# International Comparison CCQM-K111 – Propane in nitrogen

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# Field

Amount of substance

# Subject

Comparison of propane in nitrogen (track A - core competences)

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# **1** Introduction

This key comparison is one of a series of key comparisons in the gas analysis area assessing core competences (*track A key comparisons*). Such competences include, among others, the capabilities to prepare Primary Standard gas Mixtures (PSMs) [1], perform the necessary purity analysis on the materials used in the gas mixture preparation, the verification of the composition of newly prepared PSMs against existing ones, and the capability of calibrating the composition of a gas mixture.

For this key comparison, a binary mixture of propane in nitrogen has been chosen at an amount-ofsubstance fraction level of 1000  $\mu$ mol mol<sup>-1</sup>. The key comparison design follows that of the key comparisons using gas mixtures that are prepared gravimetrically as transfer standards [2,3].

# 2 Design and organisation of the key comparison

# 2.1 Participants

Table 1 lists the participants in this key comparison.

Acronym	Country	Institute		
CEDI	ID	Chemical Evaluation and Research Institute,		
CLKI	JL	Saitama, Japan		
INMETRO	DD	Instituto Nacional de Metrologia, Qualidade e Technologia,		
INVIETKO	DK	Xerém RJ, Brasil		
VDICC	VD	Korea Research Institute of Standards and Science,		
<b>KKISS</b>	ΝΛ	Deajeon, Republic of Korea		
NIST	US	National Institute of Standards and Technology,		
11151	05	Gaithersburg MD, United States of America		
NIMIS A	7.4	National Metrology Institute of South Africa,		
ININIISA	LA	Pretoria, South Africa		
NDI	CP	National Physical Laboratory,		
INFL.	OB	Teddington, United Kingdom		
VNIIIM	DII	D.I. Mendeleyev Institute for Metrology,		
V INIIIIVI	KU	St Petersburg, Russia		
VSI	NI	Van Swinden Laboratorium,		
VOL	INL	Delft, the Netherlands		

### Table 1: List of participants

## 2.2 Measurement standards

A set of mixtures was prepared gravimetrically by VSL using the procedure of ISO 6142 [1]<sup>1</sup>. For the preparation, propane was used from Scott Specialty Gases grade 3.5 and nitrogen from Air Products, grade 6.0. The mixtures were verified against a set of VSL PSMs. The propane was subjected to a

<sup>&</sup>lt;sup>1</sup> Once ISO 6142-1:2015 was published, VSL revisited its procedures which were based on the then valid edition, ISO 6142:2001. This analysis showed that the procedures used in this key comparison are also consistent with the requirements of ISO 6142-1:2015 [1].

purity analysis in accordance with ISO 19229 [4] prior to use for preparation of the gas mixtures. The nitrogen used (Air Products 6.0) is free of propane and has also been checked for impurities.

The filling pressure in the cylinders was approximately 100 bar. Aluminium cylinders having a 5 dm<sup>3</sup> water volume from Luxfer UK with an Aculife IV treatment were used. The mixture composition and its associated uncertainty were calculated in accordance with ISO 6142 [1]. The amount-of-substance fractions as obtained from gravimetry and purity verification of the parent gases were used as key comparison reference values (KCRVs). Each cylinder had its own reference value.

The nominal amount-of-substance fraction of propane was 1000 µmol/mol.

### 2.3 Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges. The laboratories were also requested to submit a summary of their uncertainty evaluation used for calculating the uncertainty of their result.

### 2.4 Schedule

The schedule of this key comparison was as follows (table 2).

Table 2: Key comparison schedule

Date	Stage
November 2013	Agreement of protocol
August 2013	Registration of participants
December 2013	Preparation of mixtures
February 2014	Verification of mixture compositions
April 2014	Dispatch of mixtures
October 2014	Reports and cylinder arrived at VSL
December 2014	Re-verification of the mixtures
January 2015	Draft A report available
May 2016	Draft B report available

### 2.5 Measurement equation

The key comparison reference values are based on the weighing data, and the purity verification of the parent gases. All mixtures underwent verification prior to shipping them to the participants. After return of the cylinders, they have been verified once more to reconfirm the stability of the mixtures.

In the preparation, the following four groups of uncertainty components have been considered:

- 1. gravimetric preparation (weighing process)  $(x_{i,grav})$
- 2. purity of the parent gases ( $\Delta x_{i, purity}$ )
- 3. stability of the gas mixture ( $\Delta x_{i,stab}$ )
- 4. correction due to partial recovery of a component ( $\Delta x_{i,nr}$ )

Previous experience has indicated that there are no stability issues and no correction is needed for the partial recovery of a component. These terms are zero, and so are their associated standard uncertainties. The verification measurements (see Figure 1) confirm that beyond the verification uncertainty, no extra uncertainty component due to instability had to be included.

The amount of substance fraction  $x_{i,prep}$  of a particular component in mixture *i*, as it appears during use of the cylinder, can now be expressed as

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

The equation for calculating the associated standard uncertainty reads as

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

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data (including uncertainty, the following condition should be met [3]

$$\left|x_{i,\text{prep}} - x_{i,\text{ver}}\right| \le 2\sqrt{u_{i,\text{prep}}^2 + u_{i,\text{ver}}^2} \tag{3}$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [5] and takes advantage of the work done in the gravimetry study CCQM-P41 [6].

The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of the key comparison reference value is

.

$$u^{2}(x_{i,\text{ref}}) = u^{2}(x_{i,\text{prep}}) + u^{2}(x_{i,\text{ver}})$$
(4)

The preparation and verification data for the gas mixtures used in this key comparison (see figure 1) agree well. The values for  $u(x_{i,ver})$  are given in the tables containing the results of this key comparison.



Figure 1: Preparation and verification data of the transfer standards used in this key comparison

#### 2.6 Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of these methods, the dates of measurement and reporting, and the way in which metrological traceability has been established is given in table 3.

Laboratory	Measurements	Calibration	Traceability	Matrix	Measurement
code				standards	technique
VNIIM	07/07/08/08 July 2014	Bracketing	Own standards	Nitrogen	NDIR
			(ISO 6142)		
NPL	18 July 2014,	Matching	Own standards	Nitrogen	GC-FID
	04/11/15 August 2014,	standard	(ISO 6142)		
	and 03 September 2014				
VSL	22/27 May 2014 and	ISO 6143	Own standards	Nitrogen	GC-FID
	11/12 June 2014		(ISO 6142)		
CERI	12/13/14/18 August 2014	Multipoint	Own standards	Nitrogen	FID
		calibration	(ISO 6142)		
KRISS	16/17/18/22/24/25	Bracketing	Own standards	Nitrogen	GC
	September 2014				
NIST	30/31 July 2014 and	ISO 6143	Own standards	Nitrogen	GC-FID
	01/05/06 August 2014				
INMETRO	26/27/28 August 2014	ISO 6143	Own standards	Nitrogen	GC-NGA-FID
NMISA	21/23 July	ISO 6143	Own standards	Nitrogen	GC-methaniser-FID
	06 August 2014		(ISO 6142)	-	

Table 3: Summary of calibration methods and metrological traceability

### 2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

$$d_i = x_i - x_{i,\text{ref}} \tag{5}$$

and the uncertainty associated with the difference  $d_i$  at 95% level of confidence. Here  $x_{i,ref}$  denotes the key comparison reference value, and  $x_i$  the result of laboratory *i*.<sup>2</sup>

The standard uncertainty associated with the difference  $d_i$  can be expressed as

$$u^{2}(d_{i}) = u^{2}(x_{i}) + u^{2}(x_{i,prep}) + u^{2}(\Delta x_{i,ver})$$
(6)

assuming that the laboratory result, the gravimetric composition and the verification result are uncorrelated. As discussed, the combined standard uncertainty associated with the key comparison reference value comprises that from preparation and that from verification for the mixture involved.

