

**EURAMET.QM-S6 / 1195:  
Bilateral comparison of liquefied hydrocarbon mixtures in  
constant pressure (piston) cylinders**

**FINAL REPORT**

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Approved on behalf of NPLML by  
Dr Michael Adeogun, Head of Analytical Science Division.

# EURAMET 1195: Bilateral comparison of liquefied hydrocarbon mixtures in constant pressure (piston) cylinders

## EXECUTIVE SUMMARY

Traceable liquid hydrocarbon mixtures are required in order to underpin measurements of the composition and other physical properties of LPG (liquefied petroleum gas) and LNG (liquefied natural gas), thus meeting the needs of an increasingly large European industrial market.

The development of traceable liquid hydrocarbon standards by National Measurement Institutes (NMIs) was still at a relatively early stage at the time this comparison was proposed in 2011. NPL and VSL, who were the only NMIs active in this area, had developed methods for the preparation and analysis of such standards in constant pressure (piston) cylinders, but neither laboratory had Calibration and Measurement Capabilities (CMCs) for these mixtures.

This report presents the results of EURAMET 1195, the first comparison of liquid hydrocarbon mixtures between NMIs, which assessed the preparation and analytical capabilities of NPL & VSL for these mixtures. The comparison operated between August 2011 and January 2012. Each laboratory prepared a liquid hydrocarbon standard with nominally the same composition and these standards were exchanged for analysis.

The results of the comparison show a good agreement between the laboratories' results and the comparison reference values for the six components with amount fractions greater than 1.0 cmol/mol (propane, propene, *iso*-butene, *n*-butane, *iso*-butane and 1-butene). Measurement of the three components with lower amount fractions (1,3-butadiene, *iso*-pentane and *n*-pentane) proved more challenging. In all but one case, the differences from the comparison reference values for these three components were greater than the expanded measurement uncertainty.



**TABLE OF CONTENTS****EXECUTIVE SUMMARY****TABLE OF CONTENTS**

<b>1. INTRODUCTION</b>	<b>1</b>
<b>2. OPERATION OF THE COMPARISON</b>	<b>1</b>
2.1. PARTICIPANTS	1
2.2. MEASUREMENT STANDARDS	1
2.3. PREPARATION OF STANDARDS	2
2.4. EXCHANGE OF STANDARDS	3
<b>3. RESULTS</b>	<b>3</b>
3.1. SUMMARY OF RESULTS	4
3.2. COMPARISON REFERENCE VALUE	4
<b>4. DISCUSSION AND CONCLUSIONS</b>	<b>6</b>
4.1. SUMMARY OF RESULTS	6
4.2. SUPPORTED CMC CLAIMS	6
<b>5. REFERENCES</b>	<b>6</b>
<b>APPENDICES</b>	<b>7</b>
APPENDIX A1 - VSL MEASUREMENT REPORT	7
APPENDIX A2 - NPL MEASUREMENT REPORT	11





## 1. INTRODUCTION

Traceable liquid hydrocarbon mixtures are required in order to underpin measurements of the composition and other physical properties of LPG (liquefied petroleum gas) and LNG (liquefied natural gas), thus meeting the needs of an increasingly large European industrial market.

The development of traceable liquid hydrocarbon standards by National Measurement Institutes (NMIs) was still at a relatively early stage at the time this comparison was proposed in 2011. NPL and VSL, who were the only NMIs active in this area, had developed methods for the preparation and analysis of such standards in constant pressure (piston) cylinders, but neither laboratory had Calibration and Measurement Capabilities (CMCs) for these mixtures.

This report presents the results of EURAMET 1195, the first comparison of liquid hydrocarbon mixtures between NMIs, which assessed the preparation and analytical capabilities of NPL & VSL for these mixtures. The comparison operated between August 2011 and January 2012. Each laboratory prepared a liquid hydrocarbon mixture with nominally the same composition and these standards were exchanged for analysis. A comparison between the results obtained by the two laboratories is presented, and the full measurement report of each participant is given at the end of this report.

