Final Report for Supplementary Comparison

APMP.QM-S9.2017: 100 μmol/mol of Carbon monoxide in nitrogen

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Field

Amount of substance

Subject

Carbon monoxide 100 μmol/mol in Nitrogen

Participants

Total six laboratories participated in this supplementary comparison. Table 1 lists the participants in this key comparison

Table 1: : List of participants

Acronym	Country	Institute
NPLI	India	CSIR-National Physical Laboratory India
KazInMetr	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 monoxide (CO) in nitrogen was one of the first types of gas mixtures used in an international key comparison. This comparison dates back to 1998 (CCQM-K1a) [1]. Another key comparison on carbon monoxide is the CCQM-K51 at the lower amount fraction of 5 μmol/mol. Since then, many National Metrology Institutes (NMIs) have developed Calibration and Measurement Capabilities (CMCs) for these mixtures. Recently, NMIs in the APMP region have actively participated in international comparisons to provide domestic services. At the 2017 APMP meeting, several NMIs requested a CO comparison to establish CO/N_2 certification for supporting industrial needs, which was to be coordinated by KRISS. Consequently,

this supplementary comparison provides an opportunity for APMP regional NMIs to meet their industrial needs . It is a replica of APMP.QM-S9.[2]

Amount of substance

Component	Nominal amount fraction
Carbon monoxide	100 μmol/mol
Nitrogen	Balance

Schedule

The schedule for this part of the comparison is presented in Table 2.

Table 2: 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 (Completed)
Dec 2018	Reanalysis
Sep 2019	Draft report A
Oct 2019	Draft report B

Preparation of measurement standards

A total of eight gas mixtures were prepared gravimetrically [4] in August 2017 by diluting twice the first step cylinders (nominal value: 2.5 cmol/mol CO/N_2) of CCQM-K84 [3] and verified with a GC (Gas Chromatograph)/FID (Flame Ionization Detector) methaniser 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. The amount fraction of carbon monoxide within the balance gas N_2 gas was less than 0.001 μmol/mol, which was considered negligible. Purity results are in the report of the former comparison, the APMP-QM.S9.[2]

Expanded uncertainties of the gravimetric preparation were evaluated as 0.10 % (k = 2), as shown in Table 3.

After weighing, all prepared mixtures were analyzed to verify their compositions [5]. As shown in figure 1, they agree within 0.1 %.

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 sequence of Rm-Sm_1- Rm -Sm_2- Rm …, and so on. 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).

$$R_i = \frac{S_i}{S_{i^{th}-drift\ corrected}}$$

where

$S_i = \frac{A_i}{C_i'}$ $S_{i^{th}-drift\ corrected} = \frac{S_{Rm,i-1}+S_{Rm,i+1}}{2}$.

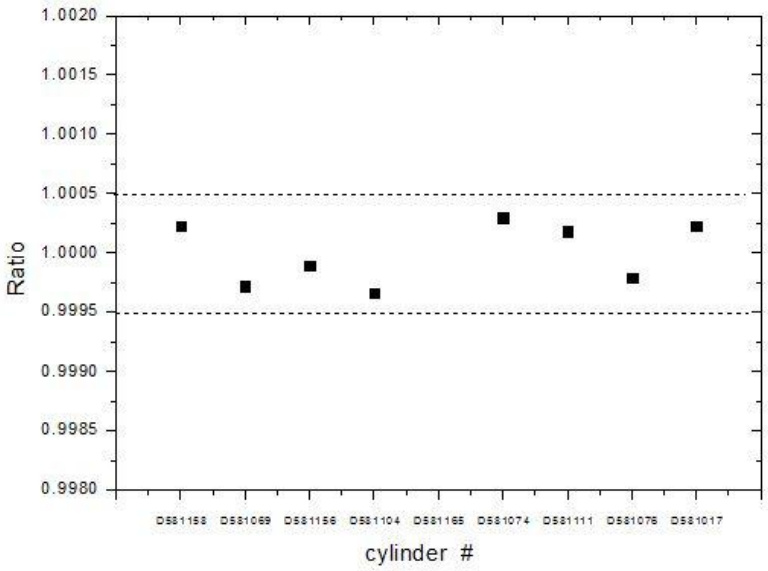

Figure 1. Consistency between gravimetrically prepared mixtures for this comparison (October 2017)

All cylinders showed agreement with the gravimetric reference value within ± 0.05% uncertainty. The prepared mixtures are summarized in Table 3, where uncertainty includes uncertainty components generated from verification analysis (< ± 0.05 %) and gravimetric preparation. Among the eight cylinders, six mixtures were used for this comparison.

Table 3: Preparation of measurement standards

Cylinder number	Gravimetric value [µmol/mol]	*U* from gravimetry (*k*=2) [µmol/mol]	*U* from preparation (*k*=2) [µmol/mol]
D581158	100.008	0.024	0.10
D581069	100.092	0.024	0.10
D581156	100.131	0.024	0.10
D581104	100.021	0.024	0.10
D581074	100.075	0.024	0.10
D581111	99.211	0.024	0.10
D581017	100.125	0.024	0.10
D581076	100.162	0.024	0.10

All cylinders were returned with sufficient pressure for re-analysis by October 2018. The results indicated that the mixtures remained stable during transport.

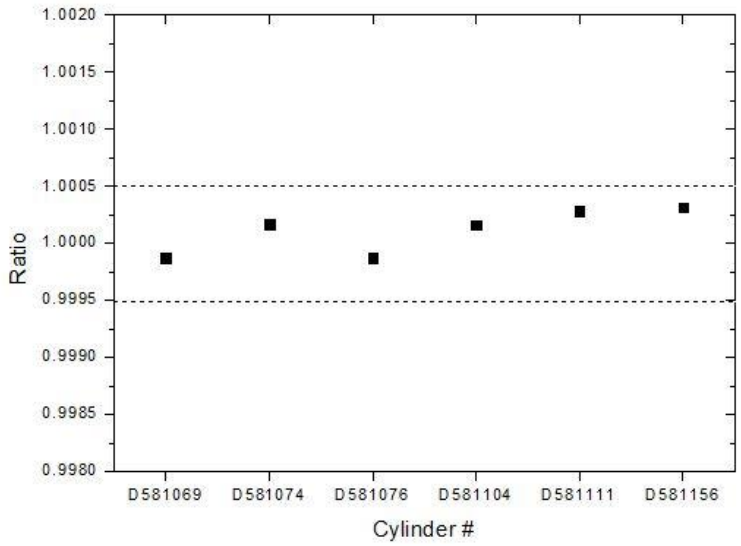

Figure 2. Reanalysis results of the returned cylinders (September 2018)

Results and Discussion

Some important items reported by the participants are summarized in Table 4. They all prepared their own standards for calibration. NIMT used NDIR (Non-dispersive InfraRed) calibrated with single point, while others used GC-FID with a single point calibration. The details of the analytical methods used by the participants are described in the individual participant reports.