# **3** Results

In this section, the results of the key comparison are summarised. In the tables, the following data is presented

- $x_{\text{prep}}$  amount of substance fraction, from preparation (µmol/mol)
- $u_{\text{prep}}$  standard uncertainty of  $x_{prep}$  (µmol/mol)
- $u_{ver}$  standard uncertainty from verification (µmol/mol)
- $u_{\rm ref}$  standard uncertainty of reference value (µmol/mol)
- $x_{\text{lab}}$  result of laboratory (µmol/mol)
- $U_{\text{lab}}$  stated uncertainty of laboratory, at 95 % level of confidence (µmol/mol)
- $k_{\text{lab}}$  stated coverage factor
- $d_i$  difference between laboratory result and reference value (µmol/mol)
- *k* assigned coverage factor for degree of equivalence
- $U(d_i)$  Expanded uncertainty of difference  $d_i$ , at 95 % level of confidence<sup>3</sup> (µmol/mol)

Laboratory	Cylinder	x <sub>prep</sub>	<i>u</i> <sub>prep</sub>	<i>u</i> <sub>ver</sub>	<i>u</i> <sub>ref</sub>	$x_{ m lab}$	$U_{ m lab}$	$k_{ m lab}$	$d_i$	k	$U(d_i)$
CERI	153748	992.99	0.27	0.35	0.44	993.1	1.1	2	0.1	2	1.4
INMETRO	153926	991.44	0.26	0.35	0.44	990.9	2.3	2	-0.5	2	2.5
KRISS	153769	991.01	0.26	0.35	0.44	991.2	1.0	2	0.2	2	1.3
NIST	153887	992.51	0.27	0.35	0.44	994.3	2.1	2.78	1.8	2	1.8
NMISA	153929	989.47	0.27	0.35	0.44	1000.20	2.00	2	10.7	2	2.2
NPL	153465	990.47	0.27	0.35	0.44	989.40	0.99	2	-1.1	2	1.3
VNIIM	153166	993.56	0.27	0.35	0.44	994.46	1.40	2	0.9	2	1.7
VSL	153513	993.40	0.27	0.35	0.44	993.4	0.7	2	0.0	2	1.1

Table 4: Results	of	CCQM-K111
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In figure 2 the degrees of equivalence for all participating laboratories are given relative to the gravimetric value. The uncertainties are, as required by the MRA [7], given as 95% coverage intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor k = 2 was used. For obtaining the standard uncertainty of the

<sup>&</sup>lt;sup>2</sup> Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

As defined in the MRA [7], a degree of equivalence is given by  $d_i$  and  $U(d_i)$ .

laboratory results, the expanded uncertainty (stated at a coverage probability of 95%) from the laboratory was divided by the reported coverage factor.



Figure 2: Degrees of equivalence

### 4 Supported CMC claims

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

- 1) For core capabilities, under the flexible scheme, using the pooling mechanism for the stated uncertainties;
- 2) For propane in nitrogen, air and automotive gas mixtures, under the default scheme.
- 3) For the purity analysis of propane.

The way in which this key comparison supports CMC claims is described in more detail in the "GAWG strategy for comparisons and CMC claims" [9].

## **5** Discussion and conclusions

The results in this Track A key comparison on 1000  $\mu$ mol mol<sup>-1</sup> propane in nitrogen are generally good. All results but one are within  $\pm 0.2$  % of the KCRV.

### References

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# **Project reference**

CCQM-K111

## **Completion date**

May 2016

# **Annex A : Measurement reports**

# **Measurement report CERI**

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

Cylinder number: 153748

#### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	12/08/2014	993.05	0.041	4

#### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	13/08/2014	993.35	0.010	4

# Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	14/08/2014	993.04	0.010	4

#### Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	18/08/2014	992.77	0.079	4

### Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor
Propane		993.1	1.1	2

#### **Calibration standards**

- Method of preparation: ISO 6142 [1]



- Weighing data (1 000 µmol/mol C<sub>3</sub>H<sub>8</sub> in N<sub>2</sub>)
  1) Evacuated cylinder Tare cylinder : 2.548 g
  2) Cylinder filled with parent gas Tare cylinder : 22.641 g
  3) Cylinder filled with nitrogen Tare cylinder : 976.242 g
- Purity tables (composition) of the parent gases
   NMIJ CRM was used for pure Propane. Purity analysis of propane was performed by NMIJ and provided as a certified reference material to CERI.
   Impurities of nitrogen were analysed by CERI.

#### Table 5: Purity table of propane

Component	Purity (certified value) mol/mol	Expanded uncertainty ( <i>k</i> =2) mol/mol
C <sub>3</sub> H <sub>8</sub>	0.9999	0.0001

#### **Table 6: Impurity table of propane**

Component	Mole fraction cmol/mol	Standard uncertainty ( <i>k</i> =1) cmol/mol
N <sub>2</sub>	0.00023	0.00013
O <sub>2</sub>	0.00018	0.00010
Ar	0.00028	0.00016
CO2	0.00028	0.00016
C <sub>2</sub> H <sub>6</sub>	0.00038	0.00022
C <sub>3</sub> H <sub>6</sub>	0.00306	0.00002
cyclo- C <sub>3</sub> H <sub>6</sub>	0.00025	0.00014
$C_4 H_{10}$	0.00019	0.00011
<i>iso</i> - C <sub>4</sub> H <sub>10</sub>	0.00019	0.00011
H <sub>2</sub> O	0.00662	0.00180

#### Table 7: Purity table of nitrogen

Component	Analytical value µmol/mol	Distribution	Mole fraction µmol/mol	Uncertainty µmol/mol
O <sub>2</sub>	≤ 0.1	Rectangular	0.05	0.02890
Ar	$\leq 1$	Rectangular	0.5	0.2890
СО	$\leq 0.01$	Rectangular	0.005	0.002890
$CO_2$	$\leq 0.01$	Rectangular	0.005	0.002890
Total hydro carbon (THC)	≤ 0.01	Rectangular	0.005	0.002890
SO <sub>2</sub>	$\leq$ 0.005	Rectangular	0.0025	0.001443
NOx	$\leq 0.005$	Rectangular	0.0025	0.001443
$N_2$	-	-	999 999.43	0.2905

Each mole fraction of impurity in nitrogen is adequately low. Therefore, the molar mass of dilution gas wasn't affected from the impurities.

Verification measures

Analytical scheme was, Std. A – Std. B – CCQM Sample – Std. C – Std. D. This scheme was repeated 4-times in a day. These measurements were carried out for 4-days.

