Final Report for Supplementary Comparison APMP.QM-S15: Carbon Dioxide in Nitrogen at 1000 µmol/mol

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Field

Amount of substance

Subject

Carbon dioxide 1000 µmol/mol in Nitrogen

Participants

A total of six laboratories participated in this supplementary comparison. Table 1 lists the participants in this supplementary comparison

Table 1: List of participants

Acronym	Country	Institute
NPLI	India	CSIR-National Physical Laboratory India
KAZ	Kazakhstan	Kazakhstan Institute of Metrology
NIMT	Thailand	National Institute of Metrology (Thailand)
NMC	Singapore	National Metrology Centre
SNSU-BSN	Indonesia	National Measurement Standards, National Standardization Agency of Indonesia
KRISS	Korea	Korea Research Institute of Standards and Science

Organizing Body

APMP TCQM

Background

Carbon dioxide (CO_2) in nitrogen was one of the first types of gas mixtures performed at an international key comparison. The comparison dates back to 1998 (CCQMK1a) [1]. Since then, many National Metrology Institutes (NMIs) have developed Calibration and Measurement Capabilities (CMCs) for these mixtures. The international comparison of CO_2 at ambient level through CCQM-K52 was compared in 2007 [2]. Recently, NMIs in the APMP region have focused on developing emission standards for regulating CO_2 released by various powered vehicles such as automobiles (motor cars). At the 2017 APMP meeting, several NMIs requested a CO_2/N_2 comparison to establish their own standards related with automotive regulation, which was to be coordinated by KRISS. Consequently, this comparison provides a CMC for APMP regional NMIs to develop CO_2/N_2 CMC claim. The nominal amount-of-substance fraction for the CO2 in nitrogen supplementary comparison is presented in table 2.

Table 2: Nominal Amount-of-substance fraction

Component	Nominal amount

Carbon dioxide	1000 μmol/mol
Nitrogen	Balance

Schedule

The schedule for this part of the comparison is presented in Table 3.

Table 3: Schedule

Time	Event
Nov 2016	Proposal for the supplementary comparison
Apr 2017	Protocol preparation by KRISS
Jun 2017	Registration and protocol circulation
Nov 2017	Preparation/Distribution of mixtures by KRISS
Aug 2018	Returning cylinder to KRISS
Dec 2018	Reanalysis
Sep 2019	Draft report A
Oct 2019	Draft report B –undergoing

Preparation of measurement standards

A total of eight gas mixtures were prepared gravimetrically in August 2017 [4] by diluting the first step cylinders of CCQM-K120 [3] and verified with a GC (Gas Chromatograph)/TCD (Thermal Conductivity Detector) analyzer in October 2017. The amount-of-substance fraction was determined based on the gravimetric method after purity analysis, which was assigned as a reference value. This implies that each cylinder has a unique reference value. CO_2 in the raw N_2 gas with high purity was around 0.011 μmol/mol, which was considered negligible. Purity results are shown in the report of the former CCQM-K120 comparison. Accordingly, the final amount of each cylinder was assigned after applying the CO_2 purity result to the gravimetric one.

After weighing, all prepared mixtures were analyzed to verify their reliability [5]. As shown in figure 1, they agree within 0.1 %. Therefore expanded uncertainties of verification were evaluated as 0.050 % (k = 2), as shown in Table 4.

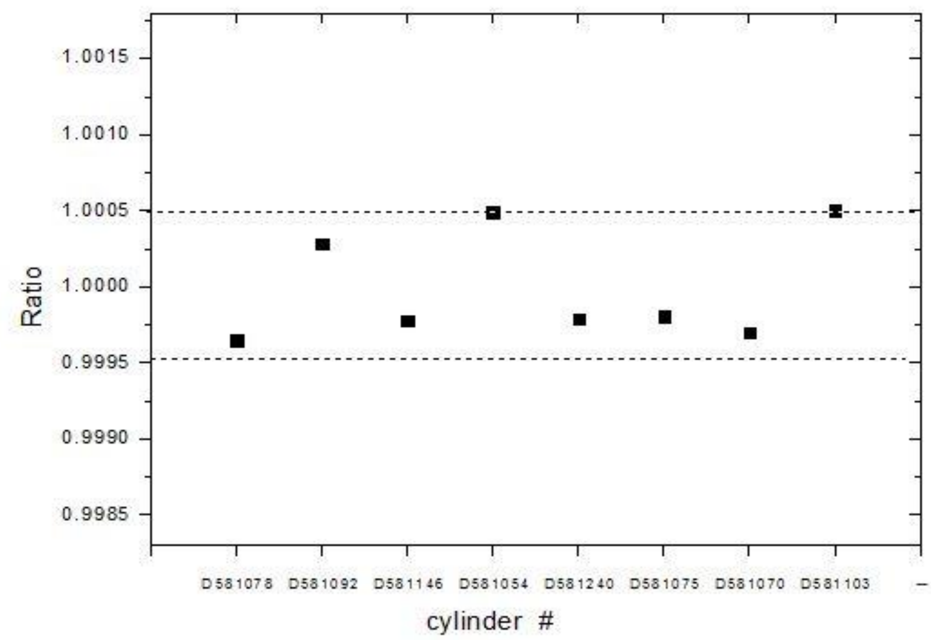

Figure 1. Consistency between gravimetrically prepared mixtures for this comparison (October 2017)

Table 4: Preparation of measurement standards

Cylinder number	Gravimetric value [μmol/mol]	*U* from gravimetry (*k*=2) [μmol/mol]	*U* from verification (*k*=2) [μmol/mol]
D581078	999.49	0.15	0.50
D581092	999.87	0.16	0.50
D581146	999.83	0.14	0.50
D581054	999.70	0.15	0.50
D581240	999.29	0.15	0.50
D581075	999.54	0.14	0.50
D581070	999.94	0.16	0.50
D581103	1001.00	0.14	0.50

A reference mixture (Rm) was analyzed between every sample mixture (Sm) to measure ratios of samples to reference and to monitor analyzer drift, for example, in a sequential set of (Rm_{j-1}-$Sm_{i,j}$- Rm_{j+1}) for *i*-th sample cylinder of *j*-th analysis. The D015343 cylinder was used as the reference (Rm). In equation (1), R_i is the ratio ($S_i/S_{i^{th}-drift\ corrected}$) where sensitivity ($S_i$) was defined as the analyzer response (A_i) of i^{th} cylinder divided by its reference value (C_i). Ratio in figure 1 denotes R_i given by equation (1).

$$R_{i,j} = \frac{S_{Sm_{i,j}}}{S_{j^{th}-drift\ corrected}} \qquad \text{(eq.1)}$$

where $S_{Sm_{i,j}} = \frac{A_{Sm_{i,j}}}{C_{Sm_i}}$ for sample *i*, $S_{j^{th}-drift\ corrected} = \frac{S_{Rm_{j-1}}+S_{Rm_{j+1}}}{2}$ for analytical sequence j

and $S_{Rm_{j-1}}$ is a sensitivity of a reference for (*j*-*1*)-th analysis, defined as $S_{Rm_{j-1}} = \frac{A_{Rm_{j-1}}}{C_{Rm}}$.

All cylinders showed agreement with the gravimetric reference value within ± 0.05 % uncertainty. The prepared mixtures are summarized in Table 4, where uncertainty includes uncertainty components generated from verification analysis and gravimetric weighing. Among the eight cylinders, six mixtures were used for this comparison.

All cylinders were returned with sufficient pressure and re-analyzed in October 2018. The results indicated that the mixtures remained stable during transport.

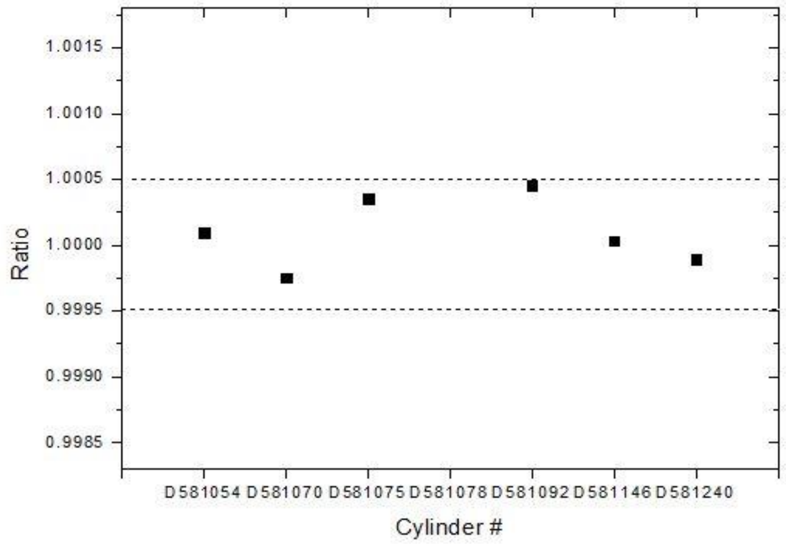

Figure 2. Reanalysis results of the returned cylinders (October 2018)

Results and Discussion

Some important items reported by the participants are summarized in Table 5. They all prepared their own standards for calibration. SNSU-BSN, NIMT and KRISS used GC-TCD calibrated with single point, while others used GC-FID, where two of them calibrated their analyzers with a single point, only

KAZ used multiple points for calibration. The details of the analytical methods used by the participants are described in the individual participant reports.

