International Comparison EURO.QM-S5 / 1166: Carbon Dioxide Mixtures in Nitrogen

Final report

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Field
Amount of Substance

Subject
Mixture containing 3.0×10^{-2} mol/mol carbon dioxide in a nitrogen balance.

Participants

Institute	Acronym	Country
Instituto Português da Qualidade	IPQ	Portugal
National Metrology Centre	A*STAR	Singapore
Central Office of Measures	GUM	Poland
Instituto Nacional de Metrologia	INMETRO	Brazil
Center for Measurement Standards	CMS	Taiwan
Bundesamt für Metrologie	METAS	Switzerland
Hungarian Trade Licensing Office	MKEH	Hungary
National Institute of Metrology	NIMT	Thailand
National Physical Laboratory India	NPLI	India
National Metrology Institute of Turkey	UME	Turkey
Van Swinden Laboratorium	VSL	The Netherlands

Organizing Body: EURAMET

Schedule of comparison

1) Preparation of cylinders: July 2011
2) Initial verification study: July 2011
3) Cylinders shipped to participants: September 2011
4) Results received from the participants: from November 2011 to February 2012
5) Cylinders received: from December 2011 to February 2012
6) Final verification study: April 2012
7) Draft A report: May 2012
8) Draft B report: June 2012
9) Final report: April 2013

Introduction

This supplementary comparison is designed to test the capabilities of the participants to measure and certify carbon dioxide in nitrogen, and will provide supporting evidence for the CMCs of institutes for carbon dioxide. Indeed this comparison aims to demonstrate the capabilities of IPQ in the production of primary gas mixtures of carbon dioxide in nitrogen and for the participant laboratories to demonstrate their capabilities on certifying primary gas mixtures of percent levels of carbon dioxide in nitrogen.
Moreover number of NMIs had already participated in the CCQM key-comparison K52, but in a lower range. This EURAMET comparison should offer an opportunity to the laboratories to submit CMC in a higher range.
In this comparison the laboratories analyzed the gas mixtures that are gravimetrically produced and analyzed by IPQ. Each cylinder had its own reference value calculated from the gravimetric preparation. The pressure in the cylinders was approximately 10 MPa; aluminium cylinders of 5 dm^3 nominal volume were used.

Supported claims

This comparison provides evidence in support of CMCs for carbon dioxide within the range of ($1.0 \times 10^{-2} – 20.0 \times 10^{-2}$) mol/mol, in a nitrogen / air balance.

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 the same conditions. The protocol informed the participants about the nominal concentration ranges. Participating laboratories were requested to specify in detail the calculation of the analyzed composition and how the evaluation of uncertainty was performed.

Preparation and certification of standard gas mixtures

IPQ prepared a set of primary gas mixtures carried out in accordance with a harmonised procedure, based on the international standard ISO 6142:2001 [1]. These primary mixtures were prepared at the highest level of accuracy by gravimetric blending methods. Their nominal compositions (amount fractions) were estimated by the ideal gas equation, corrected by a compression factor.
In a previously passivated and evacuated cylinder, each component was added through a filling station, where all equipments (pipes, valves etc.) were electro polished and free of oil. The mass of each component was determined using a mass comparator balance. The mixture was prepared by gravimetric addition of each component. The amount fractions of the components in the final mixtures were calculated using the following equation:

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{iA}\cdot m_A}{\sum_{i=1}^{n} x_{iA}\cdot M_i}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n} x_{iA}\cdot M_i}\right)}$$

Where x_i is the amount fraction of component i in the final mixture, $i = 1, \ldots, n$
P is the total number of parent mixtures
n is the total number of components in the final mixture
m_A is the mass of parent gas A determined by weighing, $A = 1, \ldots, P$
M_i is the molar mass of component i
$x_{i,A}$ is the amount fraction of component i.

The traceability of the primary gas mixtures is established by the traceability of the masses to national standards of mass, the IUPAC definition atomic/molecular masses of the components, and the purity of the components.

The composition of the gas mixtures was verified by leading individual analysis of the amount fraction of each analyte: the procedure described in ISO 6143:2001 [2] was followed. For analysis the cylinder was connected to a valve to reduce the pressure and the sample was transferred to the analyser through an auto-sampler. After the calibration of the instrument according to this standard the mixture composition was certified by comparison methods using a set of mixtures with pre-established assigned values (Table 1). The selection of analytical method is dependent on the available PSMs and the chosen range. The composition of the carbon dioxide gas mixtures was certified by Non Dispersive Infrared Spectroscopy (NDIR) and Gas Chromatography (GC-TCD).
The *B_Least* program was used to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear or quadratic function. In order to establish the relationship between equipment response and the composition of the series of calibration mixtures (table 1), the following aspects were considered, namely analytical method, calibration range, measurement conditions, number and sequence of replicate measurements.

Cylinder	Assigned value (x) (mol/mol)	Standard uncertainty ($u(x)$)
PSM104693	1.0005×10^{-2}	0.0021×10^{-2}
PSM503640	2.0011×10^{-2}	0.0026×10^{-2}
PSM104699	2.5015×10^{-2}	0.0039×10^{-2}
PSM502525	3.0028×10^{-2}	0.0040×10^{-2}
PSM408990	4.0039×10^{-2}	0.0047×10^{-2}
PSM202579	5.0040×10^{-2}	0.0075×10^{-2}

Table 1: Composition of calibration standards.

Results are expressed together with their measurement uncertainty, according to ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement" [3]. The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources, namely, uncertainty in calibration, uncertainty of repeatability and uncertainty of reproducibility. These uncertainties were combined and the result was multiplied by a coverage factor with a confidence interval of 95 %.

The obtained results show that the gravimetric and analytical amount fractions were not significantly different according to their uncertainties; consequently the preparation of the gravimetric gas mixtures is validated.
As a conclusion the gravimetric amount fractions have been assigned to each gas mixture.

The cylinders were stored at ambient temperature in a storage room.

Verification of candidate gas mixtures

The CO_2 content of each comparison mixture was verified prior to shipment to the participants using a Non Dispersive Infrared Spectroscopy (NDIR) analyzer URAS 14 and a Gas Chromatograph (GC) HP 6890 with a Porapak Q, 80/100 Mesh, conditioned column. The data collection was carried out with an auto-sampler - Software Sira version 2.0. The ISO 6143 data analysis procedure was used to evaluate the data. The gravimetric values of all comparison cylinders were within the analytical uncertainty of analytical values. The comparison cylinders fulfil the verification step and were sent to the participants.

Verification of returned gas mixtures

The participants were asked to return the comparison cylinders to IPQ after their analyses were completed. All participants except NPLI returned their cylinder, and the gas mixtures were reanalyzed in April 2012. The data are presented in Figure 1. No visible

trend in the data is apparent, the difference between the values analysed is less than 4×10^{-5} mol/mol which was within the analytical standard uncertainty of 6×10^{-5} mol/mol. Cylinder PSM105439, which was sent to NPLI was never returned to IPQ. It is assumed in this report that this cylinder's stability is in line with the rest of the cylinders population.

Participant results

The participants' reports are appended to this report. The reported instrumental method and calibration standards used are summarized in Table 2. One participant reported using primary standards obtained from another NMI (NPL). All other participants reported using primary standards prepared with their facility from pure carbon dioxide. A total of six participants used a GC-TCD instrument, two used a NDIR analyser, two used a GC-FID with methaniser instrument and one participant used two techniques NDIR and GC-TCD. There was no correlation between the degrees of equivalence and the method used, or the source of the primary standards. The eleven analytical results reported by each participant are listed in Table 3, and presented in graphical form in Figure 2. Table 4 presents all the results. The gravimetric amount fraction and the associated uncertainty were calculated according to ISO 6142. It was added to the gravimetric uncertainty, an uncertainty due to the stability of the gas mixtures calculated with the analytical results obtained before and after the comparison. Finally, the degrees of equivalence are calculated in the prescribed manner, and presented for each participant in Table 4. The degrees of equivalence are displayed graphically in Figure 3 and 4.