#### Instrumentation

Flame ionization detector, Rosemount Analytical Inc. Model 400A

#### Calibration method and value assignment

The instrument was calibrated using four gravimetrically prepared PRMs ranging in concentration from 1 200  $\mu$ mol/mol to 600 $\mu$ mol/mol. Each calibration curve was linear given by :

 $y = a_1 x_s + b_1$ 

where,

y: CCQM sample concentration

*n*: Gas standards number

- *x<sub>s</sub>*: Indicated value of sample
- xi: Indicated value of standard material i

*yi*: Concentration of standard material *i* 

$$a_{1} = \frac{S(xy)}{S(xx)}$$

$$b_{1} = \sum y_{i} - a_{1} \times \frac{\sum x_{i}}{n}$$

$$S(xx) = \sum x_{i}^{2} - \frac{(\sum x_{i})^{2}}{n}$$

$$S(xy) = \sum x_{i}y_{i} - \frac{\sum x_{i}\sum y_{i}}{n}$$

#### **Uncertainty evaluation**

Table 8: Budget Sheet for 1 000 µmol/mol C<sub>3</sub>H<sub>8</sub> in N<sub>2</sub>

Uncertainty source	Value <sub>Xi</sub>	Estimate +/-	Method of evaluation (type A or typeB)	Assumed probability distribution	Divisor	Standards uncertainty u(x <sub>i</sub> )	Sensitivity coefficient  c <sub>i</sub>	Contribution u(y <sub>i</sub> )
Parent gas	76 156.8 μg/g	9.553 μg/g	А	normal	1	9.553 μg/g	0.01312	0.1251 ·10 <sup>-6</sup>
Weighing data 1)	2.548 g	3.597 ·10⁻³g	А	normal	1	3.597 ·10⁻³g	$\begin{array}{c} 0.04872 \\ \cdot 10^{\text{-3}}\text{g}^{\text{-1}} \end{array}$	0.1752 ·10 <sup>-6</sup>
Weighing data 2)	22.641 g	3.597 ·10⁻³g	А	normal	1	3.597 ·10 <sup>-3</sup> g	$0.05069 \\ \cdot 10^{-3} g^{-1}$	0.1823 ·10 <sup>-6</sup>
Weighing data 3)	976.242 g	30.71 ·10⁻³g	А	normal	1	30.71 ·10⁻³g	1.027 $\cdot 10^{-6} g^{-1}$	0.03154 ·10 <sup>-6</sup>
Molar mass of C <sub>3</sub> H <sub>8</sub>	44.0596 g/mol	0.00140 g/mol	В	normal	2	0.00070 g/mol	22.63 ·10 <sup>-6</sup> mol/g	0.01584 ·10 <sup>-6</sup>
Molar mass of N <sub>2</sub>	28.0134 g/mol	0.00028 g/mol	В	normal	2	0.00014 g/mol	35.62 ·10 <sup>-6</sup> mol/g	0.004892 ·10 <sup>-6</sup>

Combined uncertainty: 0.2843  $\mu$ mol/mol Uncertainty of NMIJ CRM (high purity C<sub>3</sub>H<sub>8</sub>) is included in uncertainty of parent gas.

### Table 9: Budget Sheet for CCQM-K111

Uncertainty source	Value <sub>Xi</sub>	Estimate +/-	Method of evaluation (type A or typeB)	Assumed probability distribution	Divisor	Standards uncertainty u(x <sub>i</sub> )	Sensitivity coefficient  c <sub>i</sub>	Contribution u(y <sub>i</sub> )
Std. 1000	999.0 μmol/mol	0.2843 μmol/mol	А	normal	1	0.2843 µmol/mol	1	0.2843 μmol/mol
Measurement	993.1 μmol/mol	0.4526 μmol/mol	А	normal	1	0.4526 µmol/mol	1	0.4526 μmol/mol
THC(as methane) in N <sub>2</sub>	0.005 µmol/mol	0.005 µmol/mol	А	rectangular	√3	0.00289 µmol/mol	1/3	0.00096 µmol/mol
C <sub>3</sub> H <sub>6</sub> in CCQM sample	0.073 µmol/mol	0.02 µmol/mol	А	normal	1	0.02 µmol/mol	1	0.02 µmol/mol
Round off	-	0.05 µmol/mol	В	rectangular	$\sqrt{3}$	0.02877 μmol/mol	1	0.02877 μmol/mol

Combined uncertainty: 0.5356 µmol/mol

Expanded uncertainty (*k*=2): 1.1 µmol/mol

# Measurement report INMETRO

Laboratory name:	Inmetro / Lanag
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Cylinder number: 153926

#### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	26-08-2014	$991,32 \times 10^{-6}$	0,24	7

#### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	27-08-2014	990,47 $ imes 10^{-6}$	0,23	7

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Propane	28-08-2014	$990,81 \times 10^{-6}$	0,22	7

# Results

Component	Result (mol/mol)	Coverage factor	Assigned expanded uncertainty (mol/mol)
Propane	990,9 × 10 <sup>-6</sup>	2	$2,3 \times 10^{-6}$

# **Calibration standards**

INMETRO primary gas standards in the range: from  $300 \times 10^{-6}$  (mol/mol) -  $3550 \times 10^{-6}$  (mol/mol) propane in nitrogen (table 10).

#### **Table 10: Calibration standards**

Mixture code	$x \times 10^{-6}$ (mol/mol)	$u_x \times 10^{-6} \text{ (mol/mol)}$
PSM117518	300.245	0.071
PSM133643	500.47	0.11
PSM153654	750.72	0.19
PSM113677	1000.88	0.71
PSM118424	999.57	0.71
PSM110255	2000.43	0.27
PSM117528	3547.70	0.76

### Instrumentation

The measurements were performed using a gas chromatograph for natural gas (GC-NGA, CP-3800sp Varian), with a flame ionization detector, coupled to a gas sampling valve (Vici), with the following method conditions (table 11).

Parameter	Settings
Injector temperature	150°C
Split ratio	20:1
Column	CP-cil 5CB column, WCOT silica, l: 60 m,
	id: 0,25 mm
Column pressure	30,3 psi
Sample flow	3 ml/min
Column temperature	150 °C
FID temperature	250°C
FID flow's	H <sub>2</sub> : 30 ml/min, Air 300 ml/min, make up
	29 ml/min

Table 11: GC-NGA method conditions

### Calibration method and value assignment

The sample and calibration standards were connected to a reducer and after flushing connected to the multi position valve. Every line was flushed separately and the flow for each mixture was set equally. For the  $2^{nd}$  and  $3^{rd}$  day of analyses the reducers were disconnected and connected to a different cylinder, also a different position on the multi position valve was used to connect the cylinder. The flushing and setting of the flow was done equal to the first measurement.

The calibration was done according to ISO 6143 [8]. The calibration curve was made using the software XLgenline, the curve model for the data resulted in a quadratic curve, which was used for the value assignment. The goodness of fit for all 3 measurements was lower than 2.

