International Comparison CCQM K52 – Carbon dioxide in Synthetic Air

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Field

Amount of substance

Subject

Comparison in the field of carbon dioxide in air

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Introduction

The first key comparison on carbon dioxide in nitrogen dates from 1993-1994 (CCQM-K1b) [1]. It is in fact one of the first types of gas mixtures that was used in an international (key) comparison. Since then, numerous National Metrology Institutes (NMIs) have been setting up facilities for gas analysis, and have developed claims for their Calibration and Measurement Capabilities (CMCs) for these mixtures. Also, in 2003 a comparison (CCQM-P41 [2, 3]) was carried out between NMIs and WMO laboratories for the determination of greenhouse gases showing a good overall agreement between the participants. In the April 2005 meeting of the CCQM Gas Analysis Working Group, a policy was proposed to repeat key comparisons for stable mixtures every 10 years. Consequently, this comparison is consistent with the proposed policy and enables NMIs that could not participate in the previous comparison to take part.

This report describes the results of a key comparison for carbon dioxide in synthetic air (oxygen + nitrogen). The amount–of–substance fraction level of carbon dioxide chosen for this key comparison (360 µmol/mol) represents the ambient level of this component in air.

This key comparison aims to support CMC-claims for carbon dioxide in both nitrogen or air (synthetic and purified) from 100 µmol/mol to 20 cmol/mol.

Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
CSIRO	AU	Commonwealth Scientific and Industrial Research Organisation, Aspendale, Australia
NMIA	AU	National Metrology Institute of Australia, Lindfield, Australia
INMETRO	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brasil
NIM	CR	National Institute of Metrology, Beijing, PR China
BAM	DE	Bundesanstalt für Materialforschung und –prüfung, Berlin, Germany
CEM	ES	Centro Espanol de Metrologia, Madrid, Spain
LNE	FR	Laboratoire National d'Essais, Paris, France
NPLI	IN	National Physical Laboratory, New Delhi, India
INRIM	IT	Istituto Nazionale di Ricerca Metrologica, Turin, Italy
CERI	JP	Chemicals Evaluation and Research Institute, Saitama, Japan
NMIJ	JP	National Metrology Institute of Japan, Tsukuba, Japan
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
CENAM	MX	Centro Nacional de Metrologia, Queretaro, Mexico
NMi VSL	NL	NMi Van Swinden Laboratorium B.V., Delft, the Netherlands
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
NIST	US	National Institute of Standards and Technology, Gaithersburg, United States of America
NMISA	ZA	National Metrology Institute of South Africa, Pretoria, South Africa

Measurement standards

A set of mixtures were prepared gravimetrically by NMi VSL. The mixtures were verified against a set of NMi VSL Primary Standard Mixtures (PSMs).

The pressure in the cylinders was approximately 50 bar; cylinders of 5 dm^3 nominal were used. The amount-of-substance fractions as obtained from gravimetry and purity verification of the parent gases were used as reference values. Each cylinder had its own reference value.

The nominal amount-of-substance fraction was 360 μmol/mol.

Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result.

Schedule

The schedule of this key comparison was as follows:

May 2006	Draft protocol to participants
June 2006	Registration of participants
July 2006	Preparation of gravimetric mixtures + first verification measurement
August 2006	Shipment of cylinders to participating laboratories
August 2006	Start of comparison
September 29, 2006	Reports due to pilot laboratory
October 15, 2006	Cylinders due to pilot laboratory
October 2006	Second verification measurement

Measurement equation

The reference values used in this key comparison are based on gravimetry, and the purity verification of the parent gases/liquids. All mixtures underwent verification prior to shipping them to the participants. After return of the cylinders, they have been verified once more to reconfirm the stability of the mixtures.

In the preparation, the following four groups of uncertainty components have been considered:

1. gravimetric preparation (weighing process) ($x_{i,grav}$)

2. purity of the parent gases ($\Delta x_{i,purity}$)

3. stability of the gas mixture ($\Delta x_{i,stab}$)

4. correction due to partial recovery of a component ($\Delta x_{i,nr}$)

The amount of substance fraction $x_{i,prep}$ of a particular component in mixture i, as it appears during use of the cylinder, can now be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr} \tag{1}$$

The value obtained from equation (1) is sometimes referred to as "gravimetric value". Assuming independence of the terms in equation (1), the expression for the combined standard uncertainty becomes

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 + u_{i,stab}^2 + u_{i,nr}^2 \tag{2}$$

For the mixtures used in this key comparison, the following statements hold (for all components involved). First of all, the preparation method has been designed in such a way that

$$\Delta x_{i,nr} = 0 \tag{3}$$

and its standard uncertainty as well. Furthermore, long-term stability study data have shown that

$$\Delta x_{i,stab} = 0 \tag{4}$$

and its standard uncertainty as well. In practice, this means that the scattering of the results over time in the long-term stability study can be explained solely from the analytical uncertainty (e.g. calibration, repeatability of measurement). On this basis, using the theory of analysis of variance [4, 5] the conclusion can be drawn that the uncertainty due to long-term stability can be set to zero.

Summarising, the model reduces to

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} \tag{5}$$

and for the associated standard uncertainty, the following expression is obtained

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 \tag{6}$$

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data (including uncertainty, the following condition should be met [7]

$$\left| x_{i,prep} - x_{i,ver} \right| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2} \tag{7}$$

where $x_{i,ver}$ is the measurement result from verification and $u_{i,ver}$ its associated standard uncertainty.

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [11] and takes advantage of the work done in the gravimetry study CCQM-P41 [2].

The reference value of mixture i in a key comparison[1] can be defined as

$$x_{i,ref} = \left\langle x_{i,ref} \right\rangle + \delta x_{i,ref} \tag{8}$$

where

$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver} \tag{9}$$

where $\Delta x_{i,ver}$ is the correction resulting from the verification.

Since the amount of substance fraction from preparation is used as the basis, the expectation of the correction $<\Delta x_{i,ver}>$ due to verification can be taken as zero, which is consistent with the assumption made earlier that both preparation and verification are unbiased. Thus, (8) can be expressed as

$$x_{i,ref} = \left\langle x_{i,prep} \right\rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver} \tag{10}$$

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[1]   This definition of a reference value is consistent with the definition of a key comparison reference value, as stated in the mutual recognition arrangement (MRA) [5].

This expression forms the basis for the evaluation of degrees of equivalence in this key comparison. For all mixtures, it has been required that

$$\Delta x_{i,ver} = 0 \qquad (11)$$

that is, there is no correction from the verification. The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of a reference value becomes thus

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2 \qquad (12)$$

The values for $u_{i,ver}$ are given in the tables containing the results of this key comparison.

Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established is given in table 2.

Table 2: Summary of calibration methods and metrological traceability

Laboratory code	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
NMi VSL	21-10 2006	ISO 6143	Own standards	Synthetic air	ND-IR
Inmetro	4, 5 and 6-12 2006	ISO 6143	NMi VSL	Synthetic air	GC-TCD
NMIA	15, 19, 21 and 24-9 2006	Bracketing	Own standards	Synthetic air	GC-TCD
KRISS	6, 7 and 8-12 2006	Multi point calibration	Own standards	Synthetic air including 0.93 %mol/mol of Ar	ND-IR
CEM	14, 18, and 19-9 2006	ISO 6143	Own standards + NMi VSL	Nitrogen	GC-TCD
NPL	24-11 2006	Bracketing	Own standards	Synthetic air, some also containing CH_4 and Ar	GC-TCD
SMU	25, 26 and 27-9 2006	ISO 6143	Own standards	Nitrogen/synthetic air	GC-FID
NMIJ		ISO 6143	Own standards	Synthetic air	GC-TCD
CERI	8, 11 and 12-12 2006	Bracketing	Own standards	Synthetic air including Ar	GC-TCD
CENAM	7, 12, 14 and 19-9 2006	ISO 6143	Own standards	Synthetic air	GC-FID
NMI-SA	16 and 24-8, 1 and 28-9 2006	ISO 6143	Own standards	Synthetic air	ND-IR
NIST	8, 11 and 14-11 2006	ISO 6143	Own standards		GC-TCD
INRiM	2 and 3-10 2006	WLS[2]	Own Standards + NMi VSL	Synthetic air	ND-IR
NPLI	25, 26 and 27-9 2006	Single point	NIST	Nitrogen	GC-FID
CSIRO-1	2, 11 and 12-10 2006	Multi point calibration	WMO	CO2-in-dry-natural air, and CO2-in-synthetic air	GC-FID
CSIRO-2	4, 5 and 10-10 2006	Multi point calibration	WMO	CO2-in-dry-natural air	ND-IR
BAM	7, 8 and 9-11 2006	Bracketing	Own standards	Nitrogen	GC-TCD
VNIIM	13, 17 and 20-10 2006	OLS[3]	Own standards	Synthetic air	ND-IR
LNE	13, 14 and 15-6 2006	Single point	Own standard	Synthetic air	GC-
NIM	1, 7 and 9-11 2006	OLS[3]	Own standards	Nitrogen	ND-IR

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[2]   Weighted least squares
[3]   Ordinary least squares

Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as [10]

$$\Delta x_i = D_i = x_i - x_{\text{KCRV}}, \tag{13}$$

and the uncertainty of the difference D_i at 95% level of confidence. Here x_{KCRV} denotes the key comparison reference value, and x_i the result of laboratory i.[4] Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = D_i = x_i - x_{i,ref}. \tag{14}$$

The standard uncertainty of D_i can be expressed as

$$u^2(\Delta x_i) = u_{i,lab}^2 + u_{i,prep}^2 + u_{i,ver}^2, \tag{15}$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved.

Results

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

x_{prep} amount of substance fraction, from preparation (10^{-6} mol/mol)
u_{prep} uncertainty of x_{prep} (10^{-6} mol/mol)
u_{ver} uncertainty from verification (10^{-6} mol/mol)
u_{ref} uncertainty of reference value (10^{-6} mol/mol)
x_{lab} result of laboratory (10^{-6} mol/mol)
U_{lab} stated uncertainty of laboratory, at 95% level of confidence (10^{-6} mol/mol)
k_{lab} stated coverage factor
Δx difference between laboratory result and reference value (10^{-6} mol/mol)
k assigned coverage factor for degree of equivalence
$U(\Delta x)$ Expanded uncertainty of difference Δx, at 95% level of confidence[5] (10^{-6} mol/mol)

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[4]   Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

[5]   As defined in the MRA [5], a degree of equivalence is given by Δx and $U(\Delta x)$.