Table 5: Summary of the analysis methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
KRISS	D581070	Oct. 2018	Own standards	Single point	GC/TCD
SNSU-BSN	D581092	Feb. 2018	Own standards	Single point	GC/TCD
NIMT	D581146	Jan. 2018	Own standards	Single point	GC/TCD
NMC	D581054	Feb. 2018	Own standards	Single point	GC/FID/Methaniser
NPLI	D581240	Mar. 2018	Own standards	Single point	GC/FID/Methaniser
KAZ	D581075	Apr. 2018	Own standards	Multiple point	GC/FID/Methaniser

The results of the comparison are summarized in Table 6.

Table 6: Summary of the comparison of APMP.QM-S15

Lab.	Cylinder	X_{prep} [μmol/mol]	u_{prep} [μmol/mol]	x_{lab} [μmol/mol]	U_{lab} [μmol/mol]	k_{lab}	Δx [μmol/mol]	U(Δx) [μmol/mol]	k
KRISS	D581070	999.94	0.25	999.86	1.08	2	-0.08	1.19	2
SNSU-BSN	D581092	999.87	0.25	1000.1344	6.538	2	0.26	6.56	2
NIMT	D581146	999.83	0.25	999.66	1.60	2	-0.17	1.68	2
NMC	D581054	999.70	0.25	999.23	2.16	2	-0.47	2.22	2
NPLI	D581240	999.29	0.25	999.58	2.52	2	0.29	2.57	2
KAZ	D581075	999.54	0.25	1003.0	14.7	2	3.5	14.7	2

As shown in table 6, all participants agreed with their SCRV within their associated uncertainties.

Degrees of equivalence

The degree of equivalence (D_i) of the comparisons is defined as

$D_i (= \Delta x_i) = x_{i,lab} - x_{i,ref}$,

where $x_{i,ref}$ denotes the supplementary comparison reference valve and x_i the result of laboratory i. The standard uncertainty of D_i can be expressed as

$$u^2(D_i) = u_{i,lab}^2 + u_{i,prep}^2$$

The degrees of equivalence (DoE) for the APMP.QM-S15 is presented in figure 3. As shown in figure 3, all results were consistent within the uncertainties $u(D_i)$.

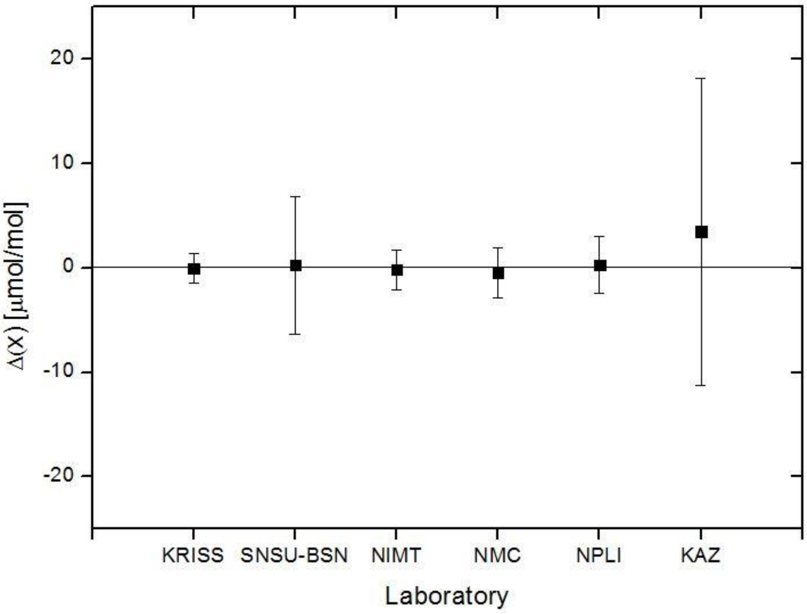

Figure 3: Degrees of equivalence for the APMP.QM-S15 (*K*=2)

Conclusions

In the comparison, all the results of the participants were consistent with their SCRV within the associated uncertainties.

How Far Does the Light Shine?

The goal of this supplementary comparison is to support CMC claim for carbon dioxide in N_2 at the range of 50 μmol/mol - 500 mmol/mol. An extended range may be supported as described in the GAWG strategy for comparisons and CMC claims [6].

Table 7: HFTLS list of each participant for CMC claims

Participant		Amount fraction (μmol/mol)	Uncertainty (%)	Amount fraction (μmol/mol)	Uncertainty (%)
KRISS	from	1.08	1.00	10	0.11
	to	10	0.11	500 000	0.11
SNSU-BSN	from	6.538	0.99	10	0.65
	to	10	0.65	500 000	0.65
NIMT	from	1.6	1.00	10	0.16
	to	10	0.16	500 000	0.16
NMC	from	2.16	1.02	10	0.22
	to	10	0.22	500 000	0.22
NPLI	from	2.52	0.99	10	0.25
	to	10	0.25	500 000	0.25
KAZ	from	-		14.7	1.47
	to	-		500 000	1.47

References

[1] A. Alink: The first key comparison of primary standard gas mixtures, Metrologia 37 (1). 2000

[2] Rob M Wessel et al. International comparison CCQM-K52: Carbon dioxide in synthetic air, Metrologia 45 08011

[3] Edgar Flores et al. International comparison CCQM-K120: (Carbon dioxide at background and urban level), Metrologia 56 1A

[4] International organization for standardization, ISO 6142-1:2015. "Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures, ISO, 2015 (E)

[5] International organization for standardization, ISO 6143:2015. "Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures", ISO, 2015(E).

[6] CCQM-GAWG strategy for comparisons and CMC claims, GAWG/19-41, https://www.bipm.org/wg/CCQM/GAWG/Restricted/October_2019/GAWG19-41-CCQM-GAWG_strategy_for_comparisons_and_CMC_claims.pdf

APMP-QM-S15: Carbon Dioxide in Nitrogen (1000 μmol/mol)

Laboratory name: Gas Metrology Laboratory, National Metrology Centre, A*STAR

Author: Liu Hui, Fang Jie, Thomas Wu, Kai Fuu Ming, Mou Jianqiang

Cylinder number: KRISS D581054

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO_2	09/02/2018	999.022	0.036	5

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO_2	12/02/2018	999.307	0.080	5

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO_2	13/02/2018	999.353	0.051	5

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor[1]
CO_2	999.23	2.16	2

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

Details of the Measurement Method Used:

A customized FID-GC (Flame Ionised Detector - Gas Chromatography) with methanizer was used to conduct the comparison. One Reference Standard which is close to transfer standard's concentration were chosen to as the one-point calibration standard. The sample cylinder was analysed with the Reference Standard in the model of Reference Standard – Sample Cylinder – Reference Standard. The number of injections from each cylinder was 8, and only the last 5 injections were used for the calculation of the mole fraction of the sample cylinder. The Reference Standards and the sample cylinder were injected directly into the FID-GC through the sampling tube. Average results obtained in each individual analysis were combined and averaged to produce a single measurement result on that day.

The purity of balance gas, nitrogen and the sample gas, carbon dioxide was analysed using PDHID/FID-GC (Pulsed Discharge Ionization Detector/ Flame Ionised Detector - Gas Chromatograph). The regulator used was SS Verifo single stage without gauges, which was purged at least 10 times based on the standard operation procedure.

Details of Sample Handling:

The sample cylinder and reference standards were stored at a room temperature (21 ± 2) °C for 3 days before an analysis. The gas mixture in the sample cylinder KRISS D581054 was analysed over 5 days against Reference Standard I maintained at NMC using FID-GC and a sampling system consisting of valves, pressure regulator and flow meter. Modified Teflon was used in the sampling line. The measurements were carried out under ambient temperature of (21 ± 2) °C and (60

± 15) % relative humidity.

Details of the Reference Standards Used:

Reference Standards used for the comparison were maintained in 2 separate cylinders with the following details:

Reference Standard	Cylinder No.	Concentration (μmol/mol)	Gravimetric Preparation Uncertainty (μmol/mol)
Reference Standard	PSM218695	1000.93	0.41

Reference Standard, which was selected as the Reference Standard in Measurement #1, Measurement #2 and Measurement #3 to measure the concentration of the sample cylinder, were prepared in NMC using gravimetric method following ISO6142 Standard.

Cylinders for Reference Standard was 5-litre aluminium cylinder with Aculife-3 treatment supplied by Scott Specialty Gases. The Reference Standards had been verified against Consistency Check with internal reference materials. The concentration of Reference Standard was the concentration after verification. The preparation of gas mixtures and measurements were carried out under ambient temperature of (21 ± 2) °C and (60 ± 15) % relative humidity based on the standard operation procedure.

Details on Uncertainty Budget:

The purity analysis of carbon dioxide and nitrogen were measured by PDHID/FID-GC. The core impurities e.g. O_2, CO, CO_2, N_2, Ar, H_2, CH_4, etc., were analysed.

1. Uncertainty Evaluation of Reference Standard

Two type of uncertainty were evaluated for the Combined Uncertainty of Reference Standard as below.

- Uncertainty of pure CO_2 and the matrix gas, pure nitrogen
- Uncertainty of reference gas mixtures by gravimetric method

1.1. Uncertainty Budget of Pure CO_2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	N_2	2.000E-07	Normal	3.325E-09
Impurity	O_2	6.000E-08	Normal	3.139E-09
Impurity	CH_4	5.000E-08	Rectangular	2.887E-08
Impurity	C_2H_4	5.000E-08	Rectangular	2.887E-08
Impurity	H_2O	2.500E-06	Rectangular	1.443E-06
Impurity	CO	2.500E-08	Rectangular	1.443E-08

Impurity	H_2	1.200E-07	Normal	6.928E-08
Impurity	Ar	9.000E-08	Normal	6.213E-09
Balance gas	CO_2	0.99999691		1.446E-06

1.2. Uncertainty Budget of Pure N_2

Components		Concentration (mol/mol)	Distribution	Standard Uncertainty (mol/mol)
Impurity	O_2	2.500E-08	Rectangular	1.44342E-08
Impurity	CO	2.500E-08	Rectangular	1.44342E-08
Impurity	H_2	2.500E-08	Rectangular	1.44342E-08
Impurity	CO_2	5.000E-08	Rectangular	2.88684E-08
Impurity	CH_4	5.000E-08	Rectangular	2.88684E-08
Impurity	H_2O	1.000E-08	Rectangular	5.77367E-09
Balance gas	N_2	0.999999815		4.82197E-08

1.3. Gravimetric Uncertainty Budget for Reference Standard

Gravimetric uncertainty of the Reference Standard at 3% CO_2 in nitrogen mixture was evaluated in the below tables.

