13 October 2020

Final Report
International Comparison APMP.QM-S7.1
Methane in nitrogen at 2000 µmol/mol

Kiryong Hong[1*], Byung Moon Kim[1], Hyun Kil Bae[1], Sangil Lee[1], James Tshilongo[2], David Mogale[2], Portia Seemane[2], Tshepiso Mphamo[2], Haslina Abdul Kadir[3], Mohamad Fauzi Ahmad[3], Noor Hidaya Abdul Nasir[3], Norliza Baharom[3], Daya Soni[4], Khem Singh[4], Sulakshina Bhat[4], Shankar G. Aggarwal[4], Prabha Johri[4].

[1]Korea Research Institute of Standards and Science (KRISS), Gas Metrology Group, 267 Gajeong-ro Yuseong-gu, Daejeon 34114, Republic of Korea
[2]National Metrology Institute of South Africa (NMISA), Gas Metrology Laboratory, Building 5N CSIR Campus, Meiring Naude Rd, Pretoria 0182, South Africa
[3]National Metrology Institute of Malaysia (NMIM), SIRIM Berhad, Lot PT 4803, Bandar Baru Salak Tinggi, 43900, Sepang, Selangor, Malaysia
[4]National Physical Laboratory-India (NPLI), Analytical Chemistry, Dr. K.S. Krishnan Road, New Delhi 110012, India

Field

Amount of substance

Organizing body

APMP

Coordinating laboratory

Korea Research Institute of Standards and Science (KRISS)

Study coordinator

Kiryong Hong (KRISS)
Correspondence to be addressed to: Kiryong Hong, khong@kriss.re.kr
(Tel: +82-42-868-5236)

Subject

Comparison of methane in nitrogen at 2000 µmol/mol.

Contents:

1 Quantities and units

In this comparison, the measurand was the amount-of-substance fraction of methane in nitrogen with measurement results being expressed in mol/mol and its submultiples μmol/mol or nmol/mol.

2 Participants

Table 1 lists the participants in this supplementary comparison.

Table 1. List of participants

Acronym	Country/Region	Institute
NMISA	South Africa	National Metrology Institute of South Africa
NMIM	Malaysia	National Metrology Institute of Malaysia
NPLI	India	National Physical Laboratory India

3 Introduction

Methane is one of the major greenhouse gases that affect climate change[1]. To mitigate anthropogenic CH_4 emissions effectively, it is necessary to measure and monitor CH_4 emissions from the production and transport of fossil fuels. Therefore, it is important for NMIs to demonstrate measurement equivalence for the standard gases of CH_4.

This is the third comparison on methane in nitrogen or air. The first comparison is the key comparison of CCQM-K82 (ambient level methane in air)[2] and the second comparison is the supplementary comparison of APMP.QM-S7 (2000 μmol/mol methane in nitrogen)[3]. As a supplementary comparison, the purpose of this comparison is to study the comparability of CH_4 standard gas mixtures at emission level (0.05 cmol/mol − 0.5 mol/mol in nitrogen or air). Furthermore, this comparison can provide a link to APMP.QM-S7 through KRISS who participated in both previous comparisons. In this comparison, KRISS prepared gas standards and sent to participants. Each participant measured the standard on their laboratory and reported their measurement results to KRISS according to the measurement protocol.

This report describes the results of a supplementary comparison for methane in nitrogen at 2000 μmol/mol.

4 Schedule

The comparison was done as in the following:

January 2018: Distribution of proposal and registration forms
February 2018: Registration
March 2018: First verification at KRISS
June 2018: Shipping cylinders to participants from KRISS
October 2018: Reporting results to KRISS
March 2019: Shipping cylinders back to KRISS
April 2019: Second verification at KRISS

July 2019: Draft A report
September 2020: Draft B report
October 2020: Final report

5 Measurement standards

A set of 4 mixtures was gravimetrically prepared for this supplementary comparison by KRISS. The methane and nitrogen that used for preparing measurement standards were analyzed their purities using several analyzers. The purity of methane and nitrogen are listed in Table 2 and 3, respectively.

Table 2. Results of purity analysis of methane

Component	Value (μmol/mol)	Standard uncertainty (μmol/mol)	Distribution	Measurement technique
H_2	0.25	0.144	Rectangular	GC/PDD
O_2	1.4	0.035	Normal	GC/PDD
CO	0.0025	0.00144	Rectangular	GC/AED
CO_2	0.11	0.00722	Normal	GC/AED
N_2	13.1	3.78	Normal	GC/PDD
C_2H_2	0.0125	0.00722	Rectangular	GC/FID
C_2H_6	0.51	0.0128	Normal	GC/FID
C_2H_4	0.0125	0.00722	Rectangular	GC/FID
C_3H_8	0.18	0.0045	Normal	GC/FID
C_3H_6	0.0065	0.00375	Rectangular	GC/FID
C_4H_{10}	0.606	0.01515	Normal	GC/FID
n-C_5H_{12}	0.11	0.00275	Normal	GC/FID
<C_6	0.05	0.0289	Rectangular	GC/FID
H_2O	11.2	1.12	Normal	Dew point
He	2.5	1.44	Rectangular	GC/TCD
Ar	2.5	1.44	Rectangular	GC/TCD
CH_4	999967.45	4.72		

