APMP.QM-S9

Final Report

- Comparison of measurement capability with 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
UME(Turkey), NPLI(India), CMS/ITRI (Taiwan), KRISS (Korea)

Background

Carbon monoxide (CO) in nitrogen was one of the first types of gas mixtures used in 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. Recently, NMIs in the APMP region have actively participated in international comparisons to provide domestic services. At the 2013 APMP meeting, several NMIs requested a CO comparison to establish CO/N_2 certification for industrial applications, which was to be coordinated by KRISS. Consequently, this comparison provides an opportunity for APMP regional NMIs to develop CO/N_2 CMC claims.

How Far Does the Light Shine

The goal of this supplementary comparison is to support CMC claim for carbon monoxide in the N_2 range of 50 – 2000 µmol/mol. An extended range may be supported as described in the GAWG strategy for comparisons and CMC claims

Amount of substance

Component	Nominal amount
Carbon monoxide	100 µmol/mol
Nitrogen	Balance

Participants

Table 1 lists the participants in this key comparison

Table 1: List of participants

Acronym	**Country**	**Institute**
UME	Turkey	Ulusal Metroloji Enstitüsü, Turkey
NPLI	India	National Physical Laboratory, New Delhi, India
CMS/ITRI	Taiwan	Center for Measurement Standards, Industrial Technology Research Institute, Hsinchu, Taiwan
KRISS	Korea	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea

Schedule

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

Table 2: Schedule

Nov. 25, 2013 Proposal for the supplementary comparison of CO/N_2 at approximately 100

	μmol/mol
Sep. 1, 2014	Protocol preparation by KRISS
Oct., 2014	Approval of the comparison
Through May, 2015	Registration and protocol circulation
Through June, 2015	Preparation and distribution of mixtures by KRISS
Through July, 2015	Measurement by participants and reports sent to KRISS
Through Feb., 2016	Cylinders returned to KRISS
Through July, 2016	Second verification of returned cylinders
Through Nov., 2016	Draft A report
Through Sep., 2017	Draft B Report

Preparation of measurement standards

A total of eight gas mixtures were prepared gravimetrically using three step dilutions in June 2015 and verified with a GC (Gas Chromatograph)/FID (Flame Ionization Detector) methaniser analyzer in July 2015. The amount fraction of each mixture was determined based on the gravimetric method, and a purity analysis was used as a reference value. This implies that each cylinder has a unique reference value. The purity of CO was checked using several measurement techniques. A GC-TCD (Thermal Conductivity Detector) was used to identify impurities in CO. A GC-PDD (Pulsed Discharge helium ionization Detector) was used to analyze the sum of oxygen and argon, because a separation of two compounds is very hard [CCQM-K53]. The analysis yielded an amount fraction of 0.93 μmol/mol with an uncertainty of 0.19 μmol/mol (k = 2). A GC-FID was used to analyze total hydrocarbons, and with the Dew Point Meter method for water vapor. The purity of CO was assigned as 99.99%. The purity of N_2 was verified in the same manner. As a result, the purity of N_2 was assigned as 99.99%. CO in the pure N_2 cylinder was less than 0.01 μmol/mol, which was considered negligible. Table 3 and 4 show summarized results of purity analyses for CO and N_2.

Table 3. Results of purity analysis of Carbon monoxide (QA8272)

component	Analytical conc. (μmol/mol)	Detector	distribution	Applied conc. (μmol/mol)	Standard uncertainty (μmol/mol)
H_2	<0.26	GC/AED	rectangular	0.13	0.075
H_2O	<1.0	Dew Point Meter	rectangular	0.5	0.289
CH_4	<0.08	GC/AED	rectangular	0.04	0.023
CO_2	<1.02	GC/TCD	rectangular	0.51	0.294
THC	<1.0	GC/FID	rectangular	0.5	0.289
N_2	4.13	GC/AED	normal	4.13	0.413
O_2+Ar	0.93	GC/PDD	normal	0.93	0.093
			impurities	6.74	0.662
			CO	**999993.26**	**1.325 (*k*=2)**

