International Comparison CCQM-K119 Liquefied Petroleum Gas

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Field

Amount of substance

Subject

Comparison of the composition of liquefied petroleum gas (track C)

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1. Introduction

Liquefied hydrocarbon mixtures with traceable composition are required in order to underpin measurements of the composition and other physical properties of LPG (liquefied petroleum gas), thus meeting the needs of an increasingly large European industrial market. NPL and VSL and recently demonstrated their capabilities for preparation and analysis of liquid hydrocarbons in Constant Pressure Cylinders (CPCs) in EURAMET 1195.[1]

This comparison aims to assess the analytical capabilities of laboratories for measuring the composition of a Liquid Petroleum Gas (LPG) mixture when sampled in the liquid phase from a CPC. Each participant was asked to measure a different mixture prepared at NPL with a nominal composition as shown in table 1.

Component	**Nominal amount fraction / cmol mol^{-1}**
Ethane	2
Propane	71
Propene	9
iso-butane	4
n-butane	10
But-1-ene	3
iso-pentane	1

Table 1 Nominal amount fractions of distributed mixtures

2. Design and organisation of the comparison

Table 2 provides is a list of the participating laboratories.

Acronym	Country	Full Institute Name and address
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NMIA	AU	National Measurement Institute, 36 Bradfield Rd, Lindfield NSW, 2070, Australia
NPL	UK	National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

Table 2 Participating laboratories

The schedule for the key comparison is shown in table 3.

Date	Event
October 2014	Draft protocol published
November 2014	Final protocol published
March – July 2015	Preparation, validation and shipment of cylinders
April – September 2015	Distribution of mixtures
June – October 2015	Re-analysis of the mixtures at NPL
April 2016	Draft A report available
May 2017	Draft B report available

Table 3 Key comparison schedule

A set of travelling standards were prepared at NPL with the nominal composition described in table 1. The calculation procedures of ISO 6142-1[2] and ISO 19229[3] have been followed to calculate the amount-of-substance fractions and associated standard uncertainties. These mixtures were prepared in constant pressure cylinders (CPCs) purchased from DCG Partnership Ltd and made by Welker Inc. All components were added from their pure parent counterparts either by direct addition or via an intermediate vessel. A purity analysis was carried out for all parent components using gas chromatography. The CPCs were pressurised using helium at approximately 20 bar, and homogenised using the gravimetric mixer within the CPC. The travelling standards were compared to NPL Primary Reference Standards (PSMs). These included gas mixtures prepared in high pressure cylinders (NG567, NG531 and NG532, table 4) and a liquid mixture prepared in a CPC (CPC38954R2, table 4). Measurements were performed within two days of preparing the travelling standards. A second set of measurements was carried out after a week to assess mixture stability. Two further measurements separated by at least a week, were performed after the travelling standards were returned by the participants.

Component	amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
CPC38954R2		
Propane	71.2087	0.0032
n-butane	10.1058	0.0013
Propene	8.8991	0.0011
iso-butane	3.9651	0.0009
But-1-ene	3.0183	0.0012
Ethane	1.7964	0.0003
iso-pentane	0.9956	0.0002
NG567		
Methane	84.7851	0.0045
Propene	8.9888	0.0025
But-1-ene	2.9894	0.0022
Ethane	2.1845	0.0035
iso-pentane	1.0313	0.0002
NG531		
Methane	857903	0.0070
iso-butane	39893	0.0048
n-butane	101725	0.0051
NG532		
Methane	59.9702	0.0064
Propane	40.0284	0.0064

Table 4 Composition of PSMs used at NPL to verify the travelling standards and monitor stability. Standard gravimetric uncertainties are shown (*k*=1)

The purity analysis information for each of these components can be found in the appendix. The participating laboratories were instructed to ensure the correct over-pressure was applied to the mixture and that it was homogenised before measurement. The results of the analysis were requested with details of the measurement procedure and associated uncertainties for each component.

All participants used gas chromatography (GC) with a flame ionisation detector (GC-FID) calibrated with LPG mixtures prepared in-house in CPCs. NMIA also used a GC with a thermal conductivity detector (GC-TCD). Table 5 list the details of the different standards and methods used at each NMI.

Laboratory identifier	Standards used for calibration	Calibration equation type	Measurement Dates
NPL	standards in 0.5 L Welker CPCs and gas standards	Direct comparison	10/09/2015 - 28/09/2015
VNIIM	3 standards prepared in 2 L Welker CPCs	Direct comparison	18/04/2015 - 21/05/2015
NMIA	6 standards in 0.5 L Welker CPCs	Calibration curve	04/08/2015 - 17/08/2015
VSL	3 standards prepared in 1 L Welker CPCs	Calibration curve	01/09/2015 - 07/09/2015
KRISS	6 standards in different (Bellows-type) CPCs models	Direct comparison	30/06/2015 - 07/07/2015

Table 5 Summary of the measurement procedures

3. Results

A unilateral degree of equivalence in key comparisons is generally expressed as:

$$d_{i,a} = x_{i,a} - x_{i,a,\mathrm{ref}}$$

Where, $x_{i,a}$ is the reported amount fraction of component *a* from laboratory *i* and $x_{i,a,\mathrm{ref}}$ is the key comparison reference value of component *a* from the mixture delivered to laboratory *i*. The combined uncertainty in this term can be expressed as:

$$u^2(d_{i,a}) = u^2(x_{i,a}) + u^2(x_{i,a,\mathrm{prep}}) + u^2(x_{i,a,\mathrm{ver}})$$

Where, $u(x_{i,a,\mathrm{prep}})$ is the uncertainty in the amount of substance fraction from preparation and $u(x_{i,a,\mathrm{ver}})$ is the uncertainty from verification.

The composition of liquid hydrocarbon mixtures in constant pressure (piston) cylinders may vary with time due to propensity of the hydrocarbon components to transfer across the piston into the pressurising gas since the piston within a constant pressure cylinder does not create a perfect seal. In this comparison, the stability of each component was monitored (before and after distribution) and a correction made for any changes in composition. A linear squares fit in accordance with ISO 6143[4] using a straight line as a calibration function, was carried out using XLgenline software for each component in each travelling standard before and after distribution. The KCRV has been calculated using:

$$x_{i,a,\mathrm{ref}} = x_{i,a,\mathrm{prep}} + x_{i,a,\mathrm{stab}}$$

Where $x_{i,a,\mathrm{prep}}$ is the amount of substance fraction from preparation and $x_{i,a,\mathrm{stab}}$ is a drift correction for each component determined from each regression at the time when it was analysed by each participant. Table 6 provides the reference values and results from the comparison.