Uncertainty source	Estimated Value	Standard Uncertainty	Distribution	Contribution to Standard Uncertainty (μ mol/mol)
Mass of CO_2 (g)	26.696	0.0065	normal	7.17
Mass of N_2 (g)	545.398	0.0082	normal	0.44
Concentration of CO_2 in pure CO_2 gas (mol /mol)	9.9999696E-01	2.04E-06	normal	0.062
Concentration of CO_2 in N_2 gas (mol/mol)	5.00E-08	2.88E-08	normal	0.028
Molar mass of CO_2 (g/mol)	44.00900	0.00072	normal	0.48
Molar mass of N_2 (g/ mol)	28.01400	0.00049	normal	0.51
Combined Uncertainty (k = 1)				**7.2**

Gravimetric uncertainty budget for Reference Standard at 1000.93 μmol/mol, which was diluted from the 3% CO_2 premix gas.

Uncertainty source	Estimated Value	Standard Uncertainty	Distribution	Contribution to Standard Uncertainty (μ mol/mol)
Mass of premix (g)	19.270	0.0065	normal	0.33
Mass of N_2 (g)	552.970	0.0082	normal	0.014
Concentration of CO_2 in premix gas (mol/mol)	3.02E-02	7.22E-06	normal	0.24
Concentration of CO_2 in N_2 gas (mol/mol)	5.00E-08	2.88E-08	normal	0.028
Molar mass of premix (g/mol)	28.49704	0.00048	normal	0.016
Molar mass of N_2 (g/mol)	28.01400	0.00049	normal	0.017
Combined Uncertainty (k = 1)				**0.41**

2. Uncertainty Evaluation for the Measurement

The GC analyser was calibrated with the calibration standard gas prepared by the gravimetric method. The A-B-A method and the one the point calibration model was used.

The concentration of sample gas was determined by the following equation:

$$X_{sample} = \frac{Y_{sample}}{Y_{std}} X_{std}$$

Where, X_{sample}*: Concentration of sample*

Y_{sample}*: GC analysis results of the sample cylinder*

Y_{std} *: GC analysis results of Reference Standard*

X_{std} *: Concentration of Reference Standard*

The uncertainties of Y_{sample} and Y_{std} have been estimated using the pooled standard deviation of analysis. The uncertainties of the X_{std} has been estimated by the uncertainty of standard concentration in preparation including the uncertainties of the standard concentration in gravimetric process and purity analysis, verification and stability check. The reproducibility of the measurements was estimated by the standard deviation of the pooled mean value of the X_{sample}.

The uncertainty of X_{std} was the combined by the uncertainties of the standard concentration in gravimetric process and purity analysis, verification and stability check. As the CO_2 gas mixtures which NMC used for this comparison were new prepared. We estimated the uncertainty of stability was negligible.

$$u^2(X_{std}) = u^2(X_{std,prep}) + u^2(X_{std,veri})$$

and: $$u^2(X_{std,prep}) = u^2(X_{std,gravi}) + u^2(X_{std,pur}) + u^2(X_{std,stab})$$

If : $$|X_{std,prep} - X_{std,ver}| \leq 2\sqrt{u^2_{std,prep} + u^2_{std,ver}}$$

Then: $$X_{std} = X_{std,prep}$$

Where, $u(X_{std})$: *Uncertainty of Standard concentration*

$u(X_{std,prep})$: *Uncertainty of Standard concentration in preparation*

$u(X_{std,veri})$: *Uncertainty of Standard concentration in analytical verification*

$u(X_{std,gravi})$: *Uncertainty of Standard concentration in gravimetric gas mixing process*

$u(X_{std,pur})$: *Uncertainty of purity analysis*

$u(X_{std,stab})$: *Uncertainty of stability check*

Uncertainty Evaluation for the Measurement					
Uncertainty Source	**Value**	**Standard Uncertainty**	**Distribution**	**Sensitivity Coefficient**	**Uncertainty Contribution (*μmol/mol*)**
Y_{sample}	1097.35	0.59	Normal	0.911	0.54
Y_{std}	1099.22	0.29	Normal	-0.909	0.26
X_{std}	1000.93	0.91	Normal	0.998	0.90
Reproducibility		0.103	Normal	1	0.103
Combined Uncertainty (*μmol/mol*)					1.08
Expanded Combined Uncertainty (*μmol/mol*) ; K = 2					2.16
Expanded Combined Uncertainty (*Relative %*) ; K = 2					0.22%

Based on the above uncertainty model, the final uncertainty evaluation for the measurement was evaluated as shown in the below table.

Measurand: 999.23 μmol/mol

Coverage factor: k = 2

Expanded Uncertainty: 2.16 μmol/mol, relative 0.22%

Report Form

Carbon dixide in nitrogen

Laboratory name: CSIR-NPLI

Cylinder number: D 581240

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO2	05/03/18	998.57	0.09	8

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO2	06/03/18	999.43	0.17	8

Measurement #3[2]

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO2	06/03/18	1000.73	0.16	8

Results

Component	**Result (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**	**Coverage factor[3]**
CO2	999.58	2.52	2

[2] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

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

Details of the measurement method used:

GC FID (Agilent 6890N) with Methanizer

Column used: Haysep D; length 12 ft, Dia 1/8" and mesh range 100/120

Oven temp: 80 °C

Carrier gas: He (20 ml/min)

Methanizer temp: 350 °C

Detector Temp: 250 °C

GSV loop: 0.25 ml

Hydrogen and air flow rate were 20 ml/min and 300 ml/min respectively

The APMP.QM-S15 gas cylinder was maintained inside a laboratory at a nominal temperature for 22 ± 5°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 through GSV into the GC-FID system for its analysis. The cylinders were rolled for two hours on homogenization system before measurement.

Details of the calibration method used:

Single point calibration method was used for the analysis of the inter-comparison cylinder. Calibration standard of concentration 1095.64± 2.59 μmol/mol is used for the calibration of GC-FID system during the analysis of APMP QM-S15 cylinder and value evaluation.

Details of the standards used:

The preparation of Primary Reference Gas Mixtures (PRGM) was done in accordance to ISO 6142: Gas Analysis -Preparation of calibration gas mixtures - Gravimetric Method.

The preconditioning of 10 litre aluminium cylinder wass done by evacuation (filling of N_2 gas + evacuation + heating at 60-70 °C & evacuation) of cylinders. This process has been repeated three times for each cylinder before preparation of gas mixture. The evacuation of cylinders is carried out using PFEIFFER HiCube 80 Eco vacuum System. The theoretical calculations for the calculation of mole fraction were carried out for the desired concentrations using model equation from ISO 6142-1:2015.

Gas mixtures of CO_2 in nitrogen gas from pure gas were prepared in two series in the concentrations around 20544 ± 33.58 and 20392.67 ± 34.73 μmol/mol. The pre-mixture of 20392.67 ± 34.73 μmol/mol was used for further dilution in the concentration 1095.64± 2.59 μmol/mol for APMP.QM S15 cylinder measurement. The initial weighing of components transferred was done using a top pan balance. And the final weighing was done using an equal arm double pan balance Raymor HCE 25G max capacity 25kg with 1mg sensitivity. These cylinders were validated in accordance to ISO 6143:2001 "Gas analysis - Comparison method for determining and checking the composition of calibration gas mixtures". Thus the prepared gas mixtures were certified as CO_2 in Nitrogen gas (Primary Reference Gas Mixtures (PRGMs)).

Purity Analysis

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

Details on uncertainty budget:

The Uncertainty for the prepared gas mixtures has been evaluated according to guideline prescribed in ISO 6142-1:2015 and EURACHEM Guide taking account of following gravimetric and analytical components:

I. Uncertainty Components in Gravimetric Preparation of calibration gas mixture (Calibration standard)

1. Raymor Balance
2. Mass Pieces
3. Buoyancy effect
4. Handling of cylinder

5. Residual gas
6. Expansion of the cylinder due to filling of gas at High pressure

II. Uncertainty Components in Analytical method

- Repeatability
- Reproducibility
- GC Response

Pooled standard deviation is taken as standard uncertainty of assigned value and GC response taking account of repeatability and reproducibility.