Table 4. Results of purity analysis of Nitrogen (NK02608)

component	Analytical conc. (μmol/mol)	Detector	distribution	Applied conc. (μmol/mol)	Standard uncertainty (μmol/mol)
H_2	<0.5	GC/PDD	rectangular	0.25	0.144
H_2O	1.2	Dew Point Meter	Normal	1.2	0.120
CO	<0.002	GC/FID	rectangular	0.001	0.001
CH_4	<0.001	GC/FID	rectangular	0.0005	0.000
CO_2	<0.01	GC/FID	rectangular	0.005	0.003
THC	<0.5	GC/FID	rectangular	0.25	0.144
Ar	<1.0	GC/TCD	Rectangular	0.5	0.289
O_2	0.35	GC/PDD	Normal	0.35	0.035
Ne	<0.1	GC/TCD	Rectangular	0.5	0.289
			impurities	3.057	0.473
			N_2	**999996.944**	**0.947 (*k*=2)**

Expanded uncertainties of the gravimetric preparation were evaluated as 0.100 % (k = 2), as shown in Table 5.

After weighing, all prepared mixtures were analyzed to verify their compositions. 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).

$$R_i = \frac{S_i}{S_{i^{th}-drift\ corrected}} \qquad \text{(eq. 1)}$$

where

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

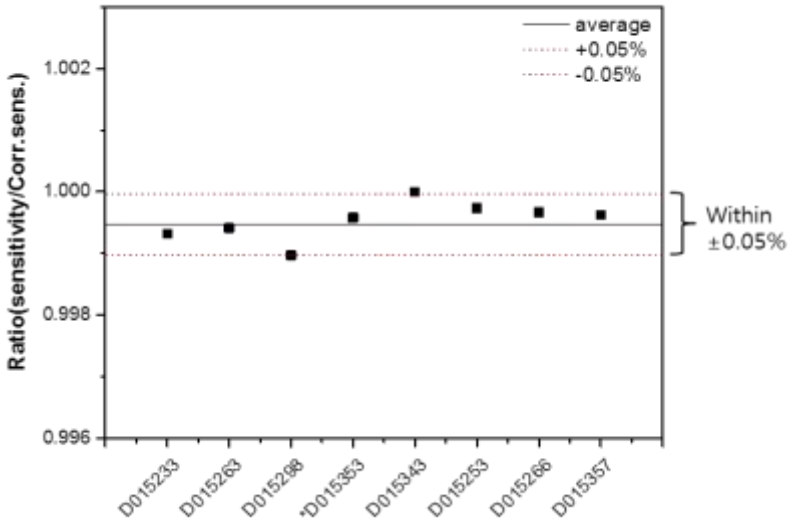

Figure 1. Consistency between gravimetrically prepared mixtures

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 %, σ) and gravimetric weighing. Among the eight cylinders, four mixtures were used for this comparison.

Table 5: Preparation of measurement standards

Cylinder number	Gravimetric value [µmol/mol]	U from gravimetry (*k*=2) [µmol/mol]	U from preparation (*k*=2) [µmol/mol]
D015233	95.637	0.031	0.1
D015298	100.941	0.033	0.1
D015343	101.151	0.034	0.1
D015253	105.080	0.034	0.1
D015263	99.987	0.032	0.1
D015266	101.594	0.032	0.1
D015353	101.086	0.032	0.1
D015357	101.158	0.031	0.1

All cylinders were returned with sufficient pressure for re-analysis in February 2016. The results indicated that

the mixtures remained stable during transport.

Results and Discussion

Some important items reported by the participants are summarized in Table 6. They all prepared their own standards for calibration. UME used CRDS (Cavity Ring-Down Spectroscopy) calibrated with multiple points, 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 6: Summary of the analysis methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
UME	D015357	Aug. 2015	in-house	Multiple point	CRDS
NPLI	D015266	Nov. 2015	in-house	Single point	GC/FID/Methanator
CMS/ITRI	D015263	Sep. 2015	in-house	Single point	GC/FID/Methanator
KRISS	D015353	Jul. 2015	in-house	Single point	GC/FID/Methanator

The results of the comparison are summarized in Table 7.

