder	$x_{K120.a}$ (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{K120.a})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{NMI})$ (µmol/mol)	$D_1(x_{NMI}\text{-}\ x_{Ref})$ (µmol/mol)	$u(D_1)$ (µmol/mol)	$U(D_1)$ *(k=2)* (µmol/mol)
BIPM	NPL 2219	483.199	0.061	483.410	0.190	0.211	0.199	0.399

Table 14. Difference from the reference value using GC-FID measurement results at the nominal mole fraction of 480 µmol mol^{-1} using the data points included in the self-consistent set of the CCQM-K120a comparison report.

	FTIR	GC-FID
b_0 / (µmol mol^{-1})	-0.013888208	-0.030057199
b_1	0.001191345	0.002163734
$u(b_0)$ / (µmol mol^{-1})	0.004956391	0.009263389
$u(b_1)$ / (µmol mol^{-1})	0.000010330	0.000019296
$cov(b_0,b_1)$	0.000000000	-0.000000179
SSD rem	0.68	0.76
GOF	1.36	1.47

Table 15. Output from the GLS Algorithm in Its Analysis Mode. ab_0, b_1, $u(b_0)$, $u(b_1)$, and $cov(b_0,b_1)$ are the parameters of a straight-line model calibration function for the FT-IR and GC-FID ratios against x_{CO_2}.

Participant	Cylinder	$x_{K120.a}$ (XLGENLINE predictied value from FTIR) (µmol/mol)	$u(x_{K120.a})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{NMI})$ (µmol/mol)	$D_1(x_{NMI}\text{-}\ x_{Ref})$ (µmol/mol)	$u(D_1)$ (µmol/mol)	$U(D_1)$ *(k=2)* (µmol/mol)
ICOS	D399085	449.299	0.039	449.140	0.125	-0.159	0.131	0.262

Table 16. Difference from the reference value using FTIR measurement results at the nominal mole fraction range of 380 µmol mol^{-1} of 480 µmol mol^{-1} using the data points included in the self-consistent set of the CCQM-K120a comparison report.

Participant	Cylinder	x_{K120} (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{K120})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{NMI})$ (µmol/mol)	$D_1(x_{NMI-}\ x_{Ref})$ (µmol/mol)	$u(D_1)$ (µmol/mol)	$U(D_1)$ (k=2) (µmol/mol)
ICOS	D399085	449.345	0.041	449.140	0.125	-0.205	0.132	0.263

Table 17. Difference from the reference value using GC-FID measurement results at the nominal mole fraction range of 380 µmol mol⁻¹ of 480 µmol mol⁻¹ using the data points included in the self-consistent set of the CCQM-K120a comparison report.

Participant	Cylinder	x_{K120} (XLGENLINE predictied value from GC-FID) (µmol/mol)	$u(x_{K120})$ (µmol/mol)	x_{NMI} (µmol/mol)	$u(x_{NMI})$ (µmol/mol)	$D_1(x_{NMI-}\ x_{Ref})$ (µmol/mol)	$u(D_1)$ (µmol/mol)	$U(D_1)$ (k=2) (µmol/mol)
BIPM	CB10422	790.908	0.342	791.060	0.265	0.152	0.433	0.865

Table 18. Difference from the reference value using GC-FID measurement results at the nominal mole fraction of 800 µmol mol⁻¹ using the data points included in the self-consistent set of the CCQM-K120.b comparison report.