Conclusion

The results of all participants in this key comparison are consistent with the RV. The relative standard measurement uncertainties reported by participants, with one exception, were in the range 0.03 % to 0.43 %.

The relative standard uncertainties of the reference values reported by the coordinating laboratory were in the range 0.11 % to 0.17 %.

Compared to other participants, NPLI reported a comparatively large relative standard measurement uncertainty of 3.2 %, which covered the 2.8 % relative difference of its measurement result from the reference value of the standard it had been supplied.

Cylinders PSM502522 and PSM902529 show a decay of ~ 0.1 % (relative difference). We do not have a concrete explanation for this situation and this difference is within the associated standard uncertainties.

Data and results:

Laboratories provided the data that are summarized in Table 2.

Participant	*Measurements*	*Reference Method*	*Calibration*	*Traceability*
A*STAR	3 Measurements each with 3 submeasurements	NDIR	calibration curve using CurveFit software	4 Primary Gas Standards prepared ISO 6142
GUM	4 Measurements each with 9 submeasurements	GC-TCD	ISO 6143	5 Primary Gas Standards prepared ISO 6142
INMETRO	4 Measurements each with 7 submeasurements	GC-TCD	ISO 6143	3 Primary Gas Standards prepared ISO 6142
IPQ	3 Measurements each with 3 submeasurements	NDIR / GC-TCD	ISO 6143	6 Primary Gas Standards prepared ISO 6142
CMS	4 Measurements each with 5 submeasurements	GC-TCD	One-point calibration	6 Primary Gas Standards prepared ISO 6142
METAS	3 Measurements each with 5 submeasurements	GC-FID with methaniser	ISO 6143	5 Primary Gas Standards prepared ISO 6142
MKEH	3 Measurements each with 20 submeasurements	GC-TCD	Single point calibration	1 Primary Gas Standards prepared ISO 6142
NIMT	5 Measurements each with 3 submeasurements	GC-TCD	ISO 6143	3 Primary Gas Standards prepared ISO 6142
NPLI	3 Measurements each with 6 submeasurements	GC-FID with methaniser	Single point calibration	1 Primary Gas Standards prepared ISO 6142
UME	4 Measurements each with 9 submeasurements	GC-TCD	ISO 6143	5 Gas Standards provided by NPL
VSL	3 Measurements each with 3 submeasurements	NDIR	ISO 6143	7 Primary Gas Standards prepared ISO 6142

Table 2: Summary of calibration methods and metrological traceability

Participant	*Comparison cylinder*	*Submitted Value (cmol/mol)*	*Reported Expanded Uncertainty (cmol/mol)*
A*STAR	PSM105443	3.0021	0.0034
GUM	PSM105538	3.002	0.024
INMETRO	PSM105530	2.992	0.014
IPQ	PSM502522	2.997	0.006
CMS	PSM105447	2.999	0.004
METAS	PSM105442	3.000	0.010
MKEH	PSM105440	2.9980	0.0055
NIMT	PSM 105441	3.009	0.025
NPLI	PSM 105439	2.92	0.196
UME	PSM105415	3.0011	0.0061
VSL	PSM902529	3.0035	0.0015

Table 3: Values reported by participating laboratories

Degree of equivalence - comparison of laboratory value and assigned amount fraction values

The degree of equivalence for each participating laboratory was calculated with the equation:

$$D = x_{lab} - x_{ref}$$

Where x_{lab} and x_{ref} are the amount fractions obtained by the participant laboratories and the gravimetric amount fractions, respectively.

The uncertainty of the degree of equivalence was calculated using the equation:

$$u(D) = \sqrt{u^2(x_{lab}) + u^2(x_{ref})}$$

Where $u\,(x_{lab})$ and $u\,(x_{ref})$ are the combined uncertainties of the participant laboratories and the one obtained by gravimetric combined with analytical method, respectively. These uncertainties are multiplied by the coverage factor to obtain the expanded uncertainties with a confidence interval of 95 %.

Participant	*Date*	*Cylinder #*	x_{ref} / *cmol/mol*	u_{ref} / *cmol/mol*	x_{lab} / *cmol/mol*	u_{lab} / *cmol/mol*	*D/ cmol/mol*	*u(D)/ cmol/mol*	*U(D)/ cmol/mol*
A*STAR	2011-11-23	PSM105443	3.003590	0.004335	3.002100	0.001700	- 0.0015	0.0047	0.0094
GUM	2011-12-07	PSM105538	3.002900	0.004747	3.002000	0.012000	- 0.0009	0.013	0.026
INMETRO	2011-12-02	PSM105530	3.001549	0.004096	2.992000	0.007000	- 0.0095	0.0081	0.0162
IPQ	2011-12-14	PSM502522	2.996929	0.003026	2.997207	0.003024	0.00028	0.0043	0.0086
CMS	2011-11-30	PSM105447	3.001929	0.005136	2.999000	0.002000	- 0.0029	0.0055	0.0110
METAS	2011-12-16	PSM105442	3.000782	0.004163	3.000000	0.005000	- 0.00078	0.0065	0.0130
MKEH	2011-12-14	PSM105440	2.998770	0.002687	2.998000	0.002750	- 0.00077	0.0038	0.0076
NIMT	2012-01-05	PSM 105441	2.997640	0.004368	3.009000	0.012500	0.011	0.013	0.026
NPLI	2011-12-29	PSM 105439	3.000820	0.003300	2.920000	0.098000	- 0.081	0.098	0.196
UME	2011-12-23	PSM105415	3.002078	0.003846	3.001100	0.003050	- 0.00098	0.0049	0.0098
VSL	2011-12-08	PSM902529	2.999600	0.003941	3.003500	0.000750	0.0039	0.004	0.008

Table 4: Comparison results table with Degrees of Equivalence.

