International Comparison CCQM-K118 Natural Gas

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Contents

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 thermophysical 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, 3] as primary standard gas mixture (PSM) [4]. An overview of the natural gas types used in previous key comparisons (CCQM-K1 [5, 6], CCQM-K16 [7], CCQM-K23 [8, 9] 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			CCQM-K16		CCQM-K23			CCQM-K118	
	I	II	III	IV	V	Ia	IIIa	IIa	IVa	LNG
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	
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	
Methane	90.8	76.2	81.5	81.85	82.16	90.6	81.4	75.4	78.85	87.52

In this key comparison two types of gas compositions have been used. Type IVa (low calorific natural gas) is similar to the type IV used in CCQM-K16 [7], but 3 % hydrogen was included in the com-

position to extend the support of Calibration and Measurement Capabilities (CMCs) to hydrogen-enriched natural gas [10, 11]. Type V from CCQM-K16 (deemed representative for high-calorific natural gas) has been replaced in this key comparison by a mixture resembling Liquefied Natural Gas (LNG), with very low amount fractions of nitrogen and carbon dioxide to support CMCs for services related to the measurement of the amount fractions nitrogen and carbon dioxide in LNG.

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) and designated institutes (DIs) in CCQM-K118

Acronym	Country	Institute
BAM	DE	Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
BFKH	HU	Government Office of the Capital City Budapest, Budapest, Hungary
CMI	CZ	Czech Metrology Institute, Prague, Czech Republic
GUM	PL	Central Office of Measures, Warsaw, Poland
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NIM	CN	National Institute of Metrology, Beijing, China
NMIA	AU	National Measurement Institute Australia, Lindfield, Australia
NMIJ	JP	Research Institute for Material and Chemical Measurement, National Metrology Institute of Japan, Ibaraki, Japan
NMISA	ZA	National Metrology Institute of South Africa, Lynnwood Ridge, South Africa
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovakia
UME	TR	TÜBİTAK Ulusal Metroloji Enstitüsü, Gebze/KOCAELİ, Turkey
VNIIIM	RU	D.I. Mendeleyev Institute for Metrology, Saint Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands

2.2 Measurement protocol

The measurement protocol requested the participating National Metrology Institutes (NMIs) to perform at least 3 measurements, each with its own calibration. The protocol informed the participants also about the nominal amount fraction ranges. The laboratories were also requested to submit a description of their calibration method, how the result was calculated, and a summary of their uncertainty evaluation used for evaluating the uncertainty of their result.

2.3 Schedule

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

Table 3: Schedule of CCQM-K118

Date	Event
January 2014	Agreement on protocol
February 2014	Call for registration opens
March 2014	Registration of participants
May 2016	Samples organised
May 2016	Calibration mixtures prepared by coordinators
February 2017	Samples verified by coordinators
December 2019	Dispatch of samples to participants
January 2019	Arrival of samples at participants
July 2019 – March 2020	Results of participants reported to VSL
July 2019 – October 2019	Dispatch of samples back to coordinators
November 2019	Arrival of samples at coordinators
October 2019 – February 2020	Re-verification of the samples by coordinators
April 2020	Draft A report available

2.4 Measurement methods used by the participants

The measurement methods used by the participants are described in annexes C and D 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 4.

3 Design of the comparison

3.1 Travelling standards

Two sets of gas mixtures were obtained from an external party. The nominal compositions of the mixtures were within the specified ranges (see table 1, types IVa and LNG). The pressure in the cylinders was approximately 70 bar; aluminium cylinders having a 5 dm^3 water volume were used. These gas mixtures were assessed for homogeneity and stability by the coordinating laboratories before and after the participating National Metrology Institutes (NMIs) took their measurements.

3.2 Analysis of the travelling standards

The travelling standards were analysed by the coordinating laboratories before shipment to the participating NMIs and after being returned. These 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 key comparison reference values (KCRVs).

Table 4: Overview of calibration methods and metrological traceability

Lab	Measurement dates type IVa	Measurement dates LNG	Calibration method	Traceability	Measurement technique
BAM	16/17 July 2019	14 August and 02/03 September 2019	Bracketing	Own standards (ISO 6142)	GC/TCD/FID
BFKH	—	27/28 March and 02 April 2019	Matching standard	Own standards (ISO 6142)	GC/TCD/FID
CMI	06 May and 03 June and 15 July 2019	13 May and 10 June and 08 July 2019	Multipoint calibration (3 standards)	Own standards (ISO 6142)	GC/TCD/FID
GUM	15/16/24 April and 17/18/30/31 July 2019	10/11 April and 27/29 May 2019	Matching standard	Own standards (ISO 6142)	GC/TCD/FID
KRISS	29/30 November 2018 and 03 December 2018	—	Bracketing	Own standards (ISO 6142)	GC/TCD/FID
NIM	15/27 August and 02 September 2019	15/23 August and 04 September 2019	Matching standard	Own standards (ISO 6142)	GC/TCD
NMIA	30 November and 03 December 2018	24/26 January and 01/04/25 February 2019	Matching standard	Own standards (ISO 6142)	GC/TCD/FID
NMIJ	23 May and 04/05/06/10/11/12/19/21/27/28 June and 12/16/29/31 July and 01/02/05/06/08/21/ 23/28 August and 09/10/11/17 September 2019	12/19/21 June and 24/25 July and 08/10/19/20/21/23/ 26/27/28/29 August and 03/04/06/09/12/13/18 September and 09/10 October 2019	Multipoint calibration (3 standards) and bracketing	Own standards (ISO 6142)	GC/FID
NMISA	20/22 August and 09 September 2019	21/23 August and 10 September 2019	Matching standard	Own standards (ISO 6142)	GC/TCD/FID
NPL	14 March and 11/13/‘4/17/18 June 2019	13/20 June and 17 July 2019	ISO 6143	Own standards (ISO 6142)	GC/TCD/FID
SMU	14/16/22/23/23/30 August and 03/06/20 September 2019	—	Multipoint calibration (3 standards)	Own standards (ISO 6142)	GC/TCD/FID
UME	16/17/19 September 2019	11/12/15/18/19 April and 18 June 2019	ISO 6143	Own standards (ISO 6142)	GC/TCD/FID
VNIIM	09/10/11/12/15/16 April 2019	04/05/06/10/13/18 June 2019	Matching standard	Own standards	GC/TCD
VSL	14/19/21 August and 02/04/05/16/20/24 September and 04 November 2019	14 August and 04/20/26 September and 04 November 2019	ISO 6143	Own standards (ISO 6142)	GC/TCD/FID

The measurements for the high-calorific natural gas were performed by VSL on an Agilent 7980A equipped with

1. 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;
2. 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 measurements of the low-calorific natural gas were performed by BAM on a specially designed Siemens Maxum II process gas analyser. The oven temperature was set to 60 °C and operated in isothermal mode with helium and nitrogen as a carrier gas. The instrument is equipped with TCD detectors and has six different separation channels

1. for helium and hydrogen with N_2 as a carrier gas and columns of type Hayesep and Molsieve columns.
2. for methane with Hayesep columns.
3. for methane, carbon dioxide, ethene and ethane with Haysep columns.
4. for propene and propane with Sorbitolchrom, TCEPCarbonblack and TCEPUnibeads columns.
5. for oxygen, nitrogen and carbon monoxide with Shincarbon and Molsieve columns.
6. for *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane and *n*-hexane with Wax columns.

3.3 Measurement equation and data evaluation

The data obtained in this key comparison can be described by the following observation equation. Let $y_{\mathrm{lab},j}$ denote the measured value of laboratory j with expanded uncertainty $U_{\mathrm{lab},j}$ and coverage factor $k_{\mathrm{lab},j}$. As each laboratory received its own transfer standard, the laboratory effects model [12] can be written as

$$y_{\mathrm{lab},j} = \mu + \lambda_j + \beta_j + \epsilon_j \tag{1}$$

where μ denotes the expected value of the amount fraction of the component concerned, λ_j denotes an effect due to laboratory j, β_j a fixed effect due to the batch homogeneity of the transfer standards, and ϵ_j a random effect due to laboratory j. It is assumed that the laboratory, homogeneity and random effects are mutually independent for each j.

In the model given in equation (1), $\epsilon_j \sim N(0, u^2_{\mathrm{lab},j})$ where $u_{\mathrm{lab},j} = U_{\mathrm{lab},j}/k_{\mathrm{lab},j}$. With only the results reported by the participants, it is not possible to independently estimate λ_j and β_j. In this key comparison, μ had to be determined as a consensus value for which the traditional procedures A and B [13,14] were considered. To apply these procedures, it is important that the β_j could be estimated, which has been done by using the data collected in the combined stability and homogeneity study. The fixed effects model for the homogeneity study can be written as

$$y_j = \mu_{\mathrm{hom}} + \beta_j + \varepsilon_j \tag{2}$$

where μ_{hom} denotes the expected value of the amount fraction of the component of interest, and ε_j the random effect due to the measurement of the amount fraction of the component of interest of transfer standard j. The random error is modelled as normally distributed with mean zero, i.e., $\varepsilon_j \sim N(0, \sigma_j^2)$ where σ_j denotes the standard uncertainty associated with the measured amount fraction in transfer standard j. Note that $y_{\mathrm{lab},j} \neq y_j$ and $\mu \neq \mu_{\mathrm{hom}}$. Should the results of any of the

coordinating laboratories be biased, this bias would affect the estimation of μ_{hom}, but not that of the β_j.

The calculation of the amount fraction y_j for a component in a set of travelling standards proceeded as follows. The stability study data (see section 4.1) were first assessed for stability issues. No issues had been expected based on previous key comparisons for natural gas [5, 7–9]. The data for the high-calorific natural gas confirmed immediately stability. For the low-calorific natural gas, some data sets suggested a stability effect for a specific mixture. Considering the evidence for all mixtures in the suite, it was also concluded that these mixtures were stable over the lifetime of the comparison. An occasional trend in the measurement data was attributed to an effect of the measurement, rather than of a change in the amount fraction. Generally, if an amount fraction would be unstable in time, it is expected that its change would be similar for the (vast) majority of the travelling standards.

The amount fractions y_j were computed as the mean from the four (high-calorific natural gas) respectively six (low-calorific natural gas) results obtained during the stability and homogeneity study. The mean was computed, as in the cases of CCQM-K112 [15] and CCQM-K117 [16] using the DerSimonian-Laird model (DL) [17, 18] to account for any extra dispersion in the data sets, thus ensuring that the measurement uncertainty is duly propagated.

For calculating the consensus value μ, the laboratory results needed to be corrected for batch homogeneity effects. To obtain these corrected laboratory results $y'_j = y_j - \beta_j$, the corrections β_j are needed. The corrections β_j have been calculated using a fixed effects model, with a weighted mean as estimator for μ_{hom}. The differences β_j were calculated in an analogous way as the differences from a weighted mean as described in procedure A [14].

To compute these corrections, an additional constraint is necessary [12, 19], as otherwise there is no unique solution. The constraint is that the net correction is zero, i.e., $\beta_1 + \cdots + \beta_n = 0$ where n denotes the number of participants (and transfer standards). Now, in equation (2), μ_{hom} can be computed as the weighted mean [20]

$$\hat{\mu}_{\text{hom}} = \frac{\sum_j v_j y_j}{\sum_j v_j} \tag{3}$$

where the weights are defined as $v_j = 1/u^2(y_j)$. If the weights are all equal, $\hat{\mu}_{\text{hom}}$ reduces to the arithmetic mean [12]. Then,

$$\hat{\beta}_j = y_j - \hat{\mu}_{\text{hom}} \tag{4}$$

The calculation of the standard uncertainty associated with $\hat{\beta}_j$ is done using the law of propagation of uncertainty. Taking into account the covariance between y_j and $\hat{\mu}_{\text{hom}}$, the expression takes the form [14]

$$u^2(\hat{\beta}_j) = u^2(y_j) - u^2(\hat{\mu}_{\text{hom}}) \tag{5}$$

if the corresponding measurement result of NMI j is included in the calculation of the KCRV and

$$u^2(\hat{\beta}_j) = u^2(y_j) + u^2(\hat{\mu}_{\text{hom}}) \tag{6}$$

otherwise. The standard uncertainty associated with $\hat{\mu}_{\text{hom}}$ can be computed from

$$\frac{1}{u^2(\hat{\mu}_{\text{hom}})} = \sum_j \frac{1}{u^2(y_j)} \tag{7}$$

The minus sign in equation (5) arises from the correlation between y_j and μ_{hom} [14].

The approach of CCQM-K112 and CCQM-K117 [15, 16] for calculating these differences was refined so that the consensus value and the KCRVs can be viewed as the best estimate of the measurand for a particular travelling standard as required by the CIPM Mutual Recognition Arrangement (CIPM MRA) of the International Committee for Weights and Measures (CIPM) [21]. This refinement concerned the weighted mean (WM) used in the fixed effects model, which in this key comparison is calculated using the homogeneity study data of only those travelling standards that belonged to the largest constistent subset (LCS). The KCRV for the NMIs that do not contribute to the consensus value is formed in the same way, i.e., by subtracting the weighted mean from the amount fraction computed from the homogeneity study data.

A slight complication was that several NMIs amended their submitted results after the release of the Draft A1 report of this key comparison (see annex D for details). Hence, it was deemed that those results could no longer be included in the formation of the KCRV. As degrees of equivalence had to be computed for these NMIs, it was decided to evaluate the homogeneity study data for all travelling standards.

To compute the consensus value, a simple Bayesian hierarchical model to fit the data was used. From the reported results, the LCS [22] was computed, after correcting the reported results for the between-bottle homogeneity $\hat{\beta}_j$, i.e.,

$$y'_j = y_{\text{lab},j} - \beta_j \tag{8}$$

The calculation of the LCS was implemented in R [23] using full enumeration. A Bayesian model was chosen to fit the corrected laboratory results y'_j, as generally these models outperform frequentist models in determining the excess variance [24–27]. An introduction to these models is available [28, section 5.4]. In the following, it is assumed that the laboratory results and the results of the homogeneity study are normally distributed.

The likelihood of the $y'_j|\theta_j, \sigma_j$ can be described as [28]

$$y'_j|\theta_j \sim \text{N}(\theta_j, \sigma_j^2)$$

where θ_j denotes the corrected laboratory mean and σ_j the standard uncertainty associated with y'_j. This standard deviation is computed as

$$\sigma_j^2 = u^2(y_{\text{lab},j}) + u^2(\beta_j)$$

The θ_j are assumed to be drawn from a normal distribution with mean μ and standard deviation τ, where μ denotes the consensus value and τ the standard deviation of the laboratory effects λ_j (see also equation (1)). Conditional on these parameters, the θ_j are normally distributed [28]

$$\theta_j|\mu, \tau, \boldsymbol{y} \sim \text{N}(\hat{\theta}_j, V_j)$$

with mean $\hat{\theta}_j$ and variance V_j, where

$$\hat{\theta}_j = \frac{\frac{1}{\sigma_j^2} y'_j + \frac{1}{\tau^2}\mu}{\frac{1}{\sigma_j^2} + \frac{1}{\tau^2}}; V_j = \frac{1}{\frac{1}{\sigma_j^2} + \frac{1}{\tau^2}}$$

For the evaluation of the key comparison, the interest is in the estimates for μ and τ. The formula for computing μ takes the form

$$\hat{\mu} = \frac{\sum_{j=1}^{N} \frac{1}{\sigma_j^2+\tau^2} y_j'}{\sum_{j=1}^{N} \frac{1}{\sigma_j^2+\tau^2}} \tag{9}$$

and

$$u^{-2}(\hat{\mu}) = \sum_{j=1}^{N} \frac{1}{\sigma_j^2+\tau^2} \tag{10}$$

One of the useful properties of such a hierarchical model is that it affects the weighting of the laboratory results if the excess variance is non-zero. From equations (9) and (10), it can be seen how the excess variance τ^2 affects the weighting of the (corrected) laboratory results (y_j'). For the computation of τ, there is no simple formula. Its estimate can be obtained from the posterior probability distribution, which is obtained by fitting the Bayesian model. Such a posterior probability distribution contains, similarly to the output probability distribution of the Monte Carlo method of GUM-S1 [29] or GUM-S2 [30], the necessary information to calculate the required output [24, 28].

The Bayesian model is complete after specifying the prior probability distributions for μ and τ. For μ, the prior probability distribution is a normal distribution with the nominal value of the amount fraction as mean and a relative standard deviation of 10 %. This is an example of a weakly informative prior, i.e., a probability distribution that adds little information to the mean μ. Its purpose is to regularise the fitting of the data by sampling from credible initial values for μ [28]. As prior for τ, a half Cauchy distribution is used with location 0 and a scale parameter equal to 2 % of the nominal amount fraction. This prior is also a weakly informative prior [24, 31]. The parameters θ have effectively a flat prior [32], i.e., a rectangular distribution over the interval $[-\infty, +\infty]$. Such a flat prior is said to contain no information about the parameter it is assigned to [28].

Fitting the Bayesian model was implemented in `R` [23] using the `RStan` package [32]. This computational environment has been introduced previously [24]. The Markov Chain Monte Carlo method (MCMC) was operated using 4 chains, each with 550000 samples, of which the first 50000 were used to initialise the method. Convergence of the MCMC was assessed as described previously [24].