Table 7: Summary of the comparison of APMP.QM-S9

Lab.	Cylinder	X_{prep}	u_{prep}	x_{lab}	U_{lab}	k_{lab}	Δx	U(Δx)	k
		[μmol/mol]					[μmol/mol]		
UME	D015357	101.16	0.05	101.13	0.09	2	-0.03	0.14	2
NPLI	D015266	101.59	0.05	99.81	1.51	2	-1.78	1.51	2
CMS/ITRI	D015263	99.99	0.05	99.74	0.50	2	-0.25	0.51	2
KRISS	D015353	101.09	0.05	101.07	0.08	2	-0.02	0.13	2

Figure 2 shows a comparison of the prepared and reported values for each cylinder. In the figure, most values agree with the preparation values. D015266 deviated from the preparation value.

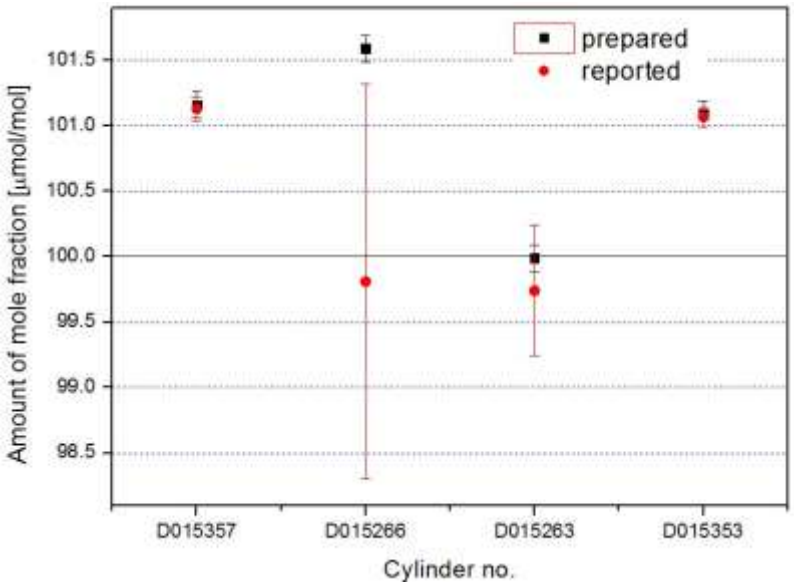

Figure 2: A comparison of the prepared (black filled square) and reported (red filled circle) values; vertical bars show each expanded uncertainty

As shown in figure 2, there was a deviation and large error in the results from the cylinder provided to NPLI (D015266). This result was due to a minor leakage problem in the sample loop of their GC that was used in the gas analysis in November 2015.

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

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

The degrees of equivalence (DoE) for the APMP.QM-S9 is presented in figure 3.