Table 4: Summary of the analysis methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
NPLI	D581074	Apr. 2018	own standards	Single point	GC/FID/Methanator
KazInMetr	D581111	Mar. 2018	own standards	Single point	GC/FID/Methanator
NIMT	D581156	Dec. 2017	own standards	Single point	NDIR analyzer
NMC	D581104	Mar. 2018	own standards	Single point	GC/FID/Methanator
SNSU-BSN	D581069	Feb. 2018	own standards	Single point	GC/FID/Methanator
KRISS	D581076	Sep. 2018	own standards	Single point	GC/FID/Methanator

The results of the comparison are summarized in Table 5.

Table 5: Summary of the comparison of APMP.QM-S9.2017

Lab.	Cylinder	X_{prep}	u_{prep}	x_{lab}	U_{lab}	k_{lab}	Δx	$U(\Delta x)$	k
		[µmol/mol]					[µmol/mol]		
NPLI	D581074	100.08	0.05	98.27	0.60	2	-1.81	0.6	2
KazIn Metr	D581111	99.21	0.05	100.18	1.75	2	0.97	1.75	2
NIMT	D581156	100.13	0.05	100.18	0.24	2	0.05	0.26	2
NMC	D581104	100.02	0.05	99.97	0.30	2	-0.05	0.32	2
SNSU-BSN	D581069	100.09	0.05	101.241	1.117	2	1.15	1.12	2
KRISS	D581076	100.16	0.05	100.19	0.26	2	0.03	0.28	2

As shown in table 5, there a considerable deviation in the results from the cylinder provided to NPLI (D581074) and a slight deviation in the results from the cylinder provided to SNSU-BSN (D581069).

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 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-S9.2017 is presented in figure 3. As shown in figure 3, there was a considerable deviation in the results from the cylinder provided to NPLI (D581074).

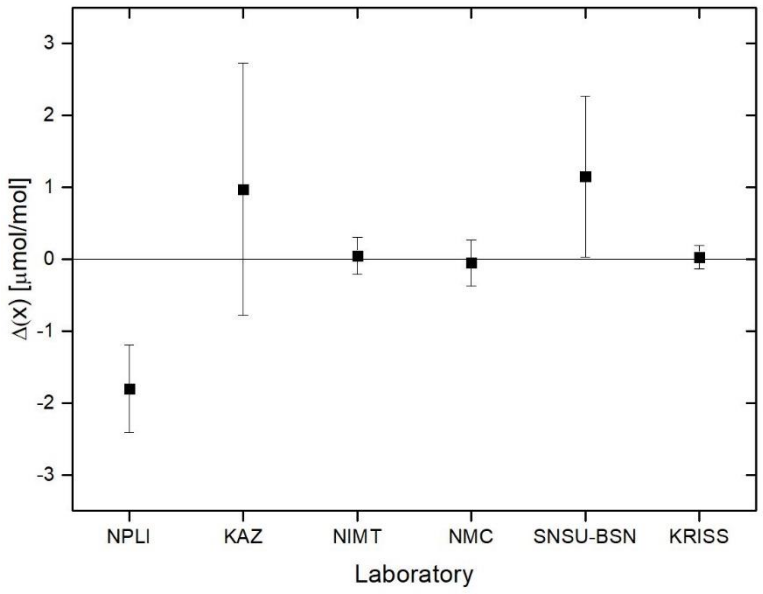

Figure 3: Degrees of equivalence for the APMP.QM-S9.2017 (*K*=2)

Conclusions

In the supplementary comparison, the results from four of the six 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 monoxide in N_2 at the range of 50 – 2000 μmol/mol. An extended range may be supported as described in the GAWG strategy [6] for comparisons and CMC claims.

Table 6: HFTLS list of each participant for CMC claims

Participant	Amount fraction (μmol/mol) from	Amount fraction (μmol/mol) to	Uncertainty (%) from	Uncertainty (%) from
NPLI	3.65	10	10	3.71
	10	500 000	3.71	3.71
KazInMetr	1.75	10	10	1.76
	10	500 000	1.76	1.76
NIMT	0.24	10	10	0.24

	10	500 000	0.24	0.24
NMC	0.30	10	10	0.30
	10	500 000	0.30	0.30
SNSU-BSN	2.56	10	10	2.53
	10	500 000	2.53	2.53
KRISS	0.26	10	10	0.26
	10	500 000	0.26	0.26

References

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

[2] Angella et al. International comparison APMP.QM-S9: Comparison of measurement capability with 100 μmol/mol of carbon monoxide in nitrogen, Metrologia 55 08007

[3] Lee et al. International comparison CCQM-K84: Carbon monoxide in synthetic air at ambient level, Metrologia 54 08016

[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

Report Form

Carbon monoxide in nitrogen

Laboratory name: CSIR-National Physical Laboratory, India (NPLI)

Cylinder number: D 581074

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	04/04/18	98.47	0.53	9

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	04/04/18	98.00	0.73	9

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	01/03/18	98.24	1.03	9

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	01/03/18	98.09	0.35	4

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	07/03/18	98.55	0.58	4

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

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor[2]
CO	98.27	0.60	*k*=2

Details of the measurement method used:

GC FID (Agilent 6890N) with Methanizer

Column used: Mol sieve 13x; length 10 ft

Oven temp: 80 ºC

Carrier gas: He (25 ml/min)

Methanizer temp.: 350 ºC

Detector Temp: 250 ºC

GSV loop: 0.25 ml

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

Details of the calibration method used:

Single point calibration method is used for the analysis. NPLI prepared CO gas standard of concentration 107.86 ± 0.33 µmole/mole is used for the calibration of GC-FID system for this analysis.