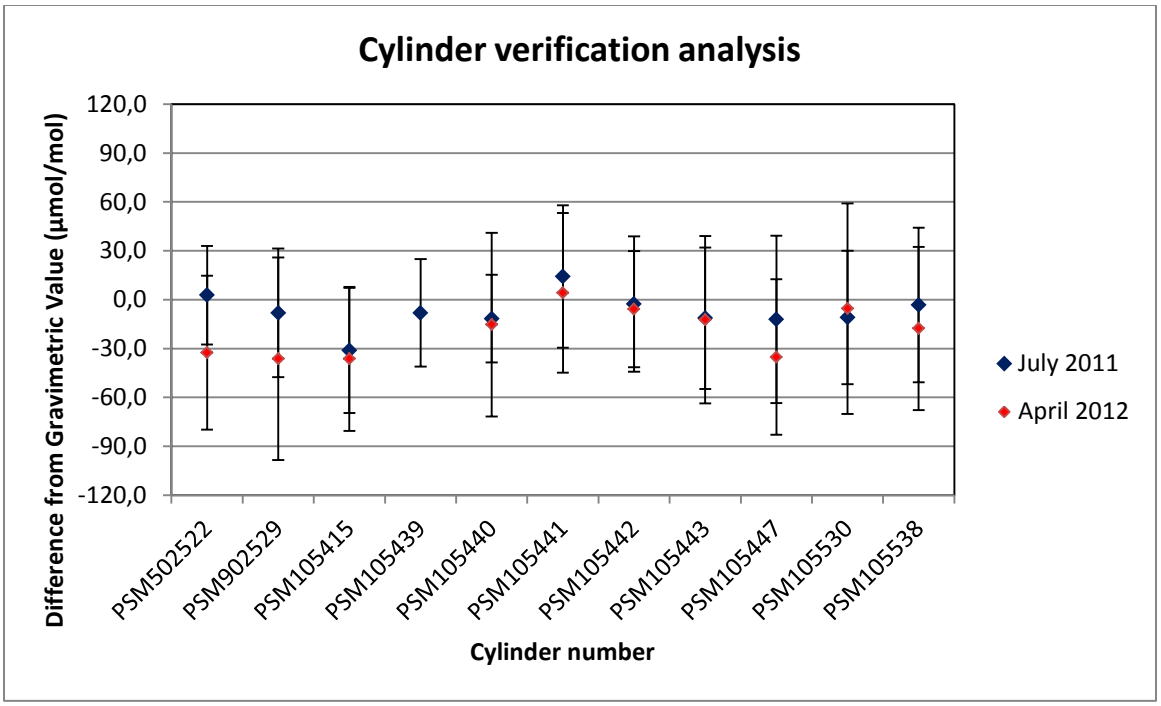

Figure 1: Verification of comparison cylinders in July 2011 and April 2012 with certified values and the associated standard uncertainties.

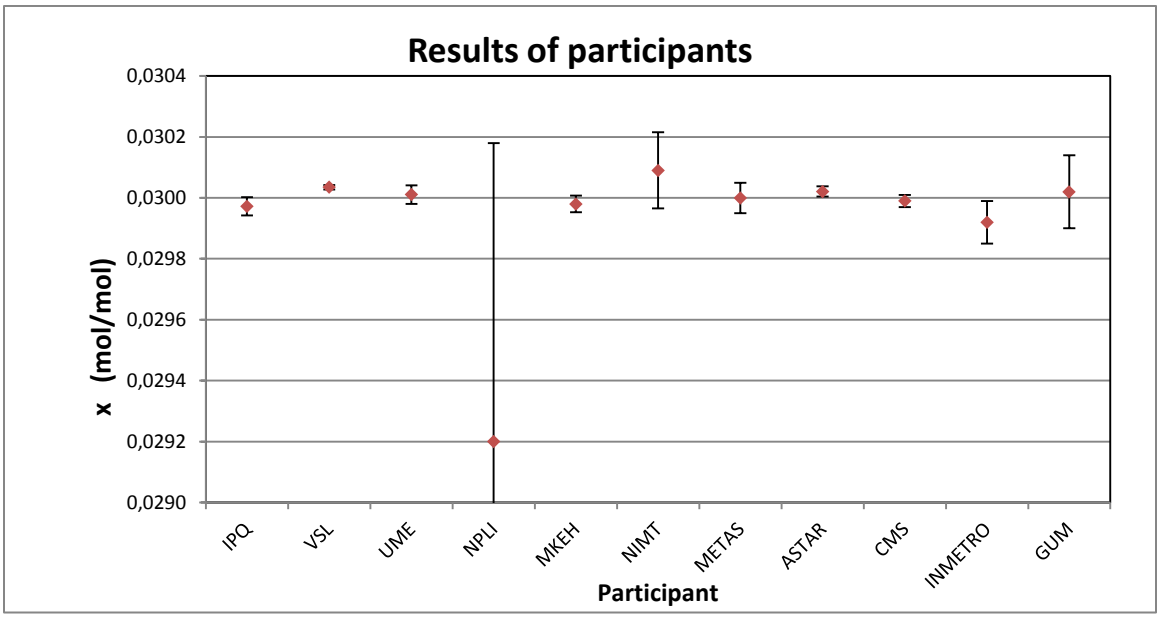

Figure 2: Results and the associated standard uncertainties submitted by participants

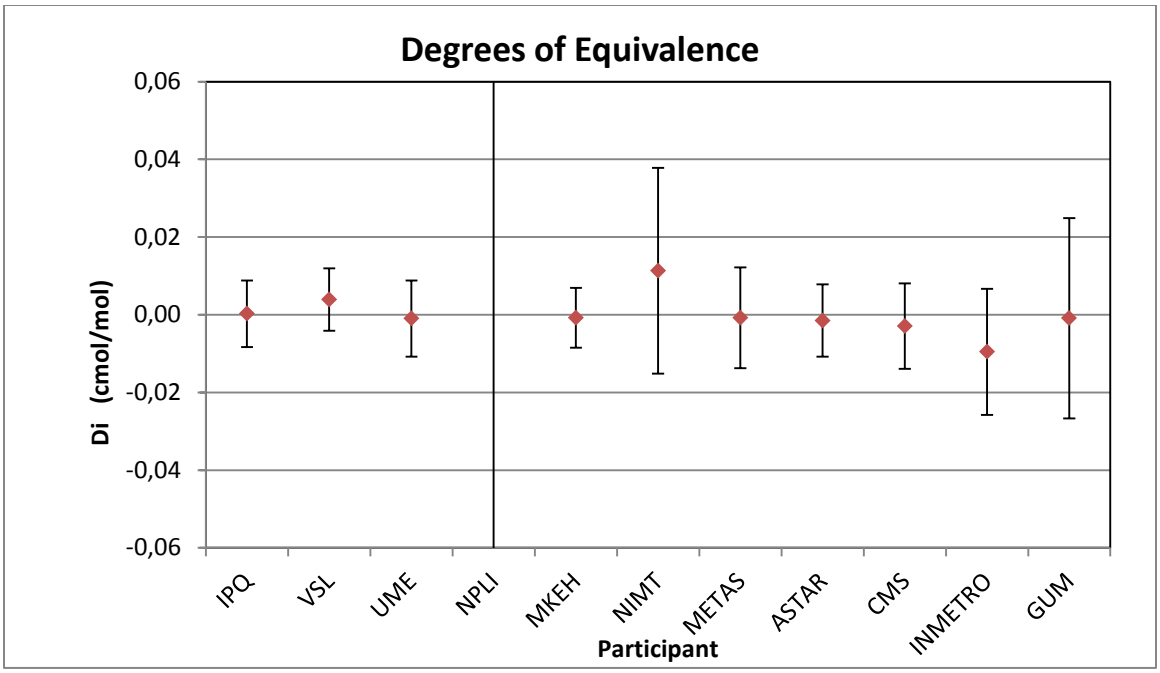

Figure 3: Degree of equivalence (*D*) and associated expanded uncertainties (*U (D)*).