Lab	Component	x_{prep}	x_{stab}	x_{ref}	u_{ref}	x_i	$u_{(x_i)}$	d_i	$U(d_i)$
NPL	**Ethane**	1.9158	-0.0156	1.9002	0.0087	1.9254	0.0193	0.0252	0.0422
	Propane	71.4424	-0.0002	71.4422	0.3069	71.4627	0.2144	0.0205	0.7487
	Propene	8.3192	-0.0102	8.3090	0.0351	8.3079	0.0291	-0.0011	0.0912
	iso-butane	3.9803	0.0011	3.9814	0.0168	3.9767	0.0139	-0.0047	0.0436
	n-butane	10.1155	0.0110	10.1265	0.0440	10.1157	0.0354	-0.0108	0.1129
	But-1-ene	3.1999	0.0012	3.2010	0.0138	3.1966	0.0128	-0.0045	0.0376
	iso-pentane	1.0154	0.0017	1.0171	0.0053	1.0151	0.0061	-0.0020	0.0162
VNIIM	**Ethane**	1.9612	0.0133	1.9745	0.0077	1.9470	0.0136	-0.0275	0.0313
	Propane	70.9346	0.0013	70.9359	0.2651	70.9300	0.1773	-0.0059	0.6379
	Propene	8.8401	0.0174	8.8575	0.0326	8.8340	0.0221	-0.0235	0.0787
	iso-butane	4.0069	-0.0073	3.9996	0.0131	3.9900	0.0080	-0.0096	0.0306
	n-butane	10.1871	-0.0148	10.1723	0.0327	10.1200	0.0253	-0.0523	0.0827
	But-1-ene	3.0445	-0.0046	3.0399	0.0107	3.0190	0.0075	-0.0209	0.0263
	iso-pentane	1.0145	-0.0034	1.0111	0.0045	0.9952	0.0040	-0.0159	0.0120
NMIA	**Ethane**	1.8154	-0.0129	1.8025	0.0083	1.8140	0.0140	0.0115	0.0326
	Propane	71.5149	0.0093	71.5242	0.2503	71.5310	0.1285	0.0068	0.5628
	Propene	8.6788	0.0093	8.6881	0.0315	8.6760	0.0255	-0.0121	0.0811
	iso-butane	3.7888	0.0014	3.7901	0.0127	3.7910	0.0170	0.0009	0.0425
	n-butane	10.0518	-0.0400	10.0117	0.0344	10.0570	0.0375	0.0453	0.1017
	But-1-ene	3.1285	-0.0125	3.1159	0.0122	3.1160	0.0245	0.0001	0.0547
	iso-pentane	1.0105	-0.0135	0.9970	0.0052	1.0150	0.0110	0.0180	0.0244
VSL	**Ethane**	2.0837	0.0490	2.1327	0.0088	2.1170	0.0100	-0.0157	0.0266
	Propane	71.0921	-0.0459	71.0462	0.2591	71.3900	0.6500	0.3438	1.3995
	Propene	8.6711	-0.0152	8.6560	0.0308	8.7300	0.0800	0.0740	0.1715
	iso-butane	3.9834	-0.0010	3.9824	0.0150	4.0230	0.0380	0.0406	0.0817
	n-butane	10.1353	0.0077	10.1431	0.0416	10.1800	0.1150	0.0369	0.2446
	But-1-ene	3.0670	0.0033	3.0703	0.0129	3.0730	0.0390	0.0027	0.0822
	iso-pentane	0.9562	-0.0005	0.9557	0.0051	0.9620	0.0130	0.0063	0.0279
KRISS	**Ethane**	2.0866	-0.0327	2.0539	0.0201	2.0178	0.0107	-0.0361	0.0455
	Propane	70.4104	0.0517	70.4621	0.2951	70.5753	0.2894	0.1132	0.8267
	Propene	8.7606	0.0079	8.7685	0.0365	8.7193	0.0349	-0.0492	0.1010
	iso-butane	4.1706	-0.0107	4.1599	0.0179	4.1535	0.0150	-0.0064	0.0467
	n-butane	10.1671	0.0070	10.1741	0.0443	10.1641	0.0457	-0.0100	0.1274
	But-1-ene	3.1113	-0.0025	3.1088	0.0137	3.1038	0.0118	-0.0050	0.0362
	iso-pentane	1.0324	-0.0130	1.0194	0.0042	1.0303	0.0088	0.0109	0.0194

Table 6 Results for the 7 components for each laboratory with units cmol mol^{-1}.

The difference for each laboratory are presented in figure 1.

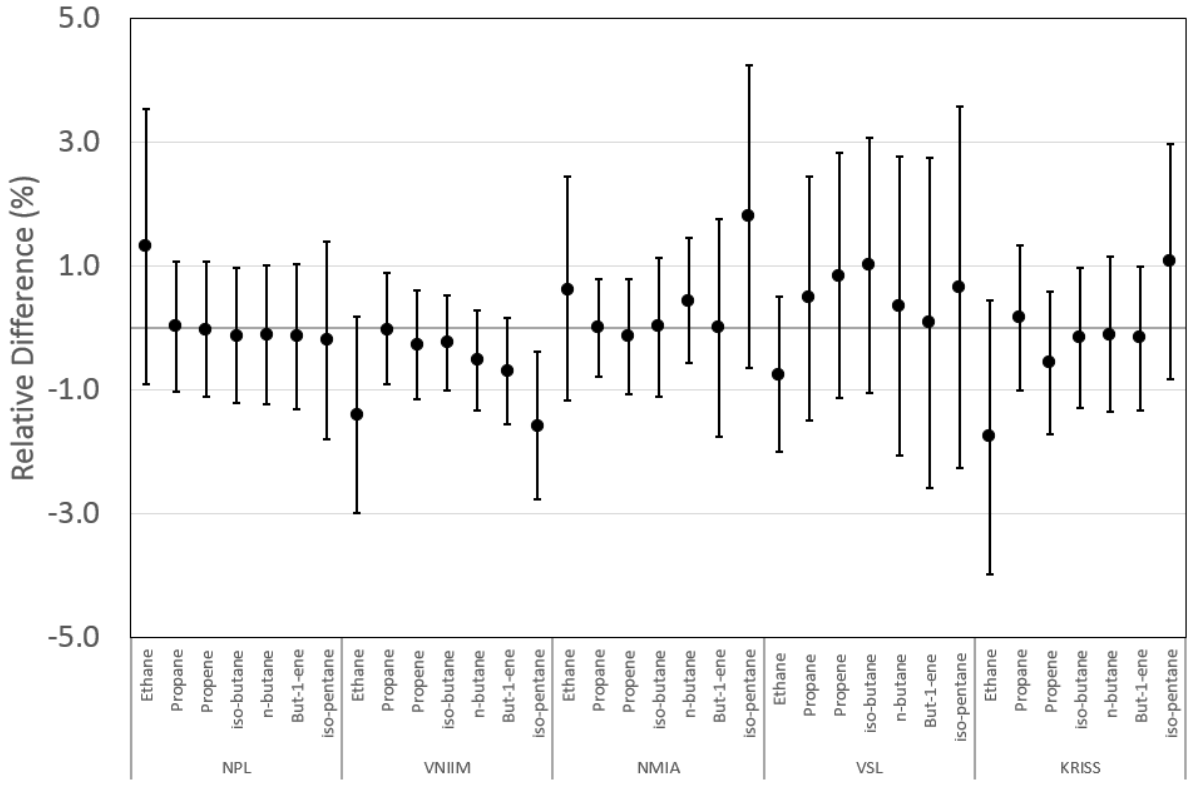

Figure 1 Results for each laboratory

4. Supported CMC claims

The results of this key comparison can be used to support CMC claims for ethane, propane, propene, *i*-butane, *n*-butane, but-1-ene and *i*-pentane in the liquid phase in CPCs with a matrix of propane, *n*-butane or *i*-butane as a track C key comparison.

The support of CMC claims is described in more detail in the GAWG strategy for comparisons and CMC claims.[5]

5. Conclusions

The results in this key comparison demonstrate good comparability between laboratories within the stated uncertainties. With the exception of one component, all measurements demonstrate equivalence with the reference value. The stability measurements indicate the limited performance of the Welker cylinder as a transfer standard of more volatile low molecular hydrocarbons such as ethane with the main potential source of uncertainty being the transfer of the component across the piston. This is particularly pronounced for ethane and further work with new technologies could focus on improving the current state of the art.

References

[1] Brown AS, Downey ML, Milton MJT, van der Veen AMH, Zalewska ET and Li J, EURAMET 1195: Bilateral comparison of liquefied hydrocarbon mixtures in constant pressure (piston) cylinders, NPL Report AS76, (2013).

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

[3] ISO 19229:2015, Gas analysis -- Purity analysis and the treatment of purity data, (2015).

[4] BS EN ISO 6143:2006 Gas analysis. Comparison methods for determining and checking the composition of calibration gas mixtures, (2001).

[5] Brewer PJ, van der Veen AMH, GAWG strategy for comparisons and CMC claims, CCQM Gas Analysis Working Group, (2016).

Appendix

Purity data with standard uncertainties (*k*=1).