### **Uncertainty evaluation**

The uncertainty was calculated according to ISO 6143 [8], using the software XLgenline. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:

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

# Measurement report KRISS

Laboratory name: KRISS

Cylinder number: 153769

### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	16/09/2014	991.0	0.04	5

### Measurement #2

Component	Date	Result	Standard deviation	number of
Component	(dd/mm/yy)	(µmol/mol)	(% relative)	replicates
Propane	17/09/2014	990.9	0.05	8

### Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	18/09/2014	991.2	0.03	8

# Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	22/09/2014	991.4	0.05	5

## Measurement #5

Component	Date (dd/mm/yyy)	Result	Standard deviation	number of
_	(dd/mm/yy)	(μποι/ποι)	(% relative)	replicates
Propane	24/09/2014	991.0	0.06	3

### Measurement #6

Component	Date	Result	Standard deviation	number of
Component	(dd/mm/yy)	(µmol/mol)	(% relative)	replicates
Propane	25/09/2014	991.4	0.04	5

### Results

Component	Date	Result	Standard deviation of	number of final
Component	(dd/mm/yy)	(µmol/mol)	the means (% relative)	replicates
Propane	25/09/2014	991.2	0.022	6

#### **Calibration standards**

Method of preparation: Six bottles of primary gas mixture cylinder were prepared by gravimetric technique; cylinder #, D233650, D233665, D233583, D233603, D233591 and D233615. We selected the cylinder D233591 as a calibration standard for the CCQM –K111

Weighing data: Two step dilution process was adopted and the weighing data on the primary gas mixture(cylinder #, D233591) was summarized as follows:

- 1) Nitrogen(614.200 g) + Propane(29.883 g) => 1st Dil. mixture(cylinder # D1234)
- 2) 1st Dil. mixture(40.022 g) + Nitrogen(1139.389 g) => Primary gas mixture(cylinder #, D233591)

Purity tables (composition) of the parent gases

Index	Impurity	Amount-of-substance fraction (µmol/mol)
1	$H_2$	<0.07
2	O <sub>2</sub> +Ar	9.18
3	CO	0.01
4	$\mathrm{CO}_2$	0.16
5	$CH_4$	< 0.05
6	$H_2O$	1.2
Purity	N <sub>2</sub>	999,989

Table 12: Purity table of pure Nitrogen gas.

#### Table 13: Purity table of pure Propane gas.

T 1	Impurity	Amount-of-substance fraction
Index		(µmol/mol)
		0.1
1	$CH_4$	< 0.1
2	$C_2H_6$	< 0.1
3	$C_2H_4$	< 0.1
4	$C_2H_2$	< 0.1
5	$C_3H_6$	< 0.1
6	$i-C_4H_{10}$	9.7
7	$n-C_4H_{10}$	4.4
8	$C_4H_8$	< 0.1
9	$C_{5}H_{12}$	< 0.1
10	$N_2$	1.5
11	$\mathrm{CO}_2$	0.7
12	СО	0.03
13	$H_2$	0.05
14	Ar and $O_2$	0.7
15	$H_2O$	0.3
Purity	Propane	999,982

#### Verification measures

Verification on the primary gas mixtures: Gravimetric results of the primary gas mixtures were compared by GC analysis and differences were tested by KRISS standard procedures. And its uncertainty was included to final uncertainty value.

Verification on the stability of cylinder adopted: Gas adsorption or any unstable effect was not observed in these gas mixtures and cylinders managed by KRISS. Previous experimental results were summarized at KRISS standard procedures. Since its uncertainty was so negligible, it was not included to final uncertainty value.

#### Instrumentation

No specific change or additional device at the GC instrument

A mass flow controller(MFC) was additionally used for constant flow of sample injection.

#### Calibration method and value assignment

Bracketing method(A-B-A) was adopted with primary reference gas mixtures, the mole fraction and filling pressure of which were very similar to sample gas. The results were directly obtained by comparison between GC responses of sample and reference gas mixtures.

#### **Uncertainty evaluation**

1) Model equation A model equation of measurand was set as followings;

 $C_{\textit{KRISS.}} = (A_{\textit{sample}} \, / \, A_{\textit{ref}}) \cdot C_{\textit{ref-grav}} \cdot f_{\textit{repro-prep}}$ 

where,  $C_{kriss}$  is mole fraction determined by KRISS,  $(A_{sample} / A_{ref})$  is ratio of sample and reference responses of GC,  $C_{ref-grav}$  is mole fraction of primary reference gas mixture determined by gravimetry, and  $f_{repro-prep}$  is a factor of error due to inconsistency of primary reference gas mixtures. Uncertainty of impurity of parent gases was combined to uncertainty of gravimetric uncertainty.

2) Combined standard uncertainty

$$\left(\frac{u(C_{KRISS.})}{C_{KRISS.}}\right)^{2} = \left(\frac{u(A_{sample} / A_{ref})}{A_{sample} / A_{ref}}\right)^{2} + \left(\frac{u(C_{ref-grav})}{C_{ref-grav}}\right)^{2} + \left(\frac{u(f_{repro-prep})}{f_{repro-prep}}\right)^{2}$$

	Estin	mate	Uncertainty				
No	x <sub>i</sub>	value	Uncertainty source	Туре	Assumed distribution	Standard Uncertainty $u(x_i)$	Contribution to total variance(%)
1	A <sub>sample</sub> /A <sub>ref</sub>	0.9904	Repeatability	А	t	0.00009	3
2	$C_{ref-grav}$	1000.8 μmol/mol	Gravimetric preparation	В	normal	0.21	17
3	f <sub>repro-prep</sub>	1	Inconsistency of gravimetric preparation	В	rectangle	0.00046	80
	$C_{kriss}$	991.2 µmol/mol	Combined			0.51	100

#### Table 14: Uncertainty budget

3) Measurand and expanded uncertainty

 $C_{kriss} = 991.2 \ \mu mol/mol \pm 1.0 \ \mu mol/mol (95 \% L.C., k = 2)$ 

# **Measurement report NIST**

Laboratory name: National Institute of Standards and Technology (NIST)

Cylinder number: 153887

### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Standard uncertainty (% relative)	Number of replicates
Propane	30/07/14	995.31	0.24	3

#### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Standard uncertainty (% relative)	Number of replicates
Propane	31/07/14	993.84	0.13	3

### Measurement #3

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Standard uncertainty (% relative)	Number of replicates
Propane	01/08/14	995.78	0.20	3

#### Measurement #4

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Standard uncertainty (% relative)	Number of replicates
Propane	05/08/14	993.56	0.16	3

#### Measurement #5

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Standard uncertainty (% relative)	Number of replicates
Propane	06/08/14	994.54	0.18	3

### Results

Component	Date (dd/mm/yy)	Result (µmol mol <sup>-1</sup> )	Expanded uncertainty (µmol mol <sup>-1</sup> )	Coverage factor
Propane	21/08/14	994.3	2.1	<i>k</i> = 2.78

#### **Calibration standards**

The CCQM-K111 sample was analyzed against NIST primary standard mixtures (PSMs), which were prepared gravimetrically on a mol-per-mol basis in accordance with the Gas Sensing Metrology Group Quality System Technical Procedure for the preparation of PSMs by gravimetry. The pure  $C_3H_8$  and nitrogen (N<sub>2</sub>) starting materials were tested for purity using gas chromatography (GC) with flame ionization detection (FID). In addition to several PSMs, one NIST Standard Reference Material (SRM), 103-CL-01, was used in the analysis to assure consistency within the NIST  $C_3H_8$  standards and measurement program. All NIST calibration standards that were used for the CCQM-K111 analysis are provided in Table 1.

