CCQM-K118.1 – Natural Gas

Adriaan M H van der Veen[1], Danique van Workum[1], Roel Beelen[1], Heinrich Kipphardt[2], Dirk Tuma[2], Florbela Dias[3], Cristina Palma[3], Jinsang Jung[4], Ji-Hwan Kang[4], One Heo[4], Hwan Lee[4], Jisik Jeong[4], Serhiy Kisel[5], Ovsiy Levbarg[5], Yaroslav Nikolaiev[5], Serhiy Shpilnyi[5], and Stanislav Yakubov[5]

[1]Van Swinden Laboratorium (VSL), Thijsseweg 11, 2629 JA Delft, The Netherlands
[2]Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstätter-Str. 11, 12489 Berlin, Germany
[3]Instituto Português da Qualidade, Rua António Gião 2, 2829-513 Caparica, Portugal
[4]Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea
[5]Pan-Ukrainian State Research and Production Center for Standardization, Metrology, Certification and Consumers Rights Protection, Metrolohichna St, 4, Kyiv, Ukraine, 03143

16 November 2026

Table of Contents

Field **1**
Subject **1**
1 Introduction **1**
2 Design and organisation of the key comparison **2**
2.1 Participants . . . 2
2.2 Measurement standards . . . 2
2.3 Measurement protocol . . . 3
2.4 Schedule . . . 3
2.5 Measurement equation . . . 3
2.6 Measurement methods used by the participants . . . 5
2.7 Analysis of the travelling standards . . . 5
2.8 Link to CCQM-K118 . . . 6
2.9 Degrees of equivalence . . . 8
3 Results **8**
4 Support to CMC claims **28**
5 Conclusions **29**
Coordinator **29**
Project reference **29**
Completion date **30**
A List of symbols and subscripts **31**
A.1 Symbols . . . 31
A.2 Subscripts . . . 31
B Measurement report of the participating institutes **32**

Field

Amount of substance

Subject

Composition of natural gas (track C key comparison)

1 Introduction

Natural gas is one of the principal energy vectors in economies around the world. It is traded either on quantity (volume or mass) or energy basis. Natural gas is a fossil fuel and its economic value per unit of volume or mass is mainly determined by its calorific value. The measurement of the composition of natural gas mixtures is commonly used for the calculation of its calorific value, among other thermodynamical properties, such as density and Wobbe index [1]. These properties are relevant for custody transfer of natural gas and related energy gases. Other aspects that may impact the economic value of natural gas, such as its sulfur content, have not been addressed in this key comparison.

At the highest metrological level, natural gas standards are commonly prepared using static gravimetry [2–4] as primary standard gas mixtures (PSMs) [5]. An overview of the natural gas types used in previous key comparisons (CCQM-K1 [6, 7], CCQM-K16 [8, 9], CCQM-K23 [10, 11]) is given in Table 1. The Roman numbers in the column headings are the designations of the compositions as used in the corresponding key comparisons.

Table 1: Nominal compositions of the travelling standards used in the natural gas key comparisons since CCQM-K1, expressed in amount fractions ($\mathrm{cmol\,mol^{-1}}$)

	CCQM-K1 1996-1997			CCQM-K16 2001-2002		CCQM-K23 2004-2006			CCQM-K118 2017	
	I	II	III	IV	V	Ia	IIIa	IIa	IVa	LNG
Methane	90.8	76.2	81.5	81.85	82.16	90.6	81.4	75.4	78.85	87.52
Ethane	3	9.4	3	0.75	11	3	3	9.4	0.75	10
Propane	1	3.4	0.5	0.3	4.5	1	0.5	3.4	0.3	2
iso-Butane				0.2	0.1	0.2	0.1	0.8	0.2	0.15
n-Butane	0.2	1	0.1	0.2	0.1	0.2	0.1	1	0.2	0.15
iso-Pentane				0.05	0.035				0.05	0.02
n-Pentane				0.05	0.035				0.05	0.02
neo-Pentane				0.05	0.05				0.05	
n-Hexane				0.05	0.02				0.05	
Nitrogen	4	7	14.4	12	1.2	4	14.4	7	12	0.12
Carbon dioxide	1	3	0.5	4	0.8	1	0.5	3	4	0.02
Helium				0.5					0.5	
Hydrogen									3	

In this follow-up key comparison of CCQM-K118 [12], travelling standards for type IVa natural gas (see Table 1) were used. After consultation with the CCQM Gas Analysis Working Group (CCQM-

GAWG), it was decided to use a protocol for this key comparison which resembled that of CCQM-K23 [10,11] and CCQM-K16 [8] instead of the consensus-value based approach of CCQM-K118 [12]. In the meantime, an assessment of the traditional approach of natural gas key comparisons using a key comparison reference value (KCRV) from static gravimetric gas mixture preparation and a consensus value was made [13], from which it was concluded that these approaches yield generally similar outcomes in terms of the degrees of equivalence (DoEs).

This key comparison aims to support Calibration and Measurement Capabilities (CMCs) for the amount fractions of the components in type IVa natural gas (i.e., nitrogen, carbon dioxide, helium, hydrogen, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, neo-pentane, n-hexane and methane) . It is organised on behalf of the CCQM-GAWG of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) in accordance with the provisions of the CIPM Mutual Recognition Arrangement (CIPM MRA) [14, 15] of the International Committee for Weights and Measures (CIPM).

2 Design and organisation of the key comparison

2.1 Participants

Table 2 lists the participants in this key comparison.

Table 2: Participating national metrology institutes (NMIs) in CCQM-K118.1

Acronym	Country	Institute
BAM	DE	Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
IPQ	PT	Instituto Português da Qualidade, Monte de Caparica, Portugal
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
UkrCSM	UA	SE “Pan-Ukrainian State Research and Production Center for Standardization, Metrology, Certification and Consumers Rights Protection” (SE “Ukrmetrteststandart”), Kyiv, Ukraine
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

BAM supported the coordinator VSL in this key comparison in confirming the KCRVs for in particular the amount fraction methane. Consequently, no degrees of equivalence were calculated in this key comparison for BAM.

2.2 Measurement standards

A set of four mixtures was prepared gravimetrically by VSL in accordance with ISO 6142-1 [2, 3], using carbon dioxide grade 5.5, ethane grade 5.5, propane grade 5.0, n-butane grade 3.8, iso-butane grade 3.8, n-pentane grade 2.5, iso-pentane grade 2.5, neo-pentane grade 2.0, n-hexane with 99.9% purity, helium grade 6.7, hydrogen grade 6.6, nitrogen grade 6.8 and methane grade 5.5. Carbon dioxide, nitrogen and methane were transferred from the pure gas.

Ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, neo-pentane and hydrogen were transferred from pre-mixtures obtained with one dilution step from the pure gas. Helium was transferred from the pre-mixture obtained with two dilution steps from the pure gas. All pure gases were subjected to a purity analysis in accordance with ISO 19229 [4] prior to use for preparation of the gas mixture. n-Hexane was transferred from a pre-mixture obtained by injection of the pure liquid into the matrix gas [2, 16].

The filling pressure in the cylinder was approximately 7 MPa. Aluminium cylinders having a volume of 5 L with an Aculife IV treatment were used. The mixture composition and its associated uncertainty was calculated in accordance with ISO 6142-1 [2,3]. The mixtures were verified against VSL's PSMs.

2.3 Measurement protocol

The measurement protocol requested the participants to perform at least three (3) measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participant about the nominal amount fraction ranges (see Table 1, type IVa). The participant was requested to submit a description of their method and a full description of their uncertainty evaluation used for evaluating the uncertainty of their result.

The results from BAM were used to confirm that the coordinating laboratory had satisfactorily addressed the issue that arose during CCQM-K118 [12] concerning the separation of hydrogen and methane which led to a discrepant result for the amount fraction methane. Prior to this key comparison, the issue had been resolved and based on the evidence of these remedial actions new CMCs were submitted by VSL and published in the key comparison database (KCDB).

2.4 Schedule

The schedule of this key comparison was as follows (see Table 3).

Table 3: Schedule

Date	Event
Apr 2023	Agreement of protocol
Sep 2023	Preparation of the mixtures
Dec 2023	Characterisation of mixture compositions
Jan 2024	Dispatch of the mixtures
Oct 2025	Measurements by the participants
Nov 2025	Measurement report due
Feb 2026	Return of cylinders
Mar 2026	Re-characterisation of the mixtures
Mar 2026	Draft A1 report available

2.5 Measurement equation

The KCRVs are based on the weighing data, the molar masses of the components and the purity verification of the parent gases. The 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:

— gravimetric preparation (weighing process) ($x_{i,\mathrm{grav}}$)

— purity of the parent gases ($\Delta x_{i,\mathrm{purity}}$)

— stability of the gas mixture ($\Delta x_{i,\mathrm{stab}}$)

— 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 [6, 8, 10, 11]. These terms are set to zero, and so are their associated standard uncertainties.

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

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

Using the law of propagation of uncertainty (LPU) from the JCGM 100:2008 [17] for mutually independent quantities provides the equation for calculating the associated standard uncertainty which takes the form

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

The results of the amount fractions of one of the travelling standards are shown in Table 4.

Table 4: Composition of the travelling standard VSL173626, expressed in amount fractions (cmol mol^{-1}). The standard uncertainties cover the preparation only.

Component	x_{prep}	$u(x_{\mathrm{prep}})$
Methane	78.8433	0.0006
Ethane	0.752 839	0.000 024
Propane	0.300 704	0.000 010
iso-Butane	0.200 733	0.000 017
n-Butane	0.200 093	0.000 020
neo-Pentane	0.050 046	0.000 010
iso-Pentane	0.050 020	0.000 012
n-Pentane	0.050 583	0.000 012
n-Hexane	0.049 977	0.000 036
Nitrogen	12.001 58	0.000 48
Carbon dioxide	3.988 57	0.000 13
Hydrogen	3.012 36	0.000 20
Helium	0.498 608	0.000 030

The validity of the compositions of the mixture 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 [2]:

$$\left|x_{i,\text{prep}} - x_{i,\text{ver}}\right| \leq 2\sqrt{u^2(x_{i,\text{prep}}) + u^2(x_{i,\text{ver}})} \tag{3}$$

The factor 2 is a coverage factor (assuming a normal distribution, 95 % level of confidence). The assumption was made that both preparation and verification are unbiased, which is in line with the assumptions made in previous key comparisons [6, 8, 10, 11] and confirmed in the literature [13]. 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-K23 [10, 11].

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

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

2.6 Measurement methods used by the participants

The measurement methods used by the participants are described in annex B of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established is given in Table 5.

Table 5: Overview of calibration methods and metrological traceability

Lab	Measurement dates	Calibration method	Gas standards	Measurement technique
BAM	3-26 March 2025	Bracketing	Own standards (ISO 6142-1)	GC/TCD/FID
IPQ	13-26 May 2025	ISO 6143	Own standards (ISO 6142-1)	GC/TCD/FID
KRISS	10-15 June 2025	Bracketing	Own standards (ISO 6142-1)	GC/TCD/FID
UkrCSM	27 October 2025 – 14 November 2025	ISO 6143	Own standards (ISO 6142-1)	GC/TCD/FID
VSL	10 September 2024 — 19 January 2025	ISO 6143	Own standards (ISO 6142-1)	GC/TCD/FID

2.7 Analysis of the travelling standards

The travelling standards were analysed by the coordinating laboratories before shipment to the participating National Metrology Institutes (NMIs) and after being returned. The data from these analyses were used to

— evaluate the stability of the amount fractions of the components;

— evaluate the homogeneity of the amount fraction of the components;

— calculate corrections to the amount fractions reported by the participants for the calculation of the KCRVs.

The verification analyses of all components save neo-pentane and n-hexane were performed on a four-channel Agilent 8890 GC custom configured for the analysis of the composition of natural gas and biogas. The configuration of this instrument is as follows:

— 1st channel, suitable for analysis of C_1 – C_6: This channel is configured with a PDMS column in the main oven with hydrogen as carrier gas, detection is performed using a FID detector.
— 2nd channel, suitable for analysis of C_1 – C_2: This channel is configured with a pre-column with backflush in the aux oven and the analytical 1/8" Porapak Q analysis column in the main oven, as carrier helium is used and detection is performed using a FID detector.
— 3rd channel, suitable for analysis of CO_2, C_2H_6, Ar/O_2, N_2, CH_4: This channel is configured with a analytical hayesep column with backflush in the aux oven and a capillary molsieve 5A column with isolation option in the aux oven, as carrier helium is used and detection is performed using a TCD detector.
— 4th channel, suitable for the analysis of He, H_2, O_2 and N_2: This channel is configured with a molsieve pre-column with backflush in the injector oven and a analytical molsieve column in the injector oven, as carrier argon is used and detection is performed using a TCD detector.

The temperature program for the 1st and 2nd channels starts at 35 °C for 10.7 minutes, followed by a temperature program of 20 °C min^{-1} to 165 °C, hold for 0.9 minutes. The other channels have no temperature program and are kept at 70 °C isothermal. The data collection is performed using Openlab software.

The analyses for neo-pentane and n-hexane were performed on an Agilent 7890A GC, configured for the analysis of the composition of natural and refinery gas. Only the front channel is used, which consists of a split/splitless inlet set to a split ratio of 1:15 and a 25 µL sample loop. On an oven programmed run all hydrocarbons are then separated using a pre-column and an aluminum oxide plot column, with helium as carrier. The temperature program for the front channel starts at 80 °C for 2 minutes, followed by a temperature program of 35 °C min^{-1} to 185 °C, hold for 2 minutes. The data collection is performed using Openlab software.

In the final verification analysis, a different gas chromatograph (GC) was used for the analysis of n-hexane. The configuration of this an Agilent 7980A equipped with [12]:

— a 30 m × 0.53 µm × 5.00 µm PDMS-1 column and a flame ionisation detector (FID) for the analysis of the hydrocarbons from ethane onward;
— a 0.25 m micropacked HayeSep Q and a 3 m Sulfinert (100/200) HayeSep T column and a thermal conductivity detector (TCD) for the analysis of methane, carbon dioxide, and nitrogen.

The relative differences with respect to the amount fractions computed in accordance with ISO 6142-1 [2] are shown in Table 6. The standard uncertainty from verification was computed by squaring the relative differences and taking the average. The suqare root of this average was used as standard uncertainty from verification.

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.

2.8 Link to CCQM-K118

The link to the KCRVs of CCQM-K118 [12] was established by including one of the retained travelling standards in the verification measurements performed by the coordinating laboratory. All mixtures were analysed using the method of ISO 6143 [18]. For the results from the static gravimetry, it

Table 6: Relative differences from the mixture verification with respect to the amount fractions gravimetric gas mixture preparation (%)

Component	Instrument	Channel	VSL173513	VSL173626	VSL173509	VSL173520	Pooled
Methane	GC-23	FIDA	0.011	-0.012	-0.017	-0.019	0.015
Ethane	GC-23	FIDA	-0.054	-0.010	-0.019	0.005	0.029
Propane	GC-23	FIDA	-0.079	-0.013	-0.006	-0.007	0.040
iso-Butane	GC-23	FIDA	-0.097	-0.050	-0.070	-0.030	0.067
n-Butane	GC-23	FIDA	-0.077	-0.020	-0.070	-0.025	0.054
neo-Pentane	GC-2	FID	0.020	0.081	0.149	0.000	0.085
iso-Pentane	GC-23	FIDA	-0.089	-0.043	-0.017	-0.032	0.053
n-Pentane	GC-23	FIDA	-0.119	-0.074	-0.042	-0.140	0.101
n-Hexane	GC-2	FID	-0.126	0.074	-0.152	0.000	0.106
Carbon dioxide	GC-23	TCDC	-0.025	-0.051	-0.077	-0.030	0.050
Nitrogen	GC-23	TCDC	0.050	0.017	0.006	-0.067	0.043
Helium	GC-23	TCDD	0.096	-0.009	-0.101	0.000	0.070
Hydrogen	GC-23	TCDD	0.133	0.074	0.002	0.000	0.076

was required that the compositions from preparation and from analysis met the criterion given in equation (3). For the retained travelling standard from CCQM-K118, the criterion for the link was

$$\left|x_{i,\mathrm{ver}} - x_{i,\mathrm{KCRV}}\right| \leq 2\sqrt{u^2(x_{i,\mathrm{ver}}) + u^2(x_{i,\mathrm{KCRV}})} \tag{5}$$

for the amount fractions of each of the components, where $x_{i,\mathrm{ver}}$ denotes the amount fraction of component i in the retained travelling standard from CCQM-K118. Based on the considerations for linking key comparisons in the gas analysis area [19], there is no adjustment necessary for the amount fractions calculated in accordance with ISO 6142-1 [2, 3]. These can be used as KCRVs in this follow-up key comparison and also be used to develop bilateral DoEs as appropriate [19].

One of the travelling standards from CCQM-K118 [12] was included in the verification measurements. The results of the comparison with the KCRV from CCQM-K118 are shown in Table 7. In the right-most column, the normalised errors are shown which indicate that the results are consistent within the respective uncertainties. So, the KCRVs established in this key comparison are comparable to that in CCQM-K118. No extra uncertainty needs to be taken into account [19].

Table 7: Comparison between the KCRV from CCQM-K118 for travelling standard WF2727 and the re-verification in this key comparison (cmol mol^{-1}). Uncertainties are stated as expanded uncertainties ($k = 2$).

Component	x_{K118}	$U(x_{K118})$	x_{ver}	$U(x_{ver})$	E_n
Methane	78.8836	0.0340	78.8577	0.0128	−0.71
Ethane	0.744 99	0.001 20	0.745 61	0.000 26	0.50
Propane	0.298 58	0.000 47	0.298 64	0.000 08	0.14
iso-Butane	0.199 83	0.000 18	0.199 66	0.000 09	−0.85
n-Butane	0.199 96	0.000 23	0.199 80	0.000 08	−0.67
neo-Pentane	0.049 357	0.000 106	0.049 359	0.000 040	0.02
iso-Pentane	0.049 875	0.000 119	0.049 863	0.000 020	−0.10
n-Pentane	0.050 193	0.000 114	0.050 240	0.000 017	0.41
n-Hexane	0.049 714	0.000 135	0.049 641	0.000 081	−0.47
Carbon dioxide	4.0049	0.0039	4.0026	0.0022	−0.50
Nitrogen	11.9843	0.0113	11.9800	0.0023	−0.38
Helium	0.502 02	0.000 83	0.501 54	0.000 18	−0.57
Hydrogen	2.9994	0.0059	3.0018	0.0012	0.41

2.9 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined in the CIPM MRA as [14]

$$d_i = x_{i,\mathrm{lab}} - x_{i,\mathrm{KCRV}}, \tag{6}$$

and the uncertainty of the difference d_i at 95 % level of confidence. Here $x_{i,\mathrm{KCRV}}$ denotes the KCRV (the amount fraction from preparation, $x_{i,\mathrm{prep}}$), and x_i the result of laboratory i. The standard uncertainty of d_i can be expressed as (see also equation (4))

$$\begin{aligned} u^2(d_i) &= u^2(x_{i,\mathrm{lab}}) + u^2(x_{i,\mathrm{prep}}) + u^2(x_{i,\mathrm{ver}}) \\ &= u^2(x_{i,\mathrm{lab}}) + u^2(x_{i,\mathrm{KCRV}}) \end{aligned}$$

assuming that the aggregated error terms are uncorrelated. As discussed, the standard uncertainty associated with the KCRVs comprises that from preparation and that from verification for the mixture involved.

The consensus values and the values for the excess standard deviation of CCQM-K118 for natural gas type IVa are given in Table 8.

3 Results

Figure 1 shows the results for the amount fraction nitrogen for the four travelling standards. The results and KCRVs are shown in Table 9 and the degrees of equivalence are shown in Figure 2. All results are consistent with the KCRV.

In Table 9 and the subsequent tables in this section, x_{ref} denotes the KCRV, $u(x_{prep})$ the standard uncertainty due to static gravimetric gas mixture preparation, $u(x_{ver})$ the standard uncertainty due

Table 8: Consensus values (μ) and the values for the excess standard deviation (τ) of CCQM-K118 for natural gas type IVa [12]

Component	μ cmol mol^{-1}	$u(\mu)$ cmol mol^{-1}	τ cmol mol^{-1}
Methane	78.881	0.013	0.017
Ethane	0.745 01	0.000 39	0.000 56
Propane	0.298 49	0.000 18	0.000 30
iso-Butane	0.199 75	0.000 08	0.000 10
n-Butane	0.199 88	0.000 11	0.000 18
iso-Pentane	0.049 85	0.000 06	0.000 11
n-Pentane	0.050 17	0.000 05	0.000 09
neo-Pentane	0.049 34	0.000 05	0.000 08
n-Hexane	0.049 70	0.000 06	0.000 11
Nitrogen	11.9848	0.0056	0.0079
Carbon dioxide	4.0044	0.0017	0.0024
Hydrogen	3.0007	0.0029	0.0046
Helium	0.502 25	0.000 39	0.000 48

to verification, $u(x_{\text{ref}})$ the standard uncertainty associated with the KCRV, x_{lab} the value stated by the participant, $U(x_{\text{lab}})$ the expanded uncertainty stated by the participant, k_{lab} the coverage factor stated by the participant, d the difference of the degree of equivalence, $U(d)$ the expanded uncertainty of the degree of equivalence and k_{d} the coverage factor of the degree of equivalence. A glossary of symbols is given in annex A.

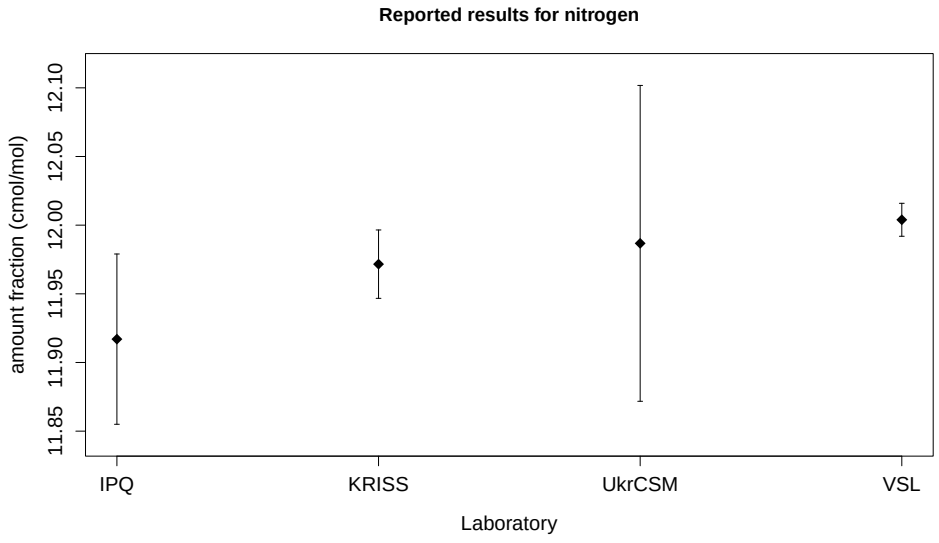


Figure 1: Reported results for the amount fraction nitrogen (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 9: Results, key comparison reference values and degrees of equivalence for the amount fraction nitrogen ($\mathrm{cmol\,mol^{-1}}$)

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	11.9317	0.0005	0.0051	0.0052	11.9170	0.0620	2	-0.015	0.063	2
KRISS	11.9767	0.0005	0.0051	0.0052	11.9716	0.0249	2	-0.005	0.027	2
UkrCSM	12.0248	0.0005	0.0052	0.0052	11.9868	0.1150	2	-0.038	0.115	2
VSL	12.0016	0.0005	0.0052	0.0052	12.0039	0.0120	2	0.002	0.016	2

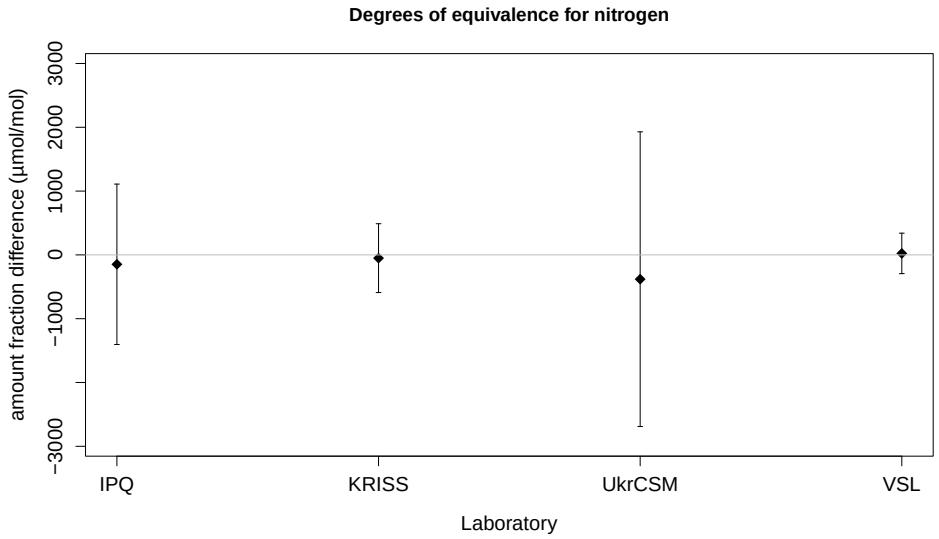


Figure 2: Degrees of equivalence for the amount fraction nitrogen ($\mu\mathrm{mol\,mol^{-1}}$). The uncertainty bars indicate expanded uncertainties.

Figure 3 shows the results for the amount fraction carbon dioxide for the four travelling standards. The results and KCRVs are shown in Table 10 and the degrees of equivalence are shown in Figure 4. All results are consistent with the KCRV.

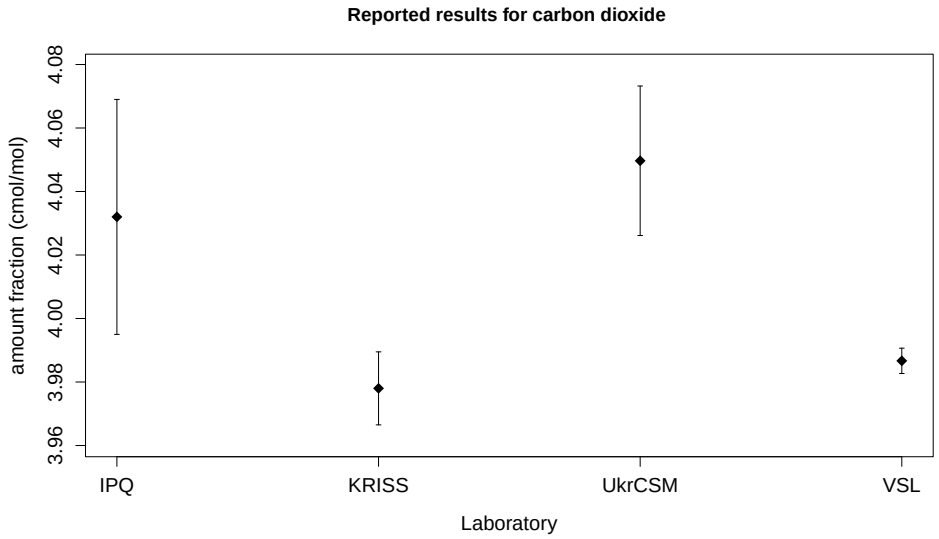


Figure 3: Reported results for the amount fraction carbon dioxide (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 10: Results, key comparison reference values and degrees of equivalence for the amount fraction carbon dioxide (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	4.02302	0.00014	0.00060	0.00062	4.0320	0.0370	2	0.0090	0.0370	2
KRISS	3.97935	0.00013	0.00060	0.00061	3.9780	0.0115	2	-0.0014	0.0116	2
UkrCSM	4.05968	0.00014	0.00061	0.00062	4.0497	0.0235	2	-0.0100	0.0236	2
VSL	3.98857	0.00013	0.00060	0.00061	3.9867	0.0040	2	-0.0019	0.0042	2

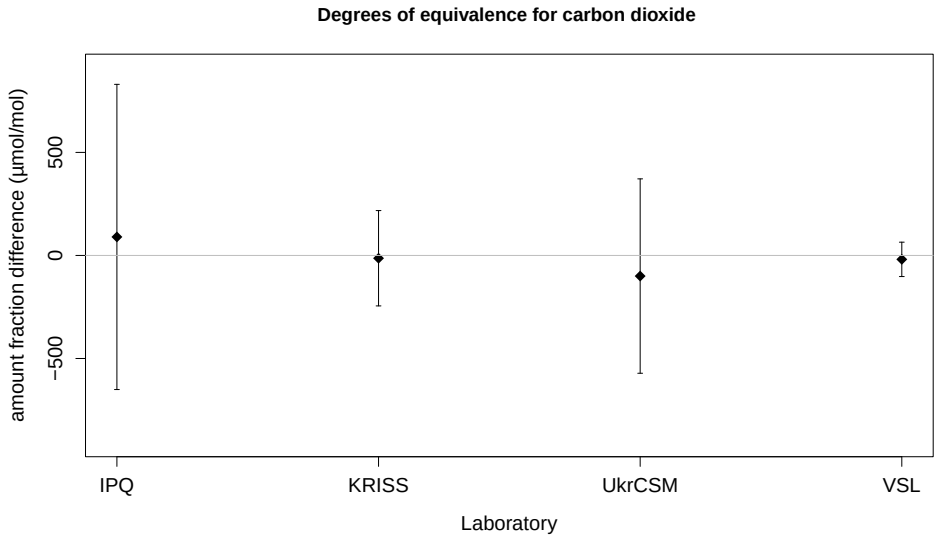


Figure 4: Degrees of equivalence for the amount fraction carbon dioxide (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 5 shows the results for the amount fraction hydrogen for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 11 and the degrees of equivalence are shown in Figure 6. All results are consistent with the KCRV.