## 2. OPERATION OF THE COMPARISON

### 2.1. PARTICIPANTS

The two participating laboratories were:

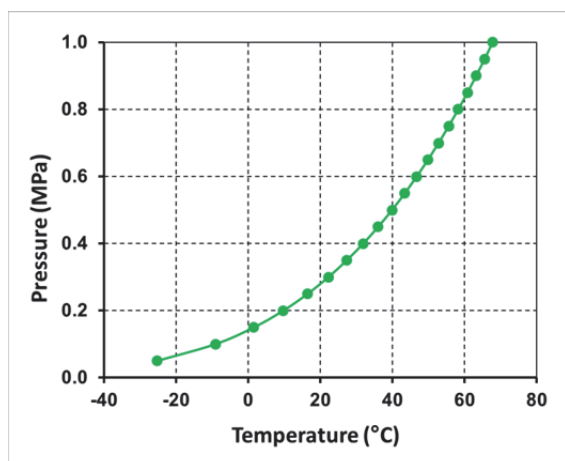
- NPL – United Kingdom (co-ordinating laboratory)
- VSL – The Netherlands

### 2.2. MEASUREMENT STANDARDS

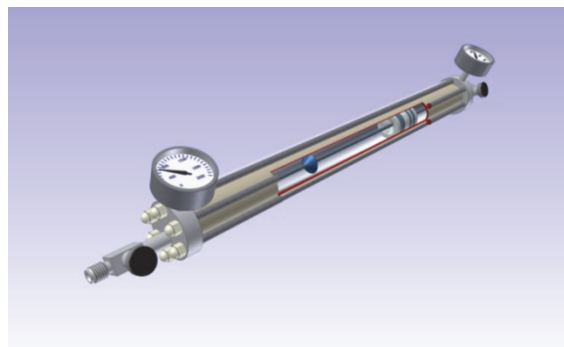
The nominal composition of the liquid hydrocarbon mixtures for the comparison, which was agreed by both participating laboratories, is shown in Table 1. (The hydrocarbon dew point curve of this mixture is shown in Figure 1.) The mixtures were prepared in constant pressure (piston) cylinders (see Figure 2). NPL used Welker constant pressure cylinders with a total internal volume of 500 mL; VSL used Welker constant pressure cylinders with a total internal volume of 1 L

Component	Amount fraction (cmol/mol)
Propane	2.0
Propene	2.0
<i>iso</i> -butane	70.8
<i>n</i> -butane	8.0
<i>iso</i> -butene	7.0
1-butene	8.0
1,3-butadiene	0.8
<i>iso</i> -pentane	0.8
<i>n</i> -pentane	0.6

**Table 1.** Nominal composition of the liquid hydrocarbon mixtures.



**Figure 1.** Hydrocarbon dew point curve of the mixture shown in Table 1



**Figure 2.** Schematic image of the constant pressure cylinders used in this comparison.

## 2.3. PREPARATION OF STANDARDS

Each participating laboratory prepared and validated one mixture with the composition shown in Table 1. Preparation of the mixtures was performed in general accordance with ISO 6142 [1], although it should be noted that because the purity data used refers to the liquid components transferred into the constant pressure cylinder, the calculated composition is only valid if the mixture remains in a single (liquid) phase.

### 2.3.1. Summary of VSL preparation method

Prior to preparing the mixture, the constant pressure cylinder was cleaned by flushing with helium, which was injected into the cylinder. During the flushing procedure, the cylinders were evacuated using a membrane pump down to a pressure of 2-3 mbar. For new cylinders, the procedure was repeated three times, for cylinders containing residual gas, the procedure was repeated five times.

In order to remove the residual gas from tubing, the system was flushed four times with each component and evacuated until the pressure reached 2-3 mbar.

The addition of each component was carried out using the pressure difference between the cylinder containing the component and the constant pressure cylinder. Whenever possible, the natural pressure difference due to the vapour pressure was used. If the pressure difference due to the vapour pressure was not large enough, the cylinder was heated. If the liquid phase of the component needed to be transferred, the cylinder was turned upside-down so that the liquid was withdrawn.

The major component (*iso*-butane) was filled from a constant pressure cylinder in order to maintain the appropriate pressure difference between the cylinders. In order to have only the liquid phase present in the mixture, the piston cylinder was pressurised with helium to between 2.7 and 4.1 MPa, which, as can be seen from Figure 1, is significantly in excess of the vapour pressure of the mixture. After completion of the filling process, the liquid mixture was homogenised for 15 minutes.

### 2.3.2. Summary of NPL preparation method

Before preparation of the mixture commenced, the constant pressure cylinder was first evacuated, then flushed with helium, then re-evacuated. Each of the components was added in turn, in order of increasing vapour pressure. All components were purity analysed before use.