Table 15:	NIST g	ravimetric c	alibration s	tandards us	ed for Mea	asurements #1	through #5	of the G	CCQM-
K111 ana	lysis								

PSM #	Cylinder number	Amount-of-substance fraction $(\mu mol mol^{-1} C_3 H_8 in N_2)$	Expanded uncertainty (µmol mol <sup>-1</sup> )	Year prepared
1	X160585	756.29	1.51	2000
2	X110542	917.2	1.8	1992
3	X302449	957.9	1.9	1999
4	X160664	1013.7	2.0	1999

#### Instrumentation

The propane ( $C_3H_8$ ) in the CCQM-K111 sample was analyzed using an Agilent 6890 GC (NIST # 632011) with FID maintained at 250 °C. The GC was equipped with a 3.66 m × 0.32 cm stainless steel column packed with Porapak Q, which was operated isothermally at 150 °C. The helium carrier gas flow rate was set to 60 mL min<sup>-1</sup>. All aliquots of the CCQM-K111 sample and the calibration standards were delivered using a computer operated gas analysis system (COGAS), and were injected onto the head of the column via a 2-mL stainless steel sample loop connected to a 6-port stainless steel gas sampling valve. This automated sampling system randomized the cylinder samples in such a manner that detector performance could be monitored for stability through use of an analytical control. The data was automatically collected using Agilent ChemStation software, and was then transferred to an Excel spreadsheet. Each sample in the measurement sequence was injected three times and the responses were averaged.

### Calibration method and value assignment

The GC-FID was calibrated using a suite of four PSMs ranging from 756.29 to 1013.7  $\mu$ mol mol<sup>-1</sup> of C<sub>3</sub>H<sub>8</sub> in a balance of N<sub>2</sub> (Table 15). For each measurement, SRM 103-CL-01 was used as the analytical control, and was sampled both before and after each CCQM-K111 and PSM sample to allow for correction of the C<sub>3</sub>H<sub>8</sub> response for instrument drift. SRM 103-CL-01 was rigorously compared to the PSMs and CCQM-K111 sample a total of five times over five analytical periods. A response ratio for each measurement was determined by dividing the measured C<sub>3</sub>H<sub>8</sub> response of each sample by the C<sub>3</sub>H<sub>8</sub> response of the control. The ratios and concentrations for the four PSMs were then plotted to a first-order regression using the ISO 6143 GenLine program, from which the CCQM-K111 sample concentration was determined (see Measurement tables).

#### **Uncertainty evaluation**

All measured certification data and calculations for the amount of substance of  $C_3H_8$  in the CCQM-K111 sample were reviewed for sources of systematic and random errors. The review identified two sources of uncertainty whose importance required quantification; these uncertainties, expressed as percent relative uncertainties, are listed in Table 16. All uncertainties in the certified gravimetric concentrations were assumed to be 0.1%. The uncertainties with respect to response ratio ( $u_{Ratio}$ ) were calculated by combining the uncertainties in measured  $C_3H_8$  response of the PSM/CCQM-K111 sample ( $u_{Sample}$ ) and adjacent control samples ( $u_{Control}$ ) (Equation 1).

$$u_{Ratio} = \sqrt{(u_{Control})^2 + (u_{Sample})^2 + (u_{Control})^2}$$
(1)

The uncertainties assigned to the CCQM-K111 sample were calculated independently for each analytical period using the ISO 6143 GenLine program, which included the uncertainties related to both the PSM concentrations and the  $C_3H_8$  response ratios.

 Table 16: Statistically significant sources of uncertainty in Measurements #1 through #5 of the CCQM-K111 analysis.

Uncertainty source, x <sub>i</sub>	Assumed distribution	Standard uncertainty, u(x <sub>i</sub> ) (% Relative)	Sensitivity coefficient, c <sub>i</sub>
Gravimetric standards (PSMs)	Gaussian	0.10	1
Response ratios	Gaussian	0.05 - 0.24	1

The final concentration ( $C_F$ ) and uncertainty ( $U_F$ ) values assigned to the CCQM-K111 sample (see Results table) were determined from the DerSimonian and Laird random-effects model for metaanalysis, using the five independently-calculated concentrations ( $C_i$ ) and uncertainties ( $u_i$ ) from Measurements #1 through #5. These values were calculated via Equations 2 and 3, such that measurements with smaller uncertainties were weighted more heavily than those with larger uncertainties. It was determined after thorough analysis that the standard deviation of all five measurements was statistically insignificant when compared to the uncertainty of each individual measurement, and was therefore excluded from the overall uncertainty calculation.

$$U_F = \sqrt{\frac{1}{\sum_{i=1}^{5} \left(\frac{1}{u_i^2}\right)}} \tag{2}$$

$$C_F = \frac{\sum_{i=1}^{5} \left( C_i \times \frac{1}{{u_i}^2} \right)}{\sum_{i=1}^{5} \left( \frac{1}{{u_i}^2} \right)}$$
(3)

# Measurement report NMISA

Laboratory name: National Metrology Institute of South Africa (NMISA)

Cylinder number: 153929

### Measurement 1<sup>#</sup>

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C <sub>3</sub> H <sub>8</sub>	21/07/2014	1002.4	0.07	8

#### Measurement 2#

Component	Date (dd/mm/vv)	Result (umol/mol)	Standard deviation (% relative)	Number of replicates
C <sub>3</sub> H <sub>8</sub>	23/07/2014	999.3	0.07	8

#### Measurement 3#

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C <sub>3</sub> H <sub>8</sub>	06/08/2014	998.8	0.06	8

#### Result

Component	Result	Expanded uncertainty	Coverage factor
	(µmol/mol)	(µmol/mol)	
C <sub>3</sub> H <sub>8</sub>	1000.2	2.0	k = 2

#### Details of the measurement method used

#### **Reference Method**

Gas chromatography with a methaniser flame ionisation detector (GC-methaniser FID).

#### Instruments

The propane was analysed using a gas chromatograph equipped with a methaniser-flame ionisation detector (GC-methaniser FID). A Hayesep-Q column was used to analyse the propane amount in the sample. The column oven was operated isothermally at 200 °C with a carrier gas pressure of 450 kPa helium. A 50  $\mu\ell$  sample loop was used to inject the sample and the standards onto the column with column flow set at 100 ml/min and column pressure set at 300 kPa. The FID-detector was operated at 300 °C and the methaniser temperature setting was 380 °C.

#### **Calibration standards:**

The primary standard gas mixtures (PSGMs) used for the calibration were prepared from pre-mixtures in accordance with ISO 6142:2001 [1] (Gas analysis - Preparation of calibration gas mixtures – Gravimetric method). The pre-mixtures were prepared from high purity gas mixtures of propane (3.5 quality) and BIP nitrogen (6.0 quality) from Air Liquide and Air Products, respectively. The purity of the high pure propane and BIP nitrogen were assessed before commencing with the preparation. After preparation, the composition was verified using the method described in ISO 6143:2001 [8]. Tables 17 and 18 show the purity tables of the purity analysis of the high purity gases.