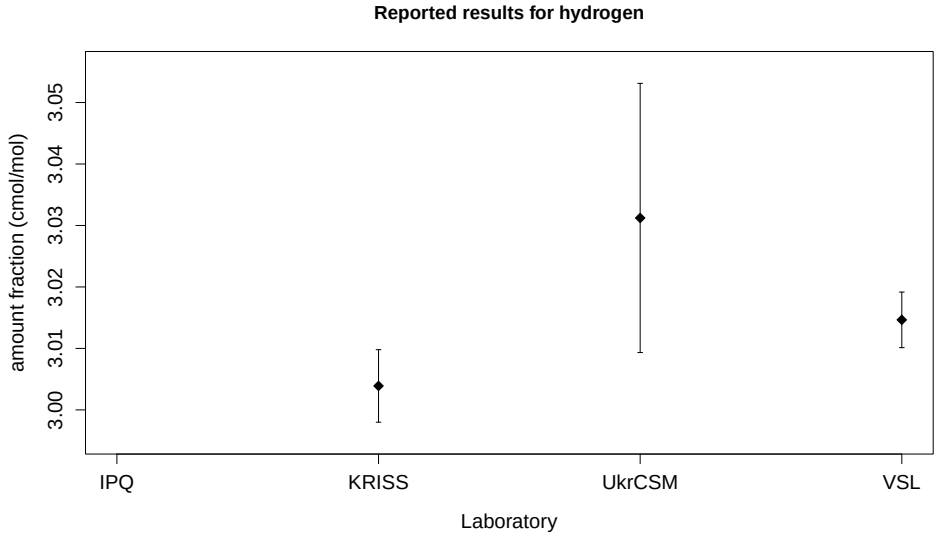


Figure 5: Reported results for the amount fraction hydrogen (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 11: Results, key comparison reference values and degrees of equivalence for the amount fraction hydrogen ($\mathrm{cmol\,mol^{-1}}$)

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	3.01572	0.00021	0.00229	0.00230						2
KRISS	3.00626	0.00020	0.00228	0.00229	3.0039	0.0059	2	-0.0024	0.0075	2
UkrCSM	3.03602	0.00021	0.00231	0.00232	3.0312	0.0219	2	-0.0048	0.0224	2
VSL	3.01236	0.00020	0.00229	0.00230	3.0146	0.0045	2	0.0023	0.0064	2

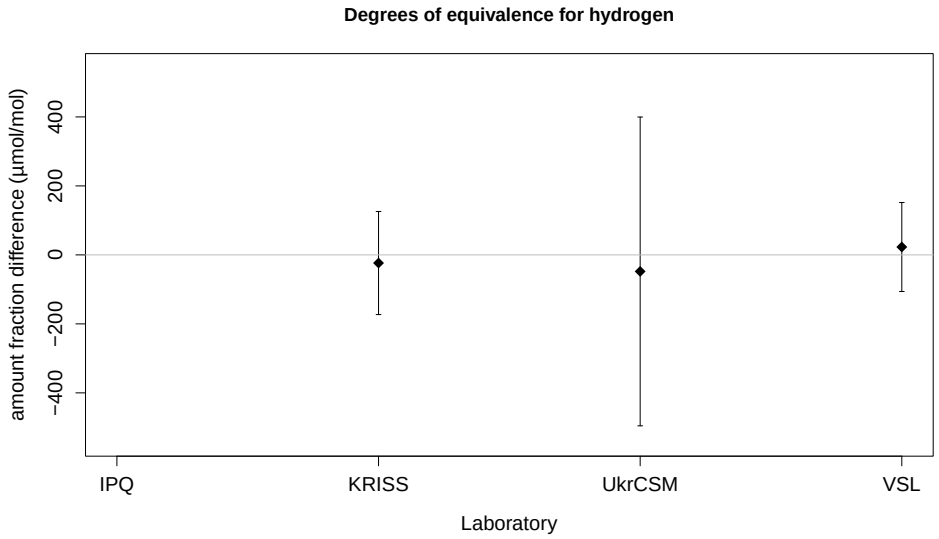


Figure 6: Degrees of equivalence for the amount fraction hydrogen ($\mu\mathrm{mol\,mol^{-1}}$). The uncertainty bars indicate expanded uncertainties.

Figure 7 shows the results for the amount fraction helium for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 12 and the degrees of equivalence are shown in Figure 8. All results are consistent with the KCRV.

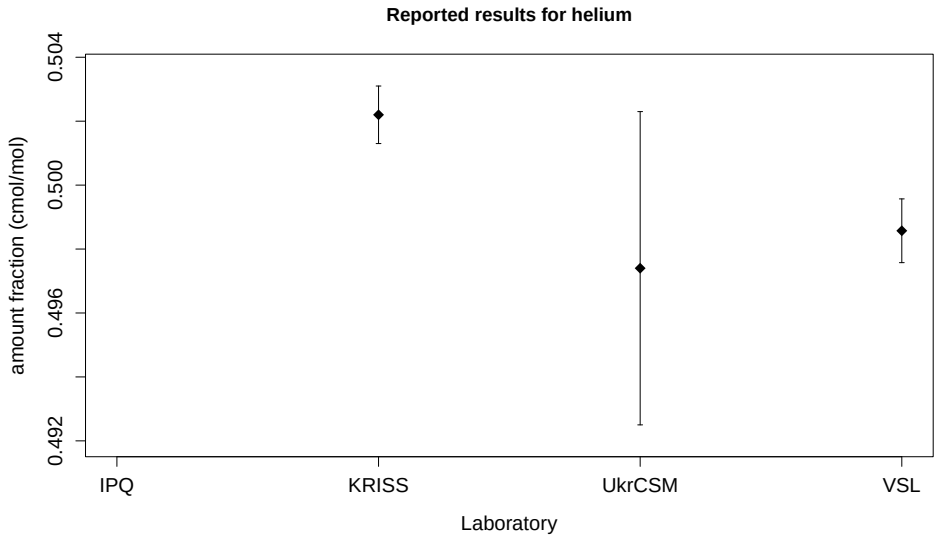


Figure 7: Reported results for the amount fraction helium (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 12: Results, key comparison reference values and degrees of equivalence for the amount fraction helium (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.50210	0.00003	0.00035	0.00035						2
KRISS	0.50279	0.00003	0.00035	0.00035	0.5022	0.0009	2	-0.0006	0.0011	2
UkrCSM	0.49801	0.00003	0.00035	0.00035	0.4974	0.0049	2	-0.0006	0.0049	2
VSL	0.49861	0.00003	0.00035	0.00035	0.4986	0.0010	2	-0.0000	0.0012	2

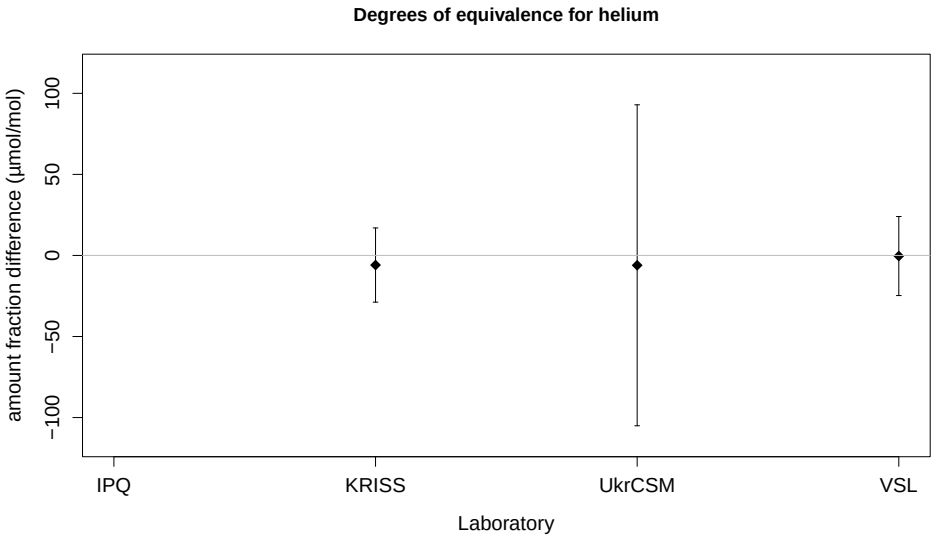


Figure 8: Degrees of equivalence for the amount fraction helium (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 9 shows the results for the amount fraction ethane for the four travelling standards. The results and KCRVs are shown in Table 13 and the degrees of equivalence are shown in Figure 10. All results are consistent with the KCRV.

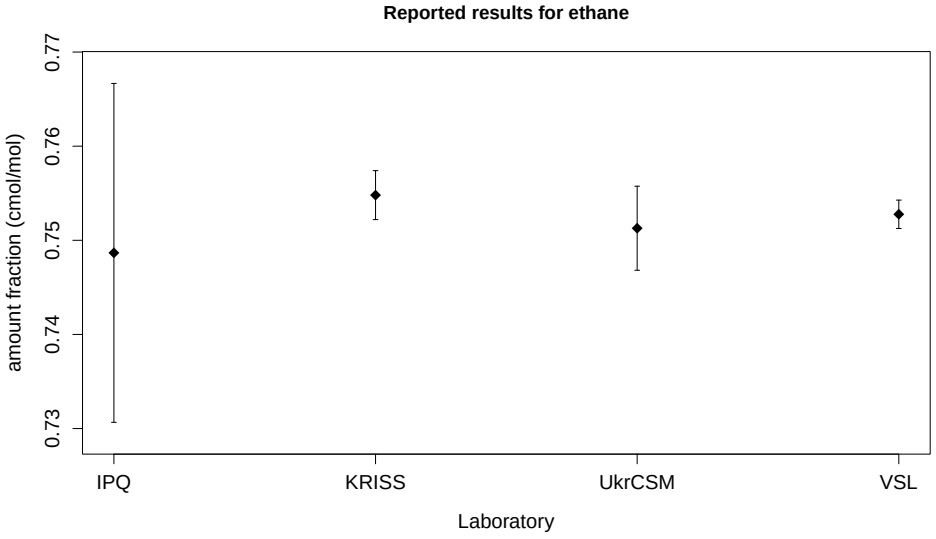


Figure 9: Reported results for the amount fraction ethane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 13: Results, key comparison reference values and degrees of equivalence for the amount fraction ethane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\text{prep}})$	$u(x_{\text{ver}})$	$u(x_{\text{ref}})$	x_{lab}	$U(x_{\text{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.74993	0.00002	0.00022	0.00022	0.7487	0.0180	2	-0.0013	0.0180	2
KRISS	0.75513	0.00002	0.00022	0.00022	0.7548	0.0026	2	-0.0003	0.0026	2
UkrCSM	0.75114	0.00003	0.00022	0.00022	0.7513	0.0045	2	0.0001	0.0045	2
VSL	0.75284	0.00002	0.00022	0.00022	0.7528	0.0015	2	-0.0001	0.0016	2

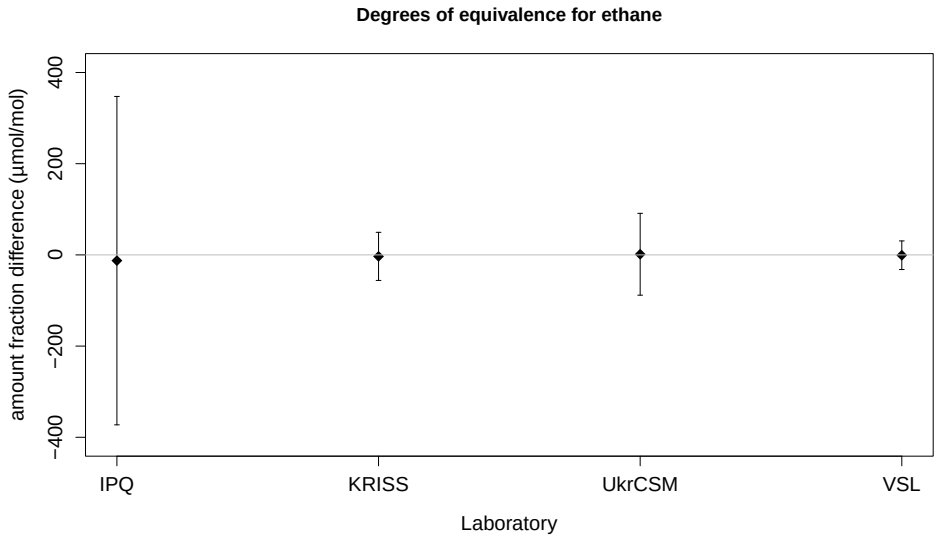


Figure 10: Degrees of equivalence for the amount fraction ethane (µmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 11 shows the results for the amount fraction propane for the four travelling standards. The results and KCRVs are shown in Table 14 and the degrees of equivalence are shown in Figure 12. All results are consistent with the KCRV.

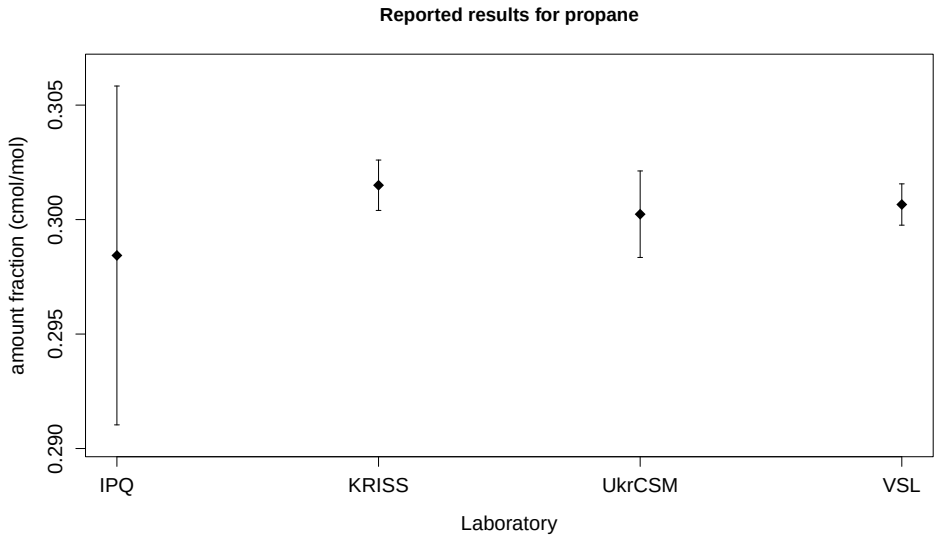


Figure 11: Reported results for the amount fraction propane ($\mathrm{cmol\,mol^{-1}}$). The uncertainty bars indicate expanded uncertainties.

Table 14: Results, key comparison reference values and degrees of equivalence for the amount fraction propane ($\mathrm{cmol\,mol^{-1}}$)

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.29954	0.00001	0.00012	0.00012	0.2984	0.0074	2	-0.0011	0.0074	2
KRISS	0.30162	0.00001	0.00012	0.00012	0.3015	0.0011	2	-0.0001	0.0011	2
UkrCSM	0.30003	0.00001	0.00012	0.00012	0.3002	0.0019	2	0.0002	0.0019	2
VSL	0.30070	0.00001	0.00012	0.00012	0.3007	0.0009	2	-0.0000	0.0009	2

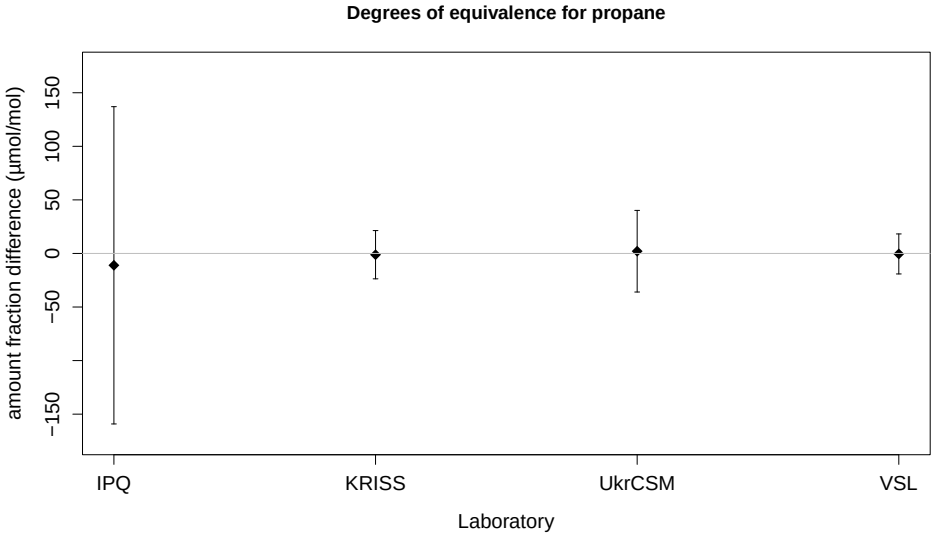


Figure 12: Degrees of equivalence for the amount fraction propane (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 13 shows the results for the amount fraction iso-butane for the four travelling standards. The results and KCRVs are shown in Table 15 and the degrees of equivalence are shown in Figure 14. All results are consistent with the KCRV.

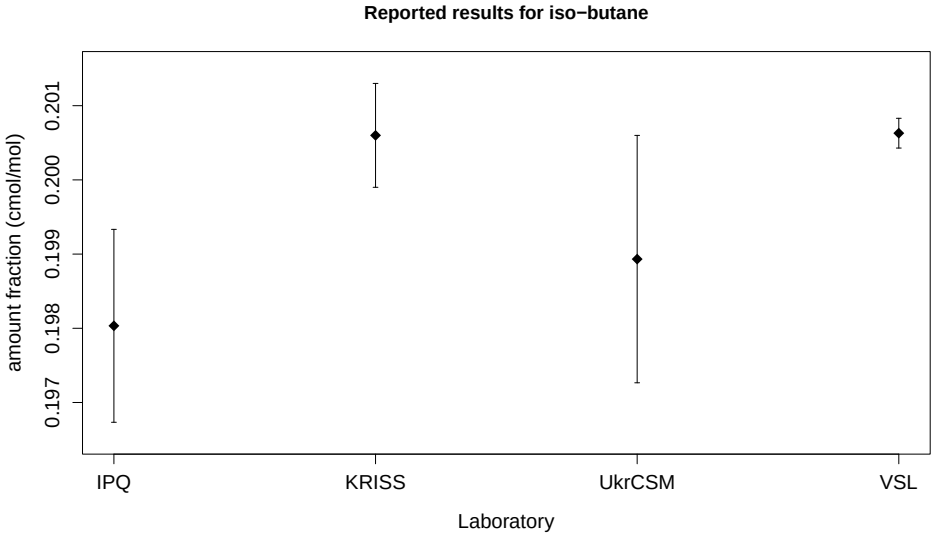


Figure 13: Reported results for the amount fraction iso-butane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 15: Results, key comparison reference values and degrees of equivalence for the amount fraction iso-butane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{prep})$	$u(x_{ver})$	$u(x_{ref})$	x_{lab}	$U(x_{lab})$	k_{lab}	d	$U(d)$	k_d
IPQ	0.19850	0.00001	0.00013	0.00013	0.19803	0.00130	2	-0.00047	0.00133	2
KRISS	0.20058	0.00001	0.00013	0.00014	0.20060	0.00070	2	0.00002	0.00075	2
UkrCSM	0.19875	0.00002	0.00013	0.00013	0.19893	0.00167	2	0.00018	0.00169	2
VSL	0.20073	0.00002	0.00013	0.00014	0.20063	0.00020	2	-0.00010	0.00034	2

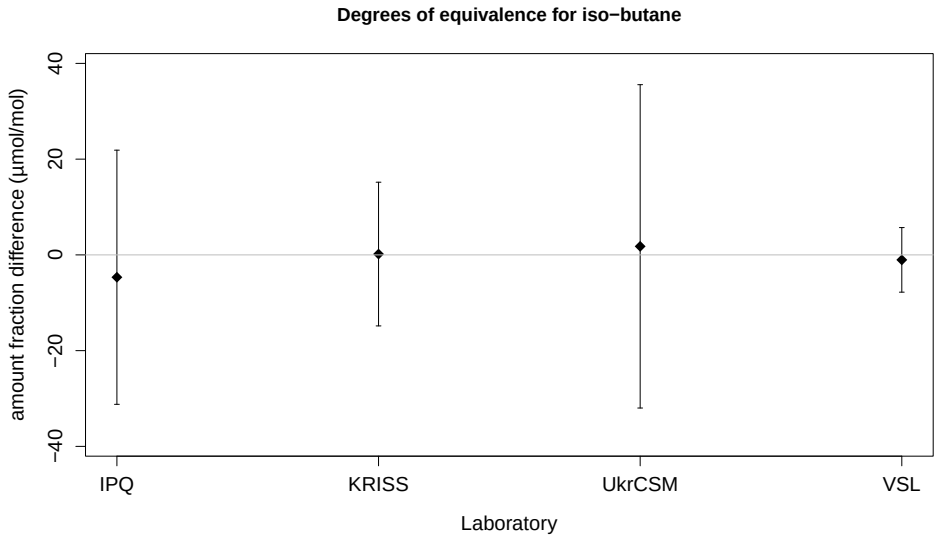


Figure 14: Degrees of equivalence for the amount fraction iso-butane (µmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 15 shows the results for the amount fraction n-butane for the four travelling standards. The results and KCRVs are shown in Table 16 and the degrees of equivalence are shown in Figure 16. All results are consistent with the KCRV.

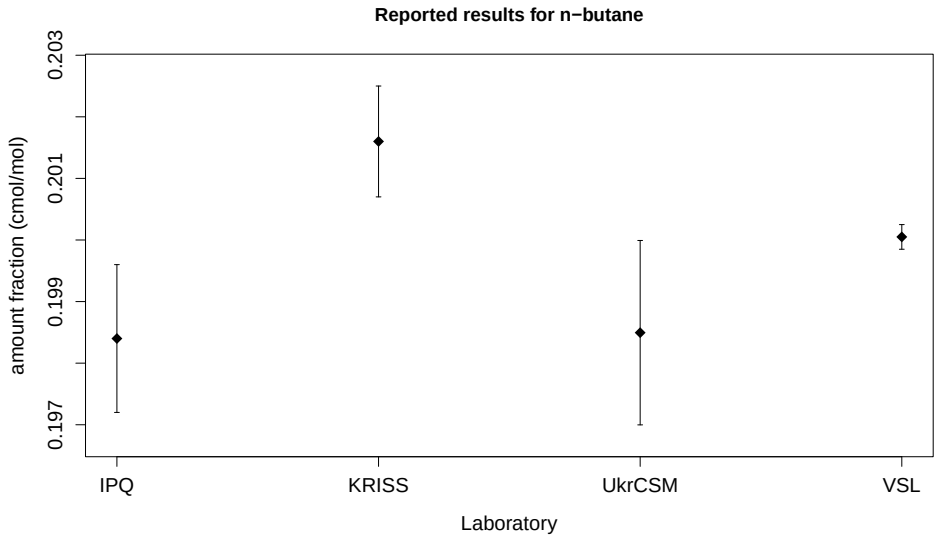


Figure 15: Reported results for the amount fraction n-butane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 16: Results, key comparison reference values and degrees of equivalence for the amount fraction n-butane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.19907	0.00002	0.00011	0.00011	0.19840	0.00120	2	-0.00067	0.00122	2
KRISS	0.20116	0.00002	0.00011	0.00011	0.20160	0.00090	2	0.00044	0.00093	2
UkrCSM	0.19812	0.00002	0.00011	0.00011	0.19850	0.00150	2	0.00038	0.00151	2
VSL	0.20009	0.00002	0.00011	0.00011	0.20005	0.00020	2	-0.00004	0.00030	2

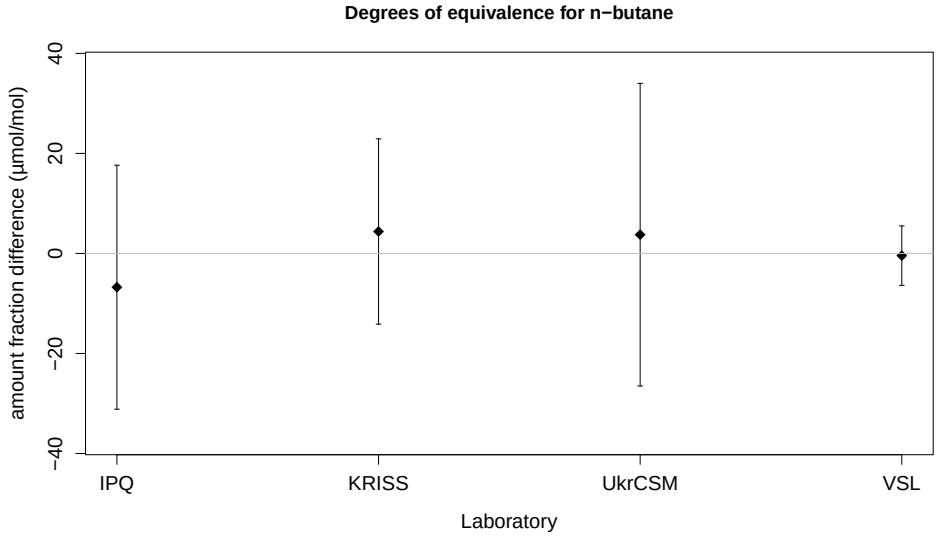


Figure 16: Degrees of equivalence for the amount fraction n-butane (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 17 shows the results for the amount fraction iso-pentane for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 17 and the degrees of equivalence are shown in Figure 18. All results are consistent with the KCRV.