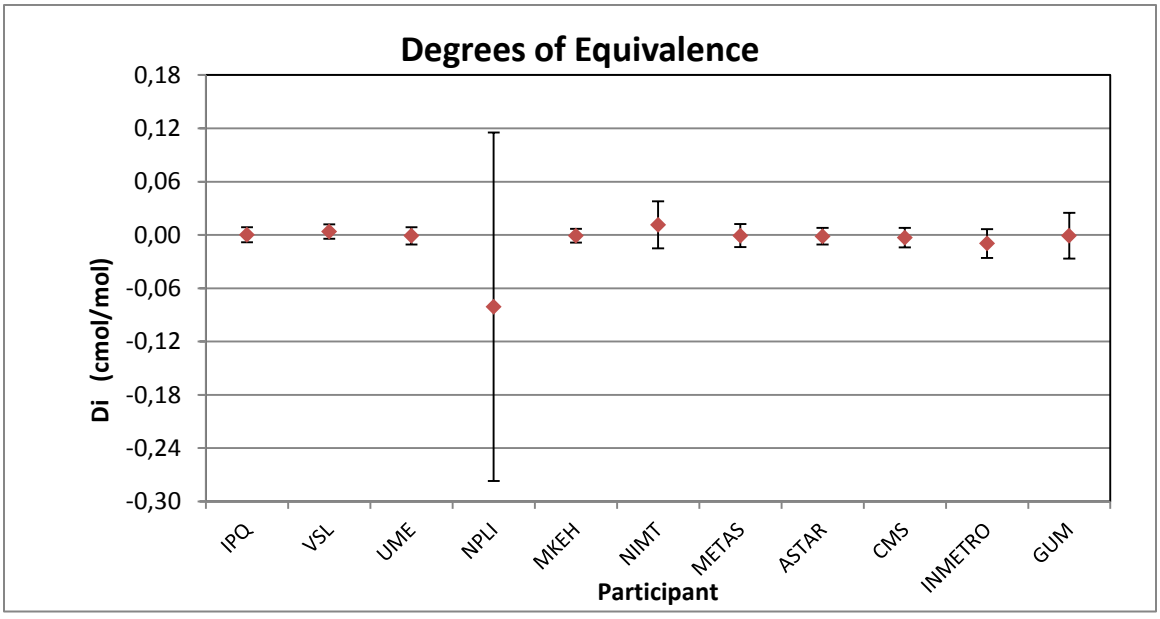

Figure 4: Degree of equivalence (*D*) and associated expanded uncertainties (*U (D)*) with expanded y-scale to include NPLI result.

References

[1] ISO 6142: Gas Analysis – Preparation of calibration gas mixtures – Gravimetric method, 2nd ed., Switzerland, 2001;
[2] ISO 6143: Gas Analysis – Determination of the composition of calibration gas mixtures, Comparison Methods, 2nd ed., Switzerland, 2001;
[3] "Guide to the expression of uncertainty of measurement in calibration laboratories", IPQ, 2005.

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Project reference

EURO.QM-S5 / 1166

Completion date

June 2012

Appendix 1: Information submitted by participating laboratories

Participant: A*STAR

EURAMET COMPARISON 1166

Measurement report

Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : National Metrology Centre, Singapore
Cylinder number : PSM105443

NOMINAL COMPOSITION
- Carbon dioxide : 1.0×10^{-2} – 5.0×10^{-2} mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	15/11/2011	0.030026	0.021	60
CO_2	15/11/2011	0.030020	0.024	60
CO_2	15/11/2011	0.030017	0.026	60

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	17/11/2011	0.030025	0.020	10
CO_2	17/11/2011	0.030027	0.029	10

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	23/11/2011	0.030020	0.024	60
CO_2	23/11/2011	0.030015	0.021	60
CO_2	23/11/2011	0.030018	0.028	60

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
CO_2	0.030021	2	0.000034

Reference Method:
The analysis was performed on three different days with ABB NDIR analyzer (URAS26) with the sampling box (MFC). The mole fraction of the compared cylinder was calculated by interpolation of a calibration curve using CurveFit software.

Calibration Standards: the following PSM were used:

PSM no	mol fraction	standard uncertainty
PSM118323	0.025123	0.000007
PSM118368	0.029006	0.000007
PSM118372	0.031006	0.000007
PSM118324	0.034615	0.000008

The above standards were prepared by gravimetric method according to ISO6142. The purity of gases was analyzed with GC PDHID technique. The cylinders used were 5l aluminum with Aculife 3 treatment from Scott Specialty Gases. The regulator used was SS Verifo single stage (no gauges) purged several times according to operational procedure.

Instrument Calibration:
The analyzer was adjusted before every analysis – in zero and span (80% of the measurement range)
The above PSM were used as the calibration curve.

Sample Handling:

Cylinders – received one and NMC PSM – were maintained inside the laboratory at room temperature for all the time.
For sample line modified Teflon was used.
The sampling to the analyzer was done under ambient pressure. However, the pressure correction was included in the calculation.

Uncertainty:

Uncertainty table: CO_2

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Repeatability	0.030021	normal	0.0000087	1	0.00087
Gas standard	0.025123	normal	0.000007	1	0.000007
Gas standard	0.029006	normal	0.000007	1	0.000007
Gas standard	0.031006	normal	0.000007	1	0.000007
Gas standard	0.034615	normal	0.000008	1	0.000008
total					0.000017

Coverage factor: 2
Expanded uncertainty: 0.000034

Participant: GUM

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : Central Office of Measures (GUM)
Cylinder number : D695538

NOMINAL COMPOSITION
- carbon dioxide : $3 \cdot 10^{-2}$ mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	01.12.2011	0,03002	0,11	9

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	02.12.2011	0,03005	0,09	9

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05.12.2011	0,02995	0,06	9

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	07.12.2011	0,03004	0,08	9

Results:

Gas mixture	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty (*) (mol/mol)
CO_2	0,03002	2	0,00024

Reference Method:

The measurements were repeated 9 times for the sample and the standards by chromatograph Varian with TCD detector.

Calibration Standards:

Five standards were prepared (by Central Office of Measures) by gravimetric method according to ISO 6142 from separate premixtures. The cylinders were evacuated on turbo molecular pump, filled up an weighted on the verification balance. The standards were prepared in aluminum (with coated layers) cylinders. The standards were (and still are) under metrological control.

Composition of calibration standards:

No.	Cylinder number	Component	Assigned value (x) [mol/mol]	Expanded uncertainty (u(x)) [mol/mol] (k=2)
1	D752102	CO_2	$1{,}000 \cdot 10^{-2}$	$0{,}004 \cdot 10^{-2}$
2	D752019	CO_2	$2{,}995 \cdot 10^{-2}$	$0{,}020 \cdot 10^{-2}$
3	D752066	CO_2	$3{,}000 \cdot 10^{-2}$	$0{,}022 \cdot 10^{-2}$
4	D518812	CO_2	$4{,}499 \cdot 10^{-2}$	$0{,}020 \cdot 10^{-2}$
5	D518819	CO_2	$6{,}114 \cdot 10^{-2}$	$0{,}014 \cdot 10^{-2}$

Instrument Calibration:

Calibration method according to ISO 6143. The calibration curve was calculated from ratios by the software B_leats.exe (linear case). Measurement sequence: standards (for calculation of calibration curve) and sample.

Sample Handling:

The cylinders (standards and sample) were in the same room for the whole time also during the measurements (temperature stabilization) and the mixtures were mixed up before the measurements. Samples were transferred to the instrument via the reducing valve and the automatic input pressure stabilization system.

Uncertainty:

The final uncertainty was calculated according to ISO 6143 and consists of the following components:

- the uncertainty of the standards
- the standard deviation of the measurement.

Resolution of the chromatograph is negligible.

