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APMP.QM-K3.2019

Automotive emission gases

KEY COMPARISON

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Final Report
International Comparison APMP.QM-K3.2019
Automotive exhaust gases

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Field

Amount of substance

Subject

Comparison of amount fractions of carbon monoxide, carbon dioxide, oxygen and propane in nitrogen (track A – core competences)

Table of contents

1 Introduction

This key comparison APMP.QM-K3.2019 is designed as linking to the appropriate CCQM comparison CCQM-K3.2019 [1], which was carried out in 2019–2022.
CCQM-K3.2019 was one of a series of key comparisons in the gas analysis area assessing core competences (*track A key comparisons*) [2]. Such competences include, among others, the capabilities to prepare Primary Standard gas Mixtures (PSMs), perform the necessary purity analysis on the materials used in the gas mixture preparation, the verification of the composition of newly prepared PSMs against existing ones, and capability of calibrating a gas mixture [3].

KRISS has participated in CCQM-K3.2019 and showed a consistent result for all of the components. (carbon monoxide, carbon dioxide, oxygen, and propane) in a gas mixture. Therefore, the results of APMP.QM-K3.2019 can be linked to CCQM-K3.2019 through the results of KRISS and can be used to support CMCs.

For this key comparison, KRISS prepared the gas mixtures that containing carbon monoxide, carbon dioxide, oxygen and propane in nitrogen for calibration of exhaust automotive gas analyzers, and sent

to participants. Each participant measured the gas mixture in their laboratory and reported their measurement results to KRISS according to the measurement protocol.

2 Design and organization of the comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1. List of participants

Acronym	Country	Institute
CENAM	Mexico	Centro Nacional de Metrologia
CERI	Japan	Chemicals Evaluation and Research Institute
CMS/ITRI	Chinese Taipei	Center for Measurement Standards/Industrial Technology Research Institute
KRISS	Korea	Korea Research Institute of Standards and Science
NIM	China	National Institute of Metrology
NIMT	Thailand	National Institute of Metrology (Thailand)
NMC	Singapore	National Metrology Centre, Agency for Science, Technology and Research
NMIA	Australia	National Measurement Institute, Australia
NMIJ	Japan	National Metrology Institute of Japan
NMIM	Malaysia	National Metrology Institute of Malaysia
NPLI	India	CSIR National Physical Laboratory of India

2.2 Measurement standards

A set of mixtures was prepared gravimetrically by KRISS, using carbon monoxide, carbon dioxide, oxygen, propane, and nitrogen pure gases. The purity of pure gases was analyzed by using several analyzers, and listed in Tables 2 – 6.

Table 2. Results of purity analysis of carbon monoxide

Component	Value μmol/mol	Standard uncertainty μmol/mol	Distribution	Method of analysis
N_2	1.207	0.129	Normal	GC-TCD
O_2	0.170	0.098	Rectangular	GC-TCD
Ar	0.171	0.099	Rectangular	GC-TCD
CH_4	0.012	0.007	Rectangular	GC-PDD
N_2O	0.0005	0.0003	Rectangular	GC-ECD
CO_2	0.848	0.283	Rectangular	GC-TCD
He	0.701	0.405	Rectangular	GC-TCD
H_2	0.271	0.001	Normal	GC-PDD
THC	0.0054	0.0014	Normal	TD-GC-FID
H_2O	2.43	0.09	Normal	Dew point
C_3H_8	0.009	0.005	Rectangular	GC-FID
CO	999994.18	0.41		

Table 3. Results of purity analysis of carbon dioxide

Component	Value µmol/mol	Standard uncertainty µmol/mol	Distribution	Method of analysis
N_2	0.956	0.039	Normal	GC-TCD
O_2	0.248	0.073	Normal	GC-TCD
Ar	0.248	0.012	Normal	GC-TCD
CH_4	0.013	0.008	Rectangular	GC-FID
N_2O	0.0005	0.0003	Rectangular	GC-ECD
CO	0.014	0.008	Rectangular	GC-FID/ methanizer
He	0.110	0.064	Rectangular	GC-TCD
H_2	0.092	0.053	Rectangular	GC-TCD
THC	0.0199	0.0009	Normal	TD-GC-FID
H_2O	2.60	1.04	Normal	Dew point
C_3H_8	0.009	0.005	Rectangular	GC-FID
CO_2	999995.69	1.04		

Table 4. Results of purity analysis of oxygen

Component	Value µmol/mol	Standard uncertainty µmol/mol	Distribution	Method of analysis
N_2	0.283	0.163	Rectangular	GC-TCD
Ar	0.171	0.099	Rectangular	GC-TCD
CO_2	0.008	0.005	Rectangular	GC-FID/ methanizer
CH_4	0.00083	0.00001	Normal	CRDS
N_2O	0.0005	0.0003	Rectangular	GC-ECD
CO	0.095	0.002	Normal	GC-FID/ methanizer
He	0.110	0.064	Rectangular	GC-TCD
H_2	0.092	0.053	Rectangular	GC-TCD
THC	0.0006	0.0001	Normal	TD-GC-FID
H_2O	1.26	0.51	Normal	Dew point
C_3H_8	0.009	0.005	Rectangular	GC-FID
O_2	999997.97	0.37		

Table 5. Results of purity analysis of propane

Component	Value µmol/mol	Standard uncertainty µmol/mol	Distribution	Method of analysis
N_2	0.283	0.163	Rectangular	GC-TCD
O_2	0.170	0.099	Rectangular	GC-TCD
Ar	0.171	0.099	Rectangular	GC-TCD
CO_2	0.065	0.007	Normal	GC-FID
CH_4	0.012	0.007	Rectangular	GC-FID
CO	0.008	0.004	Rectangular	GC-FID
H_2	0.013	0.007	Rectangular	GC-TCD

THC	0.250	0.145	Rectangular	GC-FID
H_2O	0.30	0.03	Normal	Dew point
Iso-C_4H_{10}	0.097	0.010	Normal	GC-FID
n-C_4H_{10}	0.044	0.005	Normal	GC-FID
C_3H_8	999998.509	0.147		

Table 6. Results of purity analysis of nitrogen

Component	Value µmol/mol	Standard uncertainty µmol/mol	Distribution	Method of analysis
O_2	0.159	0.004	Normal	GC-TCD
Ar	4.901	0.005	Normal	GC-TCD
CO_2	0.0010	0.002	Rectangular	GC-FID/methanizer
CH_4	0.00041	0.00001	Normal	CRDS
N_2O	0.0005	0.0003	Rectangular	GC-ECD
CO	0.008	0.004	Rectangular	GC-FID/methanizer
He	0.110	0.064	Rectangular	GC-TCD
H_2	0.092	0.053	Rectangular	GC-TCD
THC	0.00051	0.00002	Normal	TD-GC-FID
H_2O	2.07	0.49	Normal	Dew point
C_3H_8	0.009	0.002	Rectangular	GC-FID
N_2	999992.64	0.49		

Carbon monoxide, carbon dioxide, and oxygen were transferred as pure gases and propane was transferred from the premixture obtained with two dilution steps for gravimetric preparation of final gas mixtures. The gas mixtures were verified before shipment to the participants and after their return. The verification results are shown in Figures 1 – 4

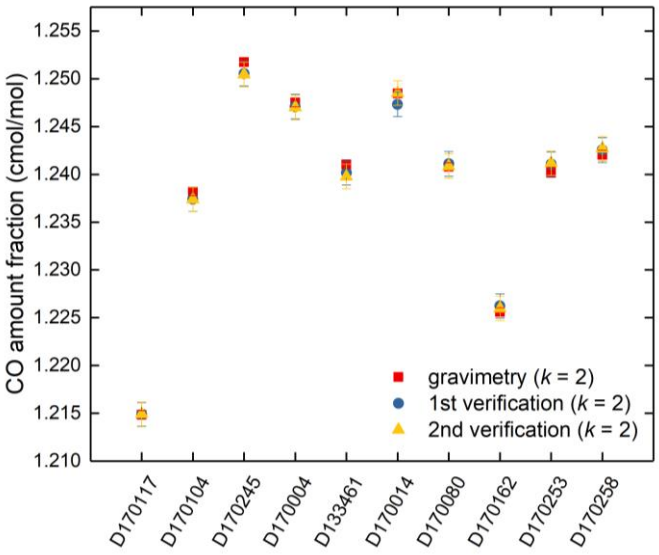

Figure 1. Verification results of carbon monoxide in gas mixtures

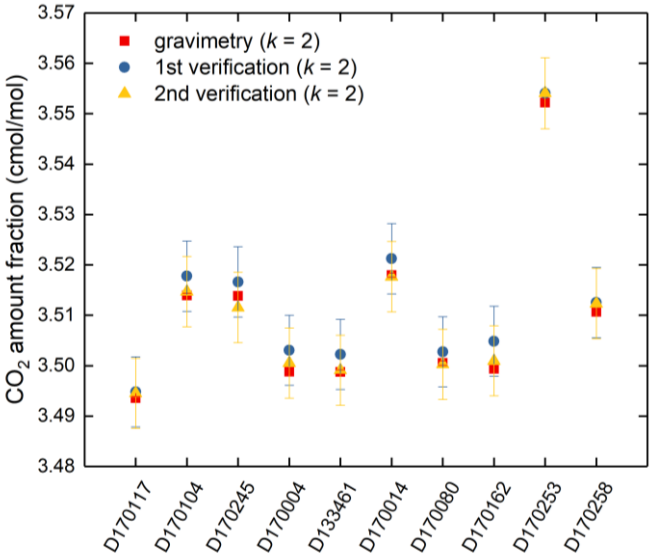

Figure 2. Verification results of carbon dioxide in gas mixtures

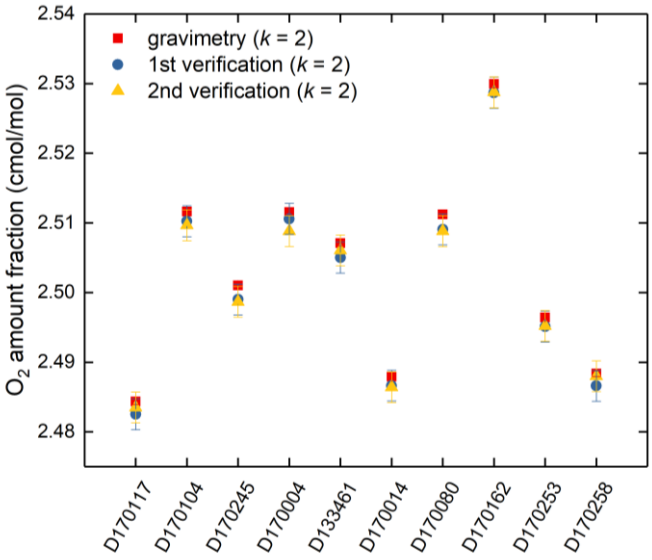

Figure 3. Verification results of oxygen in gas mixtures

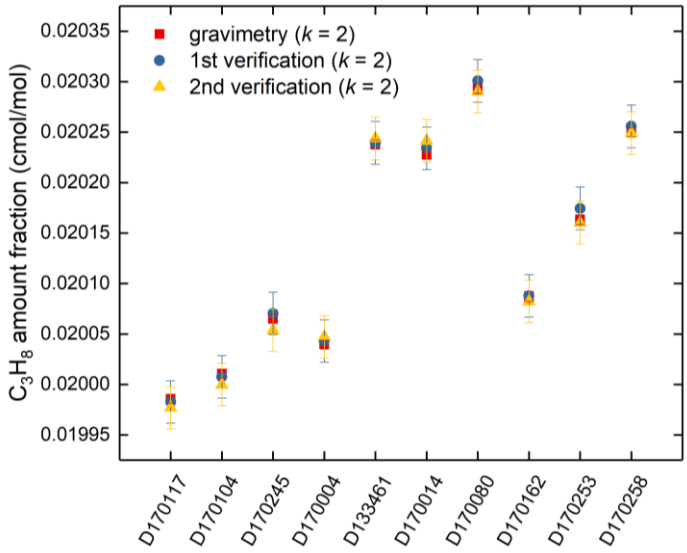

Figure 4. Verification results of propane in gas mixtures

The nominal ranges of amount fractions of the targeted components in the mixtures are given in Table 7.

Table 7. Nominal composition of mixtures, given in amount fractions

Component	Amount fraction x (cmol/mol)
Carbon monoxide	0.5 – 2
Carbon dioxide	2 – 5
Oxygen	1 – 4
Propane	0.01 – 0.03
Nitrogen	Balance

2.3 Measurement protocol

The measurement protocol requested each participant to perform at least three measurements with independent calibrations and report the final value with its expanded uncertainty including all measurement results. Each participant was also requested to provide information regarding standard mixtures, analysis method, and uncertainty budget.

2.4 Schedule

The schedule of this key comparison was as follows (Table 8).

Table 8. Key comparison schedule

Date	Event
March 2023	Agreement of protocol
May 2023	Registration of participants
November 2023	Preparation and verification of mixtures
December 2023	Dispatch of mixtures
July 2025	Reports and cylinders arrived back at KRISS

September 2025	Re-verification of the mixtures
January 2026	Draft A report available

2.5 Measurement equation

The reference values in this key comparison are determined by the gravimetric preparation, including purity analysis. All gas mixtures were verified prior to shipping to each participant. The returned cylinders were re-verified to confirm their stability.

In the gravimetric preparation, the amount fraction of a target component is determined by the following equation

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

where $x_{i,\mathrm{prep}}$ is the amount fraction of a target component in mixture *i*, $x_{i,\mathrm{grav}}$ is the amount fraction of a target component in mixture *i* gravimetrically prepared, $\Delta x_{i,\mathrm{purity}}$ is the correction based on purity analysis, and $\Delta x_{i,\mathrm{stab}}$ is the correction due to stability. For the mixtures used in this comparison, the correction due to instability is zero, since the re-verification results are agreed to the gravimetric values within their verification uncertainties. Therefore, the amount fraction of a target component can be expressed as

$$x_{i,\mathrm{prep}} = x_{i,\mathrm{grav}} + \Delta x_{i,\mathrm{purity}} \tag{2}$$

The associated uncertainties can now be expressed as

$$u^2\left(x_{i,\mathrm{prep}}\right) = u^2\left(x_{i,\mathrm{grav}}\right) + u^2\left(\Delta x_{i,\mathrm{purity}}\right) \tag{3}$$

where $u^2\left(x_{i,\mathrm{prep}}\right)$ is the uncertainty from gravimetric preparation, $u^2\left(x_{i,\mathrm{grav}}\right)$ is the uncertainty from gravimetric weighing process, $u^2\left(\Delta x_{i,\mathrm{purity}}\right)$ is the uncertainty from purity analysis. For the mixtures used in this comparison have been verified by comparing the gravimetric composition value with its analytic measurement value (i.e., verification value) as shown in the following condition.

$$\left|x_{i,\mathrm{prep}} - x_{i,\mathrm{ver}}\right| \leq 2\sqrt{u^2\left(x_{i,\mathrm{prep}}\right) + u^2\left(x_{i,\mathrm{ver}}\right)} \tag{4}$$

where $x_{i,\mathrm{ver}}$ and $u^2\left(x_{i,\mathrm{ver}}\right)$ are the measurement result from verification and its standard uncertainty, respectively. The uncertainty associated with the verification relies on the measurement capability and experiment design.

As shown in Figures 1 – 4, the verification experiments demonstrated that the verification values agreed with the gravimetric values of this comparison mixtures. Therefore, the reference value of mixture *i* is set to $x_{i,\mathrm{prep}}$. The uncertainty of the reference value is given as

$$u^2\left(x_{i,\mathrm{ref}}\right) = u^2\left(x_{i,\mathrm{prep}}\right) + u^2\left(x_{i,\mathrm{ver}}\right) \tag{5}$$

2.6 Measurement methods

Measurement methods of each participant are summarized in Table 9. More detailed descriptions about the methods are available in annex A of this report.

Table 9. Summary of calibration methods and metrological traceability

Laboratory	Measurements	calibration	Traceability	Matrix	Measurement

	(dd/mm/yyyy)			standards	technique
A*STAR	30/08/2024 04/09/2024 10/09/2024	Single point calibration	Own standards	Nitrogen	GC-TCD, GC-FID
CENAM	20-22/03/2024 01-03/03/2024 01-03/04/2024 11-13/03/2024	Multipoint calibration	Own standards	Nitrogen	ND-IR, GC-TCD, Paramagnetism GC-FID
CERI	16-19/03/2024 7-13/03/2024 22-25/03/2024 21-24/03/2024	Bracketing	Own standards	Nitrogen	GC-TCD, GC-FID
CMS/ITRI	11-18/04/2024 22-25/04/2024 11-18/04/2024 16-23/05/2024	Bracketing	Own standards	Nitrogen	GC-TCD, GC-FID
NIM	12-15/03/2024	Single point calibration	Own standards	Nitrogen	ND-IR, Paramagnetism
NIMT	18-26/03/2024	Single point calibration	Own standards	Nitrogen	GC-TCD, Paramagnetism GC-FID
NMIA	14/05/2024 03/08/2024 08/08/2024	Bracketing	Own standards	Nitrogen	GC-TCD, GC-FID
NPLI	03-29/04/2024	Single point calibration	Own standards	Nitrogen	GC-TCD, GC-FID
NMIJ	27/02/2024 05-07/03/2024 13-15/03/2024	Multipoint calibration	Own standards	Nitrogen	Paramagnetism GC-FID
NMIM	18/04/2024 29-31/05/2024 05-10/06/2024	Single point calibration	Own standards	Nitrogen	GC-TCD, GC-FID

2.7 Degrees of equivalence

A degree of equivalence of an RMO key comparison and its standard uncertainty can be calculated using following equations (6) and (7), respectively.

$$d_{\mathrm{RMO}} = x_{\mathrm{RMO,lab}} - x_{\mathrm{RMO,RV}} \tag{6}$$

$$\mathrm{u}(d_{\mathrm{RMO}}) = \sqrt{u^2\left(x_{\mathrm{RMO,lab}}\right) + u^2\left(x_{\mathrm{RMO,RV}}\right)} \tag{7}$$

where d_{RMO} is a deviation between the participant's reported value ($x_{\mathrm{RMO,lab}}$) and the reference value ($x_{\mathrm{RMO,RV}}$) in the RMO key comparison.

The RMO key comparison should be linked to a related CIPM key comparison. Therefore, the degree of equivalence that linked to the CIPM key comparison can be calculated using following equation.

$$d_{\mathrm{linked}} = d_{\mathrm{RMO}} + d_{\mathrm{CIPM,linking}} \tag{8}$$

where d_{linked} is the degree of equivalence linked to the CIPM key comparison, $d_{\mathrm{CIPM,linking}}$ is the deviation of a linking laboratory in CIPM key comparison.

The standard uncertainty of d_{linked} can be expressed as

$$\mathrm{u}(d_{\text{linked}}) = \sqrt{u^2(d_{\text{RMO}}) + u^2\left(d_{\text{CIPM,linking}}\right)} \tag{9}$$

However, if the nominal value of the target component in the RMO key comparison is not equal to that in the CIPM key comparison, the linked degree of equivalence and its uncertainty can be calculated using following equations (10) and (11), respectively.

$$rd_{\text{linked}} = rd_{\text{RMO}} + rd_{\text{CIPM,linking}} \tag{10}$$

$$\mathrm{u}(rd_{\text{linked}}) = \sqrt{u^2(rd_{\text{RMO}}) + u^2\left(rd_{\text{CIPM,linking}}\right)} \tag{11}$$

where rd_{RMO} and $rd_{\text{CIPM,linking}}$ are relative deviations from the reference value in the RMO key comparison and the KCRV in the CIPM key comparison, respectively.