Details of the standards used:

Gas mixtures of CO in nitrogen gas were prepared in two series in the concentrations ~5 %mol/mol. The same cylinder was used for further dilution in two steps to prepare the concentration ranges ~100 µmol/mol for participation in APMP.QM S9.2017. The initial weighing of components transferred has been done using a top pan balance. The final weighing has been done using an equal arm balance Raymor HCE 25G max capacity

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

25kg with 1 mg sensitivity. These cylinders were validated in accordance to "ISO 6143: Gas analysis - Comparison method for determining and checking the composition of calibration gas mixtures". Thus the prepared gas mixtures were certified as CO in nitrogen gas (Primary Reference Gas Mixtures (PRGMs)).

Details on uncertainty budget:

The Uncertainty of the prepared gas mixtures has been estimated according to ISO 6142 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 effects
4. Residual gas
5. Expansion of the cylinder due to filling of gas at high pressure

II. Uncertainty Components in Analytical Method

- Repeatability
- Reproducibility
- GC response

Uncertainty Budget of analytical measurement is given in the table:

Measurement Uncertainty Budget									
Sources of Uncertainty	**Estimates x_i**		**value**		**Distribution/ Type A & B/ Divisor**	**Standard uncertainty $u(x_i)$**		**Sensitivity cofficient c_i**	**Relative standard uncertainty $u_i(y)$**
Assigned value	98.27	µmol/mol	0.24	µmol/mol	Normal/ Type A/ √5	0.11	µmol/mol	1	0.00107
Conc. of Std	107.86	µmol/mol	0.33	µmol/mol	Normal/ Type B/ 2	0.17	µmol/mol	1	0.00153
GC Response	154.79	mV	0.83	mV	Normal/ Type A/ √5	0.37	mV	1	0.00239
Combined standard Uncertainty, u_c	0.30	µmol/mol							
Expanded Uncertainty, U	0.60	µmol/mol	k=2						

Cylinder Pressure after the measurement: ~ 60 bar

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

REPORT ON

APMP- QM-S9.*2017*

APMP Regional Comparison
Carbon monoxide in Nitrogen (100 µmol/mol)

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02 March 2018

Report Form

Carbon monoxide in nitrogen

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

Cylinder number: **D581069 (APMP QM S-9.2017)**

Measurement:

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	08/02/2018	101.222	0.080	3

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	10/02/2018	101.250	0.033	4

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	11/02/2018	101.243	0.074	6

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	12/02/2018	101.235	0.057	7

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	13/02/2018	101.245	0.055	8

Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor [3]
CO	**17/02/2018**	**101.241**	**1.117**	***k* =2**

Details of the measurement method used:

Reference Method

Gas chromatography equipped with methanizer-flame ionization detector (GC methanizer-FID).

Instruments

The concentration of CO in gas mixtures was determined by gas chromatography using methanizer- flame ionization detection (GC methanizer-FID). A stainless steel packed column (Porapak Q, 6 feet, 1/8" outer diameter) was used for the separation of the CO from the mixtures. The FID gases used were H_2 (50 mL/min) and air (400 mL/min). The oven temperature was isothermal at 40°C. Ultra high purity of helium (99.999%) was used as a carrier gas at a flow rate of 28 mL/min. The methanizer and detector temperature were kept at 375°C and 250°C, respectively. 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 0.125 mL 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 (or CSGMs in short) of CO in N_2 were prepared by SNSU-BSN using gravimetric method in compliance with ISO 6142:2001[1]. The pre-mixtures were prepared from ultra-high purity of CO (Linde Indonesia) and ultra-high purity N_2 (SII-Indonesia). The purity of CO and N_2 were assessed prior to use for the CSGMs preparation and the purity tables (compositions) of the CO and N_2 gases are shown in Table 1 and Table 2, respectively. Six cylinders of CSGMs containing CO in N_2 were individually prepared, with a

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

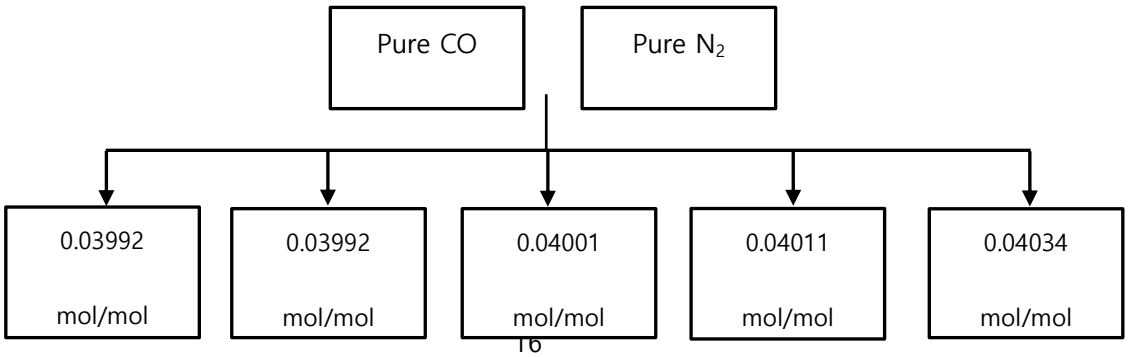
nominal concentration ~100 µmol/mol of each, by adopting a three-step dilution process as schematically shown in Figure 1. After preparation, gravimetric concentrations of CO in all prepared CSGMs cylinder were verified using method described in ISO 6143:2001[2] and the results are tabulated in Table 3.