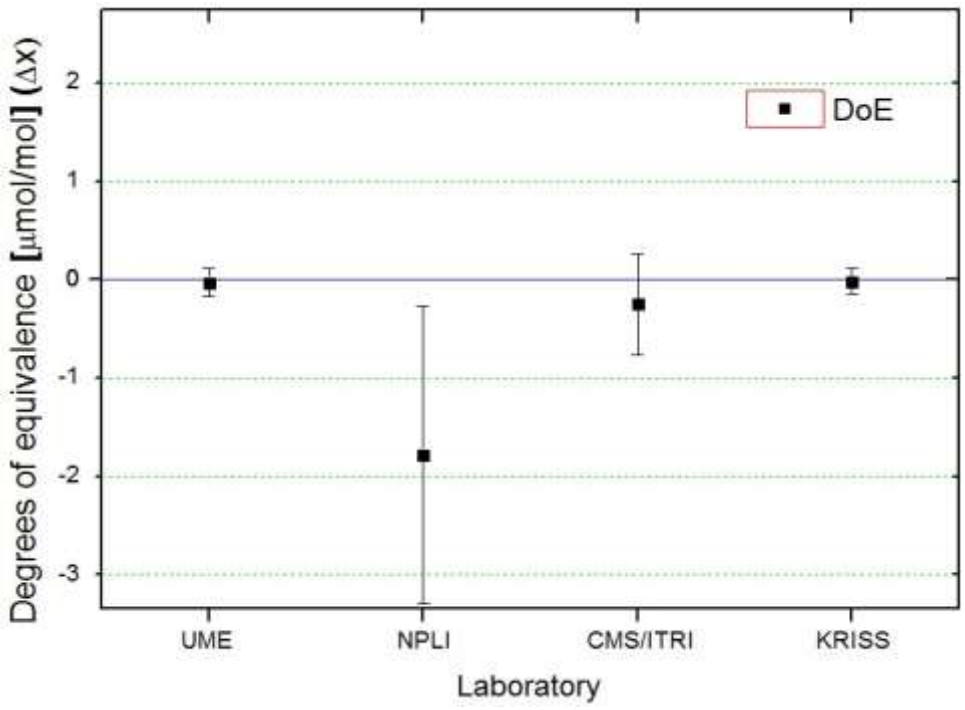

Figure 3: Degrees of equivalence for the APMP.QM-S9 (*K*=2)

Conclusions

In the comparison, the results from three of the four participants were consistent with their KCRV within the associated uncertainties. Furthermore, the negative bias against the reference value in the figure 3 suggests that the participants' in-house standards had slightly higher values than the prepared standard.

This supplementary comparison supports the measurement capability of 100 μmol/mol CO in N_2.

References

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

[2] International organization for standardization, ISO 6142. "Preparation of calibration gas mixtures, Gravimetric method", ISO, Third edition, 2001(E)

[3] International organization for standardization, ISO 6143. "Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures", ISO, 2001.

APMP.QM-S9 Carbon monoxide in nitrogen

Laboratory name: UME

Cylinder number: D015357

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	27.08.2015	101.13	0.03	60

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	28.08.2015	101.12	0.04	60

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	31.08.2015	101.14	0.02	60

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	01.09.2015	101.14	0.03	60

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	02.09.2015	101.13	0.02	60

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor[1]
CO	101.13	0.09	2

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

Details of the measurement method used:

The carbon monoxide (CO) in nitrogen (N_2) was analyzed on a cavity ring-down spectroscopy (CRDS) instrument, i.e., Picarro G2401 $CO/CO_2/CH_4/H_2O$ Analyzer equipped with 16-Port Distribution Manifold.

After the arrival of the cylinder from KRISS, it was stored in the laboratory where the analyses were carried out. Three primary standard gas mixtures were also stored in the same laboratory during all the measurements. The sample cylinder and the calibration standards were equipped with pressure reducers and connected to 16-port distribution manifold. They were flushed three times before the first measurement.

The analyzer operates vacuum pump to get the sample. Therefore, more gas than the amount of gas required by CRDS has been sent to the analyzer by adjusting the reducers. The excess gas has been sent to the atmosphere through a bypass connected to sample line in between distribution manifold and the analyzer.

Each cylinder was measured for 3 minutes which is satisfactory to obtain stable results. Zero air has been passed through the analyzer for 3 minutes in between each cylinder measurement. The measurement data was collected using CRDS software. Software takes about 280 readings for 3 minutes. For each cylinder measurement, the last 60 readings has been collected and used for determination of average values and uncertainties of the measurements.

Details of the calibration method used:

The calibration of the instrument has been carried out according to ISO 6143. Three primary standard gas mixtures were used for calibration. The software "B_Least" was utilized to determine the fitting data for the calibrations. The value for goodness of fit in each measurement was found to be less than 2 for linear function.

The assigned value was calculated by averaging the results of five independent measurements.

Details of the standards used:

Primary reference gas mixtures used in calibration are given in the Table 1. All the primary standards are binary mixtures of CO in N_2. They were prepared individually according to ISO 6142 "Gas analysis - Preparation of calibration gases - Gravimetric Method" at TÜBİTAK UME. One pre-mixture (20 % CO/N_2) was prepared from pure carbon monoxide and nitrogen gases. Then, this pre-mixture was diluted with the same pure nitrogen to lower concentrations (2.5 %, 0.25 % and 0.10 % CO/N_2). 120 ppm mixture was diluted from 0.25 % CO/N_2 mixture. 100 and 80 ppm mixtures were prepared from 0.10 % CO/N_2 mixture. Pure carbon monoxide (4.7 grade) and nitrogen (6.0 grade)

were from Linde Gas Germany and Linde Gas Turkey, respectively. The content of the impurities in the pure gases were determined based on the gas producers' specifications.