#### Table 17: Purity analysis of propane 3.5

Propane 3.5			
Chemical symbol	Mole Fraction (x 10 <sup>-6</sup> mol/mol)	Expanded uncertainty (x 10 <sup>-6</sup> mol/mol)	Analysis method

C <sub>2</sub> H <sub>6</sub>	87.2	4.4	GC-methaniser FID
$C_3H_6$ (Propene)	100	115.5	Manufacturer specification
C <sub>3</sub> H <sub>8</sub>	999432.9	119.4	Mass balance
CH <sub>4</sub>	2.04	0.2	GC-methaniser FID
CO <sub>2</sub>	2.5	2.88	Manufacturer specification
H <sub>2</sub>	20	23.1	Manufacturer specification
H <sub>2</sub> O	2.5	2.88	Manufacturer specification
N <sub>2</sub>	347.87	18	GC-TCD
O <sub>2</sub>	5	5.77	Manufacturer specification

#### Table 18: Purity analysis of BIP nitrogen 6.0

BIP nitrogen 6.0			
Chemical symbol	Mole Fraction (x 10 <sup>-6</sup>	Expanded uncertainty	Analysis method
	mol/mol)	(x 10 <sup>-0</sup> mol/mol)	
Ar	78.4	7.9	GC-PDHID
$C_2H_6$	0.001	0.001155	GC-methaniser FID
$CH_4$	0.017	0.01963	GC-methaniser FID
CO	0.006	0.006928	GC-methaniser FID
$CO_2$	0.0035	0.004041	GC-methaniser FID
$H_2$	0.5	0.57735	Manufacturer specification
$H_2O$	0.01	0.011547	Manufacturer specification
N <sub>2</sub>	999921.06	7.9	Mass balance
O <sub>2</sub>	0.005	0.005774	Manufacturer specification

#### **Instrument calibration:**

The calibration standards consisted of a set of eleven (11) PSGMs of  $C_3H_8$  in nitrogen with concentrations ranging from 900 to 5000 µmol/mol. The standards were used for the multi-point calibration of the Varian CP3800 GC-methaniser FID in accordance with ISO 6143 [8] with a 50 µℓ stainless steel sample loop, and a 8' x 1/8" SS HayeSep Q- column packed with 80/100 mesh.

Certificate/Cylinder	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>8</sub>
number	Gravimetric amount-of-	Standard uncertainty
	substance fraction	$(x \ 10^{-6} \ mol/mol)$
	(x 10 <sup>-6</sup> mol/mol)	
NMISA50006642	4996.737022	5.660675
NMISA30003779	4002.273007	1.11494
NMISA30003964	3001.093676	1.655253
NMISA20006624	2000.222228	0.782976
NMISA40003945	1505.510083	0.672492
NMISA30003949	1002.18572	1.210261
NMISA20006667	1001.158171	0.435319
NMISA20006696	1000.73138	0.857295
NMISA30006638	999.674725	0.47124
NMISA30003954	995.0874015	0.522235
NMISA40003802	899.1295055	0.766015

#### Sample handling

After arrival, the cylinder was kept in the laboratory to stabilise in the laboratory environment. The cylinder was rolled before commencing with the measurements. Each cylinder (sample and standards) was equipped with a Tescom 316L stainless steel pressure regulator that was adequately purged. The sample flow rate was set to approx. 100 mℓ/min.

#### Uncertainty

All measured data and calculations for the component concentrations of cylinder no.153929 were reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated % relative uncertainties. These uncertainty contributions were:

- a) Gravimetric uncertainties of the PSGMs in the order of 0.09%.
- b) Repeatability uncertainty (run-to-run) which ranged from 0.06 to 0.07% relative experimental standard deviation
- c) Reproducibility uncertainty (day-to-day) calculated in % relative standard deviation was 0.18%.

#### **Detailed uncertainty budget:**

The results for each day gave an average verification concentration. The average concentration and verification uncertainty were obtained from regression analysis using the method of XLGENLINE.

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

$$u_{c}^{2} = \frac{u_{Day1}^{2} + u_{Day2}^{2} + u_{Day3}^{2}}{3} + (u_{ESDM})^{2} \dots Equation 1$$

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. Equation 2

# **Measurement report NPL**

Laboratory: National Physical Laboratory

Cylinder Number: 153465

#### Measurement #1: GC-FID

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard deviation (µmol/mol)	No. of replicates
C <sub>3</sub> H <sub>8</sub>	18/07/2014	989.45	1.09	18

#### Measurement#2 : GC-FID

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard deviation (µmol/mol)	No. of replicates
C <sub>3</sub> H <sub>8</sub>	04/08/2014	989.71	1.27	19

#### Measurement#3 : GC-FID

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard deviation (µmol/mol)	No. of replicates
C <sub>3</sub> H <sub>8</sub>	11/08/2014	989.57	0.67	11

#### Measurement#4 : GC-FID

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard deviation (µmol/mol)	No. of replicates
C <sub>3</sub> H <sub>8</sub>	15/08/2014	989.28	1.62	48

#### Measurement#5: GC-FID

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard deviation (µmol/mol)	No. of replicates
C <sub>3</sub> H <sub>8</sub>	03/09/2014	989.00	0.51	33

#### **Final Result**

Component	Date (dd/mm/yy)	Result (µmol/mol)	expanded uncertainty (µmol/mol)	Coverage Factor
C <sub>3</sub> H <sub>8</sub>	19/09/2014	989.40	0.99*	2

\*The reported uncertainty is based on a standard uncertainty multiplied by a coverage factor k = 2, providing a coverage probability of 95 %.

#### Details of the measurement method used

#### **Reference method**

The amount fraction of propane in the comparison mixture was measured using two gas chromatographs with flame ionisation detectors (GC-FIDs):

- An Agilent Technologies 6890N GC with 4.4 m Porasil-P and 4.4 m Porapak-PS custommade packed columns.
- An Agilent Technologies 7890N GC with DB-624 column (L = 75 m, D = 0.530 mm, FT =  $3.00 \ \mu$ m)

#### **Calibration standards**

Two NPL Primary Reference Gas Mixtures (PRGMs) of nominally 1000  $\mu$ mol/mol propane in nitrogen were prepared in accordance with ISO 6142 [1]. The purity of the source propane (gas phase) was analysed and found to be >99.989 %. The mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. Mixtures were prepared in one stage from the gas phase of a propane source cylinder (via a transfer vessel) followed by the addition of nitrogen (by direct filling). Both mixtures were used in determining the amount fraction of the comparison mixture. The amount fractions of the two PRGMs (NPL 1601 and NPL A437) were 1000.51  $\pm$  0.25 and 989.44  $\pm$  0.30  $\mu$ mol/mol respectively. (Uncertainties are stated as expanded (*k* = 2) uncertainties.)