Table 3: Results

Laboratory code	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
NMi VSL	D240036	364.30	0.073	0.18	0.20	364.13	0.36	2	-0.17	2	0.54
Inmetro	D752038	363.18	0.073	0.18	0.20	364.0	3.6	2	0.82	2	3.6
NMIA	D751922	363.31	0.073	0.18	0.20	363.09	0.70	2.18	-0.22	2	0.75
CEM	D751928	363.67	0.073	0.18	0.20	363.38	0.73	2	-0.29	2	0.8
NPL	D751947	364.15	0.073	0.18	0.20	364.36	0.44	2	0.21	2	0.59
SMU	D751961	363.86	0.073	0.18	0.20	364.6	1.2	2	0.74	2	1.3
NMIJ	D751944	363.88	0.073	0.18	0.20	364.08	0.48	2	0.20	2	0.62
CERI	D751923	363.89	0.073	0.18	0.20	363.42	0.61	2	-0.47	2	0.73
CENAM[6]	D751924	363.91	0.073	0.18	0.20	361.6	2.2	2	-2.31	2	2.2
NMI-SA	D751918	364.00	0.073	0.18	0.20	364.9	3.883	2	0.90	2	3.9
NIST	D751954	364.03	0.073	0.18	0.20	363.72	0.34	2	-0.31	2	0.52
INRiM	D751935	364.05	0.073	0.18	0.20	364.62	0.90	2	0.57	2	1.0
NPLI	D751950	364.14	0.073	0.18	0.20	358.1	13.6	2	-6.04	2	14
CSIRO-1[7]	D751926	364.15	0.073	0.18	0.20	364.07	0.25	2			
CSIRO-2[7]	D751926	364.15	0.073	0.18	0.20	364.114	0.11	2			
BAM	D751942	363.72	0.073	0.18	0.20	363.5	2.9	2	-0.22	2	2.9
VNIIM	D751937	364.19	0.073	0.18	0.20	364.1	0.7	2	-0.09	2	0.8
LNE	D750235	364.21	0.073	0.18	0.20	363.63	1.15	2	-0.58	2	1.2
NIM	D751943	364.34	0.073	0.18	0.20	364.6	1.1	2	0.26	2	1.2

During the return analysis of the cylinders the cylinder that had been send to KRISS showed an inexplicable deviation from the gravimetric value and was therefore found not to be stable. When analysing this cylinder with a Cavity Ring Down Spectrometer an increased moisture level was found when compared to another cylinder that was part of the comparison. This level was for the "stable" mixture approx. 230 nmol/mol, the cylinder that was returned from KRISS contained approx. 630 nmol/mol. As this moisture level was not analysed before the cylinder was shipped to KRISS, it cannot be concluded that during measurements at KRISS, moisture was introduced. As no explanation could be found for this instability, in addition to this key-comparison, a bilateral comparison was organised between the coordinating laboratory and KRISS. For this comparison the coordinating laboratory prepared an additional mixture that was analysed by KRISS. In table 4, the results of this comparison are summarized.

Table 4: Results bilateral NMi-VSL - KRISS

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
KRISS	D751977	363.12	0.073	0.18	0.20	363.20	0.06	2	0.08	2	0.41

In figure 1 the relative deviation from the reference value for all laboratories, including CSIRO, is given. The uncertainties shown are those stated by the laboratories, *i.e.*, the uncertainty in the reference value is not included.

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[6] CENAM applied a correction factor to arrive to the reported values

[7] CSIRO is not a designated laboratory. For this laboratory no degree of equivalence is calculated.

In figure 2 the relative degrees of equivalence for the laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [11], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $k = 2$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

CCQM-K52 Carbon dioxide in Synthetic air
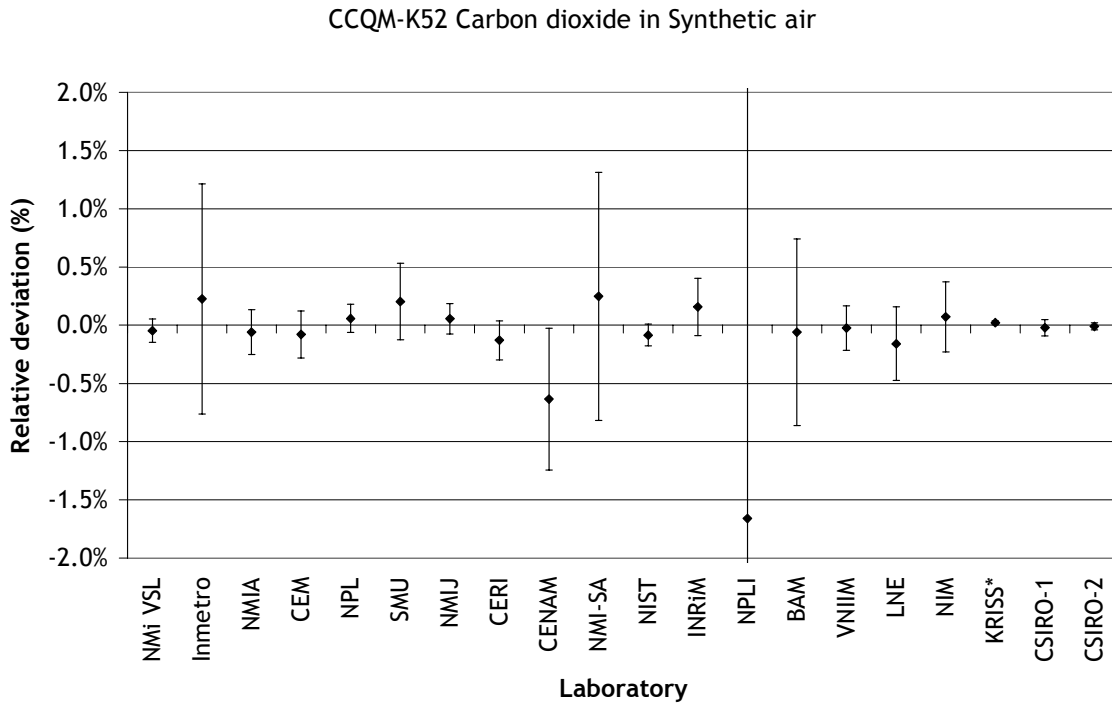
Figure 1: Relative deviation from the reference value with uncertainties stated by the laboratories (k=2)

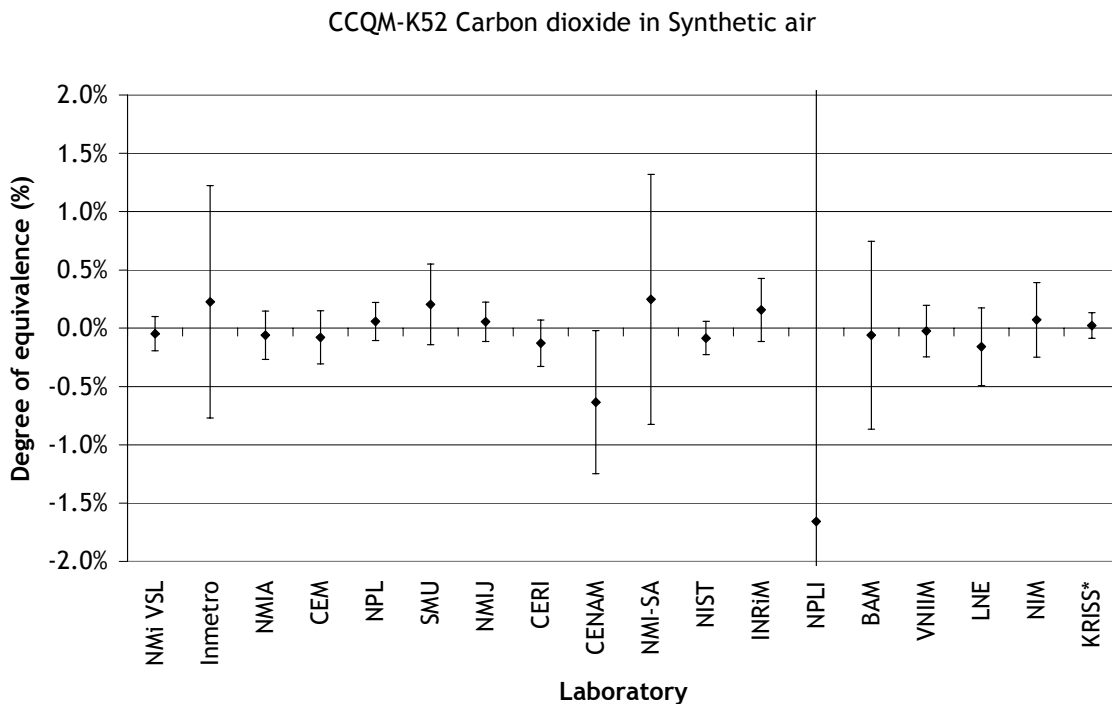CCQM-K52 Carbon dioxide in Synthetic air

Figure 2: Relative degrees of equivalence with uncertainties (k=2)

*The results of KRISS were obtained in a separate bilateral comparison carried out with NMi VSL (see text)