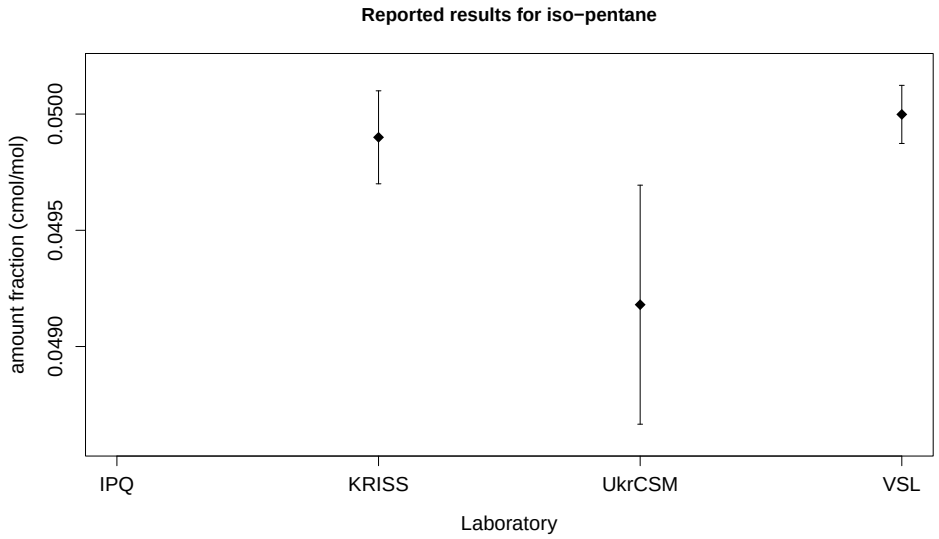


Figure 17: Reported results for the amount fraction iso-pentane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 17: Results, key comparison reference values and degrees of equivalence for the amount fraction iso-pentane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{prep})$	$u(x_{ver})$	$u(x_{ref})$	x_{lab}	$U(x_{lab})$	k_{lab}	d	$U(d)$	k_d
IPQ	0.049240	0.000011	0.000026	0.000029						2
KRISS	0.050015	0.000012	0.000027	0.000029	0.04990	0.00020	2	-0.00011	0.00021	2
UkrCSM	0.049148	0.000012	0.000026	0.000029	0.04918	0.00051	2	0.00003	0.00052	2
VSL	0.050020	0.000012	0.000027	0.000029	0.05000	0.00012	2	-0.00002	0.00014	2

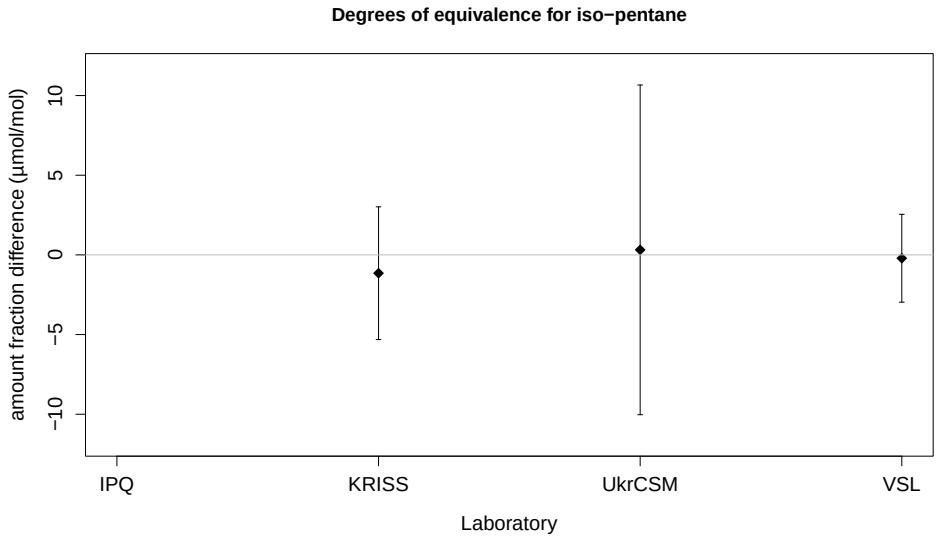


Figure 18: Degrees of equivalence for the amount fraction iso-pentane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 19 shows the results for the amount fraction n-pentane for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 18 and the degrees of equivalence are shown in Figure 20. All results are consistent with the KCRV.

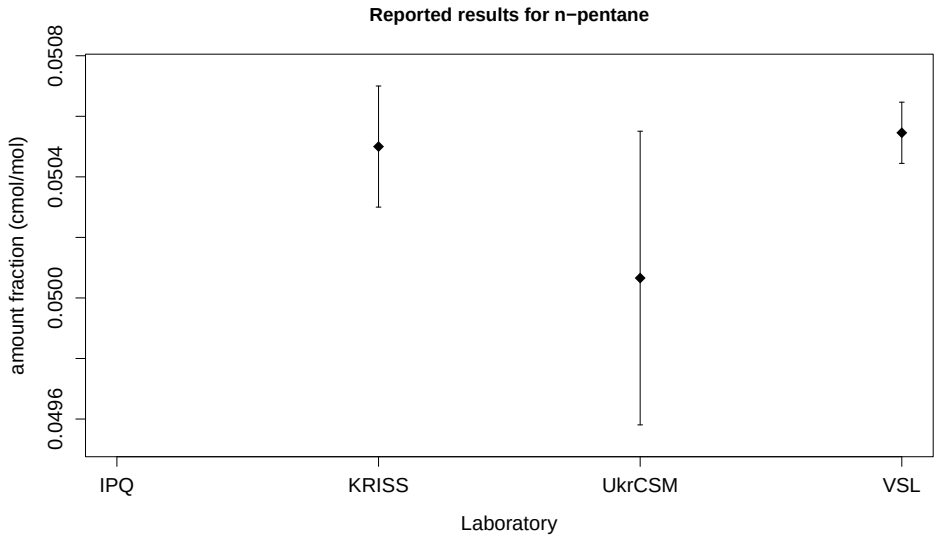


Figure 19: Reported results for the amount fraction n-pentane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 18: Results, key comparison reference values and degrees of equivalence for the amount fraction n-pentane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.049936	0.000011	0.000050	0.000052						2
KRISS	0.050579	0.000012	0.000051	0.000053	0.05050	0.00020	2	-0.00008	0.00023	2
UkrCSM	0.049702	0.000012	0.000050	0.000052	0.05007	0.00049	2	0.00036	0.00050	2
VSL	0.050583	0.000012	0.000051	0.000053	0.05055	0.00010	2	-0.00004	0.00015	2

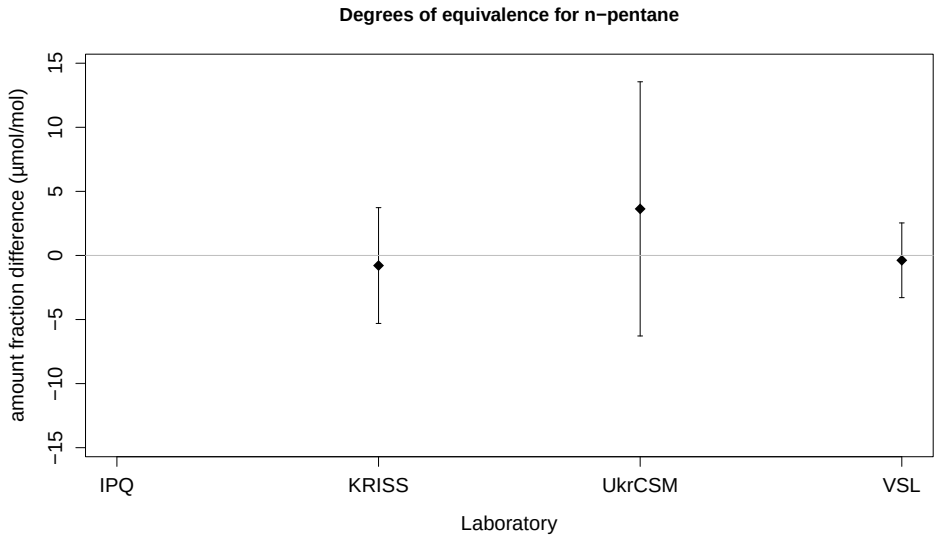


Figure 20: Degrees of equivalence for the amount fraction n-pentane (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 21 shows the results for the amount fraction neo-pentane for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 19 and the degrees of equivalence are shown in Figure 22. All results are consistent with the KCRV.

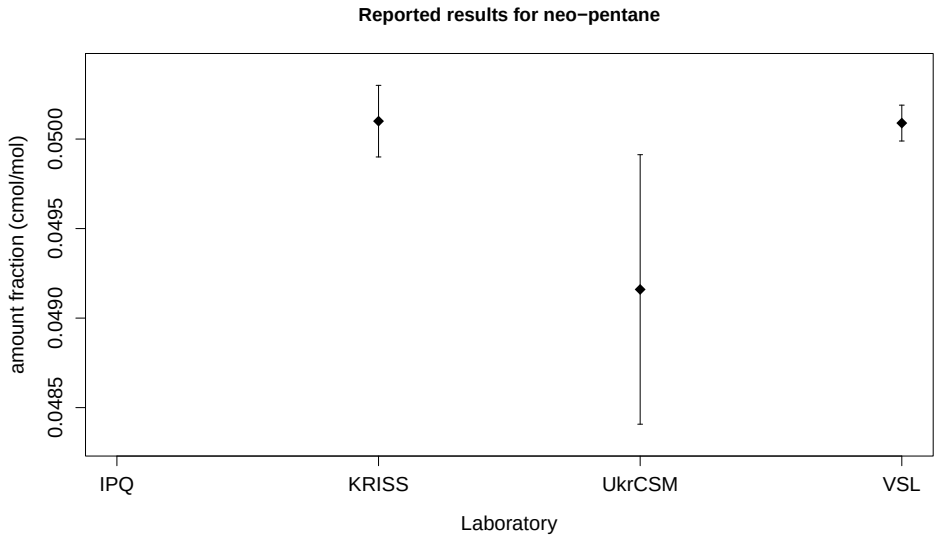


Figure 21: Reported results for the amount fraction neo-pentane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 19: Results, key comparison reference values and degrees of equivalence for the amount fraction neo-pentane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{prep})$	$u(x_{ver})$	$u(x_{ref})$	x_{lab}	$U(x_{lab})$	k_{lab}	d	$U(d)$	k_d
IPQ	0.050683	0.000010	0.000043	0.000044						2
KRISS	0.050042	0.000010	0.000043	0.000044	0.05010	0.00020	2	0.00006	0.00022	2
UkrCSM	0.049175	0.000010	0.000042	0.000043	0.04916	0.00075	2	-0.00001	0.00076	2
VSL	0.050046	0.000010	0.000043	0.000044	0.05009	0.00010	2	0.00004	0.00013	2

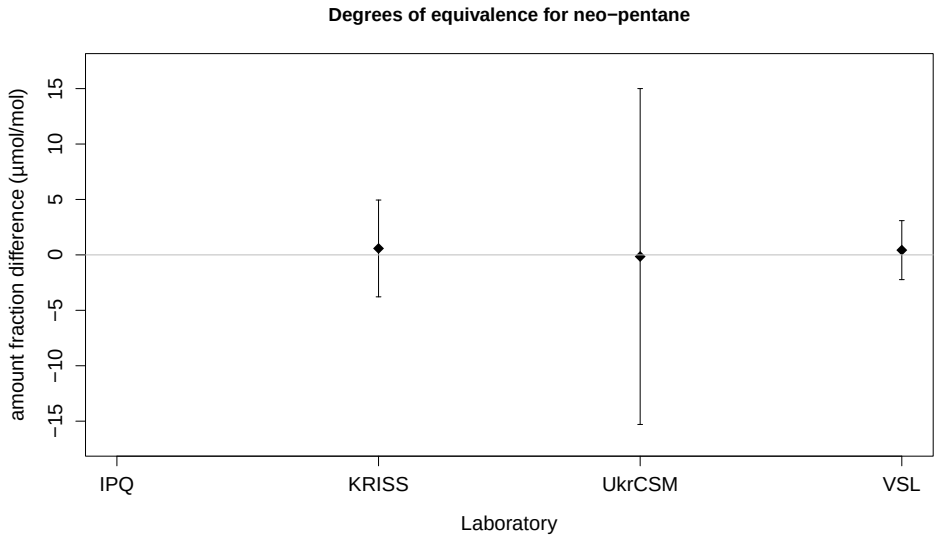


Figure 22: Degrees of equivalence for the amount fraction neo-pentane (µmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 23 shows the results for the amount fraction n-hexane for the four travelling standards. IPQ did not submit a result. The results and KCRVs are shown in Table 20 and the degrees of equivalence are shown in Figure 24. All results are consistent with the KCRV.

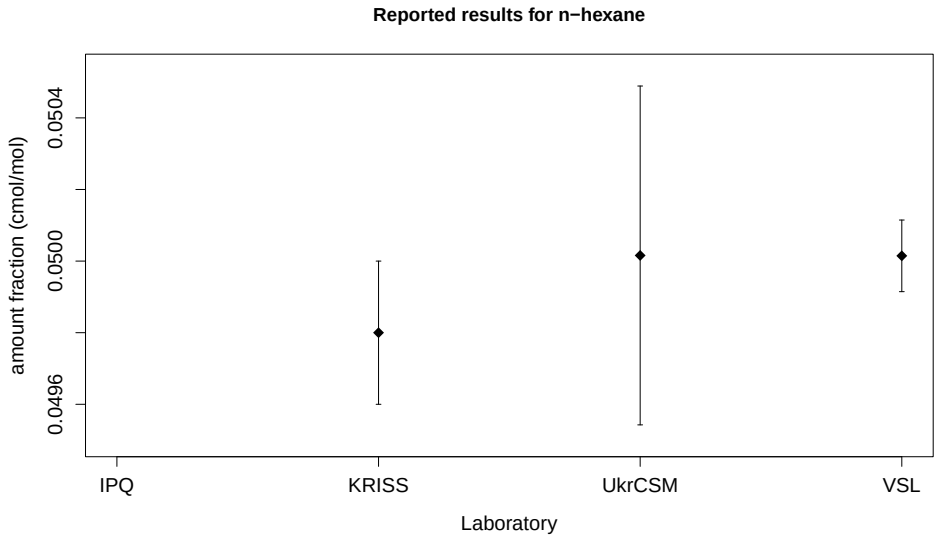


Figure 23: Reported results for the amount fraction n-hexane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 20: Results, key comparison reference values and degrees of equivalence for the amount fraction n-hexane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\mathrm{prep}})$	$u(x_{\mathrm{ver}})$	$u(x_{\mathrm{ref}})$	x_{lab}	$U(x_{\mathrm{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	0.049633	0.000011	0.000053	0.000054						2
KRISS	0.049962	0.000011	0.000053	0.000054	0.04980	0.00020	2	-0.00016	0.00023	2
UkrCSM	0.049665	0.000004	0.000053	0.000053	0.05002	0.00047	2	0.00035	0.00048	2
VSL	0.049977	0.000036	0.000053	0.000064	0.05001	0.00010	2	0.00004	0.00016	2

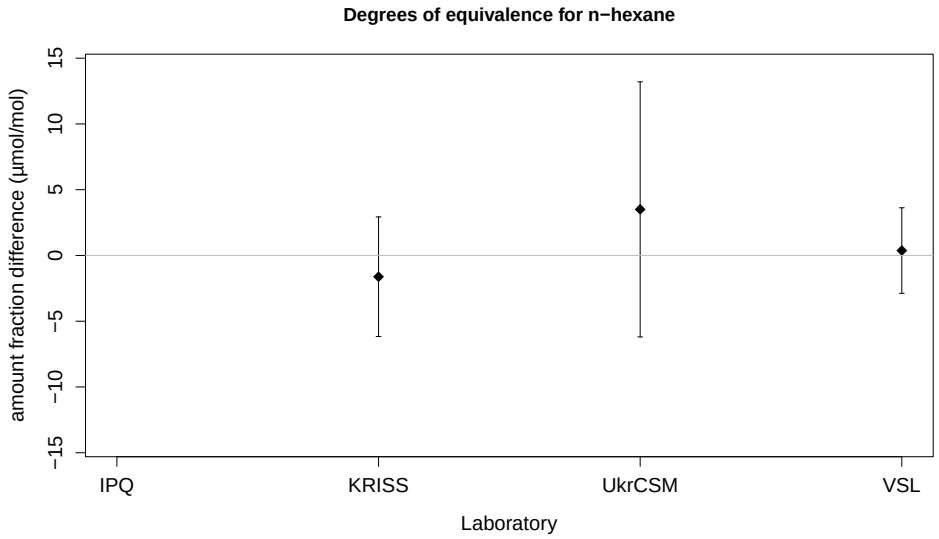


Figure 24: Degrees of equivalence for the amount fraction n-hexane (μmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Figure 25 shows the results for the amount fraction methane for the four travelling standards. The results and KCRVs are shown in Table 21 and the degrees of equivalence are shown in Figure 26. All results are consistent with the KCRV.

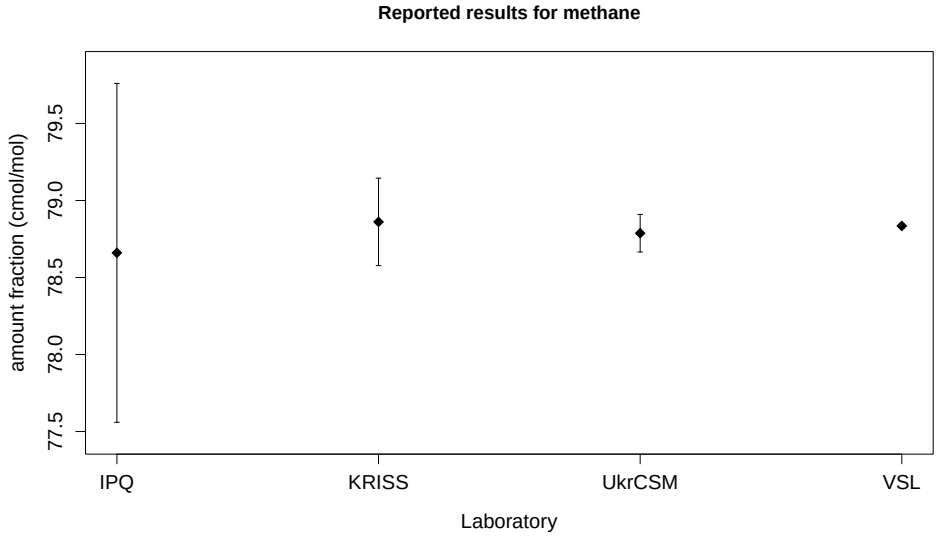


Figure 25: Reported results for the amount fraction methane (cmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

Table 21: Results, key comparison reference values and degrees of equivalence for the amount fraction methane (cmol mol^{-1})

NMI	x_{ref}	$u(x_{\text{prep}})$	$u(x_{\text{ver}})$	$u(x_{\text{ref}})$	x_{lab}	$U(x_{\text{lab}})$	k_{lab}	d	$U(d)$	k_{d}
IPQ	78.88063	0.00058	0.01183	0.01185	78.660	1.100	2	-0.221	1.100	2
KRISS	78.87559	0.00056	0.01183	0.01184	78.861	0.284	2	-0.015	0.285	2
UkrCSM	78.73550	0.00057	0.01181	0.01182	78.788	0.122	2	0.052	0.124	2
VSL	78.84327	0.00058	0.01183	0.01184	78.835	0.016	2	-0.009	0.029	2

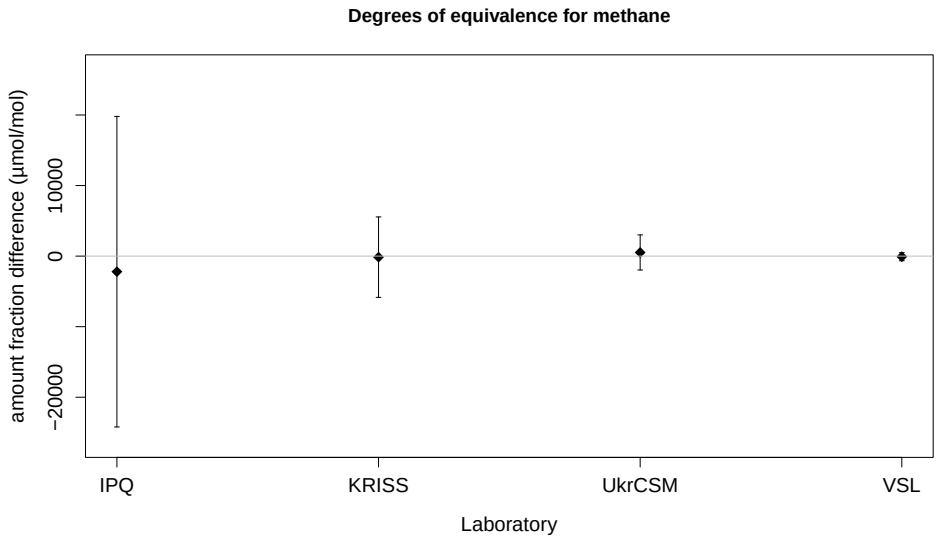


Figure 26: Degrees of equivalence for the amount fraction methane (µmol mol^{-1}). The uncertainty bars indicate expanded uncertainties.

4 Support to CMC claims

Participation in this key comparison can be used to support CMCs for natural gas under the provisions given in the report of CCQM-K118 [12] and in accordance with the CCQM-GAWG guidance [20].

When preparing CMCs, the excess standard deviation τ from CCQM-K118 shall be combined with the submitted standard uncertainty using the formula

$$u^2(x_{i,\text{CMC}}) = \tau^2 + u^2(x_{i,\text{lab}}) \tag{7}$$

where $u(x_{i,\text{CMC}})$ denotes the standard uncertainty of the CMC for the amount fraction of component i and

$$u(x_{i,\text{lab}}) = \frac{U(x_{i,\text{lab}})}{k_{i,\text{lab}}}$$

where $U(x_{i,\text{lab}})$ denotes the submitted expanded uncertainty for the amount fraction of component i and $k_{i,\text{lab}}$ the coverage factor for component i.

The values of τ are given in Table 22.

Table 22: Consensus values (x_{cv}) and excess standard deviations (τ) from CCQM-K118 for the hydrogen-enriched natural gas (cmol mol^{-1}) [12]

Component	x_{cv}	$u(x_{cv})$	τ	$u(\tau)$
Nitrogen	11.9848	0.0056	0.0079	0.0075
Carbon dioxide	4.0044	0.0017	0.0024	0.0022
Hydrogen	3.0007	0.0029	0.0046	0.0035
Helium	0.5022	0.0004	0.0005	0.0005
Ethane	0.7450	0.0004	0.0006	0.0005
Propane	0.298 49	0.000 18	0.000 30	0.000 22
iso-Butane	0.199 75	0.000 08	0.000 10	0.000 10
n-Butane	0.199 88	0.000 11	0.000 18	0.000 12
iso-Pentane	0.049 85	0.000 06	0.000 11	0.000 06
n-Pentane	0.050 17	0.000 05	0.000 09	0.000 05
neo-Pentane	0.049 34	0.000 05	0.000 08	0.000 06
n-Hexane	0.049 70	0.000 06	0.000 11	0.000 07
Methane	78.881	0.013	0.018	0.017

5 Conclusions

Equivalence with the key comparison reference value (KCRV) was shown for all submitted results for all amount fractions. This key comparison was successfully linked to CCQM-118 (natural gas type IVa). No additional uncertainty had to be taken into account.

This follow-up key comparison demonstrates how a consensus value-based key comparison can be combined with a subsequent key comparison in which an independent KCRV is used.

Coordinator

VSL
Department of Chemistry
Adriaan M.H. van der Veen
Thijsseweg 11
2629 JA Delft
the Netherlands
E-mail avdveen@vsl.nl

Project reference

CCQM-K118.1

Completion date

March 2026

A List of symbols and subscripts

A.1 Symbols

d	difference with respect to the key comparison reference value
Δx	correction to an amount fraction
k	coverage factor
U	expanded uncertainty
u	standard uncertainty
x	amount fraction

A.2 Subscripts

d	degree of equivalence
grav	gravimetry
prep	preparation
purity	purity
lab	participant (laboratory)
nr	non-recoverable
ref	key comparison reference value
stab	stability
ver	verification

B Measurement report of the participating institutes

Internal Analysis Report

BAM-1.4-2025_CCQM-K118.1_H2_enriched

Date 2025-07-28

Customer Internal

Date of order 2025-04-04

Operator Dr. Heinrich Kipphardt
Tel.: +49 30 8104-1116
heinrich.kipphardt@bam.de

Task Determination of the amount-of-substance fractions of the gas in a 5-Liter cylinder with number D153626

CCQM-K118.1 H2 enriched

Summary From the measurement campaign, the normalized amount-of-substance fractions of the gas in cylinder with cylinder number D153626 are:

normalised	Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
x_{cert} / cmol/mol	0,49914	3,0140	12,0032	78,841	3,9883	0,7525	0,30047	0,20073	0,19989
$u(x_{cert})$ / cmol/mol	0,00050	0,0023	0,0060	0,020	0,0030	0,0016	0,00030	0,00010	0,00015
$u_{rel}(x_{cert})$	1,0E-03	7,5E-04	5,0E-04	2,5E-04	7,5E-04	2,2E-03	1,0E-03	5,0E-04	7,5E-04
$U_{rel}(x_{cert})$	2,0E-03	1,5E-03	1,0E-03	5,0E-04	1,5E-03	4,3E-03	2,0E-03	1,0E-03	1,5E-03

normalised	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
x_{cert} / cmol/mol	0,050159	0,049822	0,050522	0,049923
$u(x_{cert})$ / cmol/mol	0,000088	0,000075	0,000101	0,000100
$u_{rel}(x_{cert})$	1,8E-03	1,5E-03	2,0E-03	2,0E-03
$U_{rel}(x_{cert})$	3,5E-03	3,0E-03	4,0E-03	4,0E-03

Given is in the last row the expanded relative measurement uncertainty $U_{rel} = u_c \cdot k$ with $k = 2$ according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement.

Date/Signature

Gas Analysis Group

Head of Division

CCQM-K118.1
H_2-enriched gas:

compiled by
Heinrich Kipphardt

BAM Federal Institute for Materials Research and Testing
Richard-Willstätter-Str. 11
12489 Berlin
GERMANY

Note: This technical report is for BAM-internal use. It can be quoted only after approval by the authors and referred to as a ‘private communication’.

Version of 2025-07-28

CCQM-K118 H_2-enriched gas
Determination of the amount-of-substance fractions of 13 compounds

1) Background

CCQM-K118.1 is an international interlaboratory comparison for energy gases organized by VSL as follow-up of CCQM-K118. The study covers a H_2-enriched gas. This report provides the results of BAM as a participant for the H_2-enriched gas.

2) Choice of method

For the determination of the 13 compounds the method of choice is GC with TCD or FID detection.

3) Sample: labeling, packing, pre-information

The sample was provided by VSL in a 5-L cylinder with cylinder number D153626 equipped with a valve which has DIN 477 thread No. 1 (hydrogen or, alternatively, test gas). The initial pressure upon arrival was not recorded, the final pressure after finishing the measurement campaign was 87 bar.

4) Sample pretreatment

No heating or rolling was applied. The sample was stored at laboratory conditions.

5) Devices used and flushing

A DIN 477 No. 1 (hydrogen)-VRC ¼″ fitting was adapted to the sample cylinder. A reduction valve, a needle valve for dosing, and a closing valve with an outlet to Swagelok 1/16″ capillaries were attached. For the two simultaneously employed calibration gases similar individual assemblies were used. The assembly for the sample cylinder was not changed during the entire measuring campaign, the assembly of the individual calibration gases used had to be changed (i.e., disconnected/connected).

A freshly installed assembly was evacuated down to a pressure of approximately 10^{-3} mbar and then filled with gas from the cylinder. The evacuating/flushing procedure was repeated five times before the analysis was started.

6) Measurement instruments & settings

A specially designed Siemens Maxum II process gas analyser was used applying “method 1” (a standard method developed by BAM to certify gas samples) which executes a sequence of 44 consecutive injections. The oven was set to 60 °C and the GC operated in isothermal mode with He as a carrier gas. The instrument is equipped with TCD detectors and has six different separation channels. Injection volumes vary between 30 and 500 µL. Details on Maxum operation can be found in the BAM SOP “GAS-StAA-027”.