In this comparison, the nominal values for carbon monoxide, carbon dioxide, and oxygen are not equal to those in CCQM-K3.2019, thus, the linked degrees of equivalence were calculated using equation (10). In case of propane, the nominal value is equal to that in CCQM-K3.2019, the linked degree of equivalence was calculated using equation (8).

The uncertainties of the deviation (*d*) and the relative deviation (*rd*) are expressed as the expanded uncertainty of the deviation at approximately 95% level of confidence with a coverage factor (*k*) of 2.

$$U(d) = k \times u(d) \tag{12}$$

$$U(rd) = k \times u(rd) \tag{13}$$

3 Results

A complete set of results reported from each participant is described in annex A of this report. The results are summarized in Tables 10 – 13. The degrees of equivalence are illustrated in Figures 5 – 8.

In the tables, the following data is presented

x_{ref}	amount fraction of the reference value
u_{ref}	standard uncertainty of reference value
x_{lab}	reported result from participant laboratory
U_{lab}	stated expanded uncertainty of laboratory, at 95 % level of confidence
d_{linked}	deviation between laboratory result and the KCRV in the CCQM-K3.2019
$U(d_{\text{linked}})$	expanded uncertainty of deviation *d*, at 95 % level of confidence
rd_{linked}	relative deviation between laboratory result and the KCRV in the CCQM-K3.2019
$U(\mathrm{r}d_{\text{linked}})$	expanded uncertainty of relative deviation *rd*, at 95 % level of confidence

Note – x_{ref} and u_{ref} for the linking laboratory KRISS are the KCRV and its standard uncertainty in the CCQM-K3.2019, respectively.

Table 10 shows the results for the amount fraction carbon monoxide. All results are consistent with the key comparison reference value with the exception of NPLI.

Table 10. Summary of measurement results for the carbon monoxide

Lab	Cylinder	x_{ref}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	rd_{linked}	$U(rd_{\text{linked}})$

		cmol/mol	cmol/mol	cmol/mol	cmol/mol	cmol/mol	cmol/mol ($k = 2$)	%	% ($k = 2$)
A*STAR	D170117	1.2149	0.0002	0.0005	0.0007	1.22	0.0076	0.483	0.714
CENAM	D170104	1.2382	0.0002	0.0005	0.0007	1.2400	0.0032	0.206	0.430
CERI	D170245	1.2517	0.0002	0.0006	0.0007	1.252	0.003	0.080	0.418
CMS/ITRI	D170004	1.2475	0.0002	0.0006	0.0007	1.2502	0.0016	0.274	0.366
NIM	D133461	1.2410	0.0002	0.0005	0.0007	1.2417	0.0037	0.113	0.454
NIMT	D170014	1.2485	0.0002	0.0006	0.0007	1.2491	0.0013	0.111	0.358
NMIA	D170080	1.2408	0.0002	0.0005	0.0007	1.2413	0.0012	0.101	0.356
NPLI	D170162	1.2256	0.0002	0.0005	0.0007	1.2084	0.0053	-1.343	0.552
NMIJ	D170253	1.2402	0.0003	0.0005	0.0007	1.2413	0.0012	0.148	0.356
NMIM	D170258	1.2420	0.0002	0.0006	0.0007	1.2392	0.1052	-0.170	8.480
KRISS	D751979	1.0100			0.0004	1.0106	0.0032	-0.050	0.495

Table 11 shows the results for the amount fraction carbon dioxide. All results are consistent with the key comparison reference value with the exception of A*STAR.

Table 11. Summary of measurement results for the amount fraction carbon dioxide

Lab	Cylinder	x_{ref} cmol/mol	u_{prep} cmol/mol	u_{ver} cmol/mol	u_{ref} cmol/mol	x_{lab} cmol/mol	U_{lab} cmol/mol ($k = 2$)	rd_{linked} %	$U(rd_{linked})$ % ($k = 2$)
A*STAR	D170117	3.4935	0.0002	0.0035	0.0035	3.51	0.0044	0.446	0.348
CENAM	D170104	3.5140	0.0002	0.0035	0.0035	3.5181	0.0088	0.092	0.410
CERI	D170245	3.5138	0.0002	0.0035	0.0035	3.515	0.009	0.008	0.414
CMS/ITRI	D170004	3.4988	0.0002	0.0035	0.0035	3.4976	0.0047	-0.060	0.352
NIM	D133461	3.4988	0.0002	0.0035	0.0035	3.4982	0.007	-0.041	0.382
NIMT	D170014	3.5180	0.0002	0.0035	0.0035	3.5180	0.0036	-0.024	0.340
NMIA	D170080	3.5005	0.0002	0.0035	0.0035	3.5016	0.0026	0.005	0.332
NPLI	D170162	3.4994	0.0003	0.0035	0.0035	3.4999	0.0068	-0.010	0.378
NMIJ	D170253	3.5522	0.0002	0.0035	0.0035	3.5525	0.0034	-0.017	0.338
NMIM	D170258	3.5107	0.0002	0.0035	0.0035	3.4587	1.2849	-1.5	36.6
KRISS	D751979	1.9731			0.0008	1.9726	0.0048	0.030	0.167

Table 12 shows the results for the amount fraction oxygen. All results are consistent with the key comparison reference value.

Table 12. Summary of measurement results for the amount fraction oxygen

Lab	Cylinder	x_{ref} cmol/mol	u_{prep} cmol/mol	u_{ver} cmol/mol	u_{ref} cmol/mol	x_{lab} cmol/mol	U_{lab} cmol/mol ($k = 2$)	rd_{linked} %	$U(rd_{linked})$ % ($k = 2$)
A*STAR	D170117	2.4843	0.0002	0.0011	0.0011	2.49	0.0076	0.352	0.460
CENAM	D170104	2.5116	0.0002	0.0011	0.0011	2.5099	0.0061	0.055	0.422
CERI	D170245	2.5010	0.0002	0.0011	0.0011	2.501	0.005	0.123	0.398
CMS/ITRI	D170004	2.5115	0.0002	0.0011	0.0011	2.5117	0.0079	0.130	0.466
NIM	D133461	2.5071	0.0002	0.0011	0.0011	2.5063	0.0050	0.092	0.398
NIMT	D170014	2.4879	0.0002	0.0011	0.0011	2.4855	0.0025	0.027	0.358
NMIA	D170080	2.5112	0.0003	0.0011	0.0011	2.5102	0.0019	0.084	0.352

NPLI	D170162	2.5300	0.0003	0.0011	0.0011	2.5508	0.0298	0.948	1.228
NMIJ	D170253	2.4964	0.0002	0.0011	0.0011	2.4968	0.0023	0.139	0.356
NMIM	D170258	2.4884	0.0002	0.0011	0.0011	2.4457	0.9313	-1.6	37.4
KRISS	D751979	3.0649			0.0010	3.0687	0.0100	0.124	0.333

Table 13 shows the results for the amount fraction propane. All results are consistent with the key comparison reference value.

Table 13. Summary of measurement results for the amount fraction propane

Lab	Cylinder	x_{ref} cmol/mol	u_{prep} cmol/mol	u_{ver} cmol/mol	u_{ref} cmol/mol	x_{lab} cmol/mol	U_{lab} cmol/mol ($k = 2$)	d_{linked} cmol/mol	$U(d_{linked})$ cmol/mol $k = 2$
A*STAR	D170117	0.0199858	0.000002	0.00001	0.0000107	0.01998	0.00012	-0.000001	0.000129
CENAM	D170104	0.0200107	0.000002	0.00001	0.0000107	0.019988	0.000029	-0.000018	0.000057
CERI	D170245	0.0200650	0.000002	0.00001	0.0000107	0.02002	0.00006	-0.00004	0.00008
CMS/ITRI	D170004	0.0200396	0.000002	0.00001	0.0000107	0.02007	0.00014	0.00004	0.00015
NIM	D133461	0.0202379	0.000002	0.00001	0.0000108	0.020233	0.000041	0.0000001	0.0000638
NIMT	D170014	0.0202276	0.000002	0.00001	0.0000108	0.020218	0.000021	-0.000005	0.000053
NMIA	D170080	0.0202931	0.000002	0.00001	0.0000109	0.02030	0.00002	0.000012	0.000053
NPLI	D170162	0.0200873	0.000002	0.00001	0.0000108	0.020051	0.000077	-0.000031	0.000091
NMIJ	D170253	0.0201633	0.000002	0.00001	0.0000108	0.020158	0.000005	-0.0000003	0.0000490
NMIM	D170258	0.0202499	0.000002	0.00001	0.0000109	0.01992	0.000467	-0.00033	0.00047
KRISS	D751979	0.019665			0.000009	0.01967	0.00004	0.000002	0.000043

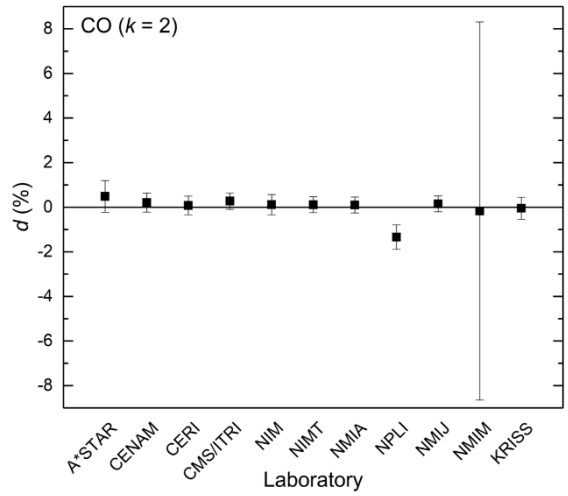

Figure 5. Degrees of equivalence for carbon monoxide linked to the CCQM-K3.2019

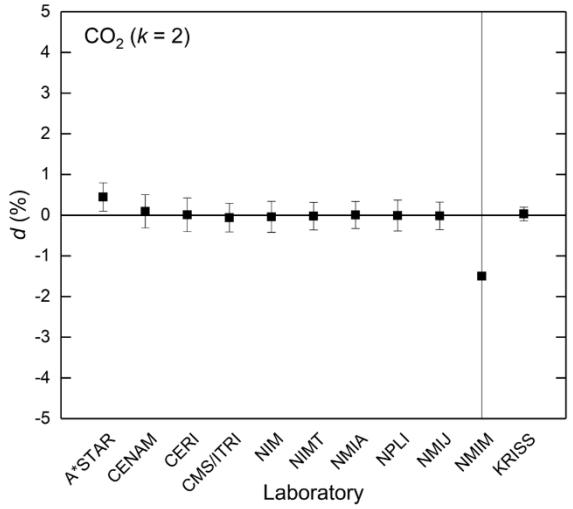

Figure 6. Degrees of equivalence for carbon dioxide linked to the CCQM-K3.2019

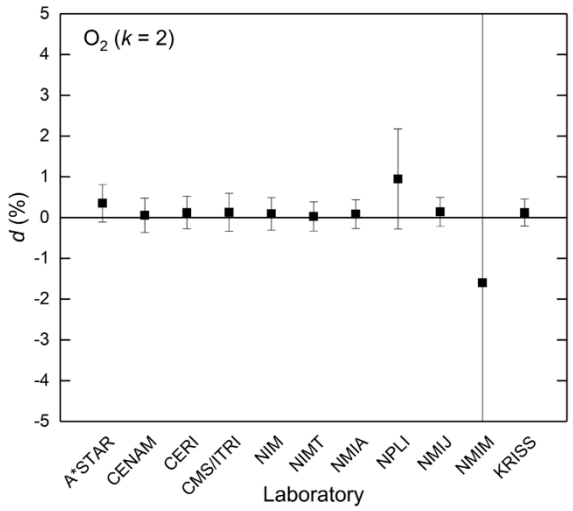

Figure 7. Degrees of equivalence for oxygen linked to the CCQM-K3.2019

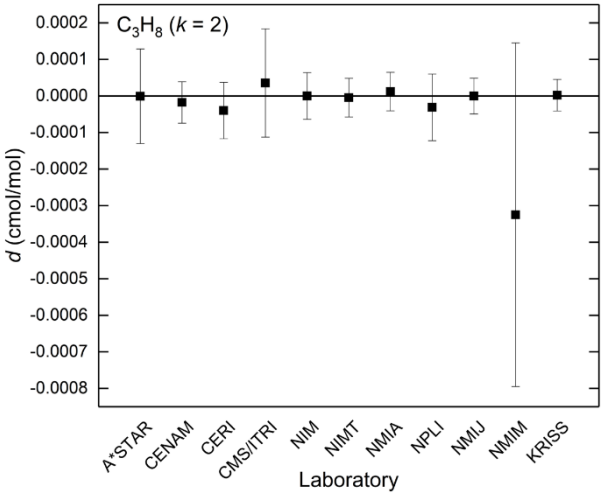

Figure 8. Degrees of equivalence for propane linked to the CCQM-K3.2019

4 Supported CMC claims

The results of this key comparison can be used to support CMC claims in two different ways:

a) For core capabilities, as track A key comparison;
b) For the components concerned (and a combination thereof) in nitrogen, as track C key comparisons.

If the results are used as track A key comparison, the support is the pooled uncertainty of the four amount fractions, i.e., the mean of the four variances.
The support of CMC claims is described in more detail in the "GAWG strategy for comparisons and CMC claims" [2].

4.1 Clarification on CMC claims for Japan (CERI and NMIJ)

Under the CCQM-GAWG track A scheme, multiple institutes from a single country are permitted to participate in a core competence key comparison to demonstrate institutional capabilities and fulfill track-record requirements. To comply with the CIPM MRA principle of having a single traceability point per country for a specific CMC claim, the future CMC application plans of the two participating Japanese institutes are clearly demarcated as follows:

a) CERI represented Japan in the corresponding CIPM key comparison (CCQM-K3.2019) to support its CMC claims, and participated in this RMO comparison primarily to confirm the linkage to the CCQM KCRV. CERI does not intend to claim any new or additional CMCs directly based on the results of this comparison.
b) NMIJ participated in this comparison to satisfy the institutional track-record requirements for track A (core capabilities) under the GAWG framework to maintain or expand its broad scope CMC claims (such as NMIJ's purity CMCs and other specific categories not claimed by CERI), using the track A and extrapolation schemes.

Therefore, there is no overlap or conflict between CERI and NMIJ regarding the single traceability point per country for CMC submissions under the CIPM MRA.

5 Discussion and conclusions

The APMP.QM-K3.2019 comparison was successfully conducted to demonstrate the calibration and measurement capabilities (CMCs) of the participating laboratories regarding automotive exhaust gas mixtures. The results, linked to the CCQM-K3.2019 through KRISS as the linking laboratory, provide a robust technical basis for supporting the CMCs of the participating NMIs. Overall, the majority of the participants demonstrated high measurement proficiency, with their reported values agreeing with the key comparison reference values (KCRVs) within their stated uncertainties. Notably, however, the results from NPLI for carbon monoxide (CO) and A*STAR for carbon dioxide (CO_2) exhibited degrees of equivalence inconsistent with the reference values, as their deviations exceeded the expanded uncertainties. In conclusion, this comparison confirms the core competencies of the participating NMIs

in the analysis of CO, CO_2, C_3H_8, and O_2.

References

[1] Adriaan M H van der Veen, Ewelina T Zalewska, Janneke I T van Wijk, Midori Kobayashi, Dai Akima, Shinji Uehara, Andreia L Fioravante, Cristiane R Augusto, Claudia C Ribeiro, Viviane Silva, Florbela Dias, Alda Botas, Carlos Costa, Joengsoon Lee, inbok Lee, Jeongsik Lim, Hyun-Kil Bae, Namgoo Kang, Christina E Cecelski, Kimberly J Harris, Walter R Miller Jr, Jennifer Carney, James Tshilongo, Napo G Ntsasa, Mudalo I Jozela, Nompumelelo Leshabane, Prelly Mohweledi Marebane, David R Worton, Eric B Mussell Webber, Sergi Moreno, Paul J Brewer, Leonid A Konopelko, Anna V Kolobova, V V Pankratov and Olga V Efremova. International comparison CCQM-K3.2019 automotive exhaust gases. Final report. Metrologia, Volume 60, Number 1A

[2] P. Brewer and A. M. H. van der Veen. GAWG strategy for comparisons and CMC claims. CCQM-GAWG/19-41, Gas Analysis Working Group, Sévres, France, October 2019

[3] 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

Coordinator

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Completion date

January 2026

ANNEX A – Measurement reports of participants

Measurement report

Report form

Laboratory name: A*STAR National Metrology Centre

Cylinder number: D 170117

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	30/08/24	1.221	0.335	5
CO_2	30/08/24	3.508	0.071	5
O_2	30/08/24	2.491	0.204	5
C_3H_8	30/08/24	0.01998	0.2946	5

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	04/09/24	1.222	1.004	5
CO_2	04/09/24	3.510	0.048	5
O_2	04/09/24	2.489	0.076	5
C_3H_8	04/09/24	0.02000	0.1920	5

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	10/09/24	1.220	0.254	5
CO_2	10/09/24	3.511	0.037	5
O_2	10/09/24	2.491	0.083	5
C_3H_8	10/09/24	0.01996	0.2169	5

Results

3

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.22	0.0076	2
CO_2	3.51	0.0044	2
O_2	2.49	0.0076	2
C_3H_8	0.01998	0.00012	2

Calibration standards

The calibration standard used were prepared gravimetrically from the dilution of higher concentration of CO2, CO, O2, C3H8 source cylinders.