A stainless steel vessel was used to add each minor component in turn. The component was added to the vessel and then transferred into the constant pressure cylinder. The vessel was weighed accurately (against a tare vessel) before and after transferring the component to the constant pressure cylinder, thus determining the mass of the component added.

For the major component (*iso*-butane), a direct filling method was used. The *iso*-butane cylinder was inverted and connected to the constant pressure cylinder *via* a series of valves connected to an evacuation system. The connecting pipework was fully evacuated and the *iso*-butane was transferred directly into the constant pressure cylinder whilst the *iso*-butane cylinder was gently heated in order to maintain a sufficiently high vapour pressure. The mass of *iso*-butane added was determined by accurate weighing of the constant pressure cylinder (against a tare constant pressure cylinder) before and after filling.

Following completion of the filling process, the constant pressure cylinder was pressurised with approximately 1.5 MPa of helium. The mixture was then homogenised by repeated rotation of the constant pressure cylinder, thus causing the internal mixing block to pass through the liquid mixture.

### 2.4. EXCHANGE OF STANDARDS

The participants then exchanged mixtures, which were transported with the cylinder piston pressurised by approximately 20 bar of helium. VSL measured the composition of the mixture prepared by NPL, and NPL measured the composition of the mixture prepared by VSL. Analysis was performed using in-house standards. Finally, the cylinders were retuned back to their original laboratories, and the analytical results exchanged. Full details of the analytical method used by each laboratory are given in the Annex, but a summary is given in Table 2.

Laboratory	Analytical method	No. of calibration standards	Calibration method
NPL	GC-FID	1	Direct comparison
VSL	GC-FID	4	ISO 6143 [2], straight line fit

**Table 2.** Summary of analytical methods used in this comparison.

It should be noted that the composition of liquid hydrocarbon mixtures in constant pressure (piston) cylinder 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. However, in this comparison, re-analysis of the mixtures when returned to their original laboratories revealed only a negligible change in composition over the short timescale involved.