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As this comparisons acted as a repeat for CCQM-K1b, the results of this first comparison are plotted in the relative degrees of equivalence figure and presented in figure 3. CCQM-K1b was organised for 3 different levels of CO_2 in nitrogen and in figure 3 the results for the 100 µmol/mol mixture are presented. The results for CCQM-K1b are presented after the results for the laboratory in this comparison and marked with an asterisk.
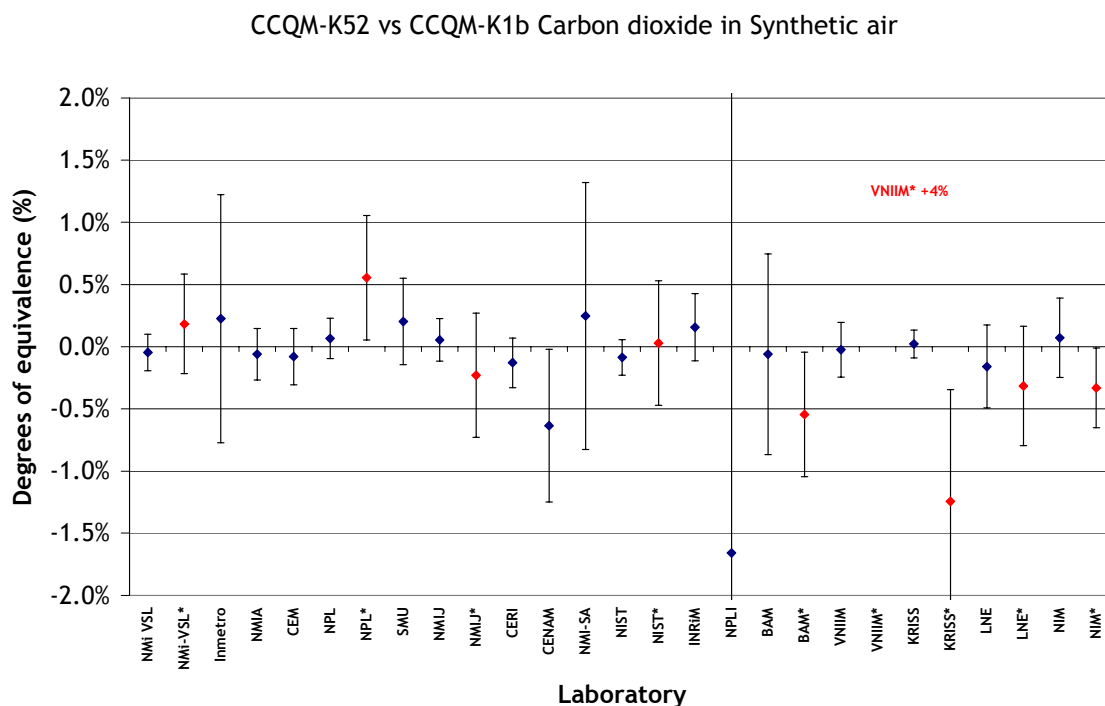

Figure 3: Relative degrees of equivalence for CCQM-K52 and CCQM-K1b at 100 µmol/mol with uncertainties (*k*=2)

Discussion of results

With the exception of the results of CENAM and NPLI, the reported results (figure 2) agree with the KCRV within 0.3% relative. In most cases, the departure from the KCRV is smaller than the associated expanded uncertainty. The only laboratory with a departure greater than the associated expanded uncertainty is CENAM.

In general, no relationship can be observed between the analytical method applied and the measurement results. Only the relatively large departure from the KCRV of the results reported by NPLI may be explained by the calibration method applied: these results were obtained by single point calibration applying a standard with a relatively high amount of substance fraction CO_2 (0.971 % mol/mol).

Totally unexpected was the failure of the standard sent to KRISS. The bilateral comparison that was organised directly after showing the first results showed extremely good results

Conclusions

The agreement of the results in this key comparison is very good. With a few exceptions, the results agree within 0.3% (or better) with the key comparison reference value.

Most of the participants that did not participate in CCQM-K1b do very well in this key comparison. In some cases, the uncertainties claimed are quite large in comparison with the NMIs for which this comparison is a true 'repeat', but the observed differences with the KCRV usually reflect that these claims are realistic. All participants in CCQM-K1b that participated in this key-comparison show improved results.

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Project reference

CCQM-K52

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Report Forms
CCQM-K52 Carbon dioxide in synthetic air

Laboratory name: CSIRO Marine and Atmospheric Research

(measurements by GAS CHROMATOGRAPHY)

Cylinder number: D751926

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	02/10/06	364.10E-6	0.047	8

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	11/10/06	364.07E-6	0.027	10

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	12/10/06	364.04E-6	0.038	10

Results

Component	Result (mol/mol)	Expanded Uncertainty (% relative)	Coverage factor
Carbon dioxide	364.07E-6	0.07	2

(measurements by LOFLO, an NDIR technique based on a Li-Cor 6251)

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	04/10/06	364.098E-6	0.0036	6

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	05/10/06	364.109E-6	0.0030	8

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	10/10/06	364.120E-6	0.0041	12

Results

Component	Result (mol/mol)	Expanded Uncertainty (% relative)	Coverage factor
Carbon dioxide	364.114E-6	0.03	2

Laboratory name: **NMIA – National Measurement Institute Australia**

Cylinder number: D751922

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	15/09/06	362.85 µmol/mol	0.22	13

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	19/09/06	363.21 µmol/mol	0.20	13

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	21/09/06	363.13 µmol/mol	0.19	13

Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	24/09/06	363.17 µmol/mol	0.23	13

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
CO2	363.09 µmol/mol	0.70 µmol/mol	2.18

Reference Method:

The concentration of carbon dioxide in the gas mixture was determined by conventional gas chromatography using a Varian 3800 gas chromatograph with TCD. The gas separation was performed on a Hayesep R (80/100 mesh, 12'x 1/8" SS) column with helium as the carrier gas. The column was held isothermally at 50°C.

Calibration Standards:

Three calibration standards were used in this study for the determination of the carbon dioxide concentration. The concentrations of the carbon dioxide in the calibration standards bracketed the expected concentration of CO_2 in the sample cylinder.

The calibration standards were prepared in our laboratory from pure carbon dioxide and internally certified synthetic air, with the concentration of CO_2 determined gravimetrically. A three stage dilution process was used to make the calibration mixtures, with CO_2 in air concentrations at 50 mmol/mol, 5 mmol/mol, and the final level around 0.36 mmol/mol. The three calibration mixtures were manufactured by three independent routes to minimise potential biases.

Calibration standard 1: ME2618

Component	Assigned value(x)	Expanded uncertainty
Carbon dioxide	366.16 µmol/mol	0.12 µmol/mol

Calibration standard 2: ME2616

Component	Assigned value(x)	Expanded uncertainty
Carbon dioxide	364.47 µmol/mol	0.12 µmol/mol

Calibration standard 3: ME2615

Component	Assigned value(x)	Expanded uncertainty
Carbon dioxide	361.59 µmol/mol	0.12 µmol/mol

Instrument Calibration:

The K52 sample cylinder was run in a sequence of runs that contained single-point and two-point bracketed calibrations with each of the reference cylinders. Each stage of the measurement sequence consisted of 27 repeat analyses of a cylinder. For calculation purposes the first 14 runs were rejected to allow for thorough flushing and equilibration of the sample gas lines, and the last 13 runs were used to determine average responses.

Single-point bracketed results were calculated using the mathematical model:

$$Cx = Cs * Rx / Rs$$

Where:
- Cx = concentration of sample
- Cs = concentration of standard
- Rx = average response of GC for sample
- Rs = average response of GC for standard

Two point bracketed results were calculated using the mathematical model:

$$Cx = (C_2-C_1)*(Rx-R_1)/(R_2-R_1)+C_1$$

Where:
- Cx = concentration of sample
- C_1 = concentration of first standard
- C_2 = concentration of second standard
- Rx = average response of GC for sample
- R_1 = average response of GC for first standard
- R_2 = average response of GC for second standard

Results from each sequence of runs were combined and averaged to produce a single table of measurement results. The sequence of runs was repeated four times over two weeks.

Analyses were performed in a laboratory with a temperature maintained at 22.5°C ± 0.2°C. Analysis results were not corrected for variations in laboratory air pressure or temperature.

Sample handling:

The K52 cylinder and calibration reference standards were connected to a Valco valve with quick-connect fittings. The Valco valve was controlled by the GC and automatically changed the cylinder for analysis. An electronic Mass Flow Controller maintained a constant amount of gas flow through the GC sample loop.

Evaluation of measurement uncertainty

For the analysis of the carbon dioxide we established two types of uncertainty:
- Gravimetric uncertainty, and
- Analytical uncertainty

The Gravimetric uncertainty related to the gas calibration standards and the contributions included:
- Balance uncertainty
- Buoyancy of cylinders
- Expansion of cylinders
- Tare mass uncertainty
- Tare mass buoyancy
- Purity of gases
- Natural variation in molar masses of source gases
- Cylinder handling

The amount of each contribution to the measurement uncertainty was determined. The gravimetric uncertainty was calculated by taking the square root of the sum of the squares for each uncertainty source.

The analytical uncertainty contributions included:
- Uncertainty from the measurement of the sample cylinder
- Uncertainty from the measurement of the reference gases

The analytical uncertainty was calculated by using the mathematical models for single-point and two-point bracketed calibrations. The standard uncertainty of the analytical response for the reference cylinders was calculated; along with the standard uncertainty for the analytical response of the sample cylinder.

The combined total uncertainty was determined using the principles described in the ISO GUM. The uncertainty obtained from the analytical measurement was combined with the gravimetric uncertainty of the gas calibration standards to give the total combined uncertainty.

Laboratory name: INMETRO – Divisão de Metrologia Química – Laboratório de Análise de Gases

Cylinder number: D752038

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	04/12/2006	363,6	0,37	5

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	05/12/2006	363,5	0,42	7

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	06/12/2006	364,8	0,42	7

Results

Component	Result (µmol/mol)	Expanded Uncertainty	Coverage factor
Carbon dioxide	364,0	3,6	2

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.)[8]:

A GC specifically set up for gas analysis was used:

-Varian CP-3800 equipped with both TCD and FID detectors. The carbon dioxide was determined using the TCD detector.

Carrier gas: Helium
Columns:

>0.5 m x 1/8" ultimetal Hayesep T   80/100
>0.5 m x 1/8" ultimetal Hayesep Q   80/100

The injection was performed automatically. The volume of sample loop was 0,5 ml and data collection was performed using Star Chromatography Workstation 6.3

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

---

[8] Please try to compile the information as short and concise as possible, for example like the description of instrumental techniques in scientific papers

It was used three standards to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by NMi-VSL.

PRM MY 9632

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty ($u(x)$) 10^{-6} mol/mol
Carbon dioxide	300,2	0,45

PRM MY 9638

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty ($u(x)$) 10^{-6} mol/mol
Carbon dioxide	392,4	0,40

PRM MY 9619

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty ($u(x)$) 10^{-6} mol/mol
Carbon dioxide	601,1	0,60

Laboratory name: NRCCRM (NIM)
Cylinder number: D751943

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO2	01/11/2006	364.2	0.1%	12

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO2	07/11/2006	364.6	0.1%	8

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO2	09/11/2006	365.1	0.1%	4

Results

Component	Result (µmol/mol)	Expanded Uncertainty	Coverage factor
CO2	364.6	0.3%	2

Reference Method:
41C CO_2 Analyzer from Thermo
EURACHEM / CITAC Guide: "Quantifying Uncertainty in Analytical measurement"

Calibration Standards:
Seven standard gas mixture cylinders were used as calibration standards to analyse the sample. The calibration standards were prepared by gravimetric method. The detail information was listed in table 1.