Table 1. Purity table of pure CO (parent)

Component	Mole fraction (µmol/mol)	Standard uncertainty (µmol/mol)	Method of evaluation (type A or type B)	Analysis method
H_2O	2.500	1.443	B	Manufacturer specification
CO_2	151.522	10.150	A	PDHID
O_2	7.669	0.555	A	PDHID
CH_4	2.786	0.241	A	PDHID
Ar	0.520	0.044	A	PDHID
N_2	77.838	5.885	A	PDHID
CO	999757.167	11.836	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



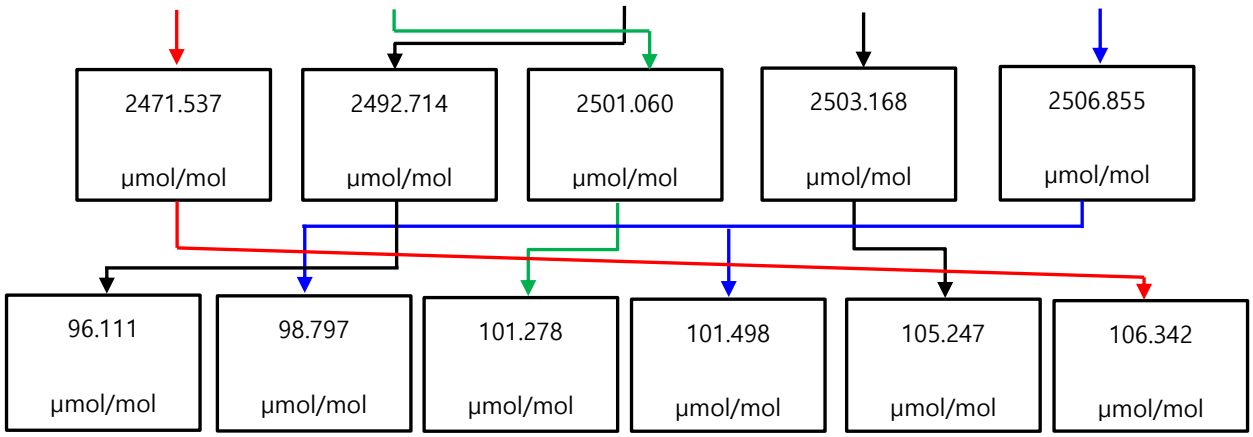


Figure 1. Three step dilution process of CSGMs at ~100 µmol/mol CO in N_2

Table 3. Calibration standard gas mixture (CSGMs)

# Cylinder	Concentration (µmol/mol)	$U_{combined}$ (µmol/mol)	$U_{expanded}$* (µmol/mol)	$U_{expanded}$ relative (%)
AH06027	96.111	0.504	1.007	1.048
AH06012	98.797	0.531	1.061	1.074
AH06005	**101.278**	**0.556**	**1.111**	**1.097**
AH06031	101.498	0.559	1.118	1.102
AH06017	105.247	0.600	1.201	1.141
AH06026	106.342	0.614	1.228	1.154

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

Weighing Data

Weighing data for cylinder #AH06005 are summarized as follows:

1st dilution mixture:

1. Evacuated cylinder #ADD007 - tare cylinder = -12.073 g (cylinder #ADD007)

2. Cylinder #ADD007 filled with parent CO - tare cylinder = -0.256 g (amount of parent CO transferred into #ADD007 = 11.817 g)
3. Cylinder #ADD007 filled with parent N_2 - tare cylinder = 283.871 g (amount of parent N_2 transferred into #ADD007 = 284.127 g)
4. Cylinder #ADD007 filled with parent CO (11.817 g) + parent N_2 (284.127 g) = 1st dilution mixture (cylinder #ADD007)

2nd dilution mixture:

1. Evacuated cylinder #AH06020 - tare cylinder = -61.171 g (cylinder #AH06020)
2. Cylinder #AH06020 filled with 1st dilution mixture #ADD007 - tare cylinder = -0.256 g (amount of 1st dilution mixture #ADD007 transferred into #AH06020 = 13.012 g)
3. Cylinder #AH06020 filled with parent N_2 - tare cylinder = 146.627 g (amount of N_2 transferred into cylinder #AH06020 = 194.787g)
4. Cylinder #AH06020 filled with 1st dilution mixture #ADD007 (13.012 g) + parent N_2 (194.787 g) = 2nd dilution mixture (cylinder #AH06020)

3rd dilution mixture:

1. Evacuated cylinder #AH06005 - tare cylinder : -44.054 g (cylinder #AH06005)
2. Cylinder #AH06005 filled with 2nd dilution mixture #AH06020 - tare cylinder = -32.288 g (amount of 2nd dilution mixture #AH06020 transferred into #AH06005 = 11.766 g)
3. Cylinder #AH06005 filled with parent N_2 - tare cylinder = -250.191 g (amount of N_2 transferred into cylinder #AH06005 = 282.479g)
4. Cylinder #AH06005 filled with 1st dilution mixture #AH06020 (11.766 g) + parent N_2 (282.479) = 3rd dilution mixture (cylinder #AH06005)

Details of the standards used for instrument calibration:

The six CSGMs were used to generate a calibration curve as a preliminary evaluation of CO concentration in the sample cylinder #D581069. The evaluation was conducted under identical

conditions. Subsequently, a prepared CSGM having a GC signal response close to that of sample cylinder #D581069 was selected for single-point calibration to determine the concentration of CO in sample cylinder. Based on our evaluation, it was found that the CO in cylinder #AH06005 had the closest GC signal response relative to that of GC signal response of CO in sample cylinder #D581069. Therefore, the CSGM cylinder #AH06005 was selected as a reference standard for the single-point calibration process to determine the CO concentration in the sample #D581069.

The single-point calibration consists of several sets of measurement (at least three set of measurements) in different period of time (days). The order of measurement was A-B-A (A is the cylinder #AH06005 as reference standard, and B is the sample cylinder #D581069). 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 in sample cylinder #D581069.

Sample handling

After arrival, the sample cylinder #D581069 was stabilised in the laboratory environmental by keeping the sample cylinder in the laboratory for 48 h. Each cylinder (CSGMs #AH06005 and sample #D581069) was equipped with an Alphagaz double stage pressure regulator that was adequately purged.

Details of uncertainty budgets:

Uncertainty evaluation for the prepared CSGM #AH06005

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

$$C_{CO} = \frac{\sum_{A=1}^{P}\left[\frac{x_{CO,A}.m_A}{\sum_{i=1}^{n} x_{i,A}.M_i}\right]}{\sum_{A=1}^{P}\left[\frac{m_A}{\sum_{i=1}^{n} x_{i,A}.M_i}\right]}$$

(**1**)

The C_{CO} was calculated as the mole of the total CO transferred from each parent gas ($\sum_{A=1}^{P}\left[\frac{x_{CO,A}.m_A}{\sum_{i=1}^{n} x_{i,A}.M_i}\right]$) 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 #AH06005, the uncertainty contributor 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 # AH06005 was calculated by means of Equation 2 (Eq. 2).