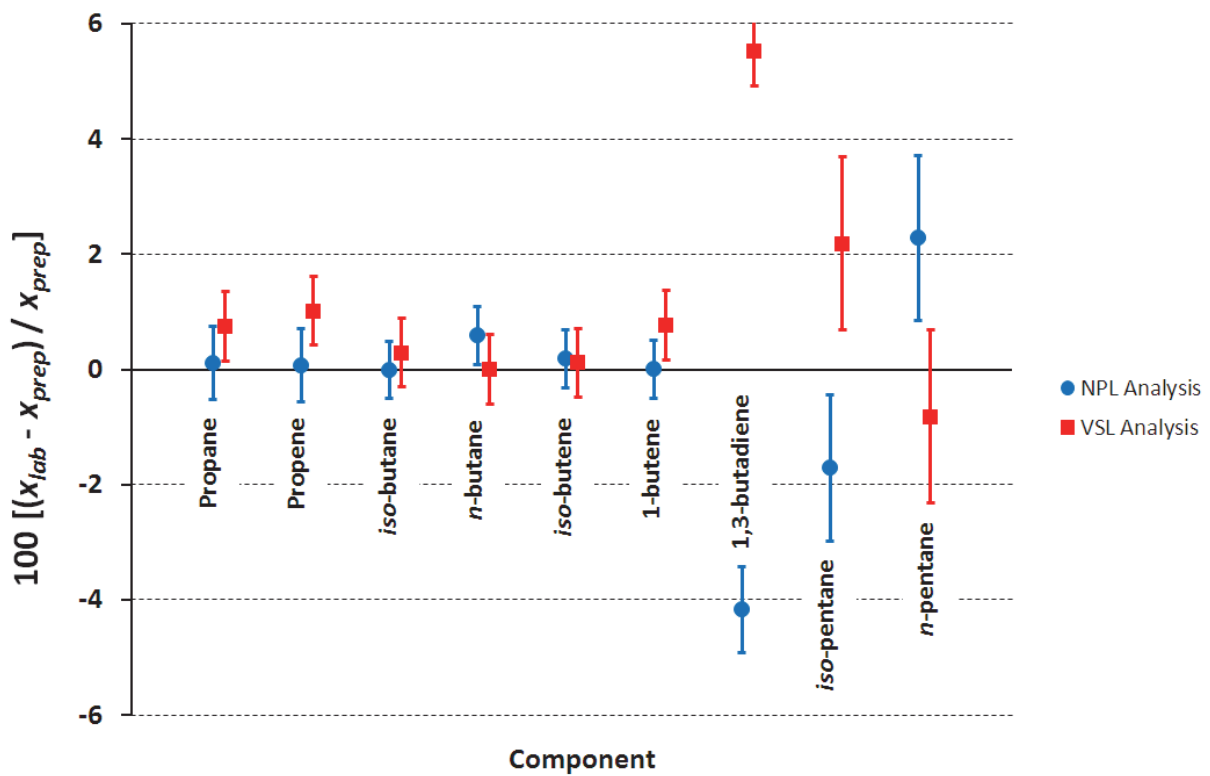
### 3. RESULTS

#### 3.1. SUMMARY OF RESULTS

The results of the comparison are summarised in Table 3 and shown graphically in Figure 3.

#### 3.2. COMPARISON REFERENCE VALUE

The results presented and discussed in this section use the values of  $x_{prep}$  (the assigned gravimetric amount fraction of component  $i$ ) as the comparison reference value.



**Figure 3.** Plot of the results from the comparison with the **NPL measurements of the VSL mixture in blue** and the **VSL measurements of the NPL mixture in red**. The data points represent the values of  $100 [(x_{lab} - x_{prep}) / x_{prep}]$  in Table 4, and the errors bars are equal to  $100 [U_{comb} / x_{prep}]$ .

Component	Cylinder number	Analysis performed by	$x_{prep}$ (cmol/mol)	$U(x_{prep})$ (cmol/mol)	$x_{lab}$ (cmol/mol)	$U(x_{lab})$ (cmol/mol)	$100 \times \frac{[(x_{lab} - x_{prep})/x_{prep}]^2}{U_{comb}/x_{prep}}$	$100 \times \frac{U_{comb}}{x_{prep}}$
Propane	VSL 230637	NPL	1.9486	0.0040	1.951	0.012	0.11	0.64
	NPL 32149	VSL	2.0389	0.0011	2.0541	0.0123	0.74	0.60
Propene	VSL 230637	NPL	1.9507	0.0039	1.952	0.012	0.07	0.64
	NPL 32149	VSL	1.9676	0.0003	1.9876	0.0119	1.02	0.60
<i>iso</i> -butane	VSL 230637	NPL	70.967	0.009	70.956	0.354	-0.02	0.50
	NPL 32149	VSL	71.7212	0.0036	71.9300	0.4316	0.29	0.60
<i>n</i> -butane	VSL 230637	NPL	7.7128	0.0032	7.758	0.039	0.59	0.50
	NPL 32149	VSL	7.5882	0.0020	7.5879	0.0455	0.00	0.60
<i>iso</i> -butene	VSL 230637	NPL	6.9466	0.0018	6.959	0.035	0.18	0.50
	NPL 32149	VSL	6.8382	0.0011	6.8458	0.0411	0.11	0.60
1-butene	VSL 230637	NPL	8.3168	0.0021	8.316	0.042	0.00	0.50
	NPL 32149	VSL	7.7499	0.0022	7.8095	0.0469	0.77	0.60
1,3-butadiene	VSL 230637	NPL	0.7767	0.0016	0.7443	0.0053	-4.17	0.74
	NPL 32149	VSL	0.7310	0.0007	0.7713	0.0046	5.52	0.61
<i>iso</i> -pentane	VSL 230637	NPL	0.771	0.009	0.7581	0.005	-1.71	1.26
	NPL 32149	VSL	0.7597	0.0007	0.7763	0.0116	2.18	1.50
<i>n</i> -pentane	VSL 230637	NPL	0.588	0.008	0.6012	0.0036	2.28	1.44
	NPL 32149	VSL	0.5877	0.0007	0.5829	0.0087	-0.82	1.50

**Table 3.** Summary of the results from the comparison.  $x_{prep}$  and  $U(x_{prep})$  are the assigned gravimetric amount fraction of the component in the liquid hydrocarbon mixture and its expanded uncertainty (as assigned by the laboratory that prepared the mixture),  $x_{lab}$  and  $U(x_{lab})$  are the measured amount fraction of component  $i$  and the assigned expanded uncertainty, and  $U_{comb}$  is the result of  $U(x_{prep})$  and  $U(x_{lab})$  combined in quadrature. All expanded uncertainties have been calculated using a coverage factor of  $k = 2$ . Note that the values of  $U(x_{prep})$  assigned by both VSL and NPL are the 'gravimetric' uncertainties calculated in accordance with ISO 6142:2001 [2] and do not include contributions for verification, stability, or any other factors.