Concentration of reference material:

Cylinder Number	Component	Assigned Concentration (cmol/mol)
PSM118977	CO	1.01
	CO_2	3.47
	O_2	2.41
	C_3H_8	0.0210

Purity table for Pure CO_2

Components		Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	N_2	2.000E-07	3.325E-09
Impurity	O_2	6.000E-08	3.139E-09
Impurity	CH_4	5.000E-08	2.887E-08
Impurity	C_2H_4	5.000E-08	2.887E-08
Impurity	H_2O	2.500E-06	1.443E-06
Impurity	CO	2.500E-08	1.443E-08
Impurity	H_2	1.200E-07	6.928E-08
Impurity	Ar	9.000E-08	6.213E-09
Balance gas	CO_2	0.99999691	1.446E-06

Purity table for Pure N_2

Components		Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	O_2	2.500E-08	1.443E-08
Impurity	CO	2.500E-08	1.443E-08
Impurity	H_2	2.500E-08	1.443E-08
Impurity	CO_2	5.000E-08	2.887E-08
Impurity	CH_4	5.000E-08	2.887E-08
Impurity	H_2O	1.000E-08	5.774E-09
Balance gas	N_2	0.99999982	4.822E-08

Purity table for pure O_2

Components		Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	N_2	5.000E-07	2.887E-07
Impurity	CO	2.500E-08	1.443E-08
Impurity	CO_2	2.500E-08	1.443E-08
Impurity	H_2	5.000E-08	2.887E-08
Impurity	H_2O	2.500E-07	1.443E-07
Impurity	CH_4	5.000E-08	2.887E-08
Impurity	Ar	5.000E-08	2.887E-08
Balance gas	O_2	0.99999905	3.272E-07

Purity Table of CO

Components		Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	N_2	2.692E-04	1.384E-06
Impurity	CH_4	5.010E-06	2.928E-07
Impurity	C_2H_6	5.000E-08	2.887E-08
Impurity	O_2	2.500E-08	1.443E-08
Impurity	H_2	1.920E-06	2.900E-07
Impurity	Ar	6.760E-05	5.459E-07
Impurity	CO_2	7.890E-06	2.963E-07
Impurity	H_2O	2.500E-06	1.443E-06
Balance gas	CO	0.99964581	2.135E-06

Purity Table of C3H8

Components		Concentration (mol/mol)	Standard Uncertainty (mol/mol)
Impurity	N_2	7.362E-05	3.681E-06
Impurity	CH_4	5.000E-08	2.890E-08
Impurity	C_2H_6	1.051E-04	5.255E-06
Impurity	O_2	8.460E-06	8.460E-07
Impurity	H_2	8.000E-08	8.000E-09
Impurity	Ar	8.460E-06	8.460E-07
Impurity	CO_2	7.900E-07	3.450E-08
Impurity	H_2O	7.790E-05	7.790E-06
Impurity	CO	5.000E-08	2.900E-08
Impurity	C4H10	6.620E-06	3.310E-07
Impurity	C2H4	6.300E-07	3.150E-08
Impurity	C3H6	4.200E-05	2.100E-06
Balance gas	C3H8	0.99967634	1.040E-05

Instrumentation

Principle: GC-FID-TCD

Manufacturer: Agilent

Type Of gas	Measurement principle
CO	TCD
CO2	TCD
O2	TCD
C3H8	FID

Calibration method and value assignment

Please provide a brief description how the equipment was calibrated and how the assigned value was calculated (including the necessary formulae):

The GC analysers were 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:

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

6

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*

Uncertainty evaluation

Please provide a brief description of the evaluation of measurement uncertainty.

PSM code KRISS, D170117	NMC Measurement result, KRISS Concentration,	Uncertainty Source: GC Analysis of Sample Gas	Uncertainty Source: GC Analysis of PRM	Uncertainty Source: Gas Preparation	Uncertainty Source: Reproducibility	Combined Uncertainty	expanded uncertainty, (k=2)
CO **(cmol/mol)**	**1.2211**	0.00149	0.00167	0.00298	0.00067	**0.00378**	**0.0076**
CO2 **(cmol/mol)**	**3.5095**	0.00113	0.00096	0.00146	0.00074	**0.00222**	**0.0044**
O2 **(cmol/mol)**	**2.4906**	0.00127	0.00233	0.00283	0.000577	**0.00393**	**0.0076**
C3H8 **(cmol/mol)**	**0.01998**	0.0000257	0.0000200	0.0000474	0.0000119	**0.000059**	**0.00012**

Authorship

Kai Fuu Ming
Lemuel Joel Kuehsamy
Cui Yuxi

Measurement report

Laboratory name: Centro Nacional de Metrología - CENAM

Cylinder number: D170104

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	20/03/2024	1.2396	0.080	10
CO_2	01/03/2024	3.5237	0.10	20
O_2	01/04/2024	2.5089	0.24	9
C_3H_8	11/03/2024	0.020030	0.29	20

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	21/03/2024	1.2402	0.11	10
CO_2	04/03/2024	3.5140	0.38	20
O_2	02/04/2024	2.5117	0.29	8
C_3H_8	13/03/2024	0.019978	0.18	20

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	22/03/2024	1.2403	0.14	10
CO_2	05/03/2024	3.5167	0.20	20
O_2	03/04/2024	2.5093	0.28	8
C_3H_8	13/03/2024	0.019983	0.17	20

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2400	0.0032	2
CO_2	3.5181	0.0088	2
O_2	2.5099	0.0061	2
C_3H_8	0.019988	0.000029	2

Calibration standards

The reference standards used for calibration in this measurement are 5 multicomponent gas mixtures individually contained in aluminium cylinders, composed of O_2, C_3H_8, CO and CO_2 in nitrogen balance, The standards (PRMs) were produced by CENAM in accordance with the requirements of ISO-6142-1:2015 and ISO-6142:2001. The ranges of the standards are described in the following table, where the value after the ± express the expanded uncertainties of the PRMs (k=2). As control samples binary PRMs for each component were used and values recovered after appropriate corrections. The origin of traceability to SI of all PRMs is to CENAM.

Cylinder	CO cmol/mol	CO_2 cmol/mol	O_2 cmol/mol	C_3H_8 cmol/mol
FF69489	0.4952 ± 0.0010	1.4889 ± 0.0038	0.9937 ± 0.0059	0.009932 ± 0.000031
FF69476	0.7985 ± 0.0010	4.9875 ± 0.0055	2.532 ± 0.011	0.024893 ± 0.000046
FF69474	0.9970 ± 0.0010	2.0017 ± 0.0027	3.0036 ± 0.0057	0.020074 ± 0.000011
FF69485	1.4927 ± 0.0015	0.9986 ± 0.0020	1.9917 ± 0.0081	0.015105 ± 0.000052
FF69486	1.9995 ± 0.0018	2.9939 ± 0.0075	3.9724 ± 0.0064	0.030237 ± 0.000043

Instrumentation

CO

Non-dispersive infrared CO gas analyzer, VIA 510, HORIBA, configured with a computerized autosampler developed by CENAM. The response is obtained through a digital multimeter added to the analyzer.

CO_2

Gas chromatograph, Agilent, model 6890, with TCD detector at 250 °C, isothermal oven 90 °C, 1.3 min, Porapak R 100/120 packed column, 2 m, 0.317 cm (1/8 inch) OD, pressure 241.3 kPa (35 psi), injector 88 °C, reference gas flow 20 ml/min, loop 0.25 ml, helium gas as carrier. Configured with a mass flow controller for sample delivery and multiposicional valve.

O_2

Paramagnetic gas analyzer, model MPA-510, HORIBA, configured with a computerized autosampler developed by CENAM. The response is obtained through a digital multimeter added to the analyzer.

C_3H_8

Gas chromatograph, Agilent, model 6890, with FID detector and packed column, oven 150 °C, 1.8 min, Porapak Q 80/100 packed column 1.83 m (6 ft), 0.317 cm (1/8 inch), pressure 189.605 kPa (27.5 psi), injector 50 °C, FID 250 °C, reference gas flow 40 ml/min, air flow 450 ml/min, hydrogen flow 40 ml/min, loop 0.25 ml, helium gas as carrier. Configured with a mass flow controller for sample delivery and multiposicional valve.

Calibration method and value assignment

Data evaluation of multipoint calibrations according to ISO 6143:2001 using the CurveFit program, version 2.16. (3 April 2019-VSL Dutch Metrology Institute).

Three sessions on different days were carried out under repeatability conditions, each of them. In each session, a calibration was carried out for each component and in each instrument and measurement method. The assigned value is the combination of the three measurement sessions.

Uncertainty evaluation

Uncertainty considers repeatability, reproducibility, and that of primary standards and the model of measurement according to reference [2].

The measurement uncertainty was obtained by multiplying the combined standard uncertainty by a coverage factor k = 2, which corresponds to a confidence level of approximately 95 % under the assumption that the probability density function of the measurand is normal. The uncertainty of the measurement was estimated in accordance with the standard Guide for the expression of uncertainty in measurements, JCGM 100:2008 (GUM 1995 with minor corrections) Evaluation of measurement data – Guide to the expression of uncertainty in measurement. Published by BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML. First edition – September 2008.

References

1. ISO 6142-1:2015 Gas Analysis-Preparation of calibration gas mixtures Part 1: Gravimetric method for Class I mixtures.
2. ISO 6143:2001 Gas analysis Comparison methods for determining and checking the composition of calibration gas mixtures.

Authorship

Jorge Koelliker-Delgado
Carlos Ramírez-Nambo
Francisco Rangel-Murillo
Diana Gabriela Ramirez-Flores
Manuel de J. Ávila-Salas

Measurement report APMP.QM-K3.2019 Automotive emission gases

Report form

Laboratory name: Chemicals Evaluation and Research Institute, Japan (CERI)

Cylinder number: D170245

Measurement 1[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	16/3/2024	1.25083	0.2916	3
CO_2	7/3/2024	3.51987	0.1216	3
O_2	22/3/2024	2.50209	0.0399	3
C_3H_8	21/3/2024	0.0200079	0.0660	3

Measurement 2[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	17/3/2024	1.25092	0.1972	3
CO_2	9/3/2024	3.51496	0.0650	3
O_2	23/3/2024	2.49694	0.3996	3
C_3H_8	22/3/2024	0.0200364	0.0952	3

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	18/3/2024	1.25219	0.1306	3
CO_2	10/3/2024	3.51354	0.1012	3
O_2	24/3/2024	2.50375	0.1348	3
C_3H_8	23/3/2024	0.0200247	0.0717	3

Measurement 4#

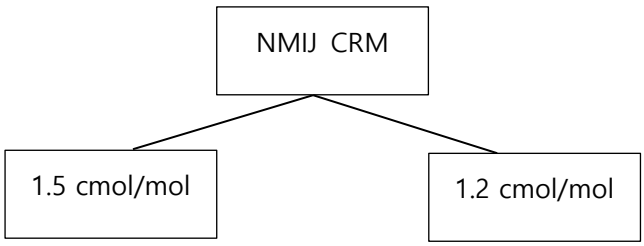
Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	19/3/2024	1.25325	0.2993	3
CO_2	13/3/2024	3.51349	0.0367	3
O_2	25/3/2024	2.50320	0.0275	3
C_3H_8	24/3/2024	0.0200272	0.1050	3

Results

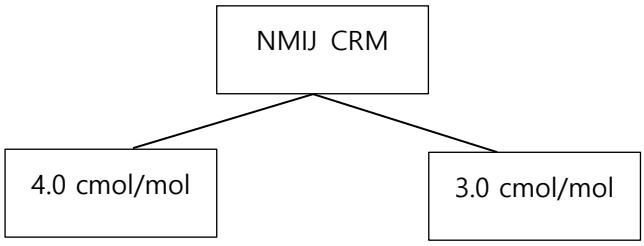
Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.252	0.003	2
CO_2	3.515	0.009	2
O_2	2.501	0.005	2
C_3H_8	0.02002	0.00006	2

Calibration standards

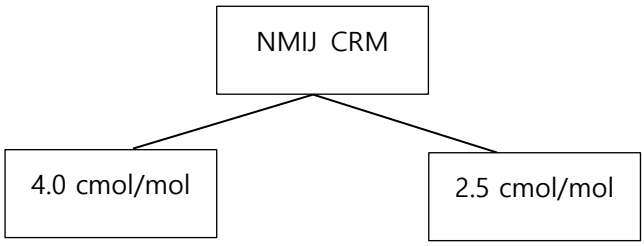
Method of preparation for CO standards



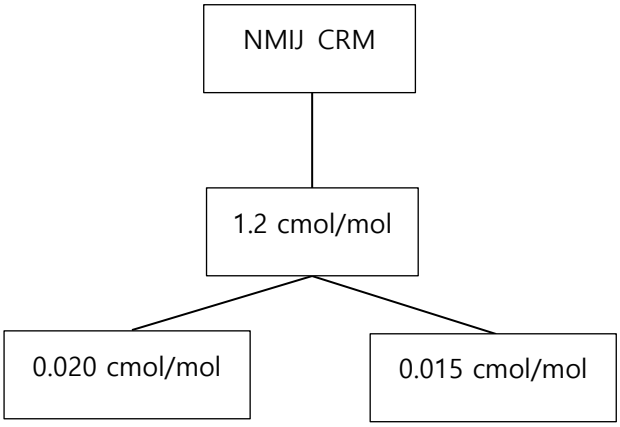
Method of preparation for CO_2 standards



Method of preparation for O_2 standards



Method of preparation for C_3H_8 standards



Instrumentation

Instruments for O_2 and CO measurement

GC-TCD (Type GC-2014, Make: Shimadzu corporation)

Column: Molecular Sieve 5A in stainless column (3 m, 3 mm i.d)

+ Porapak Q in stainless column (1 m, 3 mm i.d)

Instruments for CO_2 measurement

GC-TCD (Type GC-2014, Make: Shimadzu corporation)

Column: Porapak N in stainless column (3 m, 3 mm i.d)

Instruments for C_3H_8 measurement

GC-FID (Type 7890A, Make: Agilent technologies)

Column: Porapak Q in stainless column (3 m, 3 mm i.d)

Calibration method and value assignment

The instruments were calibrated using two gravimetrically prepared standards. Analytical scheme was, R_1 – APMP sample – R_2 or R_2 – APMP sample – R_1. This scheme was repeated 3-times in a day and iterated for 4 days.

Concentration of standards:

Component	Concentration (cmol/mol)	
	R_1	R_2
CO	1.511	1.207
CO_2	4.027	3.005
O_2	3.991	2.480
C_3H_8	0.02007	0.01507

Uncertainty evaluation

Carbon monoxide

Uncertainty source	Value (Xi)	Estimate +/-	Assumed distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient (c_i)	Contribution $u(y_i)$
R1	1.511 cmol/mol	0.000984333 cmol/mol	normal	1	0.000984333 cmol/mol	0.14803	0.00014571 cmol/mol
R2	1.207 cmol/mol	0.000660631 cmol/mol	normal	1	0.000660631 cmol/mol	0.85197	0.00056284 cmol/mol
CO in N_2 (dilution gas)	<0.0000003 cmol/mol	0.00000015 cmol/mol	rectangular	√3	0.000000087 cmol/mol	1	0.00000009 cmol/mol
Verification	0.9995 cmol/mol	0.0009 cmol/mol	normal	1	0.0009 cmol/mol	1.25263	0.00112737 cmol/mol
Measurement	1.252 cmol/mol	0.000798923 cmol/mol	normal	1	0.000798923 cmol/mol	1	0.00079892 cmol/mol
Round off	-	0.0005	rectangular	√3	0.000288675	1	0.00028868

		cmol/mol			cmol/mol		cmol/mol

Combined uncertainty 0.001527 cmol/mol

Expanded uncertainty 0.003 cmol/mol

Expanded uncertainty(relative) 0.24 %

Carbon dioxide

Uncertainty source	Value (Xi)	Estimate +/-	Assumed distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient (c_i)	Contribution $u(y_i)$
R1	4.027 cmol/mol	0.003605990 cmol/mol	normal	1	0.003605990 cmol/mol	0.49902	0.00179946 cmol/mol
R2	3.005 cmol/mol	0.002245800 cmol/mol	normal	1	0.002245800 cmol/mol	0.50098	0.00112510 cmol/mol
CO_2 in N_2 (dilution gas)	<0.0000003 cmol/mol	0.00000015 cmol/mol	rectangular	√3	0.000000087 cmol/mol	1	0.00000009 cmol/mol
Verification	2.025 cmol/mol	0.002 cmol/mol	normal	1	0.002 cmol/mol	1.7358	0.00347160 cmol/mol
Measurement	3.515 cmol/mol	0.001091949 cmol/mol	normal	1	0.001091949 cmol/mol	1	0.00109195 cmol/mol
Round off	-	0.0005 cmol/mol	rectangular	√3	0.000288675 cmol/mol	1	0.00028868 cmol/mol

Combined uncertainty 0.004223 cmol/mol

Expanded uncertainty 0.009 cmol/mol

Expanded uncertainty(relative) 0.25 %

Oxygen

Uncertainty source	Value (Xi)	Estimate +/-	Assumed distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient (c_i)	Contribution $u(y_i)$
R1	3.991 cmol/mol	0.002658882 cmol/mol	normal	1	0.002658882 cmol/mol	0.01390	0.00003696 cmol/mol
R2	2.480 cmol/mol	0. 001640421 cmol/mol	normal	1	0.001640421 cmol/mol	0.98610	0.00161762 cmol/mol
Ar in O_2 (parent gas)	<0.000005 cmol/mol	0.0000025 cmol/mol	rectangular	√3	0.000001443 cmol/mol	1	0.00000144 cmol/mol
Ar in N_2 (dilution gas)	-	0.0003 cmol/mol	normal	1	0.000300 cmol/mol	1	0.00030000 cmol/mol
O_2 in N_2 (dilution gas)	<0.00002 cmol/mol	0.00001 cmol/mol	rectangular	√3	0.000005774 cmol/mol	1	0.00000577 cmol/mol
Verification	2.503 cmol/mol	0.001 cmol/mol	normal	1	0.001 cmol/mol	0.9996	0.00099960 cmol/mol
Measurement	2.501 cmol/mol	0.001537448 cmol/mol	normal	1	0.001537448 cmol/mol	1	0.00153745 cmol/mol

Round off	-	0.0005 cmol/mol	rectangular	√3	0.000288675 cmol/mol	1	0.00028868 cmol/mol

Combined uncertainty 0.002481 cmol/mol

Expanded uncertainty 0.005 cmol/mol

Expanded uncertainty(relative) 0.20 %

Propane

Uncertainty source	Value (Xi)	Estimate +/-	Assumed distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient (c_i)	Contribution $u(y_i)$
R1	0.02007 cmol/mol	0.000025477 cmol/mol	normal	1	0.000025477 cmol/mol	0.99000	0.00002522 cmol/mol
R2	0.01507 cmol/mol	0.000019250 cmol/mol	normal	1	0.000019250 cmol/mol	0.01000	0.00000019 cmol/mol
Total hydro carbon in N_2 (dilution gas)	<0.0000003 cmol/mol	0.00000015 cmol/mol	rectangular	√3	0.000000087 cmol/mol	1	0.00000009 cmol/mol
Verification	0.01994 cmol/mol	0.00001 cmol/mol	normal	1	0.00001 cmol/mol	1.00401	0.00001004 cmol/mol
Measurement	0.02002 cmol/mol	0.000005254178 cmol/mol	normal	1	5.25418E-06 cmol/mol	1	0.00000525 cmol/mol
Round off	-	0.000005 cmol/mol	rectangular	√3	0.000002887 cmol/mol	1	0.00000289 cmol/mol

Combined uncertainty 0.000027802 cmol/mol

Expanded uncertainty 0.00006 cmol/mol

Expanded uncertainty(relative) 0.30 %

Authorship

Junji Azuma, Tomoe Nishino, Masaru Yamazawa

Measurement report

Report form

Laboratory name ： CMS/ITRI

Cylinder number ： D170004

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	11/04/2024	1.24999	0.039	5
CO_2	22/04/2024	3.49654	0.016	5
O_2	11/04/2024	2.51162	0.015	5
C_3H_8	16/05/2024	0.020076	0.004	5

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	16/04/2024	1.25021	0.065	5
CO_2	23/04/2024	3.49756	0.030	5
O_2	16/04/2024	2.51211	0.016	5
C_3H_8	17/05/2024	0.020077	0.012	5

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	18/04/2024	1.25051	0.021	5
CO_2	25/04/2024	3.49858	0.004	5
O_2	18/04/2024	2.51138	0.011	5
C_3H_8	23/05/2024	0.020072	0.013	5

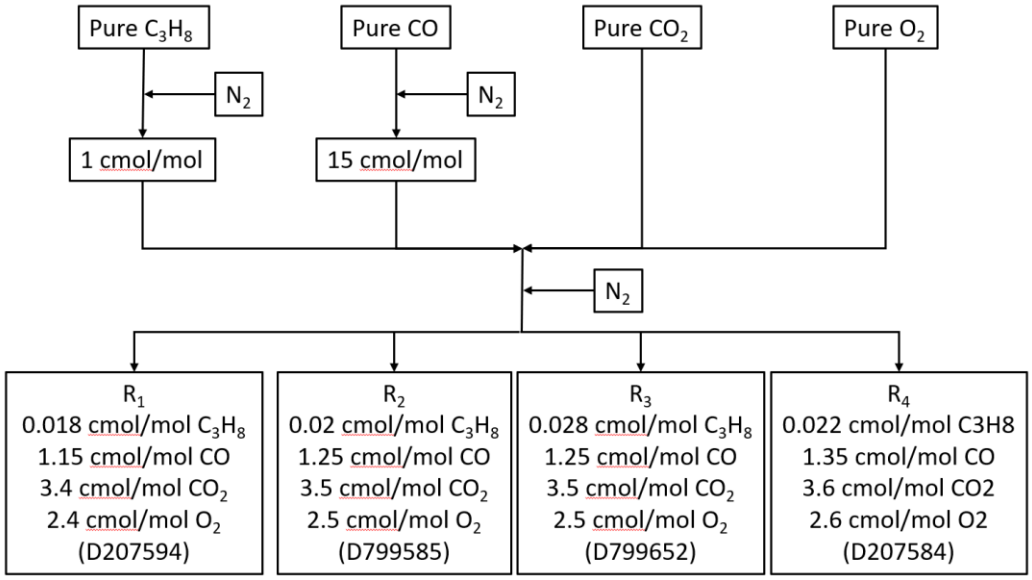
Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2502	0.0016	2
CO_2	3.4976	0.0047	2
O_2	2.5117	0.0079	2
C_3H_8	0.02007	0.00014	2

Calibration standards

The primary reference materials (PRMs) were prepared by gravimetric method according to ISO 6142-1: 2015. All source gases were analyzed to determine their impurity then used to prepare the PRMs. The PRMs were prepared by several times dilution with nitrogen from pure gases to cmol/mol or hundred μmol/mol. The PRMs at each stage were analyzed against each other for verification.