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
Ethane	99.99967	0.000088
Nitrogen	0.0001	0.00008
Oxygen	0.000025	0.00002
Methane	0.00003	0.00002
Propane	0.000025	0.00001
n-butane	0.00015	0.00002

Table 7 Purity analysis data for ethane

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
Propane	99.99579	0.000322
Propene	0.001236	0.000124
n-butane	0.002974	0.000297

Table 8 Purity analysis data for propane

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
Propene	99.997897	0.0002103
Propane	0.002103	0.0002103

Table 9 Purity analysis data for propene

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
iso-butane	99.996265	0.000373
n-butane	0.003735	0.000373

Table 10 Purity analysis data for *i*-butane

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
n-butane	99.998491	0.000015
iso-butane	0.000151	0.00001509

Table 11 Purity analysis data for *n*-butane

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
n-butane	0.075596	0.00755962
iso-butane	0.253514	0.0253514
trans-but-2-ene	0.252102	0.0252102
But-1-ene	99.350335	0.0368858
iso-butene	0.043533	0.00435329
cis-but-2-ene	0.02492	0.00249197

Table 12 Purity analysis data for but-1-ene

Component	Amount fraction / cmol mol^{-1}	Uncertainty / cmol mol^{-1}
neo-pentane	0.021742	0.00217417
iso-pentane	99.890069	0.00908296
n-pentane	0.088189	0.00881891

Table 13 Purity analysis data for *i*-pentane

NPL MEASUREMENT REPORT

Cylinder number: CPC38959

Measurements made at NPL during September 2015

Analytical comparison methods

The LPG mixtures were connected to a GC system with a low dead-volume connector and a 1/16th inch Silcosteel sample line with an NPL custom-designed flow restrictor, which were both purged thoroughly before use. A sample flow of approximately 15 ml/min was used and at least six repeat measurements were performed in all cases. The responses were recorded as peak area and the average peak area of the repeated measurement was calculated.

GC system

GC analysis was carried out using an Analytical Controls 'Hi-speed RGA' gas chromatography system (AC Analytical Controls, Rotterdam, The Netherlands) with six columns, six valves and three detectors - one flame ionisation detector (FID) and two thermal conductivity detectors (TCDs). Table 1 provides more details on the GC set up and methods parameters.

Column	Details
Column 1	3 m x 0.32 mm x 4 µm SPB-1
Column 2	25 m x 0.32 mm x 8 µm Al_2O_3 Plot 'S'
Column 3	0.25 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep Q (80/100)
Column 4	1 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep N (80/100)
Column 5	1 m x $^1/_{16}$″ (ID 1 mm) Silcosteel HayeSep Q (80/100) + 2 m x $^1/_{16}$″ (ID 1 mm) Silcosteel molecular sieve 5A (80/100)
Column 6	2 m x $^1/_{16}$″ (ID 1 mm) Silcosteel molecular sieve 13X (80/100)
Detector	
Detector 1 (FID)	All hydrocarbons
Detector 2 (TCD)	Hydrogen and helium – Not used
Detector 3 (TCD)	Carbon dioxide, oxygen, nitrogen, methane and carbon monoxide – Not used
Parameter	**Setting**
Run time	9 min
Injection mode	GSV
Main oven temperature (columns 1 and 2)	60 – 200 °C
Auxiliary oven temperature (columns 3 to 6)	70deg C isothermal
Carrier gases	Helium (detectors 1 (FID) and 3 (TCD)) Nitrogen (detector 2 (TCD))
Detector temperatures	150 °C isothermal (TCD) 250 °C isothermal (FID)

Table 1 Detailed description of the GC used for LPG analysis

Calibration standards

An LPG PSM (CPC 30974R3) of nominally the same composition as the comparison mixture was prepared in a 0.5 L Welker CPC.

Component	Amount Fraction cmol/mol	Gravimetric Standard Uncertainty cmol/mol
Ethane	2.1572	0.0003
Propane	71.6798	0.0032
Propene	8.3732	0.0010
iso-Butane	4.1581	0.0009
n-Butane	9.7237	0.0012
But-1-ene	2.9663	0.0011
iso-Pentane	0.9309	0.0002

Table 2 Composition of the LPG PSM (CPC 30974R3) used for analysis of the comparison mixture

The impurities present in the parent gases/liquids were quantified by GC-FID. The stated amount fractions are those calculated from the gravimetric preparation process. The standard uncertainties were calculated using the NPL Software GravCalc2 (following ISO 6142) by combination of the uncertainties from three sources: gravimetry, relative molar masses and purity analysis.

Evaluation of measurement uncertainty and coverage interval

The evaluation of measurement uncertainties is based on the statistical analysis of the repeated comparisons. For each of the analyses of the comparison mixture, the standard deviation was calculated from the repeated measurements comprising each analysis.

Component	Relative Uncertainty (%)			
	Gravimetric Uncertainty	Analytical Uncertainty	Combined (k=1)	Combined (k=2)
Ethane	0.017	1.0	1.0	2.0
Propane	0.0045	0.30	0.30	0.6
Propene	0.012	0.35	0.35	0.7
iso-Butane	0.024	0.35	0.35	0.7
n-Butane	0.012	0.35	0.35	0.7
But-1-ene	0.036	0.40	0.40	0.8
iso-Pentane	0.016	0.6	0.6	1.2

Table 3 Breakdown of uncertainties

Final Results and Expanded Uncertainties

We estimate that there are a very large number of degrees of freedoms in these values. Therefore, we expand the standard uncertainties using a coverage factor of two to give expanded uncertainties with a 95% confidence interval.

Component	Amount Fraction cmol/mol	Expanded Uncertainty	
		% Relative	cmol/mol
Ethane	1.925	2.0	0.039
Propane	71.463	0.6	0.429
Propene	8.308	0.7	0.058
iso-Butane	3.977	0.7	0.028
n-Butane	10.116	0.7	0.071
But-1-ene	3.197	0.8	0.026
iso-Pentane	1.015	1.2	0.012

Table 4 Final results of the analysis of the comparison mixture

VNIIM Report CCQM-K119 “Liquified petroleum gas”

Laboratory: D.I. Mendeleyev Institute for Metrology (VNIIM), Research Department for the State Measurement Standards in the field of Physico-Chemical Measurements.

Authors: L.A. Konopelko, T.A. Popova, A.V. Meshkov, O.V. Efremova

Cylinder number: 38957

Measurement 1

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
ethane	(28.04 - 18.05) 2015	1.962	0.25	3 measurements (with 5 sub-measurements)
propane		71.12	0.10	
propene		8.853	0.08	
iso-butane		3.991	0.43	
n-butane		10.13	0.61	
1-butene		3.023	0.53	
iso-pentane		0.9961	1.2	

Measurement 2

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
ethane	(29.04 - 19.05) 2015	1.941	0.72	4 measurements (with 5 sub-measurements)
propane		70.84	0.60	
propene		8.819	0.52	
iso-butane		3.986	0.73	
n-butane		10.10	0.83	
1-butene		3.016	0.73	
iso-pentane		0.9923	0.84	

Measurement 3

Component	Date	Result (cmol/mol)	Standard deviation (% relative)	Number of replicates
ethane	(13.05 - 21.05) 2015	1.938	0.60	4 measurements (with 5 sub-measurements)
propane		70.84	0.49	
propene		8.829	0.63	
iso-butane		3.994	0.75	
n-butane		10.13	0.78	
1-butene		3.019	0.90	
iso-pentane		0.9972	0.99	

Measurements №№ 1-3 were carried out with different calibration standards each.

Results

Component	Date	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Relative expanded uncertainty, %	Coverage factor
ethane	27.05.2015	1.947	0.027	1.4	k=2
propane		70.93	0.38	0.5	
propene		8.834	0.044	0.5	
iso-butane		3.990	0.016	0.4	
n-butane		10.12	0.05	0.5	
1-butene		3.019	0.015	0.5	
iso-pentane		0.9952	0.0076	0.8	

Calibration standards

Preparation of LPG calibration mixtures (liquid) was carried out by gravimety in constant pressure cylinders (floating piston cylinders, 2 dm^3). Every component was added directly from a conventional cylinder to a piston cylinder, except iso-pentane, which was transferred to the piston cylinder with a syringe. In the case of propane (major component) the cylinder was slightly heated during transferring in order to maintain enough vapour pressure.
Before and after addition of each component the piston cylinder was weighed accurately on RAYMOR HCE-25G balance against a tare cylinder.
After filling the piston cylinders were pressurized with He to 2.0 MPa.
Purity analysis of the parent substances was carried out by GC- FID, TCD

3 calibration standards were prepared in piston cylinders. Composition of calibration standards is shown in the tables 1-3.