The principal output of the MCMC is a probability distribution of the parameters in the Bayesian model. This probability distribution is called the posterior probability distribution, or short "posterior". It contains not only the relevant information about the consensus value μ and the excess standard deviation τ, but also about several auxiliary parameters that have been computed to evaluate this key comparison. The implementation of the model provides a sample of the posterior, which has been handled in a similar way as the sample of the output distribution as obtained in CCQM-K112 [15] and CCQM-K117 [16]. From the samples generated by the MCMC, the estimates of the parameters can be obtained by calculating the average of the parameter values in the samples. Analogously to the Monte Carlo method from GUM-S1 and GUM-S2 [29, 30], the standard uncertainty associated with the parameter value is obtained by calculating the standard deviation of the parameter values contained in the samples [24, 32]. Coverage intervals were computed using the standard uncertainty and using a coverage factor $k = 2$.

The KCRV is defined as

$$\mu_{\mathrm{KCRV},j} = \mu + \beta_j \tag{11}$$

and was computed using the posterior probability distribution obtained from the MCMC. The standard uncertainty was computed by calculating the standard deviation of the values of $\mu_{\mathrm{KCRV},j}$ contained in the sample of the posterior.

3.4 Degrees of equivalence

The difference of the degree of equivalence was computed as

$$d_j = y_j - \mu_{\mathrm{KCRV},j} \tag{12}$$

These parameters were defined in the Bayesian model, and hence the associated standard uncertainties were obtained like any other parameter in the model, i.e., by calculating the standard deviation of the MCMC samples (just as the values are obtained by calculating the mean of these samples).

The standard uncertainty associated with d_j is obtained in a similar fashion as implemented in the NIST Consensus Builder [26, 27]. For each of the samples from the MCMC for μ, β_j, and τ, a sample $\xi_j \sim \mathrm{N}(\mu_{\mathrm{KCRV},j}, \tau^2 + \sigma_j^2)$ is drawn using the normal distribution. The KCRV is defined in equation (11) and then the difference is computed as $d_j = y_{\mathrm{lab},j} - \xi_j$. The standard uncertainty is obtained by computing the variance of the samples of d_j, and then taking the square root. Note that the variance of ξ_j contains two components: the excess standard deviation τ and the standard uncertainty from the laboratory's result, $\sigma_j = u(y_{\mathrm{lab},j})$.

3.5 Amendments to measurement reports

Several laboratories had forwarded requests to amend their originally submitted data (see annex D). The following approach was agreed to deal with the results submitted:

- the KCRV was calculated based on the *original* data (see also annex C), excluding those results which had been superseded by corrected results;
- the degrees of equivalence were calculated based on the *original* data, which is in agreement with the CIPM MRA [33] and the applicable guidelines [34].

The amended measurement reports have been annexed to this report (see annex D).

4 Stability and homogeneity evaluation

4.1 Stability assessment

The results of the combined stability and homogeneity study are summarised in figures 1–13 for low-calorific natural gas. The measurements were taken at 2016-10-10 and 2019-10-29 for the components nitrogen, carbon dioxide, hydrogen, helium, ethane, propane iso-butane, n-butane and 2016-11-22 and 2019-11-12 for the others. At each measurement day, three measurements were taken for the amount fractions of all components. The red line in figures 1–13 denotes the mean amount fraction, and the dotted lines the 95 % coverage intervals as obtained by fitting the data to the Dersimonian-Laird model (DL).

For all component amount fractions in all travelling standards, stability has been demonstrated. The same applies for the travelling standards of high-calorific natural gas, see figures 14–22. The compositions were measured four times at different dates, two times before and two times after the measurements had been taken by the participants. Between the first and second measurement, and between the third and fourth measurement, there was typically a time period of 1–2 weeks. The red line in figures 14–22 denotes the mean amount fraction, and the dotted lines the 95 % coverage intervals as obtained by fitting the data to the DL. The stability study data are also given in annex A.

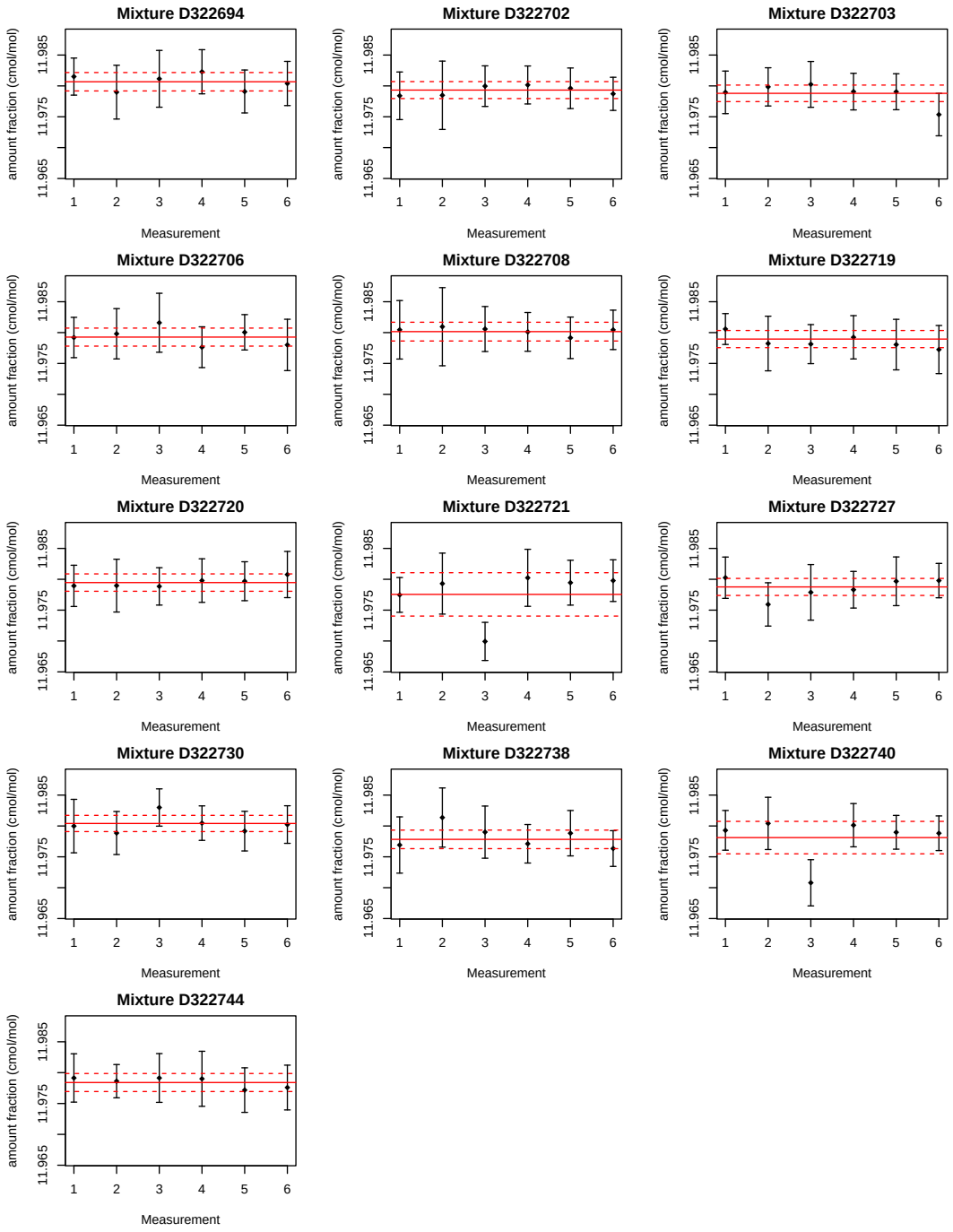


Figure 1: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for nitrogen. The uncertainty bars indicate expanded uncertainties.

The results for nitrogen in low-calorific natural gas are shown in figure 1. The numerical data are given in table 30 in annex A. The results demonstrate stability for this component. The results for carbon dioxide in low-calorific natural gas are shown in figure 2. The numerical data are given in table 31 in annex A. The results demonstrate stability for this component.

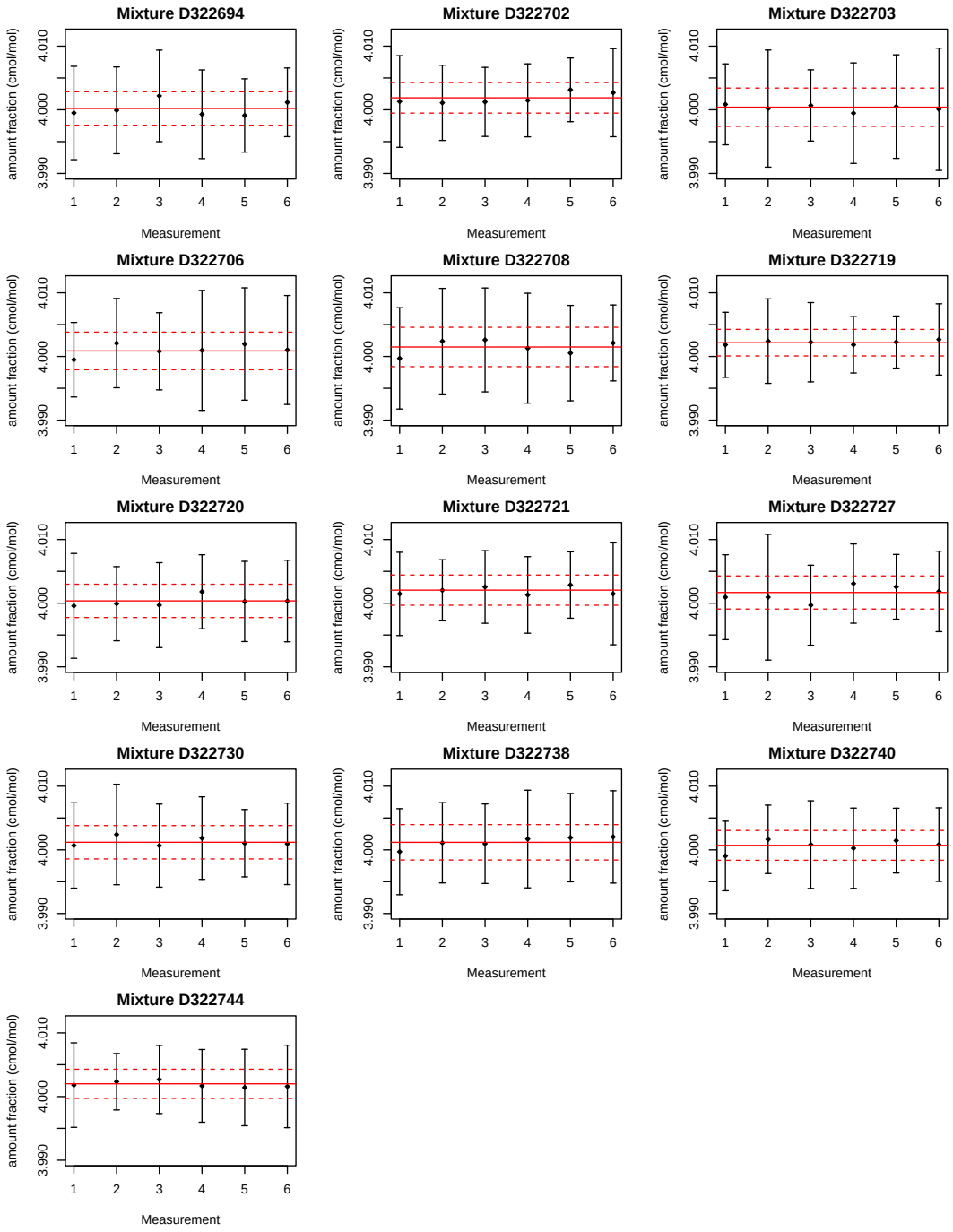


Figure 2: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for carbon dioxide. The uncertainty bars indicate expanded uncertainties.

The results for hydrogen in low-calorific natural gas are shown in figure 3. The numerical data are given in table 32 in annex A. The results demonstrate stability for this component. The results for helium in low-calorific natural gas are shown in figure 4. The numerical data are given in table 33 in annex A. The results demonstrate stability for this component.

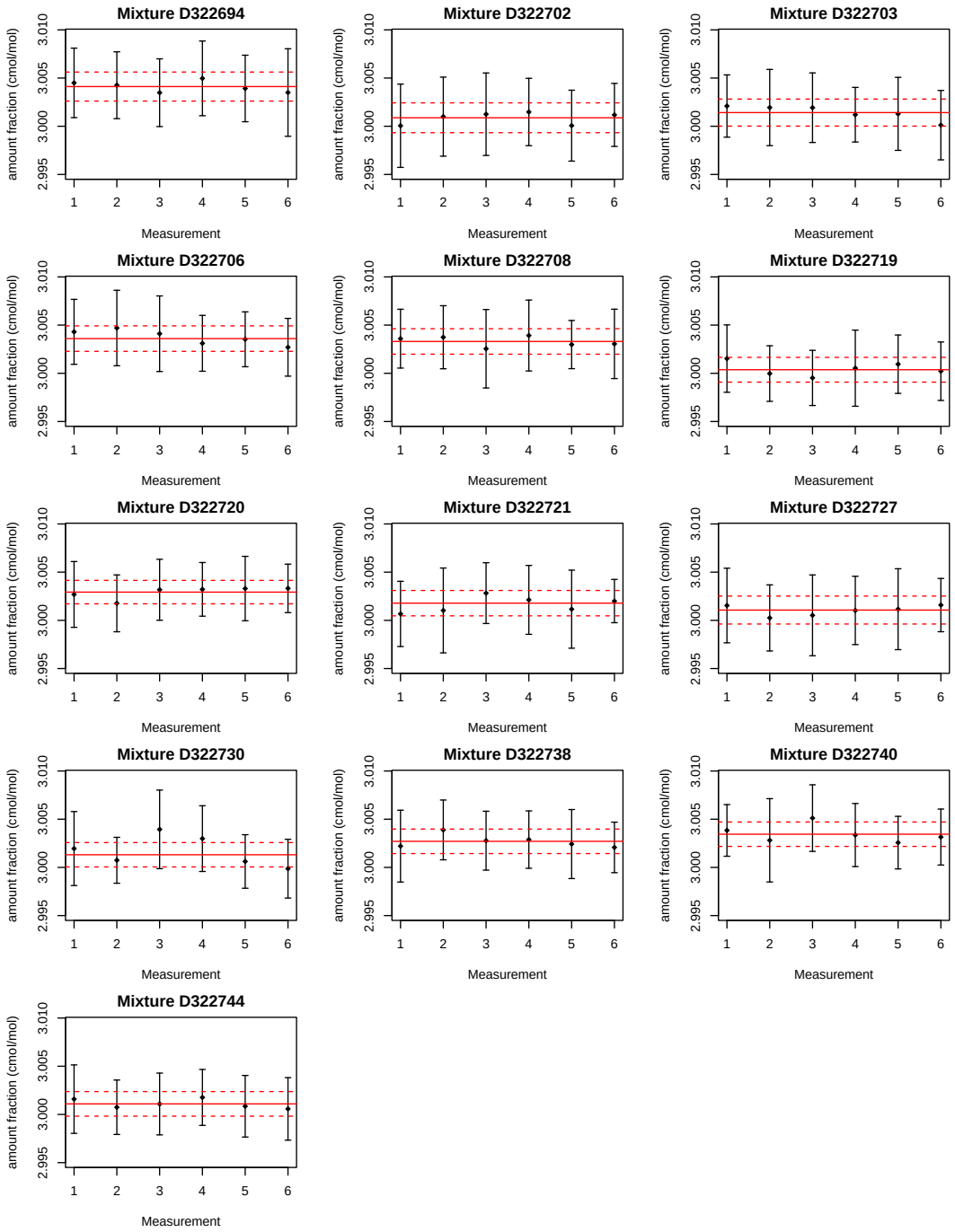


Figure 3: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for hydrogen. The uncertainty bars indicate expanded uncertainties.