The uncertainties of the mixtures given in Table 1 were determined by combining the standard uncertainties of weighing, purity and molar masses.

Table 1. List of primary reference gas mixtures

Item	**Prepared By**	**Cylinder Number**	**Mole Fraction** (µmol/mol)	**Uncertainty (k=1)** (µmol/mol)
1	UME	266320	80.04	0.03
2	UME	266300	100.05	0.03
3	UME	249372	119.99	0.04

Details on uncertainty budget:

The measurement uncertainty of sample was determined according to ISO 6143 "Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures" standard, using the B_Least software.

The combined standard uncertainty was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2}$$

where
u_m, standard uncertainty from measurements
u_g, standard uncertainty from gravimetric preparation

u_m = 0.020 % rel. (determined by selecting the largest uncertainty value among the obtained uncertainties for each measurement)
u_g = 0.039 % rel. (determined by selecting the largest uncertainty value among the uncertainties of primary reference gas mixtures)

u_c was determined as 0.044 % rel.

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

Authorship

Participant's List : Dr. Tanıl TARHAN

Report Form

Carbon monoxide in nitrogen

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

Cylinder number: **3-7 NPLI** (M9905 **00T-3AL2216** 0015266)

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO	30/11/15	98.67	0.38	03

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO	30/11/15	98.49	0.56	03

Measurement #3[2]

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO	02/12/15	101.96	0.56	08

Measurement #4

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO	03/12/15	100.11	0.50	08

Results

Component	**Result**	**Expanded Uncertainty**	**Coverage factor[3]**

[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.

	(µmol/mol)		
CO	99.81	1.51	2

Details of the measurement method used:

GC-FID (Agilent 6890N) with Methanizer
Column used: SS Mol Sieve 13x (6 feet, 1/8" diameter)
Oven temp 80 ℃
Methanizer temp.: 350 ℃
Carrier gas: He (25 ml/min)

Details of the calibration method used:

Single point external calibration method was used.

Details of the standards used:

Calibration standards used for the analysis work were prepared at NPLI using gravimetric method. Four mixtures (CO in N2 gas) were prepared using double pan balance (sensitivity 1mg) in the range of 87 to 113 µmol/mol. The mixtures were prepared in three dilution steps from pure (99.97%) CO gas targeting the final concentration of CO around 5% mol/mol, 2500 µmol/mol and 100 µmol/mol respectively. Out of these standards, 107.11±0.37 µmol/mol standard was used as calibration standard for the measurement work, and reporting the result.

Details on uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

List of Uncertainty components:

1. **Gravimetric Preparation of calibration gas mixture (Calibration standard)**
   - Balance
   - Weights used
   - Buoyancy
2. **Analytical method Components**
   - Repeatability

- Reproducibility
- GC Response

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	99.81	µmol/mol	Normal, Type A	0.52	µmol/mol	1	0.00525
Conc. of Std (JJ108900)	107.11	µmol/mol	Normal, Type A	0.37	µmol/mol	1	0.00345
GC Response	156.82	mV	Normal, Type A	0.66	mV	1	0.00420
Combined standard Uncertainty, u_c	0.75	µmol/mol					
Expanded Uncertainty, U	1.51	µmol/mol	$k = 2$				
U	1.51	%					

Report for Key Comparison on APMP.QM-S9 : Carbon monoxide in nitrogen at 100 μmol/mol

Laboratory name: CMS/ITRI
Cylinder number: D015263

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
CO	07/09/2015	99.69	0.043	5

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
CO	08/09/2015	99.67	0.028	5

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
CO	09/09/2015	99.74	0.053	5

Measurement #4

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
CO	10/09/2015	99.81	0.091	5

Measurement #5

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	Number of replicates
CO	11/09/2015	99.79	0.058	5

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor
CO	99.74	0.50	2

Calibration standards

The primary reference materials (PRMs) of carbon monoxide in N_2 were gravimetrically prepared according to ISO 6142: 2001 by CMS/ITRI. The high purity carbon monoxide and BIP nitrogen from Air Products were used to prepare the PRMs. The impurities in carbon monoxide and nitrogen were determined with various gas analyzers and were described in Table 1 and Table 2 individually. The uncertainty associated with the carbon monoxide determination was taken into account during the gravimetric calculations and uncertainty evaluation. The prepared PRMs were verified by analytical comparisons against existing gravimetrically prepared standards, and the characteristics of calibration

standards are described in Table 3.