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

(**2**)

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

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

(**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).

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

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 equationss represented by the Eq. 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.

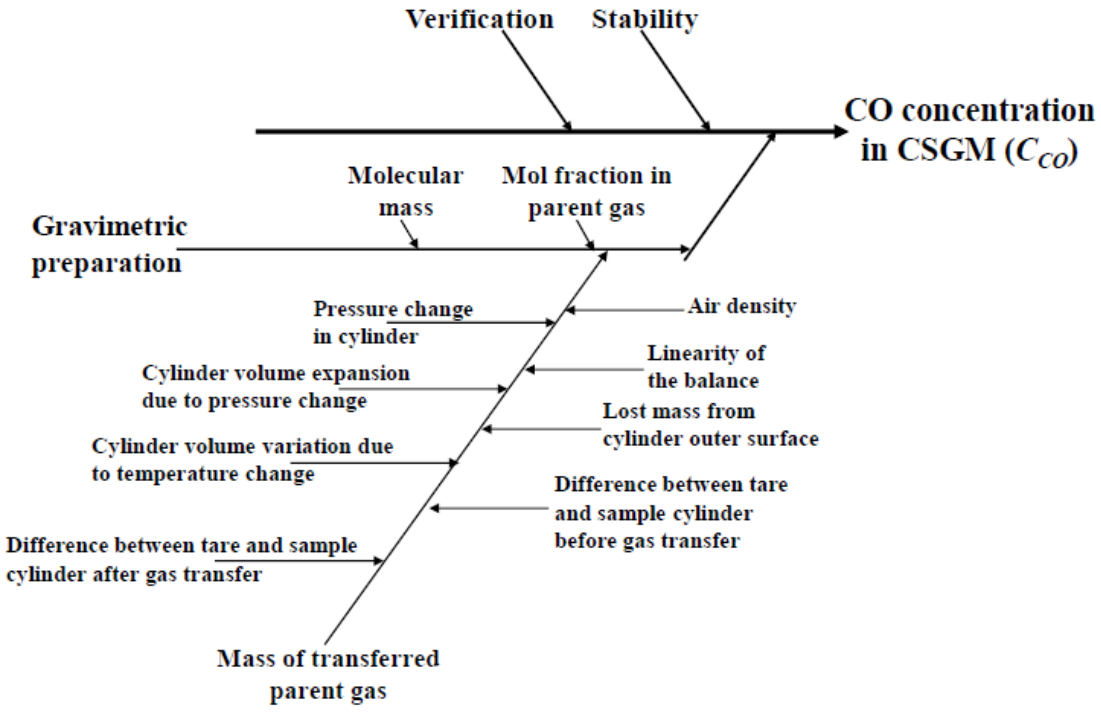


Figure 1. Fishbone diagram of uncertainty sources affecting the final concentration of CSGMs

Table 4. Uncertainty budgets for the CSGM #AH06005

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 #AH06020			

b. Weighing of transferred parent gas N_2			
2. Mole fraction of components in parent gas #AH06020 and parent N_2 :	11.766 g	0.003 g	A
a. H_2O in #AH06020	282.479 g	0.003 g	A
b. CO in #AH06020			
c. CO_2 in #AH06020			
d. O_2 in #AH06020			
e. Ar in #AH06020			
f. CH_4 in #AH06020			
g. N_2 in #AH06020	0.00000150 mol/mol	0.00000081 mol/mol	B
h. H_2O in parent N_2	0.00250106 mol/mol	0.00000787 mol/mol	B
i. CO in parent N_2	0.00000040 mol/mol	0.00000003 mol/mol	B
j. CO_2 in parent N_2	0.00000585 mol/mol	0.00000033 mol/mol	B
k. O_2 in parent N_2	0.00000091 mol/mol	0.00000006 mol/mol	B
l. Ar in parent N_2	0.00000269 mol/mol	0.00000022 mol/mol	B
m. CH_4 in parent N_2	0.99748759 mol/mol	0.00000134 mol/mol	B
n. N_2 in parent N_2	0.00000150 mol/mol	0.00000087 mol/mol	A
3. Molecular mass of all components in the mixture (based on IUPAC) :	0.00000132 mol/mol	0.00000011 mol/mol	A
a. H_2O	0.00000002 mol/mol	0.00000001 mol/mol	A
b. CO	0.00000585 mol/mol	0.00000035 mol/mol	A
c. CO_2	0.00000092 mol/mol	0.00000006 mol/mol	A
d. O_2	0.00000269 mol/mol	0.00000023 mol/mol	A
e. Ar	0.99998771 mol/mol	0.00000097 mol/mol	A
f. CH_4			
g. N_2			
	18.01528000 g/mol	0.00000087 g/mol	B
	28.01040000 g/mol	0.00000011 g/mol	B
	44.00950000 g/mol	0.00000001 g/mol	B
	31.99880000 g/mol	0.00000035 g/mol	B
	39.94800000 g/mol	0.00000006 g/mol	B
	16.04246000 g/mol	0.00000023 g/mol	B
	28.01348000 g/mol	0.00000097 g/mol	B

Combined uncertainty from the gravimetric preparation (using Eq. 3)	0.000000333 mol/mol	B
Verification of the CSGM concentration	0.000000372 mol/mol	A
Stability testing of the CSGM	0.000000227 mol/mol	A
Combined uncertainty of the CSGM (using Eq. 2)	0.000000556 mol/mol	
Expanded uncertainty for confidence level of 95% (k=2)	0.000001111 mol/mol (**1.111 µmol/mol**)	

- ***Measurand and expanded uncertainty*** . Measurand and expanded uncertainty of prepared CSGM #AH06005 are listed in table

Table 5. Measurand ($\boldsymbol{C}_{\text{CSGM\#AH06005}}$) and expanded uncertainty ($\boldsymbol{U}_{\text{CSGMs-\#AH06005}}$)

CSGM	Assigned value (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor*
#AH06005	**101.278 µmol/mol**	**1.111 µmol/mol**	**k = 2**