Table 3. Results of purity analysis of nitrogen

Component	Value (μmol/mol)	Standard uncertainty (μmol/mol)	Distribution	Measurement technique
H_2	0.025	0.0144	Rectangular	GC/PDD
O_2	0.35	0.00875	Normal	GC/PDD
CO	0.05	0.0289	Rectangular	GC/FID
CO_2	0.005	0.00289	Rectangular	GC/FID
CH_4	0.0013	0.0000325	Normal	GC/FID
<C_5	0.05	0.0289	Rectangular	GC/FID

H_2O	1.2	0.12	Normal	Dew point
Ar	0.175	0.101	Rectangular	GC/PDD
N_2	999998.144	0.163		

The mixtures were verified by checking the internal consistency among them. In addition, all sample mixtures were verified again after they returned to KRISS. Results from the verifications are shown in Figure 1.

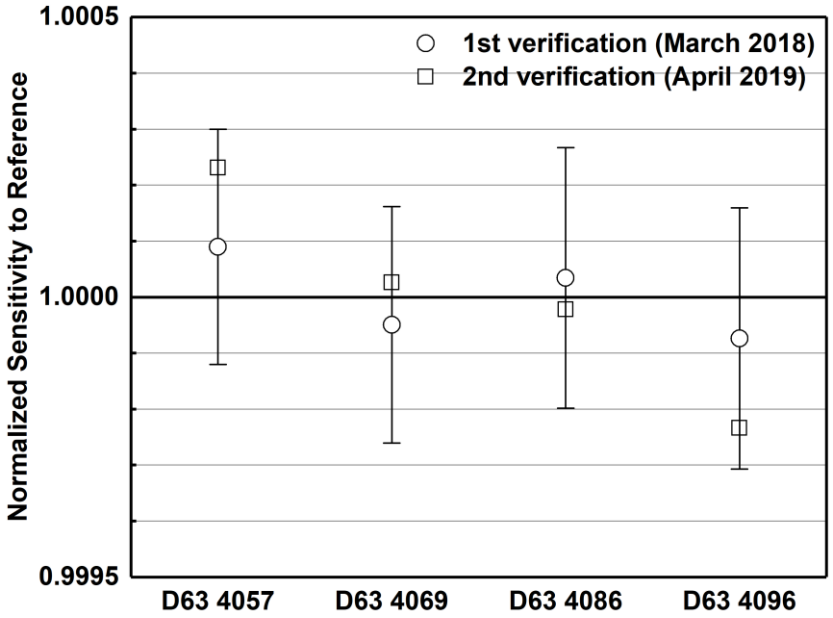


Figure 1. Verification results for sample cylinders (error bars represent their preparation uncertainty)

6 Measurement protocol

Each participant was requested 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 asked to provide information regarding standard mixtures, analysis method, and uncertainty budget.

7 Measurement equation

The reference values used in this comparison are determined by the gravimetric preparation, including purity analysis. All sample cylinders were verified prior to shipping them to each participant. The returned cylinders were re-verified to confirm their stability. Results from both verification experiments showed that the verified values were within the preparation uncertainties of all sample cylinders.

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

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

where $x_{i,\mathrm{prep}}$ is the fractional amount of substance of a target component in mixture (i), $x_{i,\mathrm{grav}}$ is the

fractional amount of substance 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. The uncertainty of the fractional amount is estimated as

$$u_{i,\mathrm{prep}}^2 = u_{i,\mathrm{grav}}^2 + u_{i,\mathrm{purity}}^2 + u_{i,\mathrm{stab}}^2 \quad (2)$$

where $u_{i,\mathrm{prep}}$ is the uncertainty from gravimetric preparation, $u_{i,\mathrm{grav}}$ is the uncertainty from gravimetric weighing process, $u_{i,\mathrm{purity}}$ is the uncertainty from purity analysis, and $u_{i,\mathrm{stab}}$ is the uncertainty due to instability. For the mixtures used in this comparison, long-term stability study data have shown that the correction due to instability and its uncertainty is zero. Therefore, the correction due to instability and its standard uncertainty is set to zero for this comparison.