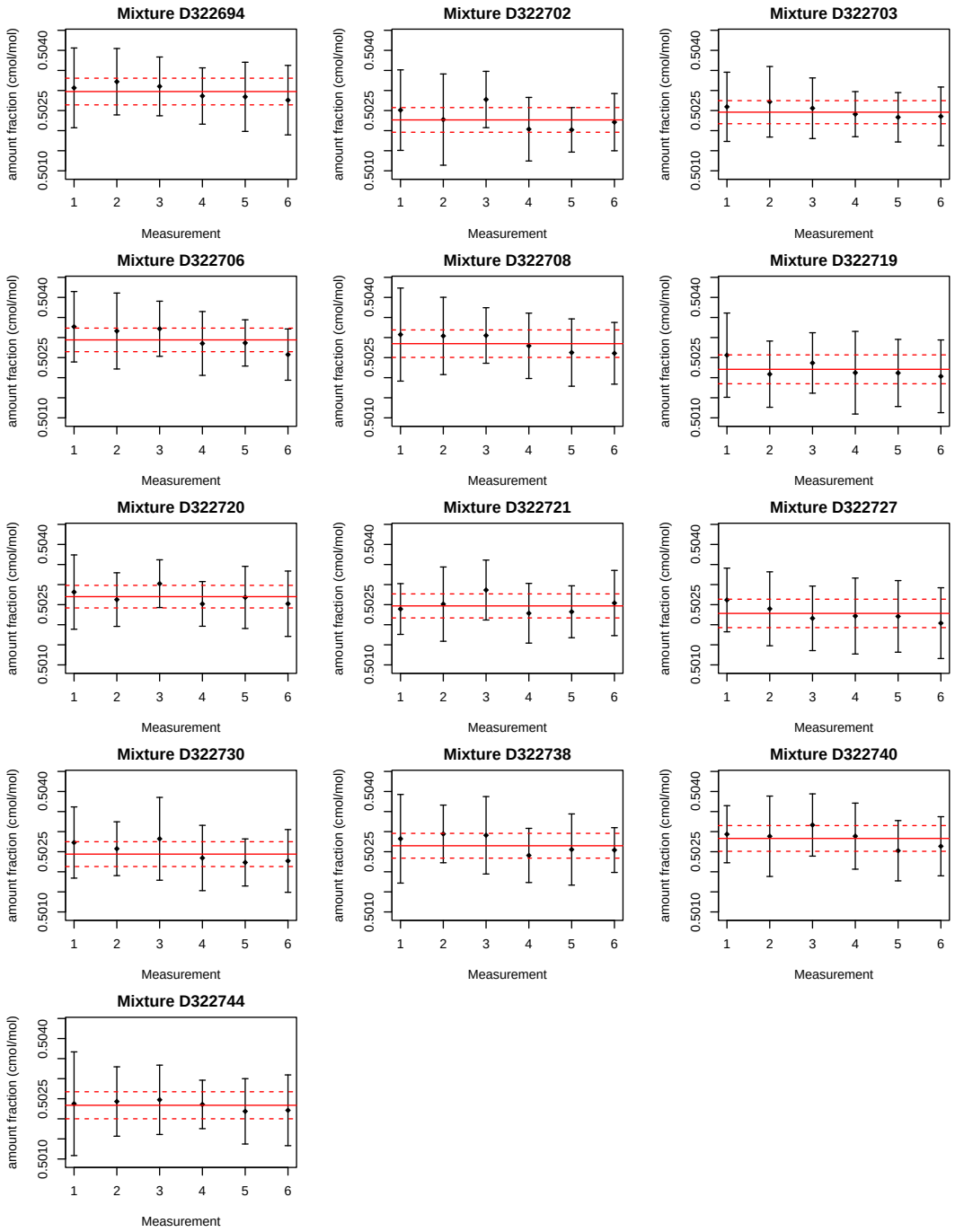


Figure 4: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for helium. The uncertainty bars indicate expanded uncertainties.

The results for ethane in low-calorific natural gas are shown in figure 5. The numerical data are given in table 34 in annex A. The results demonstrate stability for this component. The results for propane in low-calorific natural gas are shown in figure 6. The numerical data are given in table 35 in annex A. The results demonstrate stability for this component.

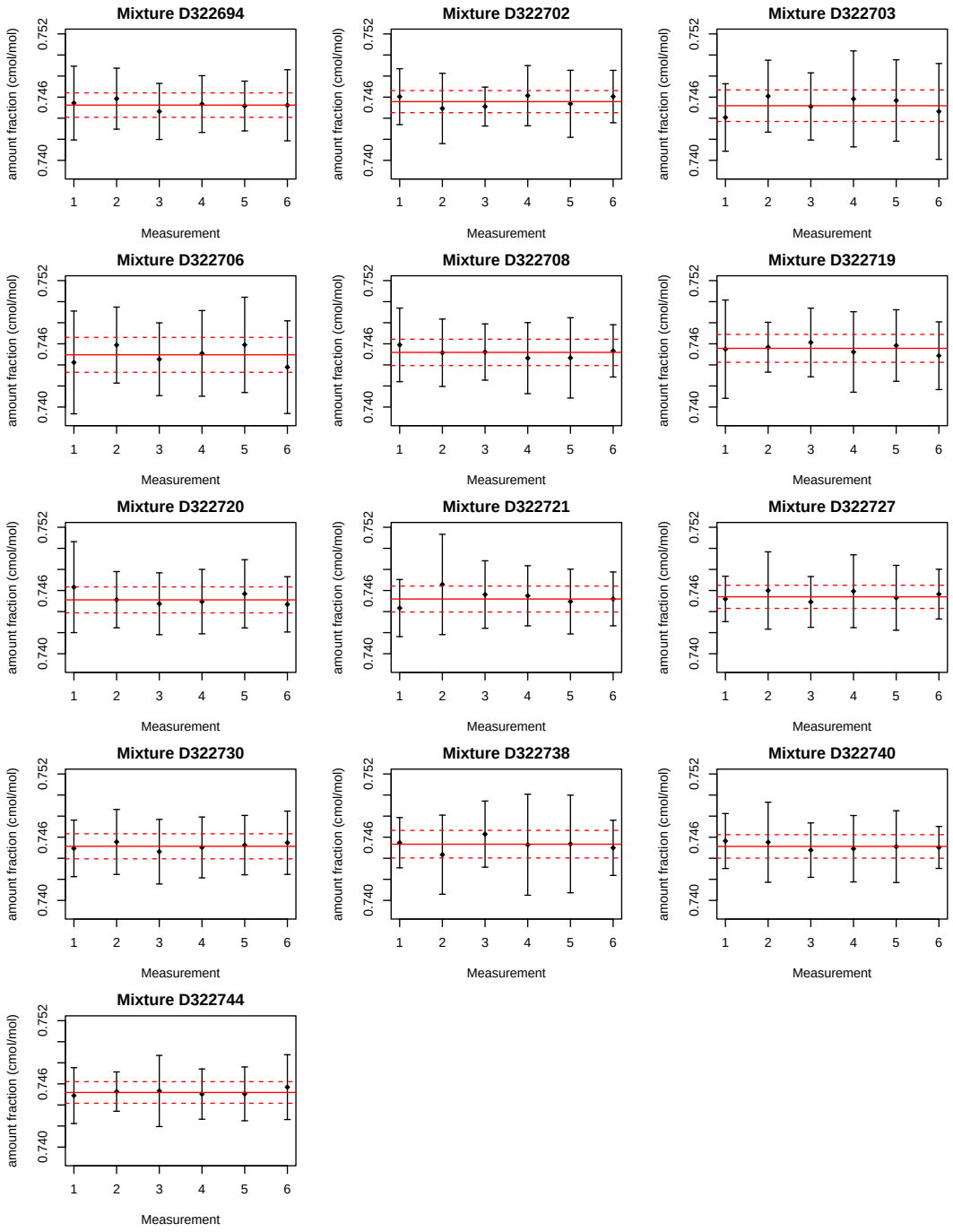


Figure 5: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for ethane. The uncertainty bars indicate expanded uncertainties.

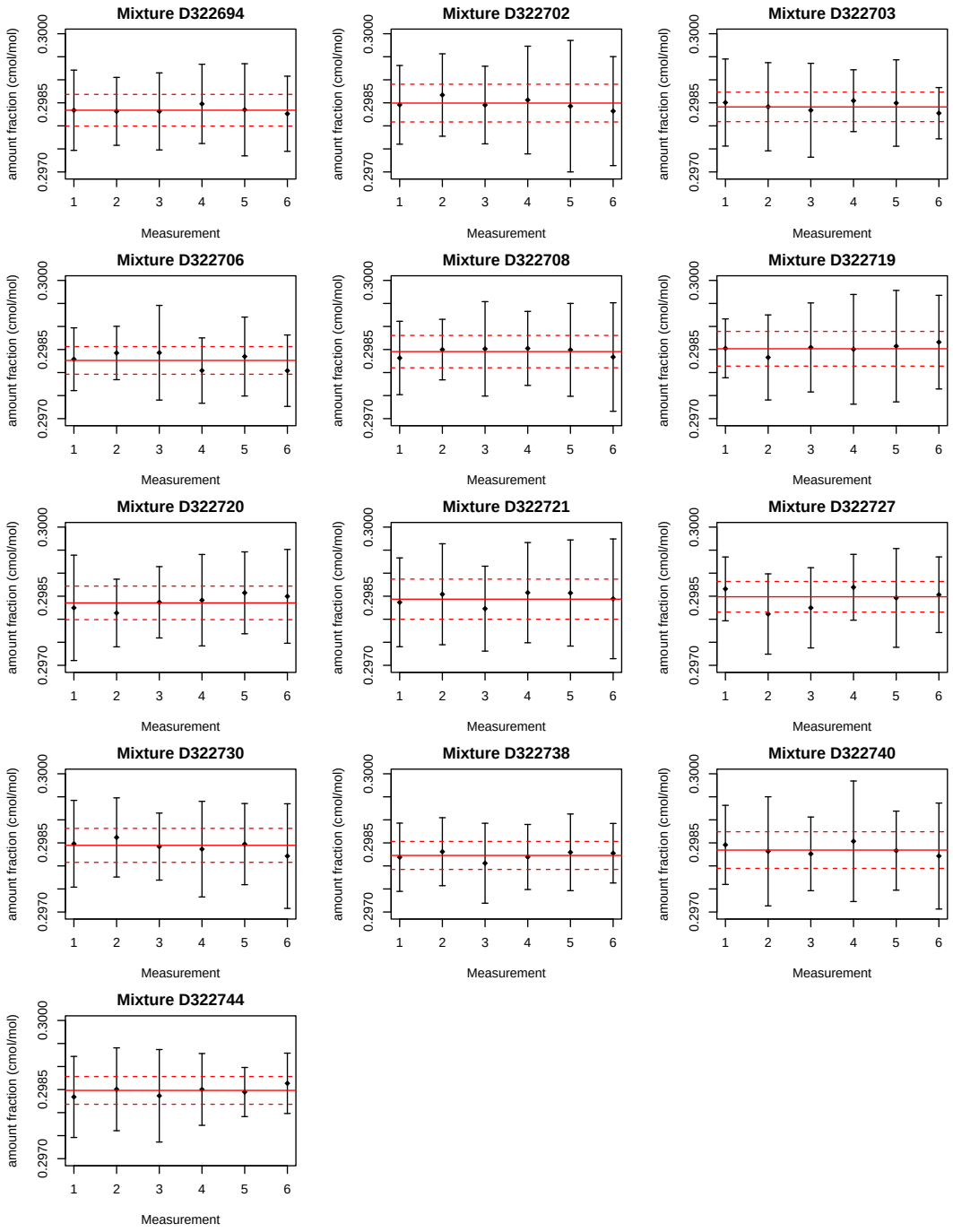


Figure 6: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for propane. The uncertainty bars indicate expanded uncertainties.

The results for *iso*-butane in low-calorific natural gas are shown in figure 7. The numerical data are given in table 36 in annex A. The results demonstrate stability for this component. The results for *n*-butane in low-calorific natural gas are shown in figure 8. The numerical data are given in table 37 in annex A. The results demonstrate stability for this component.

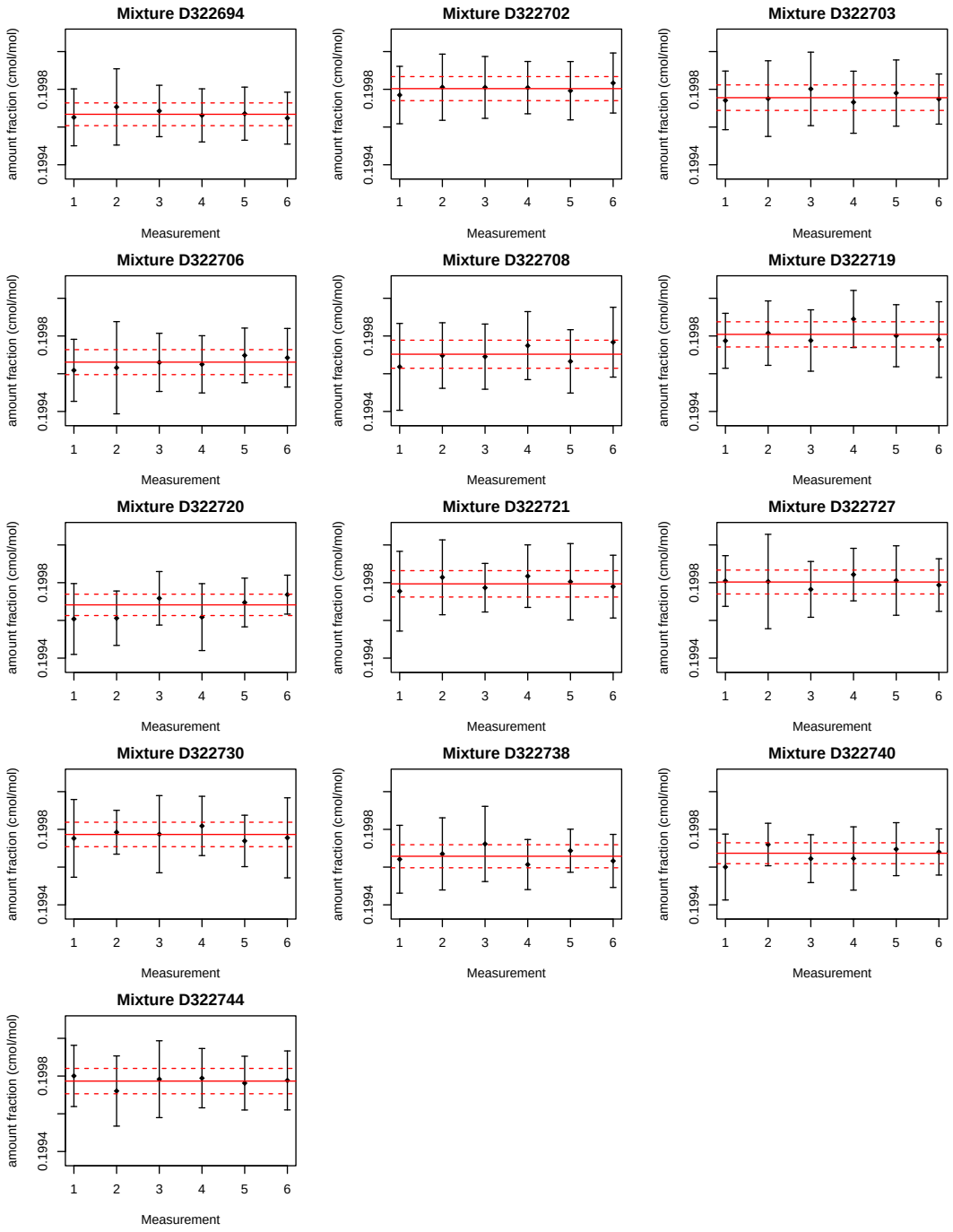


Figure 7: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *iso*-butane. The uncertainty bars indicate expanded uncertainties.

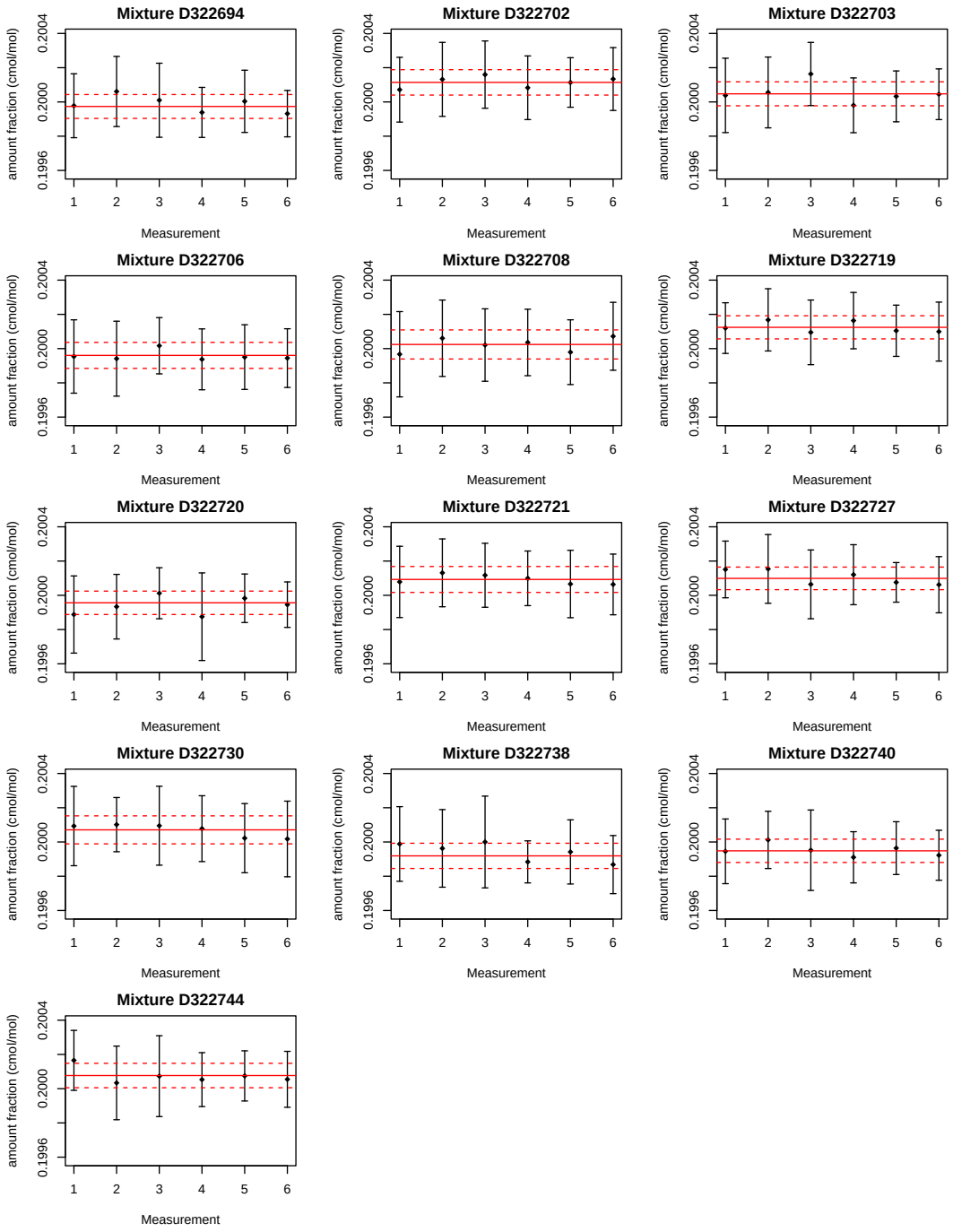


Figure 8: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *n*-butane. The uncertainty bars indicate expanded uncertainties.