Cylinder dilution tree:



Purity tables of the source gases:

C_3H_8 :

Purity Table: C_3H_8

Cylinder no : 113053	Component	Amount fraction $*10^{-6}$ mol/mol	Distribution	uncertainty, Ai $*10^{-6}$ mol/mol	Detector
	H_2	0.02	Rectangular	0.00577	GC-PDHID
	Ar	2.68	Normal	0.03002	GC-PDHID
	O_2	26.62	Normal	0.27992	GC-PDHID
	N_2	650.00	Normal	0.45223	GC-TCD
	CO	0.04	Normal	0.00085	GC-PDHID

CH_4	0.03	Normal	0.00031	GC-PDHID
CO_2	2.36	Normal	0.01001	GC-FID
C_2H_6	33.57	Normal	0.32308	GC-FID
H_2O	36.55	Normal	0.03196	Dew point
C_3H_8	**999248.122**		**0.63**	

CO :

Purity Table: CO

Cylinder no : LLH180201	Component	Amount fraction *10^{-6} mol/mol	Distribution	uncertainty, Ai *10^{-6} mol/mol	Detector
	H_2	0.026	Normal	0.00021	GC-PDHID
	Ar	0.032	Normal	0.00022	GC-PDHID
	O_2	0.212	Normal	0.00208	GC-PDHID
	N_2	3.107	Normal	0.01023	GC-PDHID
	CH_4	0.010	Rectangular	0.00577	GC-PDHID
	CO_2	3.304	Normal	0.95378	FTIR
	CO	**999993.309**		**0.96**	

CO_2 :

Purity Table: CO2

Cylinder no : BH09HKK	Component	Amount fraction *10^{-6} mol/mol	Distribution	uncertainty, Ai *10^{-6} mol/mol	Detector
	H_2	0.020	Rectangular	0.00577	GC-PDHID
	Ar	0.020	Rectangular	0.00577	GC-PDHID
	O_2	0.058	Normal	0.00051	GC-PDHID
	N_2	0.149	Normal	0.00057	GC-PDHID
	CH_4	0.020	Rectangular	0.00577	GC-PDHID
	CO	0.020	Normal	0.00577	FTIR
	H_2O	2.932	Normal	0.00108	CRDS
	CO_2	**999996.7808**		**0.02**	

O_2 :

Purity Table: O_2

Cylinder no : FJ30PJP	Component	Amount fraction *10^{-6} mol/mol	Distribution	uncertainty, Ai *10^{-6} mol/mol	Detector
	N_2	1.53	Rectangular	0.0632	QMS
	CO_2	0.27	Rectangular	0.1530	FTIR
	CO	0.78	Rectangular	0.4503	FTIR
	CH_4	0.88	Rectangular	0.5081	FTIR
	O_2	**999996.545**		**0.70**	

N_2 :

Purity Table:	N_2				
Cylinder no : AP BIP	Component	Amount fraction $*10^{-6}$ mol/mol	Distribution	uncertainty, Ai $*10^{-6}$ mol/mol	Analyzer
	O_2	0.0025	Rectangular	0.0014	GC-PDHID
	H_2	0.01	Rectangular	0.0058	GC-PDHID
	CO	0.01	Rectangular	0.0058	GC-FID
	CO_2	0.01	Rectangular	0.0058	GC-FID
	CH_4	0.01	Rectangular	0.0058	GC-PDHID
	Ar	1.086	Rectangular	0.0010	GC-PDHID
	SO_2	0.225	Rectangular	0.1299	FTIR
	H_2O	0.00571	Rectangular	0.0212	CRDS
	NO	0.025	Rectangular	0.0144	Analyzer
	N_2	**999998.6158**		**0.13**	

Instrumentation

The instruments using for this key comparison are GC systems. Separation column using Molsieve (5A, 80/100, 6 ft, 1/8 inch) for O_2 and CO. Parapak Q (80/100, 6 ft, 1/8 inch) for CO, CO_2 and C_3H_8. The oven temperature were set from 40 to 120℃. Samples and standards were passed through the mass flow controller at 50 mL/min and sample loop (0.5 and 1 mL). During measurement, the drift of instrument was corrected by response variation of standards, so take the bracketing measurement like R-S-R-S-R…. Every measurement was repeated by a set of 7.

Configuration of analysis system: gas cylinder → regulator → selection valve → mass flow controller → GC-TCD or GC-FID → vent.

Calibration method and value assignment

Primary reference materials (PRMs) and KC cylinder through selection valve were sequence introduced to the sample loop of the GC system. The GC were calibrated using four PRMs. Analytical scheme was as follows R_1-R_2-R_3-R_4-KC-R_1-R_2-R_3-R_4 for three cycles and executed in spread across three days.

The value assignment of KC sample were calculated using the formula below :

$$C_{KC} = \frac{A_{KC}}{\left(\frac{A_{PRM1} + A_{PRM2}}{2}\right)} \times C_{PRM}$$

Where :

C_{KC} : Concentration of KC sample

A_{KC} : GC response of KC sample

A_{PRM1} : GC response of PRM before KC sample

A_{PRM2} : GC response of PRM after KC sample

C_{PRM} : Concentration of PRM

Uncertainty evaluation

Its combined uncertainty value was calculated as two times the square root of the sum of the squares for both uncertainty sources u_{prep} and u_{ver}.

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

Where :

u_{prep} : uncertainty of gravimetric preparation
u_{ver}. : uncertainty of analytical verification

Factors contributed to the gravimetric uncertainty of standard cylinder included:

- Purity of pure gases
- Tare mass uncertainty (accuracy of balance)
- Uncertainty in balance measurement (measurement uncertainty in cylinder weighing)
- Molecular weight

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

- Repeatability of instrument signal response
- Reproducibility of instrument signal response

According to the mathematical model used to calculate the concentration of gases in KC sample cylinder, the uncertainty of the calculated concentration of sample included:

- Repeatability of instrument signal response ratio between sample and standard cylinder
- Reproducibility of individual analysis
- Concentration uncertainty of standard cylinder

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

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

$$S_p = \sqrt{\frac{\sum_{i=1}^{3} S_i^2}{5}}$$

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

References

(1) ISO 6142-1:2015 /Amd.1:2020 “Gas Analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures”

(2) ISO 6143:2001 “Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures”

Authorship

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Measurement report

Report form

Laboratory name: National Institute of Metrology (NIM)

Cylinder number: D133461

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	12/03/2024	1.2418	0.009	3
CO_2	12/03/2024	3.4981	0.005	3
O_2	12/03/2024	2.5063	0.025	3
C_3H_8	12/03/2024	0.020233	0.004	3

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	13/03/2024	1.2419	0.001	3
CO_2	13/03/2024	3.4983	0.012	3
O_2	13/03/2024	2.5064	0.025	3
C_3H_8	13/03/2024	0.020234	0.002	3

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	14/03/2024	1.2416	0.011	3
CO_2	14/03/2024	3.4981	0.014	3
O_2	14/03/2024	2.5060	0.009	3
C_3H_8	14/03/2024	0.020233	0.017	3

Measurement 4#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates

CO	15/03/2024	1.2416	0.014	3
CO_2	15/03/2024	3.4982	0.014	3
O_2	15/03/2024	2.5067	0.018	3
C_3H_8	15/03/2024	0.020233	0.014	3

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2417	0.0037	2
CO_2	3.4982	0.0070	2
O_2	2.5063	0.0050	2
C_3H_8	0.020233	0.000041	2

Calibration standards

The sample was analyzed against NIM PSMs of which the amount fraction is listed in Table 1. The PSMs were prepared gravimetrically by using dilution starting from pure gas (the C_3H_8 using a multiple step dilution, Fig. 1 & Fig.2) according to ISO 6142-1:2015 – Gravimetric Method [1].

The CO, CO_2 and O_2 each was diluted one step into the final mixture from pure gas. While C_3H_8 was prepared from two different raw gases (Fig. 1) and the verification was made to their mixtures. A micro-GC coupled with TCD was used, He was the carrier gas. The differences (relative) between the C_3H_8 mixtures were 0.01% and 0.03% at the point of 3% mol/mol and 0.5% mol/mol respectively. This shows good agreement between the two routes for C_3H_8. Then the 0.5% mol/mol C_3H_8/N_2 in the cylinder '200236206120' was chosen for the further dilution (Fig. 2).

After preparation, the PSMs were analyzed against each other for verification [2].

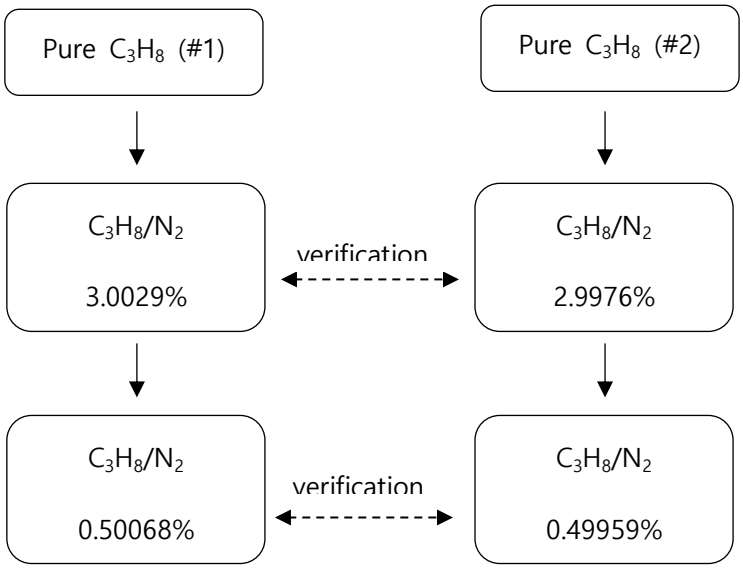

Fig. 1 Production diagram for the C_3H_8/N_2 gas mixture

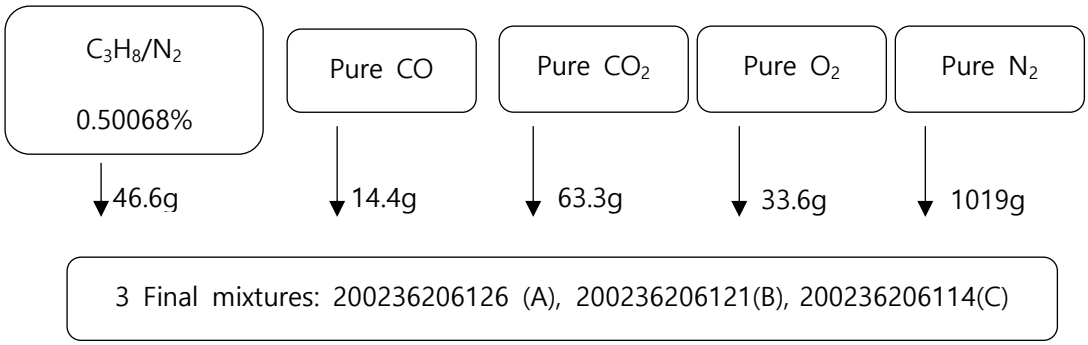

Fig. 2 Production diagram for the calibration standards with multi-components

Table 1. The amount fraction for the components in each calibration standard

Code	A	B	C	
Cylinder No.	200236206126	200236206121	200236206114	
Component	Amount fraction	Amount fraction	Amount fraction	Unit
C_3H_8	201.65	202.42	202.14	μmol/mol
CO	1.2528	1.2584	1.2547	cmol/mol
CO_2	3.5021	3.5074	3.5160	cmol/mol
O_2	2.5572	2.5586	2.5636	cmol/mol

Purity tables for the parent gases:

Purity table for N_2

Component	**Method**	**Amount fraction (μmol/mol)**	**Distribution**	**Standard uncertainty (μmol/mol, *k*=1)**
O_2	Oxygen Analyzer	0.05	Rectangular	0.03
Ar	GC-PDHID	45	Normal	2
H_2	GC-PDHID	0.05	Rectangular	0.03
H_2O	CRDs	0.2	Rectangular	0.12
CO	GC-PDHID	0.05	Rectangular	0.03
CO_2	GC-PDHID	0.05	Rectangular	0.03
CH_4	GC-PDHID	0.05	Rectangular	0.03
C_3H_8	GC-PDHID	0.05	Rectangular	0.03
N_2	—	999955	—	2

Purity table for O_2

Component	Method	Amount fraction (µmol/mol)	Distribution	Standard uncertainty (µmol/mol, *k*=1)
H_2	GC-PED	0.05	Rectangular	0.03
Ar	GC-PED	0.05	Rectangular	0.03
N_2	GC-PED	2.4	Normal	0.2
CH_4	GC-PED	0.05	Rectangular	0.03
CO	GC-PED	0.05	Rectangular	0.03
CO_2	GC-PED	0.05	Rectangular	0.03
H_2O	CRDs	1.5	Rectangular	0.9
C_3H_8	FTIR	0.05	Rectangular	0.03
O_2	—	999996	—	1

Purity table for CO_2

Component	Method	Amount fraction (µmol/mol)	Distribution	Standard uncertainty (µmol/mol, *k*=1)
H_2	GC-PDHID	0.05	Rectangular	0.03
Ar	GC-PDHID	0.05	Rectangular	0.03
O_2	GC-PDHID	0.05	Rectangular	0.03
N_2	GC-PDHID	0.38	Normal	0.04
CH_4	GC-PDHID	0.05	Rectangular	0.03
CO	GC-PDHID	0.05	Rectangular	0.03
H_2O	H_2O analyzer	1.5	Rectangular	0.9
C_3H_8	FTIR	0.05	Rectangular	0.03
CO_2	—	999998	—	1

Purity table for CO

Component	Method	Amount fraction (µmol/mol)	Distribution	Standard uncertainty (µmol/mol, *k*=1)
H_2	GC-PDHID	0.05	Rectangular	0.03
Ar	GC-PDHID	0.94	Normal	0.09
O_2	GC-PDHID	0.10	Normal	0.01
N_2	GC-PDHID	8.5	Normal	0.8
CH_4	GC-FID	0.05	Rectangular	0.03

CO_2	GC-PDHID	0.3	Normal	0.03
H_2O	CRDs	0.5	Rectangular	0.3
C_3H_8	FTIR	0.05	Rectangular	0.03
CO	—	999990	—	1

Purity table for C_3H_8

Component	Method	Amount fraction (µmol/mol)	Distribution	Standard uncertainty (µmol/mol, *k*=1)
H_2	GC-PDHID	12	Normal	1
Ar	GC-PDHID	1.5	Normal	0.2
O_2	GC-PDHID	26	Normal	3
N_2	GC-PDHID	115	Normal	12
CO_2	GC-PDHID	9	Normal	1
CO	GC-PDHID	0.05	Rectangular	0.03
H_2O	H_2O analyzer	24	Rectangular	14
CH_4	GC-FID	42	Normal	4
C_3H_6	GC-FID	11	Normal	1
C_2H_6	GC-FID	0.05	Rectangular	0.03
C_3H_8	—	999759	—	19

Instrumentation

Two analyzers (ABB AO2020) were used, the infrared analyser (module: Uras 26) was used for CO_2, CO and C_3H_8 analyses, the paramagnetic analyser (module: Magnos 206) was used for O_2 analyses. For controlling the sampling flow, a MFC was equipped for linking the sample/standard and analyser, it was set at 500mL/min. The two analyzers were connected in tandem, the sample/standard gas firstly went into the infrared analyser, then went into the paramagnetic analyser.

Calibration method and value assignment

The mixture with the cylinder No. 200236206121 was chosen as the standard to calibrate the KC sample (D133461). The calibration standard and the KC sample were alternately introduced to the analyzers. The readings were treated as response signals, the KC sample's amount fraction could be calculated through their readings in combination with standard's gravimetrical value. A single-point calibration procedure was adopted.

Uncertainty evaluation

The contributions of uncertainty for the amount fraction of KC sample were from the calibration standard and the analysis method.

$$u_{\mathrm{r}}(x_i) = \sqrt{u_{\mathrm{r}}{}^2\left(x_{i,\mathrm{ref}}\right) + u^2_{\mathrm{r,\,anal}}}$$

Here, u_{r} represents the relative standard uncertainty, x_i represents the amount fraction of a component in the KC sample, $u_{\mathrm{r,\,anal}}$ represents uncertainty comes from the analysis process for the calibration of KC sample, mainly consider the repeatability of calibration standard and the KC sample, and reproducibility of the value assigned for the KC sample during different days. $u_{\mathrm{r,\,anal}}$ was evaluated to be 0.087% in this comparison.

The uncertainty source of the calibration standard includes gravimetric preparation (weighing process, purity) and verification.

$$u_{\mathrm{r}}\left(x_{i,\mathrm{ref}}\right) = \sqrt{u^2_{\mathrm{r,\,prep}} + u^2_{\mathrm{r,}\,ver}}$$

Here, $x_{i,ref}$ represents the amount fraction of a component in the calibration standard, $u_{\mathrm{r,\,prep}}$and $u_{\mathrm{r,\,ver}}$represent uncertainty from gravimetric preparation and from verification, respectively.

$$U_{\mathrm{r}}(x_i) = k \times u_{\mathrm{r}}(x_i) \quad (k{=}2)$$

$U_r(x_i)$ represents the relative expanded uncertainty for the amount fraction of a component in the KC sample.