Table 1

Cylinder N 2221		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
ethane	2.0235	0.0011
propane	71.1176	0.0013
propene	8.8737	0.0008
iso-butane	4.0296	0.0005
n-butane	9.9484	0.0007
1-butene	2.9966	0.0004
iso-pentane	0.98996	0.0002

Table 2

Cylinder N 2217		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
ethane	2.0434	0.0010
propane	71.1325	0.0012
propene	8.7726	0.0007
iso-butane	4.0172	0.0005
n-butane	10.0331	0.0007
1-butene	2.9866	0.0004
iso-pentane	0.99393	0.0003

Table 3

Cylinder N 2218		
Component	Amount of substance fraction, cmol/mol	u_{grav}, cmol/mol (k=1)
ethane	2.0008	0.0010
propane	70.6680	0.0012
propene	9.3181	0.0007
iso-butane	4.0157	0.0005
n-butane	10.0077	0.0007
1-butene	2.9790	0.0004
iso-pentane	0.99016	0.0003

Results of purity analysis are shown in the tables 4-10

Table 4. Ethane (cylinder № 4877)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_2H_6	99.995587 cmol/mol	-
N_2	15 µmol/mol	9
O_2	15 µmol/mol	9
CO_2	10 µmol/mol	6
C_4H_{10} (n-butane)	2.13 µmol/mol	0.17
C_5H_{12} (n-pentane)	0.5 µmol/mol	0.29
C_6H_{14} (n-hexane)	0.5 µmol/mol	0.29
CH_4	0.5 µmol/mol	0.29
i-C5H_{12}	0.5 µmol/mol	0.29

Table 5. Propane (cylinder № JT111017)

Component	Amount of substance fraction, µmol/mol	u, µmol/mol (k=1)
C_3H_8	99.98662 cmol/mol	-
C_2H_6	89 µmol/mol	13
i-C_4H_{10}	27 µmol/mol	4
C_3H_6	15.5 µmol/mol	2.3
C_4H_{10} (n-butane)	2.3 µmol/mol	0.6

Table 6. Propene (cylinder № 1356)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_3H_6	99.77711 cmol/mol	-
C_3H_8	2163 µmol/mol	65
C_2H_6	34.4 µmol/mol	1.7
N_2	15 µmol/mol	9
O_2	15 µmol/mol	9
C_2H_4	0.5 µmol/mol	0.29
C_5H_{12} (n-pentane)	0.5 µmol/mol	0.29
C_6H_{14} (n-hexane)	0.5 µmol/mol	0.29

Table 7. Iso-butane (cylinder № 4874)

Component	Amount of substance fraction	u, µmol/mol (k=1)
i-C_4H_{10}	99.929169 cmol/mol	—
N_2	339 µmol/mol	34
C_3H_8	136 µmol/mol	5
C_4H_{10} (n-butane)	112 µmol/mol	6
O_2	58 µmol/mol	6
cis-C_4H_8 (cis-2-buten)	50 µmol/mol	14
i-C_4H_8 (iso-buten)	9.7 µmol/mol	0.7
C_4H_8 (1-butene)	1.11 µmol/mol	0.11
C_2H_4	0.5 µmol/mol	0.29
C_2H_6	0.5 µmol/mol	0.29
C_3H_6	0.5 µmol/mol	0.29
C_3H_6 (cyclopropane)	0.5 µmol/mol	0.29
CH_4	0.5 µmol/mol	0.29

Table 8. n- butane (cylinder № 26133)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_4H_{10} (n-butane)	99.859748 cmol/mol	—
neo-C_5H_{12}	664 µmol/mol	40
i-C_4H_{10}	347 µmol/mol	28
N_2	262 µmol/mol	26
C_3H_8	80 µmol/mol	4
O_2	46 µmol/mol	5
CH_4	0.52 µmol/mol	0.29
C_2H_4	0.5 µmol/mol	0.29
C_2H_6	0.5 µmol/mol	0.29
C_3H_6 (cyclopropane)	0.5 µmol/mol	0.29
C_5H_{12} (n-pentane)	0.5 µmol/mol	0.29
C_6H_{14} (n-hexane)	0.5 µmol/mol	0.29
i-C_5H_{12}	0.5 µmol/mol	0.29

Table 9 1-butene (cylinder № 829)

Component	Amount of substance fraction	u, µmol/mol (k=1)
C_4H_8 (1-butene)	99.40332 cmol/mol	—
C_4H_{10} (n-butane)	2975 µmol/mol	89
i-C_4H_8 (iso-buten)	1210 µmol/mol	36
i-C_4H_{10}	1190 µmol/mol	36
N_2	232 µmol/mol	23
trans-C_4H_8 (trans-2-buten)	137 µmol/mol	7
C_3H_6	68 µmol/mol	5
O_2	46 µmol/mol	5
cis-C_4H_8 (cis-2-buten)	19.9 µmol/mol	1.2
C_3H_8	17.4 µmol/mol	1.4
C_4H_6 (1,3-butadien)	12.5 µmol/mol	0.8
C_5H_{10} (2-methyl-1-butene)	7 µmol/mol	0.6
C_2H_4	0.5 µmol/mol	0.29
C_2H_6	0.5 µmol/mol	0.29
C_6H_{14} (n-hexane)	0.5 µmol/mol	0.29
CH_4	0.5 µmol/mol	0.29

Table 10 Iso-pentane (cylinder № 8027-1)

Component	Amount of substance fraction	u, µmol/mol (k=1)
i-C_5H_{12}	99.646 cmol/mol	—
C_5H_{12} (n-pentane)	2500 µmol/mol	480
C_5H_{10} (2-methyl-1-butene)	1040 µmol/mol	210

Instrumentation

The measurements were performed on GC system «Crystal-5000.2» (Chromatec, Russia)

Data collection: Software “Chromatec Analytic 2.6”
Detector: FID
Column: Restek Rt-Alumina, 30 m × 0,53 mm
Carrier gas: He
Gas flow:10 ml/min
Injected dose: 0.25 µl
Injector temperature: 50°C
Temperature of the cooling zone of the injector: 10°C
Detector temperature: 300°C
Temperature program of the column thermostat: 40°C – 5 min, 7°C/min, 130°C – 5 min.

Measurement procedure

Before each analysis the cylinder with the LPG comparison mixture was homogenized by rotating through 180° about 10 times.
The injection of the sample was carried out by sampling valve for liquefied gases, which enables to maintain single-phase state for mixtures of liquefied hydrocarbons with saturated vapor pressure higher than atmospheric. Pressure in the injection system is provided by

pressure in a working chamber of the piston cylinder (2.0 MPa).
Single point calibration method was used to determine components mole fraction in the LPG mixture to be investigated.
Measurement sequence was in the order:
Calibration mixture 1- Comparison mixture - Calibration mixture 1;
Calibration mixture 2- Comparison mixture - Calibration mixture 2;
Calibration mixture 3 - Comparison mixture - Calibration mixture 3.

Uncertainty evaluation

Component	Measurement result, cmol/mol	u_{grav} (purity+weighing), cmol/mol	u_{anal} (between and within day measurements), cmol/mol	u (combined standard uncertainty), cmol/mol	U (expanded uncertainty, k=2), cmol/mol	U_0 (relative expanded uncertainty), %
ethane	1.947	0.0011	0.0137	0.0137	0.0274	1.4
propane	70.93	0.0013	0.1897	0.1897	0.3794	0.5
propene	8.834	0.0008	0.0219	0.0219	0.0438	0.5
iso-butane	3.990	0.0005	0.0082	0.0082	0.0164	0.4
n-butane	10.12	0.0007	0.0257	0.0257	0.0514	0.5
1-butene	3.019	0.0004	0.0073	0.0073	0.0146	0.5
iso-pentane	0.9952	0.0003	0.0038	0.0038	0.0076	0.8

Report Form CCQM-K119 LPG

Laboratory name: National Measurement Institute, Australia (NMIA)

Authors: Damian Edward Smeulders, John Briton McCallum, Raymond Tendai Satumba

Cylinder number: 38958

Measurement #1 (Bruker 452 NGA)

Component	Date	**Result / cmol mol^{-1}**	**Expanded uncertainty / cmol mol^{-1}**	**Number of replicates**
Ethane	4/8/2015	1.788	0.040	9 repeats
Propane		71.498	0.217	4 Standards
Propene		8.636	0.049	Each run 3 times
iso-butane		3.808	0.029	
n-butane		10.114	0.053	
But-1-ene		3.138	0.042	
iso-pentane		1.019	0.012	

Measurement #2 (Bruker 452 NGA)