Table 1. Purity table for carbon monoxide

Component	Mole fraction (μmol/mol)	Standard uncertainty (μmol/mol)	Method
O_2	1.10	0.6351	GC-PDHID
N_2	4.36	2.5172	GC-PDHID
H_2	2.07	1.1951	GC-PDHID
CO_2	2.08	1.2009	FTIR
CH_4	0.50	0.2858	FTIR
CO	999989.895	3.11	-

Table 2. Purity table for nitrogen

Component	Mole fraction (μmol/mol)	Standard uncertainty (μmol/mol)	Method
O_2	0.005	0.0029	Trace oxygen analyzer
CO	0.011	0.0064	GC-PDHID
CO_2	0.046	0.027	GC-PDHID
CH_4	0.023	0.014	GC-PDHID
CF_4	0.005	0.0029	FTIR
SF_6	0.0045	0.0026	FTIR
SO_2	0.18	0.11	FTIR
NO	0.005	0.0029	NOx analyzer
N_2	999999.7205	0.11	-

Table 3. Carbon monoxide concentration of primary reference materials (PRMs)

Cylinder number	Assigned value (μmol/mol)	Expanded uncertainty (μmol/mol) (*k*=2)
CAL013004	100.00	0.50

Instrumentation

A GC specifically set up for carbon monoxide in N_2 analysis was described in Table 4.

Table 4. Analytical conditions

Body	Agilent GC-7890A
Software for data collection	Agilent ChemStation
Column	HP-PLOT/Q (30 m × 0.53 mm × 40 μm)
Oven temp.	30℃ isothermal
FID detector	Temp.= 400℃ Flame gases flows: air = 400 ml/min, H_2 = 40 ml/min
Methanizer temp.	375℃
Detector temp.	250℃
Carrier gas	He: 25 ml/min
Analytical time for one injection	4 min

Calibration method and value assignment

GC-FID was used to determine carbon monoxide concentration in the sample cylinder. The standard with concentration close to that of the sample cylinder D015263 was chosen for single-point calibration to determine the concentration of carbon monoxide in sample cylinder. The sample

cylinder was analyzed with a reference cylinder in the following order.
Reference – Sample – Reference – Sample – Reference – Sample – Reference – Sample – Reference – Sample – Reference
The mathematical model shown below was used to calculate the concentration of carbon monoxide in sample cylinder:

$$\overline{C} = \frac{\sum_{i=1}^{5}(C_i)}{5}; \quad C_i = \overline{r_i} \times C_s; \quad \overline{r_i} = \frac{\sum_{i=1}^{5}(r_i)}{5}; \quad r_i = \frac{2R_i}{R_{s,i} + R_{s,i+1}}$$

$\overline{C}$ =the reported concentration, D015263
C_i = the i[th] measured concentration of sample, D015263
C_s = concentration of standard, CAL013004
$\overline{r_i}$ = the average ratio of GC-FID response of sample to standard
r_i = the i[th] calculated ratio of response of sample to standard
R_i = the i[th] response of GC-FID for sample, D015263
$R_{s,i}$ = the i[th] response of GC-FID for reference standard, CAL013004

Uncertainty evaluation

The final uncertainty was estimated by combining two uncertainty components (i.e., PRM and analysis).