Component	Result (x_i, cmol/mol)	$u_{\mathrm{r,prep}}$	$u_{\mathrm{r,ver}}$	$u_{\mathrm{r,\,anal}}$	$U_{\mathrm{r}}(x_i)$ (k=2)	$U(x_i)$ (k=2, cmol/mol)
CO	1.2417	0.021%	0.08%	0.087%	0.3%	0.0037
CO_2	3.4982	0.011%	0.06%	0.087%	0.2%	0.0070
O_2	2.5063	0.009%	0.04%	0.087%	0.2%	0.0050
C_3H_8	0.020233	0.014%	0.04%	0.087%	0.2%	0.000041

References

[1] International Organization for Standardization, ISO 6142-1: 2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures.
[2] International Organization for Standardization, ISO 6143: 2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures.

Authorship

Tiqiang Zhang, Shuguo Hu, Fengran Zhou

Report Form APMP.QM-K3.2019 : CO,CO_2,O_2,C_3H_8 in N_2

Laboratory name : National Institute of Metrology (Thailand)

Cylinder number : D170014

Measurement #1

Component	Date (dd/mm/yy)	Amount fraction (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	19/3/24	1.2491	0.02	3
CO_2	19/3/24	3.5170	0.05	3
O_2	18/3/24	2.4862	0.03	3
C_3H_8	26/3/24	0.020222	0.02	3

Measurement #2

Component	Date (dd/mm/yy)	Amount fraction (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	19/3/24	1.2494	0.04	3
CO_2	19/3/24	3.5200	0.05	3
O_2	18/3/24	2.4850	0.03	3
C_3H_8	26/3/24	0.020222	0.05	3

Measurement #3

Component	Date (dd/mm/yy)	Amount fraction (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	19/3/24	1.2489	0.03	3
CO_2	19/3/24	3.5169	0.02	3
O_2	18/3/24	2.4854	0.02	3
C_3H_8	26/3/24	0.020208	0.04	3

Measurement result

Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2491	0.0013	2
CO_2	3.5180	0.0036	2
O_2	2.4855	0.0025	2
C_3H_8	0.020218	0.000021	2

Calibration standards

The primary gas reference materials (PGRMs) containing carbon monoxide, carbon dioxide, oxygen and propane in nitrogen used for calibration were prepared by gravimetric method in accordance with ISO 6142-1:2015. The amount fraction of PGRMs were verified by comparison method in accordance with ISO 12963. The PGRM used for APMP.QM-K3 2019 were newly prepared close to the amount fraction of gas sample. Purity assessment of the high pure gases were traceable to PGRMs of NIMT.

Purity data:

Table 1. Purity data of pure carbon dioxide

Component	Amount fraction (μmol/mol)	Detector	Distribution	Applied amount fraction (μmol/mol)	standard uncertainty (μmol/mol)	
O_2	0.96	GC/PDHID	Rectangular	0.96	0.007	
N_2	4.95	GC/PDHID	Rectangular	4.950	0.073	
CO	<0.07	GC/PDHID	Rectangular	0.033	0.019	
CH_4	0.21	GC/FID	Rectangular	0.207	0.01	
C_2H_4	<0.005	GC/FID	Rectangular	0.674	0.033	
H_2O	7.06	Dew Point Meter	Rectangular	7.06	4.1	
			impurities	13.88	4.08	
			CO_2 purity	999986.1	8.15	k=2

Table 2. Purity data of pure oxygen

Component	Amount fraction (μmol/mol)	Detector	Distribution	Applied amount fraction (μmol/mol)	standard uncertainty (μmol/mol)	
H_2	<0.05	GC/PDHID	Rectangular	0.02	0.014	
N_2	<0.02	GC/PDHID	Rectangular	0.009	0.005	
CO	<0.01	GC/PDHID	Rectangular	0.006	0.003	
CO_2	1.61	GC/FID*	Normal	1.61	0.12	
Ar	<1.45	GC/TCD	Rectangular	0.725	0.42	
CH_4	<0.005	GC/FID	Rectangular	0.002	0.001	
H_2O	4.32	CRDS	Rectangular	4.32	2.5	
			impurities	6.70	2.53	
			O_2 purity	999993.3	5.07	k=2

*GC-FID with Methanizer

Table 3. Purity data of pure carbon monoxide

Component	Amount fraction (μmol/mol)	Detector	Distribution	Applied amount fraction (μmol/mol)	standard uncertainty (μmol/mol)	
O_2	3.12	GC/PDHID	Normal	3.12	0.07	
N2	40.74	GC/PDHID	Normal	40.74	0.39	
CO_2	54.86	GC/FID*	Normal	54.86	0.89	
CH_4	< 0.1	GC/FID	Rectangular	0.05	0.03	
H2O	< 7	as specification	Rectangular	3.50	2.02	
			impurities	102.27	2.24	
			CO purity	999897.7	4.49	k=2

*GC-FID with Methanizer

Table4. Purity data of pure propane

Component	Amount fraction (µmol/mol)	Detector	Distribution	Applied amount fraction (µmol/mol)	standard uncertainty (µmol/mol)	
O_2	1.23	GC/PDHID	Rectangular	1.23	0.71	
N2	3.47	GC/PDHID	Rectangular	3.47	2.01	
CO	0.07	GC/FID*	Rectangular	0.07	0.04	
CO_2	1.95	GC/FID*	Rectangular	1.95	1.13	
CH_4	0.30	GC/FID	Rectangular	0.30	0.17	
C_2H_6	< 40	as specification	Rectangular	40.00	23.09	
C_3H_6	< 10	as specification	Rectangular	10.00	5.77	
H_2	<0.5	as specification	Rectangular	0.50	0.29	
H_2O	< 3	as specification	Rectangular	3.00	1.73	
			impurities	60.52	23.99	
			C_3H_8 purity	999939.5	47.98	k=2

*GC/FID with metanizer

Table 5. Purity data of pure nitrogen

Component	Amount fraction (µmol/mol)	Detector	Distribution	Applied amount fraction (µmol/mol)	standard uncertainty (µmol/mol)	
O_2	0.03	CRDS	Rectangular	0.03	0.01	
Ar	37.23	GC/PDHID	Normal	37.2	0.39	
CO	<0.05	GC/FID*	Rectangular	0.03	0.01	
CO_2	<0.05	GC/FID*	Rectangular	0.03	0.01	
CH_4	<0.07	GC/FID	Rectangular	0.04	0.02	
H_2O	0.07	CRDS	Rectangular	0.07	0.04	
			impurities	37.42	0.39	
			N_2 purity	999962.6	0.78	k=2

*GC/FID with methanizer

Weighing data:

The amount fraction of PGRMs were determined in compliance with ISO 6142-1 by using gravimetric method. These standard gas mixtures were prepared by gravimetric dilution of high purity carbon monoxide, carbon dioxide and oxygen in 1-step and from high purity propane in 3-step shown in Figure 1. The uncertainty of PGRMs were evaluated from the gravimetry, verification and measurement bias.

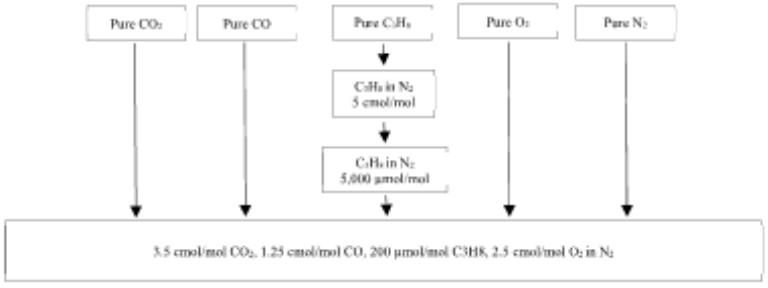

Figure 1: Step dilution of PGRM.

Uncertainty Budget of gravimetric method

Quantity	Value		Standard Uncertainty		Distribution	Sensitivity Coefficient	Uncertainty Contribution	
n_{comp1}	1.45E+00	mol	6.75E-04	mol	Normal	1	6.75E-04	%rel
n_{comp2}	4.92E-01	mol	1.60E-03	mol	Normal	1	1.60E-03	%rel
n_{comp3}	8.35E-03	mol	1.27E-02	mol	Normal	1	1.27E-02	%rel
n_{comp4}	1.01E+00	mol	2.73E-04	mol	Normal	1	2.73E-04	%rel
n_{comp5}	3.80E+01	mol	2.17E-04	mol	Normal	1	2.17E-04	%rel
m_{comp1}	63.93	g	3.21E-03	%rel	Normal	1	3.21E-03	%rel
$(Samp-Tare)_{empty}$	-6.09	g	0.663	mg				
$(Samp-Tare)_{comp1}$	57.84	g	0.748	mg				
u_{bl}	0.00	g	1.789	mg				
u_{mp}	0.00	g	0.000	mg				
mol	1.45	mol	0.000	mol				
m_{comp2}	13.78	g	1.57E-02	%rel	Normal	1	1.57E-02	%rel
$(Samp-Tare)_{empty}$	57.84	g	0.748	mg				
$(Samp-Tare)_{comp1}$	71.62	g	0.970	mg				
u_{bl}	0.00	g	1.789	mg				
u_{mp}	0.00	g	0.000	mg				
mol	0.49	mol	0.000	mol				
m_{comp3}	46.93	g	4.80E-03	%rel	Normal	1	4.80E-03	%rel
$(Samp-Tare)_{empty}$	71.62	g	0.970	mg				
$(Samp-Tare)_{comp1}$	118.55	g	0.970	mg				
u_{bl}	0.00	g	1.789	mg				
u_{mp}	0.00	g	0.000	mg				
mol	0.01	mol	0.000	mol				
m_{comp4}	32.46	g	6.85E-03	%rel	Normal	1	6.85E-03	%rel
$(Samp-Tare)_{empty}$	118.55	g	0.970	mg				
$(Samp-Tare)_{comp1}$	151.01	g	0.894	mg				
u_{bl}	0.00	g	1.789	mg				
u_{mp}	0.00	g	0.000	mg				
mol	1.01	mol	0.000	mol				
m_{comp5}	1017.69	g	1.63E-03	%rel	Normal	1	1.57E-03	%rel
$(Samp-Tare)_{empty}$	151.01	g	0.894	mg				
$(Samp-Tare)_{comp1}$	1168.70	g	1.000	mg				
u_{bl}	0.00	g	1.789	mg				
u_{mp}	0.00	g	16.414	mg				
mol	37.99	mol	0.001	mol				
MW_{comp1}	44.009	g/mol	3.26E-03	%rel	Normal	1	3.26E-03	%rel
MW_{comp2}	28.010	g/mol	4.40E-03	%rel	Normal	1	4.40E-03	%rel
MW_{comp3}	44.096	g/mol	8.35E-03	%rel	Normal	1	8.35E-03	%rel
MW_{comp4}	31.999	g/mol	2.67E-03	%rel	Normal	1	2.67E-03	%rel
MW_{comp5}	28.014	g/mol	3.50E-03	%rel	Normal	1	3.50E-03	%rel
CO_2	3.54694	cmol/mol	1.64	µmol/mol			0.00	%rel
CO	1.20070	cmol/mol	1.97	µmol/mol			0.02	%rel
C_3H_8	203.979	µmol/mol	0.05	µmol/mol			0.02	%rel
O_2	2.47655	cmol/mol	1.82	µmol/mol			0.01	%rel
N_2	92.7518	cmol/mol	0.004	cmol/mol			0.00	%rel

Results:

Quantity	Amount fraction		Expanded Uncertainty		Coverage factor	Coverage
CO_2	3.54694	cmol/mol	0.009	%rel	2.00	95%
CO	1.20070	cmol/mol	0.033	%rel	2.00	95%
C_3H_8	203.979	µmol/mol	0.032	%rel	2.00	95%
O_2	2.47655	cmol/mol	0.015	%rel	2.00	95%
N_2	92.7518	cmol/mol	0.01	%rel	2.00	95%

Table 6. Amount fraction of PGRM used for assigned value.

Cylinder number	Component	Amount fraction	Expanded uncertainty (Relative value, $k = 2$)
PRM1094477	CO	1.2007 cmol/mol	0.08%
	CO_2	3.5469 cmol/mol	0.06%
	O_2	2.4766 cmol/mol	0.08%
	C_3H_8	203.98 µmol/mol	0.08%

Instrumentation

The amount fraction of carbon monoxide and carbon dioxide were determined by using an Agilent 7890 Gas Chromatograph with Thermal Conductivity Detector (GC-TCD). The GC columns used were 8 ft Hayesep Q 80/100 Mesh for CO_2 and 8 ft Molesieve 5A 60/80 Mesh for CO. The measured condition was sample loop 1 ml, temperature of oven 30°C, temperature of detector 250°C, and He as carrier gas 30 ml/min. The flowrate of sample gas mixtures was controlled by using a mass flow controller at 45 ml/min.

The amount fraction of oxygen was determined by using a Paramagnetic Oxygen Analyzer, Model 4100 (Servomex). The sample flowrate was at 200 ml/min.

The amount fraction of propane was determined by using an Agilent 6890 Gas Chromatograph with flame ionization detector (FID). The GC column used was 1.64 ft Hayesep Q 80/100 Mesh and with nitrogen as carrier gas 25 ml/min. The measured condition was sample loop 0.25 ml, temperature of oven 65°C, temperature of detector 250°C, hydrogen flow 30 ml/min and air flow 400 ml/min. The flowrate of sample gas mixtures was controlled by using a mass flow controller at 45 ml/min.

Calibration method and value assignment

This sample gas mixture was measured against primary gas reference materials (PGRMs) of NIMT for traceable measurement results. The one-calibration point measurement was performed in accordance with ISO 12963. The composition of the PGRM used was closed to the target amount fraction of the sample gas mixture. The measurement procedure is shown as follow; "PGRM (Calibration) – Sample – PGRM (Calibration) –Sample – PGRM (Calibration) – Sample – PGRM (Calibration)". In the addition, 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.

The certified amount fraction of sample, X_s, is calculated from the following equations;

$$X_s = \frac{Y_s}{Y_{ref}} \times X_{ref}$$

- The amount fraction of standard gas mixture, X_{ref}
- Average response of standard gas mixture at j^{th}cycles, ($y_{ref,j}$)
- Average measurement response of standard gas mixture, Y_{ref}

$$Y_{ref} = \frac{\sum_{j=1}^{3} y_{ref,j}}{J}$$

- Average response of sample gas mixture at j^{th}cycles, ($y_{s,j}$)
- Average measurement response of sample, Y_s

$$Y_s = \frac{\sum_{j=1}^{J} y_{s,j}}{J}$$

J = number of series

Uncertainty evaluation

The uncertainty of the measurement was evaluated according to the following equation.

$$u(x_s) = x_s \sqrt{\frac{u^2(X_{ref})}{X_{ref}^2} + \frac{u^2(Y_{ref})}{Y_{ref}^2} + \frac{u^2(Y_s)}{Y_s^2} + \frac{u^2(x_{s,b})}{x_s^2}}$$

Where

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

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

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

$u(x_{s,b})$ is the standard uncertainty of the analytical amount fraction of the sample between cycles

X_{ref} is the amount fraction of the standard gas mixture

Y_{ref} is average measurement response of the standard gas mixture

Y_s is average measurement response of the sample

X_s is the certified amount fraction of the sample

Table 7 Uncertainty Budget for CO measurement

Uncertainty source	Estimate (absolute unit)	Standard uncertainty (%relative)	Contribution to standard uncertainty (%relative)
The standard gas mixture, (X_{grav})	1.2007	0.04	0.04
Response of standard gas mixture, u(Y_{grav})	4346.072	0.01	0.01
Response of sample, u(Y_s)	4521.298	0.01	0.01
Analytical amount fraction of sample between cycle, u(x_{sb})	-	0.01	0.01
Certified amount fraction of sample, (X_s)	1.2491	Combined uncertainty	0.05
Expanded uncertainty (k = 2), %relative			0.10

Table 8 Uncertainty Budget for CO_2 measurement

Uncertainty source	Estimate (absolute unit)	Standard uncertainty (%relative)	Contribution to standard uncertainty (%relative)
The standard gas mixture, (X_{grav})	3.5469	0.03	0.03
Response of standard gas mixture, (Y_{grav})	14553.924	0.01	0.01
Response of sample, u(Y_s)	14434.986	0.01	0.01
Analytical amount fraction of sample between cycle, u(x_{sb})	-	0.03	0.03
Certified amount fraction of sample, (X_s)	3.5180	Combined uncertainty	0.05
Expanded uncertainty ($k = 2$), %relative			0.10

Table 9 Uncertainty Budget for O_2 measurement

Uncertainty source	Estimate (absolute unit)	Standard uncertainty (%relative)	Contribution to standard uncertainty (%relative)
The standard gas mixture, (X_{grav})	2.4765	0.04	0.04
Response of standard gas mixture, (Y_{grav})	2.5331	0.01	0.01
Response of sample, u(Y_s)	2.5422	0.01	0.01
Analytical amount fraction of sample between cycle, u(x_{sb})	-	0.01	0.01
Certified amount fraction of sample, (X_s)	2.4855	Combined uncertainty	0.05
Expanded uncertainty ($k = 2$), %relative			0.10

Table 10 Uncertainty Budget for C_3H_8 measurement

Uncertainty source	Estimate (absolute unit)	Standard uncertainty (%relative)	Contribution to standard uncertainty (%relative)
The standard gas mixture, (X_{grav})	203.98	0.04	0.04
Response of standard gas mixture, u(Y_{grav})	1674.65	0.01	0.01
Response of sample, u(Y_s)	1659.85	0.01	0.01
Analytical amount fraction of sample between cycle, u(x_{sb})	-	0.02	0.02
Certified amount fraction of sample, (X_s)	202.18	Combined uncertainty	0.05
Expanded uncertainty ($k = 2$), %relative			0.10

References

[1] ISO 6142-1:2015 Gas analysis - Preparation of calibration gas mixtures
Part 1: Gravimetric method for Class I mixtures.

[2] ISO 12963:2017 Gas analysis - Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration.
[3] ISO 19229: 2015 Gas analysis – Purity analysis and the treatment of purity data

Authorship

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Measurement report

Report form.

Laboratory name: NMIA

Cylinder number: D170080

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	14/05/24	1.2420	0.0936	5
CO_2	14/05/24	3.5016	0.0470	30
O_2	14/05/24	2.5106	0.0633	12
C_3H_8	14/05/24	0.02030	0.1037	24

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	03/08/24	1.2410	0.0575	8
CO_2	03/08/24	3.5013	0.0432	15
O_2	03/08/24	2.5092	0.0286	4
C_3H_8	03/08/24	0.02029	0.0668	30

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	08/08/24	1.2412	0.1109	7
CO_2	08/08/24	3.5020	0.0360	15
O_2	08/08/24	2.5103	0.0598	7
C_3H_8	08/08/24	0.02030	0.0635	15

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2413	0.0012	k=2
CO_2	3.5016	0.0026	k=2
O_2	2.5102	0.0019	k=2
C_3H_8	0.02030	0.00002	k=2

Calibration standards

NMI primary standards were prepared gravimetrically using a Sartorius CC10000S mass comparator according to ISO 6142.1. Environmental conditions were monitored during the use of the mass comparator to allow for the correction of buoyancy. The purity of the source gases was also included in the calculation of mixture composition and for the assignment of the concentration of each gas component.
All standards were manufactured at NMIA Lindfield. Multiple stages of dilution were required to reach the desired concentration of carbon monoxide and propane.
Luxfer (USA) 5.8L aluminium cylinders were used to hold the gas mixtures. Cylinders were not coated or treated for these mixtures. Tables display the composition and combined preparation uncertainty (k=1).