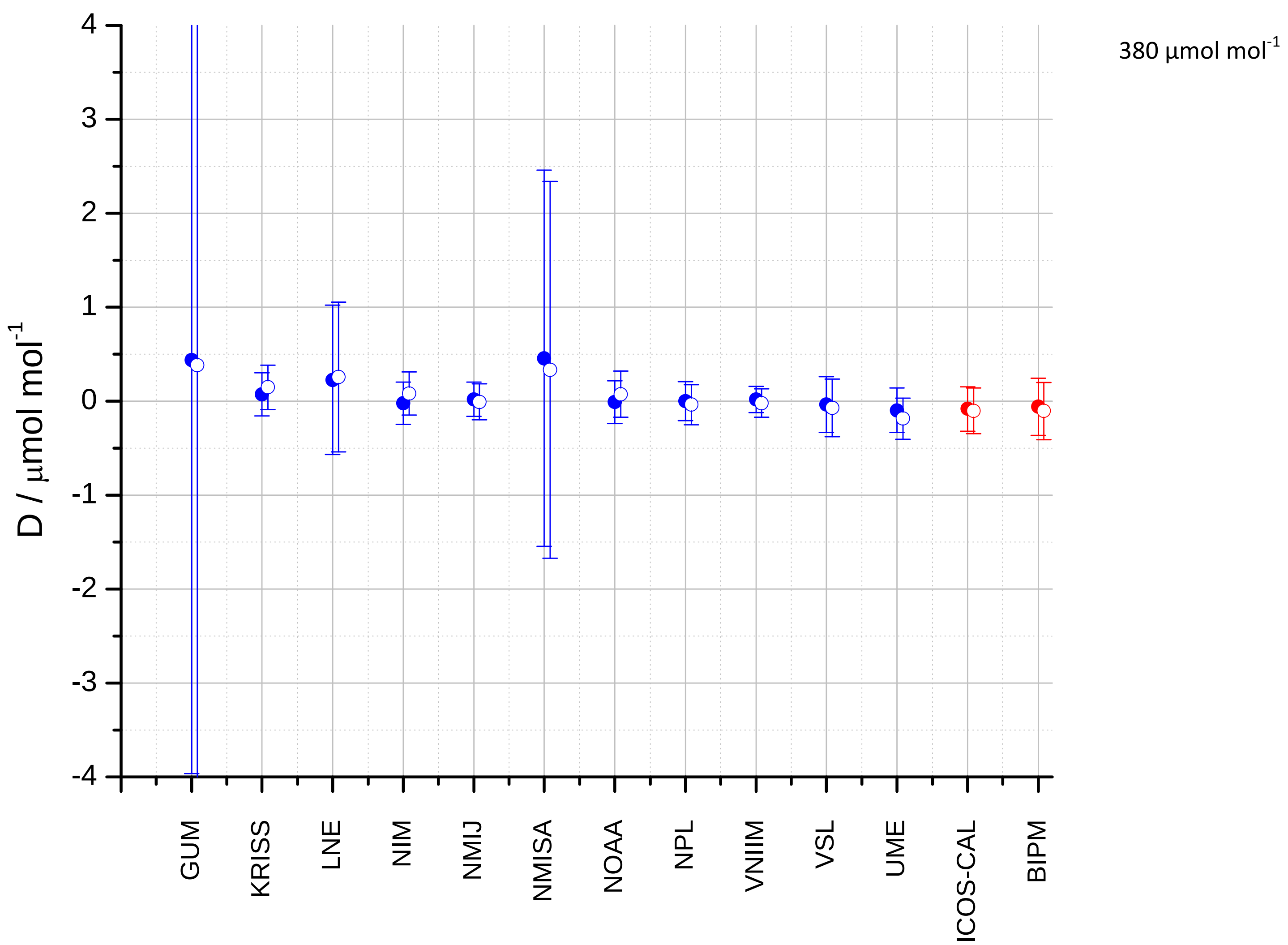

Figure 6. Difference between the CO_2 mole fractions submitted by the participants and predicted value using FTIR (full dots) and GC-FID.(empty dots) at a nominal mole fraction of *380 µmol mol^{-1}* . XLGENLINE GLS fit using *LCS* data set. The error bar represents the expanded uncertainty at a 95 % level of confidence. Blue dots CCQM-K120.a self-consistent standards used for KCRV determination.