## 4. DISCUSSION AND CONCLUSIONS

### 4.1. SUMMARY OF RESULTS

The results of the comparison, which are presented in Table 3 and Figure 3, show good agreement between the laboratories' results and the comparison reference values for the six components with amount fractions greater than 1.0 cmol/mol (propane, propene, *iso*-butene, *n*-butane, *iso*-butane and 1-butene).

Measurement of the other three components with lower amount fractions (1,3-butadiene, *iso*-pentane and *n*-pentane) proved more challenging, with the measured amount fractions differing from the comparison reference values by 4.2 and 5.5 % relative for 1,3-butadiene, and 0.8 to 2.3 % relative for *iso*-pentane and *n*-pentane. In all but one case, these differences were greater than the expanded measurement uncertainty. Of particular interest is the observation that for each of these three components, the amount fractions measured by the two laboratories were approximately equally 'high' and 'low' of the comparison reference values. This implies that for these components, one or both of the participating laboratories may have had a consistent bias in composition of the mixture sent to the other laboratory, and the in-house mixtures used for validation and analysis.

### 4.2. SUPPORTED CMC CLAIMS

It is proposed that this comparison can be used to support CMC claims for liquid hydrocarbon mixtures in constant pressure (piston) cylinders over the amount fraction ranges shown in Table 4.

Component	Amount fraction (cmol/mol)
Propane	0.5 to 5.0
Propene	0.5 to 5.0
<i>iso</i> -butane	67 to 96
<i>n</i> -butane	0.5 to 10
<i>iso</i> -butene	0.5 to 10
1-butene	0.5 to 10
1,3-butadiene	0.4 to 2.0
<i>iso</i> -pentane	0.4 to 2.0
<i>n</i> -pentane	0.3 to 2.0

**Table 4.** CMC ranges supported by this comparison.

## 5. REFERENCES

- [1] ISO 6142:2001, *Gas analysis - Preparation of calibration gas mixtures - Gravimetric method.*
- [2] ISO 6143:2001, *Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures.*

## APPENDICES

### APPENDIX A1 - VSL MEASUREMENT REPORT

Laboratory name: VSL

Cylinder number: NPL32149

**Nominal composition of the unknown mixture is within the range of Table A1.1**

**Table A1.1 Nominal ranges of amount of substance fractions**

Component	Amount of Substance Fraction $x$ (mol mol <sup>-1</sup> )
C <sub>3</sub> H <sub>8</sub>	0.020
C <sub>3</sub> H <sub>6</sub>	0.020
iso-C <sub>4</sub> H <sub>10</sub>	0.708
n-C <sub>4</sub> H <sub>10</sub>	0.080
iso-C <sub>4</sub> H <sub>8</sub>	0.070
1-C <sub>4</sub> H <sub>8</sub>	0.080
1,3-C <sub>4</sub> H <sub>6</sub>	0.008
iso-C <sub>5</sub> H <sub>12</sub>	0.008
n-C <sub>5</sub> H <sub>12</sub>	0.006

**Measurement Results of Cylinder NPL32149 as shown in Table A1.2**

**Table A1.2. Measurement Results of Cylinder NPL32149**

Component	Date (dd/mm/yy)	Result (mol/mol)	Expanded Uncertainty (%)	number of replicates
C <sub>3</sub> H <sub>8</sub>	14/11/2011	0.020541	0.6	5
C <sub>3</sub> H <sub>6</sub>	14/11/2011	0.019876	0.6	5
iso-C <sub>4</sub> H <sub>10</sub>	14/11/2011	0.719300	0.6	5
n-C <sub>4</sub> H <sub>10</sub>	14/11/2011	0.075879	0.6	5
iso-C <sub>4</sub> H <sub>8</sub>	14/11/2011	0.068458	0.6	5
1-C <sub>4</sub> H <sub>8</sub>	14/11/2011	0.078095	0.6	5
1,3-C <sub>4</sub> H <sub>6</sub>	14/11/2011	0.007713	0.6	5
iso-C <sub>5</sub> H <sub>12</sub>	14/11/2011	0.007763	1.5	5
n-C <sub>5</sub> H <sub>12</sub>	14/11/2011	0.005829	1.5	5

## Instrument

The verification is carried out using an Agilent 6890N gas chromatograph equipped with a flame ionisation detector (GC/FID). The injection part of the GC is pressurised using helium up to a pressure of 28 bar. The column used is an aluplot, J&W Scientific 19095P-825, 50 m length, 0.53 mm diameter, 15.0 µm film thickness.