The model and the associated standard uncertainty can be expressed as

$$x_{i,\mathrm{prep}} = x_{i,\mathrm{grav}} + \Delta x_{i,\mathrm{purity}} \quad (3)$$

$$u_{i,\mathrm{prep}}^2 = u_{i,\mathrm{grav}}^2 + u_{i,\mathrm{purity}}^2 \quad (4)$$

The gravimetrically prepared mixtures have been verified by comparing the gravimetric composition value with its analytic measurement value (i.e., verification value) as shown in the following condition.

$$\left|x_{i,\mathrm{prep}} - x_{i,\mathrm{ver}}\right| \leq 2\sqrt{u_{i,\mathrm{prep}}^2 + u_{i,\mathrm{ver}}^2} \quad (5)$$

where $x_{i,\mathrm{ver}}$ and $u_{i,\mathrm{ver}}$ is 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 Figure 1, the verification experiments demonstrated that the verification values agreed with the gravimetric values of this comparison mixtures within the preparation uncertainties. Therefore, the reference value of mixture (*i*) is set to $x_{i,\mathrm{prep}}$. The uncertainty of the reference value is given as

$$u_{i,\mathrm{ref}}^2 = u_{i,\mathrm{prep}}^2 + u_{i,\mathrm{ver}}^2 \quad (6)$$

8 Measurement method

Measurement methods of each participant are summarized in Table 4. More detailed descriptions about the methods are available in annex A of this report.

Table 4. Calibration methods and measurement traceability

Participant	Measurement dates	Calibration	Traceability	Number of measurements	Measurement technique
NMISA	23/08/2018	One point	Own standards	4	GC/FID
NMIM	27/08/2018 – 28/08/2018	One point	Own standards	3	GC/FID
NPLI	11/07/2018 – 17/07/2018	Multiple points	Own standards	5	GC/FID

9 Degree of equivalence

A degree of equivalence (*D*) in the comparison is determined by the following equation[4]:

$$D_i = x_{i,\text{lab}} - x_{i,\text{ref}} \tag{7}$$

where $x_{i,\text{lab}}$ is a reported value by each participant.

The standard uncertainty of the deviation is determined by the following equation.

$$u_{D_i}^2 = u_{i,\text{lab}}^2 + u_{i,\text{ref}}^2 \tag{8}$$

where $u_{i,lab}$ is the uncertainty of $x_{i,\text{lab}}$.

The uncertainty of the deviation (D) is expressed as the expanded uncertainty of the deviation at approximately 95% level of confidence with a coverage factor (k) of 2.

$$U_{D_i} = k \times u_{D_i} \tag{9}$$

10 Results and Discussion

A complete set of results reported from each participant is described in ANNEX A of this report. The results are summarized in Table 5, and presented in Figure 2. In figure 2, the degrees of equivalence for each participant are illustrated and linked to those from APMP.QM-S7[3]. The measurement results of APMP.QM-S7[3] are shown in ANNEX B.

Table 5. Summary of measurement results

Laboratory acronym	Cylinder	x_{ref} (μmol/mol)	u_{prep} (μmol/mol)	u_{ver} (μmol/mol)	u_{ref} (μmol/mol)	x_{lab} (μmol/mol)	u_{lab} (μmol/mol)	D (μmol/mol)	$U(D)$ (μmol/mol)	k
NMISA	D63 4057	1997.38	0.42	0.47	0.63	1999.4	1.15	2.02	2.62	2
NMIM	D63 4069	1998.73	0.42	0.42	0.59	2001.50	5.26	2.77	10.58	2
NPLI	D63 4086	1994.96	0.46	0.42	0.62	1993.54	3.86	-1.42	7.82	2

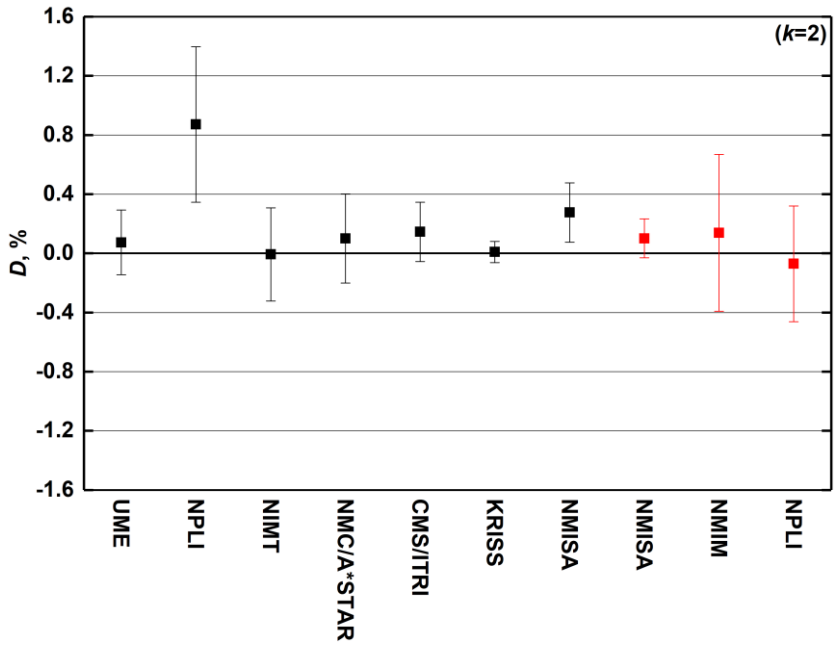


Figure 2. Relative deviations from the reference values for the APMP.QM-S7 (black squares) and the

APMP.QM-S7.1 (red squares). Note that the error bars are the relative uncertainties (k = 2) of Ds.