Uncertainty table: CO_2

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
cylinder no. D752102	$1{,}000 \cdot 10^{-2}$ mol/mol	normal	$0{,}002 \cdot 10^{-2}$ mol/mol	1	$0{,}002 \cdot 10^{-2}$ mol/mol
cylinder no. D752019	$2{,}995 \cdot 10^{-2}$ mol/mol	normal	$0{,}010 \cdot 10^{-2}$ mol/mol	1	$0{,}010 \cdot 10^{-2}$ mol/mol
cylinder no. D752066	$3{,}000 \cdot 10^{-2}$ mol/mol	normal	$0{,}011 \cdot 10^{-2}$ mol/mol	1	$0{,}011 \cdot 10^{-2}$ mol/mol
cylinder no. D518812	$4{,}499 \cdot 10^{-2}$ mol/mol	normal	$0{,}010 \cdot 10^{-2}$ mol/mol	1	$0{,}010 \cdot 10^{-2}$ mol/mol
cylinder no. D518819	$6{,}114 \cdot 10^{-2}$ mol/mol	normal	$0{,}007 \cdot 10^{-2}$ mol/mol	1	$0{,}007 \cdot 10^{-2}$ mol/mol
reading for cylinder no. D752102	$264{,}5 \cdot 10^{3}$	normal	$3{,}8 \cdot 10^{3}$	1	$3{,}8 \cdot 10^{3}$
reading for cylinder no. D752019	$789{,}0 \cdot 10^{3}$	normal	$1{,}8 \cdot 10^{3}$	1	$1{,}8 \cdot 10^{3}$
reading for cylinder no. D752066	$786{,}6 \cdot 10^{3}$	normal	$2{,}4 \cdot 10^{3}$	1	$2{,}4 \cdot 10^{3}$
reading for cylinder no. D518812	$1176{,}7 \cdot 10^{3}$	normal	$1{,}8 \cdot 10^{3}$	1	$1{,}8 \cdot 10^{3}$
reading for cylinder no. D518819	$1599{,}9 \cdot 10^{3}$	normal	$2{,}1 \cdot 10^{3}$	1	$2{,}1 \cdot 10^{3}$
reading for cylinder no. D695538	$791{,}1 \cdot 10^{3}$	normal	$0{,}7 \cdot 10^{3}$	1	$0{,}7 \cdot 10^{3}$

Coverage factor: 2

Expanded uncertainty: $0{,}024 \cdot 10^{-2}$ mol/mol

Participant: INMETRO

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory: INMETRO/LABAG
Participants: Andreia de Lima Fioravante, Claudia Cipriano Ribeiro, Cristiane Rodrigues Augusto, Denise Cristine Gonçalves Sobrinho, Elizandra Cananéa de Sá Elias.
Cylinder number: D695530

NOMINAL COMPOSITION
- Carbon dioxide: 1,0x 10^{-2} – 5,0x 10^{-2} mol/mol
- Nitrogen: matrix

Measurement No. 1	Date	Result (10^{-2} mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	09/11/2011	2.991	0.06	7

Measurement No. 2	Date	Result (10^{-2} mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	11/11/2011	2.994	0.06	7

Measurement No. 3	Date	Result (10^{-2} mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	01/12/2011	2.992	0.08	7

Measurement No. 4	Date	Result (10^{-2} mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	02/12/2011	2.991	0.07	7

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
CO_2	2.992	2	0.014

Reference Method:

To analyze the component CO2 the Micro Gas Chromatography (GC- Varian – model 4900) was used.

This Micro GC has four channels and only analyze gases. The channel B was used to analyze the component CO2, with a detector TCD and a column poraPLOT Q (0,15mmID, 10mts). The injection volume was 10uL.

Calibration Standards:

Three standards were used to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by Inmetro.

PSM103795

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty (u(x)) 10^{-2} mol/mol
Carbon dioxide	2.413	0.011

PSM103635

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty (u(x)) 10^{-2} mol/mol
Carbon dioxide	3.712	0.006

PSM103655

Component	Assigned value(x) 10^{-2} mol/mol	Standard uncertainty (u(x)) 10^{-2} mol/mol
Carbon dioxide	3.946	0.005

Instrument Calibration:

The standards used are listed above. Pressure correction was taken into account. The measurement was done automatically using an automatic multi selective valve. The order of injections was: first injection of the standards and then injection of the sample. The mixtures were injected seven times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least. The calibration model selected that was better adjusted was a linear curve.

Sample Handling:

After arrival in the laboratory, the cylinder was stabilized at room temperature (21ºC and humidity of 52%) before measurements. The standards and sample were transferred directly to the GC using a system composed of four valves, pressure regulator and flow meter.

Uncertainty:

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B_least. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:

- **Uncertainty of the standards (certificate – type B)**
- **Uncertainty of the area (analysis – type A)**
- **Linear calibration curve (type A)**

Participant: IPQ

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : IPQ
Cylinder number : PSM502522

NOMINAL COMPOSITION
- carbon dioxide : ($1{,}0 \times 10^{-2}$ – $5{,}0 \times 10^{-2}$) mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-14	$2{,}998 \times 10^{-2}$	0,042	3

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-15	$2{,}996 \times 10^{-2}$	0,060	3

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-16	$2{,}997 \times 10^{-2}$	0,060	3

Results:

Gas mixture	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty (*)(mol/mol)
CO_2	$2{,}997 \times 10^{-2}$	2	$0{,}006 \times 10^{-2}$

Reference Method:
Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS 14 and Gas Chromatography HP 6890 (GC)
Data Collection: Auto-sampler - Software Sira version 2.0

Calibration Standards:
The preparation was done according to ISO 6142:2001- Gravimetric method
The estimated uncertainty was done according ISO GUM: 1995 “Guide to the Expression of Uncertainty in Measurement”.
It was used six primary standard mixtures from IPQ.

Composition of calibrants:

Component	Assigned value(x) (mol/mol)	Standard uncertainty (u(x))
CO_2	PSM104693: $1{,}00 \times 10^{-2}$	$2{,}1 \times 10^{-5}$
	PSM503640: $2{,}00 \times 10^{-2}$	$2{,}6 \times 10^{-5}$
	PSM104699: $2{,}50 \times 10^{-2}$	$3{,}9 \times 10^{-5}$
	PSM502525: $3{,}00 \times 10^{-2}$	$4{,}0 \times 10^{-5}$
	PSM408990: $4{,}00 \times 10^{-2}$	$4{,}7 \times 10^{-5}$
	PSM202579: $5{,}00 \times 10^{-2}$	$7{,}5 \times 10^{-5}$

Instrument Calibration:
The calibration instrument was done according to ISO 6143. We have used the B_Least program to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear or quadratic function.
Were used a set of six PSM (from IPQ). At least three repeated analyses were performed in three independent days.
Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys)

Sample Handling:
The cylinder was storage at ambient temperature in a storage room.
The cylinder was connected to a valve to reduce the pressure. The samples were transferred to the analyser through an auto-sampler.

Uncertainty:
The uncertainty measurement was done according ISO GUM: 1995 “Guide to the Expression of Uncertainty in Measurement”.
The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources:

- Uncertainty in calibration;
- Uncertainty of repeatability;
- Uncertainty of reproducibility

These uncertainties were combined and the result was multiplied by a coverage factor with a confidence interval of 95 %.