Date of Analysis	**n_i**	**X_i (µmol/mol)**	**$(SD)_i$ (µmol/mol)**	**RSD (%)**	**SD_{pooled}**
05-03-2018	8	998.57	0.94	0.09	
06-03-2018	8	999.43	1.67	0.17	
06-03-2018	8	1000.73	1.63	0.16	
RESULT	**24**	**999.58**			**0.32**

$$SD_{pooled} = \sqrt{\frac{s_1^2\,(n_1 - 1) + s_2^2(n_2 - 2) + \cdots}{(n_1 + n_2 + n_3) - 3}}$$

Measurement Uncertainty Budget:

Sources of Uncertainty	Estimates x_i		Distribution/ Type A & B	Standard uncertainty $u(x_i)$		Sensitivity cofficient c_i	Contribution to standard uncertainty $u_i(y)$
Assigned value	999.58	µmol/mol	Normal, Type A	0.32	µmol/mol	1	0.00032
Conc. of Cal Std	1095.64	µmol/mol	Normal, Type B, 2	1.29	µmol/mol	1	0.00118
GC Response	2064.50	mV	Normal, Type A	0.67	mV	1	0.00033
Combined standard Uncertainty, u_c	1.26	µmol/mol					
Expanded Uncertainty, U	2.52	µmol/mol	k = 2				
U	0.25	%					

Cylinder Pressure after Analysis ~ 90 bar

Team Members: Dr Daya Soni, Dr Khem Singh, Ms Sulakshina Bhat, Dr Shankar G Aggarwal and Dr Prabha Johri.

REPORT ON

APMP- QM-S15

APMP Regional Comparison

Carbon Dioxide in Nitrogen (1000 µmol/mol)

Oman Zuas,

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Report Form

Carbon dioxide in nitrogen

Laboratory name: **Research Centre for Metrology-Indonesian Institutes of Sciences (SNSU-BSN)**

Cylinder number: **D581092 (APMP QM S-15)**

Measurement:

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	07/02/2018	999.959	0.645	3

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	08/02/2018	999.936	0.575	3

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	16/02/2018	1000.307	0.572	5

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	17/02/2018	1000.528	0.718	6

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO_2	18/02/2018	999.834	0.360	7

Results

Component	Date (dd/mm/yy)	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor [4]
CO_2	**01/03/2018**	**1000.1344**	**6.538**	***k* =2**

Details of the measurement method used:

Reference Method

Gas chromatography equipped with thermal conductivity detector (GC-TCD).

Instruments

Gas chromatography equpped with thermal conductivity detector (GC-TCD) was used to determine the concentration of CO_2 in gas mixtures. Separation of CO_2 from the gas mixture was conducted on a stainless steel packed column (Porapak Q, 6 feet, 1/8" outer diameter). The oven temperature was isothermal at 40°C. The TCD gas used was He at 20 mL/min and 7 mL/min as reference and make-up gases, repectively. The TCD temperature was kept at 250°C with negative polarity. Ultra high purity of helium (99.999%) was used as a carrier gas at a flow rate of 28 mL/min. The valve box temperature was maintained at 100ºC. The flow rate of gas mixture was set at 30 mL/min (checked at GC gas outlet by using a digital flow meter) and the gas mixture was passed through on a 500 μL sample loop. A mass flow controller was used to keep the gas mixture flow at constant rate.

Details of the calibration method used:

The calibration standard gas mixtures (hereinafter called as CSGMs) of CO_2 in N_2 were prepared by SNSU-BSN using gravimetric method in accordance to ISO 6142:2001[(1)]. The pre-mixtures were prepared from CO_2 (ultra-high purity grade, Air Liquid Indonesia) and N_2 (ultra-high purity grade, SII-Indonesia). The purity (compositions) assessment of CO_2 and N_2 were conducted prior to use and the result are presented in Table 1 and Table2, respectively. Two-step dilution processes (Figure 1) were adopted to prepare each of six cylinders of CSGMs

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

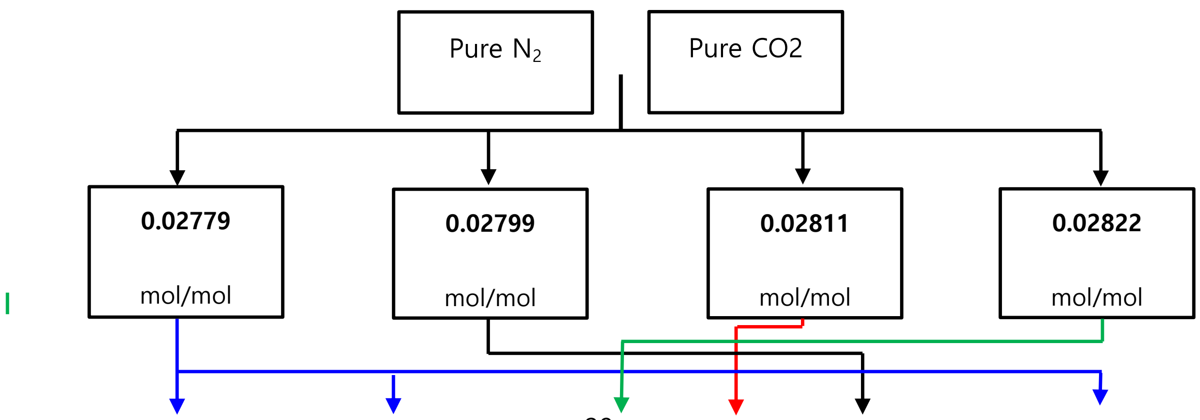
containing CO_2 in N_2 with a nominal concentration ~1000 µmol/mol. After that, the gravimetric concentrations of CO_2 in all prepared CSGM cylinders were verified using the method described in ISO 6143:2001[(2)], and the results are presented in Table 3.

Table 1. Purity table of pure CO_2 (parent)

Component	Mole fraction (µmol/mol)	Standard uncertainty (µmol/mol)	Method of evaluation (type A or type B)	Analysis method
H_2O	1.000	0.577	B	Manufacturer specification
CO	0.846	0.073	A	PDHID
O_2	0.846	0.063	A	PDHID
CH_4	0.306	0.021	A	PDHID
Ar	0.495	0.038	A	PDHID
N_2	2.254	0.167	A	PDHID
CO_2	999994.253	0.610	A	Mass balance

Table 2. Purity table of pure N_2 (parent)

Component	Mole fraction (µmol/mol)	Standard uncertainty (µmol/mol)	Method of evaluation (type A or type B)	Analysis method
H_2O	1.500	0.866	B	Manufacturer specification
CO_2	0.022	0.012	A	PDHID
O_2	5.846	0.348	A	PDHID
CH_4	2.685	0.231	A	PDHID
Ar	0.915	0.064	A	PDHID
CO	1.320	0.114	A	PDHID
N_2	999987.712	0.970	A	Mass balance



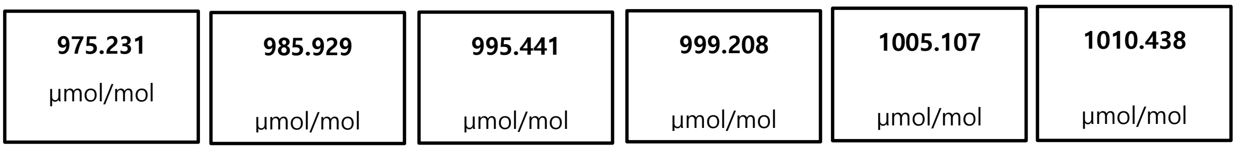


Figure 1. Two step dilution process of CSGMs at ~1000 μmol/mol CO_2 in N_2

Table 3. Calibration standard gas mixture (CSGMs)

# Cylinder	Concentration (μmol/mol)	$U_{combined}$ (μmol/mol)	$U_{expanded}$* (μmol/mol)	$U_{expanded}$ relative (%)
L150721016	975.231	3.056	6.111	0.627
L150721015	985.929	3.091	6.182	0.627
L150721006	995.441	3.119	6.237	0.627
L150721012	**999.208**	**3.212**	**6.423**	**0.643**
L150721005	1005.107	3.170	6.341	0.631
L150721003	1010.438	3.170	6.340	0.627

* The coverage factor (*k*=2) was based on approximately 95% confidence level.

Weighing Data

Weighing data for cylinder #L150721012 are summarized as follows:

1st dilution mixture:

1. Evacuated cylinder #L150721004 - tare cylinder = 70.210 g (cylinder #L150721004)

2. Cylinder #L150721004 filled with parent CO_2 - tare cylinder = 80.185 g (amount of parent CO_2 transferred into #L150721004 = 9.974 g)
3. Cylinder #L150721004 filled with parent N_2 - tare cylinder = 299.669 g (amount of parent N_2 transferred into #L150721004 = 219.462 g)
4. Cylinder #L150721004 filled with parent CO_2 (9.974 g) + parent N_2 (219.462 g) = 1st dilution mixture (cylinder #L150721004).

2nd dilution mixture:

1. Evacuated cylinder #L150721012 - tare cylinder = 3.260 g (cylinder #L150721012)
2. Cylinder #L150721012 filled with 1st dilution mixture #L150721004 - tare cylinder = 13.445 g (amount of 1st dilution mixture #L150721004 transferred into #L150721012 = 10.183 g)
3. Cylinder #L150721012 filled with parent N_2 - tare cylinder = 285.450 g (amount of N_2 transferred into cylinder #L150721012 = 271.975 g)
4. Cylinder #L150721012 filled with 1st dilution mixture #L150721004 (10.183 g) + parent N_2 (271.975 g) = 2nd dilution mixture (cylinder #L150721012)

Details of the standards used for instrument calibration:

Preliminary evaluation of CO_2 concentration in the sample cylinder #D581092 was performed by constructing a calibration curve using the six prepared CSGMs. Such evaluation was conducted under identical conditions and for a CSGM having a GC signal response close to that of sample cylinder #D581092 was selected for single-point calibration to determine the concentration of CO_2 in sample cylinder. Our evaluation showed that the CO_2 in cylinder #L150721012 was found to be the closest GC signal response relative to that of GC signal response of CO_2 in sample cylinder #D581092. Therefore, the CSGM cylinder #L150721012 was chosen as a reference standard for the single-point calibration process to determine the CO_2 concentration in the sample #D581092.