The results for *neo*-pentane in low-calorific natural gas are shown in figure 9. The numerical data are given in table 38 in annex A. The results demonstrate stability for this component. The results for *iso*-pentane in low-calorific natural gas are shown in figure 10. The numerical data are given in table 39 in annex A. The results demonstrate stability for this component.

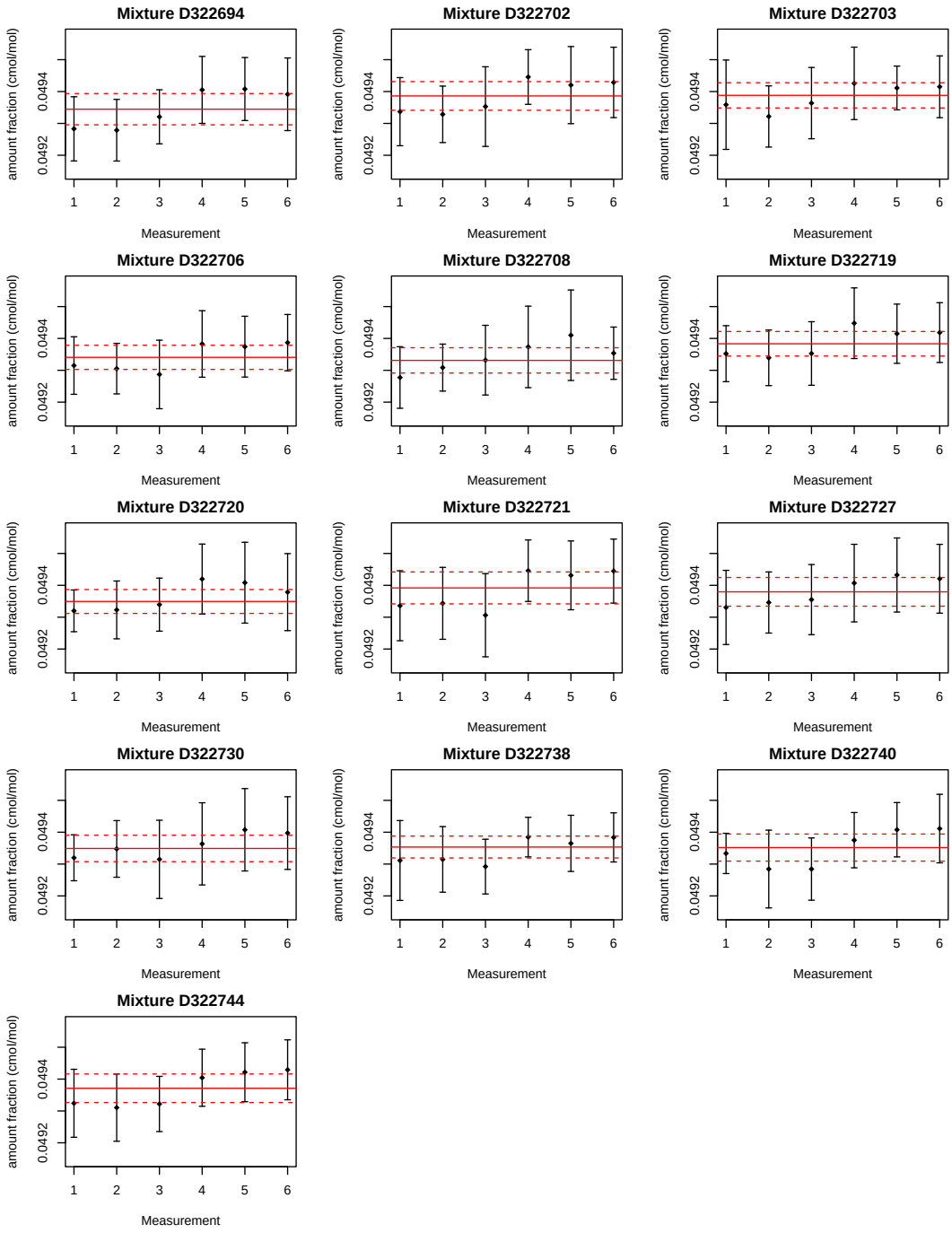


Figure 9: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *neo*-pentane. The uncertainty bars indicate expanded uncertainties.

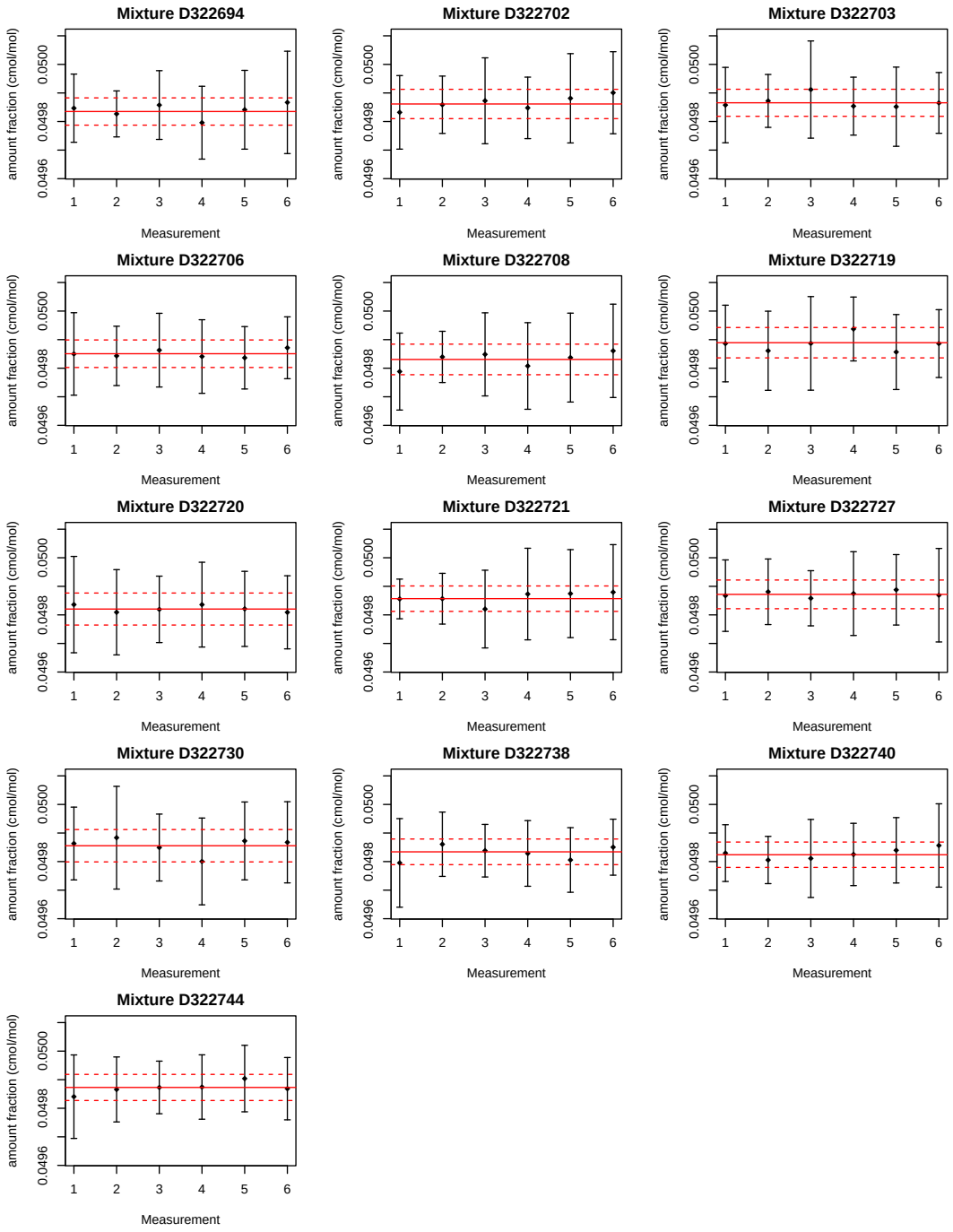


Figure 10: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *iso*-pentane. The uncertainty bars indicate expanded uncertainties.

The results for *n*-pentane in low-calorific natural gas are shown in figure 11. The numerical data are given in table 40 in annex A. The results demonstrate stability for this component. The results for *n*-hexane in low-calorific natural gas are shown in figure 12. The numerical data are given in table 41 in annex A. The results demonstrate stability for this component.

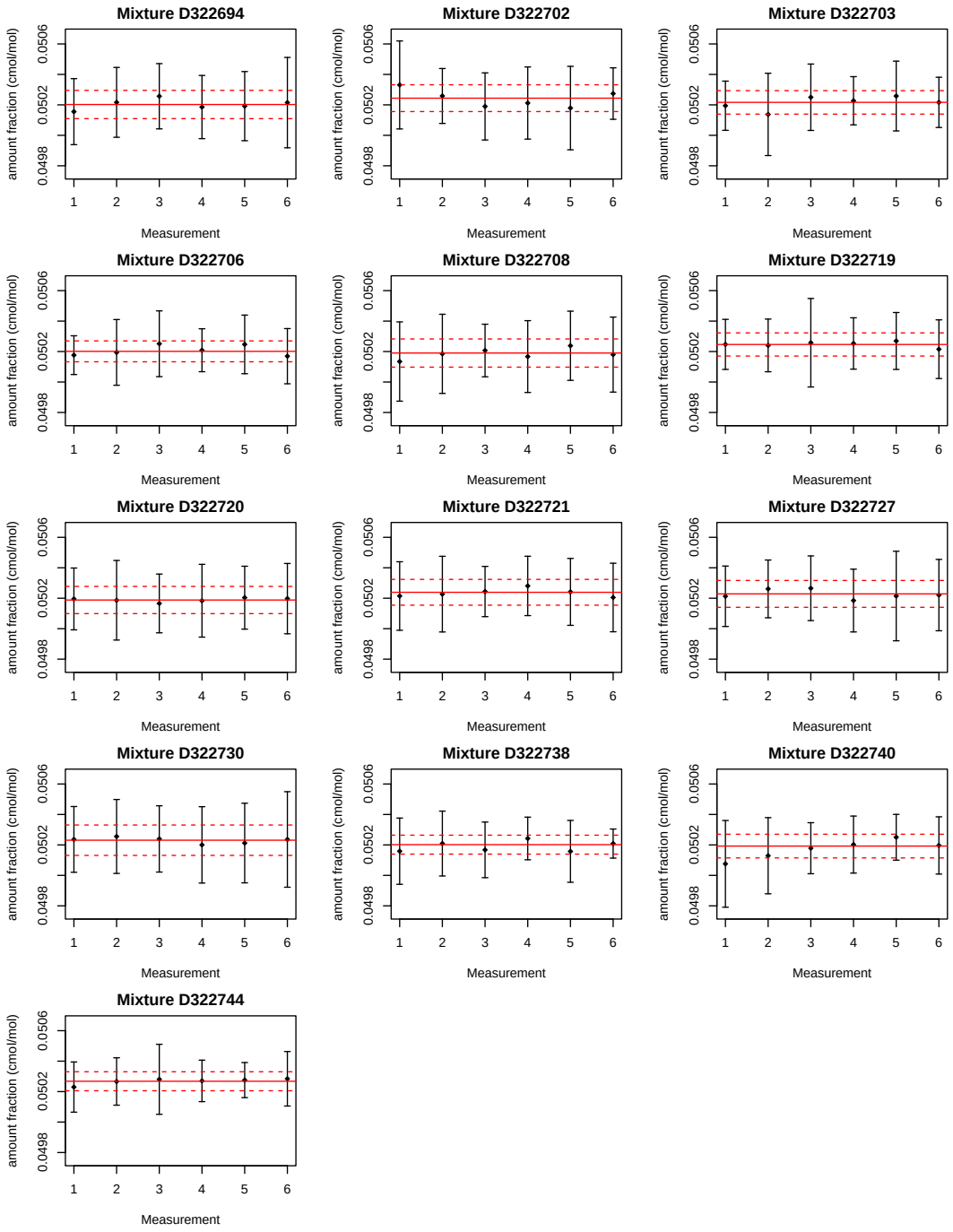


Figure 11: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *n*-pentane. The uncertainty bars indicate expanded uncertainties.

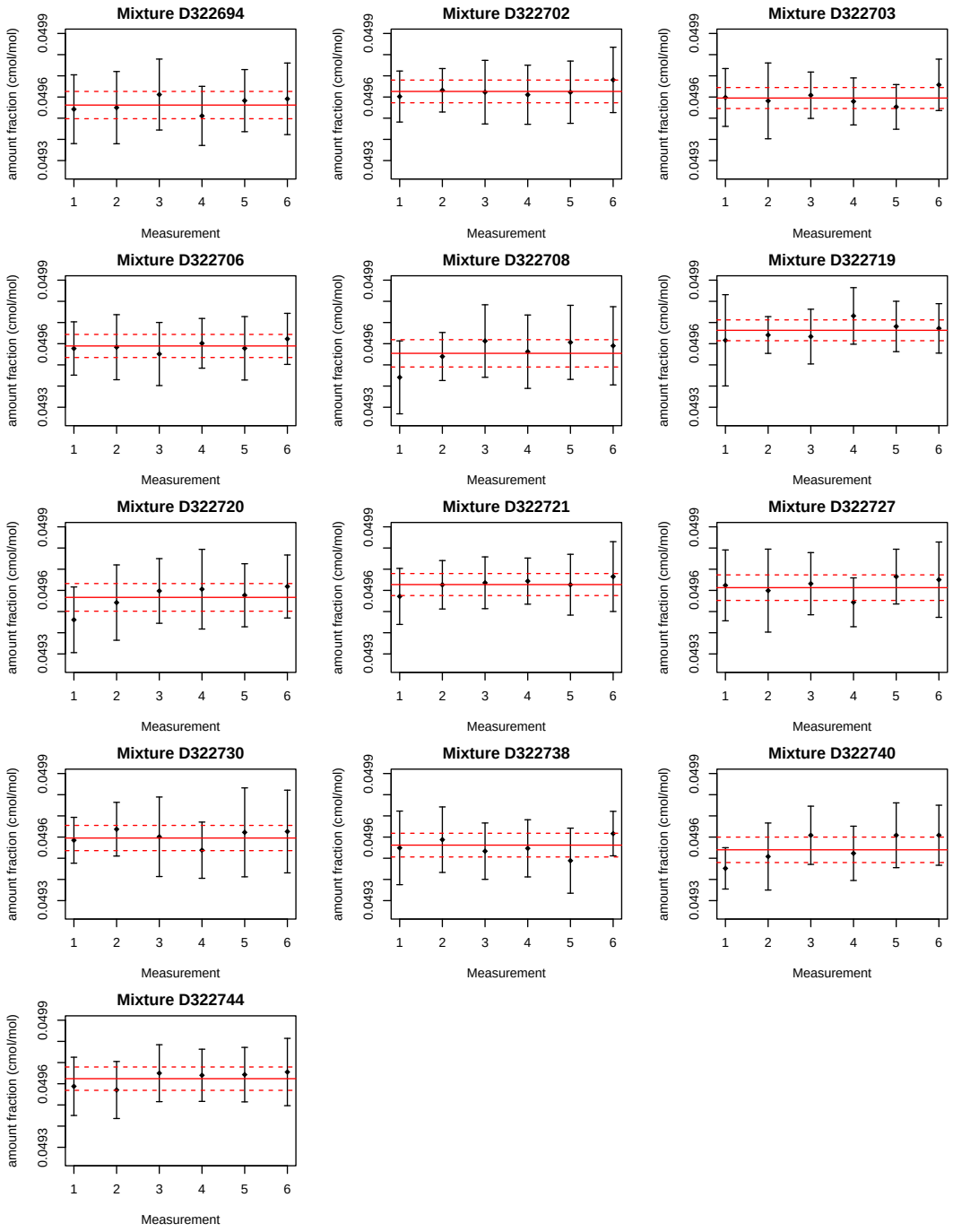


Figure 12: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for *n*-hexane. The uncertainty bars indicate expanded uncertainties.