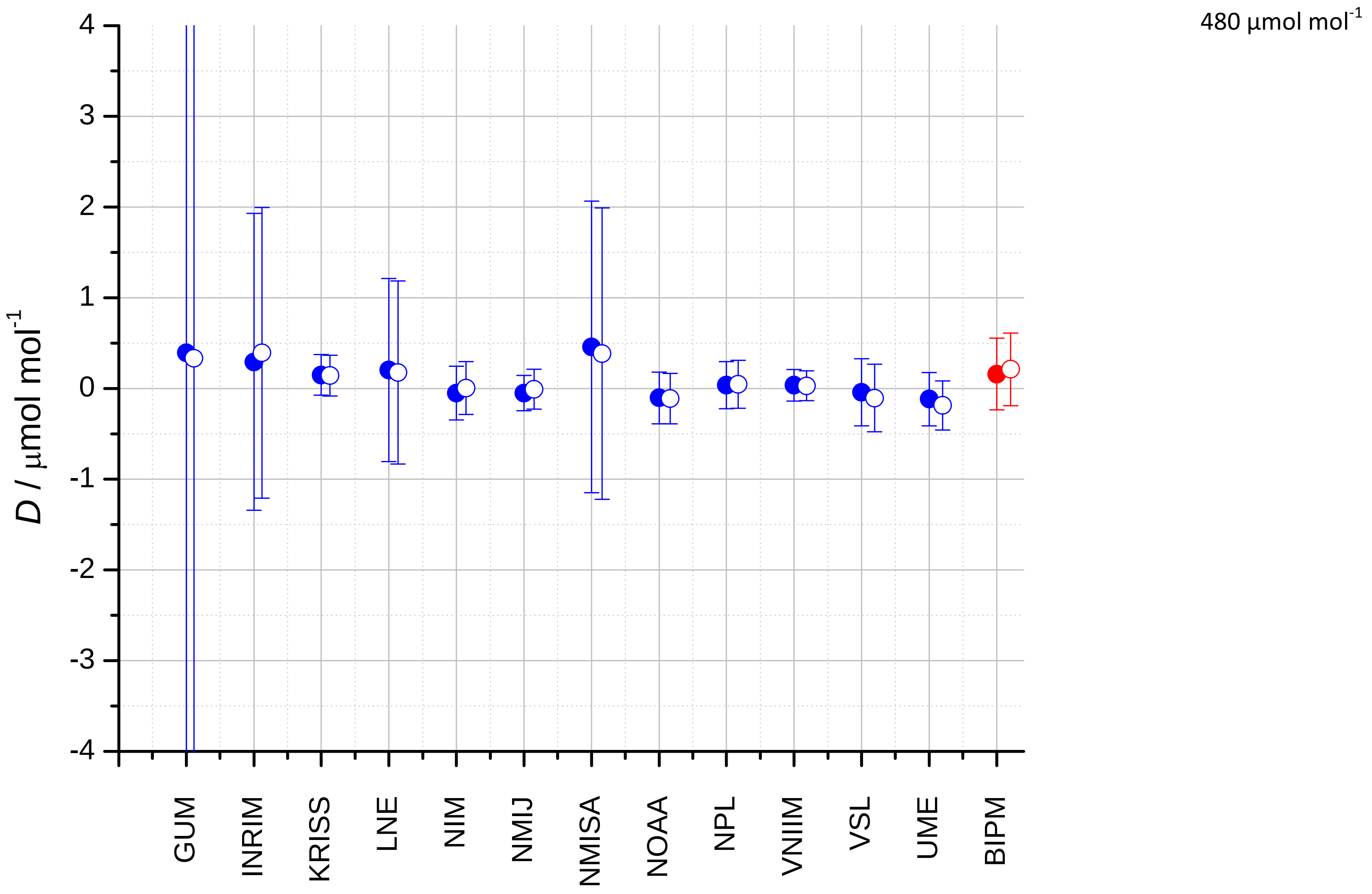

Figure 7. Difference between the CO_2 mole fractions submitted by the participants and predicted value using FTIR (full dots) and GC-FID.(empty dots) at a nominal mole fraction of 480 µmol mol^{-1}XLGENLINE GLS fit using *LCS* data set. The error bar represents the expanded uncertainty at a 95 % level of confidence. Blue dots CCQM-K120.a self-consistent standards used for KCRV determination.