Component	Date	**Result / cmol mol^{-1}**	**Expanded uncertainty / cmol mol^{-1}**	**Number of replicates**
Ethane	6/8/2015	1.819	0.103	9 repeats
Propane		71.563	0.247	4 Standards
Propene		8.677	0.068	Each run 2 times
iso-butane		3.786	0.046	
n-butane		10.037	0.124	
But-1-ene		3.1068	0.054	
iso-pentane		1.011	0.027	

Measurement #3 (Bruker 452 NGA)

Component	Date	**Result / cmol mol^{-1}**	**Expanded uncertainty / cmol mol^{-1}**	**Number of replicates**
Ethane	14/08/2015	1.826	0.033	9 repeats
Propane		71.499	0.376	3 Standards
Propene		8.670	0.045	Each run 2 times
iso-butane		3.798	0.022	

n-butane		10.070	0.050	
But-1-ene		3.117	0.020	
iso-pentane		1.020	0.013	

Measurement #4 (Varian 3800 TCD)

Component	Date	**Result / cmol mol^{-1}**	**Expanded uncertainty / cmol mol^{-1}**	**Number of replicates**
Ethane	10/08/2015	1.821	0.022	9 repeats
Propane		71.532	0.146	3 Standards
Propene		8.727	0.037	Each run 2 times
iso-butane		3.779	0.036	
n-butane		10.022	0.059	
But-1-ene		3.114	0.052	
iso-pentane		1.005	0.039	

Measurement #5 (Varian 3800 TCD)

Component	Date	**Result / cmol mol^{-1}**	**Expanded uncertainty / cmol mol^{-1}**	**Number of replicates**
Ethane	17/08/2015	1.822	0.033	9 repeats
Propane		71.551	0.365	3 Standards
Propene		8.670	0.058	Each run 2 times
iso-butane		3.784	0.031	
n-butane		10.045	0.086	
But-1-ene		3.107	0.045	
iso-pentane		1.022	0.019	

Results

Component	Result cmol /mol	Expanded uncertainty cmol/mol
Ethane	1.814	0.028
Propane	71.531	0.257
Propene	8.676	0.051
iso-butane	3.791	0.034
n-butane	10.057	0.075
But-1-ene	3.116	0.049
iso-pentane	1.015	0.022

Calibration standards

Two batches of LPG calibration standards were made for this comparison. The calibration standards were liquid mixtures made in 0.5L Welker constant pressure cylinders (Welker CP2-500ma and CP2-500gma). The compositions of the standards are detailed below and were manufactured to span the target concentration of the LPG sample:

CPC standard		Ethane	Propane	Propylene	iso-Butane	n-Butane	But-1-ene	iso-Pentane
Batch 1								
CPC31229	Concentration cmol/mol	1.8037	71.0279	9.9966	3.7803	9.6254	2.6028	1.0045
	Preparation uncertainty	0.0090	0.0170	0.0080	0.0055	0.0106	0.0115	0.0036
CPC31230	Concentration cmol/mol	5.3831	68.4453	8.6626	3.7799	9.8190	2.9848	0.7666
	Preparation uncertainty	0.0241	0.0303	0.0176	0.0132	0.0146	0.0155	0.0106
CPC31231	Concentration cmol/mol	1.2837	70.3101	8.8925	4.4116	10.6879	3.0316	1.2259
	Preparation uncertainty	0.0259	0.0327	0.0185	0.0141	0.0158	0.0170	0.0109
CPC31232	Concentration cmol/mol	2.3930	70.8754	9.0437	4.2008	8.8483	2.5724	1.9066
	Preparation uncertainty	0.0255	0.0324	0.0182	0.0138	0.0152	0.0164	0.0107
Batch 2								
CPC39961	Concentration cmol/mol	1.8412	70.9871	8.9509	4.0314	10.0760	3.0786	0.8790
	Preparation uncertainty	0.0114	0.0145	0.0094	0.0066	0.0061	0.0064	0.0066

CPC39962	Concentration cmol/mol	2.3392	70.7280	8.4584	3.9662	10.1071	3.2491	0.9971
	Preparation uncertainty	0.0104	0.0135	0.0079	0.0059	0.0063	0.0062	0.0068
CPC39963	Concentration cmol/mol	1.8427	70.8996	8.7035	3.9600	10.0250	3.3185	1.0952
	Preparation uncertainty	0.0104	0.0135	0.0079	0.0059	0.0063	0.0062	0.0068

Standards were manufactured by gravimetry using a Mettler XP32003L-EL mass comparator. The standards were manufactured in the following way:

1. The receiving CPC was evacuated on both sides of the piston
2. Each nominally pure hydrocarbon liquid was stored in individual CPCs. The CPCs were used to push the liquid into the receiving CPC. Liquids were added in the following order: iso-pentane, n-butane, butene, iso-butane, propylene, ethane, propane.
3. Weighing was performed before and after each addition.
4. CPCs were pressurised for use.

The impurities present in each nominally pure hydrocarbon were determined on a Varian 3800 GC. The pure liquids were tested by sampling the vapour phase and also by testing the liquids after they were transferred to CPCs. The GC used for purity assessment used a Varian Gasifier for sample introduction. The GC was equipped with two channels – a hydrocarbon channel using an alumina Plot Na_2SO_4 column with FID, and a second channel with molsieve and PDHID for measurement of hydrogen and air components. Purity measurements showed that hydrocarbon impurities were generally present at low levels and had little impact on the compositions of the LPG standards. However, nitrogen was detected in most of the liquids at various concentrations. Purity tables have been added at the end of this document.

Verification:

Early standards were made by a combination of loops and CPCs to transfer the hydrocarbon components into the CPCs. The procedure proved to be time-consuming and produced unreliable standards. Batches of LPG standards made by CPC addition were found to be consistent from batch to batch. For this comparison, two batches of standards (4 standards, then 3 extra standards) gave close agreement for the certification of the LPG sample.
Traditional vapour standards were also manufactured. However, the agreement between vapour standards and liquid standards was poor due to different amounts of sample being introduced onto the GC systems. The GCs did not give linear responses due to overloading of the columns when liquid is sampled.

Instrumentation

Two GCs were used for the certification. **Measurements 1-3** were obtained on a Bruker 456 GC 'configuration C' natural gas analyser. For LPG analysis, the GC uses a liquid sampling valve to introduce a volume of LPG onto an alumina PLOT KCL or Na_2SO_4 capillary column (50m x 0.53 µm) with FID detector. (Measurement 1 & 2: Al_2O_3 KCl. Measurement 3: Al_2O_3 Na_2SO_4)

Measurements 4-5 were obtained on a Varian 3800 GC with TCD detector. A Varian gasifier (100°C heated regulator) was used to vaporise the liquid sample and standards. The vapour was then injected using a gas sampling valve with a 20 µL sample loop. Alumina PLOT KCL or Na_2SO_4 capillary columns were used (50m x 0.53 µm). (Measurement 4: Al_2O_3 Na_2SO_4; Measurement 5: Al_2O_3 KCl)

Analysis Procedure

All results were normalized to 100% to correct for any differences in sampling and for different permanent gas compositions.

The sample submitted for analysis had a number of impurities that eluted around 1-butene that were not present in the NMIA standards. These impurities may have introduced a slight bias into the measurement of that component.

Mixtures in CPCs were mixed every time they were connected to the GC for analysis.

System 1:

Bruker 456 GC. NGA configuration C with liquid sampling valve. FID channel used.
Liquid injection. Sample line pressurised. Sample static during testing.
Alumina Plot Na_2SO_4 or KCl column (50m x 0.53 µm).
Helium carrier.
Oven program: 40°C for 5 minutes. 4°C/min to 100°C. Held for 0 minutes.

System 2:

Varian 3800 with TCD
Varian gasifier used. Liquid input. Vapour output metered at 10mL/minute.
Alumina Plot Na_2SO_4 or KCL column (50m x 0.53 µm).
Helium carrier.
Oven program: 50°C for 5 minutes. 10°C/min to 150°C. Held for 5 minutes.

Uncertainty evaluation

The preparation uncertainty of the gas mixtures was calculated using the principles described in ISO 6142, 2001. The preparation uncertainty budget included contributions from:

- Gravimetry
- Purity of gases
- Molar mass

Gravimetry was the dominant factor in the preparation uncertainty due to the resolution of the balance and the small mass additions.