The results for methane in low-calorific natural gas are shown in figure 13. The numerical data are given in table 42 in annex A. The results demonstrate stability for this component.

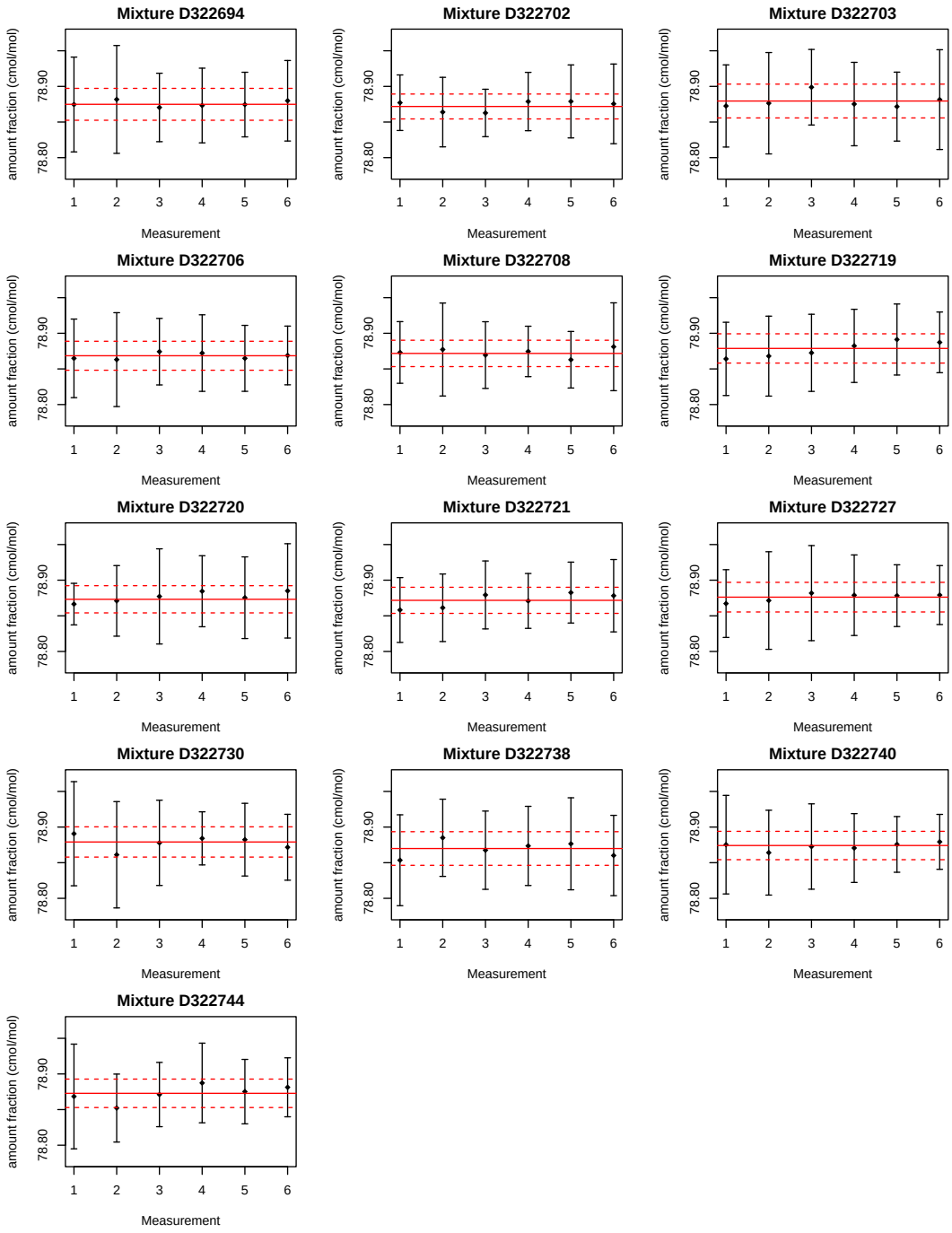


Figure 13: Results of the analysis of the travelling standards type IVa before and after analysis by the participating NMIs for methane. The uncertainty bars indicate expanded uncertainties.

The results for nitrogen in high-calorific natural gas are shown in figure 14. The numerical data are given in table 43 in annex A. Taking into consideration the excess dispersion of the data, the results demonstrate stability for this component. The results for carbon dioxide in high-calorific natural gas

are shown in figure 15. The numerical data are given in table 44 in annex A. The results demonstrate stability for this component.

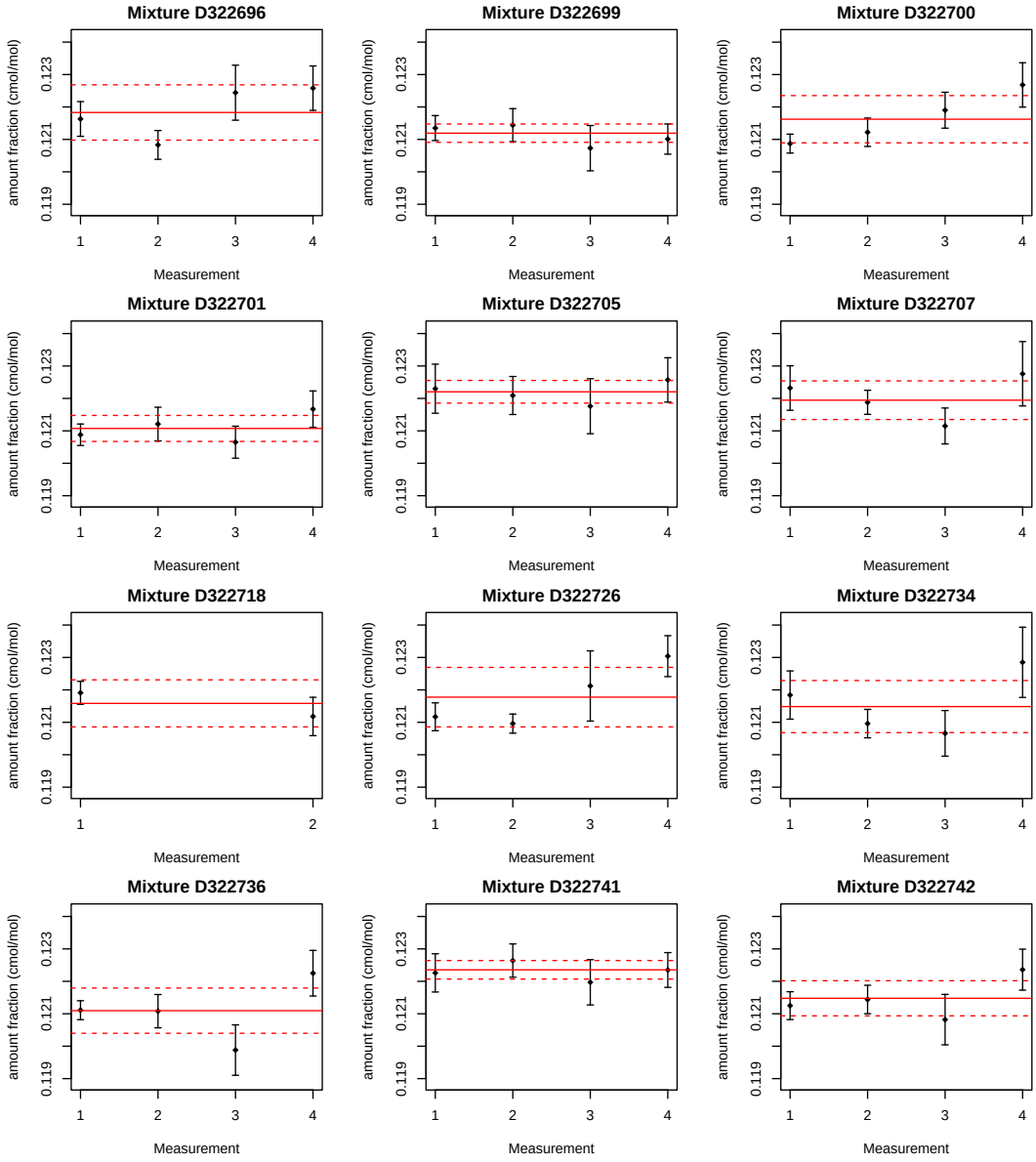


Figure 14: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for nitrogen. The uncertainty bars indicate expanded uncertainties.

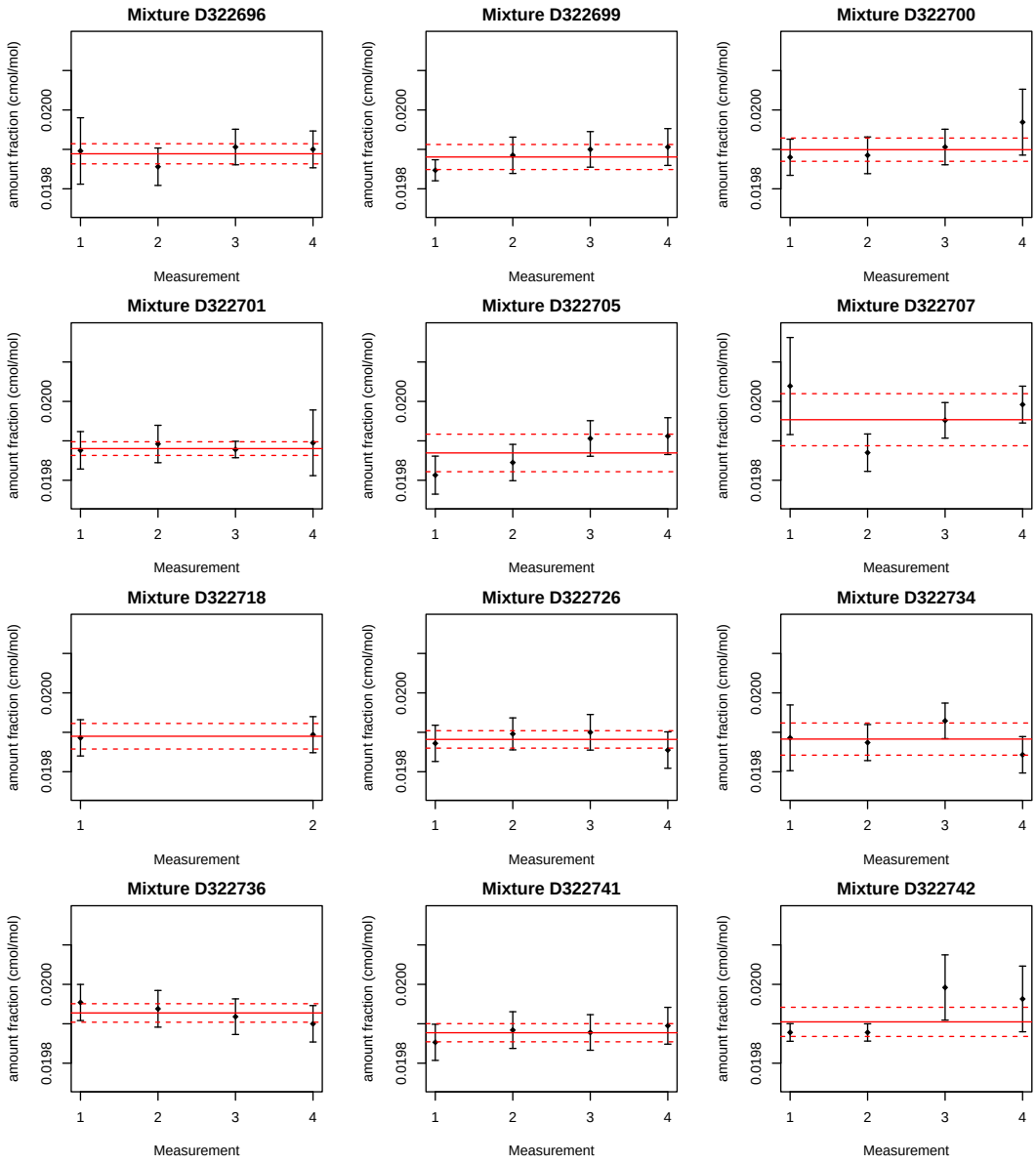


Figure 15: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for carbon dioxide. The uncertainty bars indicate expanded uncertainties.

The results for ethane in high-calorific natural gas are shown in figure 16. The numerical data are given in table 45 in annex A. The results demonstrate stability for this component. The results for propane in high-calorific natural gas are shown in figure 17. The numerical data are given in table 46 in annex A. The results demonstrate stability for this component.

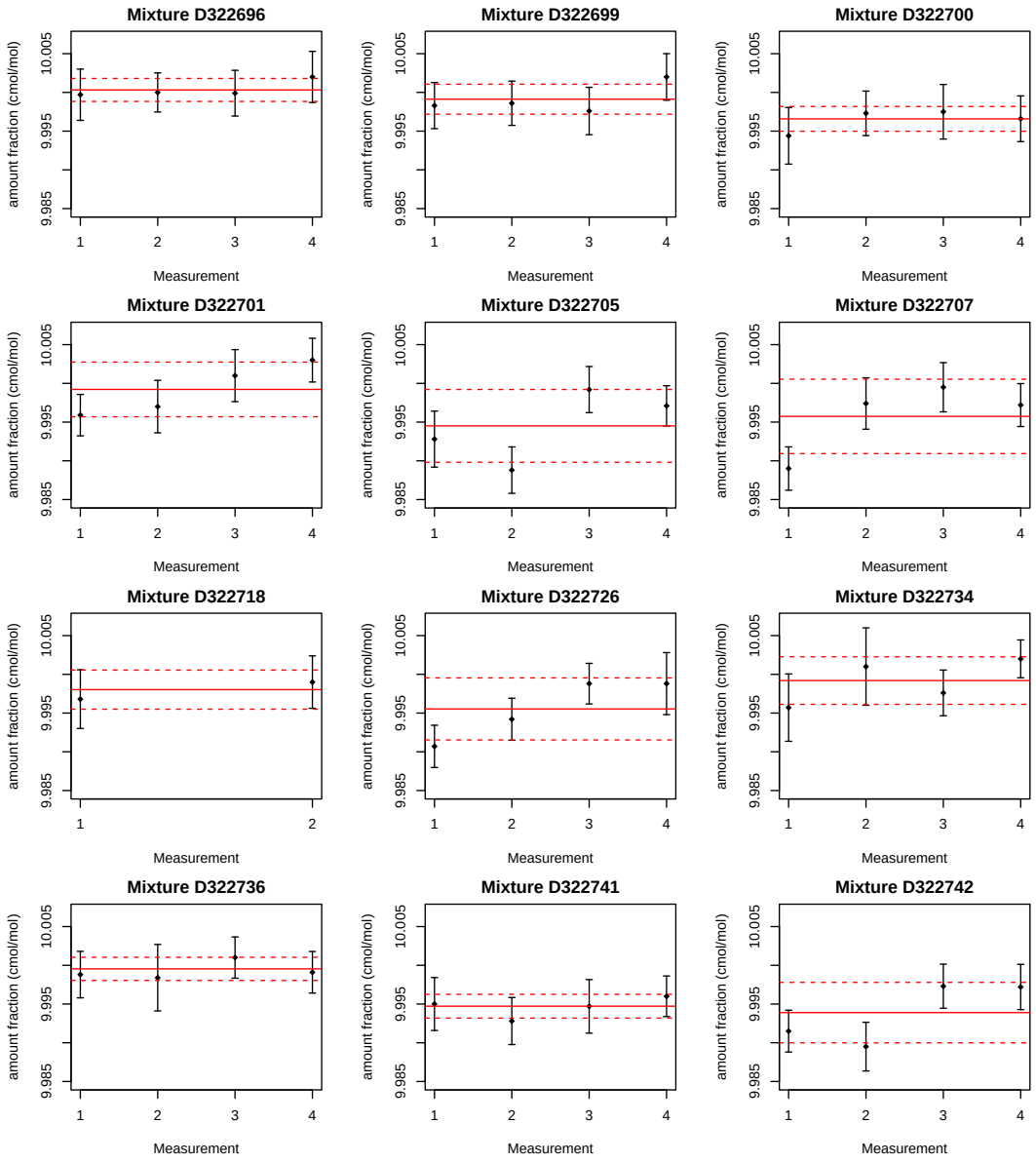


Figure 16: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for ethane. The uncertainty bars indicate expanded uncertainties.

