International Comparison CCQM-K111.1 – Propane in nitrogen

Adriaan M.H. van der Veen[1], J. Wouter van der Hout[1], Paul R. Ziel[1], Mudalo Jozela[2], James Tshilongo[2], Napo G. Ntsasa[2], Angelique Botha[2]

[1] *Van Swinden Laboratorium (VSL), Chemistry Group, Thijsseweg 11, 2629 JA Delft, the Netherlands*
[2] *National Metrology Institute of South Africa (NMISA), CSIR, Building 4 W, Meiring Naudé Road, Brummeria, Pretoria 0184, South Africa*

Field

Amount of substance

Subject

Comparison of propane in nitrogen (track B)

Table of contents

1 Introduction

This key comparison is an addition on 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 a gas mixture.

According to the Strategy of the Gas Analysis Working Group [2], the results of a subsequent (bilateral) key comparison can be used to support CMCs under the *track B* scheme, that is, for capabilities for specific groups of measurement standards.

For this key comparison, a binary mixture of propane in nitrogen has been chosen at an amount-of-substance fraction level of 1000 μmol mol^{-1}. The key comparison design follows that of the key comparisons using gas mixtures that are prepared gravimetrically as transfer standards [1,3].

2 Design and organisation of the key comparison

2.1 Participants

Table 1 lists the participants in this key comparison.

Table 1: List of participants

Acronym	Country	Institute
NMISA	ZA	National Metrology Institute of South Africa, Pretoria, South Africa
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands (coordinator)

2.2 Measurement standards

A mixture was prepared gravimetrically by VSL. For the preparation, propane was used from Scott Specialty Gases grade 3.5 and nitrogen from Air Products, grade 6.0. The mixture was verified against a set of VSL PSMs, jointly with some of the mixtures of the CCQM-K111 comparison. The propane was subjected to a purity analysis in accordance with ISO 19229 [4] prior to use for preparation of the gas mixtures.

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

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

2.3 Measurement protocol

The measurement protocol requested the participating 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 participant was also requested to submit a summary of their uncertainty evaluation used for estimating 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	Event
May 2015	Agreement of protocol
July 2015	Preparation of mixture
July 2015	Verification of mixture compositions
October 2015	Dispatch of mixture
February 2016	Reports and cylinder arrived at VSL
March 2016	Re-verification of the mixtures
March 2016	Draft A report available
November 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) ($x_{i,\mathrm{grav}}$)
2. purity of the parent gases ($\Delta x_{i,\mathrm{purity}}$)
3. stability of the gas mixture ($\Delta x_{i,\mathrm{stab}}$)
4. correction due to partial recovery of a component ($\Delta x_{i,\mathrm{nr}}$)

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

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

The equation for calculating the associated standard uncertainty reads as

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

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 [6]

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

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 [7] and takes advantage of the work done in the gravimetry study CCQM-P41 [8].

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

$$u^2\left(x_{i,\mathrm{ref}}\right) = u^2\left(x_{i,\mathrm{prep}}\right) + u^2\left(x_{i,\mathrm{ver}}\right) \tag{4}$$

The value for $u_{i,\mathrm{ver}}$ is in the table containing the results of this key comparison.

2.6 Measurement methods

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

Table 3: Summary of calibration methods and metrological traceability

Laboratory code	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
NMISA	22/23 December 2015 19 January 2016	ISO 6143	Own standards (ISO 6142)	Nitrogen	GC-FID

2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

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

and the uncertainty associated with the difference d_i at 95% level of confidence. Here $x_{i,\mathrm{ref}}$ denotes the key comparison reference value, and x_i the result of laboratory i.[1]

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

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

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 table 4, the following data is presented

x_{prep} amount of substance fraction, from preparation (µmol/mol)
u_{prep} standard uncertainty of x_{prep} (µmol/mol)
u_{ver} standard uncertainty from verification (µmol/mol)
u_{ref} standard uncertainty of reference value (µmol/mol)
x_{lab} result of laboratory (µmol/mol)
U_{lab} stated uncertainty of the laboratory, at 95 % level of confidence (µmol/mol)
k_{lab} stated coverage factor
d_i difference between the 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 (µmol/mol)

Table 4: Results of CCQM-K111.1

Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	d_i	k	$U(d_i)$
NMISA	M937404	1013.0	0.27	0.24	0.36	1012.5	3.4	2	-0.5	2	3.5