Channel 1 for helium and hydrogen with N_2 as a carrier gas and columns of type Haysep and Molesieve columns.

Channel 2 for methane with Haysep columns.

Channel 3: for methane, carbon dioxide, ethene and ethane with Haysep columns

Channel 4 for propene and propane with Sorbitolchrom, TCEPCarbonblack and TCEPUnibeads columns.

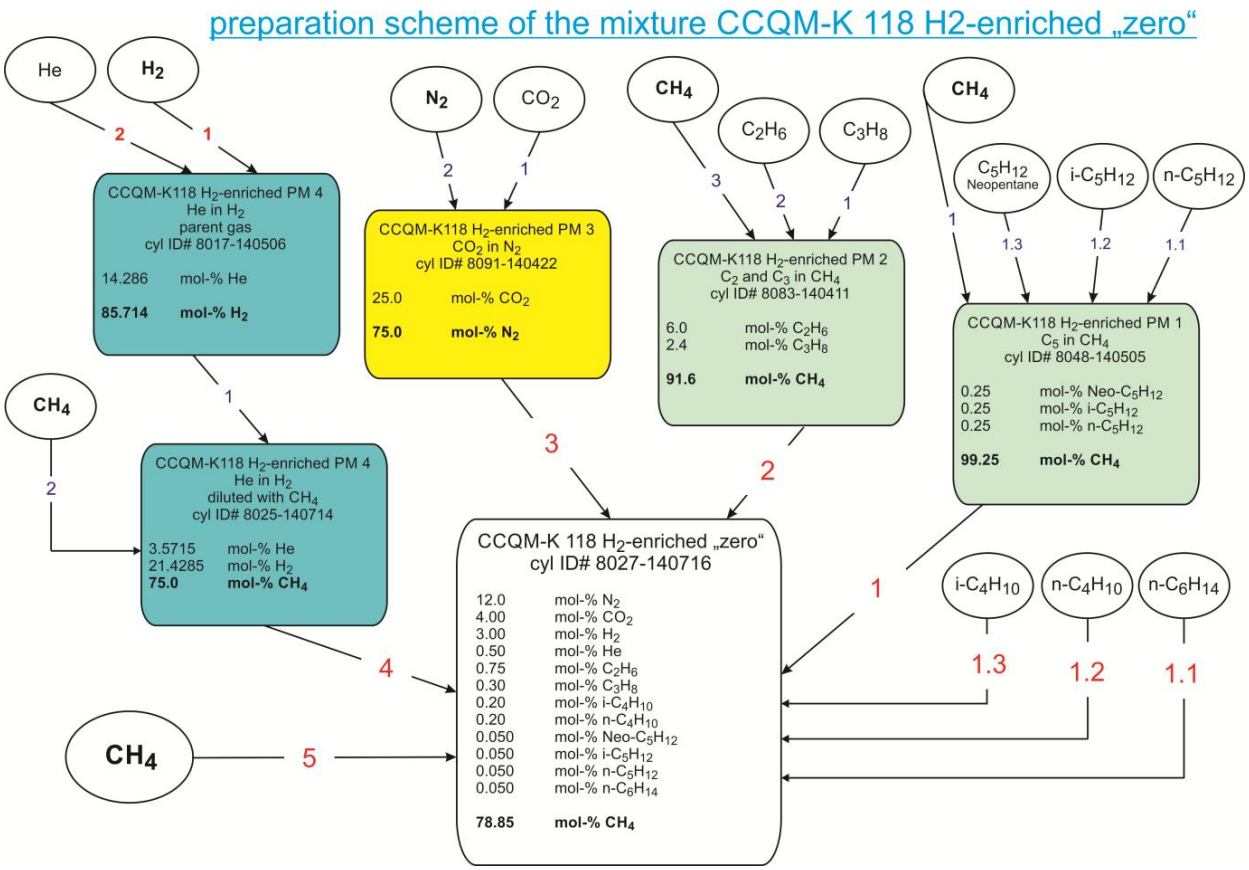
Channel 5 for oxygen, nitrogen and carbon monoxide with Shincarbon and molesieve columns.

Channel 6 for i-butane, n-butane, neo-pentane, i-pentane, n-pentane and n-hexane with Wax columns.

For measurements of propane, the butanes, the pentanes and n-hexane, a Thermo Scientific Trace 1310 analytical GC was used. It is equipped with two channels, namely a channel for permanent gases with backflush on a Restek HayesepQ and separation on a Restek Molsieve micro-packed column with TCD detection and channel for hydrocarbons with a Restek Rtx-1® capillary column for hydrocarbons and a methanizer/FID detector. A valve control circuit allows for building methods with a switch protocol. For this work, only the results from the hydrocarbon channel were used.

7) Calibration

The calibration gases used in CCQM-K118 were prepared as follows: Three calibration gases were prepared from high-purity gases by a gravimetric method according to DIN EN ISO 6142-1:2015 as shown in the following general scheme:



Filling steps and resulting pressure in the recipient cylinder (calculated amounts and pressures to create the targeted composition; the pressures are calculated for room temperature):

1, 2, 3, … indicates a filling step with pure gases or gas mixtures, respectively

1.1, 1.2, … indicates the use of a minicylinder for the compound to be introduced (purging gas “1”)

1.1.1, 1.1.2, … indicates the use of a gas-tight syringe for the compound to be introduced (purging gas “1”)

Mini-cylinders and syringes (with individual component masses > 2 g) were weighed using a balance of type Sartorius HCE 25 with an uncertainty of $U(m)$ = 0,2 mg (Type B).

Gas cylinders (with individual component masses > 30 g) were weighed using a balance of type Voland HCE 25 with an uncertainty of $U(m)$ = 15 mg (Type B).

Premixture 1 (PM 1)

1.1 8.55 g n-C_5H_{12}

1.2 8.55 g i-C_5H_{12}

1.3 8.55 g Neo-C_5H_{12} < 1 bar

1. 755.2 g CH_4 106 bar

Total: 780.85 g

Premixture 2 (PM 2)

1. 71.0 g C_3H_8 4 bar
2. 121.1 g C_2H_6 12 bar
3. 986.7 g CH_4 150 bar

Total: 1178.8 g

Premixture 3 (PM 3)

1. 590.3 g CO_2 30 bar
2. 1127.1 g N_2 120 bar

Total: 1717.4 g

Premixture 4 (PM 4) parent gas

1. 105.6 g H_2 140 bar
2. 34.9 g He 166 bar

Total: 140.5 g

Final mixture

1.1 2.02 g n-C_6H_{14}

1.2 5.46 g n-C_4H_{10}

1.3 5.46 g i-C_4H_{10} 1 bar

1. 154.5 g PM 1 21 bar
2. 103.0 g PM 2 34 bar
3. 240.5 g PM 3 51 bar
4. 82.5 g PM 4 66 bar
5. 278.5 g CH_4 105 bar

Total: 871.94 g

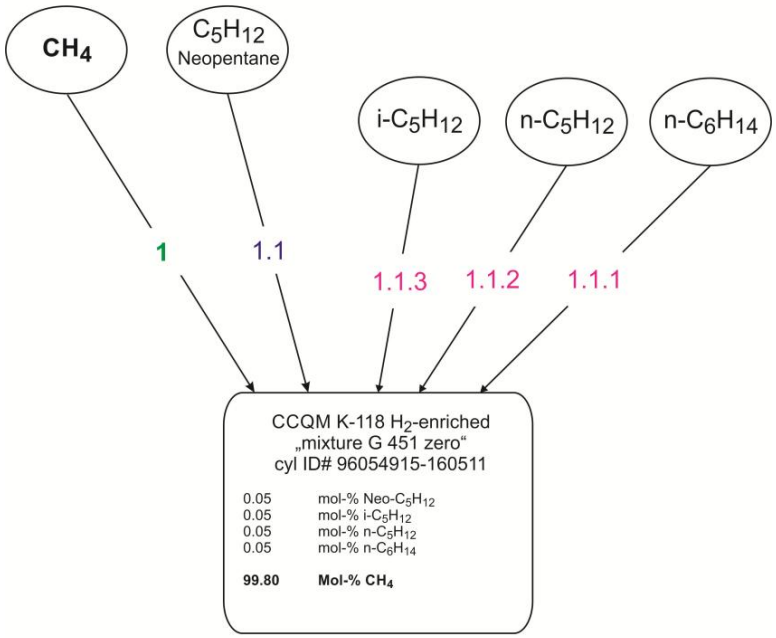
Premixture 4 (PM 4)

1. 40.0 g PM 4 parent gas 39 bar
2. 836.0 g CH_4 156 bar

Total: 876.0 g

As the validation of the three gases showed a small bias with the pentanes, a set of additional calibration gases were produced for these compounds according to the general scheme:

preparation scheme of the mixture
CCQM K-118 H2-enriched (separate mixture G 451)



Filling steps and resulting pressure in the recipient cylinder:

Final mixture

1.1.1 2.89 g n-C_6H_{14}

1.1.2 2.42 g n-C_5H_{12}

1.1.3 2.42 g i-C_5H_{12} 1 bar

1.1 2.42 g Neo-C_5H_{12} < 1 bar

1. 1074,2 g CH_4 150 bar

Total: 1084.35 g

The composition of the calibration gases was:

		Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
8056-140922	x_{cert} / %	0,471769	2,750777	11,103398	80,443530	3,700223	0,700350	0,274717	0,186453	0,184936
	$u(x_{cert})$ / %	0,000139	0,000591	0,000333	0,001609	0,000130	0,000070	0,000040	0,000018	0,000045
	$u_{rel}(x_{cert})$	3,0E-04	2,2E-04	3,0E-05	2,0E-05	3,5E-05	1,0E-04	1,5E-04	9,5E-05	2,5E-04
	$U_{rel}(x_{cert})$	5,9E-04	4,3E-04	6,0E-05	4,0E-05	7,0E-05	2,0E-04	2,9E-04	1,9E-04	4,9E-04

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
x_{cert} / %	~~0,045306~~	~~0,046163~~	~~0,046127~~	~~0,046238~~
$u(x_{cert})$ / %	~~0,000029~~	~~0,000028~~	~~0,000027~~	~~0,000042~~
$u_{rel}(x_{cert})$	~~6,4E-04~~	~~6,2E-04~~	~~5,9E-04~~	~~9,0E-04~~
$U_{rel}(x_{cert})$	~~1,3E-03~~	~~1,2E-03~~	~~1,2E-03~~	~~1,8E-03~~

		Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
8045-140923	x_{cert} / %	0,535826	3,245527	12,928316	77,208758	4,304190	0,810092	0,321367	0,215044	0,216555
	$u(x_{cert})$ / %	0,000161	0,000714	0,000452	0,002316	0,000151	0,000089	0,000050	0,000020	0,000053
	$u_{rel}(x_{cert})$	3,0E-04	2,2E-04	3,5E-05	3,0E-05	3,5E-05	1,1E-04	1,6E-04	9,5E-05	2,5E-04
	$U_{rel}(x_{cert})$	6,0E-04	4,4E-04	7,0E-05	6,0E-05	7,0E-05	2,2E-04	3,1E-04	1,9E-04	4,9E-04

		neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
	x_{cert} / %	~~0,052772~~	~~0,054195~~	~~0,054141~~	~~0,053205~~
	$u(x_{cert})$ / %	~~0,000034~~	~~0,000033~~	~~0,000032~~	~~0,000048~~
	$u_{rel}(x_{cert})$	~~6,4E-04~~	~~6,2E-04~~	~~5,9E-04~~	~~9,0E-04~~
	$U_{rel}(x_{cert})$	~~1,3E-03~~	~~1,2E-03~~	~~1,2E-03~~	~~1,8E-03~~

		Methane	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
96054955-160510	x_{cert} / %	99,813861	0,046416	0,046301	0,046514	0,046473
	$u(x_{cert})$ / %	0,000998	0,000006	0,000010	0,000010	0,000004
	$u_{rel}(x_{cert})$	1,0E-05	1,4E-04	2,1E-04	2,1E-04	9,5E-05
	$U_{rel}(x_{cert})$	2,0E-05	2,8E-04	4,2E-04	4,1E-04	1,9E-04

		Methane	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
96054952-160518	x_{cert} / %	99,785105	0,053178	0,053694	0,053785	0,053802
	$u(x_{cert})$ / %	0,000998	0,000007	0,000011	0,000011	0,000005
	$u_{rel}(x_{cert})$	1,0E-05	1,4E-04	2,1E-04	2,1E-04	9,0E-05
	$U_{rel}(x_{cert})$	2,0E-05	2,8E-04	4,1E-04	4,1E-04	1,8E-04

In a measurement campaign prior to the investigation of the sample, the two sets of calibration gases (two “bracket gases” and a “zero” sample that displays the targeted composition, see the general filling scheme) were found to be consistent [see file VAL-CCQM-K118_H2_enriched].

The purity analysis of initial gases was based on the information provided by the supplier or on the results of determination of impurities in pure gases using an analysis method developed at BAM. The least pure compound was neo-pentane containing about 1.0 % cyclobutene as major impurity.

8) Measurement outline

For a measurement sequence, the two calibration gases C1 & C2 and the sample S were connected to the GC. Using a stream selector valve, each calibration gas was connected three times, the sample gas five times to the GC in the following order: C1/S/C2/S/C1/S/C2/S/C1/S/C2. At each connection to the GC, four injections were made, from which only the last three were used for data evaluation. The complete sequence runs over a period of four hours.

Using the Maxum, two measurement campaigns (the first with the gases 8056 and 8045, the second with the gases 96054955 and 96054952 for the evaluation C5 and C6 only) with three sequences were conducted. In each campaign, the sequences were executed on two different days.

The calibration follows a special the two-point calibration with bracketing (TPC). The practical implementation is briefly described and exemplarily illustrated below with data for an arbitrary measurement of propane. Data for the other mixture compounds are also available but archived in an EXCEL spreadsheet available upon request.

From the three recorded measurements for each gas, the mean value (MW) and standard deviation (Stdev) (to be understood as uncertainty of type A) and relative standard deviation (urel) are calculated for the observed intensities.

C2,1	MW	867763
	Stdev	601
	urel	6,9E-04
S ,2	MW	804363
	Stdev	358
	urel	4,4E-04
C1,2	MW	741065
	Stdev	656
	urel	8,9E-04

Together with the gas composition with uncertainties taken as type B of the calibration gases, i.e.,

C 1	x_{cert} / %	0,27472
	$u(x_{cert})$ / %	0,00004
8056-140922	$u_{rel}(x_{cert})$	1,5E-04

C 2	x_{cert} / %	0,32137
	$u(x_{cert})$ / %	0,00005
8045-140923	$u_{rel}(x_{cert})$	1,6E-04

bracketing calculation is performed to obtain the amount of substance fraction (Kurvenwert) for the sample S, the corresponding uncertainty is calculated according to the general rules of uncertainty propagation. The obtained values are:

m	2715934
b	-5048
Kurvenwert / %	0,29802
u(Kurvenwert) / %	0,00021
u_{rel}(Kurvenwert)	7,1E-04
(X3-X1)	0,0467
(Y3-Y1)	126698
(Y3-Y2)	63401
(Y2-Y1)	-63298
(dX2/dY2)^2 * u(Y2)^2	1,733E-08
	38%
(dX2/dY3)^2 * u(Y3)^2	1,221E-08
	27%
(dX2/dY1)^2 * u(Y1)^2	1,461E-08
	32%
(dX2/dX1)^2 * u(X1)^2	3,973E-10
	1%
(dX2/dX3)^2 * u(X3)^2	6,193E-10

	1%
summe	4,517E-08

As can be seen, the uncertainty is dominated almost equally (i.e., 38 % + 27 % + 32 %) from the measurement statistics of the three gases. The uncertainty from the calibration gases has an influence of < 5% on the combined uncertainty of the amount of substance fraction.

From the measurement sequence, in total five bracketing combinations are possible. (Correlation from using C2, 1; C2, 2; C1, 2 and C1, 3 twice in the calculation is not considered.) The values and uncertainties obtained are:

Kurvenwert 1 / %	0,29831
u(Kurvenwert) / %	0,00045
Kurvenwert 2 / %	0,29802
u(Kurvenwert) / %	0,00021
Kurvenwert 3 / %	0,29821
u(Kurvenwert) / %	0,00044
Kurvenwert 4 / %	0,29789
u(Kurvenwert) / %	0,00043
Kurvenwert 5 / %	0,29813
u(Kurvenwert) / %	0,00058

All five values from the measurement sequence are compatible, i.e., agree within their uncertainty. The five individual results are pooled to:

Kurvenwert / %	0,29811
u(Kurvenwert) / %	0,00044
u_{rel}(Kurvenwert)	1,5E-03

Considering three measurement sequences, the results are:

x_{A1} / %	0,2981
$u(x_{A1})$ / %	0,0004
$u_{rel}(x_{A1})$	1,5E-03
$u^2(x_{A1})$	1,914E-07
x_{A2} / %	0,2984
$u(x_{A2})$ / %	0,0005
$u_{rel}(x_{A2})$	1,8E-03
$u^2(x_{A2})$	2,967E-07
x_{A3} / %	0,2981
$u(x_{A3})$ / %	0,0005
$u_{rel}(x_{A3})$	1,7E-03
$u^2(x_{A3})$	2,697E-07

All values from the three measurement sequences are compatible, i.e., agree within their uncertainty. These three individual results are ultimately pooled to the result of the measurement campaign:

x_{BAM_MW} / %	0,2982
$u(x_{BAM_MW})$ / %	0,0005
$u_{rel}(x_{BAM_MW})$	1,7E-03
$U_{rel}(x_{BAM_MW})$	3,4E-03
$u^2(x_{BAM_MW})$	2,526E-07

Note, square root of *n* is not used in any of these calculations.

(There are additional consistency checks for data evaluation with SPEM as basically described in ISO12963 which are not further elaborated here. The results using each calibration gas for direct match calibration are:

x_{V_1} / %	0,2982
$u(x_{V_1})$ / %	0,0005
$u_{rel}(x_{V_1})$	1,6E-03

x_{V_3} / %	0,2981
$u(x_{V_3})$ / %	0,0005
$u_{rel}(x_{V_3})$	1,7E-03

These results indicate a sufficient linearity of the measurement system.)

9) Considered sources of uncertainty

The results and uncertainties given here include the uncertainty of the composition of the calibration gases, the uncertainty from the measurement statistics (i.e., consecutive portions of three injections), the uncertainty propagation for the calibration approach, the bias within a measurement campaign over the period of time, and finally from combining the different individual measurement campaigns. Main source of uncertainty is the imprecision of the TCD and FID used.

10) Raw data: 2025-06-03/26; for more details see
\\Gfs05\g15\SERV143\DMS\Beratung+Information_CCQM_Studien\CCQM-K118.1_2025
Code 911

11) Results from the measurement campaign

The data form FID and TCD were pooled. From the direct measurement (i.e., not normalised) of all compounds the result is:

	Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
x_{cert} / %	0,49916	3,0141	12,0036	78,8444	3,9884	0,7526	0,30049	0,20074	0,19990
$u(x_{cert})$ / %	0,00042	0,0017	0,0017	0,0100	0,0014	0,0016	0,00010	0,00007	0,00010
$u_{rel}(x_{cert})$	8,4E-04	5,6E-04	1,5E-04	1,3E-04	3,5E-04	2,1E-03	3,5E-04	3,5E-04	5,1E-04
$U_{rel}(x_{cert})$	1,7E-03	1,1E-03	2,9E-04	2,5E-04	7,0E-04	4,3E-03	7,0E-04	7,0E-04	1,0E-03

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane	Sum
x_{cert} / %	0,05016	0,049824	0,050524	0,049925	100,0039
$u(x_{cert})$ / %	0,00008	0,000026	0,000033	0,000093	0,0105
$u_{rel}(x_{cert})$	1,5E-03	5,3E-04	6,5E-04	1,9E-03	1,1E-04
$U_{rel}(x_{cert})$	3,1E-03	1,1E-03	1,3E-03	3,7E-03	2,1E-04

The customers usually request normalized values (i.e., sum = 100.000) which almost does not change the values, however, the uncertainty of the main component is then further reduced.

	Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
x_{cert} / %	0,49914	3,0140	12,0032	78,8414	3,9883	0,7525	0,30047	0,20073	0,19989
$u(x_{cert})$ / %	0,00042	0,0017	0,0020	0,0033	0,0014	0,0016	0,00011	0,00007	0,00010
$u_{rel}(x_{cert})$	8,4E-04	5,5E-04	1,6E-04	4,2E-05	3,5E-04	2,1E-03	3,6E-04	3,6E-04	5,2E-04
$U_{rel}(x_{cert})$	1,7E-03	1,1E-03	3,3E-04	8,5E-05	7,0E-04	4,3E-03	7,3E-04	7,3E-04	1,0E-03

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane	Sum
x_{cert} / %	0,05016	0,049822	0,050522	0,049923	100,0000
$u(x_{cert})$ / %	0,00008	0,000040	0,000083	0,000093	0,0047
$u_{rel}(x_{cert})$	1,5E-03	8,1E-04	1,6E-03	1,9E-03	4,7E-05
$U_{rel}(x_{cert})$	3,1E-03	1,6E-03	3,3E-03	3,7E-03	9,5E-05

12) Consolidated results

Finally, the consolidated results include uncertainties that are based on experience, which are typically slightly larger than plainly calculated from the data of this measurement campaign.

	Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
x_{cert} / %	0,49914	3,01398	12,00315	78,84138	3,98829	0,75252	0,30047	0,20073	0,19989
$u(x_{cert})$ / %	0,00050	0,00226	0,00600	0,01971	0,00299	0,00162	0,00030	0,00010	0,00015
$u_{rel}(x_{cert})$	1,0E-03	7,5E-04	5,0E-04	2,5E-04	7,5E-04	2,2E-03	1,0E-03	5,0E-04	7,5E-04
$U_{rel}(x_{cert})$	2,0E-03	1,5E-03	1,0E-03	5,0E-04	1,5E-03	4,3E-03	2,0E-03	1,0E-03	1,5E-03

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane	Sum
x_{cert} / %	0,05016	0,04982	0,05052	0,04992	100,0000
$u(x_{cert})$ / %	0,00009	0,00007	0,00010	0,00010	0,0210
$u_{rel}(x_{cert})$	1,8E-03	1,5E-03	2,0E-03	2,0E-03	2,1E-04
$U_{rel}(x_{cert})$	3,5E-03	3,0E-03	4,0E-03	4,0E-03	4,2E-04

Given is in the last row the expanded relative measurement uncertainty $U_{rel} = u_c \cdot k$ with $k = 2$ according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement.

13) Remarks

The uncertainties reported are about the same as reported in the CCQM-K118 key comparison. The uncertainties reported are within the CMCs derived from CCQM-K118. For ethane, the uncertainty in this campaign is the same as reported for the hydrogen enriched gas in CCQM-K118. However, the CMC for ethane is actually slightly lower as it was generated from pooling the data for LNG and Hydrogen enriched type of gas in CCQM-K118.

14) Responsibility

The calibration gases have been prepared by the filling team consisting of Claudia Boissière, Kerstin Köster, Jeannette Pelchen, under supervision of Dr. Dirk Tuma. The measurements using the Maxum II gas chromatograph have been performed by Jeannette Pelchen. The measurements using the Thermo gas chromatograph have been performed by Dr. Dirk Tuma. Strategy, reporting and calculations have been performed by Dr. Heinrich Kipphardt.

The overall technical responsibility for the measurement result is with Dr. Heinrich Kipphardt.

Berlin, 2025-07-31 Heinrich Kipphardt FB 1.4

15) Scientific Authorship of this work

Heinrich Kipphardt and Dirk Tuma.