The single-point calibration consists of several sets of measurement (at least three set of measurements) in different days. The order of measurement was A-B-A (where A is the cylinder #L150721012 as reference standard, and B is the sample cylinder #D581092). Each set of measurement comprised of at least seven replications of analysis and the first injection was excluded from measurement repeatability evaluation. The mathematical model (Eq. 5) was used to calculate the concentration of CO_2 in sample cylinder #D581092.

Sample handling

The sample cylinder #D581092 was conditioned in the laboratory environmental by keeping the sample cylinder in the laboratory for 48 h. Each cylinder (CSGMs #L150721012 .and sample #D581092) was equipped with an Alphagaz double stage pressure regulator that was adequately purged.

Details of uncertainty budgets:

Uncertainty evaluation for the prepared CSGM #L150721012 .

- ***Model equation***: a model formula (Eq. 1) below was used to calculate CO_2 concentration in the prepared CSGMs (measurand). The concentrations of CO_2 in in CSGMs (C_{CO_2}) were calculated as the gravimetric concentration based on ISO 6142 using equation 1 (Eq. 1).

$$C_{CO_2} = \frac{\sum_{A=1}^{P}\left[\frac{x_{CO_2,A}\cdot m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right]}{\sum_{A=1}^{P}\left[\frac{m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right]} \quad (1)$$

The C_{CO2} was calculated as the mole of the total CO_2 transferred from each parent gas ($\sum_{A=1}^{P}\left[\frac{x_{CO2,A}.m_A}{\sum_{i=1}^{n} x_{i,A}.M_i}\right]$) divided by the total mole of gas components in the CSGM cylinder ($\sum_{A=1}^{P}\left[\frac{m_A}{\sum_{i=1}^{n} x_{i,A}.M_i}\right]$). Notation A corresponds to the parent gases in the amount of P, while i is corresponding to each gas components in the mixture with fraction of x_i, including the impurities, in a total of n components. M_i is the molecular mass of each component and m_A is the mass of transferred parent gas.

- ***Uncertainty budgets***. For the uncertainty estimation of the CSGM #L150721012, the uncertainty contributors are including gravimetric uncertainty (u_{grav}), uncertainty from verification (u_{ver}), and uncertainty form stability (u_{stab}). For that, the combined uncertainty of the CSGMs #L150721012 was calculated by means of equation 2 (Eq. 2).

$$u_{CO_2} = \sqrt{u_{grav} + u_{ver} + u_{stab}}$$

(**2**)

For the uncertainty from gravimetric preparation (u_{grav}) the estimation was done by modifying Eq. 1 based on the propagation rules)", resulting in an equation 3 (Eq. 3) below.

$$u^2(C_{CO_2}) = \sum_{A=1}^{P}\left[\frac{\partial x_{CO_2}}{\partial m_A}\right]^2 .u^2(m_A) + \sum_{A=1}^{P}\left[\frac{\partial x_{CO_2}}{\partial M_i}\right]^2 .u^2(M_{CO_2}) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left[\frac{\partial x_{CO_2}}{\partial x_{i,A}}\right]^2 .u^2(x_{CO_2,A})$$

(**3**)

where $u^2(m_A)$ is the uncertainty from the weighing of the transferred parent gas A. The $u^2(M_i)$ is the uncertainty of molecular mass for all gas components i in the mixture. The $u^2(x_{i,A})$ is the uncertainty of the mole fraction for all of gas components i, including the impurities of the parent gas A.

Moreover, the uncertainty from the verification (u_{ver}) was estimated from the standard deviations of the CSGM verification. The uncertainty from the stability of the CSGM (u_{stab}) was estimated from the concentration difference between some days of measurement.

For the uncertainty of weighing process of the transferred parent gas ($u^2(m_A)$), it was estimated by using following equation 4 (Eq. 4).

$$u^2{}_{m_A} = (\Delta w_A - \Delta w_{A-1})^2 u^2(e) + +(-e)^2 u^2(\Delta w_A) + (-e)^2 u^2(\Delta w_{A-1}) + (\Delta P \rho_{air})^2 u^2(K) + (K\rho_{air})^2 u^2(\Delta P) + u^2(\Delta L) + (\rho_{air})^2 u^2(\delta V) + (K\Delta P + \delta V)^2 u^2(\rho_{air}) \quad \textbf{(4)}$$

where:

- $u^2(e)$ is the uncertainty of the linearity of the balance.
- $u^2(\Delta w_A)$ is the repeatability of mass difference between the tare cylinder and CSGM cylinder after the transfer of parent gas by repeated weighing.
- $u^2(\Delta w_{A-1})$ is the repeatability of mass difference between the tare cylinder and CSGM cylinder before the transfer of parent gas by repeated weighing.
- $u^2(K)$ is the uncertainty caused by expansion of cylinder volume due to pressure change.
- $u^2(\Delta P)$ is the uncertainty from the pressure change due to gas transferring.
- $u^2(\Delta L)$ is the uncertainty caused by random loss of mass or sticking dirt in cylinder's wall.
- $u^2(\delta V)$ is the uncertainty from the volume change due to temperature rise during transfer of parent gas.
- $u^2(\rho_{air})$ is the uncertainty from the buoyancy correction caused by air density change in the weighing chamber.

By combining those three aforementioned equations represented by the Eg. 2, Eq. 3 and Eq. 4 and applying them to evaluate the sources of uncertainty of the CSGM concentration, the below fishbone diagram was obtained.

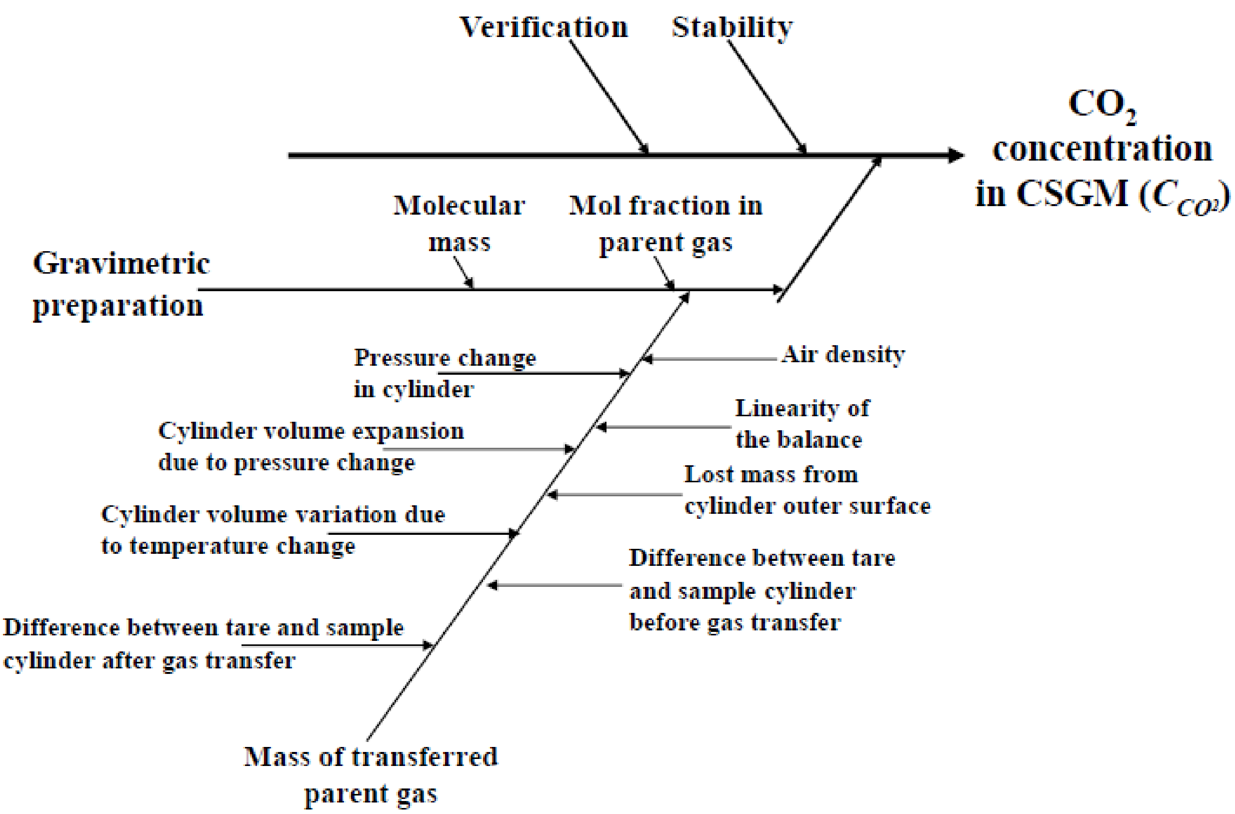


Figure 1. Fishbone diagram of uncertainty sources affecting the final concentration of CSGMs