The uncertainty for the certification incorporated uncertainties from preparation, instrument repeatability, and reproducibility (incorporating stability). The combined uncertainty was calculated by combining the different uncertainty components as the square root of the sum of squares. The expanded uncertainties were determined by multiplication of the standard uncertainty with a coverage factor equal to 2 (to give a 95% confidence interval).

	Preparation uncertainty	Analytical uncertainty (repeatability)	Reproducibility and stability	Combined standard uncertainty	Standard uncertainty	Expanded uncertainty
	(% relative)	(% relative)	(% relative)	(% relative)	cmol/mol	cmol/mol
Ethane	0.62	0.42	0.21	0.78	0.014	0.028
Propane	0.02	0.18	0.02	0.18	0.128	0.257
Propylene	0.10	0.25	0.10	0.29	0.025	0.051
iso-Butane	0.16	0.41	0.09	0.45	0.017	0.034
n-Butane	0.06	0.36	0.10	0.37	0.038	0.075
But-1-ene	0.21	0.74	0.14	0.78	0.024	0.049
iso-Pentane	0.75	0.86	0.26	1.17	0.011	0.022

Final results and expanded uncertainties.

Component	Result cmol/mol	Expanded uncertainty cmol/mol
Ethane	1.814	0.028
Propane	71.531	0.257
Propene	8.676	0.051
iso-butane	3.791	0.034
n-butane	10.057	0.075
But-1-ene	3.116	0.049
iso-pentane	1.015	0.022

Purity Tables:

Ethane

C2H6_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Nitrogen	N2	2402	240	µmol/mol	Normal	NMI analysis
Oxygen	O2	53	5	µmol/mol	Normal	NMI analysis
Ethane	C2H6	0.9975	0.0002	µmol/mol	Normal	Nominally pure component
Propane	C3H8	0.8	0.4	mol/mol	Normal	NMI analysis

Propane

C3H8_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Argon	Ar	219	44	µmol/mol	Normal	NMI analysis
Nitrogen	N2	948	190	µmol/mol	Normal	NMI analysis
Ethane	C2H6	38	8	µmol/mol	Normal	NMI analysis
Propane	C3H8	0.9988	0.0002	mol/mol	Normal	Nominally pure component

Propylene

C3H6_11A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Nitrogen	N2	4119	419	µmol/mol	Normal	NMI analysis
Propane	C3H8	58	12	µmol/mol	Normal	NMI analysis
Propylene	C3H6	0.9958	0.0004	mol/mol	Normal	Nominally pure component

iso-Butane

isoC4H10_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Argon	Ar	58	12	µmol/mol	Normal	NMI analysis
Nitrogen	N2	2184	437	µmol/mol	Normal	NMI analysis
Propane	C3H8	0.8	0.2	µmol/mol	Normal	NMI analysis
n-Butane	C4H10	91	18	µmol/mol	Normal	NMI analysis
iso-Butane	C4H10	0.9976	0.0004	mol/mol	Normal	Nominally pure component
iso-Pentane	C5H12	42	8	µmol/mol	Normal	NMI analysis

n-Butane

C4H10_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Argon	Ar	359	72	µmol/mol	Normal	NMI analysis
Nitrogen	N2	1246	249	µmol/mol	Normal	NMI analysis
Propane	C3H8	4	1	µmol/mol	Normal	NMI analysis
n-Butane	C4H10	0.9983	0.0003	mol/mol	Normal	Nominally pure component
iso-Butane	C4H10	33	7	µmol/mol	Normal	NMI analysis

n-Pentane	C5H12	13	3	µmol/mol	Normal	NMI analysis
iso-Pentane	C5H12	4	1	µmol/mol	Normal	NMI analysis

1-Butene

C4H8_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Nitrogen	N2	626	125	µmol/mol	Normal	NMI analysis
Oxygen	O2	18	4	µmol/mol	Normal	NMI analysis
Propane	C3H8	1	0	µmol/mol	Normal	NMI analysis
n-Pentane	C5H12	47	9	µmol/mol	Normal	NMI analysis
iso-Pentane	C5H12	19	4	µmol/mol	Normal	NMI analysis
But-1-ene	C4H8	0.9993	0.0001	mol/mol	Normal	Nominally pure component

Iso-Pentane

Iso-C5H12_14A		Concentration	U(Concentration)	Composition Range	Uncertainty Type	Justification of Value
Nitrogen	N2	694	134	µmol/mol	Normal	NMI analysis
n-Butane	C4H10	384	77	µmol/mol	Normal	NMI analysis
n-Pentane	C5H12	3475	95	µmol/mol	Normal	NMI analysis
iso-Pentane	C5H12	0.9954	0.0007	mol/mol	Normal	Nominally pure component

Report form for CCQM-K119 (LPG)
Laboratory name: VSL Dutch Metrology Institute

Authors: Ewelina T. Zalewska, Adriaan M.H. van der Veen

Cylinder number: NP8956

Results

Measurement 1

Component	Date	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	number of replicates
Ethane	2015-09-01	2.1255	0.0081	3
Propane	2015-09-01	71.82	0.79	3
Propene	2015-09-01	8.681	0.068	3
iso-butane	2015-09-01	4.036	0.053	3
n-butane	2015-09-01	10.174	0.078	3
But-1-ene	2015-09-01	3.054	0.052	3
iso-pentane	2015-09-01	0.963	0.012	3

Measurement 2

Component	Date	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	number of replicates
Ethane	2015-09-07	2.1128	0.0072	3
Propane	2015-09-07	71.07	0.40	3
Propene	2015-09-07	8.745	0.097	3
iso-butane	2015-09-07	4.015	0.032	3
n-butane	2015-09-07	10.142	0.196	3
But-1-ene	2015-09-07	3.101	0.040	3
iso-pentane	2015-09-07	0.959	0.013	3

Measurement 3

Component	Date	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	number of replicates
Ethane	2015-09-07	2.112	0.014	3
Propane	2015-09-07	71.28	0.84	3
Propene	2015-09-07	8.756	0.090	3
iso-butane	2015-09-07	4.017	0.042	3
n-butane	2015-09-07	10.221	0.077	3
But-1-ene	2015-09-07	3.065	0.032	3
iso-pentane	2015-09-07	0.964	0.020	3

Results

Component	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	number of replicates
Ethane	2.117	0.020	3
Propane	71.39	1.30	3
Propene	8.73	0.16	3
iso-butane	4.023	0.076	3
n-butane	10.18	0.23	3
But-1-ene	3.073	0.078	3
iso-pentane	0.962	0.026	3

Calibration standards

All Primary Standard Mixtures (PSMs) for the measurements of liquid petroleum gas are compressed liquid mixtures prepared in 1 L constant pressure cylinders. The preparation was performed in accordance with ISO 6142-1 [1].

Purity data of the parent liquids/gases

All raw materials have been checked for impurities in accordance with ISO 19229 [2]. The results of the purity analysis have been summarised in the tables in this section. In most cases, the liquid phase was sampled for the purity analysis.

Table 1. Purity table of Ethane

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Ethane	0.999970	0.000020
Propane	0.0000100	0.0000050
iso-butane	0.000020	0.000010

Table 2. Purity table of Propane

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Ethane	0.00000239	0.00000024
Propene	0.00001440	0.00000144
Propane	0.9998667	0.0000085
But-1-ene	0.00000765	0.00000077
n-butane	0.0000229	0.0000023
iso-butane	0.0000802	0.0000080
iso-pentane	0.00000580	0.00000058

Table 3. Purity table of Propene

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Ethene	0.0000355	0.0000036
Ethane	0.00000690	0.00000069
Propene	0.99578	0.00042
Propane	0.00418	0.00042

Table 4. Purity table of *iso*-butane

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Ethane	0.00000245	0.00000025
Propene	0.00000419	0.00000042
Propane	0.00000855	0.00000086
But-1-ene	0.00000965	0.00000097
iso-butene	0.000153	0.000015
n-butane	0.000481	0.000048
iso-butane	0.999332	0.000050
iso-pentane	0.00000919	0.00000092

Table 5. Purity table of *n*-Butane

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Propene	0.0000171	0.0000017
Propane	0.0000148	0.0000015
1,3-butadiene	0.0000224	0.0000022
But-1-ene	0.0000274	0.0000027
iso-butene	0.0000109	0.0000011
n-butane	0.999412	0.000047
iso-butane	0.000468	0.000047
n-pentane	0.00000403	0.00000040
iso-pentane	0.00001390	0.00000139
cis-2-butene	0.00000323	0.00000032
trans-2-butene	0.00000646	0.00000065

Table 6. Purity table of But-1-ene

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
But-1-ene	0.997914	0.000002
iso-butene	0.00081	0.00008
n-butane	0.00091	0.00009
trans-2-butene	0.00037	0.00003

Table 7. Purity table of *iso*-pentane

Component	Amount of fraction (mol/mol)	Uncertainty (mol/mol)
Ethane	0.00000740	0.00000074
Propene	0.0000582	0.0000058
Propane	0.000208	0.000021
iso-butene	0.000129	0.000013
n-pentane	0.00271	0.00027
iso-pentane	0.99687	0.00027
neo-pentane	0.000018	0.000002

Verification measures

The calibration curves for the one the measurements (second) are given in tables 8 through 14.