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

Uncertainty evaluation for the Sample #D581069

- ***Model equation***: a model equation (Eq. 5) below was used to calculate CO concentration in the sample #D581069 (measurand).

$$C_{sample\ \#D581069} = \left(\frac{Response\ area_{sample\ \#D581069}}{Response\ area_{standard\ \#AH06005}}\right) x\ C_{standard\ \#AH06005} \quad (5)$$

- ***Uncertainty budget***: For the uncertainty of sample #D581069, the estimation was performed by modifying Eq. 5 based on the propagation rules[3], resulting in an equation 6 (Eq. 6) below.

$$\left(\frac{u_{C_{sample\ \#D581069}}}{C_{sample\ \#D581069}}\right)^2 = \left(\frac{u_{\left(A_{sample\ \#D581069}/A_{standard\ \#AH06005}\right)}}{A_{sample\ \#D581069}/A_{standard\ \#AH06005}}\right)^2 + \left(\frac{u_{C_{standard\ \#AH06005}}}{C_{standard\ \#AH06005}}\right)^2 \quad (\mathbf{6})$$

Based on Eq. 6, there are two sources of uncertainty of the sample #D581069 concentration, i.e., 1). Repeatability of the ratio between detector's response of sample #D581069 and detector's response of standard #AH06005 ($u_{\left(A_{sample\ \#D581069}/A_{standard\ \#AH06005}\right)}$), and 2). Uncertainty of standard concentration #AH06005 ($u_{C_{standard\ \#AH06005}}$). The details of uncertainty budgets for the sample #D581069 are listed in Table 6.

Table 6. Uncertainty budgets for the sample #D581069

Uncertainty source $\mathbf{X_i}$	**Estimated value** $\mathbf{x_i}$	**Assumed distribution**	**Standard uncertainty** $\boldsymbol{u}$ **(**$\mathbf{x_i}$**)**	**Sensitivity coefficient** $\mathbf{c_i}$	**Contribution to standard uncertainty** $\mathbf{u_i}$ **(%)**
Ration of detector's					

response to sample and standard, $u_{(A_{sample}/A_{standard})}$	0.9996	normal	0.001	101.278	1.073
Uncertainty of CSGM #AH06005	101.278 µmol/mol	normal	0.556 µmol/mol	0.9996	98.927
Combined Uncertainty of sample #D581069			**0.558** µmol/mol		
Expanded Uncertainty, confidence level 95% (*k*=2)			**1.117** µmol/mol		

- ***Measurand and expanded uncertainty*** : Measurand and expanded uncertainty of sample #D581069 are listed in Table 7**.**

Table 7. Measurand and expanded uncertainty of sample #D581069

Sample	*Concentration* (µmol/mol)	*Expanded uncertainty* (µmol/mol)	Coverage factor*
#D581069	**101.241**	**1.117**	***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).

APMP-QM-S9: Carbon Monoxide in Nitrogen (100 µmol/mol)

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

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

Cylinder number: KRISS D581104

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO	28/2/2018	100.016	0.122	5

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO	1/3/2018	99.979	0.071	5

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard Deviation (% relative)	Number of Replicates
CO	2/3/2018	99.924	0.084	5

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor[4]
CO	**99.97**	**0.30**	2

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:

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

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 D581104 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 3 separate cylinders with the following details:

Reference Standard	Cylinder No.	Concentration (μmol/mol)	Gravimetric Uncertainty (μmol/mol)
Reference Standard	PSM118720	99.86	0.043

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

1.1. Uncertainty Budget of Pure CO

Components		Distribution	Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	N_2	Normal	2.692E-04	1.384E-06
Impurity	CH_4	Normal	5.010E-06	2.928E-07

Impurity	C_2H_6	rectangular	5.000E-08	2.887E-08
Impurity	O_2	rectangular	2.500E-08	1.443E-08
Impurity	H_2	Normal	1.920E-06	2.900E-07
Impurity	Ar	Normal	6.760E-05	5.459E-07
Impurity	CO_2	Normal	7.890E-06	2.963E-07
Impurity	H_2O	rectangular	2.500E-06	1.443E-06
Balance gas	CO		0.99964581	2.135E-06

1.2. Uncertainty Budget of Pure N_2

Components		Distribution	Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	O_2	rectangular	2.500E-08	1.443E-08

Impurity	CO	rectangular	2.500E-08	1.443E-08
Impurity	H_2	rectangular	2.500E-08	1.443E-08
Impurity	CO_2	rectangular	5.000E-08	2.887E-08
Impurity	CH_4	rectangular	5.000E-08	2.887E-08
Impurity	H_2O	rectangular	1.000E-08	5.774E-09
Impurity	Ar	normal	8.630E-07	2.101E-07
Balance gas	N_2		0.999998952	2.155E-07

1.3. Gravimetric Preparation Uncertainty Budget for Reference Standard

Preparation uncertainty budget for Reference Standard at 4.75% CO in nitrogen mixture was evaluated in the below table.

Uncertainty source	Estimated Value	Standard Uncertainty	Distribution	Contribution to Standard Uncertainty (μ

				mol/mol)
Mass of CO (g)	27.182	0.0065	normal	10.87
Mass of N_2 (g)	544.915	0.0082	normal	0.68
Concentration of CO in pure CO gas (mol/mol)	9.9964581E-01	2.13E-06	normal	0.10
Concentration of CO in N_2 gas (mol/mol)	2.50E-08	1.44E-08	normal	0.014
Molar mass of CO (g/mol)	28.01080	0.00062	normal	0.99
Molar mass of N_2 (g/mol)	28.01372	0.00049	normal	0.79
Combined Uncertainty (k = 1)				**11.0**

Preparation uncertainty budget for Reference Standard at 2329.65 μmol/mol, which was diluted from the 4.75% CO premix gas.