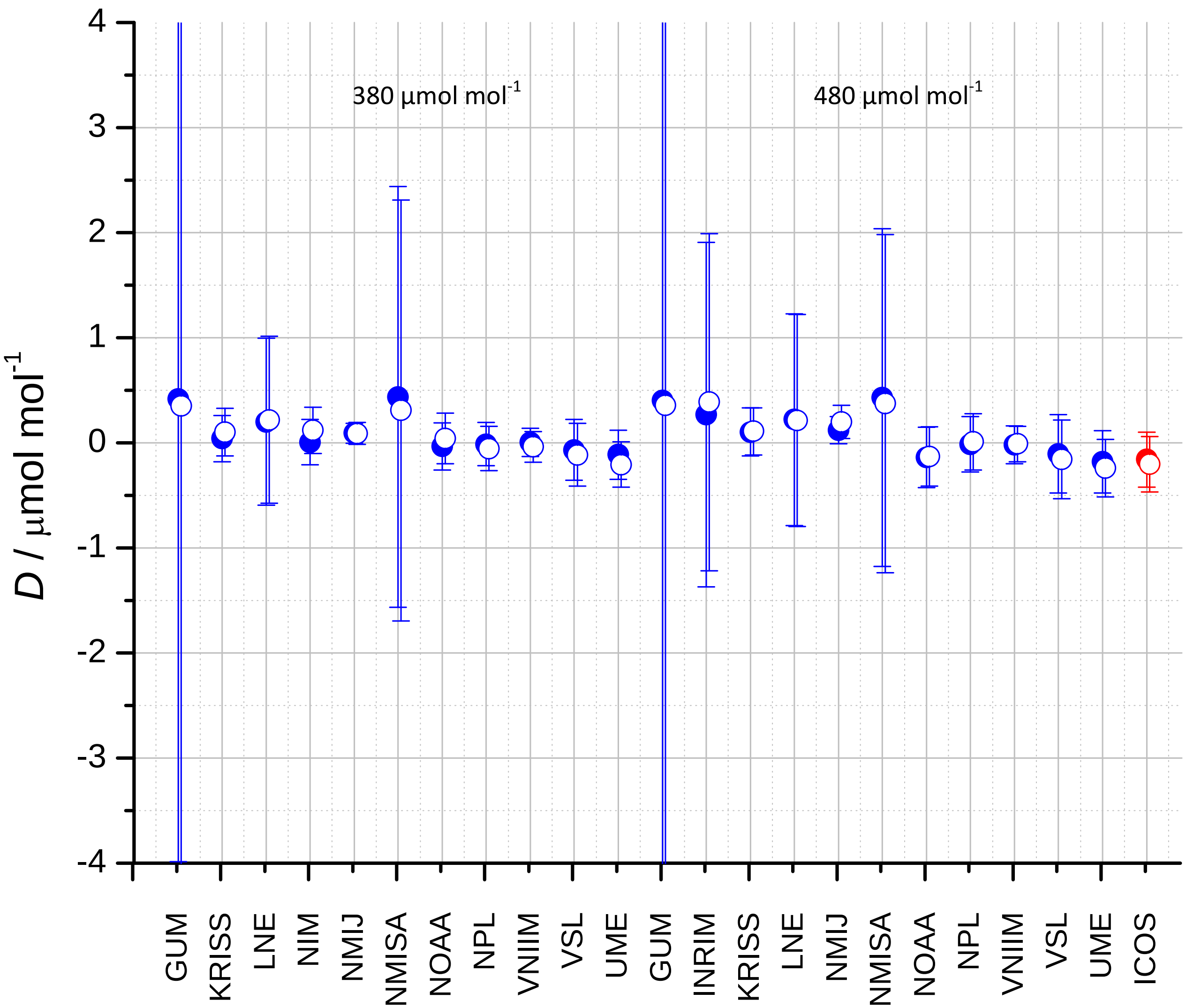

Figure 8. Difference between the CO_2 mole fractions submitted by the participants and predicted value using FTIR (full dots) and GC-FID.(empty dots) over the nominal mole fraction range of *380 µmol mol*$^{-1}$ to *480 µmol mol*$^{-1}$ XLGENLINE GLS fit using *LCS* data set. The error bar represents the expanded uncertainty at a 95 % level of confidence. Blue dots CCQM-K120.a self-consistent standards used for KCRV determination. Red dot: ICOS value.