- total standard uncertainty of carbon monoxide mole fraction in PRMs (including uncertainty of weighing of parent gases and pre-mixture, uncertainty in the purity of the parent gas and balance gas);

- standard uncertainty of the measurement result of carbon monoxide mole fraction in cylinder number D015263 (including uncertainties of repeatability and reproducibility)

The equations described below were used to evaluate the uncertainty for carbon monoxide measurement.

$$\overline{C} = \frac{\sum_{i=1}^{5}(C_i)}{5}; \quad C_i = \overline{r_i} \times C_s; \quad \overline{r_i} = \frac{\sum_{i=1}^{5}(r_i)}{5}; \quad r_i = \frac{2R_i}{R_{s,i} + R_{s,i+1}}$$

$$u^2(C_i) = \left(\overline{r_i}\right)^2 \times u^2(C_s) + (C_s)^2 \times u^2\left(\overline{r_i}\right)$$

$$S_p = \sqrt{\frac{\sum_{i=1}^{5} S_i^2}{5}}$$

$$u^2\left(\overline{C}\right) = \left(\overline{\overline{r_i}}\right)^2 \times u^2(C_s) + (C_s)^2 \times \left(\frac{S_p}{\sqrt{5}}\right)^2$$

=

$\overline{r_i}$ = the average of calculated mean ratios, $\overline{r_i}$, for the five sets of measurements
s_p = pooled standard deviation of the five sets of measurements
s_i = standard deviation of each set of measurements

The uncertainty budget for carbon monoxide measurement in the cylinder number D015263 is shown in Table 5.

Table 5. Uncertainty budget for carbon monoxide measurement

Uncertainty source X_i	**Estimate** x_i	**Evaluation type and distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution to the uncertainty of the reporting value** $u_i(y)$
Repeatability and reproducibility of ratio of signal, *r*	$\overline{r_i}$; 1.016	Type A; Normal	2.30×10^{-4}	1.00×10^{-4}	2.30×10^{-8}

Uncertainty of calibration standard	C_s ; 20.0078	Type A; Normal	2.5×10^{-7}	9.97×10^{-1}	2.49×10^{-7}
Combined Uncertainty, (µmol/mol)					0.25
Expanded Uncertainty, (*k=2*) , (µmol/mol)					0.50
Expanded Uncertainty, (*k=2*) , (% relative)					0.50

Authorship

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APMP.QM-S9 Carbon monoxide in nitrogen

Laboratory name: KRISS

Cylinder number: D015353

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates
CO	29.07.2015	101.09	0.04	5

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates
CO	30.07.2015	101.13	0.04	5

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates
CO	31.07.2015	101.00	0.04	5

Results

Component	Result (μmol/mol)	Expanded Uncertainty (μmol/mol)	Coverage factor[4]
CO	101.07	0.08	2

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

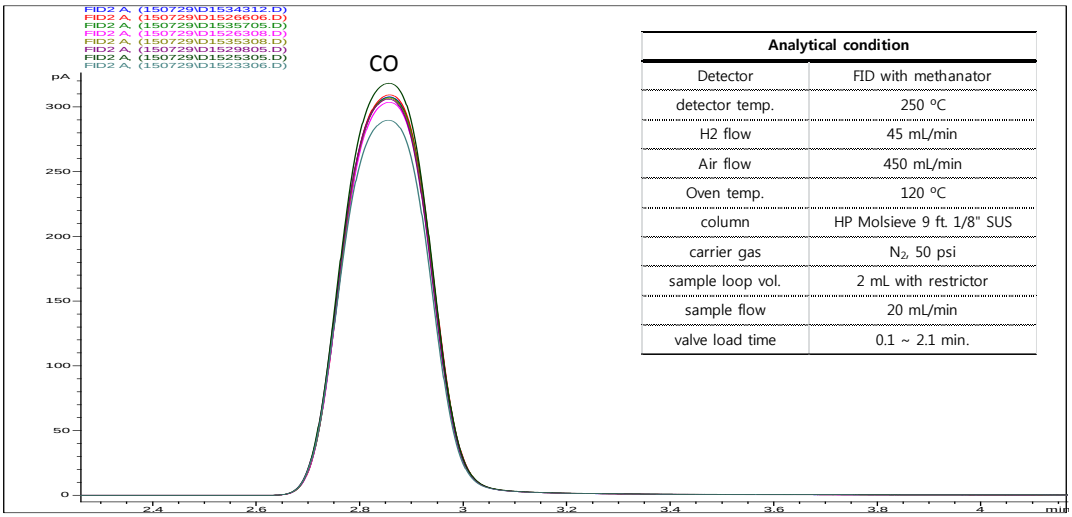
Details of the measurement method used:

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.