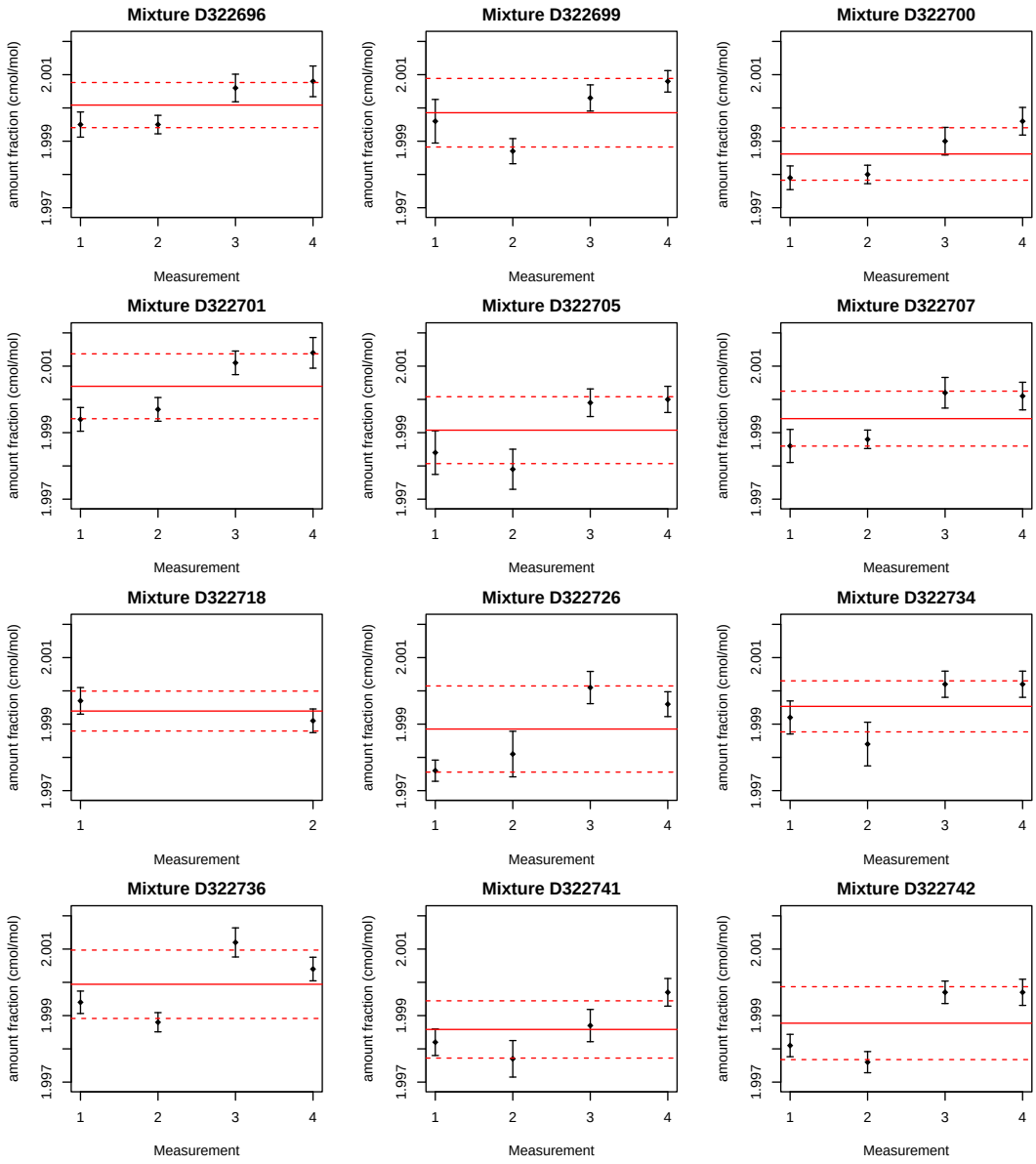


Figure 17: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for propane. The uncertainty bars indicate expanded uncertainties.

The results for *iso*-butane in high-calorific natural gas are shown in figure 18. The numerical data are given in table 47 in annex A. The results demonstrate stability for this component. The results for *n*-butane in high-calorific natural gas are shown in figure 19. The numerical data are given in table 48 in annex A. The results demonstrate stability for this component.

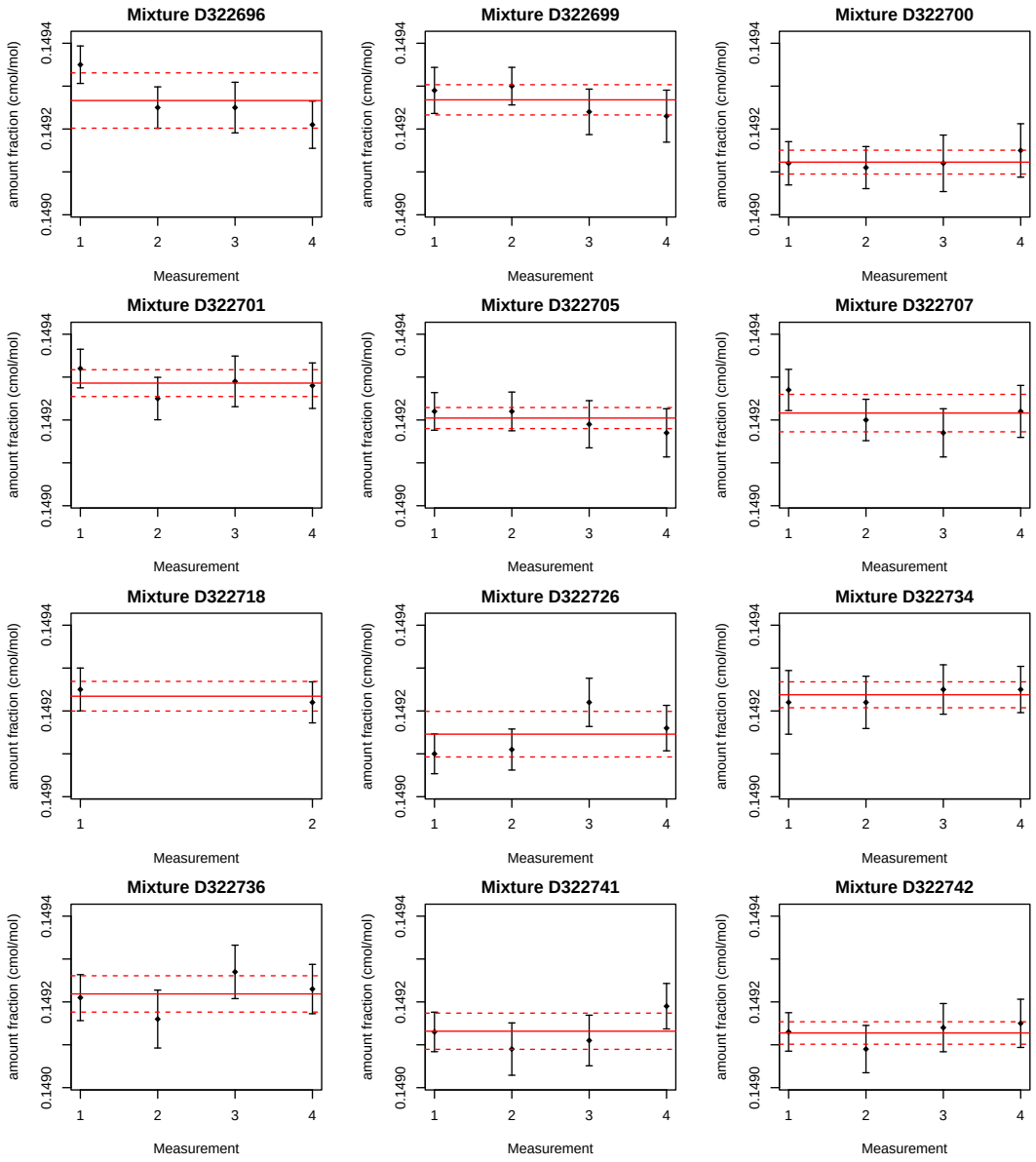


Figure 18: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for *iso*-butane. The uncertainty bars indicate expanded uncertainties.

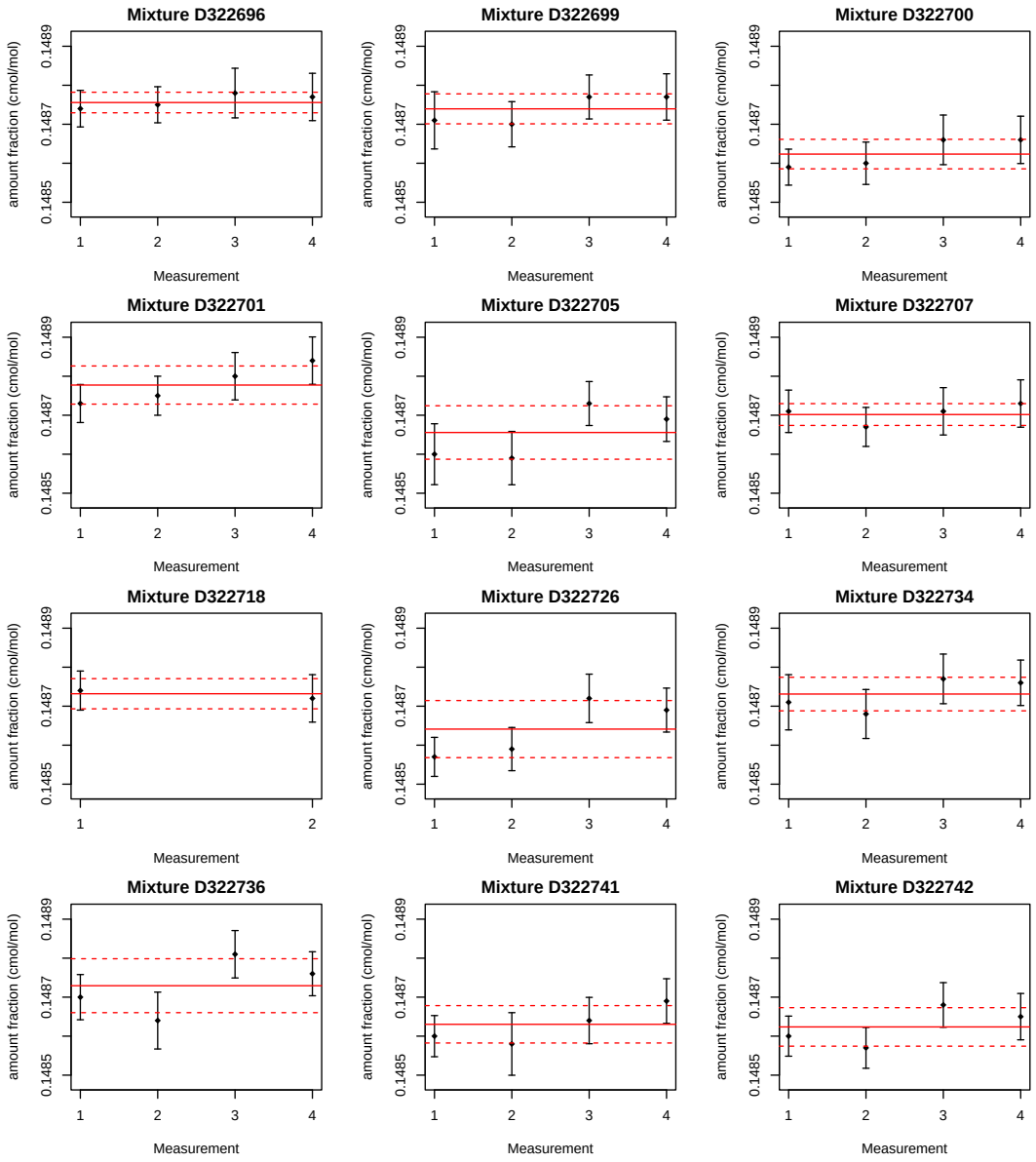


Figure 19: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for *n*-butane. The uncertainty bars indicate expanded uncertainties.

The results for *iso*-pentane in high-calorific natural gas are shown in figure 20. The numerical data are given in table 49 in annex A. The results demonstrate stability for this component. The results for *n*-pentane in high-calorific natural gas are shown in figure 21. The numerical data are given in table 50 in annex A. The results demonstrate stability for this component.

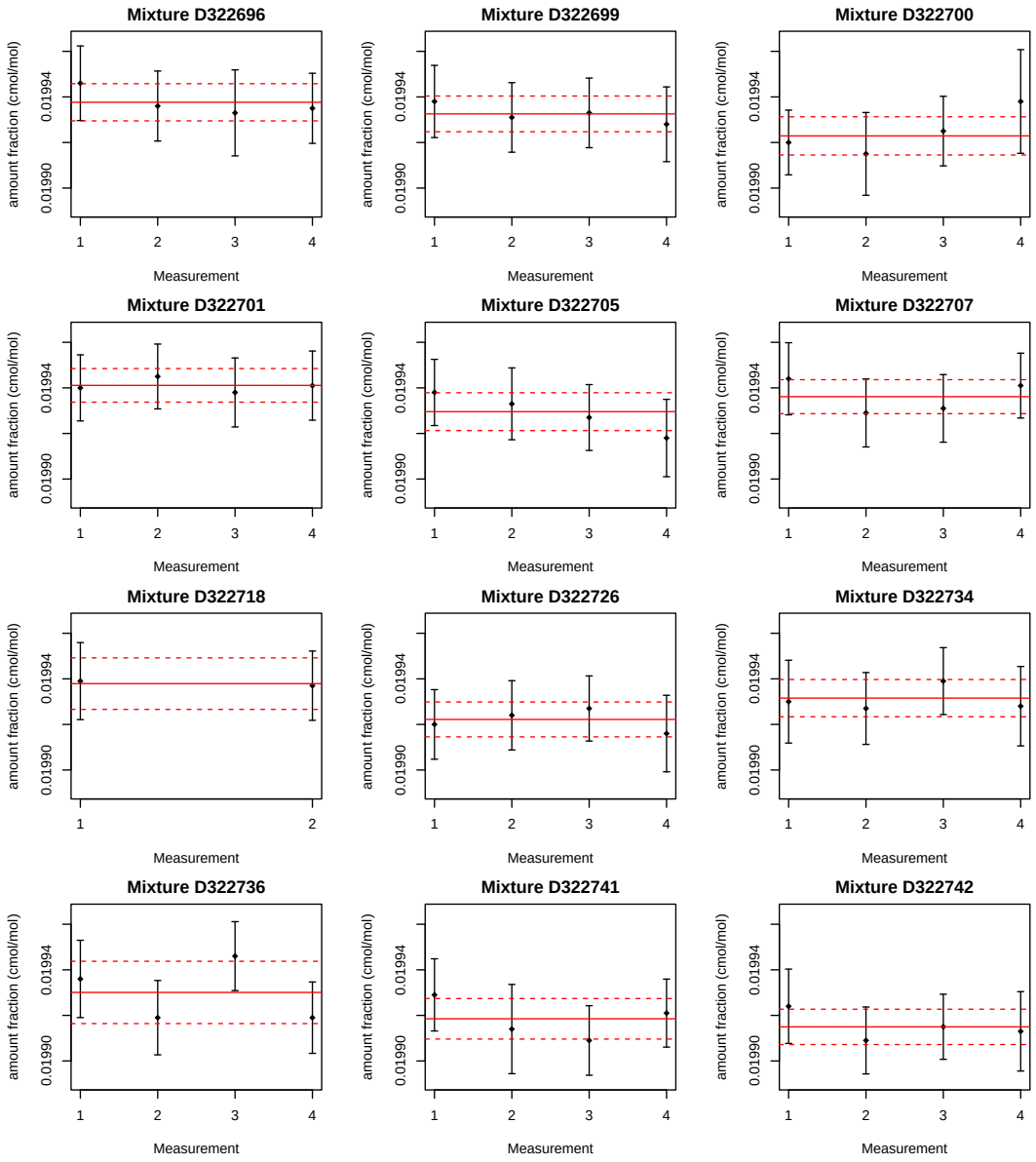


Figure 20: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for *iso*-pentane. The uncertainty bars indicate expanded uncertainties.