In figure 1 the degrees of equivalence for the participating laboratory are given, together with those from CCQM-K111 [11], relative to the gravimetric value. The uncertainties are, as required by the MRA [9], given as 95% confidence 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 laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

[1] Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

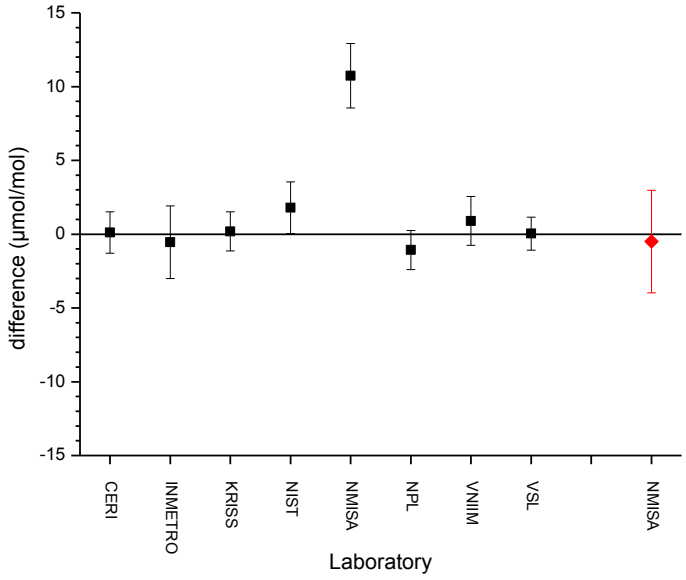

Figure 1: Degrees of equivalence in CCQM-K111 (squares) and CCQM-K111.1 (diamond)

4 Supported CMC claims

The results of this key comparison can be used to support CMCs as described in the final report of CCQM-K111 [11], with the exception of the track A regime (see also the GAWG Strategy [2]).

5 Discussion and conclusions

The result of the participating laboratory is consistent with the key comparison reference value within the respective expanded uncertainties and deviates less than 0.1 %.

References

[1] Alink A., "The first key comparison on Primary Standard gas Mixtures", Metrologia **37** (2000), pp. 35-49

[2] Brewer P.J., Van der Veen A.M.H., "GAWG strategy for comparisons and CMC claims", CCQM Gas Analysis Working Group, April 2016

[3] Van der Veen A.M.H., Cox M.G., "Degrees of equivalence across key comparisons in gas analysis", Metrologia **40** (2003), pp. 18-23

[4] International Organization for Standardization, ISO 19229:2015 Gas analysis -- Purity analysis and the treatment of purity data, 1st edition

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

[6] Alink A., Van der Veen A.M.H., "Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry", Metrologia **37** (2000), pp. 641-650

[7] Van der Veen A.M.H, De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report, 2000

[8] Van der Veen A.M.H., Brinkmann F.N.C., Arnautovic M., Besley L., Heine H.-J., Lopez Esteban T., Sega M., Kato K., Kim J.S., Perez Castorena A., Rakowska A., Milton M.J.T., Guenther F.R., Francy R., Dlugokencky E., "International comparison CCQM-P41 Greenhouse gases. 2. Direct comparison of primary standard gas mixtures", Metrologia **44** (2007), Techn. Suppl. 08003

[9] CIPM, "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes", Sèvres (F), October 1999

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

[11] Van der Veen A.M.H., Van der Hout J.W., Ziel P.R., Oudwater R.J., Fioravante A.L., Augusto C.R., Brum M.C., Uehara S., Akima D., Bae H.K., Kang N., Woo J.C., Liaskos C.E., Roderick G.C., Jozela M., Tshilongo J., Ntsasa N.G., Botha A., Brewer P.H., Brown A.S., Bartlett S., Downey M.L., Konopelko L.A., Kolobova A.V., Pankov A.A., Orshanskaya A.A., Efremova O.V., "International Comparison CCQM-K111 – Propane in nitrogen", Final Report, Metrologia Techn. Suppl. **54** (2017), 08009

Coordinator

VSL
Chemistry Group
J. Wouter van der Hout
Thijsseweg 11
2629 JA Delft
the Netherlands
Phone +31 15 269 1500
E-mail wvdhout@vsl.nl

Project reference

CCQM-K111.1

Completion date

October 2016

Measurement Report NMISA

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

Cylinder number: M93 7404

Measurement 1[#]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_3H_8	22/12/2015	1012,59	0,10	4

Measurement 2[#]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_3H_8	23/12/2015	1012,54	0,02	11

Measurement 3[#]

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_3H_8	19/01/2016	1012,49	0,01	10

Result

Component	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
C_3H_8	1012,5	3,4	k =2

Reference Method:

The value assigned to the comparison mixture was obtained by comparing the comparison sample against gravimetrically prepared NMISA C_3H_8 in nitrogen gas mixtures. The comparison was done using a Gas chromatography coupled with a flame ionisation detector (GC- FID).