16) Additional information

Customer:	VSL, CCQM-K118.1 H2-enriched
PAZ-No.	-
Sample arrival:	2025-04-04
Internal No.:	\\Gfs05\q15\SERV143\DMS\Beratung+Information_CCQM_Studien\CCQM-K118.1_2025 Code 911
Sample No.:	cylinder with cylinder number D153626
Task:	Determination of amount-of-substance fractions
Period of measurement:	2025-06-03/26
Location:	Building AH 08.05 Room O1.285
Method:	GC with TCD and FID

17) Appendix: Purity Tables with typical examples

Material	Helium	99,99989	0,00003	2,9E-07
gas quality	6.0			
supplier	Linde			
batch				
	Impurities	0,00012	0,00003	2,6E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00003	0,00001	5,8E-01
3	Oxygen	16,00	0,00		0,00003	0,00001	5,8E-01
4	Carbon dioxide	44,01	0,01		0,00001	0,00000	5,8E-01
5	Carbon monoxide	28,01	0,01		0,00001	0,00000	5,8E-01
17	Hydrogen	1,01	0,00		0,00003	0,00001	5,8E-01
18	Helium	4,00	0,00		99,99989	0,00003	2,9E-07
31	Moisture	18,01	0,00		0,00003	0,00001	5,8E-01
36	UNKNOWN	80,00	20,00		0,00001	0,00000	5,8E-01

Material	Hydrogen	99,99993	0,00002	2,2E-07
gas quality	6.0			
supplier	Linde			
batch	276311-19029784			
	Impurities	0,00007	0,00002	3,0E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00001	0,00001	5,8E-01
2	Argon	39,95	0,00		0,00000	0,00000	5,8E-01
3	Oxygen	16,00	0,00		0,00000	0,00000	5,8E-01
4	Carbon dioxide	44,01	0,01		0,00001	0,00000	5,8E-01
5	Carbon monoxide	28,01	0,01		0,00000	0,00000	5,8E-01
6	Methane	16,04	0,01		0,00003	0,00001	5,8E-01
17	Hydrogen	1,01	0,00		99,99993	0,00002	2,2E-07
31	Moisture	18,01	0,00		0,00003	0,00001	5,8E-01

Material	Nitrogen	99,99991	0,00003	3,3E-07
gas quality	6.0			
supplier	Linde			
batch	276311-21144639			
	Impurities	0,00010	0,00003	3,4E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		99,99991	0,00003	3,3E-07
2	Argon	39,95	0,00		0,00005	0,00003	5,8E-01
3	Oxygen	16,00	0,00		0,00000	0,00000	5,8E-01
4	Carbon dioxide	44,01	0,01		0,00001	0,00000	5,8E-01
5	Carbon monoxide	28,01	0,01		0,00000	0,00000	5,8E-01
6	Methane	16,04	0,01		0,00000	0,00000	5,8E-01
17	Hydrogen	1,01	0,00		0,00000	0,00000	5,8E-01
31	Moisture	18,01	0,00		0,00003	0,00001	5,8E-01
36	UNKNOWN	80,00	20,00		0,00001	0,00000	5,8E-01
37	2-Butine	54,09	0,01				

Material	Methane	99,99983	0,00006	6,5E-07
gas quality	5.5			
supplier	Linde			
batch	27611-21588356			
	Impurities	0,00017	0,00006	3,9E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00001	0,00000	5,8E-01
2	Argon	39,95	0,00		0,00000	0,00000	5,8E-01
3	Oxygen	16,00	0,00		0,00001	0,00000	5,8E-01
5	Carbon monoxide	28,01	0,01		0,00000	0,00000	5,8E-01
6	Methane	16,04	0,01		99,99983	0,00006	6,5E-07
7	Ethane	30,07	0,01		0,00005	0,00003	5,8E-01
17	Hydrogen	1,01	0,00		0,00000	0,00000	5,8E-01
31	Moisture	18,01	0,00		0,00010	0,00006	5,8E-01

Material	Carbon dioxide	99,99971	0,00009	8,9E-07
gas quality	5.5			
supplier	AL			
batch	A8509			
	Impurities	0,00029	0,00009	3,1E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00010	0,00006	5,8E-01
3	Oxygen	16,00	0,00		0,00005	0,00003	5,8E-01
4	Carbon dioxide	44,01	0,01		99,99971	0,00009	8,9E-07
5	Carbon monoxide	28,01	0,01		0,00003	0,00002	5,8E-01
17	Hydrogen	1,01	0,00		0,00001	0,00000	5,8E-01
31	Moisture	18,01	0,00		0,00011	0,00003	3,0E-01

Material	Ethane	99,99968	0,00004	4,4E-07
gas quality	5.0			
supplier	Matheson			
batch	EGB000095			
	Impurities	0,00032	0,00004	1,4E-01
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00003	0,00001	3,0E-01
3	Oxygen	16,00	0,00		0,00001	0,00000	5,8E-01
4	Carbon dioxide	44,01	0,01		0,00001	0,00000	5,8E-01
5	Carbon monoxide	28,01	0,01		0,00001	0,00000	5,8E-01
6	Methane	16,04	0,01		0,00001	0,00000	5,8E-01
7	Ethane	30,07	0,01		99,99968	0,00004	4,4E-07
8	Ethylene	28,05	0,01		0,00007	0,00002	3,0E-01
9	Propane	44,10	0,01		0,00004	0,00001	3,0E-01
11	n-Butane	58,12	0,01		0,00004	0,00001	3,0E-01
12	i-Butane	58,12	0,01		0,00001	0,00000	5,8E-01
31	Moisture	18,01	0,00		0,00010	0,00003	3,0E-01

Material	Propane			99,99848	0,00028	2,8E-06
gas quality	4.5					
supplier	Matheson					
batch	FF032424					
	Impurities			0,00153	0,00028	1,8E-01
	Sum			100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00001	0,00000	3,0E-01
3	Oxygen	16,00	0,00		0,00001	0,00000	5,8E-01
4	Carbon dioxide	44,01	0,01		0,00001	0,00000	5,8E-01
6	Methane	16,04	0,01		0,00001	0,00000	5,8E-01
7	Ethane	30,07	0,01		0,00005	0,00003	5,8E-01
8	Ethylene	28,05	0,01		0,00005	0,00003	5,8E-01
9	Propane	44,10	0,01		99,99848	0,00028	2,8E-06
10	Propylene	42,08	0,01		0,00010	0,00006	5,8E-01
11	n-Butane	58,12	0,01		0,00040	0,00012	3,0E-01
12	i-Butane	58,12	0,01		0,00080	0,00024	3,0E-01
31	Moisture	18,01	0,00		0,00010	0,00003	3,0E-01

Material	i-Butane			99,97700	0,00690	6,9E-05
gas quality	3.8					
supplier	Scott					
batch	VCN1000056					
	Impurities			0,02300	0,00690	3,0E-01
	Sum			100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
12	i-Butane	58,12	0,01		99,97700	0,00690	6,9E-05
15	Neo-Pentane	72,15	0,01		0,02300	0,00690	3,0E-01

Material	n-Butane				99,97225	0,01450	1,5E-04
gas quality	3.5						
supplier	AL						
batch							
	Impurities				0,02775	0,01450	5,2E-01
	Sum				100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
1	Nitrogen	28,01	0,00		0,00200	0,00116	5,8E-01
3	Oxygen	16,00	0,00		0,00050	0,00029	5,8E-01
11	n-Butane	58,12	0,01		99,97225	0,01450	1,5E-04
31	Moisture	18,01	0,00		0,00025	0,00014	5,8E-01
36	UNKNOWN	80,00	20,00		0,02500	0,01445	5,8E-01

Material	Neo-Pentane				98,94500	0,01600	1,6E-04
gas quality	2.0						
supplier	Linde						
batch	35888						
	Impurities				1,05500	0,01600	1,5E-02
	Sum				100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
15	Neo-Pentane	72,15	0,01		98,94500	0,01600	1,6E-04
38	Cyclobutane	58,12	0,01		1,05500	0,01600	1,5E-02

Material	i-Pentane				99,77050	0,01910	1,9E-04
gas quality	2.7						
supplier	Sigma						
batch	BCBM0088V						
	Impurities				0,22950	0,01910	8,3E-02
	Sum				100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
13	n-Pentane	72,15	0,01		0,18680	0,01868	1,0E-01
14	i-Pentane	72,15	0,01		99,77050	0,01910	1,9E-04
15	Neo-Pentane	72,15	0,01		0,03750	0,00375	1,0E-01
16	n-Hexane	86,18	0,01		0,00240	0,00096	4,0E-01
34	Xylol	106,17	0,01		0,00120	0,00060	5,0E-01
35	Pentene	70,13	0,10		0,00160	0,00080	5,0E-01

Material	n-Pentane				99,80300	0,05590	5,6E-04
gas quality	2.7						
supplier	Sigma						
batch	BCBK0693V						
	Impurities				0,19700	0,05590	2,8E-01
	Sum				100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
13	n-Pentane	72,15	0,01		99,80300	0,05590	5,6E-04
14	i-Pentane	72,15	0,01		0,18600	0,05580	3,0E-01
26	2-Methyl-Pentane	86,18	0,01		0,01100	0,00330	3,0E-01

Material	n-Hexane	99,88000	0,00873	8,7E-05
gas quality	2.7			
supplier	Sigma			
batch	BCBP5147V			
	Impurities	0,12000	0,00873	7,3E-02
	Sum	100,00000		

Index	compound	M / g/mol	$u(M)$ / g/mol	vq	x / %	$u(x)$ / %	$u_r(x)$
13	n-Pentane	72,15	0,01		0,00040	0,00020	5,0E-01
16	n-Hexane	86,18	0,01		99,88000	0,00873	8,7E-05
25	3-Methyl-Pentane	86,18	0,01		0,03670	0,00367	1,0E-01
26	2-Methyl-Pentane	86,18	0,01		0,00220	0,00066	3,0E-01
28	Methyl-Cyclopentane	86,18	0,01		0,07880	0,00788	1,0E-01
29	2-Methy-Butane	72,15	0,01		0,00030	0,00015	5,0E-01
30	Octane	114,23	0,01		0,00160	0,00048	3,0E-01

Measurement details for CCQM-K118.1

Laboratory : Instituto Português da Qualidade

Laboratory code : D153520

Calibration standards

– Six primary standard mixtures were used for natural gas analysis. Two of them are from NPL and the other four come from VSL.

	NPL		NMI			
	NG002	NG005	0540E	0541E	0542E	0543E
N_2 (%)	11,996±0,063	1,204±0,011	7,492±0,039	4,977±0,031	10,022±0,052	2,536±0,018
CO_2(%)	4,009+/-0,031	0,8098±0,0098	1,0009±0,0075	2,015±0,016	0,4958±0,0060	0,2035±0,0044
C_2H_6 (%)	0,752±0,015	11,037±0,022	9,995±0,020	7,529±0,025	2,515±0,013	5,022±0,013
C_3H_8 (%)	0,3001±0,0070	4,488±0,026	2,984±0,015	2,0008±0,0099	0,4978±0,0062	1,0047±0,0061
n-C_4H_{10} (%)	0,1998±0,0013	0,10011±0,00092	0,6890±0,0051	0,4970±0,0032	0,0989±0,0012	0,2996±0,0017
i-C_4H_{10} (%)	0,1988±0,0013	0,10017±0,00092	0,4999±0,0030	0,6985±0,0042	0,1000±0,0010	0,2994±0,0018
CH_4 (%)	81,22±0,79	82,23±0,74	77,07±0,80	80,99±0,78	86,51±0,87	90,0±1,1
He (%)	0,5030+/-0,005	-	0,1026+/-0,0005	0,4022+/-0,0020	0,2014+/-0,0010	0,3029+/-0,0015
neo-C_5H_{12} (%)	0,04927+/-0,00049	0,04989+/-0,00050	-	-	-	-
i-C_5H_{12} (%)	0,04944+/-0,00044	0,03489+/-0,00031	0,0999+/-0,0009	0,2933+/-0,0024	0,0490+/-0,0005	0,1998+/-0,0017
n-C_5H_{12} (%)	0,05063+/-0,00046	0,03485+/-0,00031	0,0996+/-0,0009	0,2987+/-0,0024	0,0488+/-0,0005	0,1982+/-0,0017
n-C_6H_{14} (%)	0,04972+/-0,00044	0,02002+/-0,00018	-	-	-	-

Instrumentation

A Gas Chromatograph was used for natural gas analyses.
GC: HP 6890
Columns: 20% Sebaconitrile on Chromosorb PAW, 80/100 Mesh
25% Sebaconitril DC200 PAW, 80/100 Mesh,15 ft
Porapak Q, 80/100 Mesh, 6 ft
Molecular Sieve 13Xx, 45/60 Mesh,4 ft
Molecular Sieve 13Xx, 45/60 Mesh, 10 ft
Detector: 2 Thermal Conductivity Detectors (TCD)
Valves: System of four valves
Sample introduction: Multi position gas sampling valves, injection at 2 bar pressure.
Carrier: N_2 and He
Data Collection: Software Clarity 9.1, 2024

Calibration method and value assignment

The calibration instrument was done according to ISO 6143. We have used the *XGENLINE* to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear function.

For all components were used a set of six PSM (from VSL and NPL). At least six repeat analyses were performed and sometimes the first of these was rejected.

Uncertainty evaluation

The uncertainty measurement was done according to ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".

The uncertainty of measurement associated with the final result has been evaluated and includes two uncertainty sources:

- Uncertainty of Primary Standard mixtures;
- Standard deviation of the mean (GC-Analysis)

these uncertainties were combined and the result was multiplied by a coverage factor of 2 with a confidence interval of 95 %.

References

ISO 6142-1:2015 – Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures

ISO 6143:2001 - Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures

ISO 17034 – General requirements for the competence of reference material producers

Measurement details for CCQM-K118.1

Laboratory : Korea Research Institute of Standards and Science (KRISS)
KC sample cylinder : D153509

Results

Component	Amount fraction (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor*
Nitrogen	0.119716	0.000249	2
Carbon dioxide	0.039780	0.000115	2
Hydrogen	0.030039	0.000059	2
Helium	0.005022	0.000009	2
Ethane	0.007548	0.000026	2
Propane	0.003015	0.000011	2
iso-Butane	0.002006	0.000007	2
n-Butane	0.002016	0.000009	2
iso-Pentane	0.000499	0.000002	2
n-Pentane	0.000505	0.000002	2
neo-Pentane	0.000501	0.000002	2
n-Hexane	0.000498	0.000002	2
Methane	0.788610	0.002840	2

*Coverage factor (k) at approximately 95% of confidence level.

Measurement #1 (June 10, 2025)

Component	Amount fraction (mol/mol)	Relative standard deviation (%)	Number of replicates
Nitrogen	0.119693	0.07	3
Carbon dioxide	0.039779	0.04	3
Hydrogen	0.030039	0.09	3
Helium	0.005024	0.09	3
Ethane	0.007546	0.02	3
Propane	0.003014	0.01	3
iso-Butane	0.002005	0.02	3
n-Butane	0.002016	0.04	3
iso-Pentane	0.000499	0.02	3
n-Pentane	0.000504	0.01	3
neo-Pentane	0.000501	0.04	3

n-Hexane	0.000498	0.03	3
Methane	0.788500	0.02	3

Measurement #2 (June 12, 2025)

Component	Amount fraction (mol/mol)	Relative standard deviation (%)	Number of replicates
Nitrogen	0.119746	0.01	3
Carbon dioxide	0.039774	0.06	3
Hydrogen	0.030047	0.02	3
Helium	0.005022	0.02	3
Ethane	0.007554	0.05	3
Propane	0.003017	0.05	3
iso-Butane	0.002007	0.05	3
n-Butane	0.002018	0.07	3
iso-Pentane	0.000500	0.04	3
n-Pentane	0.000505	0.05	3
neo-Pentane	0.000502	0.08	3
n-Hexane	0.000499	0.07	3
Methane	0.789303	0.07	3

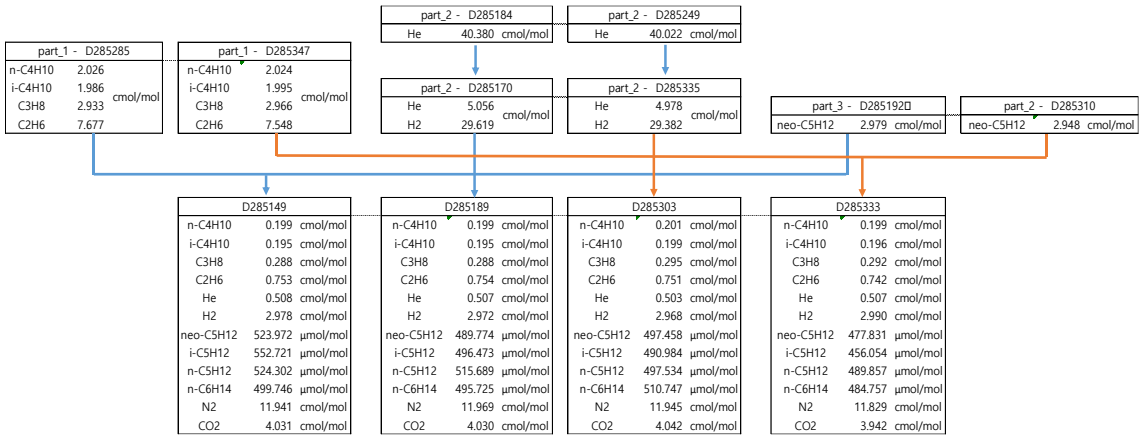
Measurement #3 (June 15, 2025)

Component	Amount fraction (mol/mol)	Relative standard deviation (%)	Number of replicates
Nitrogen	0.119708	0.06	3
Carbon dioxide	0.039788	0.04	3
Hydrogen	0.030030	0.01	3
Helium	0.005022	0.04	3
Ethane	0.007544	0.04	3
Propane	0.003013	0.03	3
iso-Butane	0.002005	0.02	3
n-Butane	0.002015	0.02	3
iso-Pentane	0.000499	0.03	3
n-Pentane	0.000504	0.03	3
neo-Pentane	0.000501	0.04	3
n-Hexane	0.000498	0.03	3
Methane	0.788027	0.06	3

1. Calibration standards

- **Method of preparation**

For this key comparison (KC), KRISS prepared a set of new primary reference gas mixtures (PRMs) using the gravimetric method in accordance with ISO 6142. Four primary reference gas mixtures at the nominal values of this key comparison were prepared through two- or three-step dilutions. Two PRMs (D285149, D285303) were used as calibration standards for measuring this KC sample from VSL. A preparation hierarchy of the PRMs is shown below.



- **Weighing data**

The masses of the pure liquid reagents and the source or the parent gas mixtures used in the preparation of D285149 is summarized in the following table.

Component	Source	Mass (g)	Standard uncertainty (g)
n-hexane	Pure liquid reagent	1.2364	0.0006
n-pentane	Pure liquid reagent	1.0805	0.0005
iso-pentane	Pure liquid reagent	1.1343	0.0005
neo-pentane (2.979 cmol/mol) in methane	Parent gas mixture	8.8802	0.0017
carbon dioxide	Pure gas	50.552	0.002
nitrogen	Pure gas	95.329	0.002
ethane (7.6771 cmol/mol), propane (2.9333 cmol/mol), *iso*-butane (1.9859 cmol/mol), *n*-butane (2.0260 cmol/mol) in methane	Parent gas mixture	54.880	0.002
hydrogen (29.6187 cmol/mol), helium (5.0555 cmol/mol) in methane	Parent gas mixture	32.316	0.002
methane	Pure gas	284.605	0.004

The amount fraction of each component in D285149, along with their standard uncertainties, are summarized in the following table.

Component	Amount fraction (cmol/mol)	Standard uncertainty (cmol/mol)	Relative standard uncertainty (%)
Nitrogen	11.9406	0.0190	0.16
Carbon dioxide	4.0305	0.0064	0.16
Hydrogen	2.9776	0.0053	0.18
Helium	0.5083	0.0010	0.20
Ethane	0.7531	0.0010	0.13
Propane	0.2878	0.0004	0.14
iso-Butane	0.1949	0.0003	0.14
n-Butane	0.1988	0.0004	0.19
iso-Pentane	0.0553	0.0001	0.14
n-Pentane	0.0524	0.0001	0.14
neo-Pentane	0.0524	0.0001	0.15
n-Hexane	0.0500	0.0001	0.15
Methane	78.8976	0.1101	0.14

Similarly, the masses of the pure liquid reagents and the sources or the parent gas mixture cylinders used in the preparation of D285303 are summarized in the following table.

Component	Source	Mass (g)	Standard uncertainty (g)
n-hexane	Pure liquid reagent	1.2680	0.0006
n-pentane	Pure liquid reagent	1.0289	0.0005
iso-pentane	Pure liquid reagent	1.0110	0.0005
neo-pentane (2.948 cmol/mol) in methane	Parent gas mixture	8.5419	0.0028
carbon dioxide	Pure gas	50.872	0.002
nitrogen	Pure gas	95.696	0.001
ethane (7.5478 cmol/mol) propane (2.9661 cmol/mol) *iso*-butane (1.9949 cmol/mol) *n*-butane (2.0236 cmol/mol) in methane	Parent gas mixture	55.846	0.003
hydrogen (29.3820 cmol/mol) helium (4.9782 cmol/mol) in methane	Parent gas mixture	32.709	0.002
methane	Pure gas	285.005	0.004

The amount fraction of each component in D285303, along with their standard uncertainties, are summarized in the following table.

Component	Amount fraction (cmol/mol)	Standard uncertainty (cmol/mol)	Relative standard uncertainty (%)

Nitrogen	11.9452	0.0085	0.07
Carbon dioxide	4.0421	0.0048	0.12
Hydrogen	2.9683	0.0021	0.07
Helium	0.5029	0.0003	0.06
Ethane	0.7511	0.0011	0.14
Propane	0.2953	0.0004	0.13
iso-Butane	0.1986	0.0002	0.13
n-Butane	0.2014	0.0004	0.22
iso-Pentane	0.0491	0.0001	0.22
n-Pentane	0.0498	0.0001	0.21
neo-Pentane	0.0497	0.0001	0.23
n-Hexane	0.0511	0.0001	0.26
Methane	78.8948	0.0973	0.12

- **Purity of the pure liquids and gases**

Impurities in the pure gases (nitrogen, carbon dioxide, hydrogen, helium, ethane, propane, *iso*-butane, *n*-butane, and methane) were analysed primarily using gas chromatographs (GC) equipped with different detectors such as a pulsed discharge detector (PDD), a flame ionization detector (FID), a thermal conductivity detector (TCD). Moisture content was analysed by cavity ring down spectroscopy (CRDS). Impurities in the pure liquids (*iso*-pentane, *n*-pentane, and *n*-hexane) and in the pure gas of *neo*-pentane were analysed using GC-FID. Moisture content in the pure liquid reagents was determined using a Karl-Fisher Analyser (KFA).

Purity table for pure He.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.00005	0.00003
i-C_4H_{10}	0.00005	0.00003
C_3H_8	0.00005	0.00003
C_2H_6	0.00005	0.00003
He	**999997.0**	**0.4**
H_2	0.17	0.11
neo-C_5H_{12}	0.00005	0.00003
i-C_5H_{12}	0.00005	0.00003
n-C_5H_{12}	0.00005	0.00003
n-C_6H_{14}	0.00005	0.00003
N_2	0.58	0.39
CO_2	0.023	0.000
CH_4	0.001	0.001
H_2O	2.20	0.13

Purity table for pure H_2.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.0009	0.0006
i-C_4H_{10}	0.0009	0.0006
C_3H_8	0.0009	0.0006
C_2H_6	0.0009	0.0006
He	0.92	0.62
H_2	**999992.8**	**0.7**
neo-C_5H_{12}	0.0009	0.0006
i-C_5H_{12}	0.0009	0.0006
n-C_5H_{12}	0.0009	0.0006
n-C_6H_{14}	0.0009	0.0006
N_2	0.28	0.01
CO_2	0.036	0.003
CH_4	0.018	0.008
O_2 (+ Ar)	1.73	0.03
H_2O	4.15	0.24

Purity table for pure N_2.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.00005	0.00003
i-C_4H_{10}	0.00005	0.00003
C_3H_8	0.00005	0.00003
C_2H_6	0.00005	0.00003
He	0.21	0.14
H_2	0.06	0.04
neo-C_5H_{12}	0.00005	0.00003
i-C_5H_{12}	0.00005	0.00003
n-C_5H_{12}	0.00005	0.00003
n-C_6H_{14}	0.00005	0.00003
N_2	**999995.7**	**0.2**
CO_2	0.027	0.002
CH_4	0.023	0.000
O_2 (+ Ar)	2.57	0.03
H_2O	1.36	0.08

Purity table for pure CO_2.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.002	0.002

i-C_4H_{10}	0.002	0.002
C_3H_8	0.002	0.002
C_2H_6	0.041	0.001
He	0.21	0.14
H_2	0.12	0.08
neo-C_5H_{12}	0.002	0.002
i-C_5H_{12}	0.002	0.002
n-C_5H_{12}	0.002	0.002
n-C_6H_{14}	0.002	0.002
N_2	0.79	0.01
CO_2	**999997.1**	**0.2**
CH_4	0.004	0.003
O_2 (+ Ar)	1.54	0.09
H_2O	0.18	0.01

Purity table for pure CH_4.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.03	0.02
i-C_4H_{10}	0.26	0.02
C_3H_8	1.36	0.01
C_2H_6	0.11	0.07
He	0.21	0.14
H_2	0.13	0.08
neo-C_5H_{12}	0.03	0.02
i-C_5H_{12}	0.03	0.02
n-C_5H_{12}	0.03	0.02
n-C_6H_{14}	0.03	0.02
N_2	0.57	0.01
CO_2	0.19	0.01
CH_4	**999994.3**	**0.2**
O_2 (+ Ar)	0.14	0.01
H_2O	2.56	0.15

Purity table for pure C_2H_6.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	0.31	0.02
i-C_4H_{10}	0.02	0.01
C_3H_8	3.71	0.03
C_2H_6	**999990.3**	**0.3**
He	0.21	0.14

H_2	1.29	0.07
neo-C_5H_{12}	0.02	0.01
i-C_5H_{12}	0.02	0.01
n-C_5H_{12}	0.02	0.01
n-C_6H_{14}	0.02	0.01
N_2	0.43	0.05
CO_2	0.14	0.01
CH_4	0.03	0.01
O_2 (+ Ar)	0.16	0.01
H_2O	3.28	0.19

Purity table for pure C_3H_8.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	4.07	0.24
i-C_4H_{10}	5.98	0.35
C_3H_8	**999938.9**	**3.4**
C_2H_6	39.17	2.27
He	0.21	0.14
H_2	0.13	0.08
neo-C_5H_{12}	0.02	0.02
i-C_5H_{12}	0.02	0.02
n-C_5H_{12}	0.84	0.05
n-C_6H_{14}	0.02	0.01
N_2	0.39	0.01
CO_2	0.07	0.01
CH_4	0.02	0.01
O_2 (+ Ar)	0.23	0.01
H_2O	0.95	0.11
C_3H_6	7.2	0.4
Unknown C_4	1.8	0.1

Purity table for pure *n*-C_4H_{10}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	**999821.9**	**5.4**
i-C_4H_{10}	51.7	3.0
C_3H_8	0.90	0.05
C_2H_6	0.03	0.02
He	29.5	0.4
H_2	0.17	0.11
neo-C_5H_{12}	0.03	0.02

i-C_5H_{12}	0.03	0.02
n-C_5H_{12}	0.03	0.02
n-C_6H_{14}	0.03	0.02
N_2	29.9	0.5
CO_2	0.88	0.01
CH_4	1.15	0.07
O_2 (+ Ar)	15.8	0.8
H_2O	19.3	2.2
C_3H_6	1.4	0.1
1-C_4H_8	7.1	0.4
i-C_4H_8	6.9	0.4
c-2-C_4H_8	13.2	0.8

Purity table for pure *i*-C_4H_{10}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	1.09	0.06
i-C_4H_{10}	**999893.5**	**5.6**
C_3H_8	65.31	3.79
C_2H_6	2.05	0.12
He	0.23	0.16
H_2	0.17	0.11
neo-C_5H_{12}	0.03	0.02
i-C_5H_{12}	0.03	0.02
n-C_5H_{12}	0.03	0.02
n-C_6H_{14}	0.03	0.02
N_2	0.35	0.23
CO_2	0.27	0.00
CH_4	0.71	0.04
H_2O	9.9	0.7
1-C_4H_8	1.4	0.1
Unknown C_4	24.9	1.5

Purity table for pure *neo*-C_5H_{12}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	786.5	4.7
i-C_4H_{10}	767.7	4.8
C_3H_8	10.55	0.09
C_2H_6	1.16	0.03
He	0.23	0.16
H_2	0.17	0.11

neo-C_5H_{12}	**996152.3**	**34.0**
i-C_5H_{12}	0.03	0.02
n-C_5H_{12}	0.03	0.02
n-C_6H_{14}	1.00	0.01
N_2	1967	15
CO_2	4.6	0.2
CH_4	0.07	0.01
H_2O	257.4	29.7
Unknown C_4	50.9	0.4
CO	0.15	0.01

Purity table for pure *i*-C_5H_{12}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_4H_{10}	99.2	5.7
i-C_5H_{12}	**999653.7**	**8.6**
n-C_5H_{12}	219.9	6.4
Unknown C_4	13.9	0.8
H_2O	13.2	0.7

Purity table for pure *n*-C_5H_{12}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
i-C_5H_{12}	2288.9	66.0
n-C_5H_{12}	**997416.3**	**66.5**
Unknown C_4	264.3	7.6
H_2O	30.6	2.5

Purity table for pure *n*-C_6H_{14}.

Component	Amount fraction (µmol/mol)	Standard uncertainty (µmol/mol)
n-C_6H_{14}	**992440.4**	**32.3**
C_6H_{14} (2-methyl)	1368.7	7.9
C_6H_{14} (3-methyl)	5127.7	29.6
C_6H_{12}	736.5	4.3
Unknown C_4	225.0	6.5
H_2O	101.7	6.8

- **Verification measures**
  - **Internal consistency between the KRISS calibration gas standards**

The amount fractions of each component in a verification gas standard (D285333), used to assess internal consistency with the calibration gas standards (D285149 and D285303), together with their standard uncertainties, are summarized in the following table.

Component	Amount fraction (cmol/mol)	Standard uncertainty (cmol/mol)	Relative standard uncertainty (%)
Nitrogen	11.8293	0.0151	0.13
Carbon dioxide	3.9422	0.0050	0.13
Hydrogen	2.9896	0.0034	0.11
Helium	0.5065	0.0006	0.12
Ethane	0.7420	0.0009	0.12
Propane	0.2917	0.0003	0.12
iso-Butane	0.1962	0.0002	0.12
n-Butane	0.1990	0.0004	0.18
iso-Pentane	0.0456	0.0001	0.14
n-Pentane	0.0490	0.0001	0.13
neo-Pentane	0.0478	0.0001	0.16
n-Hexane	0.0485	0.0001	0.14
Methane	79.1120	0.1037	0.13

The response factors of each component in the calibration gas standards (D285149 and D285303) were compared with those in the verification gas standard (D285333) using a comparative analysis method in accordance with ISO 6143.

The relative expanded uncertainties of internal consistency among the verification and calibration gas standards are summarized in the following table. The relative differences between the calibration gas standards and the verification gas standard were smaller than their relative expanded uncertainties, indicating the internal consistence of the calibration gas standards were successfully verified.