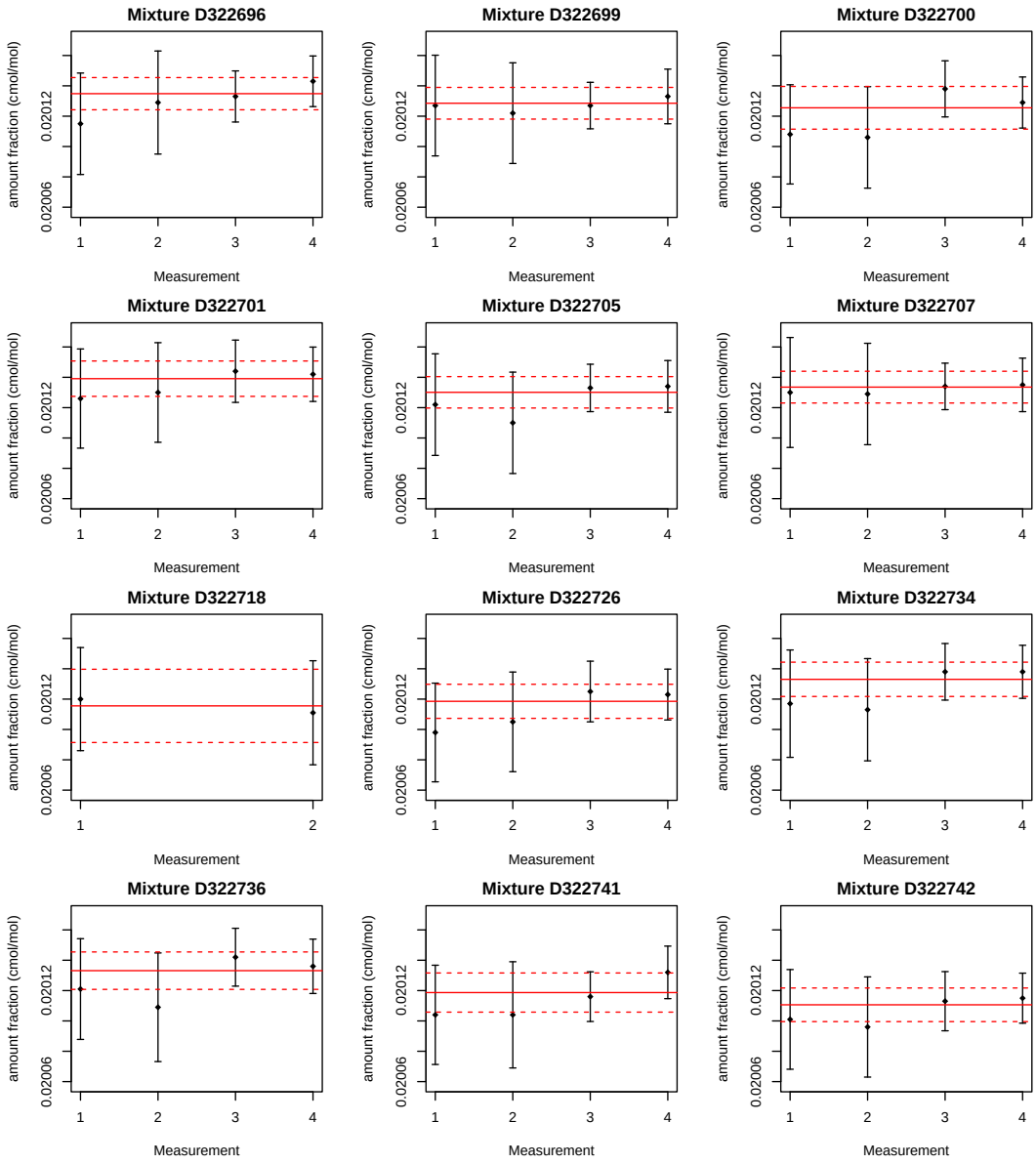


Figure 21: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for *n*-pentane. The uncertainty bars indicate expanded uncertainties.

The results for methane in high-calorific natural gas are shown in figure 22. The numerical data are given in table 51 in annex A. The results demonstrate stability for this component.

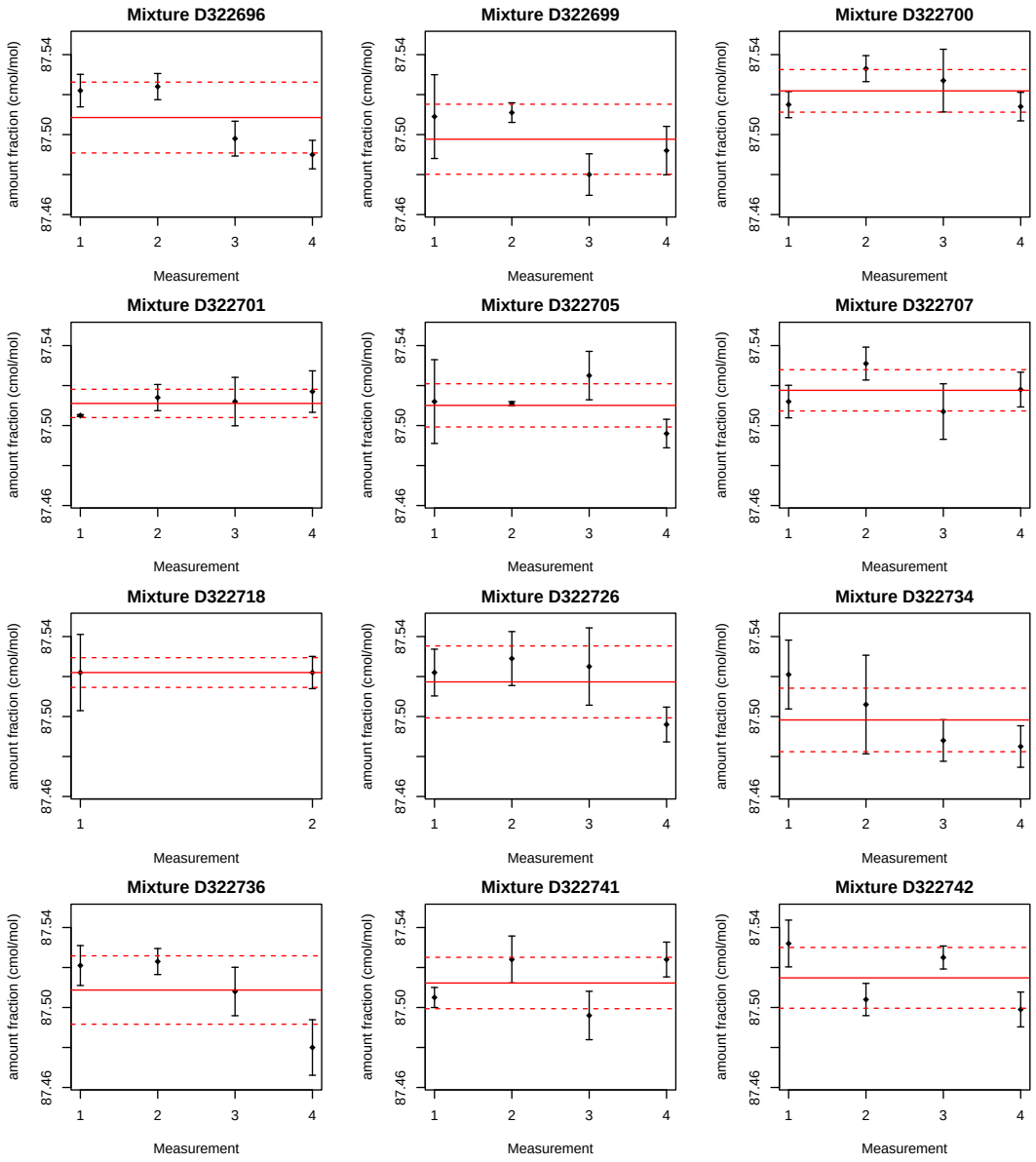


Figure 22: Results of the analysis of the travelling standards type LNG before and after analysis by the participating NMIs for methane. The uncertainty bars indicate expanded uncertainties.

4.2 Calculation of corrections due to between-bottle inhomogeneity

In this section, the corrections due to between-bottle homogeneity are shown and discussed. In the figures, the uncertainty bars represent probabilistically-symmetric 95 % coverage intervals. If these invervals contain zero, then the correction is not significant at the 95 % probability level.

Irrespective of whether the corrections were significant at this probability level, all corrections have been applied in the subsequent calculations. Annex B provides tabulated values of these corrections, their associated standard uncertainties, as well as the computed degrees of equivalence. It is important to emphasise that all corrections were applied, even if they were not significant, to ensure that

the small differences in the composition of the travelling standards does not contribute to flagging a participant's result as discrepant.

Figure 23 shows the results for nitrogen. Most corrections are insignificant at the 95 % probability level; three are (close to be) meaningful. The numerical data of the corrections are given in table 52 in annex B.

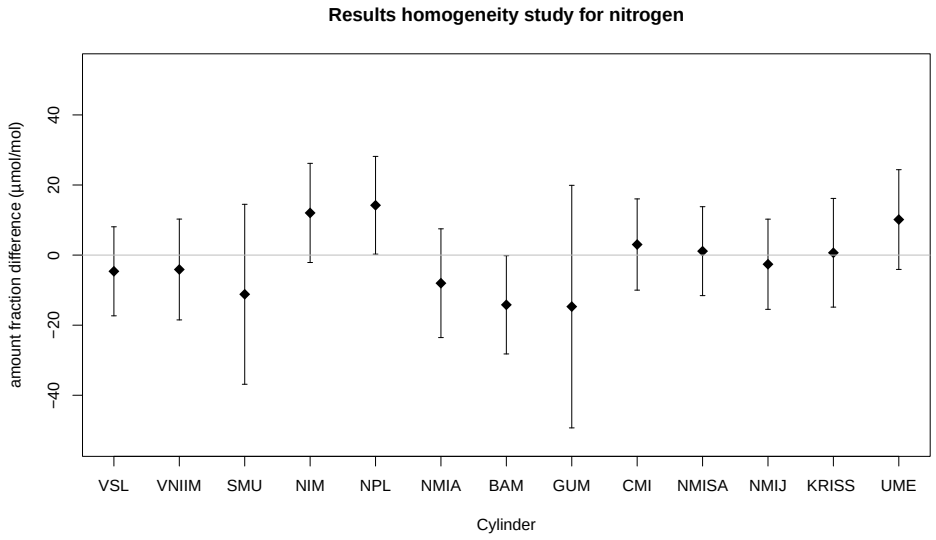


Figure 23: Corrections due to between-bottle homogeneity calculated for the amount fraction nitrogen (type IVa).

Figure 24 shows the results for carbon dioxide. None of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 53 in annex B.

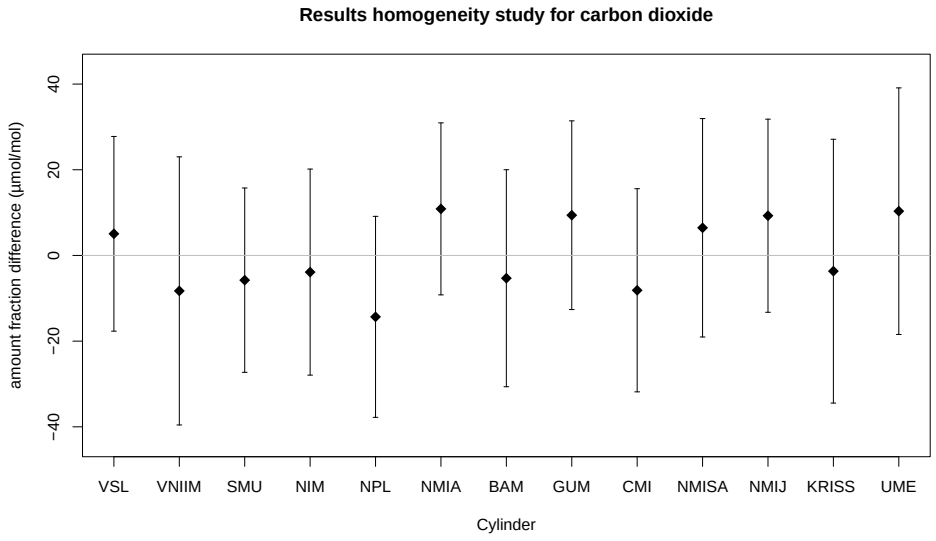


Figure 24: Corrections due to between-bottle homogeneity calculated for the amount fraction carbon dioxide (type IVa).

Figure 25 shows the results for hydrogen. Two corrections are significant at the 95 % probability level; three are (close to be) meaningful. The numerical data of the corrections are given in table 54 in annex B.

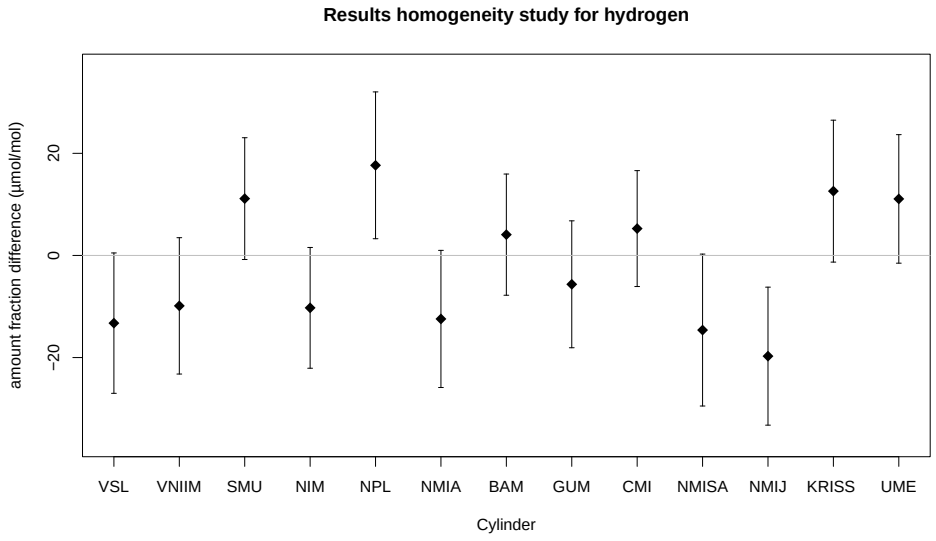


Figure 26: Corrections due to between-bottle homogeneity calculated for the amount fraction hydrogen (type IVa).

Figure 26 shows the results for helium. Two corrections are significant at the 95 % probability level; three are (close to be) meaningful. The numerical data of the corrections are given in table 55 in annex B.

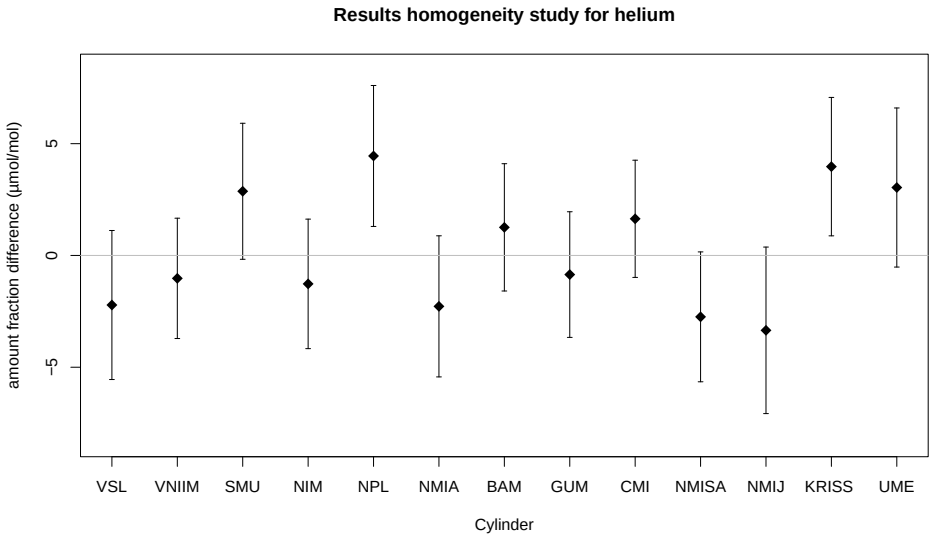


Figure 26: Corrections due to between-bottle homogeneity calculated for the amount fraction helium (type IVa).

Figure 27 shows the results for ethane. None of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 56 in annex B.

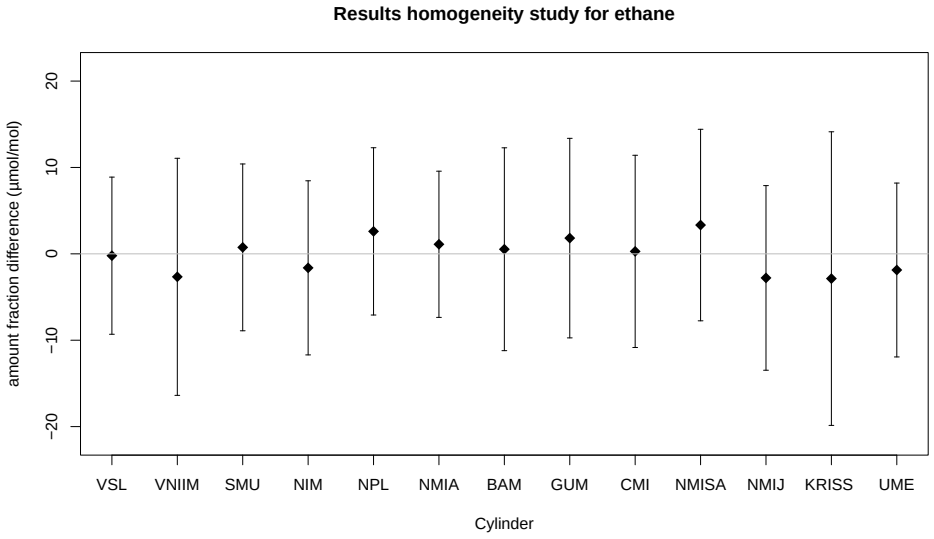


Figure 27: Corrections due to between-bottle homogeneity calculated for the amount fraction ethane (type IVa).

Figure 28 shows the results for propane. None of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 57 in annex B.