The degrees of equivalence for the results from the participants are shown in Figure 3, together with those from the APMP.QM-S7[3]. The results from the participant are consistent with the reference values as the deviations from the reference values are within the associated uncertainties.

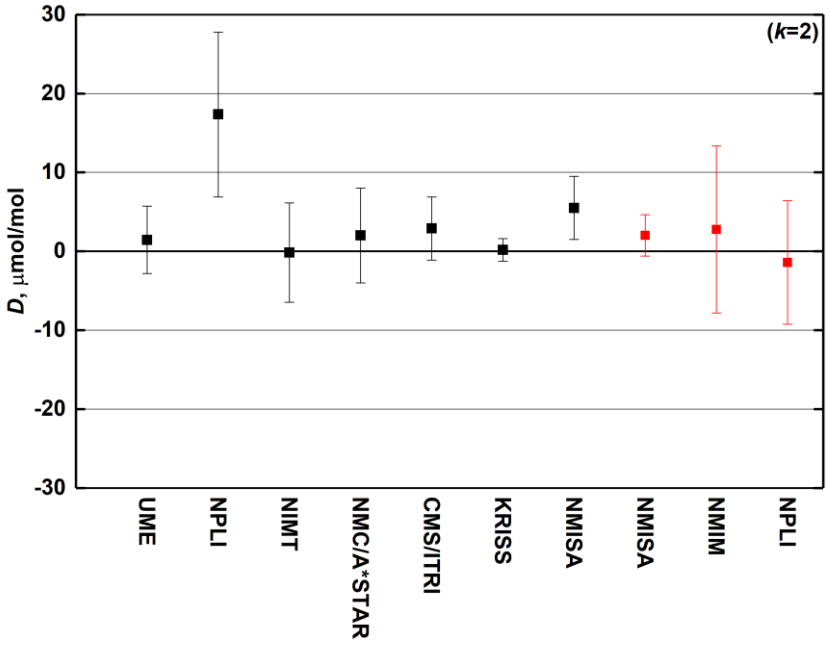


Figure 3. Degree of equivalence for the APMP.QM-S7 (black squares) and the APMP.QM-S7.1 (red squares). Note that the error bars are the expanded uncertainties (k = 2) of Ds.

11 Conclusion

This study compares the measurement capability of CH_4 at a level of 2000 µmol/mol. Results from all participants agree with the SCRV within their associated uncertainties.

12 How far the light shines

The results of this comparison can be used to support calibration and measurement capability (CMC) claims for methane in air and/or nitrogen according to following Table 6 with amount fraction ranges and those relative expanded uncertainties (k = 2).

Table 6. HFTLS list of each participant for CMC claims

Participant	Amount fraction (µmol/mol) from	Amount fraction (µmol/mol) to	Uncertainty (%) from	Uncertainty (%) from
NMISA	0.012	10	100	0.12
	10	500 000	0.12	0.12
NMIM	0.053	10	100	0.53
	10.51	500 000	0.53	0.53
NPLI	0.039	10	100	0.39
	10	500 000	0.39	0.39

13 References

[1] IPCC 2013 Climate Change 2013: The Physical Science Basis. Contribution to Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stoker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J.Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

[2] Flores E, Viallon J, Choteau T, Moussay P, Wielgosz R I, Kang N, Kim B M, Zalewska E, van der Veen A, Konopelko L, Wu H, Han Q, Rhoderick G, Guenther F R, Watanabe T, Shimosaka T, Kato K, Hall B, and Brewer P, 2015, International comparison CCQM-K82: methane in air at ambient level (1800 to 2200) nmol/mol.

[3] Kim B M, Bae H K, Lee S, Oh S, Lin T-Y, Huang C-K, Sinweeruthai R, Rattanasombat S, Laongsri B, Wongjuk A, Li H, Hui L, Keat T B, Mogale D, Johri P, Tarhan T, Engin E, 2015, Final report: international comparison APMP.QM-S7 methane in nitrogen at 2000 μmol/mol.

[4] CIPM MRA 2014 *Measurement comparisons in the CIPM MRA*, CIPM MRA-D-05 version 1.5

ANNEX A – Measurement reports of participants

National Metrology Institute of South Africa (NMISA)

Report Form APMP_QM_S7.1: Methane in nitrogen

Laboratory name: National Metrology Institute of South Africa

Cylinder number: D63 4057

Measurement 1#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	23 Aug 2018	1999,072	0,033	3

Measurement 2#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	23 Aug 2018	1999,137	0,025	3

Measurement 3#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	23 Aug 2018	1999,318	0,029	5

Measurement 4#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	23 Aug 2018	2000,044	0,026	5

Results

Component	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
CH_4	1999,4	2,3	2

Calibration Standards

The calibration standards were prepared gravimetrically according to ISO 6142 at NMISA. High pure CH_4 and N_2 were analysed for impurities prior to preparation of calibration standards. Table **1** and **2** shows the results of the purity analyses.