Instrumentation:

The propane was analyzed using a Varian CP3800 gas chromatography technique coupled flame ionisation detector (GC/FID). A packed 1.83 m stainless steel column with 80/100 mesh Porapak-Q was used to separate the C_3H_8 from other components in the mixture. The column temperature was 150 ^{0}C with a helium carrier flow of 40 mL/min. The GC-FID system, set at 300 ^{0}C, was fuelled with synthetic air at 330 mL/min and hydrogen at 30 mL/min. Samples were introduced onto the column via a 6-port stainless steel gas sampling valve equipped with a 250 µL stainless steel sample loop. Each sample in the measurement sequence was injected seven (7) times and the responses were averaged.

Sample handling:

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

Calibration standards:

The calibration standards consisted of a set of six (6) PSGMs of 1000 µmol/mol C_3H_8 in nitrogen. Primary standard gas mixtures (PSGMs) used for the calibration were prepared from pre-mixtures in accordance with ISO 6142:2001 (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.Table 5 summarises the six (6) calibration PSGMs prepared.

The six gas mixtures were analysed using substitution method (A-B-A method), where 'A' and 'B' represents the reference and sample respectively. One of the gas standards was chosen as a reference cylinder. The reference mixture was analysed before and after the sample, a typical sequence follows: A, B, A_1, C, A_2 until all six samples have been analysed. This was to ensure that the repeatability, correction of drift and changes during the analysis was accurately done. Cylinder M39 5419, M39 5413 and M9 3802 were selected as the calibration standards for the CCQM-K111.1 comparison.

Table 5: Calibration standards prepared for the intercomparison

Certificate/Cylinder number	**C_3H_8 gravimetric concentration ($\times 10^{-6}$ mol/mol)**	**C_3H_8 Standard uncertainty ($\times 10^{-6}$ mol/mol)**
NMISA10005402	998,8	0,90
NMISA10005413	1000,2	0,85
NMISA10005419	999,9	0,90
NMISA10005427	1001,6	0,90
NMISA50003802	1009,6	0,90
NMISA40003954	1023,4	0,90

Calibration method and value assignment

The reference mixture was analyzed before and after the sample analysis using the Borda (substitution) method (i.e brackets the sample, ABA method). Data analysis calculation for the CCQM-K111.1 cylinder and the reference cylinder included the following: average response (peak area), standard deviation, %RSD, ESDM and drift during the analysis and sensitivity of the reference cylinder. Sensitivity is calculated as (average response/mole fraction of the reference gas standard).

The model equation used to calculate the mole fraction of the sample is showed in equation 1:

$$C_{sample} = \frac{A_{Sample}}{A_{Reference}} \times C_{reference} \quad (1)$$

where the C_{sample}, A_{sample}, $A_{reference}$, and $C_{reference}$ represent mole fraction of the sample, area of the sample, area of the reference and the mole fraction of the reference, respectively.

Uncertainty:

All measured data and calculations for the component concentrations of cylinder no. M39 7404 were reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose significance required quantification. These uncertainty contributions are shown in table 6.

Table 6: The uncertainty budget of the standard uncertainties for the comparison sample

Parameter		**Standard uncertainty**
Gravimetric uncertainty	- Weighing uncertainty - Purity analysis	0,085 % rel.
Verification uncertainty		0,14 % rel.
Stability uncertainty		0,006 % rel.

Table 7 shows the final mole fraction and uncertainty for the comparison sample after analysis the sample for a minimum of three measurements.

Table 7: Final results for the comparison sample

Reported Value (µmol/mol)	1012,5
Combined uncertainty (µmol/mol)	1,7
Reported Uncertainty (µmol/mol)	3,4
Coverage Factor (k =2)	2

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

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