		FF34142		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N_2	92.73254435	0.001281325	0.001381742
Oxygen	O_2	2.694881613	0.001045593	0.038799222
Carbon Monoxide	CO	1.167149425	0.000382139	0.032741194
Carbon Dioxide	CO_2	3.386278748	0.000890551	0.026298822
Propane	C_3H_8	0.01911319	9.64797E-06	0.050478053

		FF34144		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N_2	92.561795	0.001201308	0.001297845
Oxygen	O_2	2.385890897	0.000952171	0.039908409
Carbon Monoxide	CO	1.28960427	0.000390767	0.030301286
Carbon Dioxide	CO_2	3.741559939	0.000867685	0.023190474
Propane	C_3H_8	0.021118506	1.03331E-05	0.048929034

		FF34145		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N_2	95.16839723	0.00141208	0.00148377
Carbon Monoxide	CO	1.225680076	0.000351883	0.0287092
Carbon Dioxide	CO_2	3.585210347	0.001397248	0.03897254
Propane	C_3H_8	0.020698305	1.2761E-05	0.061652198

		FF56364		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N2	97.46872481	0.000482244	0.000494768
Oxygen	O2	2.530969307	0.00048273	0.019072938

Source gas purity tables:

		Nitrogen		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Argon	Ar	0.000184	0.0000035	1.902173913
Nitrogen	N2	99.9996525	4.64579E-06	4.6458E-06
Oxygen	O2	1E-05	0.0000025	25.00000001
Carbon Dioxide	CO2	0.000151	0.000001	0.662251656
Methane	CH4	0.0000025	1.44338E-06	57.73502692

		Carbon Dioxide		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N2	0.00008	0.00002	25
Oxygen	O2	0.000018	0.000006	33.33333333
Carbon Dioxide	CO2	99.999862	2.1616E-05	2.1616E-05
Methane	CH4	8E-06	0.0000025	31.25000002
Ethane	C2H6	0.000032	0.000005	15.625

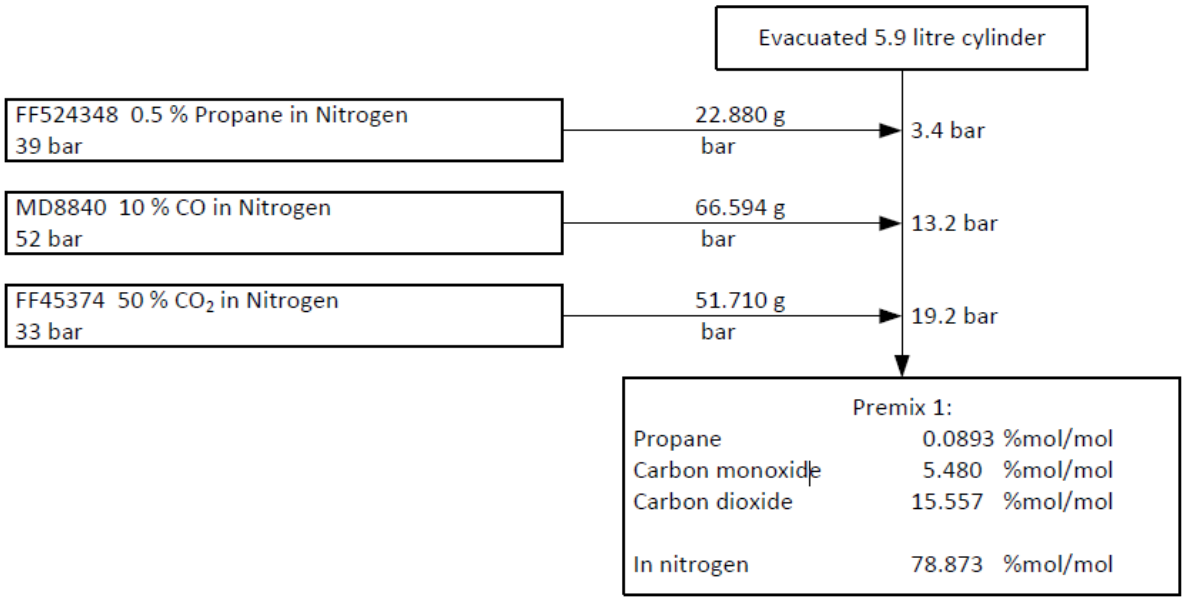
		Carbon Monoxide		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N2	0.00039	0.000115	29.48717949
Oxygen	O2	0.00015	0.00001	6.666666667
Carbon Monoxide	CO	99.99935	0.000115866	0.000115867
Carbon Dioxide	CO2	0.00011	0.00001	9.090909091

		Propane		
Chemical Name	**Formula**	**(%mol)**	**u (%mol)**	**u (% Rel)**
Nitrogen	N2	0.0024	0.00015	6.25
Oxygen	O2	0.00015	0.00003	20
Ethane	C2H6	0.0017	0.0001	5.882352941
Propane	C3H8	99.99575	0.000182757	0.000182764

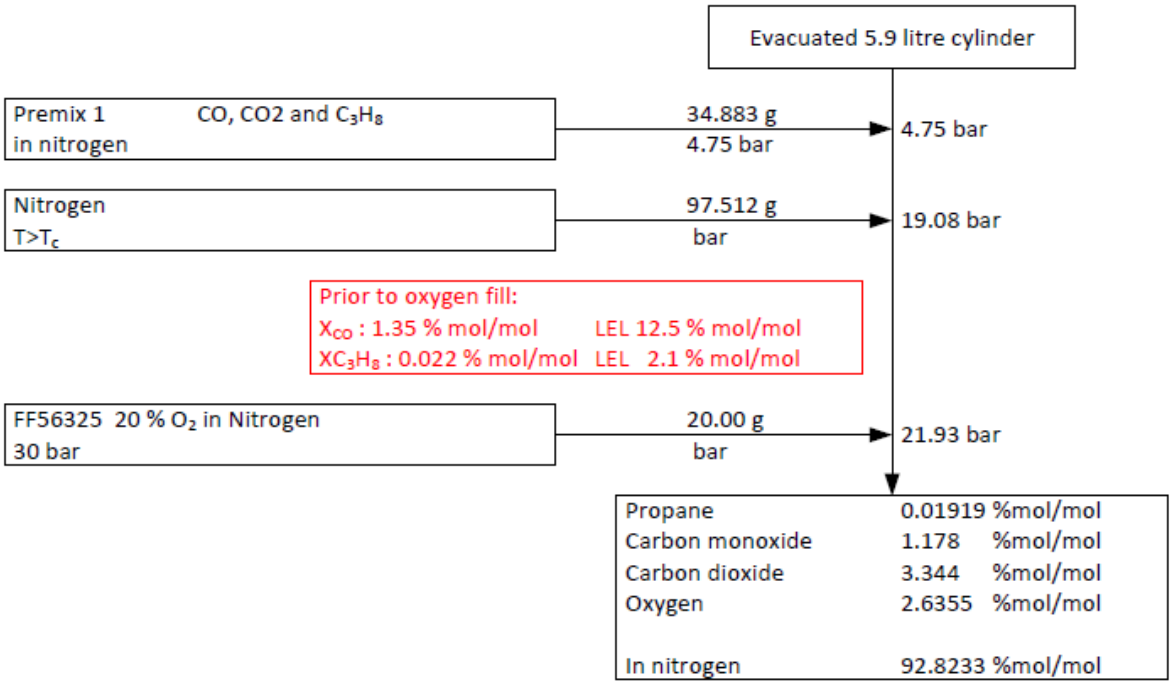
Mixture preparation stages:

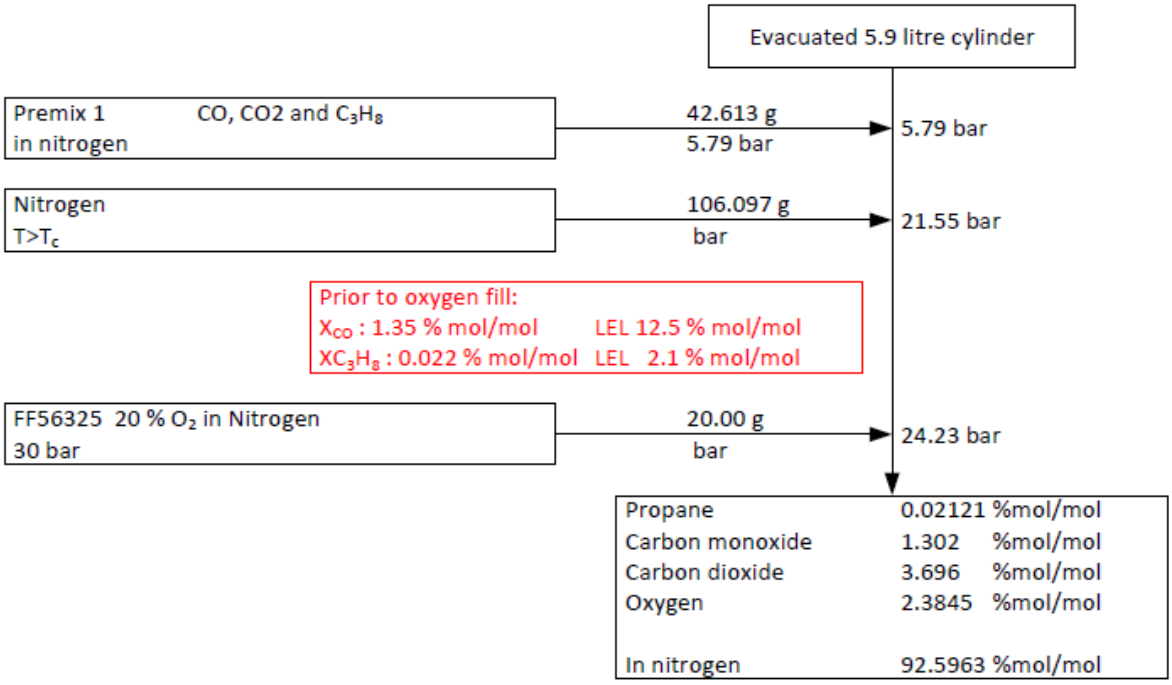
Stage 1:

APMP QM-K3 analysis
Automotive Emission
Oxygen, CO, CO_2 and propane in Nitrogen



Stage 2:





Instrumentation

1. GC6 Varian CP3800: PPQ 6'x1/8" + HayesepR 12'x2mm (Argon carrier FID). Used for the analysis of propane.
2. GC7 Varian 450-GC: HayesepR 2.6m x 1/8" (He carrier FID). Used for the analysis of propane.
3. GC9 Bruker/SCION 456 GC (NGA configuration C). The system is configured with a 14 port valve and 6 port valve. The valves are installed in the multi-valve oven for flexible operation of the conventional column oven. The 14 port valve enables the system to introduce the

sample stream simultaneously to three independent columns with automated detector switching. Two of the sample paths flow onto Molsieve and porous polymer columns to separate oxygen, nitrogen and carbon dioxide, ethane, methane, and the other via a non-polar capillary column (BR-1) to separate the hydrocarbon components up through C16. The 6 port valve is used to direct the separated components fraction to the TCD detector while components remaining on the Molsieve column are flushed to vent. Scion 456-GC: BR1 60m x 0.25mmID x 1.0µm (FID), Molsieve 13X 4'x 1/8" (He carrier TCD). This GC was used for the analysis of propane and carbon dioxide.

4. GC10 Agilent 7890B GC: HayesepQ 3'x 1/8" backflush + Molsieve5A 20'x 1/8" (Argon carrier TCD). Used for the analysis of oxygen, carbon monoxide and carbon dioxide.

Calibration method and value assignment

Instruments were calibrated at the time of use with closely matched reference standards. The standards were run with the sample for analysis.

During the certification measurements, each gas cylinder was equipped with a conditioned low volume Messer pressure regulator. The regulators were connected to 10-port VICI stream selection valves and then to common Bronkhorst mass flow controllers mounted on each GC to give a highly consistent sample pressure and flow through the GC sample loops.

Analysis and value assignment was performed using equation 2 from ISO 12963 using single point calibrations. The equation for single point calibration was employed:

$C_A = S_{sample} / S_{standard} * C_{standard}$

The sample was analysed many times relative to the reference gases in an S R_1 S R_1 type sequence or when more than one standard was employed in a S R_1 S R_2 S R_3 S R_4 S type sequence (S is sample; R_1 to R_4 are reference standards) with each step comprising at least 7 repeat injections. The whole sequence was repeated three times (starting on the 14/5/24, 3/8/24 and the 8/8/2024).

The calculated concentration from each analysis on each GC against the individual standards was tabulated. The mean was then determined for the amount fraction of each component. For several components the amount fraction was determined on more than one instrument.

Uncertainty evaluation

Measurement uncertainty was calculated using equation 3 from ISO 12963. Uncertainties were calculated from the uncertainties of the preparation of the reference standards (including balance, buoyancy, expansion, purity, molar mass etc) and the uncertainties due to the repeat analyses (Repeatability of standard within run; Repeatability of sample within run; Repeatability between runs; Instrument resolution). As the standards had uncertainties that were nominally the same and the performance of the instrument was consistent, the uncertainties from each standard/sample pairing were common and a value was chosen approximately halfway through the sequence as the value then represents what is routinely achievable during testing of a commercial sample with unknown composition. When the component was measured on several detectors, the detector that gave the smaller uncertainty was generally chosen as the basis of the uncertainty.

References

- ISO 6142-1:2015 – Gas analysis - Preparation of calibration gas mixtures
- JCGM 100:2008 (GUM 1995 with minor corrections) Evaluation of measurement data – Guide to the expression of uncertainty in measurement

Authorship

Damian Smeulders, John McCallum, Mona Safari Jurshari, Raymond Satumba.

Measurement report

Report form

Laboratory name: National Metrology Institute of Japan (NMIJ)

Cylinder number: D170253

Measurement 1[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	05/03/2024	1.242 0	0.026	5
CO_2	05/03/2024	3.554 4	0.030	5
O_2	27/02/2024	2.499 0	0.018	3
C_3H_8	13/03/2024	$2.015\ 9\times10^{-2}$	0.022	5

Measurement 2[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	06/03/2024	1.240 3	0.029	5
CO_2	06/03/2024	3.549 4	0.025	5
O_2	27/02/2024	2.496 2	0.018	3
C_3H_8	14/03/2024	$2.015\ 8\times10^{-2}$	0.022	5

Measurement 3[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	07/03/2024	1.241 8	0.035	5
CO_2	07/03/2024	3.553 8	0.035	5
O_2	27/02/2024	2.495 2	0.024	3
C_3H_8	15/03/2024	$2.015\ 6\times10^{-2}$	0.023	5

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.241 3	0.001 2	2
CO_2	3.552 5	0.003 4	2
O_2	2.496 8	0.002 3	2
C_3H_8	$2.015\ 8\times10^{-2}$	$0.000\ 5\times10^{-2}$	2

Calibration standards

Source gases and materials for calibration gas mixtures

NMIJ CRMs 3406-e, 3407-c, 3403-c, and 4052-c were used as source gases for calibration gas mixtures of carbon monoxide, carbon dioxide, oxygen, and propane, respectively. Pure nitrogen was purchased from Japan Fine Products Co., Ltd. (Kawasaki, Kanagawa, Japan). Purity tables of carbon monoxide, carbon dioxide, oxygen, propane, and nitrogen were shown in Tables 1, 2, 3, 4, and 5, respectively.

Table 1 Purity table with uncertainties for the pure carbon monoxide (units: μmol/mol)

Component *i*	x_i	$u(x_i)$
Carbon monoxide	999966	10
Nitrogen	1.52	0.88
Helium	26.20	0.58
Oxygen	0.52	0.30
Water	1.47	0.85
Carbon dioxide	0.42	0.24
Hydrogen	3.97	0.34

Table 2 Purity table with uncertainties for the pure carbon dioxide (units: μmol/mol)

Component *i*	x_i	$u(x_i)$
Carbon dioxide	999995.0	3.0
Nitrogen	0.89	0.51
Oxygen	0.43	0.25
Water	2.8	1.4
Carbon monoxide	0.156	0.090
Methane	0.40	0.23
Hydrogen	0.89	0.52

Table 3 Purity table with uncertainties for the pure oxygen (units: μmol/mol)

Component *i*	x_i	$u(x_i)$
Oxygen	1000000.0	1.5
Nitrogen	negligible	
Carbon monoxide	negligible	
Carbon dioxide	negligible	
Propane	negligible	

Note: The purity of oxygen in this table was quantified by using a magneto-pneumatic oxygen analyzer, which was calibrated by using another pure oxygen gas with its purity determined by the subtraction method.

Table 4 Purity table with uncertainties for the pure propane (units: μmol/mol)

Component *i*	x_i	$u(x_i)$
Propane	999 469.93	118.04
Nitrogen	9.39	0.58
Oxygen	13.44	1.76
Carbon dioxide	5.85	3.38
Ethane	5.58	0.70
Propene (propylene)	23.85	0.98
Cyclopropane	1.00	0.58
Butane	2.17	0.11
2-Methylpropane (isobutane)	20.69	2.21
Butene	1.00	0.58
Water	447.10	117.94

Table 5 Purity table with uncertainties for the pure nitrogen (units: μmol/mol)

Component *i*	x_i	$u(x_i)$
Nitrogen	999 999	1
Oxygen	0.08	0.05
Carbon monoxide	0.16	0.09
Carbon dioxide	0.58	0.33
Propane	negligible	

Preparation of calibration gas mixtures

The calibration gas mixtures were prepared by a gravimetric method using NMIJ's reported weighing systems.[1],[2],[3] Preparation schemes of the gas mixtures were shown in Figure 1.

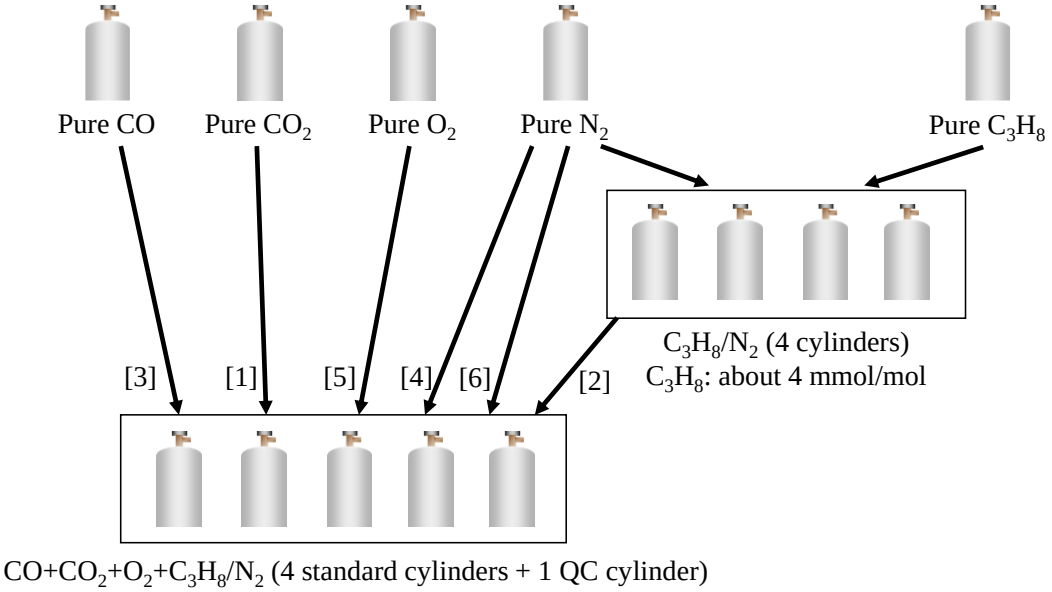


Figure 1 Preparation scheme for calibration gas mixtures of carbon monoxide, carbon dioxide, oxygen, and propane in nitrogen. The numbers in square brackets mean the order of the filled raw material gases.