Uncertainty source	Estimated Value	Standard Uncertainty	Distribution	Contribution to Standard Uncertainty (μmol/mol)
Mass of CO (g)	26.439	0.0065	normal	0.55

Mass of N_2 (g)	512.650	0.0082	normal	0.04
Concentration of CO in premix gas (mol/mol)	4.75E-02	1.10E-05	normal	0.54
Concentration of CO in N_2 gas (mol/mol)	2.50E-08	1.44E-08	normal	0.014
Molar mass of premix (g/mol)	28.01358	0.00047	normal	0.037
Molar mass of N_2 (g/mol)	28.01372	0.00049	normal	0.039
Combined Uncertainty (k = 1)				**0.77**

Preparation uncertainty budget for Reference Standard at 99.86 μmol/mol, which was diluted from the 2329.65 μmol/mol CO premix gas.

Uncertainty source	**Estimated Value**	**Standard Uncertainty**	**Distribution**	**Contribution to Standard Uncertainty (μmol/mol)**
Mass of CO (g)	26.839	0.0065	normal	0.023
Mass of N_2 (g)	599.432	0.0082	normal	0.0013
Concentration of CO i	2.33E-03	7.70E-07	normal	0.033

n premix gas (mol/mol)				
Concentration of CO in N_2 gas (mol/mol)	2.50E-08	1.44E-08	normal	0.014
Molar mass of premix (g/mol)	28.01371	0.00049	normal	0.0017
Molar mass of N_2 (g/mol)	28.01372	0.00049	normal	0.0017
Combined Uncertainty (k = 1)				**0.043**

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 uncertainty of gravimetric process, purity analysis, verification and stability check. As the CO gas mixtures which NMC used for this comparison were new prepared. We estimated the uncertainty of stability was negligible.

Uncertainty Evaluation for the Measurement					
Uncertainty Source	**Value**	**Standard Uncertainty**	**Distribution**	**Sensitivity Coefficient**	**Uncertainty Contribution (*µmol/mol*)**
Y_{sample}	109.04	0.095	Normal	0.917	0.09
Y_{std}	108.92	0.042	Normal	-0.918	0.04
X_{std}	99.86	0.112	Normal	1.001	0.11
Reproducibility		0.027	Normal	1	0.027
Combined Uncertainty (*µmol/mol*)					0.15
Expanded Combined Uncertainty (*µmol/mol*) ; k = 2					0.30
Expanded Combined Uncertainty (*Relative %*) ; k = 2					0.30%

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

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

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

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

Based on the above uncetainty model, the final uncetainy evaluation for the measuremwrnt w as evaluated in the below table.

Measurand: 99.97 μmol/mol

Coverage factor: k = 2

Expanded Uncertanty: 0.30 μmol/mol, relative 0.30%

Report Form

Carbon monoxide in nitrogen

Laboratory name: National Institute of Metrology (Thailand)

Cylinder number: D581156

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	14/12/2017	100.171	0.052	3

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	14/12/2017	100.170	0.010	3

Measurement #3[5]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	14/12/2017	100.191	0.006	3

Results

Component	Result (µmol/mol)	Expanded Uncertainty (% relative)	Coverage factor[6]
CO	100.18	0.24	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 NDIR analyzer at the inlet pressure 100 kPa and flow rate 1.2 LPM. 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 monoxide 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 three times for each measurement series.

Details of the calibration method used:

The NDIR analyzer was performed following the single point calibration by primary gas reference material (PGRM) at the inlet pressure 100 kPa and flow rate 1.2 LPM. The mole fraction of the PGRM used was closed to the target mole fraction of carbon monoxide in the sample cylinder.

Details of the standards used:

The PGRMs used in the measurements are binary mixtures of the carbon monoxide in nitrogen. They are traceable to the National Institute of Metrology (Thailand). The mole fraction of PGRM s used was determined in compliance with ISO 6142-1 by using gravimetric method and verified by using NDIR analyzer calibrated by using one of the PGRM s. The purity of Nitrogen is more than 99.9995% and the purity of carbon monoxide is more than 99.95%. These standard gas mixtures used were prepared by 3-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.

.

Table 1. Concentration of PGRMs.

Cylinder number	Assigned value	Expanded uncertainty (Relative value, $k = 2$)

PRM 112708	100.17 μmol/mol	0.2%
PRM 112727	100.06 μmol/mol	0.2%

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 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	100.17	B	Normal	0.100	1.0	0.100
Response of standard gas mixture	99.592	A	Normal	0.041	1.0	0.041
Response of sample gas mixture	99.600	A	Normal	0.043	1.0	0.043
Analytical content of sample	100.18	Combined Uncertainty, (%relative)				0.12
		Expanded Uncertainty, ($k=2$) , (%relative)				0.24

Authorship

Ms.Ratirat Sinweeruthai, Mr.Soponrat Rattanasombat

APMP Regional Comparison

Carbon monoxide in Nitrogen (100 µmol/mol)

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

Cylinder number: D581111

I. Measurement

Measurement #1	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	15.03.2018	100,16	0,30	5

Measurement #2	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	16.03.2018	100,49	0,27	5

Measurement #3	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	19.03.2018	99,57	0,57	5

Measurement #4	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	20.03.2018	100,20	0,29	5

Measurement #5	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	21.03.2018	100,28	0,18	5

Measurement #6	Date	Result, µmol/mol	Standart deviation (% relative)	Number of replicates
Carbon monoxide in Nitrogen	22.03.2018	100,36	0,26	5

Result

Component	Result, µmol/mol	Coverage factor*)	Expanded Uncertainty, µmol/mol
Carbon monoxide in Nitrogen	100,18	2	1,75

*) The coverage factor based on 95% confidence.

II. Measurement Details for APMP-QM-S9.2017

Instruments

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

Carrier gas: argon.

Volume size: 1 ml.