The impurities of complementary gas and impurities of components interested were also analysed. Experiments showed that the impurities of the material gases have no effects to the results within the measurement uncertainties. So the purity of pure gases used for preparation was taken from the certifications of producer. Their uncertainties were calculated by type B evaluation.

Table 1 Calibration Standards

Components	CO₂ in air							Average relative standard uncertainty
Cylinder No.	290526	290500	284144	290513	291536	290586	291410	
Assigned value (µmol/mol)	319.9	357.3	356.6	357.8	360.2	375.8	400.8	0.1%

Instrument Calibration:

The concentration of CO_2 in nitrogen is calculated using a manually prepared calibration curve. For this purpose seven gas calibration standards were prepared by gravimetric method. More than three subsequent measurement results were obtained under repeatable conditions by the linear least squares calibration.

Sample Handling:

Sample cylinder after arrival was stored in the room temperature. Sample and standard gas were all directly led to monitor by a regulator, a flow meter and a piece of teflon pipe, after flushing the regulator several times. Each sample flows into the monitor for at least 5 minutes with flow rate 600 ml/min.

Uncertainty Evaluation:

Two source of uncertainties were considered:
- Gravimetric uncertainty
- Analytical uncertainty

The Gravimetric uncertainty contributions included:
- Balance uncertainty
- Buoyancy of cylinders
- Impurity of gases
- Leakage
- Absorption

The analytical uncertainty was evaluated by RSD% of the repeating measurement.

The relative standard uncertainty of CO_2 in sample mixture was evaluated by equation (1)

$$u^2(C_{sample}) = u^2_{gravi} + u^2_{analysis} \qquad (1)$$

Expanded uncertainty can be calculated with a confidence interval 95% and a coverage factor k= 2. The expanded uncertainty was:

$$U = k \cdot u(C_{sample}) \qquad (2)$$

Laboratory name: Bundesanstalt für Materialforschung und –Prüfung (BAM)

Cylinder number: **D 751 942**

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	07/11/06	0,0003644		3 * 3

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	08/11/06	0,0003631	0,3	3 * 3

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	09/11/06	0,0003630	0,3	4 * 3

Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	11/11/06	0,0003636		4 * 3

Results

Component	Result (mol/mol)	Expanded Uncertainty (% relative)	Coverage factor
CO2	0,0003635	0,8	2

Reference Method:

For the determination of Carbon Dioxide (CO_2:

GC: Perkin Elmer AutoSystem XL (two channel system) with a stream selection valve for 4 streams and 2 gas sampling valves.

> Channel A: Carrier Gas: Helium
> Columns: Column system with two packed columns
> (6 ft x 1/8" Porapak R, 80/100 mesh and
> ~~6 ft x 1/8" Mol-Sieve 13X, 80/100 mesh.)~~
> Oven Temperature 75 °C
> Detector: μ-TCD
> Data Collection: Total Chrom Workstation

Data Collection: Total Chrom Workstation

Comment:

The applied method does not correspond to the method, which is normally used by BAM for certifying by reference materials.
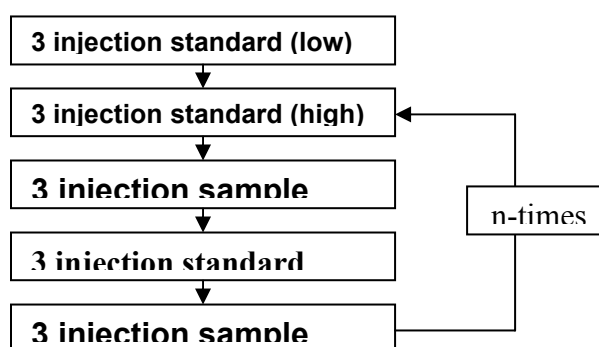
Channel B of the GC was defective. Therefore the content of CO_2 could not be determined by use of Methanizer with the FID (Channel A).   The TCD had to be use!

Therefore the value of the Standard deviation becomes larger substantially, since the content is appropriate for only little over the limit of determination for CO2 with the TCD.

Instrument Calibration:

For the instrument calibration the bracketing technique was used. The fraction of the current used standards deviated no more than +10%rel. and -10%rel. respectively from those of the sample.

Measurement sequence

```
┌─────────────────────────────┐
│  3 injection standard (low)  │
└──────────────┬──────────────┘
               ▼
┌─────────────────────────────┐
│  3 injection standard (high) │◄──────┐
└──────────────┬──────────────┘       │
               ▼                       │
┌─────────────────────────────┐       │
│      3 injection sample      │     ┌─────────┐
└──────────────┬──────────────┘     │ n-times │
               ▼                     └─────────┘
┌─────────────────────────────┐       │
│      3 injection standard    │       │
└──────────────┬──────────────┘       │
               ▼                       │
┌─────────────────────────────┐       │
│      3 injection sample      │───────┘
└─────────────────────────────┘
```

Sample handling:

Each cylinder was equipped with a pressure regulator that was purged three times by sequential evacuation and pressurisation with the gas mixture used.
Continous flow (2 – 3ml/min) through the sample loop.

Calibration Standards:

All standards are prepared via pre-mixtures according to ISO 6142
"Gas analysis - Preparation of calibration gases - Gravimetric Method".
The content of the impurities in all pure gases were determined before use by GC-DID, GC-FID and / or GC-TCD.

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition is found, the "new prepared candidate " is accepted as a new standards

Composition of calibrants :

Component	Assigned value mol/mol	Standard uncertainty ($u(x)$) (k=2) %rel
Nitrogen	Balance	0,01
Carbon dioxide	0,00036922	0,04

BAM 6018-061010

Component	Assigned value	Standard uncertainty ($u(x)$)

	mol/mol	(k=2) %rel
Nitrogen	Balance	0,01
Carbon dioxide	0,00034959	0,04

BAM 6052-061030

Component	Assigned value mol/mol	Standard uncertainty ($u(x)$) (k=2) %rel
Nitrogen	Balance	0,01
Carbon dioxide	0,0005270	0,04

Laboratory name: CENTRO ESPAÑOL DE METROLOGÍA (CEM)

Cylinder number: D751928

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	14/09/2006	363,58	0,07	10

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	18/09/2006	363,00	0,08	10

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	19/09/2006	363,57	0,10	10

Measurement #4

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	19/09/2006	363,36	0,08	10

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor
CO_2	363,38	0,73	2

Laboratory name: Laboratoire National de métrologie et d'Essais (LNE)

Cylinder number: D752035

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CO_2	13/06/2006	363.71	0.21	10

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CO_2	14/06/2006	363.49	0.29	10

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CO_2	15/06/2006	363.69	0.28	10

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor
CO_2	363.63	1.15	2

Laboratory name: Istituto Nazionale di Ricerca Metrologica

Cylinder number: D751935

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	2/10/06	$364,63*10^{-6}$	0,035	9

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	2/10/06	$364,61*10^{-6}$	0,034	9

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	3/10/06	$364,63*10^{-6}$	0,023	9

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
CO2	$364,62*10^{-6}$	$0,90*10^{-6}$	2

Reference Method:

The instrument used for CO_2 determination is a NDIR analyser ABB URAS 14, with measurement range from 0 to 1000 μmol mol^{-1} and resolution of 0,1 μmol mol^{-1}. The data are visualized on the instrument display and manually recorded.

Calibration Standards:

The Calibration Standards used are Primary Reference Gas Mixtures of CO_2 in a matrix of synthetic air gravimetrically prepared at INRIM by diluting a gravimetric standard purchased from NMi-VSL (concentration: 2001 μmol/mol, standard uncertainty: 4 μmol/mol) with air N 57 for mixtures n. 1 and n. 3 (see following section) and air N 50 for mixture n. 2. The standard compositions were verified by means of NDIR spectroscopy using a set of certified reference gas mixtures having similar composition.

As for purity, the data certified by the producers were used, i.e. a maximum content of CO_2 of 0,1 μmol/mol for air N 57, and of 1 μmol/mol for air N 50 which were taken into account in the uncertainty budget assuming a rectangular distribution.

Instrument Calibration:

Three standards were used at the following concentrations:

CO_2 328,45·µmol mol^{-1} $U = 0,66$ µmol mol^{-1} (k=2)

CO_2 360,03 µmol mol^{-1} $U = 0,92$ µmol mol^{-1} (k=2)

CO_2 390,08 µmol mol^{-1} $U = 0,78$ µmol mol^{-1} (k=2)

The measurements were carried out at a flow of approximately 30 L h^{-1}. It was previously proved that small flow variations do not affect the measurement value. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.

No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:

Standard n. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times). A control standard was analysed at the beginning and at the end of the entire sequence.

No correction for ambient temperature was made.

Three different calibration curves were determined, one for each measurement day and they were used to estimate the final result for CO_2.

Determination of calibration curves

The calibration curves were determined by means of an Excel worksheet, developed at INRIM, based on the Weighted Least Squares method, which calculates a linear correction, to be applied to the instrument readings according to the following equation:

$$x = y + d(y) = y + \alpha_0 + \alpha_1 y \qquad (2)$$

where x is the concentration of the analyte in the reference gas mixtures, y is the instrument output and $d(y) = \alpha_0 + \alpha_1 y$ is the correction. The measurands are the polynomial coefficients α_0 and α_1. The estimation algorithm takes care of different sources of uncertainty: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. Being the reference gas mixtures prepared at INRIM by diluting the same pre-mixture, a correlation coefficient of 0,9 was adopted in the calculation. For detailed information see the reference: Plassa M., Mosca M., Sega M. "Carbon Dioxide Determination for High Accuracy Weighings" in: *Proceedings of the 16th International Conference IMEKO TC3/APMF '98*, Myung Sai Chung Ed.; Taejon, Korea, 1998, pp. 183-191.

Calibration curves data are summarized in the following tables (tab. 1-3):

	α	$u_c(\alpha)$	ψ_α	
α_0	-40,98	2,5	6,37E+00	-1,74E-02
α_1	0,11	7,0E-3	-1,74E-02	4,87E-05

Tab. 1: calibration curve parameters of 02/10/06 (first set)

	α	$u_c(\alpha)$	ψ_α	

	α	$u_c(\alpha)$	$\boldsymbol{\psi_\alpha}$	
α_0	-41,45	2,6	6,95E+00	-1,91E-02
α_1	0,11	7,3E-03	-1,91E-02	5,39E-05

Tab. 2: calibration curve parameters of 02/10/06 (second set)

	α	$u_c(\alpha)$	$\boldsymbol{\psi_\alpha}$	
α_0	-40,66	2,3	5,32E+00	-1,47E-02
α_1	0,11	6,5E-03	-1,47E-02	4,18E-05

Tab. 3: calibration curve parameters of 03/10/06 (third set)

Sample Handling:

The cylinder was kept indoor and in a horizontal position.