Preparation of gas mixture for propane in nitrogen:

Four-gas mixtures of propane in nitrogen were prepared. The amount fraction of propane in the prepared gas mixtures (x_{C3H8}) and its standard uncertainty ($u(x_{C3H8})$) were summarized in Table 6. Examples of preparation procedures for gas mixture of propane and nitrogen (cylinder ID: CPB-29173) were described below. An evacuated cylinder was weighed and transferred to a filling room. The cylinder was connected to a filling apparatus, and the pure propane (5.450 g) was filled into the cylinder. The cylinder was weighed and transferred to the filling room again and connected to the filling apparatus. The nitrogen as dilution gas (868.960 g) was filled into the cylinder, and the cylinder was weighed. Standard uncertainties of the masses of the propane and the nitrogen were 2.1 mg and 2.1 mg, respectively. The amount fraction of propane in the prepared gas mixture and its standard uncertainty were 3.967 5 mmol/mol and 0.001 56 mmol/mol, respectively.

Table 6 The amount fraction of propane in the prepared pre-mixtures and its standard uncertainty (units: mmol/mol)

Cylinder ID	Amount fraction of propane / x_{C3H8}	$u(x_{C3H8})$
CPB-16262	3.989 5	0.001 49
CPB-16264	4.097 5	0.001 53
CPB-29173	3.967 5	0.001 56
CPB-29221	3.977 6	0.001 34

Preparation of gas mixture for carbon monoxide, carbon dioxide, oxygen, and propane in nitrogen: Five-gas mixtures of carbon monoxide, carbon dioxide, oxygen, and propane in nitrogen were prepared. Four of the five gas mixtures (cylinder ID: CPC-00554, CPB-16467, CPB-21274, and CPB-16263) were used as standard gas mixtures. The other one was used as a quality control (QC) cylinder. The amount fractions of each component in the prepared gas mixtures and their standard uncertainties were summarized in Table 7. An example of preparation procedures for the gas mixture (cylinder ID: CPB-16263) was described below.

An evacuated cylinder was weighed and transferred to a filling room. The cylinder was connected to a filling apparatus, and pure carbon dioxide (57.546 g) was filled into the cylinder. The cylinder was weighed and transferred to the filling room again and connected to the filling apparatus. Gas mixture of propane in nitrogen (CPB29221, 49.103 g) was filled into the cylinder. The cylinder was transferred to the filling room a third time and connected to the filling apparatus. Filling with pure gas and weighing of the cylinder were carried out in the same manner in the order of carbon monoxide (14.597 g), nitrogen (405.004 g), and oxygen (25.544 g). The cylinder was transferred to the filling room a final time and connected to the filling apparatus. Nitrogen gas (499.810 g) was refilled into the cylinder. Standard uncertainties of the masses of the propane in nitrogen gas mixture, the carbon monoxide, the carbon dioxide, and the oxygen were 2.1 mg, 2.1 mg, 2.1 mg, and 2.1 mg, respectively. Standard uncertainties of the masses of the first nitrogen filling were 2.1 mg. At the second time, it was 2.1 mg. The amount fraction of carbon monoxide in the prepared gas mixture and its standard uncertainty were 1.421 0 cmol/mol and 0.000 2 cmol/mol, respectively. The amount fraction of carbon dioxide and its standard uncertainty were 3.565 4 cmol/mol and 0.000 1 cmol/mol, respectively. The amount fraction of oxygen and its standard uncertainty were 2.176 7 cmol/mol and 0.000 2 cmol/mol, respectively. The amount fraction of propane and its standard uncertainty were $1.896\ 7\times10^{-2}$ cmol/mol and $0.000\ 6\times10^{-2}$ cmol/mol, respectively.

Table 7 Amount fractions of carbon monoxide, carbon dioxide, oxygen, and propane in the prepared gas mixture and their own standard uncertainties.

Cylinder ID	Amount fraction *				
	CO (cmol/mol)	CO_2 (cmol/mol)	O_2 (cmol/mol)	C_3H_8 (10^{-2} cmol/mol)	N_2
CPC-00554	1.712 4±0.000 2	3.922 7±0.000 1	3.141 1±0.000 8	2.081 4±0.000 4	balance
CPB-16467	0.788 6±0.000 2	3.042 5±0.000 2	2.793 0±0.001 0	1.800 1±0.000 3	balance
CPB-21274	1.517 3±0.000 3	3.501 1±0.000 2	2.374 5±0.000 3	2.120 3±0.000 7	balance
CPB-16263	1.421 0±0.000 2	3.56 54±0.000 1	2.176 7±0.000 4	1.896 7±0.000 6	balance

*: The numeric value after the symbol ± of each mean value indicates a standard uncertainty.

Instrumentation

When determining amount fractions of target components in APMP.QM.K3.2019's samples, we used two instruments, MPA-510 (HORIBA, Ltd., Kyoto, Japan) and GC-14B (Shimadzu Corporation, Kyoto, Japan). Analytical conditions were summarized in Tables 7, 8, and 9.

Table 7 Analytical condition for measuring amount fraction of oxygen in the sample.

Analyzer	Magnetopneumatic oxygen analyzer
Oxygen analyzer	HORIBA MPA-510
Range	5.00 vol%

Table 8 Analytical condition for measuring the amount fraction of CO and CO_2 in the sample.

Analyzer	Methanizer equipped GC-FID
Gas chromatograph	Shimadzu GC-14B
Injection method	Direct injection using 6-ports sampling valve
Sample volume	0.1 mL
Valve box temperature	Room temperature
Column	Porapak Q (Length 1 m, 3 mm i.d.)
Carrier gas, flow rate	N_2, 30 mL/min
Oven temperature	1.2 min hold at 60 ºC, 40 ºC/min up to 120 ºC, and hold 1.5 min
FID Temperature	200 ºC
FID fuel gas	H_2, 97 kPa (also used as reduction gas in the methanizer)
FID supporting gas	Purified air, 59 kPa
Methanizer	Shimadzu MTN-1
Temperature	400 ºC

Table 9 Analytical condition for measuring the amount fraction of propane in the sample.

Analyzer	GC-FID
Gas chromatograph	Shimadzu GC-14B
Injection method	Direct injection using 6-ports sampling valve
Sample volume	0.1 mL
Valve box temperature	Room temperature
Column	Porapak Q (Length 1 m, 3 mm i.d.)
Carrier gas, flow rate	N_2, 30 mL/min
Oven temperature	120 ºC isothermal
FID Temperature	200 ºC
FID fuel gas	H_2, 97 kPa
FID supporting gas	Purified air, 59 kPa

Calibration method and value assignment

The calibration was carried out by "ISO6143 method" (3-points calibration line). Peak areas of the target components except oxygen in a chromatogram were recorded for the calibration. The values of peak area were corrected by using a quality control cylinder (QC cylinder)[4][5]. For oxygen, obtained values were recorded, because the oxygen analyzer MPA-510 provided continuous monitoring of the amount fraction of oxygen in the calibration and the sample gases.

Uncertainty evaluation

The final reported analytical amount fraction x was estimated by using the following equation.

$$x = \sum_{k=1}^{J} x_k / J \ldots (1)$$

where J was the total number of "measurement #", k was the number of "measurement #" and x_k was amount fraction of analyte. The standard uncertainty of the analytical amount fraction $u(x)$ was evaluated from the following equations.

$$u^2(x) = u^2(x)_{\mathrm{ISO6143}} + u^2(x)_{\mathrm{between-day}} \ldots (2)$$

$$u^2(x)_{\mathrm{ISO6143}} = \sum_{k=1}^{J} u^2(x_k)_{\mathrm{ISO6143}} / J^2 \ldots (3)$$

$$u^2(x)_{\text{between-day}} = \sum_{k=1}^{J}(x_k - x)^2/J(J-1) \ldots (4)$$

where $u(x_k)_{\text{ISO6143}}$ was a standard uncertainty of analytical amount fraction by a set of "calibration" and "sample measurement" on each date. The parameter $u(x)_{\text{between-day}}$ was a standard uncertainty of between-day variation. The difference, $D_{m,n}$, was calculated using the following equation (5). If $D_{m,n}$ <2 for all combination of $D_{m,n}$, all x_k were assumed to agree within the uncertainty range and the standard uncertainty of between-day variation was considered to be zero.

$$D_{m,n} = |x_m - x_n|/\sqrt{u^2(x_m)_{ISO6143} + u^2(x_n)_{ISO6143}} \ \ldots (5)$$

where *m* and *n* were the numbers of "measurement #", and $m \neq n$.

References

[1] N. Matsumoto, T. Watanabe, M. Maruyama, Y. Horimoto, T. Maeda, K. Kato, "Development of mass measurement equipment using an electronic mass-comparator for the gravimetric preparation of reference gas mixtures", *Metrologia*, **41**, pp.178–188 (2004).

[2] N. Aoki, S. Ishidoya, N. Matsumoto, T. Watanabe, T. Shimosaka, S. Murayama, "Preparation of primary standard mixtures for atmospheric oxygen measurements with less than 1 μmol mol^{-1} uncertainty for oxygen molar fractions", *Atmos. Meas. Tech.*, **12**, pp.2631–2646 (2019).

[3] ISO 6142-1, "Gas analysis – Preparation of calibration gas mixtures– ", (2015).

[4] M. J. T. Milton, F. Guenther, W. R. Miller, A. S. Brown, "Validation of the gravimetric values and uncertainties of independently prepared primary standard gas mixtures", *Metrologia* **43**, L7–L10 (2006).

[5] N. Matsumoto, F. Noguchi, N. Aoki, K. Kato, R. Isaki, S. Sakata, H. Yoshida, T. Ikeda, "Development of primary reference gas mixture of CF_4 and SF_6 in N_2 as CRM for measurements of their emission from semiconductor process tool", *Bunseki Kagaku*, **58**, pp. 407–416 (2009).

Authorship

MATSUMOTO Nobuhiro

WATANABE Takuro

SHIMOSAKA Takuya

Report Form APMP.QM-K3.2019 Automotive emission gases

Laboratory name: **National Metrology Institute of Malaysia (NMIM), SIRIM Berhad, MALAYSIA**.

Cylinder number: **D 170258**

Measurement 1[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	18/4/24	1.23	0.28	3
CO_2	18/4/24	3.42	0.31	3
O_2	29/5/24	2.45	0.69	3
C_3H_8	05/06/24	0.0198	0.00008	3

Measurement 2[#]

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	05/06/24	1.23	0.25	3
CO_2	05/06/24	3.46	0.57	3
O_2	30/05/24	2.45	0.61	3
C_3H_8	06/06/24	0.0199	0.00009	3

Measurement 3[#]

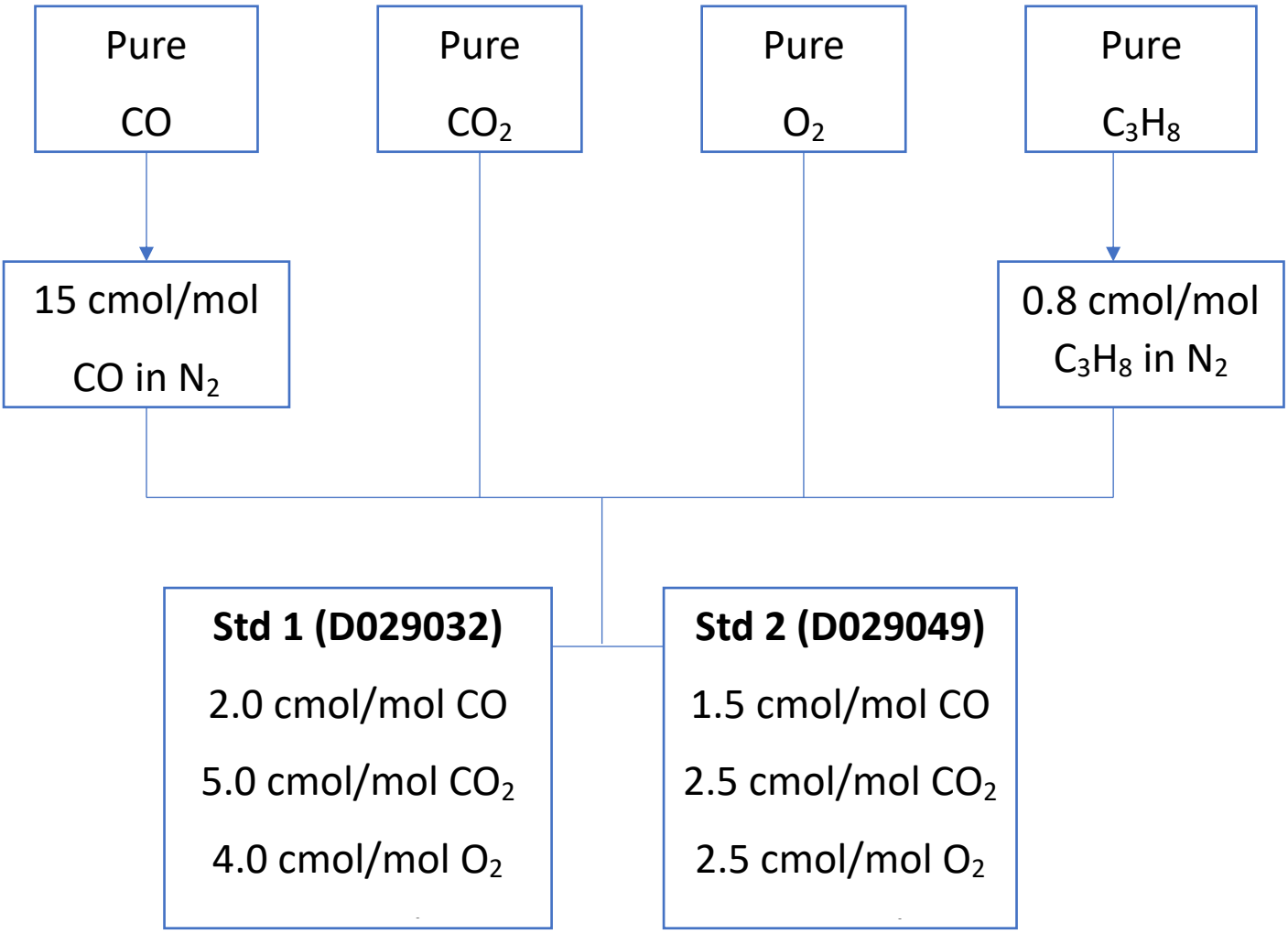
Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	07/06/24	1.23	0.25	3
CO_2	07/06/24	3.44	0.38	3
O_2	31/5/24	2.46	0.62	3
C_3H_8	10/06/24	0.0199	0.00008	3

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2392	0.1052	2
CO_2	3.4587	1.2849	2
O_2	2.4457	0.9313	2
C_3H_8	0.01992	0.000467	2

Calibration standards

Preparation of Calibration Standard (ISO 6142) and use 10L size of Luxfer aluminium alloy cylinders



Carbon Monoxide

Calibration Standard

NMIM was prepared and verified the standard 1 (D029032) of PRM according to ISO 6142 and ISO 6143. CO components in this inter-comparison analysis used a single-point calibration method.

Instrumentation

A standards and sample gases were injected into 6 port valves of Agilent Technology Model 7890A GC equipped with a Methanizer Flame Ionization Detector.

GC conditions: -

Carrier gas: Purified Hydrogen

Column type: Porapak Q 9ft x 1/8 in SS & Porapak Q 2.5M x 1/8 in SS

Oven:

Temperature: Isothermal @ 40ºC
Duration: 10 min

Detector:

Temperature: 300 ºC
H_2 Flow: 50mL/min
Air flow: 400mL/min

Calibration method and value assignment

The data was collected using Chemstation software. Each sample was injected 3 times and the first injection in each case was discarded which was considered as flushing of the sample loop. The responses were averaged.

The calibration of the instruments has carried out according ISO 6143. Sample flow of each cylinder was constantly at 40ml/min by a mass flow controller. The sample was analyzed with reference cylinder in the following order.

Reference – Sample – Reference – Sample – Reference – Sample- Reference.

Sample Handling

During the measurement, the cylinders of standards and sample were stabilized at room temperature.

Uncertainty evaluation

Uncertanty Budget					
	cmol/mol	cmol/mol			
Source of Uncertainty	u	u2	contribution	DoF	Evaluation type
Sample gas peak area detrmination	1.60861E-08	2.58763E-16	4.91896E-13	26	A
Std gas peak area determination	0.002111529	4.45856E-06	0.008475499	35	A
Std gas	0.01	0.000100	0.190095181	∞	B
Adsoption cylinder	0.0406810	0.001655	3.145967746	∞	B
Gravimetric weighing	0.0001733	0.000000	5.70643E-05		combine A&B
Combined Uncertainty		**0.052605**	**3.34**		
Expended uncertainty (95%)		**0.10521**			

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

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)

Carbon Dioxide

Calibration Standard

NMIM was prepared and verified the standard 1 (D029032) of PRM according to ISO 6142 and ISO 6143. CO2 components in this inter-comparison analysis used a single-point calibration method.

Instrumentation

A standards and sample gases were injected into 6 port valves of Agilent Technology Model 7890A GC equipped with a Methanizer Flame Ionization Detector.

GC conditions: -

Carrier gas: Purified Hydrogen

Column type: Porapak Q 9ft x 1/8 in SS & Porapak Q 2.5M x 1/8 in SS

Oven:

Temperature: Isothermal @ 40ºC
Duration: 10 min

Detector:

Temperature: 300 ºC
H_2 Flow: 50mL/min
Air flow: 400mL/min

Calibration method and value assignment

The data was collected using Chemstation software. Each sample was injected 3 times and the first injection in each case was discarded which was considered as flushing of the sample loop. The responses were averaged.

The calibration of the instruments has carried out according ISO 6143. Sample flow of each cylinder was constantly at 40ml/min by a mass flow controller. The sample was analyzed with reference cylinder in the following order.

Reference – Sample – Reference – Sample – Reference – Sample- Reference.

Sample Handling

During the measurement, the cylinders of standards and sample were stabilized at room temperature.