Table 4. Uncertainty budgets for the CSGM #L150721012

Uncertainty sources	Value	Standard Uncertainty	Type
Gravimetric preparation of CSGM; Combined from : 1. Weighing of the transferred parent gas (a combination of the uncertainty sources stated in equation 4) : a. Weighing of transferred parent gas #L150721004			
b. Weighing of transferred parent gas N_2	10.1832 g	0.0064 g	A
2. Mole fraction of components in parent gas #L150721004 and parent N_2 :	271.9754 g	0.0075 g	A

a. H_2O in #L150721004	0.00000149 mol/mol	0.00000084 mol/mol	B
b. CO in #L150721004	0.00000131 mol/mol	0.00000010 mol/mol	B
c. CO_2 in #L150721004	0.02811440 mol/mol	0.00001024 mol/mol	B
d. O_2 in #L150721004	0.00000571 mol/mol	0.00000034 mol/mol	B
e. Ar in #L150721004	0.00000091 mol/mol	0.00000006 mol/mol	B
f. CH_4 in #L150721004	0.00000262 mol/mol	0.00000021 mol/mol	B
g. N_2 in #L150721004	0.97187357 mol/mol	0.00001028 mol/mol	B
h. H_2O in parent N_2	0.00000150 mol/mol	0.00000087 mol/mol	A
i. CO in parent N_2	0.00000132 mol/mol	0.00000011 mol/mol	A
j. CO_2 in parent N_2	0.00000002 mol/mol	0.00000001 mol/mol	A
k. O_2 in parent N_2	0.00000585 mol/mol	0.00000035 mol/mol	A
l. Ar in parent N_2	0.00000092 mol/mol	0.00000006 mol/mol	A
m. CH_4 in parent N_2	0.00000269 mol/mol	0.00000023 mol/mol	A
n. N_2 in parent N_2	0.99998771 mol/mol	0.00000097 mol/mol	A
3. Molecular mass of all components in the mixture (based on IUPAC) :			
a. H_2O	18.01528000 g/mol	0.00000087 g/mol	B
b. CO	28.01040000 g/mol	0.00000011 g/mol	B
c. CO_2	44.00950000 g/mol	0.00000001 g/mol	B
d. O_2	31.99880000 g/mol	0.00000035 g/mol	B
e. Ar	39.94800000 g/mol	0.00000006 g/mol	B
f. CH_4	16.04246000 g/mol	0.00000023 g/mol	B
g. N_2	28.01348000 g/mol	0.00000097 g/mol	B
Combined uncertainty from the gravimetric preparation (using Eq. 3)		0.00000070 mol/mol	B

Verification of the CSGM concentration	0.00000261 mol/mol	A
Stability testing of the CSGM	0.00000173 mol/mol	A
Combined uncertainty of the CSGM (using Eq. 2)	0.00000321 mol/mol	
Expanded uncertainty for confidence level of 95% (*k*=2)	0.00000642 mol/mol (**6.423 µmol/mol**)	

- ***Measurand and expanded uncertainty*** . Measurand and expanded uncertainty of prepared CSGM #L150721012 are listed in Table 5.

Table 5. Measurand ($C_{CSGM\#L150721012}$) and expanded uncertainty ($U_{CSGMs\text{-}\#L150721012}$)

CSGM	Assigned value (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor*
#L150721012	**999.208 µmol/mol**	**6.423 µmol/mol**	**k = 2**

* The coverage factor (k=2) was based on approximately 95% confidence level.

Uncertainty evaluation for the Sample #D581092

- ***Model equation***: a model equaation (Eq. 5) below was used to calculate CO_2 concentration in the sample #D581092 (measurand).

$$C_{sample\ \#D581092} = \left(\frac{Response\ area_{sample\ \#D581092}}{Response\ area_{standard\ \#L150721012}}\right) x\ C_{standard\ \#L150721012}$$

(5)

- ***Uncertainty budget***: For the uncertainty of sample #D581092, the estimation was performed by modifying Eq. 5 based on the propagation rules[3], resulting in an equation 6 (Eq. 6) below.

$$\left(\frac{u_{C_{sample\ \#D581092}}}{C_{sample\ \#D581092}}\right)^2 = \left(\frac{u_{(A_{sample\ \#D581092}/A_{standard\ \#L150721012})}}{A_{sample\ \#D581092}/A_{standard\ \#L150721012}}\right)^2 + \left(\frac{u_{C_{standard\ \#L150721012}}}{C_{standard\ \#L150721012}}\right)^2$$

(**6**)

Based on Eq. 6, there are two sources of uncertainty of the sample #D581092 concentration, i.e., 1). Repeatability of the ratio between detector's response of sample #D581092 and detector's response of standard #L150721012. ($u_{(A_{sample\ \#D581092}/A_{standard\#L150721012})}$), and 2). Uncertainty of standard concentration #L150721012. ($u_{C_{standard\ \#L150721012}}$). The details of uncertainty budgets for the sample #D581092 are listed in Table 6.

Table 6. Uncertainty budgets for the sample #D581092

Uncertainty source **X_i**	**Estimated value** **x_i**	**Assumed distribution**	**Standard uncertainty** ***u*** **(x_i)**	**Sensitivity coefficient** **c_i**	**Contribution to standard uncertainty** **u_i (%)**
Ratio of detector's response to sample and standard, $u_{(A_{sample}/A_{standard})}$	1.001	normal	0.001	999.208	3.285

Uncertainty of CSGM #L150721012	999.208 µmol/mol	normal	3.212 µmol/mol	1.001	96.716
Combined Uncertainty of sample #D581092			**3.269** µmol/mol		
Expanded Uncertainty, confidence level 95% (*k*=2)			**6.538** µmol/mol		

- ***Measurand and expanded uncertainty*** : Measurand and expanded uncertainty of sample #D581092 are listed in Table 7**.**

Table 7. Measurand and expanded uncertainty of sample #D581092.

Sample	*Concentration* (µmol/mol)	*Expanded uncertainty* (µmol/mol)	Coverage factor*
#D581092	**1000.134**	**6.538**	***k* =2**

References

[1]. International Organization for Standardization, ISO 6142:2001 “Gas analysis - Preparation of calibration gas mixtures – Gravimetric method”, 2nd Edition.

[2]. International Organization for Standardization, ISO 6143:2001 “Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures”, 2nd Edition.

[3]. Joint Committee for Guides in Metrology, JCGM 2008. Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM).

Report Form

Carbon dioxide in nitrogen

Laboratory name: National Institute of Metrology (Thailand)

Cylinder number: D581146

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO_2	24/01/2018	999.80	0.01	3

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO_2	24/01/2018	1000.28	0.03	3

Measurement #3[5]

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO_2	24/01/2018	998.89	0.02	3

Results

Component	**Result (µmol/mol)**	**Expanded Uncertainty (% relative)**	**Coverage factor[6]**
CO_2	999.66	0.16	2

[5] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary
[6] The coverage factor shall be based on approximately 95% confidence.

Details of the measurement method used:

The measurements were performed using a 6890 Gas Chromatograph with Thermal conductivity detector (TCD). The measurement procedure is shown as follow; "PGRM (Calibration) – Sample – PGRM (Calibration) – PGRM (Assurance) – PGRM (Calibration)– Sample – PGRM (Calibration) – PGRM (Assurance) – PGRM (Calibration) – Sample – PGRM (Calibration) – PGRM (Assurance) – PGRM (Calibration)". The single point calibration was used for determining the mole fraction of carbon dioxide in sample. In the addition, one of the primary gas reference material (PGRM) was used in the measure to assure consistency with the standard gas mixtures used and measurement system. The average response was calculated by using the last three of six times for each cylinder.

Details of the calibration method used:

The GC-TCD was performed following the single point calibration by primary gas reference material (PGRM). The mole fraction of carbon dioxide in the PGRM used was closed to the target mole fraction of carbon dioxide in the sample cylinder. The GC column used was Hayesep Q, 8 ft and mesh 80/100, and with helium as carrier gas. The measured condition was sample loop 1 ml, temperature of oven 45°C, temperature of detector 250°C, reference gas flow 30 ml/min. The flow rate of gas mixtures was controlled by using a mass flow controller at 40 ml/min.

Details of the standards used:

The PGRMs used in the measurements are binary mixtures of the carbon dioxide in nitrogen. They are traceable to the National Institute of Metrology (Thailand). The mole fraction of PGRMs used was determined in compliance with ISO 6142-1 by using gravimetric method and verified by using GC-TCD calibrated by using one of the PGRMs. The purity of Nitrogen is more than 99.9995% and the purity of carbon dioxide is more than 99.995%. These standard gas mixtures used were prepared by 2-step of dilution. Uncertainty values of PGRM s are evaluated from the gravimetry, verification, stability and measurement bias. The characteristics of the standard gas mixtures used are listed in Table as below.

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Table 1. Concentration of PGRMs.

Cylinder number	Assigned value	Expanded uncertainty (Relative value, *k* = 2)
PRM 112694	1000.68 μmol/mol	0.14%
PRM 112684	1001.33 μmol/mol	0.18%

Details on uncertainty budget:

The certified value applies to only this cylinder, and the uncertainty is expressed as an expanded uncertainty obtained by multiplying the standard uncertainty at 95% confidence interval by the coverage factor k=2. The standard uncertainty $u(x_s)$ of the sample gas mixture is calculated from the following equations;

$$u(x_s) = x_s\sqrt{\frac{u^2(X_{crm})}{X_{crm}^2} + \frac{u^2(Y_{crm})}{Y_{crm}^2} + \frac{u^2(Y_s)}{Y_s^2}}$$

Where

$u(X_{crm})$ is the standard uncertainty of the standard gas mixture

$u(Y_{crm})$ is the standard uncertainties of measurement response of standard gas mixture

$u(Y_s)$ is the standard uncertainties of measurement response of sample

X_{crm} is the standard gas mixture contents

Y_{crm} is average measurement response of standard gas mixture

Y_s is average measurement response of sample

Uncertainty Budget for of CO_2 measurement

Quantity (Uncertainty source), X_i	Estimate x_i *(µmol/mol)*	Evaluation type (A or B)	Distribution	Standard uncertainty *(%relative)*	Sensitivity coefficient c_i	Contribution *(%relative)*
The standard gas mixture	1000.68	B	Normal	0.070	1.0	0.070
Response of standard gas mixture	330.44	A	Normal	0.014	1.0	0.014
Response of sample gas mixture	330.10	A	Normal	0.013	1.0	0.013
Analytical content of sample	999.66	Combined Uncertainty, (%relative)				0.08
		Expanded Uncertainty, (*k=2*) , (%relative)				0.16