## Calibration Standard

Composition ranges of VSL primary LPG standards as shown in Table A1.3.

**Table A1.3. Composition ranges of VSL primary LPG standards**

Component	Nominal of unknown mixture $x$ (mol mol <sup>-1</sup> )	VSL standards $x$ (mol mol <sup>-1</sup> )
C <sub>3</sub> H <sub>8</sub>	0.020	0.005 – 0.026
C <sub>3</sub> H <sub>6</sub>	0.020	0.005 – 0.026
iso-C <sub>4</sub> H <sub>10</sub>	0.708	0.670 – 0.957
n-C <sub>4</sub> H <sub>10</sub>	0.080	0.005 – 0.096
iso-C <sub>4</sub> H <sub>8</sub>	0.070	0.005 – 0.099
1-C <sub>4</sub> H <sub>8</sub>	0.080	0.005 – 0.103
1,3-C <sub>4</sub> H <sub>6</sub>	0.008	0.004 – 0.010
iso-C <sub>5</sub> H <sub>12</sub>	0.008	0.004 – 0.010
n-C <sub>5</sub> H <sub>12</sub>	0.006	0.003 – 0.008

The linear (straight line) calibration function was made using 4 PSM's divided over the range as shown in Table A1.3. The repeatability of the measurements is determined. In most cases, the repeatability standard deviation of 5 injections is about 0.1% - 0.35% relative. The calibration function was obtained as described in ISO 6143 and used for value assignment.

The repeatability of the measurement of NPL32149 is reported in Table A1.4.

**Table A1.4. Relative Standard Deviation of GC response values**

Component	R.S.D. (%) NPL32149
C <sub>3</sub> H <sub>8</sub>	0.19
C <sub>3</sub> H <sub>6</sub>	0.25
iso-C <sub>4</sub> H <sub>10</sub>	0.19
n-C <sub>4</sub> H <sub>10</sub>	0.18
iso-C <sub>4</sub> H <sub>8</sub>	0.18
1-C <sub>4</sub> H <sub>8</sub>	0.18
1,3-C <sub>4</sub> H <sub>6</sub>	0.22
iso-C <sub>5</sub> H <sub>12</sub>	0.19
n-C <sub>5</sub> H <sub>12</sub>	0.19



The data and regression results for the nine components are given in tables A1.5 –A1.13.

**Table A1.5. Calibration results of C<sub>3</sub>H<sub>8</sub>**

C <sub>3</sub> H <sub>8</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL230371	0.0050576	0.0000092	855.05	1.91	-0.0000077	-0.83	1.89	0.99
VSL129035	0.0101860	0.0000217	1780.58	6.28	0.0000515	2.38	-25.00	-3.98
VSL129248	0.0176700	0.0000362	3061.75	10.63	0.0000277	0.77	-13.83	-1.3
VSL230870	0.0255470	0.0000507	4372.00	8.55	-0.0001057	-2.08	17.34	2.03

**Table A1.6. Calibration results of C<sub>3</sub>H<sub>6</sub>**

C <sub>3</sub> H <sub>6</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL230371	0.0049433	0.0000073	849.36	0.57	-0.0000032	-0.43	0.11	0.20
VSL129035	0.0101780	0.0000213	1776.80	6.59	0.0000320	1.5	-17.75	-2.69
VSL129248	0.0176810	0.0000359	3065.05	10.36	0.0000252	0.7	-12.15	-1.17
VSL230870	0.0255800	0.0000505	4384.70	8.93	-0.0000770	-1.52	13.96	1.56

**Table A1.7. Calibration results of iso-C<sub>4</sub>H<sub>10</sub>**

iso-C <sub>4</sub> H <sub>10</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL129035	0.6700600	0.0000509	151969.00	542.23	-0.0000009	-0.02	519.15	0.96
VSL129248	0.7712300	0.0000918	174248.00	587.24	0.0000049	0.05	-985.12	-1.68
VSL230870	0.8300300	0.0001416	183144.00	3377.35	-0.0000008	-0.01	2191.27	0.65
VSL230371	0.9574300	0.0000892	211481.00	122.71	-0.0000015	-0.02	13.53	0.11