Uncertainty evaluation

Uncertanty Budget					
	cmol/mol	cmol/mol			
Source of Uncertainty	u	u2	contribution	DoF	Evaluation type
Sample gas peak area detrminatio	3.052E-08	9.313E-16	1.44963E-13	26	A
Std gas peak area determination	0.0032372	1.0479E-05	0.001631162	35	A
Std gas	0.001	0.000001	0.000155656	∞	B
Adsoption cylinder	0.1860721	0.034623	5.389239157	∞	B
gravimetric weighing	0.0000500	0.000000	3.89235E-07		combine A&B
Combined Uncertainty		**0.6424436**	**5.39**		
Expended uncertainty (95%)		**1.2848872**			

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

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)

Oxygen

Calibration Standard

NMIM was prepared and verified the standard 2 (D029049) of PRM according to ISO 6142 and ISO 6143. The oxygen component in this inter-comparison analysis used a single-point calibration method.

Instrumentation

A standards and sample gases were injected into 6 port valves of Agilent Technology Model 7890A GC equipped with a Thermal Conductivity Detector.

GC conditions: -

Carrier gas: Purified Helium

Column type: 45/60 MolSieve 13x

Oven:

Temperature: Isothermal @ 50ºC

Duration: 6 min

Detector:

Heater: 200 ºC

Reference Flow: 40 mL/min

Make up Flow (He): 2 mL/min

Calibration method and value assignment

The data was collected using Chemstation software. Each sample was injected 3 times and the first injection in each case was discarded which was considered as flushing of the sample loop. The responses were averaged.

The calibration of the instruments has carried out according ISO 6143. Sample flow of each cylinder was constantly at 40ml/min by a mass flow controller. The sample was analyzed with reference cylinder in the following order.

Reference – Sample – Reference – Sample – Reference – Sample- Reference.

Sample Handling

During the measurement, the cylinders of standards and sample were stabilized at room temperature.

Uncertainty evaluation

Uncertanty Budget					
	cmol/mol	cmol/mol			
Source of Uncertainty	u	u2	contribution	DoF	Evaluation type
Sample gas peak area detrminatio	3.612E-06	1.3045E-11	2.80145E-09	26	A
Std gas peak area determination	0.0012463	1.5533E-06	0.000333579	35	A
Std gas	0.0025	0.000006	0.0013422	∞	B
Adsoption cylinder	0.1872747	0.035072	7.531740504	∞	B
Gravimetric weighing	0.0029013	0.000008	0.001807632		combine A&B
Combined Uncertainty		**0.4656533**	**7.54**		
Expended uncertainty (95%)		**0.9313067**			

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

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)

Propane

Calibration Standard

NMIM was prepared and verified the standard 2 (D029049) of PRM according to ISO 6142 and ISO 6143. The propane component in this inter-comparison analysis used a single-point calibration method.

Instrumentation

A standards and sample gases were injected into 6 port valves of Agilent Technology Model 7890A GC equipped with a Flame Ionization Detector.

GC conditions: -

Carrier gas: Purified Helium

Column type: GS Gas Pro (30 m x 0.32 mm)

Oven:

Temperature: Isothermal @ 60ºC
Duration: 6 min

Detector:

Heater: 250 ºC
H_2 Flow: 40mL/min

Air flow: 400mL/min

Calibration method and value assignment

The data was collected using Chemstation software. Each sample was injected 3 times and the first injection in each case was discarded which was considered as flushing of the sample loop. The responses were averaged.

The calibration of the instruments has carried out according ISO 6143. Sample flow of each cylinder was constantly at 40ml/min by a mass flow controller. The sample was analyzed with reference cylinder in the following order.

Reference – Sample – Reference – Sample – Reference – Sample- Reference.

Sample Handling

During the measurement, the cylinders of standards and sample were stabilized at room temperature.

Uncertainty evaluation

Uncertanty Budget					
	umol/mol	umol/mol			
Source of Uncertainty	u	u2	contribution	DoF	Evaluation type
Sample gas peak area detrmination	0.005454651	2.97532E-05	0.001274238	26	A
Std gas peak area determination	0.000578818	3.35031E-07	1.43483E-05	35	A
Std gas	0.01	0.000100	0.004282688	∞	B
Adsoption cylinder	0.0026703	0.000007	0.000305388	∞	B
gravimetric weighing	0.0002888	0.000000	3.57251E-06		combine A&B
Combined Uncertainty		**2.334982**	**0.01**		
Expended uncertainty (95%)		**4.669965**			

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

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)

References

1. ISO 6142- Gas Analysis- Preparation of calibration gas mixtures- Gravimetric method, 2001.
2. ISO 6143- Gas Analysis- Comparison methods for determining and checking the composition of calibration gas mixtures.
3. EURACHEM/ CITAC Guide – Quantifying Uncertainty in Analytical Measurement, 2nd Edition

Authorship

1. Dr. Mohamad Fauzi Ahmad
2. Mrs. Haslina Abdul Kadir

Measurement report

Report form

Laboratory name: National Physical Laboratory, India (NPLI)

Cylinder number: D170162

Cylinder Pressure before measurement: 90 bar

Cylinder pressure after measurement: 75 bar

Measurement 1#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	05.04.24	1.2051	0.0012	20
CO_2	08.04.24	3.5034	0.0041	18
O_2	03.04.24	2.5627	0.0048	7
C_3H_8	22.03.24	0.020071	0.000017	7

Measurement 2#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	22.04.24	1.2033	0.0014	16
CO_2	08.04.24	3.5037	0.0017	20
O_2	05.04.24	2.4922	0.0049	9
C_3H_8	26.03.24	0.020048	0.000047	19

Measurement 3#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	22.04.24	1.2158	0.0014	16
CO_2	09.04.24	3.5014	0.0039	32
O_2	24.04.24	2.5617	0.0063	11
C_3H_8	27.03.24	0.020006	0.000025	17

Measurement 4#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	23.04.24	1.2077	0.0008	16
CO_2	18.04.24	3.4915	0.0022	28
O_2	24.04.24	2.5664	0.0023	11
C_3H_8	26.04.24	0.020042	0.000066	17

Measurement 5#

Component	Date (dd/mm/yy)	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
CO	23.04.24	1.2099	0.0005	16
CO_2	18.04.24	3.4995	0.0023	30
O_2	25.04.24	2.5709	0.0073	23
C_3H_8	29.04.24	0.020089	0.000051	16

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
CO	1.2084	0.0053	2
CO_2	3.4999	0.0068	2
O_2	2.5508	0.0298	2
C_3H_8	0.020051	0.000077	2

Calibration standards

Calibration standards used for the measurement of all the four components were prepared gravimetrically at NPL India following ISO 6142-1:2015 standard [1]. Binary component primary reference gas mixtures (PRGMs) of each component in nitrogen were prepared separately and used as calibration standard for measurement by gas chromatograph. Each prepared gas mixture is rotated clockwise and anticlockwise for two hours sufficiently stabilized in the analytical at room temperature before measurement. Impurities of H_2O, CO, CO_2, CH_4 etc are checked using CRDS and NDIR technique in commercially purchased nitrogen gas and given in purity table 1. Pure component gases with certificates are purchased from commercial supplier and their purities are given in Table 2-5.

Table 1. Purity Table for pure N_2

Component	Method	Amount Fraction (mol/mol)
N_2	Specification	> 0.999995
H_2O	CRDS	$< 2 \times 10^{-6}$
O_2	Specification	$< 1.5 \times 10^{-6}$
CO	CRDS	$< 0.3 \times 10^{-6}$
CO_2	NDIR	$< 0.5 \times 10^{-6}$
CH_4	CRDS	$< 0.002 \times 10^{-6}$

Table 2. Purity Table for nominally pure CO

Component	Method	Amount Fraction (mol/mol)
CO	specification	> 0.9997
CH_4	GC FID	< DL*

*Detection limit

Table 3. Purity Table for nominally pure CO_2

Component	Method	Amount Fraction (mol/mol)
CO_2	specification	> 0.9998
CH_4	GC FID	< LOD

Table 4. Purity Table for certified pure C_3H_8

Component	Method	Amount Fraction (mol/mol)
O_2	specification	> 0.995
N_2	N_2 Trace analyser	$\leq 360 \times 10^{-6}$
O_2	O_2 analyser	$\leq 80 \times 10^{-6}$
H_2O	Moisture analyser	$\leq 4 \times 10^{-6}$
THC	HC analyser	$\leq 3800 \times 10^{-6}$

Table 5. Purity Table for nominally pure O_2

Component	Method	Amount Fraction (mol/mol)
O_2	specification	> 0.99999
H_2O	CRDS	$< 1 \times 10^{-6}$
CH_4	CRDS	$< 0.002 \times 10^{-6}$

Verification of all calibration gas mixtures prepared gravimetrically was done according to ISO 6143:2001 [2]. The amount fractions of gravimetrically prepared gas mixtures with expanded uncertainties are given in tables 6-9.

Table 6. PRGMs of CO used for calibration of GC-TCD for APMP.QM-K3.2019 sample D170162

Cylinder number	Amount fraction (cmol mol^{-1})*	Year of preparation	Binary Gas mixture
M2101027038	0.5008 ± 0.0019	March 2022	CO/N_2
M2012008032**	2.5329 ± 0.0054	November 2021	CO/He
M2012008013**	5.0575 ± 0.0103	March 2022	CO/N_2

*uncertainties given are expanded uncertainties at *k*=2.
****** used for single point calibration scheme for calculation of measurement result of sample cylinder.

Table 7. PRGMs of CO_2 used for calibration of GC-TCD for APMP.QM-K3.2019 sample D170162

Cylinder number	Amount fraction (cmol mol^{-1})*	Year of preparation	Binary Gas mixture
D001471	0.9866 ± 0.0019	March 2023	CO_2/N_2
M1702003020	2.6743 ± 0.00285	August 2018	CO_2/N_2
D013184**	4.4305 ± 0.0046	April 2024	CO_2/N_2
M1702003078**	11.522 ± 0.0112	Feb 2018	CO_2/N_2

*uncertainties given are expanded uncertainties at *k*=2.
**used for single point calibration scheme for calculation of measurement result of sample cylinder.

Table 8. PRGMs of O_2 used for calibration of GC-TCD for APMP.QM-K3.2019 sample D170162

Cylinder number	Amount fraction (cmol mol^{-1})*	Year of preparation	Binary Gas mixture
D013202	4.0247 ± 0.0044	March 2024	O_2/N_2

*uncertainties given are expanded uncertainties at *k*=2.

Table 9. PRGMs of C_3H_8 used for calibration of GC-FID for APMP.QM-K3.2019 sample D170162

Cylinder number	Amount fraction (cmol mol^{-1})*	Year of preparation	Binary Gas mixture
M1812010019	0.026503 ± 0.000071	January 2020	C_3H_8/N_2
M1812010030**	0.050745 ± 0.000158	January 2020	C_3H_8/N_2

*uncertainties given are expanded uncertainties at *k*=2.
**used for single point calibration scheme for calculation of measurement result of sample cylinder.

Instrumentation

Gas Chromatograph (Model: 6890N, Make: Agilent Technologies) with FID and TCD detectors was used for the measurement of gases. Each component is analysed separately using

different condition according to the detector response using binary component calibration gas mixtures prepared gravimetrically at NPLI following ISO 6142-I. Sample introduction in GC is done through gas sampling valve (GSV) loop using mass flow controller (MFC) in connection with multi position valve(MPV). During measurement instrumental drift was taken care by monitoring response of calibration standard before and after the sample in sequence of Cal-S-Cal-S…. Every measurement was repeated by a set of minimum 5. Detail of the method conditions and column used in GC for each component is given in below table 10.

Table 10. Instrument method conditions used for measurement of APMP sample

Components >	**CO**	**CO_2**	**O_2**	**C_3H_8**
Method	GC-TCD	GC-TCD	GC-TCD	GC-FID
Oven Temperature (°C)	60	80	25	100
Detector Temp (°C)	250	250	250	270
GSV box Aux-1 Temp (°C)	100	120	100	120
Column used (Packed SS Columns)	Molecular Sieve 13x 10 ft, 1/8" OD, 80/100 mesh	Haysep D 12 ft, 1/8" OD, 100/120 mesh	Molecular Sieve 13x 10 ft, 1/8" OD, 80/100 mesh	Porapak Q 10 ft, 1/8" OD, 80/100 mesh
Carrier gas	Helium	Helium	Helium	Helium
Carrier gas flow (mL/min)	20	25	20	60
Hydrogen flow (mL/min)*	-	-	-	35
Air flow (mL/min)*	-	-	-	400
GSV loop size (mL)	1	1	1	0.5
MFC flow (mL/min)	40	40	40	40

*Not required in TCD

Configuration of GC analysis is given as follow:

Gas cylinders—regulators—MPV—MFC—GSV loop—GC column—Detector (TCD or FID)—Response—Result

Calibration method and value assignment

The instrument was calibrated using gravimetrically prepared standard. Single point calibration method scheme was used using sequence run method. The scheme was repeated twice in a day and measurements were done more than 5 days for each component. The amount fraction of APMP sample was calculated using the formula below:

$$x_s = \frac{x_{std} \times A_s}{A_{std}} \quad (1)$$

where,

x_s : amount fraction of sample
x_{std} : amount fraction of calibration standard
A_s : peak area of sample
A_{std} : peak area of the calibration standard

Gravimetrically prepared calibration gas mixtures with higher amount fractions of the component are used for value assignment of respective component in the APMP sample using equation (1).

Uncertainty evaluation

The main uncertainty components that have been considered for gravimetric preparation of calibration gas mixtures are:

1. Weighing of components which include uncertainty of E2 class mass pieces used for weighing and atomic masses of the component gases.
2. Purity of component gas and diluent gas.

$$x_{\mathrm{i,prep}} = x_{\mathrm{i,grav}} + \Delta x_{\mathrm{i,purity}} \tag{2}$$

$$u^2(x_{\mathrm{i,prep}}) = u^2(x_{\mathrm{i,grav}}) + u^2(\Delta x_{\mathrm{i,purity}}) \tag{3}$$

Stability of gas mixtures is not taken into account as the gas mixture compositions are assumed to be stable for a long period. Uncertainty in preparation of binary mixtures is explained in detail in literature [5].

The analytical uncertainty components used for estimation of reported uncertainty are:

1. Repeatability and reproducibility
2. Instrument response in form of peak area
3. Calibration standard

Result reported for each component is the average of five measurements. The standard uncertainty is calculated as standard deviation (sd) of the mean of *n* measurements taken from experiment as given is equation (4).

$$u_{\mathrm{std}} = \frac{SD}{\sqrt{n}} \tag{4}$$

In the case of calculation of amount fraction of a gas using GC (i.e., concentration against peak area), the sensitivity coefficient is taken as 1. Hence, the combined uncertainty is calculated using equation (5):

$$\left[\frac{u_{ver(sample)}}{x_{sample}}\right] = \sqrt{\left[\frac{u(x_r)}{x_{sample}}\right]^2 + \left[\frac{u(GC_{response})}{GC_{response}}\right]^2 + \left[\frac{u(x_{PRGM})}{x_{PRGM}}\right]^2} \quad (5)$$

Verification uncertainties of all the five measurement results are pooled as per given equation (6) to get the result of verification uncertainty

$$u_c(verification) = \sqrt{\frac{u_1^2+u_2^2+u_3^2+u_4^2+u_5^2}{5}} \quad (6)$$

Uncertainty in the result reported is calculated by combining uncertainties of measurements and uncertainty of verification as given in equation (7)

$$u(x_{reported\ sample}) = \sqrt{u^2_{\text{reproducibility}} + u^2_{\text{c(verification)}}} \quad (7)$$

The final uncertainty is expressed as expanded uncertainty as:

$$U = ku$$

Where, the coverage factor *k* is equal to 2 at approximate 95 % confidence interval. Detail of measurement uncertainty budget for CO and CO_2 measurement in APMP sample is given in tables 11-12 below. Similarly measurement uncertainty of O_2 and C_3H_8 in sample is estimated.

Table 11. Measurement uncertainty budget for CO measurement in APMP sample

Date of measurement	Amount fraction	sd	n	u	u(rel)	Peak area	u	u(rel)	PRGM Amount fraction	u(prep)	u(rel)	u(verification)
	cmol/mol			(cmol/mol)		(µV)			(cmol/mol)			(cmol/mol)
05.04.2024	1.2051	0.0012	20	0.0003	2.17E-04	1299	0.15	1.14E-04	5.0575	0.0052	1.02E-03	0.0013
22.04.2024	1.2033	0.0014	16	0.0003	2.87E-04	1731	0.83	4.81E-04	5.0575	0.0052	1.02E-03	0.0014
22.04.2024	1.2158	0.0014	16	0.0003	2.87E-04	858	0.61	7.11E-04	2.5329	0.0027	1.07E-03	0.0016
23.04.2024	1.2077	0.0008	16	0.0002	1.68E-04	828	1.36	1.64E-03	2.5329	0.0027	1.07E-03	0.0024
23.04.2024	1.2099	0.0005	16	0.0001	1.00E-04	823	0.34	4.17E-04	2.5329	0.0027	1.07E-03	0.0014
Average	**1.2084**											
SD	0.0049											
u(reproducibility)	**0.0022**											
u(verification)	**0.0017**											
uc	0.0027											
U	0.0055	at *k* =2										
% rel	0.45											

Table 12. Measurement uncertainty budget for CO2 measurement in APMP sample

Measurement uncertainty budget for CO2 measurement in APMP sample												
Date of measurement	**Amount fraction**	**sd**	**n**	**u**	**u(rel)**	**Peak area**	**u**	**u(rel)**	**PRGM Amount fraction**	**u(prep)**	**u(rel)**	**u(verification)**
	cmol/mol			**(cmol/mol)**		**(µV)**			**(cmol/mol)**			**(cmol/mol)**
08.04.2024	3.5034	0.0041	18	0.0010	2.78E-04	3341	1.23	3.69E-04	11.522	0.0056	4.86E-04	0.0023
08.04.2024	3.5037	0.0017	20	0.0004	1.07E-04	3341	0.58	1.72E-04	11.522	0.0056	4.86E-04	0.0018
9.04.2024	3.5014	0.0039	32	0.0007	1.99E-04	3237	0.44	1.36E-04	11.522	0.0056	4.86E-04	0.0019
18.04.2024	3.4915	0.0022	28	0.0004	1.18E-04	1217	1.27	1.05E-03	4.4305	0.0023	5.19E-04	0.0041
18.04.2024	3.4995	0.0023	30	0.0004	1.21E-04	1212	0.23	1.88E-04	4.4305	0.0023	5.19E-04	0.0020
Average	**3.4999**											
SD	0.0050											
u(reproducibility)	**0.0022**											
u(verification)	**0.0026**											
uc	0.0034											
U	0.0068	at k =2										
% rel	0.20											

References

[1] ISO 6142-1: 2015 Gas analysis – Preparation of calibration gas mixtures-Part 1: Gravimetric method for Class I mixtures

[2] ISO 6143: 2001(E) Gas analysis – Comparison methods for determination and checking the composition of calibration gas mixtures.

[3] Guide to the expression of uncertainty in measurement. ISO, Geneva (1993). (Reprinted 1995: Reissued as ISO Guide 98-3 (2008), JCGM 100:2008.

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[5] A practical approach of measurement uncertainty evaluation for gravimetrically prepared binary component calibration gas mixture. (2022) Komal, Soni, D., Kumari, P., Gazal, Singh, K., & Aggarwal, S. G. MAPAN, 37(3), 653-664. https://doi.org/10.1007/s12647- 022-00600-2.

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