Samples were transferred into the NDIR analyser by means of a needle valve and a sample line of stainless steel at a flow of 30 L h^{-1}.

Uncertainty:

The contributions to the combined standard uncertainty of the results are due to the calibration curve and to the repeatability of readings of sample measurements. From each of the three calibration curves a CO_2 concentration value with its combined standard uncertainty was estimated. The final result is the mean of these three values and its combined standard uncertainty is the largest one among the obtained uncertainties, as they were very close.

The contribution of the calibration curve takes into account different sources: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. These sources are merged together in the Excel worksheet for the calibration curves calculation, hence it is very difficult to separate each contribution.

After the calibration process α_0 and α_1 being known, if a set of n_r instrument readings, arranged in a vector r, are to be corrected by the calibration algorithm, the matrix R can be defined, whose columns are the first two powers of r:

$R = (r^0 \ r)$

The correction vector $d(r)$ can be computed from $d(r) = R\,\alpha$, where α is the vector of the coefficients α_0 and α_1. The corrected readings are:

$$q = d(r) + r \qquad\qquad\qquad (3)$$

The covariance matrix of the readings is $\psi_r = s^2 I$, where s is the repeatability standard uncertainty of the instrument and I an identity matrix. The covariance matrix ψ_d of d can be estimated starting from the law of propagation of uncertainty:

$$\psi_d = \nabla_\alpha(d)\ \psi_\alpha\ \nabla_\alpha(d)^\mathrm{T} + \nabla_r(d)\ \psi_r\ \nabla_r(d)^\mathrm{T}$$

where the symbol $\nabla_z(w)$ means the Jacobian matrix, i.e. the matrix derivative, of the vector w with respect to the vector z and ψ_α is the variance-covariance matrix of the coefficients α_0 and α_1.

Laboratory name: Chemicals Evaluation and Research Institute, Japan

Cylinder number: D751923

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	08/12/2006	363.44	0.08	4

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	11/12/2006	363.40	0.06	5

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	12/12/2006	363.43	0.08	5

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
CO2	363.42	0.61	2

Reference Method:

Instruments for CO2 measurement
Principles : GC-TCD (Type:GC-14A, Make : Shimadzu corporation)
          Column : Porapak-N 5m x 3mm
                  50 degree constant
                  He : 40ml/min
   Data collection : output of integrator of data C-R6A (Shimadzu corporation)

Calibration Standards:

Preparation : Gravimetric method

Purity analysis ;
   CO2 : certified by NMIJ(National Metrology Institute of Japan)
   O2, Ar, N2: The impurities in O2, Ar and N2 are determined by analyses and the amount
       of the major component is conventionally determined by,

$$X_{pure} = 1 - \sum_{i=1}^{N} x_i$$

   where:
   x_I = mole fraction of impurity i , determined by analysis
   N = number of impurities likely in the final mixture
   X_{pure} = mole fraction 'purity' of the 'pure' parent gas

Instrument Calibration:

Table 1   concentration of PSMs

Component	Concentration (μmol/mol)	
	R_1	R_2
CO2	380.11	360.08

 This procedure is for the determination of CO2 in a sample using GC-TCD.
  1) Inject the calibration standard (R_1) into GC-TCD. Record the output.
  2) Inject the sample to be tested in same manner as the calibration standard. Record the
     output.
  3) Inject the calibration standard (R_2). Record the output.
  4) Calculate the concentration of CO2 using the formula below.

$$Y = \frac{A(E-D) + B(C-E)}{(C-D)}$$

   where Y: Concentration of sample
           A: Concentration of standard (R_1)
           B: Concentration of standard (R_2)
           C: Standard (R_1) output
           D: Standard (R_2) output

E: Sample output

Following above procedure, 5 measurements are repeated subsequently in a day and iterated for 3 days.

Uncertainty:

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatability of analysis	363.42	normal	0.27	1	0.27
Reference gas R1 preparation	380.11	normal	0.10	1	0.10
Reference gas R2 preparation	360.08	normal	0.10	1	0.10
total					0.30

Coverage factor: 2
Expanded uncertainty: 0.61 µmol/mol

Laboratory name: NMIJ

Cylinder number: D751944

The following results are obtained by the method described in the Ref.[1]. This method uses a quality control (QC) cylinder.

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor[9]
CO_2	364.08	0.48	2

Reference Method:

Our analysis used a gas chromatograph described in table 1.

Table 1. Analytical conditions.

Body	Shimadzu GC-14B
Software for data collection	GC solution (Shimadzu)
Column	Porapak Q 2m
Oven temp.	50 ºC
Detector	TCD
Current of detector	100 mA
Temp. of detector	130 ºC
Carrier gas	He
Volume of sample loop	2 mL
Analytical time for one injection	4.5
Number of injections per one cylinder	5

Calibration Standards:

All measurements used the calibration gas standards in Table 2. These standards were prepared by gravimetric method, according to ISO 6142:2001.

Table 2. Gravimetric concentrations in calibration standards. (Units are μmol/mol).

(a) calibration standard 1

Component	Gravimetric concentration	Expanded uncertainty [k=2]
Carbon dioxide	365.074	0.0619
Oxygen	206904.0	4.74
Nitrogen	792730.5	4.75

---

[9] The coverage factor shall be based on approximately 95% confidence.

(b) calibration standard 2

Component	Gravimetric concentration	Expanded uncertainty [k=2]
Carbon dioxide	358.396	0.0662
Oxygen	203125.3	4.94
Nitrogen	796515.8	4.94

(c) calibration standard 3

Component	Gravimetric concentration	Expanded uncertainty [k=2]
Carbon dioxide	361.025	0.0613
Oxygen	209679.3	5.08
Nitrogen	789959.2	5.08

(d) calibration standard 4

Component	Gravimetric concentration	Expanded uncertainty [k=2]
Carbon dioxide	374.496	0.0787
Oxygen	189995.0	5.12
Nitrogen	809630.1	5.12

Preparation method:

All calibration gas standards were prepared by using an electronic mass-comparator (Mettler Toledo model KA10-3/P, capacity 15 kg , readability 1 mg) with automatic loading system of cylinders [Ref.2]. These calibration gas standards were prepared by two-step dilution.

Purity analyses :

The impurities in nominally "pure" parent gases are determined with various gas analyzers. The mole fractions of the major components are conventionally calculated from equation (1) in ISO6142:2001.
Tables 3-5 show the results of impurity analyses.

Table 3. Purity table for high-purity carbon dioxide gas used as parent gas.

Component	Mole fraction μmol/mol	Standard uncertainty μmol/mol	Distribution	method
N_2	1.55	0.90	-	GC-TCD
O_2	0.68	0.39	Rectangular	GC-TCD
H_2O	0.44	0.25	Rectangular	Capacitance type moisture meter
CH_4	0.00155	0.00090	Rectangular	GC-FID
H_2	2.0	1.1	Rectangular	GC-TCD
CO_2	999995.36	1.5	-	-

Table 4. Purity table for high-purity oxygen gas used as parent gas.

Component	Mole fraction μmol/mol	Standard uncertainty μmol/mol	Distribution	method
N_2	0.025	0.015	Rectangular	GC-TCD
Ar	0.027	0.015	Rectangular	GC-TCD
CO_2	0.02283	0.00091	Normal	FT-IR
CH_4	0.0020	0.0011	Rectangular	FT-IR
CO	0.0077	0.0044	Rectangular	FT-IR
H_2O	0.44	0.25	Rectangular	Capacitance type moisture meter
O_2	999999.48	0.25	-	-

Table 5. Purity table for nitrogen gas used as parent gas.

Component	Mole fraction μmol/mol	Standard uncertainty μmol/mol	Distribution	method
N_2	999999.50	0.25	-	-
O_2	0.03135	0.00031	Normal	Oxygen analyzer with galvanic cell
H_2O	0.44	0.25	Rectangular	Capacitance type moisture meter
CO	0.0078	0.0045	Rectangular	FT-IR
CO_2	0.0091	0.0028	Normal	FT-IR
CH_4	0.0022	0.0013	Rectangular	FT-IR
Ar	0.0170	0.0098	Rectangular	GC-TCD

Sample handling:

Stabilization

The sample cylinder was kept in air conditioned room at about 22 $^{\circ}$C for 1 day since the sample cylinder had arrived at our laboratory. After that, we started our measurements for this comparison.

Transfer of sample gas to the instrument
A pressure regulator with two gauges was attached with the sample cylinder via an adaptor (DIN-1 – JIS 22 mm left). The pressure of sample gas from the regulator to a flow controlled valve was controlled at 0.01 MPa. The flow rate of sample gas was controlled at approximately 30 mL/min. The injection of sample gas was injected with 6-port valve.

Instrument Calibration:

A QC cylinder gas and other cylinder gases were injected into the GC-TCD, alternatively. These cylinders were exchanged manually after each measurement for one cylinder had finished.

These cylinders were measured within one day by the following order ;

"QC(i=1st)-calibration standard 1- QC(i=2nd)-calibration standard 2- QC(i=3rd)-calibration standard 3- QC(i=4th)-calibration standard 4- QC(i=5th)-sample cylinder-QC(i=6th)"

Record 5 peak heights per cylinder.

The following calibration data set can be obtained at j th day (j=1,…,6);

· average values of responses to the QC, $y_{qc,i=1,j}$, ….., $y_{qc,i=6,j}$,

· average heights of responses for calibration standards, $y_{1,j}$, $y_{2,j}$, $y_{3,j}$, , $y_{4,j}$,

· average height of responses for sample cylinder, $y_{s,j}$,

The corrected peak height for calibration standard k at j th day, $Y_{k,j}$, was calculated from :

$$Y_{k,j} = y_{k,j} / \left[(y_{qc,i=k,j} + y_{qc,i=k+1,j})/2 \right] .$$

The corrected peak height for sample cylinder at j th day, $Y_{s,j}$, was calculated from :

$$Y_{s,j} = y_{s,j} / \left[(y_{qc,i=5,j} + y_{qc,i=6,j}) / 2 \right] .$$

Furthermore, the measurements of Y_k and Y_s were repeated 6 times(6 days).

$$Y_k = \sum_{j=1}^{J=6} x_{k,j} \Big/ J \quad,$$

$$Y_s = \sum_{j=1}^{J=6} x_{s,j} \Big/ J \quad,$$

These standard uncertainties are ;

$$u^2(Y_k) = \sum_{j=1}^{J=6} (Y_{k,j} - Y_k)^2 \Big/ J(J-1) \quad,$$

$$u^2(Y_s) = \sum_{j=1}^{J=6} (Y_{s,j} - Y_s)^2 \Big/ J(J-1) \quad.$$

Here, we set that the gravimetric concentration and its uncertainty of calibration standard k are X_k and $u(X_k)$.