Component	Difference between D285149 vs D285333	Relative expanded uncertainty	Difference between D285303 vs D285333	Relative expanded uncertainty
	$\lvert C\text{-}V \rvert^*$ (%)	(%)	$\lvert C\text{-}V \rvert$ (%)	(%)
Nitrogen	0.03	0.41	0.03	0.30
Carbon dioxide	0.11	0.41	0.10	0.37
Hydrogen	0.07	0.42	0.03	0.27
Helium	0.06	0.46	0.01	0.27
Ethane	0.05	0.39	0.07	0.37
Propane	0.06	0.39	0.12	0.35
iso-Butane	0.02	0.38	0.03	0.38
n-Butane	0.23	0.64	0.00	0.64
iso-Pentane	0.06	0.65	0.07	0.69
n-Pentane	0.01	0.79	0.04	0.82

neo-Pentane	0.13	0.72	0.37	0.64
n-Hexane	0.01	0.71	0.05	0.76
Methane	0.10	0.37	0.11	0.35

* Relative deviations (%) were calculated using the expression $|C - V|/V \times 100$, where C is the response factor of each component in the calibration gas standards (D285149 and D285303), and V is the corresponding response factor in the verification gas standard (D285333).

2. Instrumentation

The amount fractions of ethane, propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane, *n*-hexane, and methane were determined using GC-FID (Agilent 8890) with a calibration gas standard, D258149. The amount fractions of nitrogen, hydrogen, helium, and carbon dioxide were determined using GC-TCD (Agilent 8890) with a calibration gas standard, D285303. A constant gas flow rate for introducing gas sample to GC was maintained using a mass flow controller (MFC), and GC signals were integrated as peak areas.

Measurement parameter	He, H_2, N_2
Detector	Agilent 8890 GC-TCD
Column	MS5A, 9 ft*4
Column flow rate	70 psi
Oven temperature	125 ºC, 45 min
Sample loop	1 mL
Carrier gas	Ar

Measurement parameter	CO_2
Detector	Agilent 8890 GC-TCD
Column	Porapak Q, 9 ft*2
Column flow rate	45 psi
Oven temperature	200 ºC, 15 min
Sample loop	0.05 mL
Carrier gas	He

Measurement parameter	ethane, propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane, *n*-hexane, methane
Detector	Agilent 8890 GC-FID
Column	AL203/KCL Capillary 50 m x 500 µm x 10 µm
Column flow rate	5 mL/min
Oven temperature	120 ºC, 30 min
Sample loop	0.5 mL
Carrier gas	N_2

3. Calibration method and value assignment

The KC sample (D153509) from VSL was contained in an aluminium cylinder with a nominal volumetric capacity of 5 L. Prior to analysis, the cylinder was stored for more than two days in a temperature-controlled laboratory at 22 ± 1°C. The overall procedures and value-assignment procedures followed ISO 6143. A one-point calibration method was applied to determine the amount fractions of the components in the KC sample relative to the KRISS calibration gas standards (D285149 and D285303). For value assignment and uncertainty evaluation, a bracketing method (KRISS calibration gas standards – KC sample – KRISS calibration gas standards) was used as the comparison procedure. After averaging the multiple response values of the calibration gas standards with drift compensation applied, the amount fractions of the components in the KC sample were calculated by directly comparing the averaged response values with the assigned amount fractions of the calibration gas standards.

4. Uncertainty evaluation

- **Model equation for a measurement data set**

The amount fraction of the KC sample was determined by the following equation for each measurement.

$$x_{KC,i,j} = x_{KRISS} \times R_{i,j}$$

$$u\left(x_{KC,i,j}\right) = x_{KC,i,j} \times \sqrt{\left(\frac{u(x_{KRISS})}{x_{KRISS}}\right)^2 + \left(\frac{u(R_{i,j})}{R_{i,j}}\right)^2}$$

where $x_{KC,i,j}$ is the amount fraction of KC sample, x_{KRISS} is the amount fraction of KRISS calibration gas standards, and $R_{i,j}$ is the analyser's response ratio of 3 repeated measurements (i.e., injections) (i.e., response of KC sample to response of KRISS calibration gas standard). At three different days (i=1, 2, 3), three repeated measurements (j= 1, 2, 3) have been conducted. The total number of measurements are 9 for three days.

	Average	1st analysis	2nd analysis	3rd analysis
1st day measurement	$x_{KC,1,avg}$	$x_{KC,1,1}$	$x_{KC,1,2}$	$x_{KC,1,3}$
2nd day measurement	$x_{KC,1,avg}$	$x_{KC,2,1}$	$x_{KC,2,2}$	$x_{KC,2,3}$
3rd day measurement	$x_{KC,1,avg}$	$x_{KC,3,1}$	$x_{KC,3,2}$	$x_{KC,3,3}$
Reported final results	$\boldsymbol{x_{KC,f}}$	$\boldsymbol{u(x_{KC,f})}$		

$$x_{KC,i,avg} = \frac{x_{KC,i,1} + x_{KC,i,2} + x_{KC,i,3}}{3}$$

$$x_{KC,f} = \frac{x_{KC,1,avg} + x_{KC,2,avg} + x_{KC,3,avg}}{3}$$

The standard uncertainty of reported final results ($x_{KC,f}$) was calculated using the following equation, taking into account the uncertainties of the KRISS calibration gas standard, repeatability and reproducibility of the KC sample analyses.

$$u(x_{KC,f}) = \sqrt{u^2_{KRISS\ CAL\ gas\ standard} + u^2_{repeatibility} + u^2_{reproducibility}}$$

Measurement report of SE «UKRMETRTESTSTANDART»

1. Results

Cylinder number: D153513.

Final results are given in Table 1.

Table 1. **Final results**

Component	Fraction (cmol/mol)	Expanded uncertainty (cmol/mol)	Coverage factor
Nitrogen	11.99	0.12	2
Carbon dioxide	4.050	0.024	2
Hydrogen	3.031	0.022	2
Helium	0.4974	0.0049	2
Ethane	0.7513	0.0045	2
Propane	0.3002	0.0019	2
i-Butane	0.1989	0.0017	2
n-Butane	0.1985	0.0015	2
i-Pentane	0.04918	0.00051	2
n-Pentane	0.05007	0.00049	2
neo-Pentane	0.04916	0.00075	2
n-Hexane	0.05002	0.00047	2
Methane	78.79	0.12	2

2. Calibration standards

Three Primary Standard Gas Mixtures (PSGM) were used as calibration standards. PSGMs were prepared gravimetrically according to ISO 6142-1 [1]. Parent gases were pure n-hexane, pure n-butane, pure i-butane, pure methane and previously prepared five pre-mixtures: 1) helium amount fraction of 14.3 % in hydrogen, 2) helium amount fraction of 3.57 % and hydrogen amount fraction of 21.5 % in methane, 3) carbon dioxide amount fraction of 25.0 % in nitrogen, 4) ethane amount fraction of 6.0 % and propane amount fraction of 2.4 % in methane, 5) n-pentane, i-pentane and neo-pentane amount fractions of 0.25 % in methane.

Composition of the PSGMs is given in Tables 2 to 4.

Table 2. Composition of PSGM No 1, cylinder number 81205104

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	813097	13
N_2	108603	9
CO_2	36160	3
H_2	24758	5
C_2H_6	6062.2	0.8
He	4115	1
C_3H_8	2411.3	0.4
n-C_4H_{10}	1602.6	1.6
i-C_4H_{10}	1585.2	1.6
neo-C_5H_{12}	407.91	0.22
n-C_6H_{14}	404.5	1.1
i-C_5H_{12}	393.89	0.22
n-C_5H_{12}	391.04	0.22
c-C_5H_{10}	4.86	0.09
O_2	1.47	0.02
H_2O	1.22	0.04
Ar	0.54	0.03
c-C_6H_{12}	0.067	0.002
1-C_4H_8	0.065	0.002
trans-2-C_6H_{12}	0.054	0.001
cis-2-C_6H_{12}	0.033	0.001
2-C_4H_8	0.030	0.001
CO	0.0005	0.0003

Table 3. Composition of PSGM No 2, cylinder number 81205128

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	787723	14
N_2	120528	9
CO_2	40131	3
H_2	30128	6
C_2H_6	7504.5	1.0
He	5007.6	1.2
C_3H_8	2985.0	0.5
n-C_4H_{10}	1995.4	1.4
i-C_4H_{10}	1991.4	1.4
neo-C_5H_{12}	511.24	0.28
n-C_6H_{14}	500.36	0.93
i-C_5H_{12}	493.69	0.27
n-C_5H_{12}	490.12	0.28
c-C_5H_{10}	6.03	0.11
O_2	1.43	0.02
H_2O	1.35	0.05
Ar	0.60	0.03
c-C_6H_{12}	0.082	0.002
1-C_4H_8	0.082	0.002
trans-2-C_6H_{12}	0.067	0.002
cis-2-C_6H_{12}	0.040	0.001
2-C_4H_8	0.037	0.001
CO	0.0006	0.0004

Table 4. Composition of PSGM No 3, cylinder number 81205023

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	758289	16
N_2	135270	10
CO_2	45040	4
H_2	36932	7
C_2H_6	7886	1
He	6138.4	1.4
C_3H_8	3137.5	0.5
n-C_4H_{10}	2448.2	1.7
i-C_4H_{10}	2427.9	1.7
neo-C_5H_{12}	624.10	0.34
n-C_6H_{14}	602.64	0.34
i-C_5H_{12}	598.30	0.34
n-C_5H_{12}	594.13	1.14
c-C_5H_{10}	7.21	0.13
O_2	1.52	0.05
H_2O	1.40	0.02
Ar	0.68	0.03
c-C_6H_{12}	0.100	0.002
1-C_4H_8	0.098	0.002
trans-2-C_6H_{12}	0.079	0.002
cis-2-C_6H_{12}	0.048	0.001
2-C_4H_8	0.046	0.001
CO	0.0007	0.0004

Composition of the premixtures is given in Tables 5 to 9.

Table 5. Composition of the premixture He – H_2, cylinder number 70491

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
H_2	857449	25
He	142515	25
N_2	29.5	0.7
O_2	6.13	0.13

Table 6. Composition of the premixture He – H_2 – CH_4, cylinder number 81215176

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	749286	44
H_2	214971	38
He	35730	8
N_2	11.5	0.2
O_2	2.32	0.04

Table 7. Composition of the premixture CO_2 – N_2, cylinder number D200354

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
N_2	750186	11
CO_2	249801	11
H_2O	8.42	0.39
Ar	3.75	0.19
O_2	0.645	0.025
CH_4	0.240	0.011
CO	0.004	0.002
H_2	0.004	0.002

Table 8. Composition of the premixture C_2H_6 – C_3H_8 – CH_4, cylinder number 81205016

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	915755	9
C_2H_6	60291	8
C_3H_8	23947	4
N_2	5.73	0.14
O_2	1.19	0.02
H_2	0.241	0.006
CO_2	0.066	0.002

Table 9. Composition of the premixture n-C_5H_{12} – i-C_5H_{12} – neo-C_5H_{12} – CH_4, cylinder number 81205019

Component	Amount fraction, µmol/mol	Std. uncertainty (gravimetric), µmol/mol
CH_4	992478	3
neo-C_5H_{12}	2551.1	1.4
i-C_5H_{12}	2469.9	1.4
n-C_5H_{12}	2452.1	1.4
C_2H_6	21.7	0.5
n-C_4H_{10}	8.52	0.13
c-C_5H_{10}	7.70	0.20
N_2	5.46	0.15
C_3H_8	3.51	0.09
O_2	1.03	0.02
n-C_6H_{14}	0.816	0.015
i-C_4H_{10}	0.465	0.013
2-C_4H_{10}	0.187	0.005

Purity data for parent gases are given in Tables 10 to 23.

Table 10. Purity data for methane used to prepare premixtures

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.00000104	0.00000025
N_2	0.0000055	0.0000015
CH_4	0.9999935	0.0000015

Table 11. Purity data for methane used to prepare final PSGMs.

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.00000171	0.00000005
N_2	0.0000125	0.0000003
CH_4	0.9999858	0.0000003

Table 12. Purity data for helium

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.00000152	0.00000005
N_2	0.00000210	0.00000005
He	0.99999643	0.00000007

Table 13. Purity data for hydrogen

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.00000692	0.00000015
N_2	0.00003401	0.00000085
H_2	0.9999591	0.0000009

Table 14. Purity data for carbon dioxide

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
CH_4	0.00000084	0.00000004
O_2	0.00000240	0.00000010
N_2	0.00000980	0.00000025
H_2O	0.000022	0.000001
CO_2	0.999965	0.000001

Table 15. Purity data for nitrogen

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
H_2	0.000000005	0.000000003
CO	0.000000005	0.000000003
CH_4	0.000000040	0.000000005
CO_2	0.000000040	0.000000005
O_2	0.000000060	0.000000005
H_2O	0.0000039	0.0000002
Ar	0.00000500	0.00000025
N_2	0.99999095	0.00000032

Table 16. Purity data for propane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.00000950	0.00000025
N_2	0.0000270	0.0000007
C_3H_8	0.9999635	0.0000007

Table 17. Purity data for ethane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
O_2	0.000000172	0.000000005
CH_4	0.000000203	0.000000005
N_2	0.00000073	0.00000002
CO_2	0.00000110	0.00000003
H_2	0.0000040	0.00000010
C_2H_6	0.999993802	0.000000011

Table 18. Purity data for n-pentane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
2-C_4H_8	0.000076	0.000002
n-C_6H_{14}	0.000213	0.000005
i-C_5H_{12}	0.002930	0.000075
c-C_5H_{10}	0.00313	0.00008
n-C_5H_{12}	0.99365	0.00011

Table 19. Purity data for i-pentane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
n-C_6H_{14}	0.000118	0.000003
neo-C_5H_{12}	0.001020	0.000025
n-C_5H_{12}	0.00312	0.00008
i-C_5H_{12}	0.995742	0.000084

Table 20. Purity data for neo-pentane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
i-C_4H_{10}	0.000180	0.000005
C_3H_8	0.001360	0.000035
n-C_4H_{10}	0.00330	0.00005
C_2H_6	0.00840	0.00020
neo-C_5H_{12}	0.98676	0.00021

Table 21. Purity data for n-butane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
CO_2	0.0000020	0.0000005
i-C_5H_{12}	0.0000060	0.0000005
O_2	0.0000110	0.0000005
N_2	0.0000520	0.0000015
C_3H_8	0.0000970	0.0000025
neo-C_5H_{12}	0.000670	0.000015
i-C_4H_{10}	0.00214	0.00005
n-C_4H_{10}	0.997022	0.000052

Table 22. Purity data for i-butane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
i-C_5H_{12}	0.00000100	0.00000005
1-C_4H_8	0.000041	0.000001
CH_4	0.0000180	0.0000005
CO_2	0.0000220	0.0000005
C_2H_6	0.000495	0.000013
n-C_4H_{10}	0.00210	0.00005
C_3H_8	0.00280	0.00005
i-C_4H_{10}	0.994523	0.000072

Table 23. Purity data for n-hexane

Component	Amount fraction, mol/mol	Std. uncertainty, mol/mol
cis-2-C_6H_{12}	0.000080	0.000002
trans-2-C_6H_{12}	0.0001320	0.0000035
c-C_6H_{12}	0.000163	0.000004
c-C_5H_{10}	0.0089	0.0002
n-C_6H_{14}	0.99072	0.00020

PSGMs were prepared gravimetrically according to ISO 6142-1 [1]. PSGM composition was calculated by formula (3) from ISO 6142-1 [1].

Amount fraction of impurities was measured/calculated according to ISO 19229 [2].

Example weighing data for PSGM No 1 are given in Table 24.

Table 24. Weighing data for PSGM No 1

Parent gas	Transferred mass, g	Std. uncertainty, g
n-C_6H_{14}	1.4700	0.0039
n-C_4H_{10}	3.9000	0.0039
i-C_4H_{10}	3.8600	0.0039
Premixture n-C_5H_{12} – i-C_5H_{12} – neo-C_5H_{12} –CH_4	109.9080	0.0057
Premixture CO_2 – N_2	193.9740	0.0071
Premixture He – H_2 – CH_4	60.7360	0.0049
Premixture C_2H_6 – C_3H_8 – CH_4	73.8620	0.0051
CH_4	730.0280	0.0092

3. Instrumentation

Balance used for PSGM preparation by gravimetric method: Mettler Toledo electronic balance XP26003L.

Helium, hydrogen, nitrogen, carbon dioxide and hydrocarbons C2-C4 amount fractions were measured using gas chromatograph HP 6890 with a thermal conductivity detector (GC-TCD) and column HayeSep Q 10ft 80/100 mesh. Carrier gas – Argon. Oven temperature 30 - 200 °C.

Hydrocarbons C5-C6 amount fraction was measured using gas chromatograph Agilent 6890N with a flame ionisation detector (GC-FID) and column GS-Alumina 50 m × 0.53 mm. Carrier gas – Helium. Oven temperature 35 - 190 °C.

Purity analysis of parent gases was performed using Agilent 6890N gas chromatographs with helium ionization detector, flame ionization detector, thermal conductivity detector and mass spectrometry detector.

4. Calibration method and value assignment

Calibration was performed according to ISO 6143 [3] using linear model. Four measurements were made, each for two days: one day for all the components, except for pentanes and hexane, using chromatograph with TCD and another day for pentanes and hexane using chromatograph with FID. Three runs, each including three PSGMs and the mixture to be analysed, were performed for each measurement. For each measurement, peak areas obtained during the runs were averaged, and the averaged values were used to obtain linear function coefficients and, consequently, measured values of the component amount fraction according to ISO 6143. Calculations were performed using B_LEAST software. The values from the four measurements were pooled to give the final values (see Table 1). Methane mole fraction x_{CH4}, cmol/mol, was calculated by difference:

$$x_{CH4} = 100 - \sum x_j$$

where x_j are measured mole fractions of the non-methane components, cmol/mol.

5 Uncertainty evaluation

5.1 Uncertainty of PSGMs

PSGM gravimetric uncertainty was calculated by formula (4) from ISO 6142-1 [1], with no

correlations taken into account. Stability term was not included into the uncertainty budget as no significant short-term drift was revealed. Also, from the long-time experience it is known that for the kind of gas mixtures concerned this term can be regarded negligible compared to the claimed uncertainty level. Thus, preparation uncertainty to be calculated by formula (7) from ISO 6142-1 [1] becomes equal to the gravimetric uncertainty.

The PSGMs were verified by examining their mutual consistency according to ISO 6143 [3]. Uncertainty term from verification was estimated for each component of the PSGMs via the differences, Δ, between gravimetric values of amount fractions, x_{grav}, and those determined using linear analysis function for each component of the PSGMs, x_{ver}:

$$\Delta = x_{grav} - x_{ver}$$

Value of Δ for each component was determined as an average of three measurements. In each case the compatibility criterion established by formula (8) from ISO 6142-1 [1] was met. Then the combined uncertainties in component amount fractions, $u_c(x)$, were calculated in accordance with formula (9) from ISO 6142-1 [1].

5.2 Uncertainty of analysis results

Uncertainty of analysis results for each of four measurements was evaluated according to ISO 6143 [3], taking into account uncertainty of PSGMs and variability of output signal (peak areas). Calculations were performed using B_LEAST software. Then the uncertainties of the four measurements for each non-methane component j were combined to obtain the standard uncertainty of a final averaged amount fraction, $u(x_j)$, by formula:

$$u(x_j) = \sqrt{\sum_{i=1}^{n} u(x_{ij})^2 / n}$$

where $u(x_{ij})$ is a standard uncertainty of an amount fraction of component j in the i-th measurement and n is a number of measurements. In our case n = 4.

For methane, a standard uncertainty was calculated by formula:

$$u(x_{CH4}) = \sqrt{\sum_{j=1}^{m} u(x_j)^2}$$

where $u(x_j)$ is a standard uncertainty of an amount fraction of component j and m is a number of non-methane components. In our case m = 12.

6 References

1. ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures

2. ISO 19229:2019 Gas analysis – Purity analysis and the treatment of purity data

3. ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures

Measurement details for CCQM-K118.1

Institute name	Van Swinden Laboratorium
Institute acronym	VSL
Address	Thijsseweg 11
ZIP	2629JA
City	Delft
Country	Netherlands
Contact name	Roel Beelen
Phone	015-2691500
Fax	
E-mail	rbeelen@vsl.nl

Cylinder number	D153626

Results

Measurement 1

Component	Date	Unit	x	std.dev.	u(x)	n
Nitrogen	13/11/2024	cmol/mol	12.003	0.06	8.48E-04	7
Carbon dioxide	22/11/2024	cmol/mol	3.9856	0.19	7.92E-04	7
Hydrogen	13/11/2024	cmol/mol	3.0145	0.06	3.23E-04	7
Helium	13/11/2024	cmol/mol	0.49871	0.06	6.04E-05	7
Ethane	22/11/2024	cmol/mol	0.75283	0.08	6.95E-05	7
Propane	22/11/2024	cmol/mol	0.30058	0.08	2.72E-05	7
iso-Butane	22/11/2024	cmol/mol	0.20061	0.08	1.93E-05	7
n-Butane	22/11/2024	cmol/mol	0.20002	0.07	1.88E-05	7
iso-Pentane	22/11/2024	cmol/mol	0.049999	0.11	8.63E-06	7
n-Pentane	22/11/2024	cmol/mol	0.050538	0.11	8.44E-06	7
neo-Pentane	10/09/2024	cmol/mol	0.050116	0.25	1.87E-05	7
n-Hexane	14/01/2025	cmol/mol	0.049941	0.02	3.62E-05	7
Methane	13/11/2024	cmol/mol	78.831	0.07	5.73E-03	7

Measurement 2

Component	Date	Unit	x	std.dev.	u(x)	n
Nitrogen	16/11/2024	cmol/mol	12.004	0.07	1.02E-03	7
Carbon dioxide	28/11/2024	cmol/mol	3.9869	0.11	4.94E-04	7
Hydrogen	16/11/2024	cmol/mol	3.0141	0.07	3.91E-04	7
Helium	16/11/2024	cmol/mol	0.49844	0.11	8.17E-05	7
Ethane	28/11/2024	cmol/mol	0.75252	0.06	5.83E-05	7
Propane	28/11/2024	cmol/mol	0.30071	0.06	4.01E-05	7
iso-Butane	28/11/2024	cmol/mol	0.20056	0.04	1.80E-05	7
n-Butane	28/11/2024	cmol/mol	0.19999	0.05	1.82E-05	7
iso-Pentane	28/11/2024	cmol/mol	0.049979	0.06	7.36E-06	7
n-Pentane	28/11/2024	cmol/mol	0.050531	0.05	7.03E-06	7
neo-Pentane	11/09/2024	cmol/mol	0.05009	0.21	1.68E-05	7
n-Hexane	15/01/2025	cmol/mol	0.050073	0.01	3.35E-05	7
Methane	16/11/2024	cmol/mol	78.833	0.04	4.81E-03	7

Measurement 3

Component	Date	Unit	x	std.dev.	u(x)	n
Nitrogen	19/01/2025	cmol/mol	12.005	0.06	0.000937	7
Carbon dioxide	10/12/2024	cmol/mol	3.9872	0.06	0.000419	7
Hydrogen	19/01/2025	cmol/mol	3.0153	0.04	0.000317	7
Helium	19/01/2025	cmol/mol	0.49855	0.15	9.61E-05	7
Ethane	10/12/2024	cmol/mol	0.75295	0.05	5.96E-05	7
Propane	10/12/2024	cmol/mol	0.30069	0.06	2.41E-05	7
iso-Butane	10/12/2024	cmol/mol	0.20072	0.05	1.7E-05	7

n-Butane	10/12/2024	cmol/mol	0.20014	0.05	1.58E-05	7
iso-Pentane	10/12/2024	cmol/mol	0.050017	0.08	7.74E-06	7
n-Pentane	10/12/2024	cmol/mol	0.050568	0.08	7.88E-06	7
neo-Pentane	18/09/2024	cmol/mol	0.050053	0.39	2.60E-05	7
n-Hexane	16/01/2025	cmol/mol	0.050028	0.02	3.62E-05	7
Methane	19/01/2025	cmol/mol	78.837	0.02	0.002933	7

Final result

Component	Unit	x	U(x)	k	u(x)	probability distribution
Nitrogen	cmol/mol	12.004	0.012	2	0.60%	Normal distribution
Carbon dioxide	cmol/mol	3.987	0.004	2	0.20%	Normal distribution
Hydrogen	cmol/mol	3.0146	0.0045	2	0.23%	Normal distribution
Helium	cmol/mol	0.4986	0.0010	2	0.05%	Normal distribution
Ethane	cmol/mol	0.7528	0.0015	2	0.08%	Normal distribution
Propane	cmol/mol	0.3007	0.0009	2	0.05%	Normal distribution
iso-Butane	cmol/mol	0.2006	0.0002	2	0.01%	Normal distribution
n-Butane	cmol/mol	0.2000	0.0002	2	0.01%	Normal distribution
iso-Pentane	cmol/mol	0.05000	0.00012	2	0.01%	Normal distribution
n-Pentane	cmol/mol	0.05055	0.00010	2	0.01%	Normal distribution
neo-Pentane	cmol/mol	0.05009	0.00010	2	0.01%	Normal distribution
n-Hexane	cmol/mol	0.05001	0.00010	2	0.01%	Normal distribution
Methane	cmol/mol	78.835	0.016	2	0.80%	Normal distribution

Method of Preparation

The preparation of PSMs (Primary Standard gas Mixtures) is carried out in accordance with ISO 6142-1 [1]. The weighing of the gas cylinder in which the gas mixture is prepared is done using the well-known substitution method. The automated weighing device used for these preparations has a standard uncertainty between 1 mg and 2 mg, taking into consideration the repeatability of the balance and the buoyancy effect on the cylinder. After transferring of a gas, the cylinder is allowed to equilibrate with the temperature in the weighing laboratory, prior to being weighed. An example of the uncertainty calculations of the weighing method has been published [2][3].

A natural gas standard mixture is prepared using the parent gases. For some components a pre-mixture was required, this was then first prepared using the parent gases, the final mixture was then prepared using these pre-mixtures. The purity analysis of these parent gases were performed in

accordance with ISO 19229[4], using a variety of analytical techniques. In cases where an expected impurity is not detected, the limit of detection is taken as basis for assigning a value to the corresponding amount-of-substance fraction, assuming a rectangular distribution. The associated standard uncertainty is computed accordingly. The composition of the gravimetrically prepared mixtures is calculated using the formulas for the amount-of-substance fraction given in ISO 6142-1. For propagating the uncertainty due to weighing, purity of the parent gases and the atomic weights, the formula of ISO 6142-1 is used, thus ignoring the correlations that exist between the masses recorded for the transferred gases and the molar masses. The magnitude of these effects has recently been evaluated for the preparation of synthetic natural gas mixtures, where these correlation effects are substantially greater. The approach regularly used by VSL is consistent with ISO 6142-1, and deviates in the same way from the requirements of the Guide to the expression of Uncertainty in Measurement (GUM) [5] as the documentary standard does.