Table 1. Purity table with uncertainties for the nominally pure CH_4 parent gas (cyl# 157108)

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol)	Measurement Technique
CO_2	0,054	0,031	GC-meth/FID
N_2	3,114	0,025	GC-PDHID
Ar	0,26	0,15	GC-PDHID
H_2	0,73	0,079	GC-PDHID
H_2O	2,5	1,4	Spec
C_2H_6	0,065	0,037	GC-FID
O_2	0,109	0,063	GC-PDHID
CH_4	999993,2	1,4	

Table 2. Purity table with uncertainties for the nominally pure BIP nitrogen (cyl#310557)

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol)	Measurement Technique
Ar	128,4	5,8	GC-PDHID
O_2	0,0050	0,0029	Spec
CO	0,044	0,025	GC-meth/FID
CO_2	0,054	0,031	GC-meth/FID
CH_4	0,0069	0,0040	GC-FID
C_2H_6	0,065	0,037	GC-TCD
H_2O	0,01	0,0058	Spec
H_2	0,50	0,29	Spec

N_2	999870,9	5,8

A 2-step dilution was carried out during the preparation of the nominal value of CH_4 gas mixture (Figure **1**). A set of 5 standard gases with similar mole fraction were prepared and verified by GC-FID to check their accuracy. Cylinder number D67 9524 was chosen to analyse the methane sample (D63 4057) using a one-point calibration method.

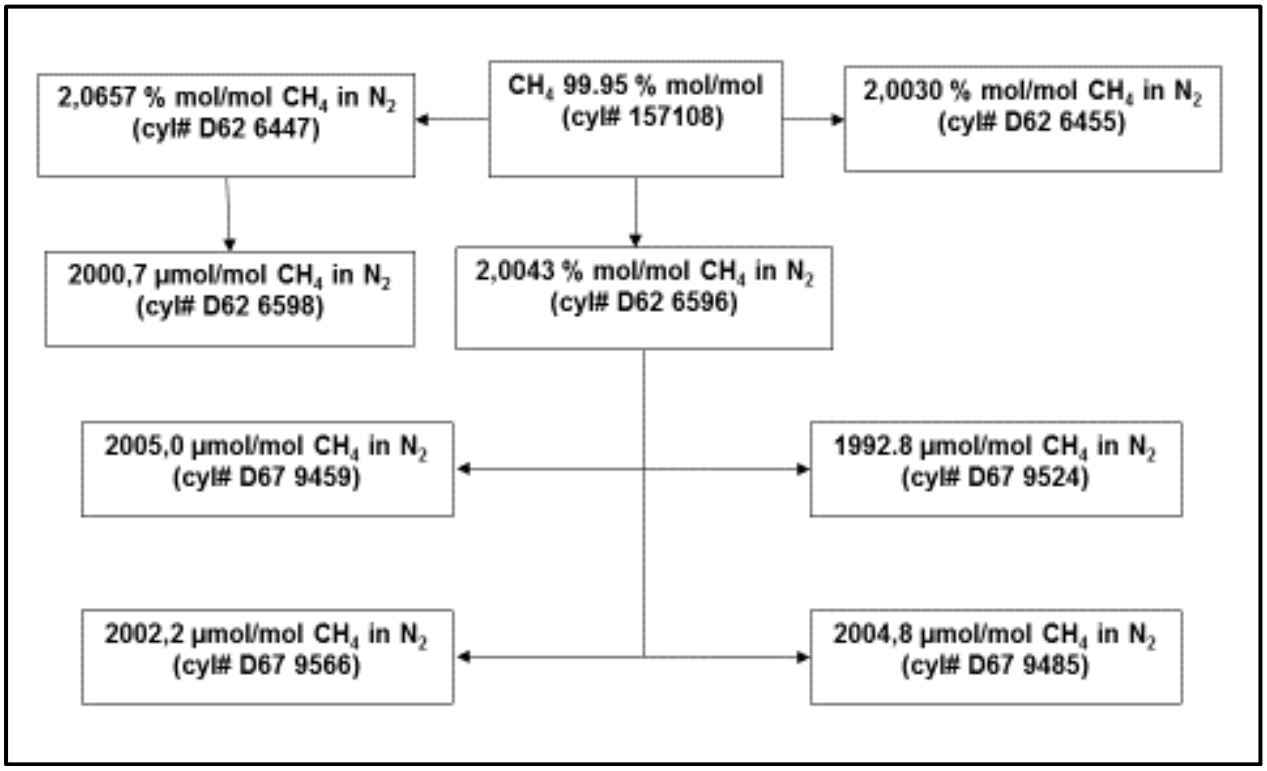


Figure **4**: The dilution steps of the gravimetric preparation of calibration standards

The preparation uncertainty of the primary standards was 0.02 %, k=1. Table **3** shows the characteristics of the calibration standards.