Uncertainty table: CO_2

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatability		normal	$1{,}645 \times 10^{-5}$	1	$1{,}645 \times 10^{-5}$
Reproducibility		normal	$5{,}901 \times 10^{-6}$	1	$5{,}901 \times 10^{-6}$
Calibration		normal	$2{,}468 \times 10^{-5}$	1	$2{,}468 \times 10^{-5}$

Coverage factor: 2
Expanded uncertainty: $0{,}006 \times 10^{-2}$ mol/mol

Participant: CMS

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : CMS/ITRI, Center for Measurement Standards
Cylinder number : D247959 / PSM105447

Measurement No. 1	Date (dd/m/yy)	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	22/11/2011	2.999E-2	0.042	5
	22/11/2011	3.001E-2	0.058	5
	22/11/2011	3.001E-2	0.033	5

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	23/11/2011	2.993E-2	0.076	5
	23/11/2011	2.995E-2	0.094	5
	23/11/2011	3.002E-2	0.024	5

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	28/11/2011	2.998E-2	0.036	5
	28/11/2011	2.997E-2	0.020	5
	28/11/2011	3.000E-2	0.071	5

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	30/11/2011	2.999E-2	0.023	5
	30/11/2011	2.997E-2	0.051	5
	30/11/2011	3.001E-2	0.057	5

Results:

Gas mixture	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty (*)
CO_2	2.999E-2	2	0.004E-2

Reference Method:
The concentration of CO_2 gas mixture was determined by gas chromatograph with TCD. Separation column of HP-PLOT/Q column (30 m* 0.537 mm* 40.00 μm) was applied with Helium as the carrier gas. The column was held at 30 ^oC.

Calibration Standards:
Six calibration standards were used for multipoint calibration to check the concentration of CO_2 in sample cylinder. After that, standard with expected concentration similar to sample cylinder was chosen for one-point calibration measurement to determine the concentration of CO_2 in sample cylinder. All calibration standards were prepared in CMS/ITRI from pure CO_2 and N_2. Gravimetric preparation method that follows ISO 6142 was applied in our mixture preparation and dilution process.

Standard	Assigned value (mol/mol)	Gravimetric expanded uncertainty (mol/mol)
Calibration standard 1: CAL012986	4.999E-2	0.002E-2
Calibration standard 2: FF10424	4.000E-2	0.002E-2
Calibration standard 3: FF6191	3.002E-2	0.002E-2
Calibration standard 4: FF6742	2.002E-2	0.002E-2
Calibration standard 5: CAL013002	2.001E-2	0.001E-2
Calibration standard 6: FF19440	1.000E-2	0.001E-2

Instrument Calibration:
The sample cylinder was analyzed in a same sequence with six calibration standards to check its concentration. Then, standard with near signal response to the sample was chosen to as the one-point calibration standard. When proceeding the one-point calibration, each stage of measurement sequence consisted of six repeat analyses. The first injection run was taken as flushing step and the last 5 runs were used to determine average responses.

The mathematical model showed below was used to calculate the concentration of CO_2 in sample cylinder:

$$\overline{C_i} = \frac{\sum_{i=1}^{12}(r \times C_s)}{12}; \quad r = \frac{R_x}{R_s}$$

C_i = concentration of sample
C_s = concentration of standard, FF6191
R_x = average response of GC-TCD for sample
R_s = average response of GC-TCD for standard, FF6191
r = ratio of average response of sample to standard

Average results obtained in each individual run were combined and averaged to produce a single measurement result. The analysis was repeated four times over 10 days.

Sample Handling:
Cylinders including sample and standards were stayed in analysis laboratory over 24 hours for conditioning. A homemade auto injection device with a Valco 16-way valve was used to lead the gas flow through the GC sample loop. Mass flow controller was applied to control the loop flow rate at 75 ml/min.

Uncertainty:
For the standard, two types of uncertainty contributed to its concentration expanded uncertainty:

- Gravimetric uncertainty
- analytical verification uncertainty

Its combined uncertainty value was calculated by taking the square root of the sum of the squares for both uncertainty sources.

$$U_{FF6191} = 2 \times \sqrt{u_{prep}^2 + u_{ver}^2}$$

Standard	Assigned value (mol/mol)	Expanded uncertainty (mol/mol)
Calibration standard: FF6191	3.002E-2	0.0031E-2

Factors contributed to the gravimetric uncertainty of standard FF6191 included:

- Balance uncertainty
- Buoyancy of cylinders and tare mass
- Purity of pure CO_2 and N_2
- Tare mass uncertainty

Factors contributed to the analytical verification uncertainty of standard FF6191 included:

- Repeatability of GC-TCD signal response
- Linearity of calibration curve
- Stability monitoring data for homemade CO_2 gas mixture

According to the mathematical model used to calculate the concentration of CO_2 in sample cylinder, the analytical verification uncertainty of sample included:

- Repeatability of GC-TCD signal response for sample
- Repeatability of GC-TCD signal response for standard, FF6191
- Reproducibility of individual analysis
- Concentration uncertainty of standard FF6191

$$\overline{C_i} = \frac{\sum_{i=1}^{12} (r \times C_s)}{12}; \quad r = \frac{R_x}{R_s}$$

Uncertainty table: CO_2

$$u^2(\overline{C_i}) = \left(\frac{\partial \overline{C_i}}{\partial C_s}\right)^2 \times u^2(C_s) + \left(\frac{\partial \overline{C_i}}{\partial r}\right)^2 \times \left(u^2(r) + \left(\frac{S_p}{\sqrt{12}}\right)^2\right)$$

$$u^2\left(\overline{C_i}\right) = (r)^2 \times u^2(C_s) + (C_s)^2 \times \left(u^2(r) + \left(\frac{S_p}{\sqrt{12}} \right)^2 \right)$$

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatability of ratio of signal, r	r; 0.999	Normal; type A	3.13E-06	3.002	9.40E-06
Reproducibility	r; 0.999	Normal; type A	2.60E-06	3.002	7.81E-06
Uncertainty of calibration standard	C_s; 3.002E-2	Normal; type A	1.55E-05	0.999	1.55E-05

Coverage factor: 2
Expanded uncertainty: 3.94E-5 mol/mol

Participant: METAS

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : Swiss Federal Office of Metrology METAS
Cylinder number : PSM105442

NOMINAL COMPOSITION
- Carbon Dioxide : 0.010 mol/mol … 0.050 mol/mol
- Nitrogen : Matrix

Measurement No. 1	Date	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.12	0.02998	0.02%	5

Measurement No. 2	Date	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.13	0.02999	0.07%	5

Measurement No. 3	Date	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.16	0.03003	0.04%	5

Measurement No. 4	Date	Result (mol/mol)	Stand. deviation (% relative)	number of sub-measurements
CO_2	-	-	-	-

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)

CO_2	0.03000 mol/mol	2	± 0.00010 mol/mol

Reference Method:

The transfer standard has been compared against 5 mixtures by means of a fully automatic pressure controlled GC with methaniser and FID. The mixtures have been prepared by dilution of 3 gravimetric premixtures with nitrogen. The binary gravimetric premixtures were cylinders out of the set of national reference gas mixtures for CO_2 in nitrogen in the range between 0.07 mol/mol to 0.11 mol/mol.

A preliminary analysis of the transfer standard revealed an approximate amount of substance fraction of 0.03 mol/mol. The calibration points for referencing the transfer standard readings have therefore been adapted. Five different dilutions have been produced for each cylinder. The area results (responses) of known calculated mixtures and the unknown mixture have been evaluated.

Calibration Standards:

Reference 1: Cylinder No. CB 6271 with METAS value (0.070077 ± 0.000177) mol/mol
Reference 2: Cylinder No. PG 104777 with METAS value (0.110100 ± 0.000209) mol/mol
Reference 3: Cylinder No. Messer 8667B with METAS value (0.069995 ± 0.000177) mol/mol

The premixtures were diluted with nitrogen of quality 6.0 (Alphagaz II from Carbagas, Quality: 99.9999%), using a molbloc-molbox system for the flow measurements.

Instrument Calibration:

A Gas-Chromatograph (Orthodyne S.A., Belgium) was used with an autosampler (Swagelok IGC-III, all gas conduits are electro polished and pneumatically controlled).