**Table A1.8. Calibration results of n-C<sub>4</sub>H<sub>10</sub>**

n-C <sub>4</sub> H <sub>10</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL230371	0.0053323	0.0000316	1228.74	1.47	0.0000172	0.54	-0.16	-0.11
VSL230870	0.0233180	0.0000295	5338.39	9.37	-0.0000204	-0.69	8.96	0.96
VSL129248	0.0533070	0.0000302	12262.80	43.23	0.0000031	0.10	-28.15	-0.65
VSL129035	0.0963880	0.0000316	22197.90	79.54	0.0000028	0.09	-77.05	-0.97

**Table A1.9. Calibration results of iso-C<sub>4</sub>H<sub>8</sub>**

iso-C <sub>4</sub> H <sub>8</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL230371	0.0049888	0.0000071	1143.01	8.59	0.0000001	0.01	-0.41	-0.05
VSL230870	0.0330140	0.0000127	7312.63	122.68	-0.0000003	-0.02	118.76	0.97
VSL129248	0.0625480	0.0000156	14059.10	50.07	0.0000000	0.00	-0.21	0.00
VSL129035	0.0987720	0.0000176	22202.30	79.80	0.0000002	0.01	-14.69	-0.18

**Table A1.10. Calibration results of 1-C<sub>4</sub>H<sub>8</sub>**

1-C <sub>4</sub> H <sub>8</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL230371	0.0050538	0.0000072	1143.65	8.56	0.0000004	0.06	-2.55	-0.30
VSL230870	0.0343690	0.0000133	7775.17	14.46	-0.0000020	-0.15	10.66	0.74
VSL129248	0.0580730	0.0000158	13178.20	95.33	0.0000001	0.01	-18.56	-0.19
VSL129035	0.1030300	0.0000193	23453.20	85.01	0.0000012	0.06	-102.28	-1.20

**Table A1.11. Calibration results of 1,3-C<sub>4</sub>H<sub>6</sub>**

1,3-C <sub>4</sub> H <sub>6</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL129035	0.0040527	0.0000087	886.48	1.90	0.0000015	0.17	-0.33	-0.17
VSL129248	0.0070403	0.0000147	1529.15	4.99	0.0000168	1.14	-9.20	-1.84
VSL230371	0.0080234	0.0000112	1717.18	1.74	-0.0000207	-1.85	2.37	1.36
VSL230870	0.0101850	0.0000206	2194.49	5.08	0.0000288	1.40	-8.27	-1.63

**Table A1.12. Calibration results of iso-C<sub>5</sub>H<sub>12</sub>**

iso-C <sub>5</sub> H <sub>12</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL129035	0.0040259	0.0000448	1142.97	4.02	-0.0000083	-0.18	0.24	0.06
VSL230371	0.0049056	0.0000613	1394.40	1.18	0.0000133	0.22	-0.02	-0.01
VSL129248	0.0069920	0.0000781	1976.20	6.34	0.0000134	0.17	-0.32	-0.05
VSL230870	0.0101140	0.0001135	2836.35	5.13	-0.0000206	-0.18	0.15	0.03

**Table A1.13. Calibration results of n-C<sub>5</sub>H<sub>12</sub>**

n-C <sub>5</sub> H <sub>12</sub>	<i>x</i> mol/mol	<i>u(x)</i> mol/mol	<i>y</i> (a.u.)	<i>u(y)</i> (a.u.)	$\Delta x$ mol/mol	$\Delta x/u(x)$	$\Delta y$ (a.u.)	$\Delta y/u(y)$
VSL129035	0.0030671	0.0000400	910.02	1.44	0.0000569	1.42	-0.25	-0.18
VSL230371	0.0041310	0.0000565	1155.35	1.06	-0.0001644	-2.91	0.20	0.19
VSL129248	0.0053280	0.0000697	1571.76	4.93	0.0000619	0.89	-1.06	-0.22
VSL230870	0.0077082	0.0001011	2256.46	4.22	0.0000320	0.32	-0.19	-0.05

### Uncertainty evaluation

The composition of cylinder NPL32149 was obtained by fitting the measured GC response value to the corresponding calibration straight line in accordance with ISO 6143. Detailed results see Table A1.2, with the assigned expanded uncertainty.