Table 3: Gravimetric mole fractions and uncertainties of PSGMs

Certificate number	**Gravimetric mole fraction (µmol/mol)**	**Gravimetric uncertainty (µmol/mol) (k = 1)**
D67 9524	1992,80	0,38

Analytical method

The amount of CH_4 in N_2 has been analysed using GC-FID (Agilent 7890B). Table **4** shows the conditions of the analysis system.
Configuration of analysis system: gas cylinder >> regulator >> MFC >> sample injection valve >>column >> detector >> integrator >> area comparison >> results.

Table 4: Analytical condition of instrument used to measure CH_4 in nitrogen.

Parameters	Analytical conditions
Column	Shincarbon ST, 2 m long, 2 mm ID, 1/8'' SS, mesh 80/100
Column oven temperature	150 °C, isothermal
Carrier gas flow (He)	30 mℓ/min
Column pressure	65 kPa
Make-up gas flow (N_2)	9 mℓ/min
Detector temperature	350 °C
Sample flow	35 mℓ/min
Sample loop	0,5 mℓ
Valve box temperature	100°C

Uncertainty evaluation

All measured certification data and calculations for the component concentrations of D63 4057 have been reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated percentage relative uncertainties. These uncertainties are:

a) Gravimetric uncertainties of the PSGMs in the order of 0,02 % relative.
b) Repeatability uncertainty (run-to-run) is 0,033 % relative standard deviation.
c) Reproducibility uncertainty (day-to-day) which gives the 0,065 % relative standard deviation.
d) Long term stability of the NMISA CH_4 gas mixtures is 0,96 µmol/mol.

The results for each day yielded an average concentration and a standard deviation. The average concentration and ESDM were obtained by the method of bracketing.

The predicted concentrations for the sample for four measurements were averaged, and a standard deviation calculated for the four values. The uncertainties of four measurements and the verification uncertainty (ESDM) were combined as shown in Equation 1:

$$u_c{}^2 = \frac{u_{Day1}{}^2 + u_{Day2}{}^2 + u_{Day3}{}^2 + u_{Day4}{}^2}{4} + (u_{ESDM})^2 \qquad (1)$$

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor k = 2 as in Equation 2.

..... $U = k \times u_c$, where k = 2. (2)

National Metrology Institute of Malaysia (NMIM)

Report Form APMP.QM-S7.1 CH_4 in Nitrogen

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

Cylinder number: D 634069

Measurement 1#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	27/08/18	1998.22	0.09	3

Measurement 2#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	27/08/18	2003.82	0.02	3

Measurement 3#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
CH_4	28/08/18	2002.47	0.03	3

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor
CH_4	**2001.50**	**10.51**	2

Calibration Standard

Using in-house PRM at concentration 2002.43 µmol/mol. The PRM was prepared according to ISO 6142 and ISO 6143. Single point calibration method was used for this inter-comparison analysis.

Analysis Method

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: Hydrogen

Column type: Porapak Q 9ft x 178 in SS

Oven:

Temperature: Isothermal @ 40ºC
Duration: 7 min

Detector:

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

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

Source of Uncertainty	u (umol/mol)	u2 (umol/mol)	Contribution	DoF	Evaluation type
Sample gas peak area determination	0.000158	2.50276E-08	4.76099E-07	8	A
Std gas peak area determination	0.000707	5.00416E-07	9.51939E-06	11	A
Std gas	0.0025	0.000006	0.000118893	∞	B
Adsoption cylinder	0.0000581	0.000000	6.41519E-08	∞	B
Gravimetric weighing	0.0003466	0.000000	2.28574E-06		combine A&B

Combined Uncertainty	**5.256807**	**0.0001312**
Expended uncertainty (95%)	**10.51361**	

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 comp osition of calibration gas mixtures.
3. EURACHEM/ CITAC Guide – Quantifying Uncertainty in Analytical Measurement, 2nd Edition

CSIR-National Physical Laboratory India (CSIR-NPLI)

Report Form APMP.QM-S7.1 – CH_4 in nitrogen (2000 μmol/mol)

Methane in nitrogen

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

Cylinder number: D634086

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CH_4	11/07/18	1994.93	0.058	9

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CH_4	13/07/18	1996.15	0.338	7

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CH_4	16/07/18	1990.75	0.013	9

Measurement #4

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CH_4	17/07/18	1995.44	0.314	9

Measurement #5

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (% relative)	number of replicates
CH_4	17/07/18	1990.42	0.040	9