From the data set of $X_1, X_2, X_3, X_4, Y_1, Y_2, Y_3$, and, Y_4, the parameters and its uncertainty of the analytical function, $X_s = b_0 + b_1 \cdot Y_s$, were calculated with ISO6143 implementation software "B_LEAST version 1.11". After that, the analytical content X_s and its standard uncertainty $u(X_s)$ of the sample cylinder were calculated from the peak height, Y_s, and its uncertainty, $u(Y_s)$. The value of goodness-of-fit for this analytical function was 0.69, which was much less than 2.

Reference

[1] M.J.T Milton, F. Guenther, W.R. Miller, A.S. Brown, Metrologia **43** (2006) pp.L7-L10.

[2] N. Matsumoto, T. Watanabe, M. Maruyama, H. Horimoto, T. Maeda, K. Kato (2004) Metrologia **41** : 178-188.

Laboratory name: KRISS (ADDITIONAL BILATERAL COMPARISON)

Participants' Names: Jin Seog Kim, Dong Min Moon, Jin Bok Lee

Cylinder number: D751977

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO2	05/16/2007	363.20	0.001	3

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO2	05/19/2007	363.20	0.001	3

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CO2	05/21/2007	363.20	0.002	4

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor
CO2	363.20	0.06	2

Reference Method:
We used NDIR for this measurement (Siemens, Ultramat 6E).
Configuration of analysis system: gas cylinder -> regulator -> MFC -> NDIR-> response comparison-> results

Sample cell flow: 800 mL/min, Reference cell flow: 800 mL/min
Cell pressure: 1.94 Kg/cm^3

Calibration Standards:
The calibration standards for CCQM-K52 were prepared by gravimetric method including 0.93 %mol/mol of Ar in KRISS. Therefore, the matrix is different from that of coordinating Lab., which does not contain Ar. All source gases were analyzed impurities for purity analysis. The primary standards with 0.014% overall uncertainty (k=2) are used.

Instrument Calibration:

The seven sets of standard gas with similar concentration were prepared by gravimetric method and checked by GC and NDIR to make sure their accuracy. Finally we used six standard gases for multi-point calibration in CO2 measurement. The list of PRM is below.

No	Cylinder.no	Gravimetric value(umol/mol)	Expanded uncertainty(umol/mol)
1	ME0398	361.469	0.05
2	ME0399	373.018	0.05
3	ME5501	385.738	0.05
4	ME5590	387.052	0.05
5	ME5599	392.426	0.05
6	ME0434	402.362	0.06

Sample Handling:

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).:

The sample cylinders were stood for more than one week at room temperature before measurements. We used mass-flow controllers to transfer sample gases.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

In support of this action, a list of potential uncertainty sources is given. This list may not be complete and is compiled from draft ISO-Standards currently under development in ISO/TC158
We estimated the uncertainty in the gravimetric methods and measurements. Their uncertainties are given in Tables.

Uncertainty evaluation of weighing

Uncertainty related to the balance & the weights	Value (mg)	Distribution	Standard uncertainty (mg)
1. Resolution of balance	1	Rectangular	0.289
2. Accuracy of balance including linearity	1	Rectangular	0.577
3. Incorrect zero point	1	Rectangular	0.289
4. Drift(thermal and time effects)	1	Rectangular	0.289
5. Instability due to draught	Negligible		
6. Location of cylinder on the balance pan	Negligible		
7. Uncertainties in the weights used	0.05	Rectangular	0.025
8. Buoyancy effects on the weights used	1.68	Rectangular	0.97
Total (mg)			1.235

Uncertainty related to the gas cylinder	Value (mg)	Distribution	Standard uncertainty (mg)
1. Loss of metal, paints or labels from surface of cylinder	0.1	Rectangular	0.058
2. Loss of metal from threads of valve/fitting	0.5	Rectangular	0.289
3. Dirt on cylinder, valves or associated fitting	0.1	Rectangular	0.058
4. Adsorption/desorption effects on the external cylinder surface	0.1	Rectangular	0.058
5. Buoyancy effects on the cylinder itself			
5.1 Cylinder temperature differs from surrounding air due to e.g. filling with gas	0.6	Rectangular	0.346
5.2 Change of cylinder volume during filling	1.1	Rectangular	0.635
5.3 Change of density of surrounding air due to change in temperature, air, pressure, humidity and CO_2 content	Negligible		
6. Uncertainty in determination of external cylinder volume	Negligible		
Total (mg)			0.783

Uncertainties related to the component gases	Value(mg)	Distribution	Standard uncertainty(mg)
1. Residual gases in cylinder	0.057	Rectangular	0.033
2. Uncertainties of leakage of gas			
2.1 Leakage of air into the cylinder after evacuation	1	Rectangular	0.289
2.2 Leakage of gas from the cylinder valve during filling	1	Rectangular	0.289
2.3 Escape of gas from cylinder into transport lines	Negligible		
3. Gas remaining in transfer system when weight loss method is used	Negligible		
4. Absorption/reaction of components on internal cylinder surface	Negligible		
5. Reaction between components	Negligible		
6. Insufficient homogenization	Negligible		
Total (mg)			0.410

Total uncertainties in weighing (1.519 mg: standard uncertainty)

Purity table for O_2

component	analytical conc. (umol/mol)	distribution	applied conc. (umol/mol)	standard uncertainty (umol/mol)
H2	< 0.1	rectangular	0.05	0.029
H2O	1.1	normal	1.1	0.550

CO	0.08	normal	0.08	0.016
CH4	< 0.005	rectangular	0.0025	0.001
CO2	0.195	normal	0.195	0.039
THC	< 0.1	rectangular	0.05	0.029
N2	3.1	normal	3.1	0.620
Ar	< 1.0	rectangular	0.5	0.289
O2			999994.923	1.759

Purity table for N_2

component	analytical conc. (umol/mol)	distribution	applied conc. (umol/mol)	standard uncertainty (umol/mol)
H2	< 0.1	rectangular	0.05	0.029
H2O	1.6	normal	1.6	0.800
CO	< 0.005	rectangular	0.0025	0.001
CH4	< 0.005	rectangular	0.0025	0.001
CO2	0.002	normal	0.002	0.001
THC	-	-	-	-
O2	0.003	normal	0.003	0.003
Ar	21.6	rectangular	21.6	4.320
N2			999976.740	8.787

Purity table for Ar

component	analytical conc. (umol/mol)	distribution	applied conc. (umol/mol)	standard uncertainty (umol/mol)
H2	< 0.1	rectangular	0.05	0.029
H2O	0.9	normal	0.9	0.450
CO	< 0.005	rectangular	0.0025	0.001
CH4	< 0.005	rectangular	0.0025	0.001
CO2	< 0.002	rectangular	0.001	0.001
THC	< 0.1	rectangular	0.05	0.029
N2	2.4	normal	2.4	0.480
O2	0.003	normal	0.003	0.002
Ar			999996.591	1.318

Purity table for CO_2

component	analytical conc. (umol/mol)	distribution	applied conc. (umol/mol)	standard uncertainty (umol/mol)
H2	< 0.1	rectangular	0.05	0.029

H2O	4.5	normal	4.5	2.250
CO	0.3	normal	0.3	0.060
CH4	2.6	normal	2.6	0.520
C2(C2H4+C2H6)	2.8	normal	2.8	0.560
C3-C5	0.7	normal	0.7	0.350
N2	12.8	normal	12.8	2.560
O2+Ar	< 0.1	rectangular	0.05	0.029
CO2			999976.200	7.022

Evaluation of Measurement uncertainty:

Uncertainty from calibration curve: 0.03 μmol/mol (k=2) type A

Uncertainty of primary standards : 0.05 μmol/mol (k=2) type B

Uncertainty from comparison : 0.01 μmol/mol (k=2) type A

Laboratory name: CENAM. Centro Nacional de Metrología. México

Cylinder number: D751924

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	07/09/2006	3,614E-04	2,7E-01	4

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	12/09/2006	3,618E-04	2,8E-01	4

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	14/09/2006	3,615E-04	3,4E-01	4

Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon dioxide	19/09/2006	3,616E-04	3,6E-01	4

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
Carbon dioxide	3,616E-04	2,2E-06	2

Reference Method:

Agilent Technologies 6890 Gas Chromatograph Separation System, with FID, split/splitless injector, with Ni catalytic methanizer and injection valve, including Chemstation NT to collect and process data. Regulator of low pressure in the outlet of cylinder, with SS tubing of 1/16; and mass and volumetric precision gas flow meter, HP-Plot Q capillary column of 30 m X 0.53 mm X 40 µm.

Oven program: 50 ºC, 3 min, isothermal
He flow = 7,7 ml/min (65 cm/s) , at 64.81 kPa, constant
Make up N_2: 30 ml/min
FID temperature = 200 ºC

Injector temperature = 150 ºC
Flame gases flows: air = 400 ml/min, H_2 = 40 ml/min

Calibration Standards:

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs), prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 4.8 of purity and 5.0 for balance. Their uncertainties were calculated by type B evaluation or/and type A evaluation.

Preparation of the cylinders before the filling
The used cylinders to prepare the mixtures are aluminum made type ALH, they were provided by the Praxair Mexico (manufacturer LUXFER). Praxair Mexico carry out routine tests on the cylinders: Vent hydrostatic pressure, leaks, humidity analysis, passivation, vacuum level, and cleaning.

Before weighing each cylinder
The external surface and valve of each cylinder was cleaned using a cotton cloth with alcohol to eliminate dust or remainders of the cylinder. It was carried out a vacuum to each cylinder < 0,7 Pa, using the filling panel of the gas mixture preparation system. The cylinders with low pressure and cleaned were introduce to the gas mixture preparation lab to let acclimate to reach the laboratory temperature (24 h).