Analytical condition	
Detector	FID with methanator
detector temp.	250 °C
H2 flow	45 mL/min
Air flow	450 mL/min
Oven temp.	120 °C
column	HP Molsieve 9 ft. 1/8" SUS
carrier gas	N_2, 50 psi
sample loop vol.	2 mL with restrictor
sample flow	20 mL/min
valve load time	0.1 ~ 2.1 min.

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 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 20 mL/min using the mass-flow controller.

Calibration standards:

Preparation method

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

Table 1. Gravimetric value and expanded uncertainty in calibration standards

Cylinder number	Gravimetric value (μmol/mol)	Expanded uncertainty [*k*=2] (μmol/mol)
D015233	95.637	0.031
D015298	100.941	0.033
D015343	101.151	0.034
D015253	105.080	0.034

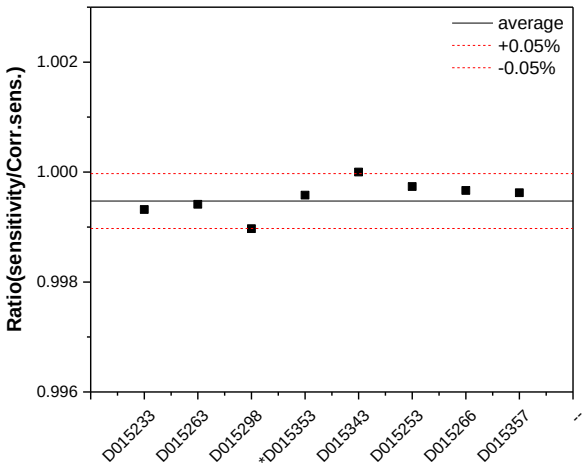


Figure 2. Consistency among primary standard mixtures

Purity analysis

The impurities of carbon monoxide, nitrogen, and oxygen 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 and N_2.

Table 2. Results of purity analysis of Carbon monoxide (QA8272)

component	Analytical conc. (μmol/mol)	Detector	distribution	Applied conc. (μmol/mol)	Standard uncertainty (μmol/mol)
H_2	<0.26	GC/AED	rectangular	0.13	0.075
H_2O	<1.0	Dew Point Meter	rectangular	0.5	0.289
CH_4	<0.08	GC/AED	rectangular	0.04	0.023
CO_2	<1.02	GC/TCD	rectangular	0.51	0.294
THC	<1.0	GC/FID	rectangular	0.5	0.289
N_2	4.13	GC/AED	normal	4.13	0.413
O_2+Ar	0.93	GC/PDD	normal	0.93	0.093
			impurities	6.74	0.662
			CO	**999993.26**	**1.325 (*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	<0.5	GC/PDD	rectangular	0.25	0.144
H_2O	1.2	Dew Point Meter	Normal	1.2	0.120
CO	<0.002	GC/FID	rectangular	0.001	0.001
CH_4	<0.001	GC/FID	rectangular	0.0005	0.000
CO_2	<0.01	GC/FID	rectangular	0.005	0.003
THC	<0.5	GC/FID	rectangular	0.25	0.144
Ar	<1.0	GC/TCD	Rectangular	0.5	0.289
O_2	0.35	GC/PDD	Normal	0.35	0.035
Ne	<0.1	GC/TCD	Rectangular	0.5	0.289
			impurities	3.057	0.473
			N_2	**999996.944**	**0.947 (*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.

Detailed uncertainty budget:

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

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

Typical evaluation of the of the measurement uncertainty for CO:

Quantity X_i		Estimate x_i	Evaluation Type (A or B)	Distribution	Standard uncertainty $u(x_i)$ [µmol/mol]	Sensitivity coefficient $Rel.u(x_i)$ [%]	Contribution $u_i(y)$
References			A	Gaussian	6.2×10^{-4}	6.4×10^{-4}	
Sample	D015353		A	Gaussian	0.0386	0.0382	
References prepared grav.	D015266		A	Gaussian	0.0158	0.0155	
	D015357				0.0157	0.0155	
	D015263				0.0158	0.0158	
Combined standard uncertainty					0.0473	0.0468	