Purity data of the parent gases (mol mol^{-1})

Table 1 Purity data helium (mol mol^{-1})

Component	APHE6B (helium)	
	x	u(x)
Methane	0.000000025	0.000000014
Carbon monoxide	0.000000013	0.000000008
Carbon dioxide	0.000000013	0.000000008
Helium	0.999999800	0.000000050
Hydrogen	0.000000050	0.000000029
Water	0.000000010	0.000000006
Nitrogen	0.000000050	0.000000029
Oxygen	0.000000005	0.000000003

Table 2 Purity data nitrogen (mol mol^{-1})

Component	APN26B (nitrogen)	
	x	u(x)
Argon	0.000005000	0.000003000
Methane	0.000000001	0.000000001
Carbon monoxide	0.000000001	0.000000001
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000025	0.000000015
Water	0.000000010	0.000000006
Nitrogen	0.999994900	0.000006000
Oxygen	0.000000100	0.000000030

Table 3 Purity data carbon dioxide (mol mol^{-1})

Component	AP9358 (carbon dioxide)	
	x	u(x)
Methane	0.000000100	0.000000060
Carbon monoxide	0.000000500	0.000000300
Carbon dioxide	0.999988000	0.000004000
Water	0.000001850	0.000000100
Nitrogen	0.000004300	0.000002100
Oxygen	0.000005300	0.000002600

Table 4 Purity data methane (mol mol^{-1})

Component	APCH4 (methane)	
	x	u(x)
Methane	0.999998500	0.000001000
Carbon monoxide	0.000000050	0.000000029
Carbon dioxide	0.000000050	0.000000030
Ethane	0.000000050	0.000000030
Propane	0.000000005	0.000000003
Hydrogen	0.000000050	0.000000030
Nitrogen	0.000001000	0.000000600
Oxygen	0.000000250	0.000000140

Table 5 Purity data ethane (mol mol^{-1})

Component	SC0084 (ethane)	
	x	u(x)
Ethane	0.999975600	0.000003000
Nitrogen	0.000011200	0.000001800
Oxygen	0.000013200	0.000001100

Table 6 Purity data propane (mol mol^{-1})

Component	AL3643 (propane)	
	x	u(x)
Ethane	0.000000100	0.000000010
Propene	0.000114000	0.000011000
Propane	0.999855600	0.000015000
Iso-butene	0.000000060	0.000000030
n-butane	0.000001610	0.000000160
Iso-butane	0.000000230	0.000000030
1-pentene	0.000000400	0.000000200
n-pentane	0.000000040	0.000000020
Nitrogen	0.000028000	0.000006000

Table 7 Purity data iso-butane (mol mol^{-1})

Component	SC0737 (iso-butane)	
	x	u(x)
Methane	0.000000105	0.000000010
Carbon dioxide	0.000013000	0.000002000
Propane	0.000000510	0.000000050
n-butane	0.000180000	0.000020000
Iso-butane	0.999786300	0.000041000
Iso-pentane	0.000000105	0.000000010
Water	0.000005000	0.000002500
Nitrogen	0.000015000	0.000002000

Table 8 Purity data n-butane (mol mol^{-1})

Component	SC0175 (n-butane)	
	x	u(x)
Argon	0.000000700	0.000000200
Methane	0.000007000	0.000002000
Carbon dioxide	0.000010000	0.000005000
Ethene	0.000000060	0.000000006
Ethane	0.000000250	0.000000020
Propene	0.000000014	0.000000003
Propane	0.000010300	0.000000500
n-butane	0.999614700	0.000030000
Iso-butane	0.000243000	0.000013000
Helium	0.000005000	0.000002000
Water	0.000005000	0.000002500
Nitrogen	0.000022000	0.000003000
Oxygen	0.000005000	0.000001000
Neo-pentane	0.000077000	0.000003000

Table 9 Purity data iso-pentane (mol mol^{-1})

Component	AL9865 (iso-pentane)	
	x	u(x)
n-butane	0.000108000	0.000011000
Iso-butane	0.000017000	0.000002500
1-pentene	0.000432000	0.000005000
n-pentane	0.004941000	0.000030000
Iso-pentane	0.994471000	0.000060000
Neo-pentane	0.000031000	0.000004500

Table 10 Purity data n-pentane (mol mol^{-1})

Component	AL8821 (n-pentane)	
	x	u(x)
1-pentene	0.001098000	0.000034000
n-pentane	0.997518000	0.000080000
Iso-pentane	0.000964000	0.000012000
Hydrocarbons	0.000420000	0.000017000

Table 11 Purity data neo-pentane (mol mol^{-1})

Component	SC0152 (neo-pentane)	
	x	u(x)
Ethane	0.000001220	0.000000122
Propane	0.000004440	0.000000444
n-butane	0.001681000	0.000010000
Iso-butane	0.000005650	0.000000565
Hydrocarbons	0.000026000	0.000010000
Oxygen	0.000500000	0.000290000
Neo-pentane	0.997781700	0.000581000

Table 12 Purity data n-hexane (mol mol^{-1})

Component	ME3010 (n-hexane)	
	x	u(x)
n-pentane	0.000006900	0.000003000
n-hexane	0.996833100	0.001000000
cyclohexane	0.001550000	0.000500000
3-methyl-pentane	0.000805000	0.000250000
2-methyl-pentane	0.000805000	0.000250000

Analysis equipment

Three gas chromatographs (GC) were used for the analysis.

GC-23
The analyses were performed on a four channel Agilent 8890 GC custom configured for the analysis of the composition of natural gas and biogas.

1ste channel, suitable for analysis of $C_1 – C_6$: This channel is configured with a PDMS column column in the main oven with hydrogen as carrier gas, detection is performed using a FID detector.

2nd channel, suitable for analysis of $C_1 – C_2$: This channel is configured with a pre-column with backflush in the aux oven and the analytical 1/8” Porapak Q analysis column in the main oven, as carrier helium is used and detection is performed using a FID detector.

3rd channel, suitable for analysis of CO_2, C_2H_6, Ar/O_2, N_2, CH_4: This channel is configured with a analytical hayesep column with backflush in the aux oven and a capillary molsieve 5A column with isolation option in the aux oven, as carrier helium is used and detection is performed using a TCD detector.

4th channel, suitable for the analysis of He, H_2, O_2 and N_2: This channel is configured with a molsieve pre-column with backflush in the injector oven and a analytical molsieve column in the injector oven, as carrier argon is used and detection is performed using a TCD detector.

The temperature program for the 1st and 2nd channel starts at 35 °C for 10.7 minutes, followed by a temperature program of 20 °C/min^{-1} to 165 °C, hold for 0.9 minutes. The other channels have no temperature program and are kept at 70 °C isothermal. The data collection is performed using openlab software.

GC-2
The analyses for neopentane and n-hexane were performed on an Agilent 7890A GC, configured for the analysis of the composition of natural and refinery gas. Only the front channel is used, which consists of a split/splitless inlet set to a split ratio of 1:15 and a 25 µL sample loop. On an oven programmed run all hydrocarbons are then separated using a pre-column and an aluminum oxide plot column, with helium as carrier. The temperature program for the front channel starts at 80 °C for 2 minutes, followed by a temperature program of 35 °C/min^{-1} to 185 °C, hold for 2 minutes. The data collection is performed using Openlab software.

Calibration method and value assignment

Most Primary Standard gas Mixtures (PSMs) used for the measurement of the Key Comparison mixture are multi compound mixtures, except those for n-hexane and neo-pentane. As the recorded peak areas are generally prone to drift due to, e.g., fluctuations in ambient pressure, these peak areas are usually corrected for this influence.

The measurements were performed as described below:

The measurement was carried out by using a correction cylinder (except for neopentane and n-hexane) and a control cylinder, both containing all components, together with the the transfer standards and PSMs. The response after correction is calculated using

$$y_i = \frac{A_i}{A_{\mathrm{ref},i}}$$

where y_i denotes the response of component i, A_i the peak area, and $A_{ref,i}$ the peak area of the correction cylinder. The value for $A_{ref,i}$ is obtained as follows. From the two injections before and after the cylinder, the averages are calculated, i.e.,

$$f_0 = \frac{1}{m_0}\sum_j A_{ij}$$

where f_0 denotes the divisor for the peak area before the cylinder, m_0 the number of repeated injections and j the index over the repeat injections. Likewise, after analysing the cylinder, the average peak area is computed using

$$f_1 = \frac{1}{m_1}\sum_j A_{ij}$$

where f_1 denotes the divisor for the peak area after the cylinder and m_1 the number of repeated injections. The actual divisor is calculated using

$$A_{\mathrm{ref},i} = j \times \Delta f + f_0$$

where

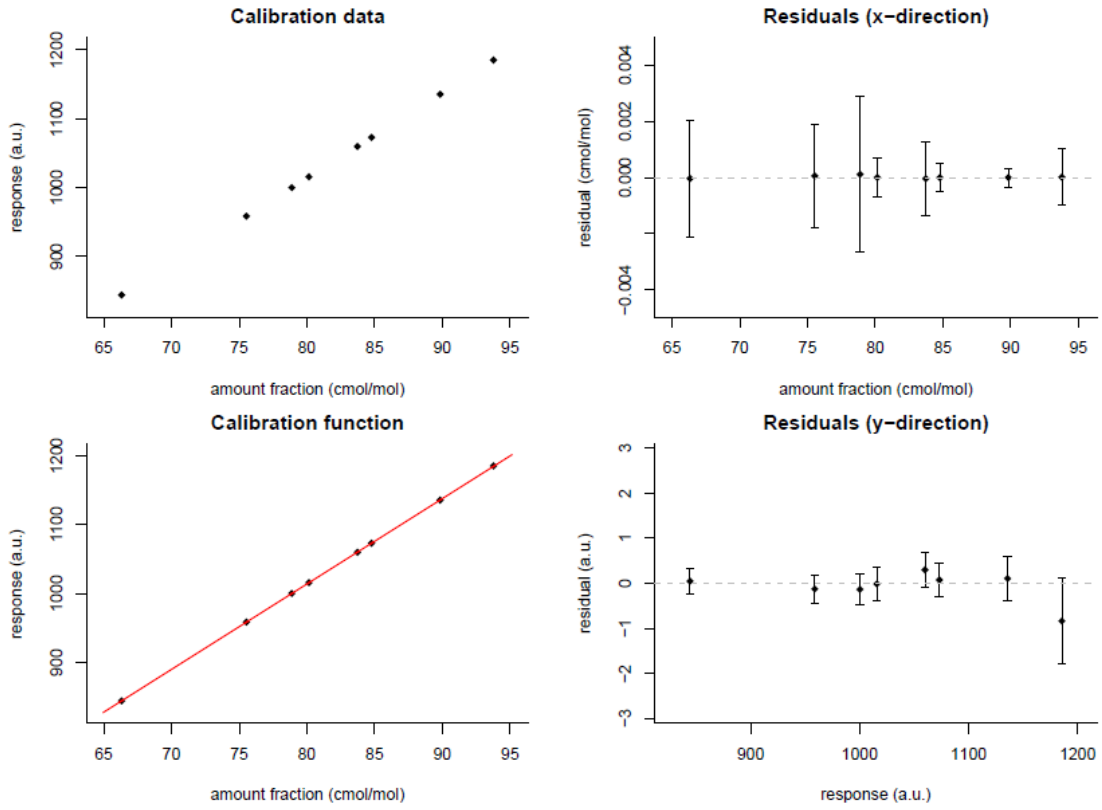
$$\Delta f = \frac{f_1 - f_0}{n-1}$$

In this expression, n denotes the number of repeat injections of the cylinder in question.

After the corrections the calibration curve was obtained in accordance with ISO 6143 [6]**.** A 2nd order curve was used as calibration function for all components.

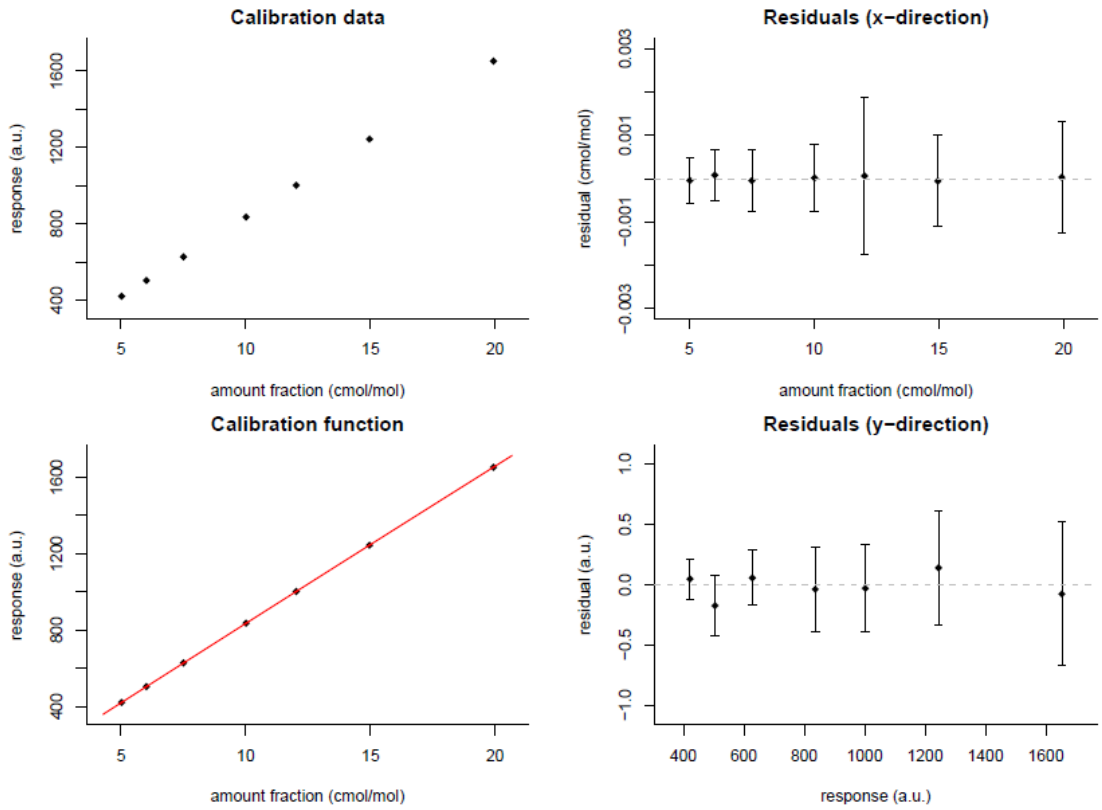
Fitting the calibration data

Mehane



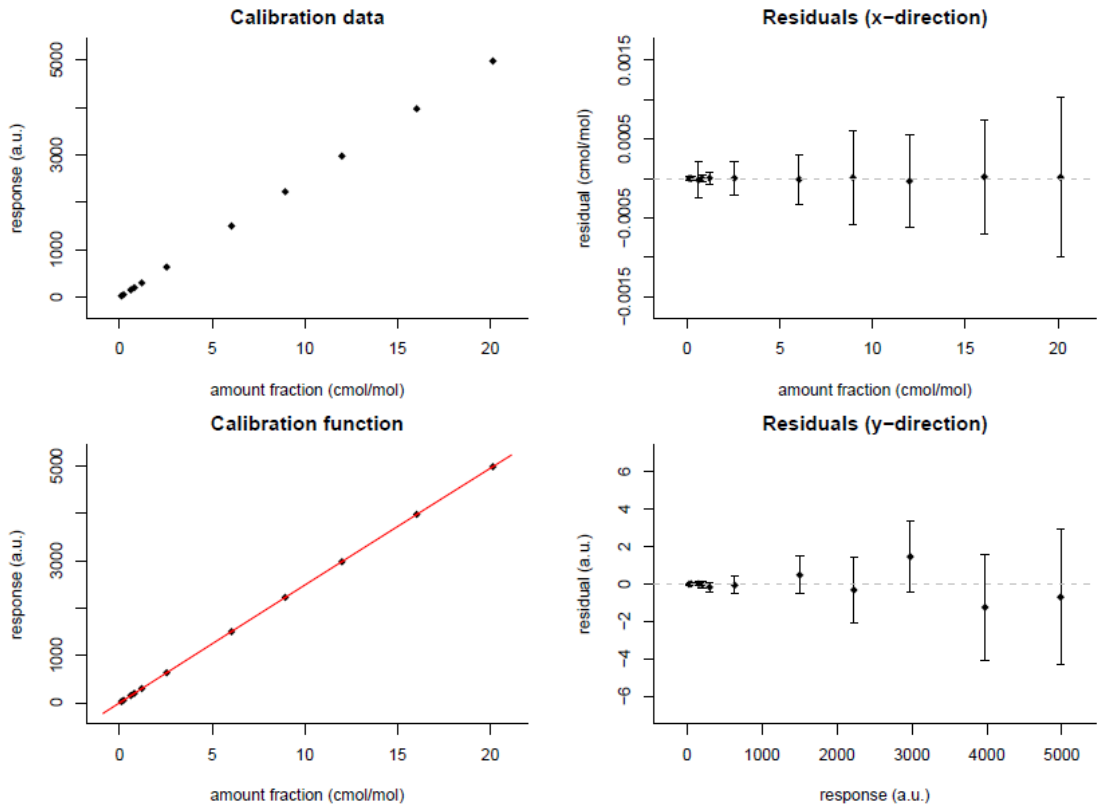
	y	u(y)	x	u(x)
D153626	999.40	0.22	78.831	0.006

Nitrogen



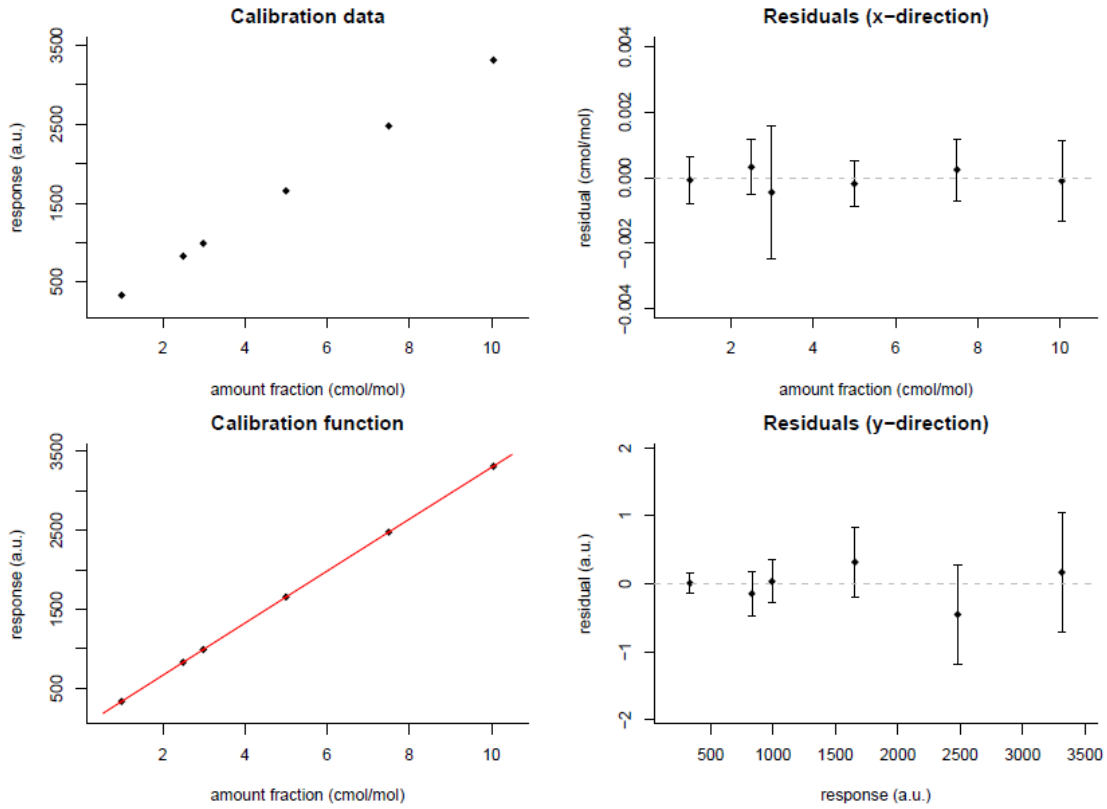
	y	u(y)	x	u(x)
D153626	1000.68	0.21	12.003	0.0008

Carbon dioxide



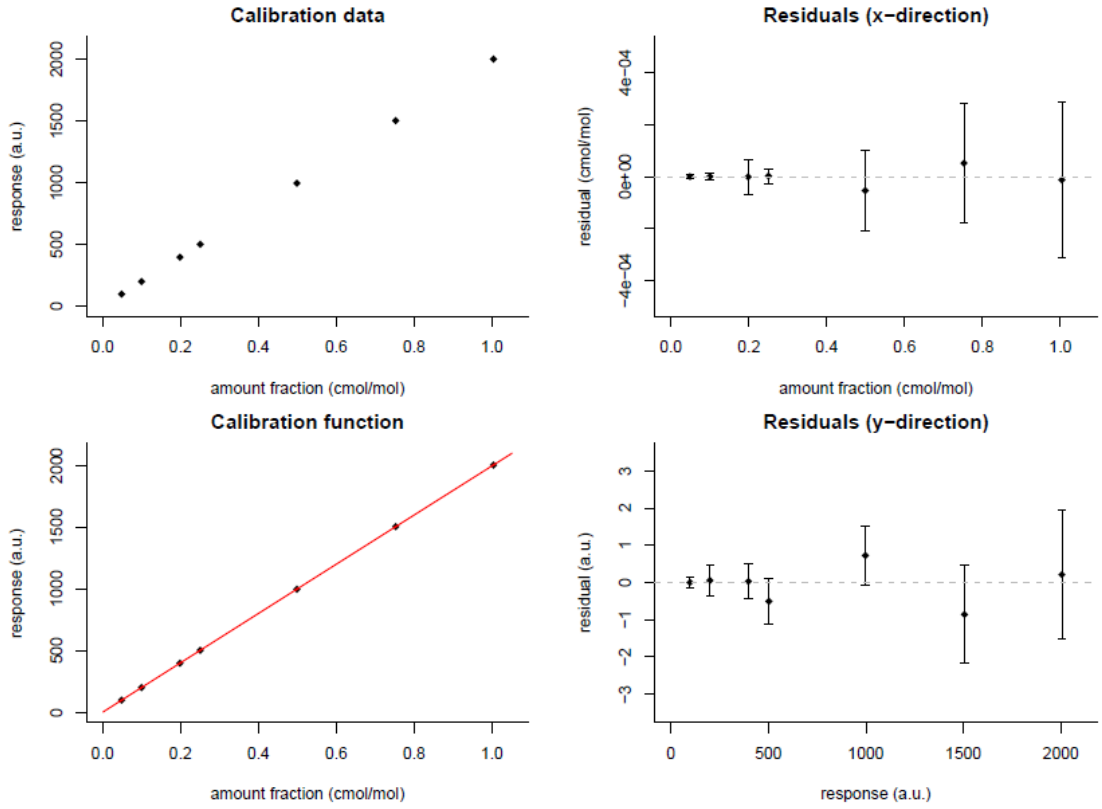
	y	u(y)	x	u(x)
D153626	993.46	0.43	3.9856	0.0008

Hydrogen



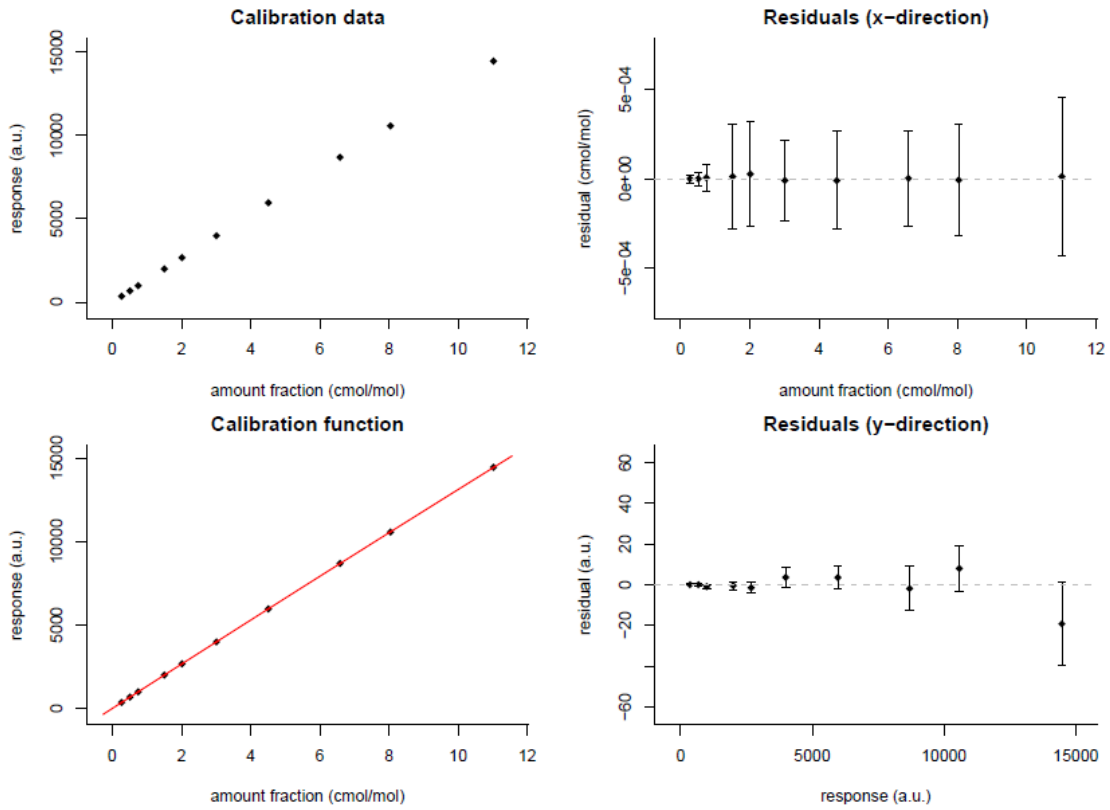
	y	u(y)	x	u(x)
D153626	1000.539	0.160	3.0145	0.0003

Helium



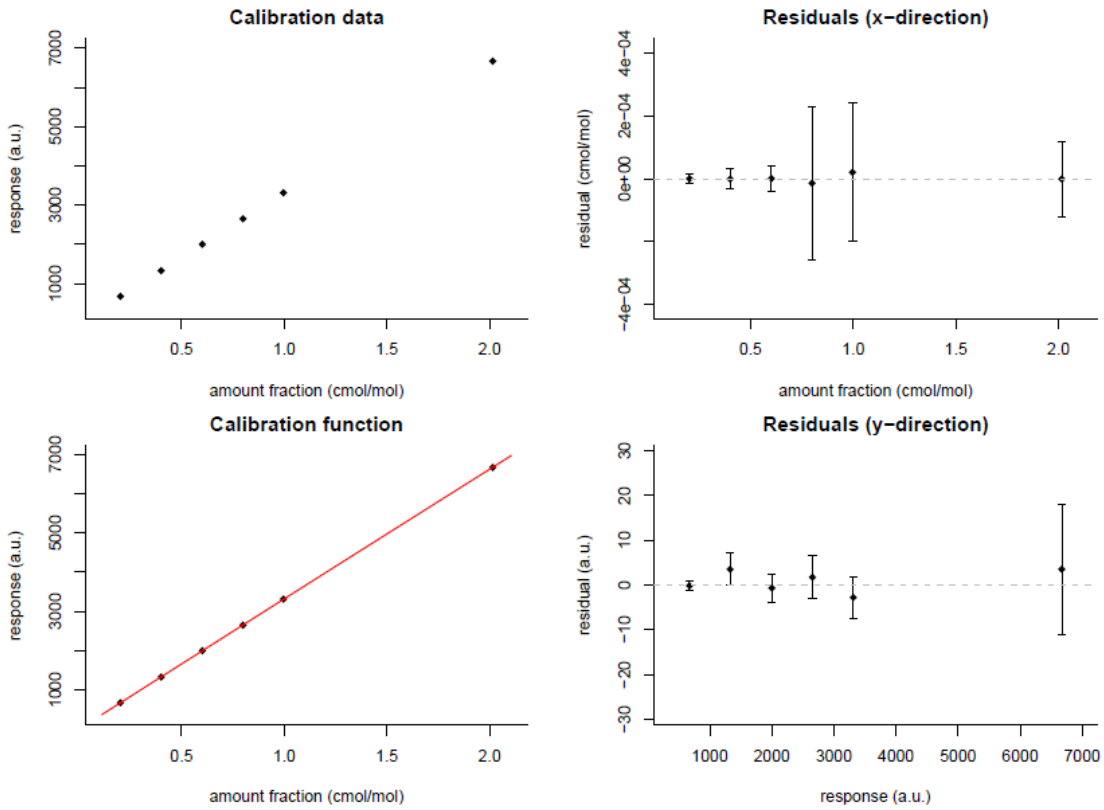
	y	u(y)	x	u(x)
D153626	997.896	0.409	0.49871	0.00006