Results

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

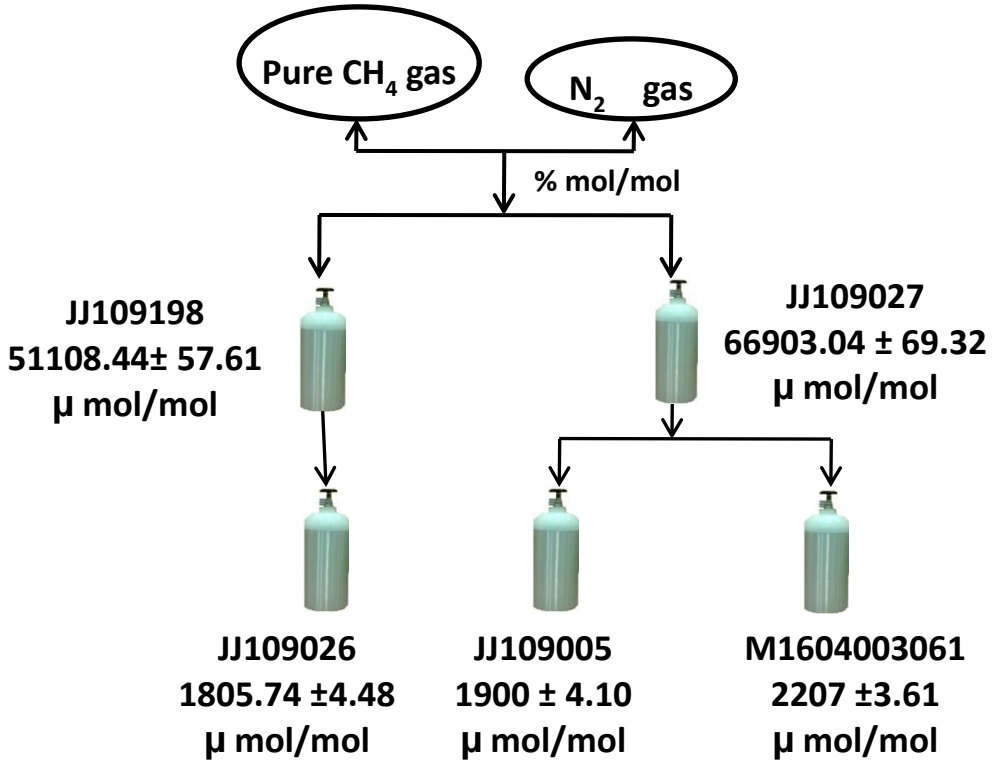
Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor[2]
CH_4	1993.54	7.72	2

Calibration standards

The calibration standards used were prepared in 10 litre aluminium cylinders. The cylinders were evacuated with heating of the cylinders at 60-70^{o}C. After wards cylinders were purged with nitrogen gas. This process is repeated thrice before actual preparation of gas mixture was carried out. The theoretical calculations were carried out for the desired concentrations.

Gas mixtures of methane in nitrogen gas from pure methane gas were prepared in two series in the concentrations around 5.1 and 6.6 % mol/mol. These gas mixtures were diluted in the concentration ranges from (1800~ 2207 µmol/mol). Total of 3 cylinders were prepared. All the preparation of Primary Reference Gas Mixtures (PRGM) standards were done in accordance to ISO 6142: Gas Analysis -Preparation of calibration gas mixtures - Gravimetric Method. These cylinders were validated in accordance to ISO 6143: Gas analysis - Comparison method for determining and checking the composition of calibration gas mixtures. Thus the prepared Methane gas mixtures were certified as Methane in Nitrogen gas Primary Reference Standard Gas Mixtures (PRGM). The preparation Scheme for the prepared methane gas mixture in nitrogen is given below

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



Gravimetric preparation scheme for Methane standards

All these standards are put to rotation for homogenization over night. After that the cylinders are put to rest for one day before it is used for the analysis.

The above mentioned standards are used for the analysis of APMP S7.1 cylinder

Analytical method
Details of the measurement method used:

GC FID (Agilent 6890N) with Methanizer

Column used: Porapak Q

Oven temp: 80 ºC

Carrier gas: He (30 ml/min)

Detector Temp: 250 ºC

GSV loop: 0.5 ml

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

The APMP.QM-S7.1 gas cylinder is stored inside gas laboratory at a nominal temperature for 23 ± 5ºC for all the period of its storage at NPL India. A dual stage regulator is fitted on the

cylinder to inject the gas sample through GSV into the GC-FID system for its analysis. The cylinders were rolled for two hours on homogenization system before doing measurements.