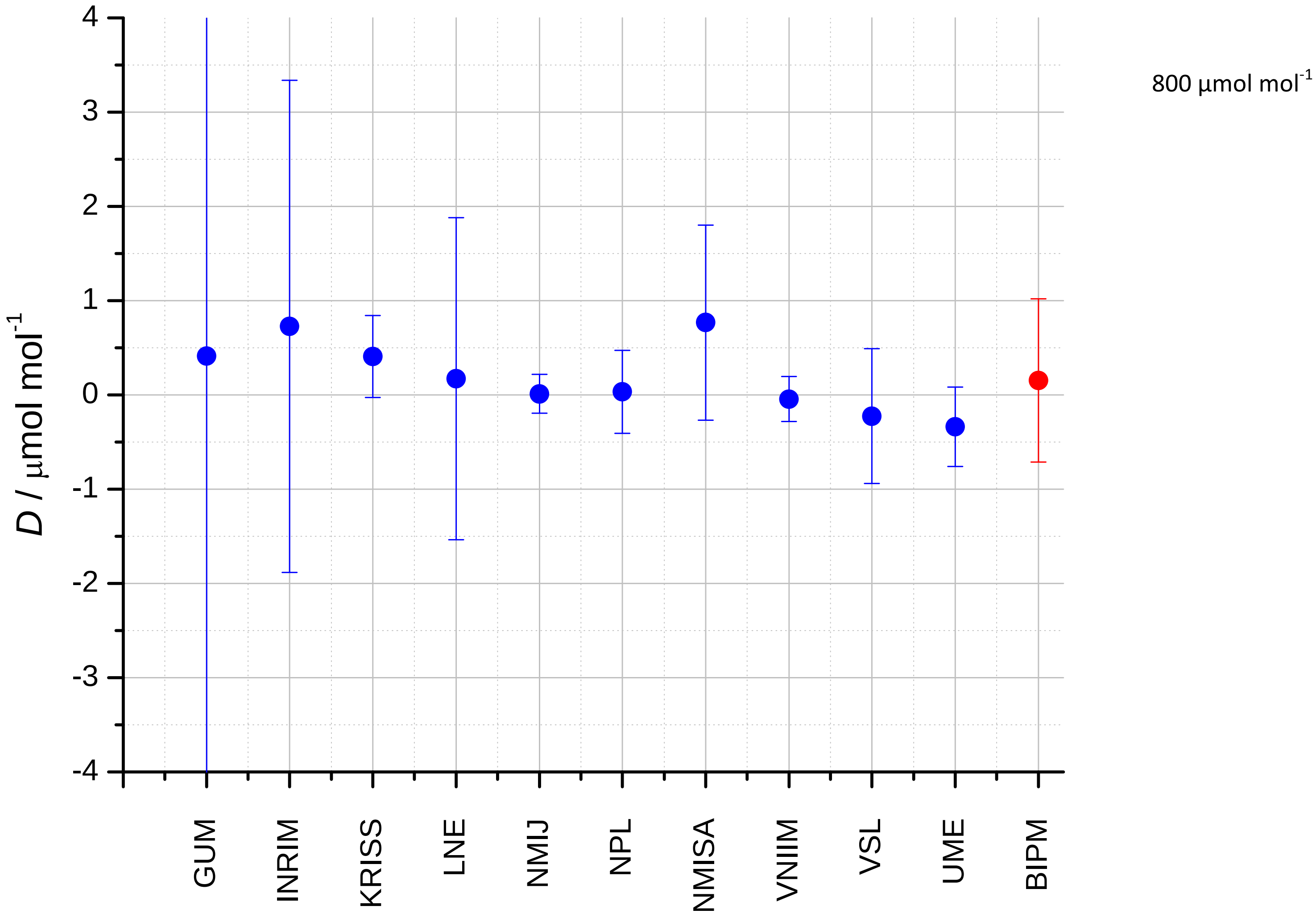

Figure 9. Difference between the CO_2 mole fractions submitted by the participants and predicted value using GC-FID at a nominal mole fraction of 800 µmol mol^{-1} XLGENLINE GLS fit using *LCS* data set. The error bar represents the expanded uncertainty at a 95 % level of confidence. Blue dots CCQM-K120.b self-consistent standards used for KCRV determination.

7. Conclusions

The values of the standards assigned by both ICOS and the BIPM were consistent within their stated uncertainties with the reference values and uncertainties derived from the CCQM-K120 comparison.

In the case of the BIPM, the values had been derived from the CO_2-PVT facility, for which further development is foreseen, and had been compared to benchmark the current state of performance of the system. The agreement with the reference values at all mole fractions as well as measurement uncertainties achieved, which are of similar magnitude to those of standards produced by gravimetric methods, is very encouraging. The BIPM facility is an analytical one, which can operate without reference to other carbon dioxide in air standards, and therefore is an ideal candidate for the reference facility for on-demand and on-going comparisons for CO_2 in air standards from NMIs. Further activity at the BIPM will focus on reducing measurement uncertainty of the facility and verifying the stability of the system in order to be able to implement BIPM.QM-K2, a CO_2 in air standard on-going comparison.