Five dilutions have been produced for each cylinder to give nominal fractions of 0.026 mol/mol, 0.028 mol/mol, 0.030 mol/mol, 0.032 mol/mol and 0.034 mol/mol. The area results (responses) of known calculated mixtures and the unknown mixture have been evaluated using the bracketing technique with a linear regression according to ISO standard 6143 by using the B-Least software.

Sample Handling:

The sample flow through the sample loop of the injector is controlled at 400 ml/min, the pressure of the sample flow after the sample loop is also controlled at 1000 mbar absolute.

Uncertainty:

Uncertainty table: CO_2
Example budget for single measurement

Quantity	Value	Unit	Standard Uncertainty	Degrees of Freedom	Distri-bution	Sensitivity Coefficient	Uncertainty Contribution	Index
$X_{CO2r}1$	30.0193	mmol/mol	0.0485	74				
$X_{CO2}S1$	70.0770	mmol/mol	0.102	50	normal	0.43	0.043	77.9%
$q_V S1$	171.291	ml/min	0.128	50	normal	0.10	0.013	6.8%
$q_{VN2}1$	228.571	ml/min	0.229	50	normal	-0.075	-0.017	12.1%
Anz_{TR}	2424700	a.u.	214	4	normal	0.000012	0.0027	0.3%
Anz_{r1}	2427718	a.u.	684	4	normal	-0.000012	-0.0085	2.9%
$X_{CO2}TR$	29.9819	mmol/mol	0.0493	160				

List of Quantities:

$X_{CO2r}1$	Amount of substance fraction of diluted premixture (for calibration)
$X_{CO2}S1$	Amount of substance fraction of premixture
$q_V S1$	Mass Flow of premixture @ STP
$q_{VN2}1$	Mass Flow of dilution gas @ STP
$X_{CO2}TR$	Amount of substance fraction of transfer standard
Anz_{TR}	Area integral of transfer standard measurement
Anz_{r1}	Area integral of reference mixture measurement

Coverage factor: 2
Expanded uncertainty: 0.33% rel.

Participant: MKEH

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Tamás Büki, Zsófia Nagyné Szilágyi, Judit Fükö

Laboratory: Hungarian Trade Licensing Office (MKEH)
Cylinder number: PSM105440

NOMINAL COMPOSITION
- carbon dioxide : 0.01 - 0.05 mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.12.	0.029973	0.026	20

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.13.	0.029989	0.023	24

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011.12.14.	0.029977	0.027	33

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
CO_2	2.9980 %(mol/mol)	2	0.0055 %(mol/mol)

Reference Method:
Gas chromatography (HP6890) was used to analyze CO_2 gas. The measurement method was direct comparison with a standard which has the same nominal concentration as the sample.
Column: HS-A 120/140 8.8 m 0.75 mm ID; Oven temp.: 190˚C; TCD temp.: 250˚C; Carrier gas: helium.

Calibration Standards:
10 L aluminum cylinder (Luxfer) with stainless steel valve, high purity CO_2 (99.998%, Siad, Hungary) and N_2 (99.995%, Messer, Hungary) gases were used for the preparation of the primary standard gas.
The mass measurements of the gases were carried out by a balance (PM 16, Mettler) with repeatability of 0.082 g and capacity of 16 kg.

Instrument Calibration:
MKEH primary standard:
DC2419/2011.10.28. CO_2: 2.9653 % ± 0.0042 %(mol/mol)
The measurements were taken with a MKEH primary standard by 3 % CO_2 nominal concentration.
The standard gas and the sample gas were changed automatically in every 1.5 minute.
The temperature and pressure correction were not done.

Sample Handling:
We used stainless steel gas regulator for the cylinders and 40 mbar was set up on flow measurement, and the flow was stable.

Uncertainty:

Uncertainty table: CO_2

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Standard reference material	2.9653 %(mol/mol)	Normal	0.00071	1	0.00071
Gas chromatography	2.9980 %(mol/mol)	Normal	0.00050	1	0.0005
Standard deviation of the 3 measurement series	2.9980 %(mol/mol)	Normal	0.00028	1	0.00028
Variancia					0.00091

Coverage factor: 2
Expanded uncertainty: 0.0055 %(mol/mol)

Participant: NIMT

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : National Institute of Metrology (Thailand)
Cylinder number : PSM 105441

NOMINAL COMPOSITION
- Carbon dioxide : 30 mmol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mmol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05-01-2012	30.13	0.14	3

Measurement No. 2	Date	Result (mmol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05-01-2012	30.20	0.13	3

Measurement No. 3	Date	Result (mmol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05-01-2012	30.06	0.12	3

Measurement No. 4	Date	Result (mmol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05-01-2012	30.04	0.12	3

Measurement No. 5	Date	Result (mmol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	05-01-2012	29.99	0.13	3

Results:

Gas mixture	Result (assigned value) (mmol/mol)	Coverage factor	Assigned expanded uncertainty (*) (mmol/mol)
CO_2	30.09	2	0.250

Reference Method:

The procedure for the estimation of measurement uncertainty is following a 3-point calibration and according to ISO 6143 using B_least software and ISO. Guide to the expression of uncertainty in measurements (GUM).

Calibration Standards:

All measurements used the standard gas mixtures in Table 1. These standards were prepared by NIMT accordance with ISO 6142:2001 and the composition was verified by using B_Least Software.

Table 1. Concentration of carbon dioxide gas mixture.

Cylinder number	**Certified concentration**	**Expanded uncertainty (Relative value, *k* = 2)**
PRM 200766	19.90 mmol/mol	0.7%
PRM 200782	30.08 mmol/mol	0.7%
PRM 200793	39.85 mmol/mol	0.7%

Instrument Calibration:

A reference and sample gases were injected into 10 port valves of the 6890 Gas Chromatograph with Thermal Conductivity Detector. The average response was calculated by using the last 3 of 6 times for each cylinder. The condition of measurement is,

Column: Porapak Q

Temperature of Oven: 40 ^{o}C

Temperature of Detector: 180 ^{o}C

Flowrate: 30 ml/min

Pressure: 1.2 bar

Carrier Gas: Helium

Sample Handling:

The sample cylinder was stabilized at room temperature, 23±3 ^{o}C, before measurements.

Participant: NPLI

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : National Physical Laboratory, New Delhi, India
Cylinder number : PSM 105439

NOMINAL COMPOSITION
- Carbon dioxide : 1,0x 10^{-2} – 5,0x 10^{-2} mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
	27/12/2011	2.93E-02	7.31E-04	6

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
	28/12/2011	2.94E-02	1.51E-04	6

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
	29/12/2011	2.90E-02	2.94E-04	5

Results:

Gas mixture	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty (*) (mol/mol)
CO_2			
	2.92E-02	2	1.96E-03

Reference Method:
Agilent GC model 6890N with FID and methanizer is used for analysis of the mixture. GSV valve is used with 2 ml sample loop to inject the gas into GC-FID. The sample is injected through 2 ml loop during analysis. The GC column used is Haysep D 12 ft, (1/8)" OD and mesh 80/120 with nitrogen as a carrier gas at the flow rate 14ml/min. GC

conditions maintained for the analysis are; Oven temperature 50^{O}C, Injector temperature 150^{O}C, Methanizer at 350^{O}C and FID Detector temperature 250^{O}C.

Calibration Standards:

The required gas standards are prepared at NPL India. The preparation of CO_2 gas is carried out according to ISO 6142 : Preparation of Calibration gas mixtures – Gravimetric method. The preconditioning of 10 liter aluminum cylinder is done by evacuation (filling of N2 gas + evacuation + heating &evacuation). This process has been repeated three times. After that the standard is prepared by weight mixing of two gases CO2 and N2.