Determination of mass by means of weight
Specification of Balance
The instrument for weighing was a Mettler balance model KB-50 (60 kg capacity and 0,05 g resolution) and sets of weights class E2 (serial number 520779750101, from 1 to 5 kg – 4 pieces) and E2 (serial number 41003979, from 1 mg to 1 kg – 25 pieces) according to the R 111 of OIML, all of them traceable to SI by CENAM´s Standards. CENAM experts prepared the gas mixtures at the gas producer facilities (Praxair).

The value concentration and associated uncertainty of the primary standard mixtures used to quantify the sample are the following:

Cylinder Number	Component	Assigned Value (mol/mol)	Expanded Uncertainty
FF43767	Carbon dioxide	3,191E-04	9,5E-07
	Oxygen	2,092E-01	1,2E-04
	Nitrogen	7,905E-01	1,2E-04
FF43855	Carbon dioxide	3,399E-04	1,0E-06
	Oxygen	2,101E-01	1,3E-04
	Nitrogen	7,896E-01	1,3E-04
FF43789	Carbon dioxide	3,605E-04	1,1E-06
	Oxygen	2,099E-01	9,8E-05
	Nitrogen	7,897E-01	9,8E-05
FF43849	Carbon dioxide	3,600E-04	9,5E-07

	Oxygen	2,101E-01	9,6E-05
	Nitrogen	7,896E-01	9,6E-05
FF43700	Carbon dioxide	3,810E-04	1,1E-06
	Oxygen	2,098E-01	1,1E-04
	Nitrogen	7,898E-01	1,1E-04
FF43709	Carbon dioxide	4,007E-04	1,0E-06
	Oxygen	2,101E-01	9,2E-05
	Nitrogen	7,895E-01	9,2E-05

Instrument Calibration:

The calibration procedure was according to ISO 6143 using B_Least program software for multipoint Calibration. It was used 5 concentration levels in one control sample in the following sequence: $CStd_1MStd_2Std_3Std_4MCStd_2$…..

Uncertainty:

The main sources of uncertainty considered to estimate the combined standard uncertainty are derived from the:

Model used for evaluating measurement uncertainty:

$$C = \mu + \delta_T + \delta_s + \delta_m$$

The combined uncertainty has three contributions:

a) Reproducibility and Repeatability.

   The combined effect (δ_T) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.

b) Mathematical model effect (δ_m).

   This component corresponds to the estimated uncertainty which come from the B_Least program software for multipoint Calibration.

c) Performance instrument (δ_s)

   Variability observed using a Primary Standard Mixture as a sample control.

Coverage factor: k=2

Expanded uncertainty: It was obtained by the product of the combined standard uncertainty and a factor of 2 and it was calculated according to the "Guide to the Expression of Uncertainty in Measurement, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1995)"

Ucertainty Measurement to CO_2

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
Repeatibility and Reproducibility	-----------	A	Normal	0,41	1	0,41
Model	-----------	A	Normal	0,36	1	0,36
Performance Instrument	-----------	B	Rectangular	0,91	----------------	0,91

CENAM Participants List:

Francisco Rangel Murillo, Carlos Ramírez Nambo, Victor M. Serrano Caballero, Manuel de Jesús Avila Salas, and Alejandro Pérez Castorena.

Laboratory name: NMi-VSL

Cylinder number: D 240036

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	21/10/06	0,00036419	0,04	3*30

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	21/10/06	0,00036413	0,03	3 * 30

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	21/10/06	0,00036407	0,03	3 * 30

Results

Component	Result (mol/mol)	Expanded Uncertainty (% relative)	Coverage factor
CO2	0,00036413	0,10	2

Reference Method:

For the determination of Carbon Dioxide (CO_2:
ISO 6143 was used and the generalized distance regression (GDR) method was applied using 5 NMi PSM's and a quadratic regression model.

Instrument Calibration:

The following NMi-VSL PSMs were used to calibrate the ND-IR analyser (ABB URAS 14). All 5 PSMs contained CO_2 in a matrix of nitrogen and 20.9% mol/mol oxygen similar to the sample mixture.

Cylinder No	Gravimetric composition	standard uncertainty
VSL228471	$200,21 \cdot 10^{-6}$ mol/mol	$0,06 \cdot 10^{-6}$ mol/mol

VSL228445	$300,22 \cdot 10^{-6}$ mol/mol	$0,06 \cdot 10^{-6}$ mol/mol
VSL151981	$400,10 \cdot 10^{-6}$ mol/mol	$0,07 \cdot 10^{-6}$ mol/mol
VSL408620	$500,54 \cdot 10^{-6}$ mol/mol	$0,10 \cdot 10^{-6}$ mol/mol
VSL508565	$600,46 \cdot 10^{-6}$ mol/mol	$0,11 \cdot 10^{-6}$ mol/mol

Sample handling:

Each cylinder was equipped with a stainless steel pressure regulator that was adequately purged. A flow of approx. 350 mL/min was flushed for three minutes through the ND-IR analyser before the readings were taken.

Calibration Standards:

The PSM's used in calibration are prepared from pre-mixtures in accordance with ISO 6142: 2001(Gas analysis - Preparation of calibration gas mixtures - Gravimetric method).
After preparation the composition was verified.
The oxygen used in preparation was from Scott Specialty Gases and from Hoek Loos and contained less then $50 \cdot 10^{-9}$ mol/mol of CO_2. For nitrogen the 6.0 Quality with Build-in-Purifier from Air Products was used. The Quality is frequently analysed to contain less then $50 \cdot 10^{-9}$ mol/mol of CO_2. The uncertainty on the CO_2 determination is taken into account when doing the gravimetric calculations.

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition is found, the "new prepared candidate" is accepted as a PSM. Mixtures were prepared in 2004 (4) and 2006 (1).

Evaluation of measurement uncertainty

The listed gravimetric uncertainty is a combined standard uncertainty and comes from:
- The uncertainty in the weighings (pooled estimate of 3 mg on minimum 20 g)
- The effect on the buoyancy correction due to cylinder expansion when pressurizing to 120 bar (approx. 20 mg on 600 g)
- The uncertainty on the purity analysis
- The uncertainty in the molar masses

The listed standard deviations in the three measurements come from the GDR taking into account gravimetric uncertainties on the PSMs and the standard deviation in the responses.

Both uncertainties can be combined in quadrature

Standard uncertainty measurements: (0,04 % / 0,03% / 0,03%) = 0,04% rel.
Standard uncertainty in gravimetry: 0,03% rel.

Combined: 0.05 % rel.
Expanded: 0.1 % rel. (k=2)

RESEARCH DEPARTMENT FOR THE STATE MEASUREMENT STANDARDS IN THE FIELD OF PHYSICO-CHEMICAL MEASUREMENTS

REPORT

Authors: L.A. Konopelko, Y.A. Kustikov, A. V. Kolobova, V.V. Pankratov
                O.V. Efremova

Reference method: **Non-dispersive IR Spectroscopy**
Instrument: "Aeronica" VNIIM, Russia

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in tables 1-3.

Table 1 – Purity table for N_2

Component	Mole fraction 10^{-6} mol/mol	Standard uncertainty 10^{-6} mol/mol
H_2	0,020	0,003
O_2	0,50	0,03
Ar	2,80	0,06
H_2O	1,50	0,09
CO_2	0,200	0,012
CO	0,5	0,3
CH_4	0,050	0,012
N_2	999994,4	0,3

Table 2 – Purity table for O_2

Component	Mole fraction 10^{-6} mol/mol	Standard uncertainty 10^{-6} mol/mol
H_2	0,010 (< 0,02)	0,006
Ar	1,00	0,06
N_2	4,2	0,3
Kr	0,060	0,006
CH_4	1,20	0,06
Xe	0,005(< 0,01)	0,003
H_2O	3,80	0,23
CO_2	0,300	0,017
O_2	999989,4	0,4

Table 3 – Purity table for CO_2

Component	Mole fraction 10^{-6} mol/mol	Standard uncertainty 10^{-6} mol/mol
O_2+ Ar	1,20	0,10
N_2	4,1	0,25
CH_4	2,5 (< 5)	1,4
CO	3,5(< 7)	2,0
H_2O	4,00	0,23
CO_2	999984,7	2,5

All standard gas mixtures were prepared in aluminium cylinders, V= 5 l ("Luxfer UK")

Weighing was performed on the balances 81-V-HCE-20kg (hnu-Voland, USA). Experimental standard deviation for 5 l cylinders: 7 mg.

Preparation of standard gas mixtures was carried out in 2 stages

1 stage:

Preparation of gas pre-mixtures CO_2/N_2 with carbon dioxide mole fraction of $\approx$ 2 %.

Verification of mole fraction was carried out by NDIR analyzer "Aeronica" (VNIIM, Russia). Standard deviation for each measurement series was not more than 0,02 %.

2 stage:

Preparation of standard gas mixtures CO_2/ synthetic air with carbon dioxide mole fraction of $\approx$ 360 ppm.

There were prepared 4 standard gas mixtures.

Verification of mole fraction was carried out by NDIR analyzer "Aeronica" (VNIIM, Russia). Standard deviation for each measurement series was not more than 0,07 %.

The characteristics of calibration standards are shown in table 4.

Table 4 – Characteristics of calibration standard

Standard gas mixture N	Component	Assigned value, 10^{-6} mol/mol	Standard uncertainty, 10^{-6} mol/mol
1	CO_2	359,41	0,24
	Synthetic air	balance	-
2	CO_2	361,18	0,24
	Synthetic air	balance	-
3	CO_2	361,19	0,24
	Synthetic air	balance	-
4	CO_2	362,01	0,24
	Synthetic air	balance	-

Instrument calibration

Linear regression by 4 calibration points (4 standard gas mixtures with similar concentrations) was used for instrument calibration.

There were made 3 independent measurements under repeatability conditions with 3 independent calibrations. One single measurement consisted of 5 sub-measurements.

Sample handling

Prior to measurements the cylinder was stabilized to room temperature.

Results of measurements

Results of measurements of carbon dioxide mole fraction in cylinder № D751937 are shown in the table 5

Table 5 - Results of measurements of carbon dioxide mole fraction in cylinder № D751937

Measurement #1

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (% relative)	number of replicates

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	13/10/06	364,34	0,07	5

Measurement #2

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	17/10/06	364,11	0,02	5

Measurement #3

Component	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	20/10/06	363,86	0,04	5

Evaluation of uncertainty of measurements

Total standard uncertainty of carbon dioxide mole fraction was calculated on the base of the following constituents:
- total standard uncertainty of carbon dioxide mole fraction in standard gas mixture (including uncertainty of weighing of parent gases and pre-mixture, uncertainty in the purity of the parent gases);
- standard deviation of the measurement result of carbon dioxide mole fraction in investigated gas mixture in cylinder № D751937

Uncertainty budget for carbon dioxide mole fraction in gas mixture in the cylinder № D751937 is shown in the table 6.