Authorship
Mr.Arnuttachai Wongjuk , Ms.Ratirat Sinweeruthai

APMP Regional Comparison

Carbon dioxide in Nitrogen (1000 μmol/mol)

Laboratory: Karaganda branch of RSE "Kazakhstan Institute of Metrology" Republic of Kazakhstan

Cylinder number: D581075

I. Measurement

Measurement #1	**Date**	**Result, μmol/mol**	**Standart deviation (% relative)**	**Number of replicates**
Carbon dioxide in Nitrogen	03.04.2018	1004,7	3,2	5

Measurement #2	**Date**	**Result, μmol/mol**	**Standart deviation (% relative)**	**Number of replicates**
Carbon dioxide in Nitrogen	04.04.2018	1001,3	2,9	5

Measurement #3	**Date**	**Result, μmol/mol**	**Standart deviation (% relative)**	**Number of replicates**
Carbon dioxide in Nitrogen	06.04.2018	999,3	3,0	5

Measurement #4	**Date**	**Result, μmol/mol**	**Standart deviation (% relative)**	**Number of replicates**
Carbon dioxide in Nitrogen	10.04.2018	1007,6	3,1	5

Measurement #4	**Date**	**Result, μmol/mol**	**Standart deviation (% relative)**	**Number of replicates**
Carbon dioxide in Nitrogen	10.04.2018	1002,0	2,9	5

Result

Component	Result, µmol/mol	Coverage factor*)	Expanded Uncertainty, µmol/mol
Carbon dioxide in Nitrogen	1003,0	2	14,7

*) The coverage factor based on 95% confidence.

II. Measurement Details for APMP-QM-S15.2017

Instruments

Measurements were carried out using gas chromatograph "Crystal 5000" combined with flame-ionization detector and methanazer for conversion carbon dioxide.

Carrier gas: argon.

Volume size: 1 ml.

Chromatographic column: Hayesep N 80/100 mesh, 2m x 2mm.

Computers and software "Chromatech Analytic" were used to control chromatograph and collect and process chromatographic data.

Calibration standards

1. The calibration gas standards were prepared by gravimetric method multiple dilutions, according to ISO 6142. An electronic mass-comparator (Mettler Toledo model XP10003S, capacity 10,1 kg, readability 1 mg) was used for preparation of all calibration gas standards. Manufacturer, type and metrological characteristics of the equipment used for the preparation of the gravimetric gas mixtures are given in Table 1.

Table 1.

Type	Manufacturer	Metrological characteristics
Model XP10003S	«Mettler-Toledo», Swizerland	The maximum limit weighing 10100 g Resolution 1 mg The standard deviation of 10 mg The maximum change in temperature for 1 h. ± 0.5 ° C
Gas mixing plant, GSU-3	OOO «PGS-Servise», Russian Federation	Pressure measuring range: from 0.001 to 16.0 MPa Residual pressure cylinders before filling 10 Pa.

For the production of calibration gas mixtures were used aluminum cylinders with a capacity of 4 dm3 complete with brass diaphragm valve type VBM-1. The internal surface of the cylinders was coated by paraffin grade P2.

2. Analysis of the purity of the clean gases.

Analysis of the purity of the original pure gases was based on information provided by the suppliers of pure gases (passports, certificates), as well as on the results of the measurement of impurities in pure gases using measurement techniques developed and approved by the RSE "KazInMetr".

In cases where the analytical method can not determine the content of the alleged impurities molar fraction of the expected impurity was assumed to be half the detection limit of the analytical method. The content of impurities unmeasured assumes a rectangular probability distribution, whereby the standard uncertainty is calculated as half the detection limit.

Determination of impurities in the starting pure gases (carbon dioxide , nitrogen) used to prepare calibration samples was conducted by gas chromatography using a flame ionization, thermal chemical and thermal conductivity detector.

The content of impurities in the pure gas used for preparing the calibration gas mixtures shown in Table 2.

Table 2.

The metrological characteristics of pure gases.

Clean gas	**Component**	**Content mole fraction, %**	**The standard uncertainty, mole fraction,%**
Carbon dioxide The cylinder capacity of 40 dm3 Manufacturer: - Kazakhstan	CO_2	99,99	0,01
Nitrogen The cylinder capacity of 40 dm3 Manufacturer: The Republic of Kazakhstan	N_2	99,9999	0,0001

In measuring the mass of gas filled and comparative cylinder identical volume being weighed according to the scheme and the method of substitution RMMR.

Based on previous studies RMS measurement result is taken to be 30 mg (standard uncertainty evaluated by type A).

3. After making the balloon with the calibration gas mixture was placed in a laboratory, where the at least 72 hours. Before the measurement tanks rolled the calibration gas mixtures for 10 minutes.

Calibration of instrument

1. Calibration was performed using GC calibration gas mixtures are identical in composition to sample comparisons. The content of each component and its expanded uncertainty (k = 2) is shown in Table 3.

Table 3 - Calibration gas mixtures

Cylinder number, passport number, size, material, date of manufacture	Component	Content, x (μmol/mol)	The standard uncertainty of the calibration samples (rel.), u (x),%
PV-214, 4 dm^3	CO_2	1055,4	0,5
	N_2	-	
PV-216, 4 dm^3	CO_2	962,1	0,5
	N_2	-	
PV-218, 4 dm^3	CO_2	1032,7	0,5
	N_2	-	
PV-219, 4 dm^3	CO_2	1022,7	0,5
	N_2	-	

The total content of components standard uncertainty in calibration gas mixtures are calculated according to the formula:

$$u_{total} = \sqrt{u_m + u_p}$$

u_m – standard uncertainty weighing, %;

u_p – standard uncertainty of frequency source gases, %.

The standard uncertainty of the molar mass of gases, as well as uncertainty due to air buoyancy, with the pressure and volume of a cylinder is filled not taken into account in connection with a minor contribution.

2. The measurements were carried out under repeatability conditions. Before each measurement was conducted by the chromatograph calibration. Each measurement includes 5 observations.

3. Analytical function used to determine the components in the sample is as follows:

$$x(y) = b_1 y + b_0$$

were,

x – measured content, µmol/mol;

y – chromatographic response of the analyte;

b_1 – coefficient of linear dependence;

b_0 – offset coefficient.

Sample preparation

The sample with the sample and the calibration sample was stored prior to measurement for 24 hours in the laboratory. The change in temperature in the laboratory at the time of measurement is ± 2 ° C, the change in pressure within ± 0,5 kPa.

Calculation of measurement uncertainty

Uncertainty value *u(x)* was calculated in accordance with ISO 6143 taking into account the uncertainties of the calibration standards and instrument response variability during calibration and measurements under reproducibility conditions:

$$u(x) = \sqrt{u^2(x, x_{cs}) + u^2(x, y)}$$

were

$u(x, x_{cs})$ – the standard uncertainty associated with the amount-of-substance fractions of the calibration standards;

$$u(x, x_{cs}) = \sqrt{\sum_{i=1}^{n} \left(\frac{u(x_{cs_i})}{n}\right)^2},$$

where

$u(x_{cs_i})$ – uncertainty of the calibration standards;

n - number of the calibration standards;

$u(x, y)$ – uncertainty associated with the instrument response,

$$u(x, y) = \sqrt{\frac{u^2(y) + x^2 \cdot u^2(a_1) + 2x \cdot cov(a_0, a_1) + u^2(a_0)}{a_1^2}},$$

where

u(y) – uncertainty of instrument response during measurements;

$a_0, a_1, u(a_0), u(a_1), cov(a_0, a_1)$ – calibration function parameters obtained from B_Least for linear function.

The calibration function parameters of all measurements are given in Table 4.

Table 4 - Calibration function parameters.

Parameter	1st measurement	2nd measurement	3rd measurement	4rd measurement	5rd measurement
Regression coefficient a_1	4,097824E+01	4,142879E+01	3,839535E+01	4,017443E+01	4,931432E+01
Regression coefficient a_1 uncertainty $u(a_1)$	3,071293E+00	3,087130E+00	2,802749E+00	3,162043E+00	3,765568E+00
Regression coefficient a_0	-2,816330E+03	-2,813569E+03	5,315462E+02	-8,128793E+02	1,576403E+04
Regression coefficient a_0 uncertainty $u(a_0)$	3,128914E+03	3,148256E+03	2,854800E+03	3,213045E+03	3,836918E+03
Covariance $cov(a_0, a_1)$	-9,602676E+03	-9,713637E+03	7,996633E+03	-1,015268E+04	-1,444015E+04

Table 5

Uncertainty table

Uncertainty source X_i	**Estimate x_i**	**Assumed distribution**	**Standart uncertainty $u(x_i)$**	**Sensitivity coefficient c_i**	**Contribution to standard uncertainty $u_i(y)$**
Uncertainty associated with the amount-of substance fractions of the calibration standards	-	Normal	2,9 μmol/mol	1	2,9 μmol/mol
Uncertainty associated with the instrument response	-	Normal	7,3 μmol/mol	1	7,3 μmol/mol

Coverage factor: k = 2.

Expended uncertainty: 14,7 μmol/mol.