Table 8. Calibration curve second measurement Ethane

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	1.990224	0.000363	10301.15	36.53	-0.08	1.69
VSL328191	2.079734	0.000374	10818.18	15.6	0.12	-0.98
VSL230871	2.332578	0.000401	12041.54	12.33	-0.03	0.2

Table 9. Calibration curve second measurement Propane

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	72.69207	0.006943	45358.43	118	-0.01	0.28
VSL328191	70.92723	0.007434	44719.76	60.92	0.01	-0.28
VSL230871	68.98176	0.007598	43942.48	15.09	-0.01	0.03

Table 10. Calibration curve second measurement Propene

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	8.262334	0.003608	7284.281	47.04	-0.01	0.28
VSL328191	9.02115	0.003862	7792.968	21.77	0.05	-0.41
VSL230871	9.373106	0.00397	8008.837	7.76	-0.03	0.1

Table 11. Calibration curve second measurement *iso*-butane

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	3.751566	0.000965	5583.345	14.15	-0.04	0.62
VSL328191	3.919975	0.000979	5781.369	19.16	0.06	-1.13
VSL230871	4.395363	0.001003	6226.519	19.94	-0.02	0.31

Table 12. Calibration curve second measurement *n*-butane

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	9.486644	0.001305	10178.44	44.44	-0.0008	0.05
VSL328191	10.06309	0.001342	10569.57	29.18	0.0022	-0.08
VSL230871	10.44363	0.001362	10819.84	38.59	-0.0015	0.07

Table 13. Calibration curve second measurement But-1-ene

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	2.862832	0.000485	4940.85	13.61	-0.03	0.71
VSL328191	2.991567	0.000498	5106.281	11.48	0.04	-0.81
VSL230871	3.355207	0.00053	5506.985	14.36	-0.01	0.26

Table 14. Calibration curve second measurement *iso*-pentane

Mixture	*x* cmol mol^{-1}	*u*(*x*) cmol mol^{-1}	*y* a.u.	u(*y*) a.u.	Δ*x*/*u*(*x*)	Δ*y*/*u*(*y*)
VSL135869	0.948173	0.000268	2516.178	11.55	-0.03	0.74
VSL328191	0.990794	0.000278	2607.02	5.59	0.04	-0.48
VSL230871	1.111192	0.000305	2825.863	11.86	-0.01	0.27

Instrumentation

The verification is carried out using an Agilent 6890N gas chromatograph equipped with a flame ionisation detector (GC/FID). The GC/FID is equipped with a liquid sampling valve (LSV) with a volume of 0.2 µL. The injection part of the GC is pressurised using helium up to a pressure of 35 bar. The vapour pressure of the mixtures to be analysed should be well below this pressure, because otherwise bubbles can be formed, leading to unrepresentative sampling. The splitter is set at a ratio 1:6. The carrier gas is helium. The GC is equipped with a stream selector and multi position valve. The column used is an aluplot, J&W Scientific 19095P-825, 50 m length, wide bore, 0.53 mm diameter, 15.0 µm film thickness.

Procedure

The piston cylinders where pressurized with helium up to 35 bar. Each measurement consisted of five injections of PSM's and three injections of the comparison mixture. It was needed to reduce the amount of injections up to three per measurement due to low amount of the liquid and high consumption of the flushing system of the measurement facility.

Uncertainty evaluation

The calibration curves where obtained in accordance with ISO 6143 [3]. As indicated, a straight line was used. The value for amount of fraction (results) is obtained by reverse use of the calibration curve [4]. The associated uncertainty is obtained using the law of propagation of uncertainty.

To arrive at the final result, the results of the three measurements were averaged. The standard error of the mean was combined with the pooled uncertainty from evaluating the data. The expanded uncertainty was obtained by multiplying the standard uncertainty with a coverage factor of $k = 2$.

References

[1] International Organization for Standardization, "ISO 6142-1 Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures", 3rd edition, ISO, Geneva, 2015

[2] International Organization for Standardization, "ISO 19229 Gas analysis -- Purity analysis and the treatment of purity data", ISO, Geneva, 2015

[3] International Organization for Standardization, "ISO 6143 – Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures", 2nd edition, ISO, Geneva, 2001

[4] Van der Veen A.M.H., "Generalised distance regression in gas analysis", Report S-CH.10.28, VSL, Delft, the Netherlands, June 2010

CCQM-K119 Liquefied Petroleum Gas (LPG)

• Laboratory name: KRISS

• Authors: Yong Doo Kim, Hyun Kil Bae, Jin Chun Woo, Namgoo Kang* (correspondence)
• Cylinder number: NPL CPC38955

Measurement Results of NPL Sample Cylinder (CPC38955)

Component	Result (cmol mol^{-1})	Relative expanded uncertainty (%)	Coverage factor	Number of replicates
Ethane	**2.0178**	**1.06**	2	5
Propane	**70.5753**	**0.82**	2	5
Propene	**8.7193**	**0.80**	2	5
***iso*-butane**	**4.1535**	**0.72**	2	5
***n*-butane**	**10.1641**	**0.90**	2	5
But-1-ene	**3.1038**	**0.76**	2	5
***iso*-pentane**	**1.0303**	**1.70**	2	5

1. Calibration standards

1.1. Type of standard used

KRISS prepared several primary standard mixtures (PSMs) with regard to the nominal mole fractions for liquefied petroleum gas (LPG) presented in the final protocol of CCQM-K119. A KRISS PSM was used as the calibration standard (BCPC001) prepared as of April 10, 2015. The gravimetric mole fractions of the LPG components in the KRISS calibration standard (BCPC001) are presented where hydrocarbon impurities originated from the pure gas/liquid cylinders were taken into account.

Component	Mole fraction (cmol mol^{-1})
Methane (impurity)	*0.000081*
Ethane	**2.160455**
Ethene (impurity)	*0.000076*
Ethyne (impurity)	*0.018310*
Propane	**69.737576**
Propene	**9.651142**
***iso*-butane**	**4.428542**
***n*-butane**	**9.720572**
But-1-ene	**3.444854**
C_4H_8 (impurities)	*0.013461*
***iso*-pentane**	**0.823054**
n-pentane (impurity)	*0.001690*
Total	99.999813

1.2. Cylinder type

A total of 6 KRISS PSMs were prepared from January 8, 2015 to June 19, 2015. Three 2 KRISS PSMs (BCPC001, BCPC002, and BCPC003) were prepared in specialty (leak-free) constant pressure cylinders with a total internal volume of 700 mL. These cylinders are designed and patented by KRISS. These CPCs were designed by KRISS to eliminate potential gas leak between LPG mixtures and pressurizing gas. The other three KRISS PSMs (CPC001, CPC002, and CPC003) were prepared in commercially available constant pressure sample cylinders (Welker® CP2-1000GMAP) with a total internal volume of 1,000 mL.