Table 6– Uncertainty budget for carbon dioxide mole fraction in gas mixture in cylinder № D751937

№	Source of uncertainty			Type of evaluation	Standard uncertainty, 10^{-6} mol/mol
1	Preparation of standard gas mixtures	Weighing of the pre-mixtures		A	0,061
		Weighing of the final mixtures		A	0,23
		Purity of gases	CO_2 in N_2	A;B	0,010
			CO_2 in O_2	A;B	0,0034
			Other impurities in N_2	A;B	0,00002
			Other impurities in O_2	A;B	0,000008
			Impurities in CO_2	A;B	0,00033
2	Standard deviation of the measurement result			A	0,24
Combined standard uncertainty					0,34
Expanded uncertainty					0,7

Final result of measurements

Final result of measurements of carbon dioxide mole fraction in investigated gas mixture in cylinder № D751937 is shown in the table 7

Table 7

Component	Result (10^{-6} mol/mol)	Expanded Uncertainty (10^{-6} mol/mol)	Relative Expanded Uncertainty (%)	Coverage factor
CO_2	364,1	0,7	0,19	2

Laboratory name: SMU

Cylinder number: D751961

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	25/9/2006	0.00036485	0.13%	6

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	26/9/2006	0.00036452	0.18%	6

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO2	27/9/2006	0.00036430	0.16%	6

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
CO2	0.0003646	0.0000012	2

Reference Method:

Measured on Thermoquest Trace 2000 gas chromatograph using Porapack&molsieve packed column (2.2m), FID detector, methanizer.
Carrier gas: nitrogen @ 30mL/min
Sample loop: 1 ml
Oven temperature: 80°C
Method time: 14 min. 6 automated runs.
Pressures of all mixtures in sample loop were regulated by pressure controller before entering.

Calibration Standards:

All PSMs as calibration standards were made gravimetrically according ISO 6142 and 6143 in SMU. Impurities in parent gases were checked on GC. Mole fraction range of CO_2 in calibration standards was from 25 to 800 ppm CO_2. 7 standards were prepared with nitrogen as a matrix gas and 1 standard was prepared in air (360ppm CO_2/air).

Instrument Calibration:

All measurements were done in automated way (only in one direction) using electric selector valve. Sequence of 6 measurement cycles with 8 PSMs was used for measurements. All PSMs were used to create calibration curves.

To calculate results following calibration curves were used

- Linear (b_least): FID-height

No corrections were used.

Sample handling:

Cylinders with CO_2 were all days at SMU kept at 17 – 22 °C. Before measurement cylinders were kept at laboratory temperature for more than 4 hours.

Evaluation of measurement uncertainty

Uncertainty of component response was constructed from immediate repeatability based on experience and from signal drift estimated from signals between measurements of the same mixture in two consecutive cycles. Calibration curves were made from each cycle using b_least program (weighted least square regression taking into account both standard uncertainties of mole fractions and standard uncertainties of responses).

From each calibration curve using b_least unknown sample molar fraction with its standard uncertainty was determined. For each i-th day the average x_i was calculated (*1*). Standard uncertainty assigned *to* each i-th day *result (4)* is from standard deviation of the average *(2)* and average from all b_least uncertainties that day *(3)*.

$$\bar{x}_i = \frac{\sum_{j=1}^{n} x_j}{n} \qquad (1)$$

$$u_1(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} (x_j - \bar{x}_i)^2}{n*(n-1)}} \qquad (2)$$

$$u_2(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}} \qquad (3)$$

$$u(\bar{x}_i) = \sqrt{u_1(\bar{x}_i)^2 + u_2(x_i)^2} \qquad (4)$$

To estimate result uncertainty we have kept "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{s_{\bar{x}}^2 + s_r \frac{n-1}{n}} \qquad (5)$$

$$s_r = \sqrt{\frac{\sum_{i=1}^{p} u(\bar{x}_i)^2}{p}} \qquad (6)$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}} \qquad (7)$$

$$\Delta x = \bar{x}_1 - \bar{x}_2 \qquad (8)$$

Final result is average from 3 day results

$$\bar{x} = \frac{\sum_{i=1}^{p} \bar{x}_i}{p} \qquad (9)$$

As final **standard uncertainty** we assigned to the result *(9)* max(s_R or s_r)

$$u(\bar{x}) = \max(s_r; s_R) \qquad (10)$$

Expanded uncertainty (k=2) of final result

$$U(\bar{x}) = 2 \cdot u(\bar{x})$$

p – number of days (3)
n – number of measurements in 1 day
index i represents particular day
index j represents particular result (evaluated) from one calibration curve

29.9.2006   Ing. Stanislav Musil, PhD.
Slovak Institute of Metrology   Head of gas laboratory

Laboratory name: **National Physical Laboratory (NPL)**

Cylinder number: D751947

Primary Standards

NPL has prepared a suite of PRMs of carbon dioxide in synthetic air. Some of these PRMs also contain methane and argon.

They were prepared gravimetrically from pure carbon dioxide at amount fractions of 10% and 5000 ppm.

1.1.1.1 Standard	NPL NG 35	NPL 425	NPL 1190
Matrix	CH_4, Ar, N_2, O_2.	CH_4, Ar, N_2, O_2.	N_2, O_2.
CO_2 amount fraction [µmol/mol]	372.75	365.27	351.41

Uncertainty in Pure Components

The uncertainty in the final PRMs imposed by purity analysis due to a detection limit of 20 nmol/mol of carbon dioxide in the pure nitrogen (Air Products BIP plus). This corresponded to a relative standard uncertainty of 0.005% and has been taken to represent $k=1$.

Uncertainty in Gravimetric Preparation Procedure

The uncertainty arising purely from gravimetry was 0.03% (relative, $k=1$) for the carbon dioxide/nitrogen and the methane/nitrogen mixtures. (This corresponds to a weighing uncertainty of 20 mg in the smallest mass of 60 g used in the first step in the process).

Analysis of Carbon Dioxide

    GC   Agilent 6900
    Column   Haysep A (4.4m, micropacked 120/140 mesh)
    Column Temp   85 Celsius
    Carrier Gas   Helium (8 bar head pressure)

Results of Analysis

The full analytical data is given as an Annex to this report.

The relative standard deviation of the complete set of 22 repeated measurements of peak height in four independent runs is 0.10%. We calculate the standard error of the mean of this value over the four independent runs to be 0.05% ($k=1$).

Calculation of Final Result for D751947

The uncertainties have been combined (in quadrature):

	$U(x)/x*100$
analysis	**0.05**
gravimetry	**0.03**
purity	**0.005**
Combined k=1	**0.06 %**
Expanded k=2	0.12 %

Reference value for cylinder D751947: 364.36 ± 0.44 μmol/mol (k=2)

Annex

1.1.1.2 Measured cylinder 1.1.1.3 D751947	CO2 results based on Peak area measurements	CO2 results based on Peak height measurements
Standards	(μmol/mol)	(μmol/mol)
NPL 1190 & NPL NG 35	363.90	363.88
NPL 1190 & NPL NG 35	363.25	364.01
NPL 1190 & NPL NG 35	365.44	365.17
NPL 1190 & NPL NG 35	363.51	364.14
NPL 425	364.16	363.91
NPL 425	364.79	364.38
NPL 425	364.77	364.48
NPL 425	364.49	364.47
NPL 425	364.72	364.52
NPL 425	364.43	364.20
NPL 425	364.04	364.19
NPL 425	364.27	364.49
NPL 425	364.25	364.49
NPL 425	364.20	364.50
NPL 425	364.66	364.81
NPL 425	365.05	365.10
NPL 1190 & NPL NG 35	365.06	364.43
NPL 1190 & NPL NG 35	364.21	364.38
NPL 1190 & NPL NG 35	364.00	364.07
NPL 1190 & NPL NG 35	363.51	363.80
NPL 1190 & NPL NG 35	364.33	363.89
NPL 1190 & NPL NG 35	364.65	364.52
Average	364.35	364.36
Standard Deviation	*0.536*	*0.367*
% RSD	*0.15*	*0.10*

Laboratory name: NIST

Cylinder number: D751954

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	08/11/06	0.00036359	0.04 %	2

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	13/11/06	0.00036370	0.05 %	2

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2	14/11/06	0.00036391	0.01 %	2

Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor
CO_2	0.00036372	0.00000034	2

Laboratory name: CSIR National Metrology Laboratory

Cylinder number: **D751918**

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2/Air	16-08-2006	365,0	0,40	3

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2/Air	24-08-2006	365,7	0,71	3

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2/Air	01-09-2006	364,6	0,44	3

Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO_2/Air	28-09-2006	364,5	0,52	3

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor
CO_2/Air	364,9	3,883	2

Measurement Details:

Analytical Method:

The measurement technique used was NDIR with 6 standards of CO_2/synthetic air over the concentration range 100-1000 $\mu mol.mol^{-1}$ prepared gravimetrically at CSIR NML.

A Quadratic model fit was used in the B-LEAST software for the calibration curve.

Uncertainty budget

The weighing uncertainty is calculated the same way as the following example.

Example of weighing uncertainty calculation

Parameter	Estimate	u	Sensitivity coefficient propagation	Sensitivity coefficient	Uncertainty contribution	Degrees of freedom
e (sensitivity)	1.0000	0.001000		0.3197500000	0.000319754	1
qm-r (weigh difference)	0.3197	0.002555		0.99999	0.002554917	2
Wr-m (mass pieces)	84.0000	0.000028		0.99986983	2.82806E-05	infinity
Air density	1.0414	0.000206		-0.021	-4.3263E-06	infinity
Vm-r	-0.0105	0.000005		1.0413634085	5.09396E-06	infinity
Density (stainless steel)	8000.0000	0.002000		-1.36679E-06	-2.73358E-09	infinity
Mass	84.2979				2.575012593	

The budget of the standard uncertainties for the comparison sample is:

Parameter		Standard uncertainty
Gravimetric uncertainty	- Weighing uncertainty - Purity analysis	0,02% rel.
Verification uncertainty (U)		0,3% rel.
Stability uncertainty (U)		0,15% rel.
Regression uncertainty (U)		0,06% rel.