Ethane



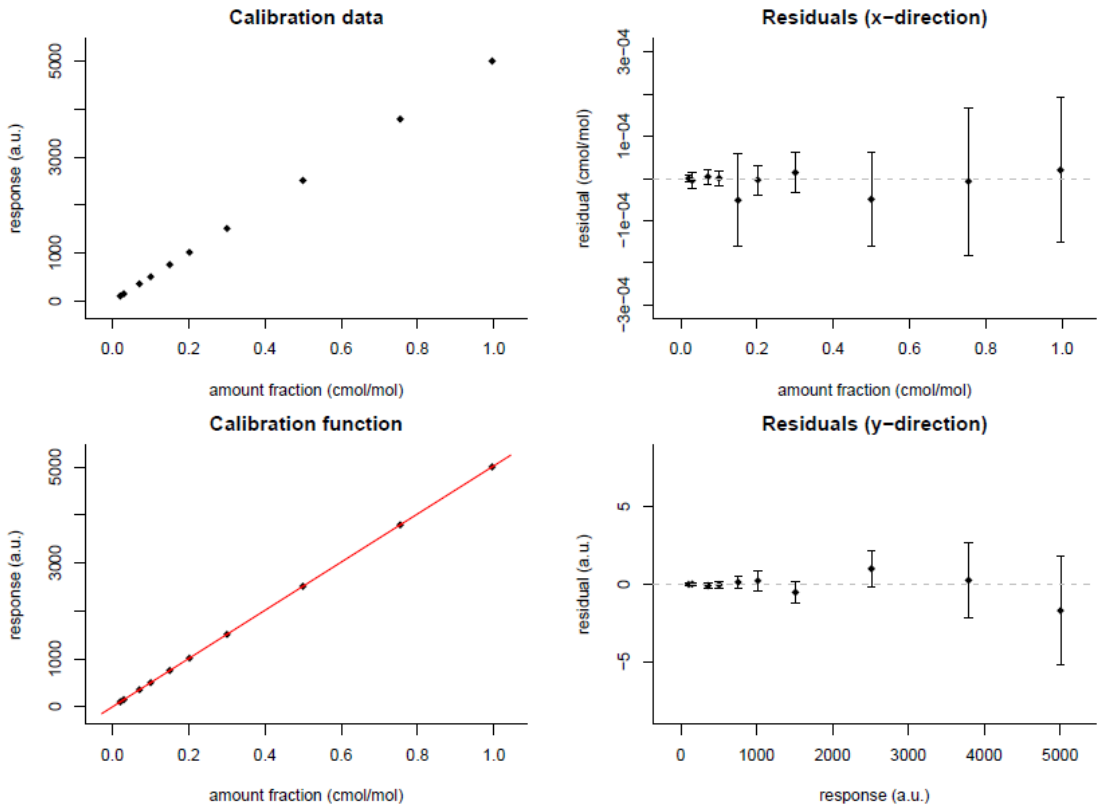
	y	u(y)	x	u(x)
D153626	1001.525	0.530	0.75283	0.00007

Propane



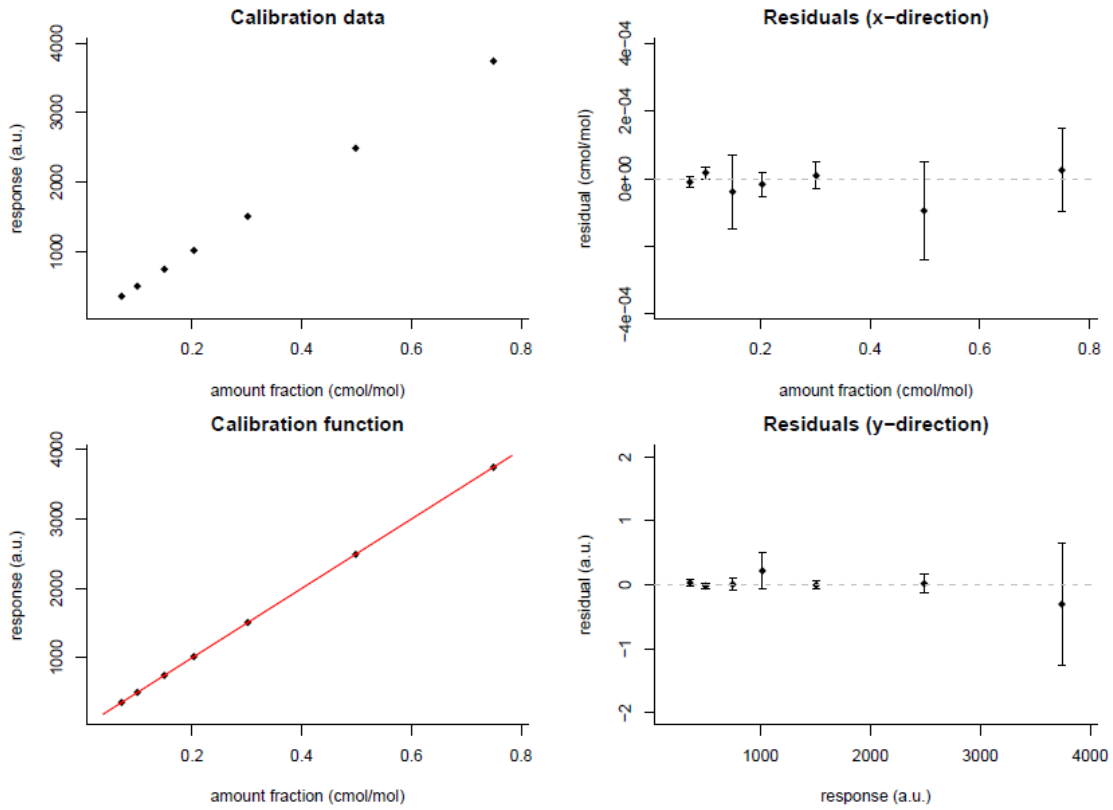
	y	u(y)	x	u(x)
D153626	1000.656	0.660	0.30058	0.00003

Isobutane



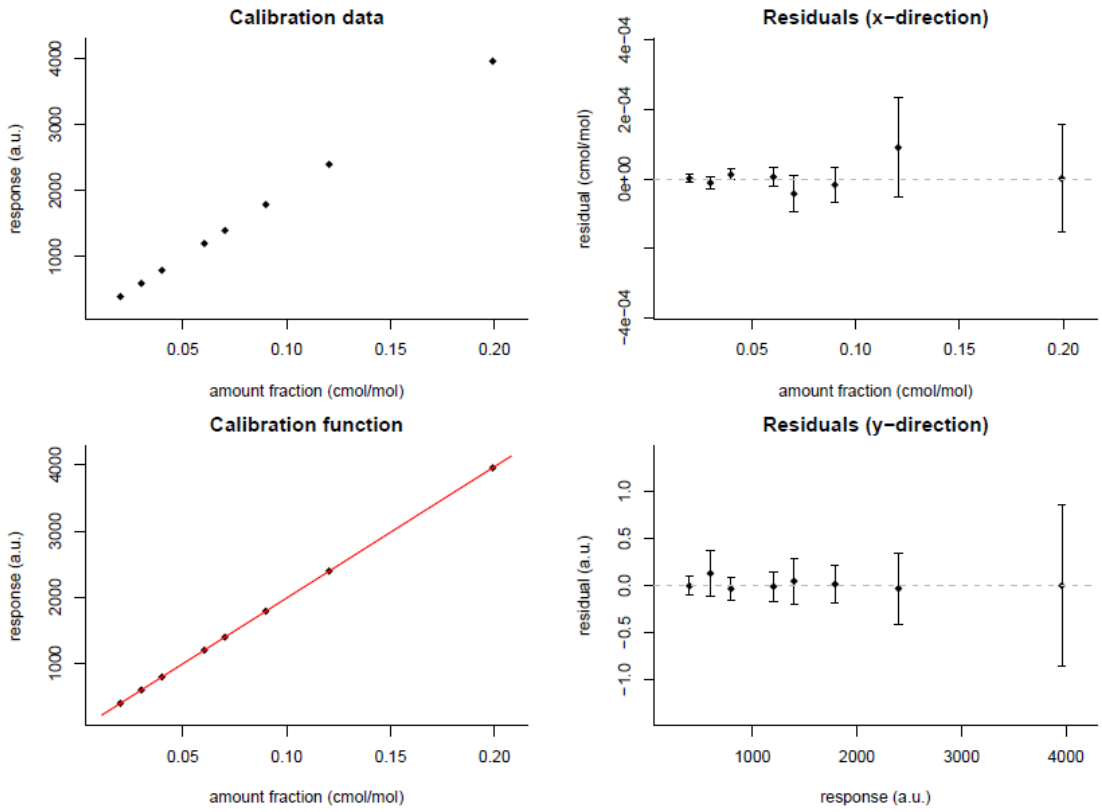
	y	u(y)	x	u(x)
D153626	1010.529	0.282	0.20061	0.00002

n-butane



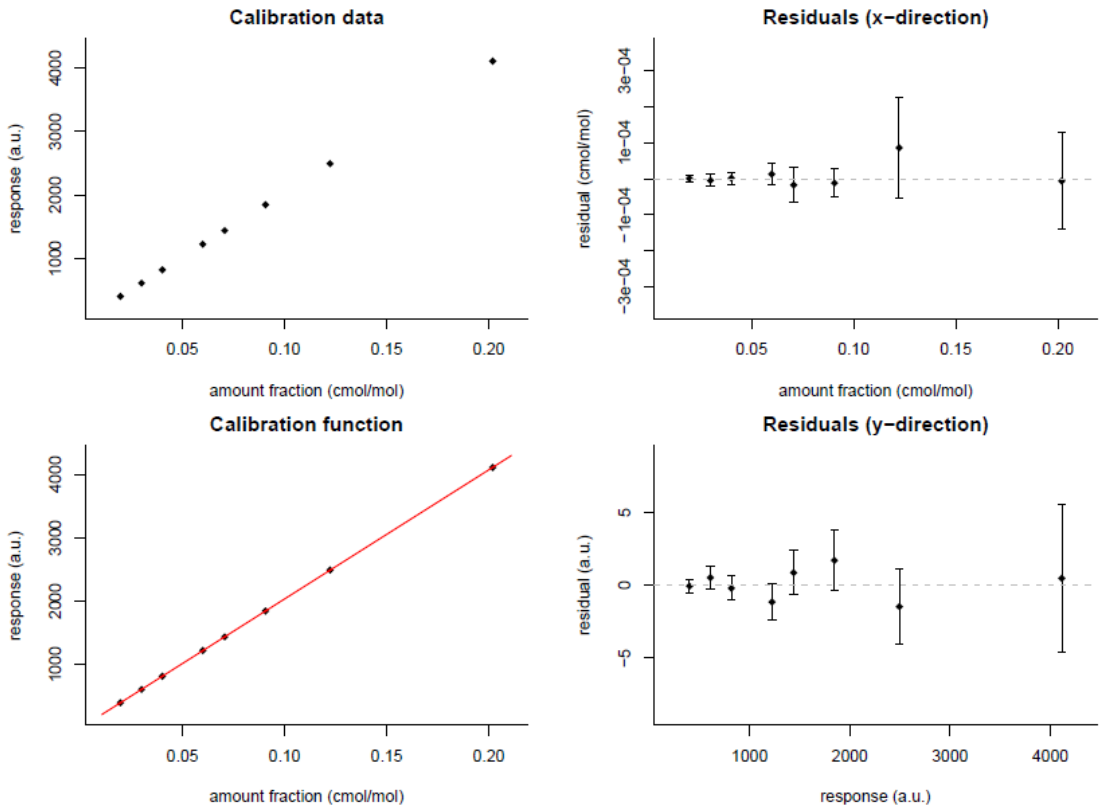
	y	u(y)	x	u(x)
D153626	999.77	0.07	0.20002	0.00002

Isopentane



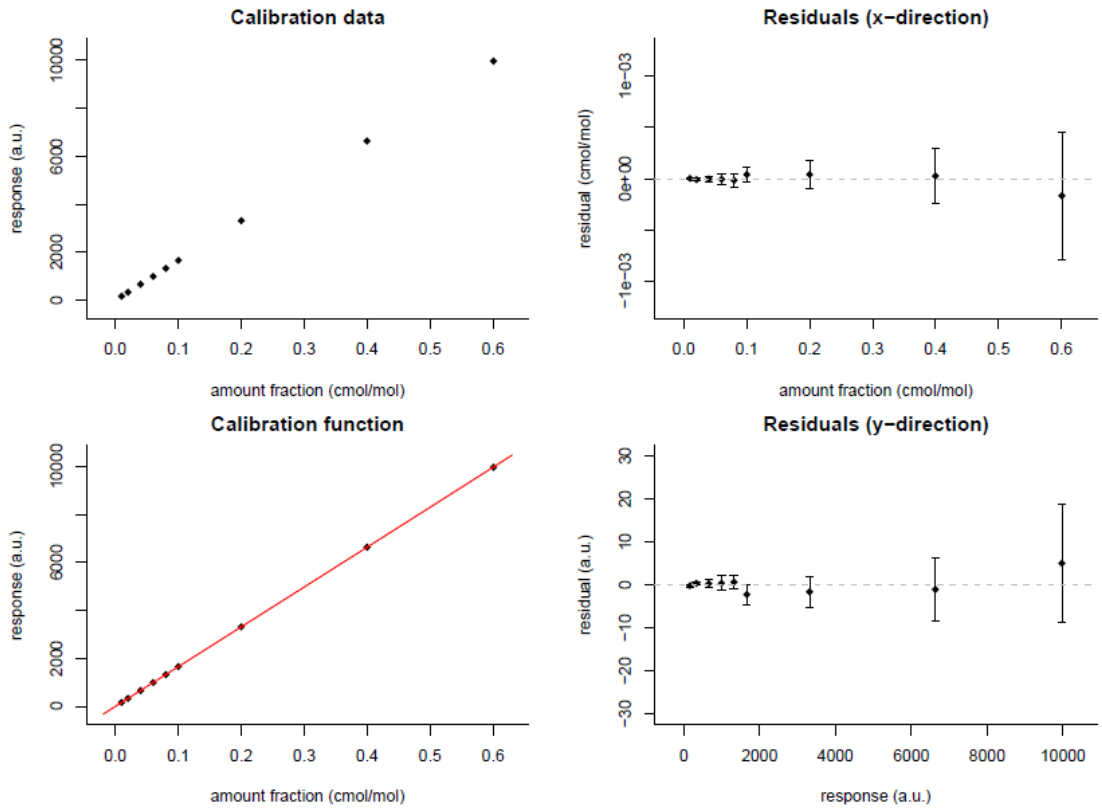
	y	u(y)	x	u(x)
D153626	995.26	0.11	0.049999	0.000008

n-pentane



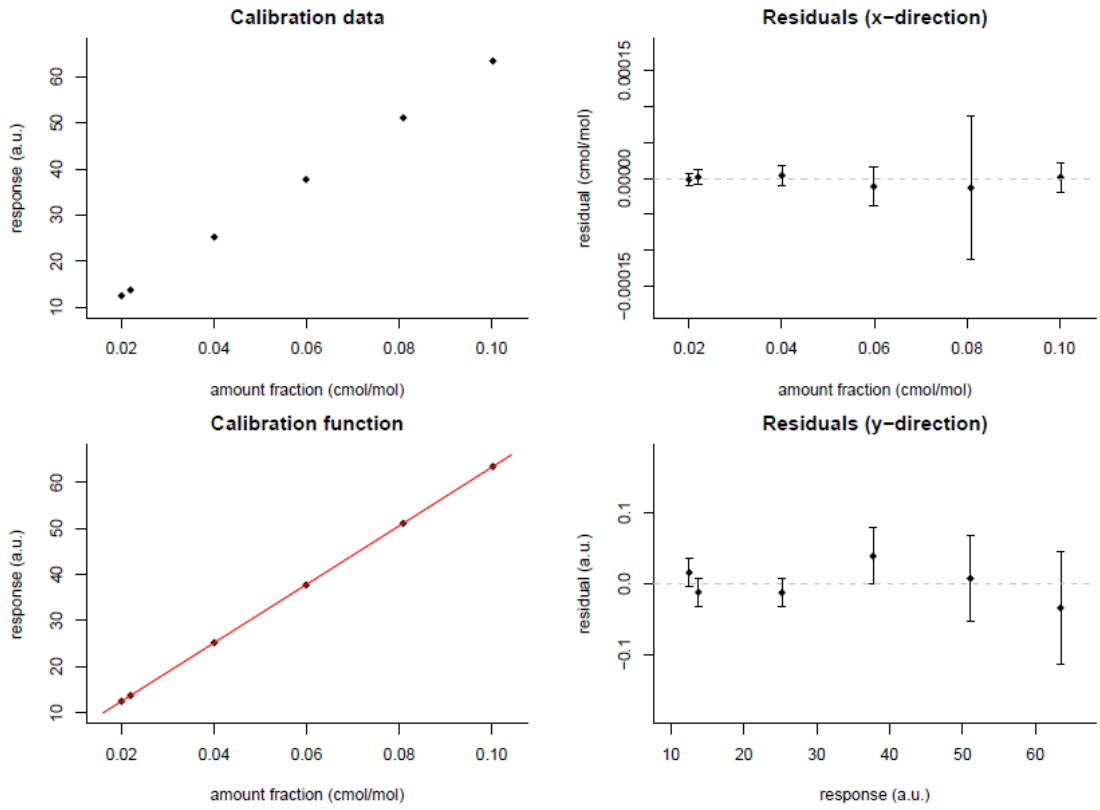
	y	u(y)	x	u(x)
D153626	1029.68	0.57	0.050538	0.000008

Neopentane



	y	u(y)	x	u(x)
D153626	828.95	0.58	0.050116	0.00002

n-hexane



	y	u(y)	x	u(x)
D153626	31.48	0.02	0.049941	0.000036

Uncertainty evaluation

The standard uncertainty associated with the assigned values has been obtained based on the calibration functions as determined in accordance with ISO 6143 [6]. The values and standard uncertainties have been obtained as described in [7]. The mean of each amount fraction is calculated using the DerSimonian-Liard model. In tables 49 and 50, the results are given. τ denotes the excess standard deviation and μ the mean. The standard uncertainty associated with μ has been taken as basis for the stated expanded uncertainty. The expanded uncertainty has been obtained using a coverage factor $k = 2$.

Component	x_1	u(x_1)	x_2	u(x_2)	x_3	u(x_3)	τ	μ	u(μ)
Nitrogen	12.00300	0.00085	12.00400	0.00102	12.00500	0.00094	0.00164	12.00392	0.00250
Carbon dioxide	3.98560	0.00079	3.98690	0.00049	3.98720	0.00042	0.00097	3.98667	0.00151
Hydrogen	3.01450	0.00032	3.01410	0.00039	3.01530	0.00032	0.00082	3.01465	0.00122
Helium	0.49871	0.00006	0.49844	0.00008	0.49855	0.00010	0.00018	0.49857	0.00028
Ethane	0.75283	0.00007	0.75252	0.00006	0.75295	0.00006	0.00030	0.75277	0.00040
Propane	0.30058	0.00003	0.30071	0.00004	0.30069	0.00002	0.00010	0.30066	0.00014
iso-Butane	0.20061	0.00002	0.20056	0.00002	0.20072	0.00002	0.00010	0.20063	0.00014
n-Butane	0.20002	0.00002	0.19999	0.00002	0.20014	0.00002	0.00010	0.20005	0.00014
iso-Pentane	0.05000	0.00001	0.04998	0.00001	0.05002	0.00001	0.00002	0.05000	0.00003
n-Pentane	0.05054	0.00001	0.05053	0.00001	0.05057	0.00001	0.00002	0.05055	0.00004
neo-Pentane	0.05012	0.00002	0.05009	0.00002	0.05005	0.00003	0.00003	0.05009	0.00004
n-Hexane	0.04994	0.00004	0.05007	0.00003	0.05003	0.00004	0.00005	0.05001	0.00007
Methane	78.83100	0.00573	78.83300	0.00481	78.83700	0.00293	0.00686	78.83469	0.01189

References

[1] International Organization for Standardization, “ISO 6142-1 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods”, ISO Geneva, 2015

[2] Van der Veen A.M.H., Ziel P.R., Li J., ”Validation of ISO 6974 for the measurement of the composition of hydrogen-enriched natural gas”, International Journal of Hydrogen Energy **40(46)** (2015), pp. 15877-15884

[3] 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

[4] International Organization for Standardization, “ISO 19229 Gas analysis - Gas analysis — Purity analysis and the treatment of purity data”, ISO Geneva, 2015

[5] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (2008) “Evaluation of measurement data — Guide to the expression of uncertainty in measurement”, first edition, GUM:1995 with minor corrections

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

[7] Milton M.J.T., Harris P.M., Smith I.M., Brown A.S., Goody B.A., “Implementation of a generalised least-squares method for determining calibration curves from data with general uncertainty structures”, Metrologia **43** (2006), pp. S291-S298

[8] DerSimonian R, Laird N. Meta-analysis in clinical trials. Control Clin Trials. **7** (1986), pp. 177–188.

References

[1] ISO 6976 Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition. ISO, International Organization for Standardization, Geneva, Switzerland, third edition, 2016.

[2] ISO 6142–1 Gas analysis — Preparation of calibration gas mixtures — Gravimetric method for Class I mixtures. ISO, International Organization for Standardization, Geneva, Switzerland, 2015. First edition.

[3] ISO 6142-1:2015/Amd 1:2020 Amendment 1: Corrections to formulae in Annex E and Annex G. ISO, International Organization for Standardization, Geneva, Switzerland, 2020.

[4] ISO 19229 Gas analysis — Purity analysis and the treatment of purity data. ISO, International Organization for Standardization, Geneva, Switzerland, 2019. Second edition.

[5] Adriaan M H van der Veen, Gerard Nieuwenkamp, Ewelina T Zalewska, Jianrong Li, Iris de Krom, Stefan Persijn, and Heleen Meuzelaar. Advances in metrology for energy-containing gases and emerging demands. *Metrologia*, 58(1):012001, jan 2021.

[6] A Alink. The first key comparison of primary standard gas mixtures. *Metrologia*, 37(1):35–49, feb 2000.

[7] A. Alink, M.J.T. Milton, F. Guenther, E.W.B. de Leer, H.J. Heine, A. Marschal, Gwi Suk Heo, C. Takahashi, Wang Lin Zhen, Y. Kustikov, and E. Déak. Final report of key comparison CCQM-K1. Technical report, NMi Van Swinden Laboratory, Department of Chemistry, P.O. Box 645, 2600 AR Delft, The Netherlands, September 2001.

[8] Adriaan M H van der Veen, Hans-Joachim Heine, Freek N C Brinkmann, Paul R Ziel, Ed W B de Leer, Wang Lin Zhen, Kenji Kato, Leonid A Konopelko, Tatjana A Popova, Yuri I Alexandrov, Elena N Kortchagina, Yuri A Kustikov, Stanislav Musil, Martin J T Milton, Franklin Guenther, and George Rhoderick. International comparison CCQM-K16: Composition of natural gas types IV and V. *Metrologia*, 42(1A):08003, 2005.

[9] Adriaan M H van der Veen, Hans-Joachim Heine, Freek N C Brinkmann, Paul R Ziel, Agata Rakowska, Adam Radlicz, and Laurie Besley. Final report of CCQM-P49: Natural gas types IV and V. *Metrologia*, 42(1A):08004–08004, jan 2005.

[10] Adriaan M H van der Veen, Paul R Ziel, Ed W B de Leer, Damian Smeulders, Laurie Besley, Valnei Smarçao da Cunha, Zei Zhou, Han Qiao, Hans-Joachim Heine, Jan Tichy, Teresa Lopez Esteban, Tatiana Mace, Zsófia Nagyné Szilágyi, Jin-Chun Woo, Hyun-Kil Bae, Alejandro Perez Castorena, Melina Perez Urquiza, Francisco Rangel Murillo, Victor M Serrano Caballero, Carlos E Carbajal Alarcón, Carlos Ramírez Nambo, Manuel de Jesús Avila Salas, Agata Rakowska, Florbela Dias, Leonid A Konopelko, Tatjana A Popova, V V Pankratov, M A Kovrizhnih, A V Meshkov, O V Efremova, Yury A Kustikov, Stanislav Musil, Frantisek Chromek, Miroslava Valkova, and Martin J T Milton. Final report on international comparison CCQM-K23ac: Natural gas types I and III. *Metrologia*, 44(1A):08001–08001, dec 2006.

[11] Adriaan M H van der Veen, Hima Chander, Paul R Ziel, Ed W B de Leer, Damian Smeulders, Laurie Besley, Valnei Smarçao da Cunha, Zei Zhou, Han Qiao, Hans-Joachim Heine, Jan Tichy, Teresa Lopez Esteban, K Kato, Zsófia Nagyné Szilágyi, Jin Seog Kim, Jin-Chun Woo, Hyun-Gil Bae, Alejandro Pérez Castorena, Francisco Rangel Murillo, Victor M Serrano Caballero, Carlos Ramírez Nambo, Manuel de Jesús Avila Salas, Agata Rakowska, Florbela Dias, Leonid A Konopelko, Tatjana A Popova, V V Pankratov, M A Kovrizhnih, T A Kuzmina, O V Efremova, Yury A Kustikov, Stanislav Musil, and Martin J T Milton. International comparison CCQM-K23b: Natural gas type II. *Metrologia*, 47(1A):08013, 2010.

[12] Adriaan M H van der Veen, Ewelina T Zalewska, Heinrich Kipphardt, Roel R Beelen, Dirk Tuma, Michael Maiwald, Judit Fükő, Tamás Büki, Zsófia Nagyné Szilágyi, Jan Beránek, Dariusz Cieciora, Grzegorz Ochman, Piotr Kolasiński, Magdalena Garnuszek, Anna Lis, Namgoo Kang, Hyun-Kil Bae, Dong-Min Moon, Sangil Lee, Hai Wu, Haomiao Ma, Qiao Han, Damian E Smeulders, John B McCallum, Raymond Satumba, Takuya Shimosaka, Takuro Watanabe, Nobuhiro Matsumoto, James Tshilongo, David Mphara Mogale, Mudalo Jozela, Lucy P Culleton, Abigail Morris, Nirav Shah, Arul Murugan, Paul J Brewer, Richard J C Brown, Miroslava Val'ková, Tanıl Tarhan, Erinç Engin, L A Konopelko, Yu A Kustikov, A V Kolobova, V V Pankratov, T A Popova, A V Meshkov, and O V Efremova. International comparison CCQM-K118 Natural gas. *Metrologia*, 59(1A):08017, jan 2022.

[13] Adriaan M H van der Veen. Dark uncertainty in key comparisons in the gas analysis area. *Metrologia*, 60(6):064002, sep 2023.

[14] CIPM. Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes, October 1999.

[15] CIPM MRA-G-11 Measurement comparisons in the CIPM MRA. guidelines for organizing, participating and reporting. CIPM MRA, Bureau International des Poids et Mesures, BIPM, Pavillon de Breteuil, F-92312 Sèvres Cedex, 2021. Version 1.1.

[16] I van Andel, A M H van der Veen, and E T Zalewska. A robot for weighing syringes used in reference gas mixture preparation. *Metrologia*, 49(4):446, 2012.

[17] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML. Evaluation of measurement data — Guide to the expression of uncertainty in measurement, JCGM 100:2008, GUM:1995 with minor corrections, 2008.

[18] ISO 6143 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures. ISO, International Organization for Standardization, Geneva, Switzerland, 2025. Third edition.

[19] Adriaan M H van der Veen and Maurice G Cox. Degrees of equivalence across key comparisons in gas analysis. *Metrologia*, 40(2):18, 2003.

[20] P. Brewer and A. M. H. van der Veen. GAWG strategy for comparisons and CMC claims. GAWG 19/41, Gas Analysis Working Group, Sèvres, France, October 2019.