1.3. Method of preparation

Before gravimetric preparation, leak tests were conducted for all KRISS CPCs used for this comparison. KRISS prepared all PSMs for the LPG components using a gravimetric technique based on the KRISS Standard Procedures (R-112-001-2012). The KRISS BCPCs and CPCs were cleaned 5 times by flushing with nitrogen and helium, respectively. During flushing, all cylinders were evacuated to 10^{-3} torr using a rotary pump and then further down to 10^{-7} torr using a turbo-molecular pump. Before preparation, purity analyses (both gas and liquid phases) were conducted for all components. The addition of each component of the LPG mixtures was conducted using the pressure difference between the cylinder containing the pure component and the receiving cylinder. The LPG components were filled in the order of increasing vapour pressure (*iso*-pentane, *n*-butane, 1-butene, *iso*-butane, propene, propane, and ethane). A direct filling method was used using a customized gas filling and liquid transfer device designed by KRISS to minimize potential liquid loss and gas leak during operation. The pure gas cylinders of *n*-butane, 1- butene, *iso*-butane, propane were heated during filling whereas the pure gas cylinders of *iso*-pentane, propene, and ethane were not. The liquid phase of *iso*-pentane from the pure *iso*-pentane cylinder was injected into the receiving cylinder using a glass syringe (8.2 mL for BCPC001).

1.4. Weighing data

The gravimetrically determined masses of the LPG components of the KRISS calibration standard (BCPC001) are presented as follows:

Component	Mass (g)
Ethane	**4.6151**
Propane	**218.4982**
Propene	**28.8591**
***iso*-butane**	**18.2943**
***n*-butane**	**40.1949**
But-1-ene	**13.7776**
***iso*-pentane**	**4.2263**
Total	328.4655

1.5. Purity data of the parent gases

The impurities in the high-purity gas/liquid cylinders used for the preparation of all KRISS PSMs were analytically determined using GC-FID. Impurities and the uncertainties due to impurities were incorporated into gravimetric composition of the KRISS PSMs and the

uncertainties of the gravimetric mole fractions of the LPG components in all KRISS PSMs. Gas phase analysis was applied to high-purity ethane cylinder. Liquid-phase analysis was applied to high-purity iso-pentane cylinder. Propane, propene, iso-butane, n-butane, but-1-ene were analyzed for both gas- and liquid-phases.

Component	Purity (μmol mol^{-1})
Ethane	**999,992**
Propane	**999,994**
Propene	**999,931**
***iso*-butane**	**999,697**
***n*-butane**	**998,631**
But-1-ene	**993,879**
***iso*-pentane**	**996,660**
Helium	**999,996**

1.6. Verification measures

Verification was conducted using internal consistency among all KRISS PSMs. The verification results were incorporated into the uncertainty evaluation. Gravimetric results of the KRISS PSMs were compared by GC analysis. The uncertainty of gravimetric preparation was included in the uncertainty budget. Experimental results indicate that unstable effects were not observed within 3 months for KRISS BCPCs. However, changes in mole fractions due probably to potential leak were observed for ethane and due to inconsistent sampling for iso-butane within 6 months for KRISS CPCs. Potential uncertainty due to these effects were not explicitly included to the uncertainty budget.

2. Instrumentation

Determination of mole fractions of LPG components was conducted using a GC-FID (Agilent 6890N). The chromatographic column used was HP-AL/KCL capillary with dimension of 50 m (length) x 320 μm (inner diameter) x 5.00 μm (thickness). The sample valve temperature was 100 oC. The column temperature was 110 ^{o}C. The total time for a single analysis took 15 min. The nominal volume of the sample loop was 100 μL. The carrier gas was pure N_2 with a flow rate of 1.5 mL min^{-1}. The split mode was used at 70:1. The FID temperature was 250 ^{o}C. The retention time of ethane that appeared on the chromatogram first of major components of the LPG mixtures was approximately 4.8 min.

3. Procedure

3.1.Sampling method

Before analysis, the NPL CPC38955 and all KRISS cylinders used for this comparison were rotated over 40 times for complete mixing. The pressure of helium to overpressurize the piston of the test cylinder (NPL CPC38955) was maintained over 10.3 bar by refilling helium once during analysis at KRISS and one more time just after analysis. The LPG mixtures in NPL CPC38955 and the KRISS calibration cylinder (BCPC001) were alternately connected to the GC-FID system through a 1/8-inch and 1/16-inch stainless steel sample loop (a total length of lines estimated about 2 m). Sample gas flow was maintained about 20 mL min-1 which was monitored using a bubble meter.

3.2.Calibration and value assignment method

Comparison measurements of the NPL sample cylinder (CPC38955) and the KRISS calibration cylinder (BCPC001) were conducted at the KRISS laboratory during 5 days (number of replicates) from June 30 through July 7, 2015. GC responses were obtained in triplicates on each measurement day. The overall procedures for calibration and value assignment are based on the KRISS Standard Procedure (R-112-004-2012). KRISS used a one-point calibration (direct comparison) method for the determination of the mole fractions (x) of the LPG components in the NPL sample cylinder (CPC38955). The responses were recorded as peak area and the average peak area of the repeated measurements was use for calculation of amount of mole fractions. The calibration cylinder of KRISS was BCP001. KRISS adopted a bracketing method (Test cylinder- Calibration cylinder-Test cylinder-Calibration cylinder) for value assignment. Results were obtained by direct comparison of GC-FID responses between the KRISS calibration cylinder (BCPC001) and the NPL sample cylinder (CPC38955) where drift compensation was taken into account. Most standard deviations for response peak areas for each day measurement were was less than 0.20 % except iso-pentane (less than 0.34%). During 5- day measurements, standard deviation (data reproducibility) of mole fraction of all LPG components in the NPL sample cylinder (CPC38955) was less than 0.10 % except isopentane (less than 0.22%). Consistency in gravimetric preparation and sampling of the KRISS calibration cylinder (BCPC001) and the other five KRISS PSMs (BCPC002, BCPC003, CPC001, CPC002, and CPC003) was verified by comparison of response factors from GC analysis. The uncertainty due to the factor of consistency in preparation (including gas/liquid filling) was quantified and incorporated into the uncertainty budget.

4. Uncertainty evaluation

1) Model equation

A model equation of the measurand (xKRISS) was used for the one-point calibration method:

$$x_{KRISS} = (A_{sample} / A_{cal}) \cdot x_{cal} \cdot f_{consistency}$$

where

x_{KRISS} : the mole fraction of each LPG component in the NPL sample cylinder (CPC38955) determined by KRISS

(A_{sample} /A_{cal}) : the ratio of response areas from GC-FID for each LPG component in between the NPL sample cylinder (CPC38955) and the KRISS calibration cylinder (BCPC001) based on the one-point calibration method

x_{cal} : the gravimetric mole fraction of each LPG component in the KRISS calibration cylinder (BCPC001)

$f_{consistency}$: the factor of error deviating from perfect consistency in preparation among the KRISS PSMs for where the factor is assumed 1.

2) Combined standard uncertainty

$$\left(\frac{u(x_{KRISS})}{x_{KRISS}}\right)^2 = \left(\frac{u(A_{sample}/A_{cal})}{A_{sample}/A_{cal}}\right)^2 + \left(\frac{u(x_{cal})}{x_{cal}}\right)^2 + +\left(\frac{u(f_{consistency})}{f_{consistency}}\right)^2$$

3) Uncertainty budget

KRISS used the GUM Workbench Pro (Version 2.3.6.141, Metrodata Gmbh) for uncertainty analysis. The uncertainty budgets for the LPG components were determined. The uncertainty budget for propane is just for example.

No.	Estimate		Uncertainty Analysis				
	Variable	Value	Uncertainty Source	Type	Assumed Distribution	Standard Uncertainty $u(x_i)$	Contribution to total variance(%)
1	A_{sample}/A_{cal}	1.0120	Analytical Reproducibility	A	t	0.001943	26
2	x_{cal}	69.7376 cmol mol^{-1}	Gravimetric preparation	B	Normal	0.3623	7
3	$f_{consistency}$	1	Consistency in preparation	B	Rectangular	0.003602	67
4	x_{KRISS}	70.5753 cmol mol^{-1}	Combined	-	Normal	0.2656	100

4) Measurand and expanded uncertainty for propane in the LPG mixtures

$x_{KRISS} \pm U_{KRISS}$ = (70.5753 ± 0.5821) cmol mol^{-1} (k = 2)

The uncertainties for all LPG components were calculated in the same manner. The same procedures were used to calculate uncertainty budgets of the other 6 components of the LPG mixtures.

References

KRISS Standard Procedures including but not limited to:

1) R-112-001-2012 Preparation and certification procedure of primary reference gas mixtures by gravimetric method, 2nd revision. (in Korean)

2) R-112-004-2012 Procedure for determining the composition of gas mixtures by comparison analysis, 1st revision. (in Korean)