The prepared standard gas mixture of CO_2 in N_2 gas is having concentration 2.67x 10^{-2} ±1.56x10-3 mole/mole (at 95% , k=2). This standard is used for the calibration of GC-FID system during the analysis of EURAMET 1166 cylinder.

Instrument Calibration:

The GC-FID is calibrated using above prepared calibration standard. Single point calibration method is used for the analysis of the inter-comparison cylinder.

Sample Handling:

The EURAMET COMPARISON 1166 gas cylinder is maintained inside a laboratory at a nominal temperature for 25±5^{o}C for all the period of its storage at NPL India. A dual stage regulator is fitted on the cylinder to inject the gas sample into the GC-FID system for its analysis.

Expanded Uncertainty Estimation:

Uncertainty budget table: for CO_2 Analysis

Uncertainty source X_i	Estimate x_i	Assumed distribution/ Type A & B	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Assigned value (mol/mol)	2.92E-02	Normal Type A	4.73E-04	1	1.62
Concentration of CO2 Std (mol/mol)	2.67E-02	Normal Type B	7.78E-04	1	2.92
GC response	2.71E+05	Normal Type A	7.11E+02	1	0.26
Combined Standard Uncertainty (mol/mol)	9.78E-04				
Expanded Standard Uncertainty (mol/mol)	1.96E-03				
U (%)	6.69				

Coverage factor: 2

Expanded uncertainty: 1.96E-03 mol/mol

Participant: UME

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : TÜBİTAK UME
Participant's List : Dr. Tanıl TARHAN and Dr. Fatma AKÇADAĞ
Cylinder number : PSM105415

1. Measurements:

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
111220R9	20-12-2011	0.030003	0.06	9

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
111221R4	21-12-2011	0.030002	0.07	9

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
111222R1	22-12-2011	0.030038	0.05	9

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2				
111223R1	23-12-2011	0.030003	0.05	9

Result:

Gas mixture	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty (mol/mol)
CO_2			
	0.030011	2	0.000061

2. Reference Method:

The CO_2 was analyzed on an Agilent 6890N GC equipped with TCD, split/splitless injector, gas injection valve, including Chemstation software (ver Rev. A. 10.02 [1757]) to collect and process data.

Conditions:

Carrier gas : Helium

Inlet:
Mode : Split
Split ratio : 10:1
Injection temperature : 150 ºC
Sample loop : 1 ml

Column:
Type : HP-PLOT Q 30 m, 0.32 mm, 20 µm (19091P-Q04)
Flow rate : 4.0 ml/min (constant flow)

Oven:
Temperature : Isothermal @ 50 ºC
Duration : 4 min

Detector:
Temperature : 250 ºC
Reference flow rate : 25.0 ml/min
Make-up flow rate : 8.0 ml/min

Aux:
Valve box temperature : 150 ºC

Signal:
Data rate : 10 Hz

Sample injection:
Duration : between 0.1 and 0.6 min.

Five primary standard gas mixtures and the sample cylinder were connected to a computer programmed multiposition valve gas sampling box. Low pressure regulators were placed at the outlet of cylinders. Sample flow of each cylinder was kept constant at 40 ml/min by a mass flow controller.

The data was collected using Chemstation software. Each sample in the sequence was injected for 10 times, and the first injection in each case was discarded as they were considered as flushing of sample loop. The responses were averaged.

3. Calibration Standards:

All primary standard gas mixtures used in the measurements are binary mixtures of the CO_2 in N_2. They were purchased from NPL. The details are given in Table 1.

Table 1. List of calibration standards

Item	Prepared By	Cylinder Number	Assigned Value (mmol/mol)	Assigned Uncertainty (k=2) (mmol/mol)
1	NPL	221709 SG	10.00	0.01
2	NPL	221719 SG	25.00	0.02
3	NPL	221722 SG	49.96	0.05
4	NPL	221724 SG	75.02	0.06
5	NPL	221726 SG	99.94	0.07

4. Instrument Calibration:

The calibration of the instrument has been carried out according to ISO Guide 6143. Five primary standard gas mixtures were used for calibration. The software “B_Least” was utilized to determine the best fitting model for data. Goodness of fit values in each measurement were found to be higher than 2 for linear function. They were less than the value of 2 for second order polynomial function. Therefore, second order analysis functions were used for calibration.

5. Sample Handling:

After the arrival of the cylinder, it was stored in the laboratory where the analyses were carried out. Calibration standards were also stored in the same laboratory during all the measurements. The cylinder and the calibration standards were equipped with pressure reducers and connected to sample box. They were flushed three times before the first measurement. The flow rates of sample and standard gases were controlled by a mass flow controller.

6. Uncertainty:

The measurement uncertainty of sample was determined according to ISO Guide 6143, using the B_Least software. The assigned value was calculated by averaging the results of four measurements. Its combined standard uncertainty was determined by selecting the largest uncertainty value among the obtained uncertainties for each measurement. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%.

Participant: VSL

EURAMET COMPARISON 1166
Measurement report
Comparison of standards and calibration facilities for CO_2 measurements

Laboratory : VSL
Cylinder number : 902529

NOMINAL COMPOSITION
- Carbon dioxide : 0.03 mol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-05	$3.0036 \cdot 10^{-2}$	0.02	3

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-06	$3.0039 \cdot 10^{-2}$	0.02	3

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
CO_2	2011-12-08	$3.0030 \cdot 10^{-2}$	0.02	3

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
CO_2	0.030035 mol/mol	2	0.000015 mol/mol (0.05% relative)

Reference Method: NDIR (URAS 14)

Calibration Standards: VSL primary gas standards in the range from 1 to 10 % mol/mol CO_2 in Nitrogen

Instrument Calibration: a cubic calibration function was made using 7 PSM's divided over the range from 1 to 10 % CO_2. The calibration function was obtained as described in ISO 6143 and used for value assignment.

Table 1: Calibration results first measurement

PSM	*x* mol/mol	*u*(*x*) mol/mol	*y* mV	*u*(*y*) mV	Δ*x* mol/mol	Δ*x*/*u*(*x*)	Δ*y* mV	Δy/u(*y*)
VSL147826	0.0100010	0.0000013	1.22776	0.00065	-0.0000002	-0.15	0.00039	0.61
VSL206397	0.0251190	0.0000048	2.92048	0.00072	0.0000058	1.22	-0.00125	-1.74
VSL206299	0.0400430	0.0000047	4.43701	0.00100	-0.0000019	-0.40	0.00086	0.87
VSL428515	0.0549810	0.0000047	5.82754	0.00092	-0.0000033	-0.70	0.00144	1.56
VSL329375	0.0695290	0.0000049	7.07773	0.00090	0.0000007	0.14	-0.00028	-0.31
VSL353533	0.0850720	0.0000051	8.31610	0.00104	0.0000029	0.57	-0.00157	-1.51
VSL353531	0.1000900	0.0000053	9.43316	0.00112	-0.0000014	-0.27	0.00088	0.79

Sample Handling: The mixtures were kept in the lab to ensure temperature stability. The samples were fed to the analyzer by using suitable reducing valves and inert tubing.

Uncertainty:

Table 2: Value assignment and uncertainty evaluation unknown (single run)

Mixture	y	u(y)	$x_{nominal}$	$x_{assigned}$	$u(x_{assigned})$
EM2529*	3.433860	0.000150	0.0300000	0.0300369	0.0000068

Coverage factor: 2
Expanded uncertainty: 0.000015mol mol^{-1} (0.05% relative)