APMP.QM-S15 Carbon dioxide in nitrogen

Laboratory name: KRISS

Cylinder number: D581070

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (µmol/mol)**	**number of replicates**
CO_2	11.8.2017	1000.13	0.55	4

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (µmol/mol)**	**number of replicates**
CO_2	18.9.2018	999.78	0.50	4

Measurement #3

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (µmol/mol)**	**number of replicates**
CO_2	1.10.2018	999.70	0.50	5

Measurement #4

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (µmol/mol)**	**number of replicates**
CO_2	2.10.2018	999.84	0.50	5

Results

Component	**Result (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**	**Coverage factor**[7]
CO_2	999.86	1.08	2

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

Details of the measurement method used:

Analysis method:

Carbon dioxide concentration in nitrogen has been quantified using gas chromatograph thermal conductivity detector (GC-TCD). Figure 1 shows an analytical condition of the analyzer and its chromatogram.

Configuration of analysis system: gas cylinder >> regulator >> MFC >> sample injection valve >> column >> detector >> integrator >> area comparison >> results

To achieve analytical interval of ± 0.1 % (standard deviation) the instrument drift and standard deviation of the response were controlled carefully. Two cylinders D581078 and D581103 were analyzed as the reference mixture against the distributed sample cylinder (D581070).

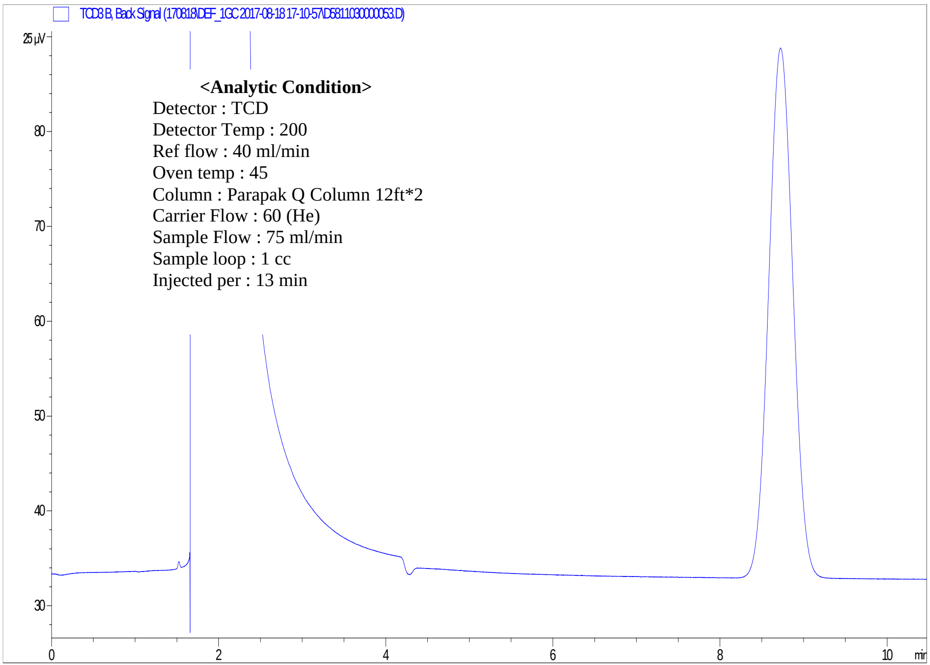

Figure 1. Analytical condition and chromatogram of CO_2

Details of the calibration method used:

Instrument calibration is performed using KRISS primary standard mixtures. One point calibration was done with a cylinder of nominal value ~ 1000 µmol/mol which was very close to the target cylinder.

Sample handling:

The sample cylinder had put in the laboratory with room temperature for several days after preparation. Each cylinder was equipped with a stainless steel pressure regulator that was purged more than 5 times after connection to the analysis line. Samples were transferred to sample loop at flow rate of 75 mL/min using the mass-flow controller.

Calibration standards:

Preparation method

Total 8 cylinders were prepared for this comparison (figure 1) and 2 primary standard mixtures among them were used for determining amount of carbon dioxide in Nitrogen. The standards were prepared from pure carbon dioxide and pure nitrogen in accordance with ISO6142:2001 (Gas analysis-preparation of calibration gases-gravimetric method). Pure carbon dioxide was diluted by 2 step and purity analysis for every pure gases were done(pure CO_2 used at CCQM-K120). Table 1 shows gravimetric value and expanded uncertainty of the calibration standards.

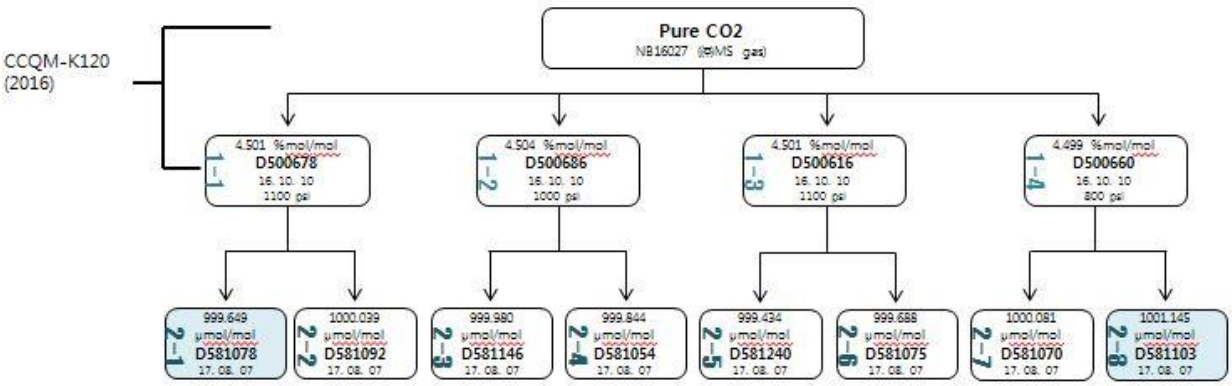

Figure 2. Preparation cylinder tree of CO_2 for this comparison

Table 1. Gravimetric value and expanded uncertainty in calibration standards

Cylinder number	Gravimetric value (μmol/mol)	Expanded uncertainty [*k*=2] (μmol/mol)
D581078	999.49	0.15
D581103	1001.00	0.14

Purity analysis

The impurities of carbon dioxide and nitrogen were determined by analytical methods and the amount of the major component is conventionally determined from the following equation,

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

Where

x_i : the mole fraction of impurity i, determined by analysis;

N: the number of impurities likely to be present in the final mixture;

x_{pure}: the mole fraction “purity” of the “pure” parent gas.

Table 2 and 3 show the results of purity analysis of CO_2 and N_2.

Table 2. Results of purity analysis of Carbon dioxide (NB16027)

component	Analytical conc. (μmol/mol)	Detector	distribution	Applied conc. (μmol/mol)	Standard uncertainty (μmol/mol)
H_2	6.4	GC/TCD	Normal	6.4	0.6
O2	79.5	GC/TCD	Normal	79.5	7.9
Ar	3.5	GC/TCD	normal	3.5	0.4
N2	214.8	GC/TCD	Normal	214.8	21.5
CO	39.6	GC/TCD	Normal	39.6	4.0
CH_4	15.2	GC/TCD	Normal	15.2	1.5
H_2O	0.54	dew point meter	Normal	0.54	0.05
THC	<0.2	GC/AED	Rectangular	0.1	0.06
Total Sulfur	<0.01	GC/AED	Rectangular	0.01	0.003
			impurities	359.67	23.30
			CO_2 purity	**99,640.34**	46.60 (*k*=2)

Table 3. Results of purity analysis of Nitrogen (NK02608)

component	Analytical conc. (μmol/mol)	Detector	distribution	Applied conc. (μmol/mol)	Standard uncertainty (μmol/mol)
H_2	< 0.1	GC/PDD	Rectangular	0.050	0.029
O2	0.11	Galvanic Sensor oxygen analyzer	Normal	0.110	0.011
Ar	4.48	GC/TCD	Normal	4.480	0.448
CO	< 0.003	GC/FID	Rectangular	0.002	0.001
CO_2	0.011	GC/FID	Normal	0.011	0.001
CH_4	< 0.002	GC/FID	Rectangular	0.001	0.001
H_2O	0.55	dew point meter	Normal	0.550	0.055
N2O	0.00014	GC/μECD	Normal	0.00014	0.00001
THC	< 0.5	GC/FID	Rectangular	0.250	0.144
			impurities	5.454	0.47
			N_2 purity	**999,994.55**	0.95 (*k* = 2)

Uncertainty:

The uncertainty used for the calibration mixtures contains all source of gravimetric preparation. Uncertainty for stability is not included because no instability has been detected. An analysis uncertainty is calculated based on repeatability and drift of analyzer of the acquired area.

<u>Detailed uncertainty budget:</u>

Please include a list of the uncertainty contribution, the estimate of the standard uncertainty, probability distribution, sensitivity coefficients, etc.

$$C_{\mathrm{final}} = \frac{A_{sample}}{A_{ref}} \times \mathrm{C}_{\mathrm{crm\_ref}}$$

Typical evaluation of the of each measurement uncertainty for CO_2:

Quantity X_i		Estimate x_i Area[arb.] [μmol/mol]	Evaluation Type (A or B)	Distribution	Standard uncertainty $u(x_i)$ Area[arb.] [μmol/mol]	Sensitivity coefficient	Contribution $u_i(y)$
Response_reference			A	Gaussian			
D581078(before)		3319.512			0.322	-0.15	-0.049
D581078(after)		3316.000			0.370	-0.15	-0.056
Area[arb.]							
Response_Sample D581070 Area[arb.]		3318.690	A	Gaussian	0.205	0.30	0.062
Reference prepared grav. [μmol/mol]	D581078	999.49	B	Gaussian	0.5	1.0	0.50
	D081103	1001.00			-	-	
Amount_sample [μmol/mol]		999.78					
Combined standard uncertainty [μmol/mol]					0.5		