#### **Propane purity table**

component	amount fraction <i>x</i> (mol/mol)	standard uncertainty u <sub>x</sub> (mol/mol)
$C_3H_8$	0.9998921900	0.0000033000
$C_3H_6$	0.0000443000	0.0000044300
$i-C_4H_{10}$	0.0000063200	0.000000095
$n-C_4H_{10}$	0.0000047900	0.000000153
cis-2-butene	0.0000047900	0.000000077
but-1-ene	0.0000410900	0.0000041100
trans-2-butene	0.0000065200	0.0000009100

#### Nitrogen purity table

Component	Amount fraction $x$ (mol/mol)	Standard uncertainty u <sub>x</sub> (mol/mol)
$N_2$	0.999999483	0.00000874
Ar	0.000000500	0.00000050
$O_2$	0.000000005	0.00000003
CxHy	0.000000005	0.000000005
H <sub>2</sub> O	0.000000005	0.000000005
CH <sub>4</sub>	0.000000001	0.000000001
H <sub>2</sub>	0.000000001	0.00000001

#### Instrument calibration, data analysis and quantification

As the PRGMs described above were prepared with propane amount fractions that differed by less than 1% (relative) from the nominal composition of the comparison mixture, this ensured that the uncertainty contribution from any deviation from the linearity of the analyser response was negligible.

The comparison mixture and an NPL PRGM were connected to the GC (via an automated switching valve) using purpose-built minimised dead volume connectors and Silcosteel-passivated 1/16'' internal diameter stainless steel tubing. NPL-designed flow restrictors were used to allow a stable sample flow of 20 ml min<sup>-1</sup> to be maintained throughout the analysis.

The lines were thoroughly purged and flow rates were allowed to stabilise before commencing analysis. The method was set up to alternate between the NPL and comparison mixtures every 3 minutes. Up to 48 injections of each mixture were performed in order to obtain a comprehensive dataset.

#### **Uncertainty evaluation**

The ratio of the GC-FID response from the comparison mixture and the NPL PRGM was calculated using:

$$r = \frac{2A_{u,m}}{(A_{s,m} + A_{s,m+1})}$$

Where  $A_{u,m}$  is the peak area from repeat *m* of the VSL mixture, and  $A_{s,m}$  is the peak area from repeat *m* of the NPL PRGM.

And the average ratio  $(\bar{r})$  is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Note that the number of ratios. The amount fraction of the propane in the comparison mixture,  $x_u$ , is then calculated by:

$$x_u = x_s \bar{r}$$

Where  $x_s$  is the amount fraction of propane in the standard. The standard uncertainty of the measurand,  $u(x_u)$ , is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{x_s^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$

The table which follows details the uncertainty analysis for an example measurement.

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
$x_s$	µmol/mol	1000.51	0.13	0.99	0.13	Α	normal
ī	-	0.9889	0.0011	1000.51	1.08	Α	normal
$x_{u}$	µmol/mol	989.45					
$u(x_n)$	µmol/mol	1.09					
$U(x_u)$	µmol/mol	2.17					

To obtain the final result for the comparison, an average was taken for the five measurements. The following table shows the calculation of the final results and its uncertainty.

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
$x_1$	µmol/mol	989.45	1.09	0.20	0.22	Α	normal
$x_2$	µmol/mol	989.71	1.27	0.20	0.25	Α	normal
<i>x</i> 3	µmol/mol	989.57	0.67	0.20	0.13	Α	normal
x 4	µmol/mol	989.28	1.62	0.20	0.32	А	normal
<i>x</i> 5	µmol/mol	989.00	0.51	0.20	0.10	А	normal
$x_f$	µmol/mol	989.40					
$u(x_f)$	µmol/mol	0.49					
$U(x_f)$	µmol/mol	0.99					

Where  $x_1$ - $x_5$  is the measurement number and  $x_f$  is the final value of the amount fraction of propane in the comparison mixture.

# **Measurement report VNIIM**

Laboratory name: D.I.Mendeleyev Institute for Metrology (VNIIM)

Cylinder number: 153166

#### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	07/07/14	994.435	0.037	10

#### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	07/07/14	994.499	0.056	10

#### Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	08/07/14	994.499	0.067	10

#### Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Propane	08/07/14	994.388	0.033	10

#### Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Propane	23/07/14	994.46	1.40	2

### **Calibration standards**

Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.

Characteristics of pure substances used for preparation of the calibration standards are shown in the tables 19 and 20.

Table 19 -	– Purity	table for	Propane	(cylinder	№ 15049)
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Component	Mole fraction	Standard uncertainty
_	(µmol/mol)	(µmol/mol)
C <sub>3</sub> H <sub>8</sub>	999932	2.2
N <sub>2</sub>	21.3	1.6
O <sub>2</sub>	3.4	0.26
CH <sub>4</sub>	1	0.6
$C_2H_6$	5.7	0.28

Component	Mole fraction	Standard uncertainty
	(µmol/mol)	(µmol/mol)
$C_3H_6$	18.9	1.1
i-C <sub>4</sub> H <sub>10</sub>	1.8	0.11
$n-C_4H_{10}$	15.4	0.8

Table 20 – Purit	y table for Nitrogen	(purification y	with Entegris Gas	purifier "Gatekeeper-HX")
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Component	Mole fraction	Standard uncertainty
	(µmol/mol)	(µmol/mol)
$\mathbf{N}_2$	999999.13	0.027
H <sub>2</sub> O	0.50	0.017
Ar	0.313	0.006
CO <sub>2</sub>	0.03	0.017
O <sub>2</sub>	0.030	0.001
$CH_4$	0.015	0.009
СО	0.010	0.006
H <sub>2</sub>	0.0025	0.0014

Preparation from pure substances was carried out in 2 stages. On the first stage 3  $C_3H_8/N_2$  gas mixtures were prepared on the concentration level of 2.5 %. On the second stage these mixtures were diluted to the target concentration level. 3 calibration gas mixtures on the level of 1000  $\mu$ mol/mol were prepared.

The exact values of propane amount of substance fraction in the calibration gas mixtures and their standard uncertainties are shown in the table 21.

Table 21: Values and standard uncertainties for the mole fraction propane

Cylinder number	Component	Mole fraction (µmol/mol)	Standard uncertainty due to weighing and purity (µmol/mol)
D158048	C <sub>3</sub> H <sub>8</sub>	994.9	0.13
D158049	C <sub>3</sub> H <sub>8</sub>	1006.1	0.15
D158053	C <sub>3</sub> H <sub>8</sub>	1005.2	0.13

All standard gas mixtures were prepared in aluminum cylinders (Luxfer),  $V = 5 \text{ dm}^3$ .

#### Instrumentation

All the measurements were carried out by NDIR method on the gas analyzer AERONICA (VNIIM, Russia).

Verification measurements for pre-mixtures (2.5 %) were performed using cuvette with optical path 1.5 mm. Standard deviation for each measurement series was not more than 0.09 %.

Verification of the target calibration gas mixtures and measurements for investigated gas mixture (cylinder number: № 153166) were performed using cuvette with optical path 35 MM. Standard deviation for each measurement series was not more than 0.07 %.

#### Calibration method and value assignment

Single point calibration method was used to determine propane mole fraction in the investigated gas mixture.

Measurement sequence was in the order:

zero gas - standard1 - zero gas - sample - zero gas - standard1 - zero gas; zero gas - standard2 - zero gas - sample - zero gas - standard2- zero gas;

zero gas - standard3 - zero gas - sample - zero gas - standard3- zero gas.