Chromatographic column: Carboxen 1000, 3m 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 monoxide, 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 monoxide The cylinder capacity of 40 dm3 Manufacturer: - Certified in the Federal State Unitary Enterprise "VNIIM" them. D.I. Mendeleev	CO	99,588	0,1
Nitrogen The cylinder capacity of 40 dm3 Manufacturer: The Republic of Kazakhstan	N_2	99,98	0,01

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-147, 4 dm^3, 01.2016 r.	CO	105,29	0,3
	N_2	-	
PV-147-1, 4 dm^3, 01.2018 r.	CO	99,66	0,3
	N_2	-	
PV-147-2, 4 dm^3, 01.2018 r.	CO	110,55	0,3
	N_2	-	
PV-147-3, 4 dm^3, 01.2018 r.	CO	93,96	0,3
	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 (PV-147, PV-147-1, PV-147-2, PV-147-3). 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	6rd measurement
Regression coefficient a_1	3,703197E+01	3,914021E+01	3,851304E+01	3,483946E+01	3,488498E+01	3,757696E+01
Regression coefficient a_1 uncertainty $u(a_1)$	1,575342E+00	1,601883E+00	1,599352E+00	1,683833E+00	1,398628E+00	1,601179E+00
Regression coefficient a_0	-1,157817+02	-3,540308E+02	-3,449929E+02	1,527315E+02	2,431744E+02	-2,537749E+02
Regression coefficient a_0 uncertainty $u(a_0)$	1,6657930E+02	1,682289E+02	1,682656E+02	1,664969E+02	1,394972E+02	1,678173E+02
Covariance $cov(a_0, a_1)$	-2,609398E+02	-2,692473E+02	-2,688789E+02	-2,801022E+02	-1,949008E+02	-2,684727E+02

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	0,29 µmol/mol	1	0,29 µmol/mol
Uncertainty associated with the instrument response	-	Normal	0,83 µmol/mol	1	0,83 µmol/mol

Coverage factor: k = 2.

Expended uncertainty: 1,75 µmol/mol.

APMP.QM-S9.2017 Carbon monoxide in nitrogen

Laboratory name: KRISS

Cylinder number: D581076

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
CO	29.10.2017	100.16	0.07	4

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
CO	20.9.2018	100.08	0.05	4

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
CO	2.10.2018	100.33	0.05	5

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor[7]
CO	100.19	0.26	2

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

Details of the measurement method used:

Analysis method:

Carbon monoxide concentration in nitrogen has been quantified using gas chromatograph Flame ionization detector with Methanator (GC-FID/Methanator). 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. The cylinder D015343 were analyzed as the reference mixture against the prepared seven cylinders.

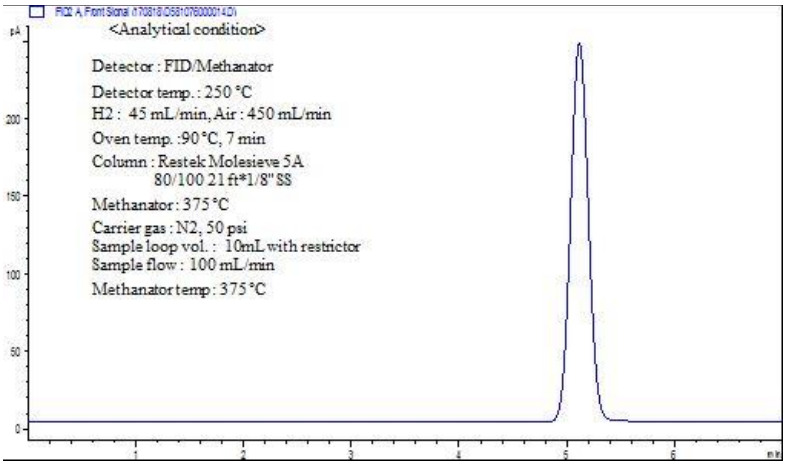


Figure 1. Analytical condition and chromatogram of CO

Details of the calibration method used:

Instrument calibration is performed using KRISS primary standard mixtures. One point calibration (D081198 and D581165) was done with a cylinder of nominal value ~ 100 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 100 mL/min using the mass-flow controller.

Calibration standards:

Preparation method

The standards were prepared from pure carbon monoxide, pure nitrogen, and pure oxygen in accordance with ISO6142:2001 (Gas analysis-preparation of calibration gases-gravimetric method). Pure carbon monoxide was diluted by 3 stages and purity analysis for every pure gases were done. Table 1 shows gravimetric value and expanded uncertainty of the calibration standards. They agreed within 0.1 % as shown in Figure 2.

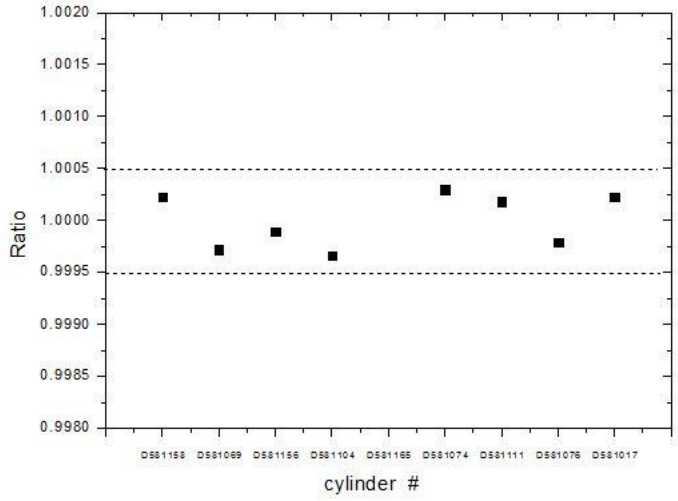


Figure 2. Consistency among primary standard mixtures

2 primary standard mixtures were used for the determination of carbon monoxide in Nitrogen.

Table 1. Gravimetric value and expanded uncertainty in calibration standards

Cylinder number	Gravimetric value (μmol/mol)	Expanded uncertainty [*k*=2] (μmol/mol)
D581165	100.03	0.031
D081198	100.26	0.034

Purity analysis

The impurities of carbon monoxide, nitrogen, and oxygen were determined by analytical method whose results are from APMP-QM.S9[ref].

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.

Detailed uncertainty budget:

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

$$C_{\text{final}} = \frac{A_{sample}}{A_{crm}} \times \mathrm{C_{crm}}$$

Typical evaluation of the of the measurement uncertainty for CO:

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 D081198(before)		3146.27	A	Gaussian	0.25	-0.016	-0.0018
D081198(after)		3147.09			0.24	-0.016	-0.0018
Area[arb.]							
Response_Sample D581076 Area[arb.]		3141.05	A	Gaussian	0.06	0.032	0.0019
Reference prepared grav. [µmol/mol]	D081198	100.26	B	Gaussian	0.05	1.0	0.050
	D081103	100.03			-	-	
Amount_sample [µmol/mol]		100.08					
Combined standard uncertainty [µmol/mol]					0.05		