Used coverage factor: 2

## APPENDIX A2 - NPL MEASUREMENT REPORT

Cylinder number: VSL230637

Measurements made at NPL during October and November 2011.

### Analytical Comparison Methods

The LPG mixtures were connected to the GC system with a low dead-volume connector and a 1/16<sup>th</sup> 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 A2.1 gives a more detailed description of the GC system and method 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 <sub>2</sub> O <sub>3</sub> 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	Species detectable
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 A2.1.** Detailed description of the GC used for LPG analysis.

## Calibration Standards

An LPG PSM of nominally the same composition as the VSL unknown mixture was used for the calculation of the unknown composition. The exact composition of the NPL LPG PSM is given below in Table A2.2.

Component	Amount Fraction (cmol/mol)	Gravimetric Uncertainty (cmol/mol)
Propane	2.0868	0.0012
Propene	2.0640	0.0010
<i>iso</i> -Butane	70.298	0.035
<i>n</i> -Butane	8.211	0.005
But-1-ene	7.995	0.005
<i>iso</i> -Butene	7.1187	0.0036
<i>iso</i> -Pentane	0.8171	0.0010
<i>n</i> -Pentane	0.6074	0.0008
1,3-Butadiene	0.7832	0.0016

**Table A2.2.** Composition of the LPG PSM (CPC 32148) used for analysis of the unknown 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 [1A]) by combination of the uncertainties from three sources: gravimetry, relative molar masses and purity analysis.

## Evaluation of measurement uncertainty and coverage interval

### *Repeatability of analysis*

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

In the case of the series of measurements with the refinery gas GC, the typical standard deviation for 6 measurements was approximately 0.15%.

### *Type B error sources*

There was one source of uncertainty estimated by Type B methods. This was due to the extra difficulty in preparing a liquid mixture in comparison to a gaseous mixture, particularly the C<sub>5</sub> species and the 1,3-butadiene as they are added to the cylinder very early and were followed by components of much higher vapour pressures. This is estimated to correspond to a standard uncertainty of 0.05% for all C<sub>3</sub> and C<sub>4</sub> species (except 1,3-butadiene which was 0.2%) and 0.12% for all C<sub>5</sub> species.

To calculate the combined uncertainty, the analytical and gravimetric uncertainties described above were combined as the square root of the sum of squares. Expanded uncertainties were determined by multiplication of the standard uncertainties by a coverage factor of two (corresponding to a 95% confidence interval).

Component	Relative Uncertainty (%)				Total Combined	
	Preparation Uncertainty		Analytical Uncertainty		k=1	k=2
	Gravimetric	Liquid Filling	Liquid Sampling	Repeatability		
<b>Propane</b>	0.027	0.05	0.25	0.16	0.30	<b>0.60</b>
<b>Propene</b>	0.008	0.05	0.25	0.16	0.30	<b>0.60</b>
<i>iso</i> -Butane	0.003	0.05	0.20	0.14	0.25	<b>0.50</b>
<i>n</i> -Butane	0.014	0.05	0.20	0.14	0.25	<b>0.50</b>
<b>But-1-ene</b>	0.014	0.05	0.20	0.14	0.25	<b>0.50</b>
<i>iso</i> -Butene	0.008	0.05	0.20	0.14	0.25	<b>0.50</b>
<i>iso</i> -Pentane	0.044	0.12	0.22	0.15	0.30	<b>0.59</b>
<i>n</i> -Pentane	0.060	0.12	0.22	0.15	0.30	<b>0.60</b>
<b>1,3-Butadiene</b>	0.051	0.20	0.25	0.15	0.36	<b>0.71</b>

**Table A2.3.** Breakdown of uncertainty calculations and factors.

### 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
<b>Propane</b>	<b>1.951</b>	0.60	0.012
<b>Propene</b>	<b>1.952</b>	0.60	0.012
<i>iso</i> -Butane	<b>70.96</b>	0.50	0.35
<i>n</i> -Butane	<b>7.758</b>	0.50	0.039
<b>But-1-ene</b>	<b>8.316</b>	0.50	0.042
<i>iso</i> -Butene	<b>6.959</b>	0.50	0.035
<i>iso</i> -Pentane	<b>0.7581</b>	0.59	0.0045
<i>n</i> -Pentane	<b>0.6012</b>	0.60	0.0036
<b>1,3-Butadiene</b>	<b>0.7443</b>	0.71	0.0053

**Table A2.4.** Final results of the analysis of the unknown mixture.