Uncertainty evaluation

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

Details on uncertainty budget calculation :

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

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

1. Raymor Balance
2. Mass Pieces
3. Buoyancy effect
4. Handling of cylinder
5. Residual gas
6. Expansion of the cylinder due to filling of gas at High pressure

II. Uncertainty Components in Analytical method

1. Repeatability
2. Calibration standards
3. GC-FID instrument Response

Measurement Uncertainty Budget for analysis:

Parameter (x_i)	Source of uncertainty	Standard uncertainty, $u(x_i)$		Unit	Relative standard uncertainty, $u_{rel}(x_i)$	Type (A/ B)
C_x	Measured result of Methane	1993.54	1.22	µmol/mol	0.000612458	A
C_{std1}		1805.74	2.05	µmol/mol	0.001135269	B
C_{std2}		1900.82	2.24	µmol/mol	0.001178439	B
C_{std3}		2207.31	1.81	µmol/mol	0.000817737	B
$Gc_{response}$	Instrument response	6853.70	1.19	mV	0.000173716	A
u_c	3.86	µmol/mol				
U	7.72	µmol/mol				
U (%)	0.39					

ANNEX B – Measurement results of APMP.QM-S7

11. Results and Discussion

A complete set of results reported from each participant is described in annex A of this report. The results are summarized in Table 3, and presented in Figure 2.

Table 3. Summary of measurement results (μmol/mol)

Laboratory acronym	Cylinder	x_{ref}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	D	$U(D)$	k
UME	D081228	1950.45	0.44	0.38	0.58	1951.89	4.11	2	1.44	4.27	2
NPLI	D081220	1991.50	0.40	0.38	0.55	2008.85	10.40	2	17.35	10.46	2
NIMT	D081209	1998.75	0.40	0.38	0.55	1998.6	6.2	2	-0.15	6.3	2
NMC/A*STAR	D081215	1990.78	0.38	0.38	0.53	1993	6	2	2	6	2
CMS/ITRI	D081158	2000.37	0.37	0.38	0.53	2003.3	3.9	2	2.9	4.0	2
KRISS	D081235	1999.30	0.40	0.38	0.55	1999.48	0.93	2	0.18	1.44	2
NMISA	D081134	1995.76	0.39	0.38	0.54	2001.3	3.8	2	5.5	4.0	2

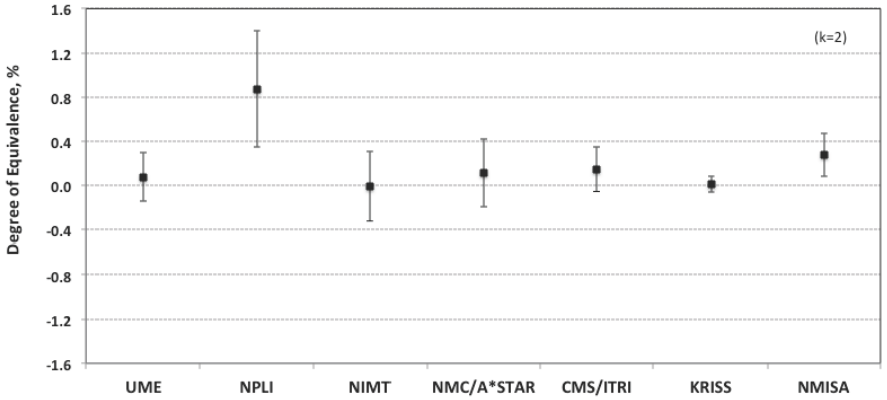


Figure 2. Relative deviations from the reference values ($k = 2$).
Note that the error bars are the relative uncertainties of Ds.

The degrees of equivalence for the results from the participants are shown in Figure 3. The results from the participants are consistent with the reference values as the deviations from the reference values are within the associated uncertainties except for two participants.

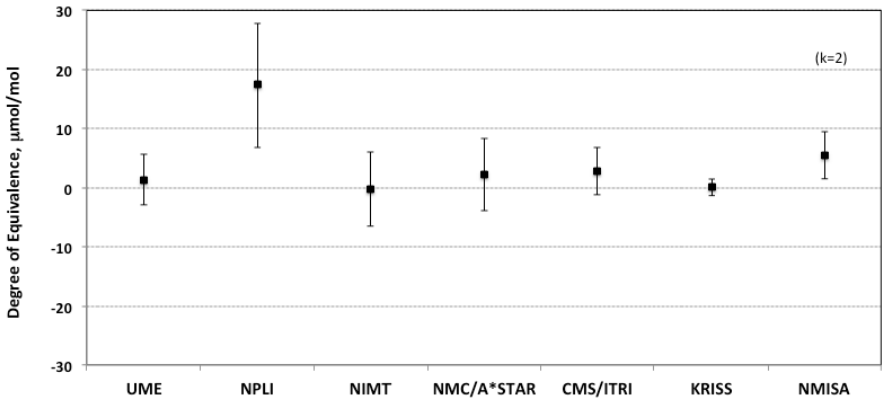


Figure 3. Degree of equivalence for the APMP.QM-S7 ($k = 2$).
Note that the error bars are the expanded uncertainties of Ds.