Temperature corrections were not applied due to use of above-mentioned measurement sequence. Four independent measurement series were carried out under repeatability conditions. The amount of substance fraction of propane for a single measurement was calculated according to the formula

$$C_x = C_{st} \frac{A_x}{(A'_{st} + A''_{st})/2}$$
,

where  $C_x$  and  $C_{st}$  – amount of substance fractions of propane in the investigated and standard mixtures;

 $A_x$  – analytical signal of propane in the investigated gas mixture (minus zero gas signal)

 $A'_{st}$  and  $A''_{st}$  analytical signals of propane in the standard gas mixture before and after measurement for the investigated mixture (minus zero gas signals).

### Uncertainty evaluation

#### Uncertainty table:

Uncertainty source	Estimate	Assumed	Standard uncertainty	Sensitivity	Contribution to
$X_i$	$x_i$ ,	distribution	$u(x_i)$	coefficient	standard
	µmol/mol		µmol/mol	$C_i$	uncertainty ui(y),
					µmol/mol
Calibration standards	1006.1	Normal	0.15	0.988	0.15
(weigning + purity)					
within and between day measurements	994.46	Normal	0.67	1	0.67

Combined standard uncertainty: 0.686 µmol/mol Coverage factor: k=2 Expanded uncertainty: 1.40 µmol/mol Relative expanded uncertainty: 0.14 %

### **Measurement report VSL**

Laboratory	: Van Swinden Labratorium B.V.
Cylinder number	: 153513

#### Measurement #1 (GC-6)

Component	Date (yyyy-mm-dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
$C_3H_8$	2014-05-22	$993.90 \times 10^{-6}$	0.02	6

#### Measurement #2 (GC-6)

Component	Date (yyyy-mm-dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
$C_3H_8$	2014-05-27	$993.80 \times 10^{-6}$	0.03	6

#### Measurement #3 (GC-3)

Component	Date (yyyy-mm-dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
C <sub>3</sub> H <sub>8</sub>	2014-06-11	$992.77 \times 10^{-6}$	0.02	6

#### Measurement #4 (GC-6)

Component	Date (yyyy-mm-dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
C <sub>3</sub> H <sub>8</sub>	2014-06-12	$993.30 \times 10^{-6}$	0.02	6

#### Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	<b>Coverage factor</b> <sup>4</sup>
C <sub>3</sub> H <sub>8</sub>	993.4 × 10 <sup>-6</sup>	$0.7 imes10^{-6}$	2

#### **Reference Method and calibration:**

Propane is analyzed on an Agilent 6890 GC equipped with a FID. Three times the sample is injected on a 10 ft Porapak N column at 145 °C with a helium carrier (GC-6). One time the sample is injected on a 10 ft Porapak T column at 150 °C with a hydrogen carrier (GC-3). Together with the CCQM-K111 sample cylinder also 4 PSMs of  $C_3H_8$  in N<sub>2</sub> are connected to a computer programmed multiposition valve gas sampling box. A sample loop, 1 mL in GC-6 and 0.25 mL in GC-3, is flushed for 3 minutes before performing 6 injections for each mixture. A straight line is used as calibration function in the regression analysis for propane. A correction cylinder is used for eliminating the instrument drift. Each measurement is preformed in compliance with ISO 6143 [8].

#### **Calibration Standards:**

All Primary Standard gas Mixtures (PSMs) for the measurements of  $C_3H_8$  are binary mixtures in nitrogen. Preparation is performed according ISO 6142 [1]. The standard uncertainty is based on the uncertainty of the gravimetric preparation process and the purity analysis of the parent gases.

<sup>&</sup>lt;sup>4</sup> The coverage factor shall be based on approximately 95% confidence.

**Table 22:** Purity table of propane.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u <sub>x</sub> (mol/mol)
$C_2H_6$	0.0000001	0.00000001
C <sub>3</sub> H <sub>6</sub>	0.000114	0.000011
C <sub>3</sub> H <sub>8</sub>	0.9998556	0.000015
$C_4H_8$	0.00000006	0.00000003
$n-C_4H_{10}$	0.0000016	0.00000016
i-C <sub>4</sub> H <sub>10</sub>	0.0000023	0.00000003
$1-C_5H_{10}$	0.0000004	0.0000002
$n-C_5H_{10}$	0.00000004	0.00000002

 Table 23: Purity table of nitrogen.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u <sub>x</sub> (mol/mol)
H <sub>2</sub>	0.000005	0.000003
H <sub>2</sub> O	0.00000001	0.000000006
$CH_4$	0.00000008	0.000000005
$N_2$	0.999994927	0.000006
CO	0.00000015	0.00000009
$O_2$	0.000000005	0.000000003
Ar	0.000005	0.000003
CO <sub>2</sub>	0.00000001	0.000000006

 Table 24: Composition of PSMs and correction cylinder.

Component	Cylinder number	Assigned value <i>x</i> (mol/mol)	Standard uncertainty $u_{(x)}$ (mol/mol)
C <sub>3</sub> H <sub>8</sub>	VSL303807	$400.17\times10^{\text{-6}}$	$0.06  imes 10^{-6}$
	VSL204663	$600.35 \times 10^{-6}$	$0.08 imes10^{-6}$
	VSL328517	$799.06  imes 10^{-6}$	$0.10  imes 10^{-6}$
	VSL238482	$999.60  imes 10^{-6}$	$0.27  imes 10^{-6}$
Correction cylinder	VSL423616	$1000.90 \times 10^{-6}$	$0.27  imes 10^{-6}$

### Sample handling:

The CCQM-K111 cylinder 153513 and the PSMs used for calibration are equipped with a pressure regulator. Sampling takes place with automated multiposition valve sample boxes as described in VSL's work instructions for routine analyses.

### **Evaluation of measurement uncertainty:**

The calibration curves where obtained in accordance with ISO 6143 [8]. As indicated, a straight line was used. From the uncertainty associated with the amount-of-substance fractions propane of the calibration mixtures and the repeatability standard deviation of the analyses of the calibration mixtures and the sample mixture, the amount-of-substance fraction propane and its associated standard uncertainty where calculated.

To arrive at the final result, the results of the four measurements were averaged. The standard error of the mean was combined with the pooled uncertainty from evaluating the data from the calibration of the GCs.

Table 25: Uncertainty evaluation

	fit value (mol/mol)	standard uncertainty u <sub>#x</sub> (mol/mol)	Expanded Uncertainty
#1	$9.9390 \times 10^{-4}$	$1.97 \times 10^{-7}$	
#2	$9.9380 \times 10^{-4}$	$2.69 \times 10^{-7}$	
#3	$9.9277 \times 10^{-4}$	$1.97 \times 10^{-7}$	
#4	$9.9330 \times 10^{-4}$	$1.97 \times 10^{-7}$	
Standard deviation	$5.1951 \times 10^{-7}$	$2.60  imes 10^{-7}$	
mean	$9.9344 \times 10^{-4}$		$6.77 \times 10^{-7}$

The standard error of the mean is  $2.17 \times 10^{-7}$  and the pooled standard uncertainty is  $2.60 \times 10^{-7}$ . These standard uncertainties were combined using the law of propagation of uncertainty. The expanded uncertainty was obtained by multiplying the standard uncertainty with a coverage factor of k = 2.