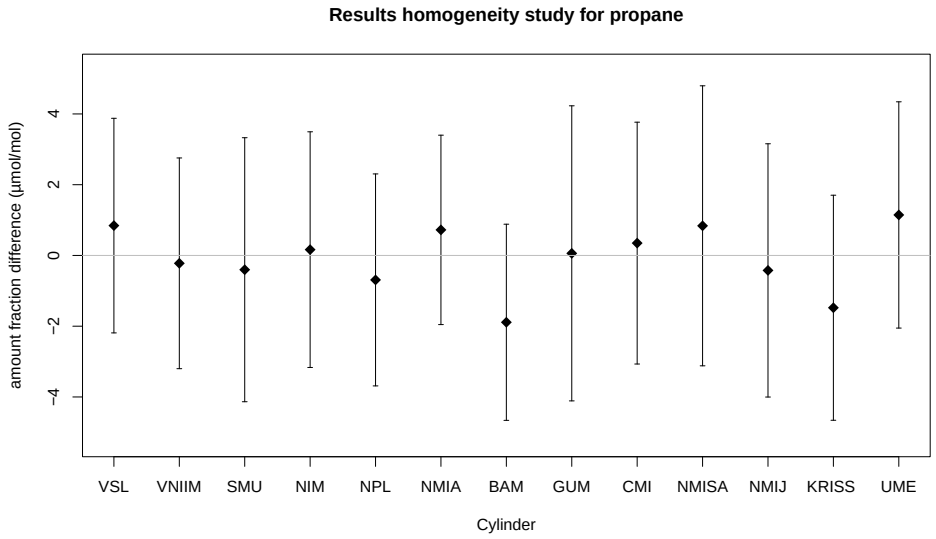


Figure 28: Corrections due to between-bottle homogeneity calculated for the amount fraction propane (type IVa).

Figure 29 shows the results for iso-butane. Several of the corrections are significant at the 95 % probability level. Many others are close to be significant. The numerical data of the corrections are given in table 58 in annex B.

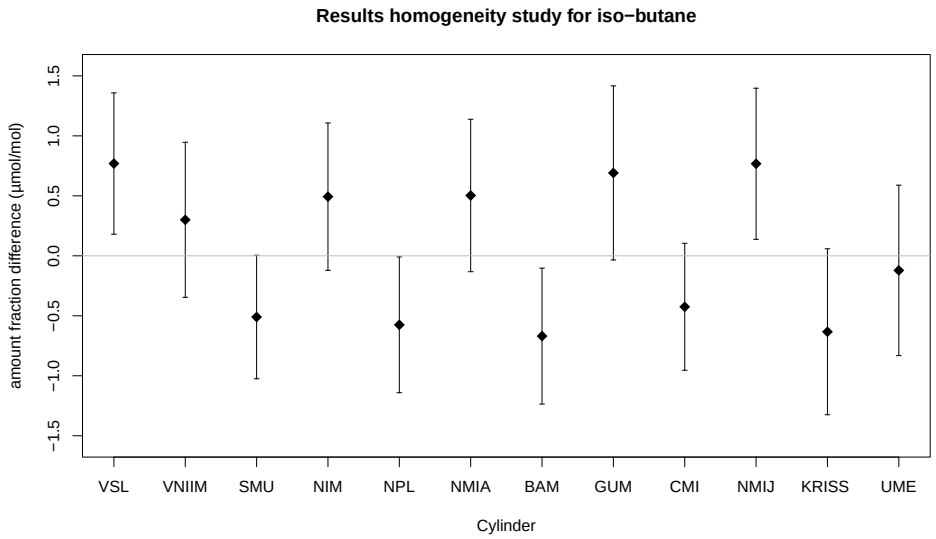


Figure 29: Corrections due to between-bottle homogeneity calculated for the amount fraction *iso*-butane (type IVa).

Figure 30 shows the results for n-butane. Several of the corrections are significant at the 95 % probability level. Many others are close to be significant. The numerical data of the corrections are given in table 59 in annex B.

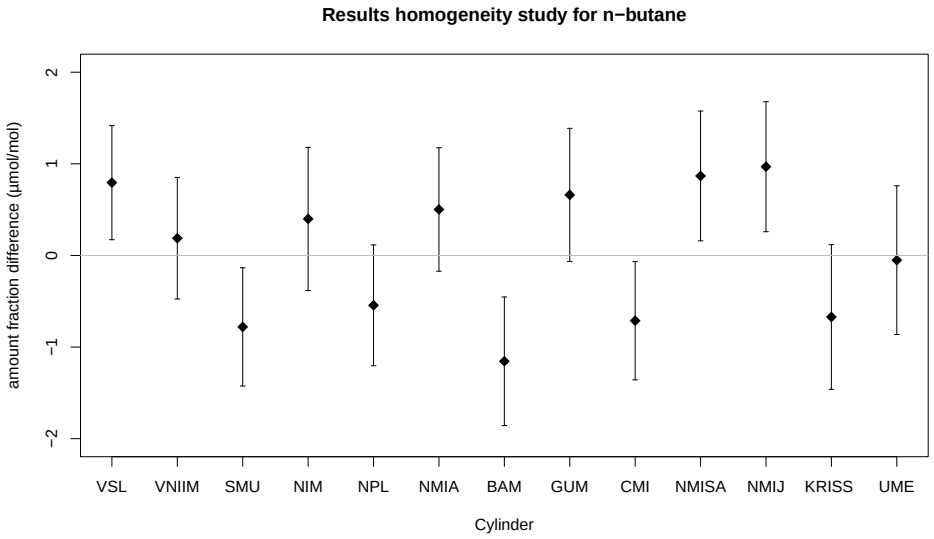


Figure 30: Corrections due to between-bottle homogeneity calculated for the amount fraction *n*-butane (type IVa).

Figure 31 shows the results for iso-pentane. None of the corrections is significant at the 95 % probability level. The numerical data of the corrections are given in table 60 in annex B.

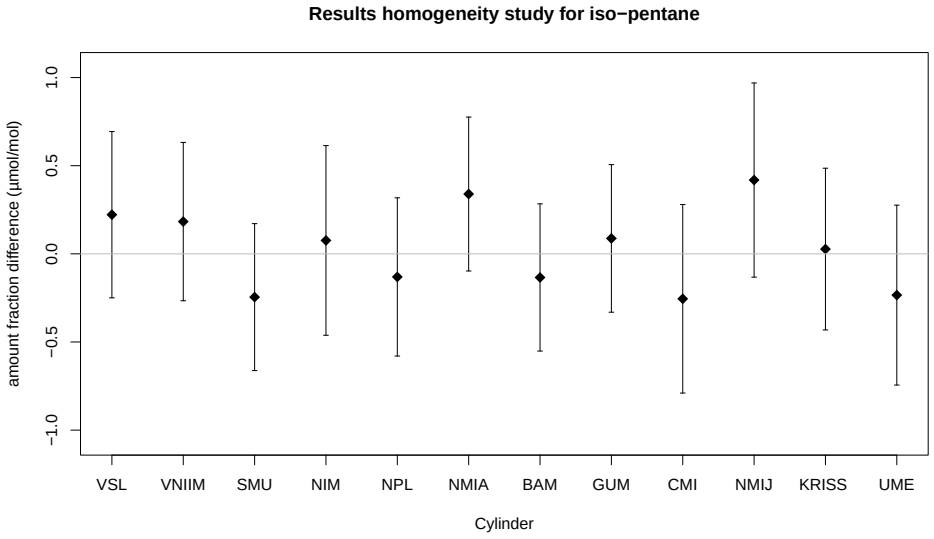


Figure 31: Corrections due to between-bottle homogeneity calculated for the amount fraction *iso*-pentane (type IVa).

Figure 32 shows the results for n-pentane. None of the corrections is significant at the 95 % probability level. The numerical data of the corrections are given in table 61 in annex B.

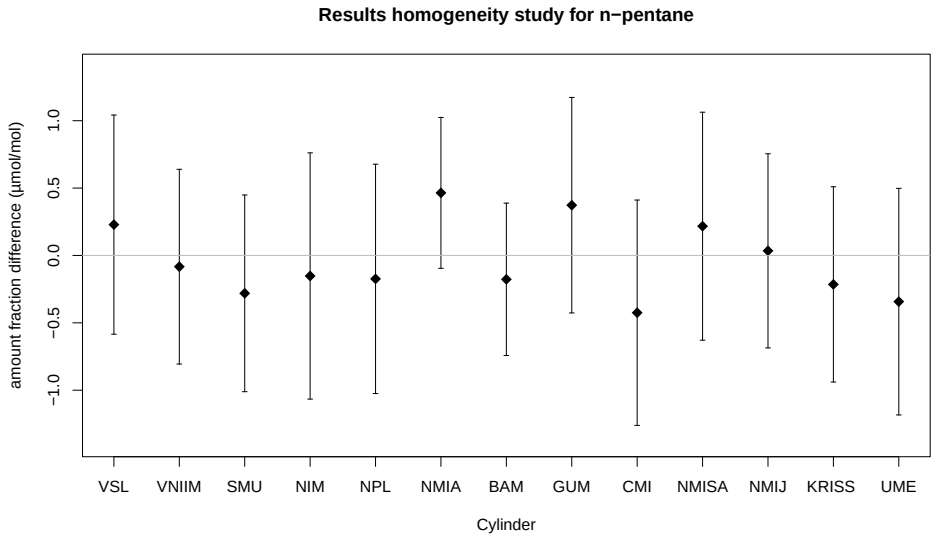


Figure 32: Corrections due to between-bottle homogeneity calculated for the amount fraction *n*-pentane (type IVa).

Figure 33 shows the results for neo-pentane. None of the corrections is significant at the 95 % probability level. The numerical data of the corrections are given in table 62 in annex B.

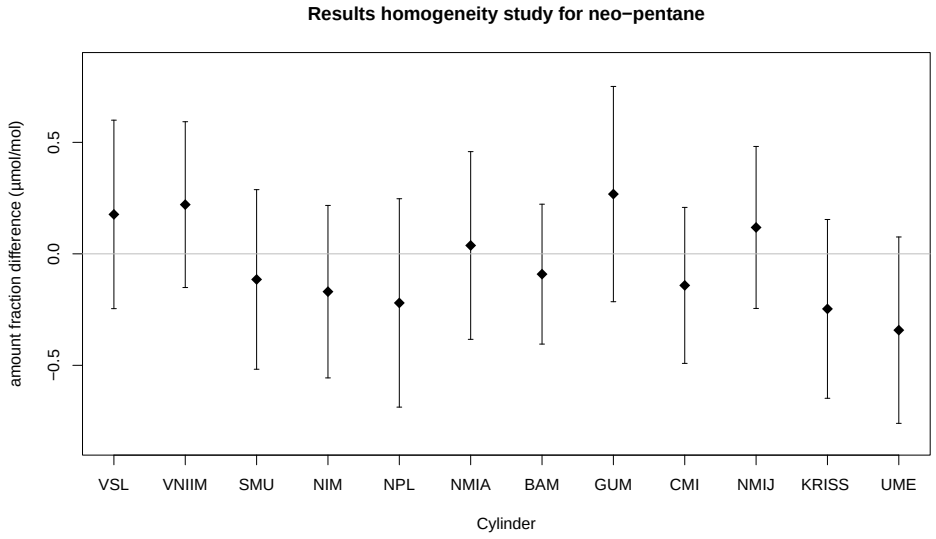


Figure 33: Corrections due to between-bottle homogeneity calculated for the amount fraction *neo*-pentane (type IVa).

Figure 34 shows the results for n-hexane. One correction are significant at the 95 % probability level. The numerical data of the corrections are given in table 63 in annex B.

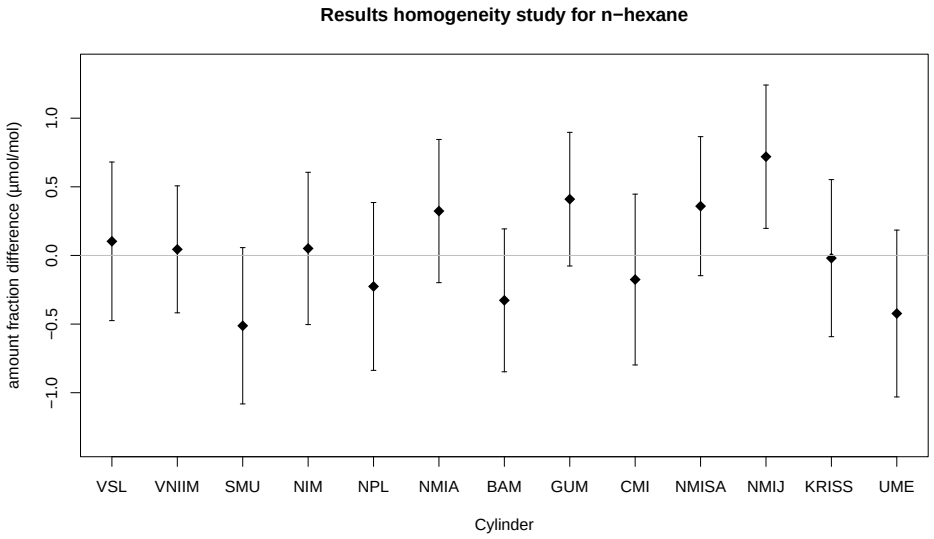


Figure 34: Corrections due to between-bottle homogeneity calculated for the amount fraction *n*-hexane (type IVa).

Figure 35 shows the results for methane. None of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 64 in annex B.

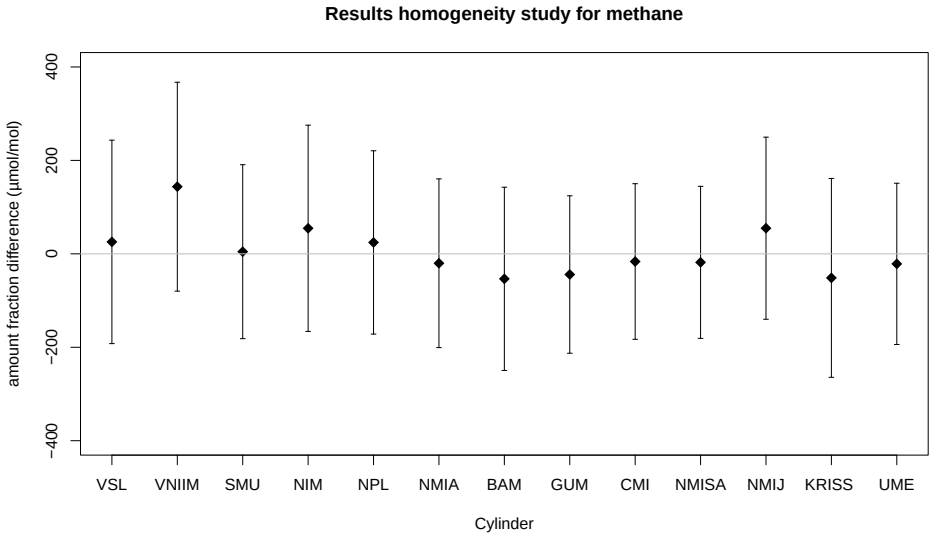


Figure 35: Corrections due to between-bottle homogeneity calculated for the amount fraction methane (type IVa).

Based on these results, it can be concluded that the batch of low-calorific natural gas travelling standards is very homogeneous. The vast majority of the corrections computed are insignificant at the 95 % probability level. The computed corrections may be seemingly small, they are in a similar

order of magnitude as the difference of the degree of equivalence. Hence, to be safe, the corrections and their associated uncertainties have been used in the subsequent evaluation of the data of this key comparison to ensure that if a result is considered discrepant, it is not so due to ignoring an effect from the between-bottle homogeneity.

Figure 36 shows the results for nitrogen in high-calorific natural gas. Four of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 65 in annex B.

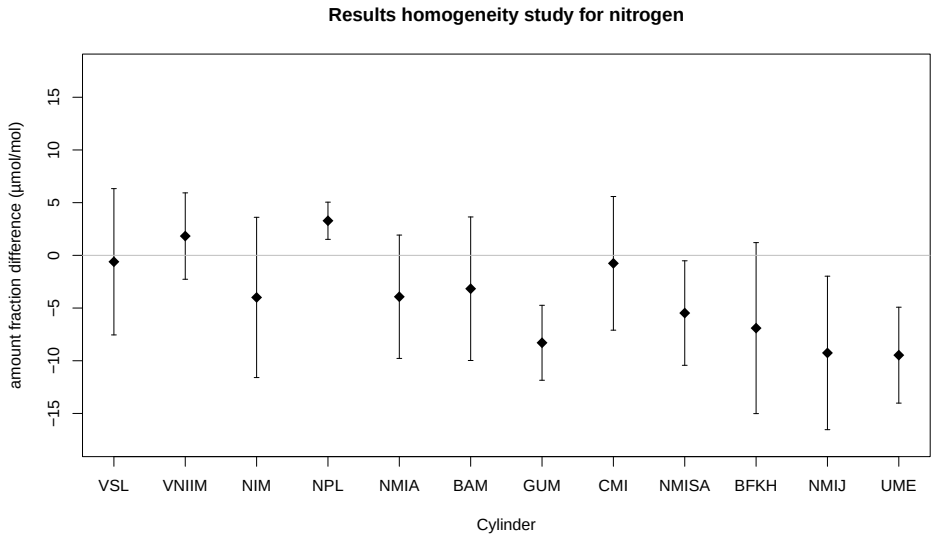


Figure 36: Corrections due to between-bottle homogeneity calculated for the amount fraction nitrogen (type LNG).

Figure 37 shows the results for carbon dioxide in high-calorific natural gas. Two of the corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 66 in annex B.

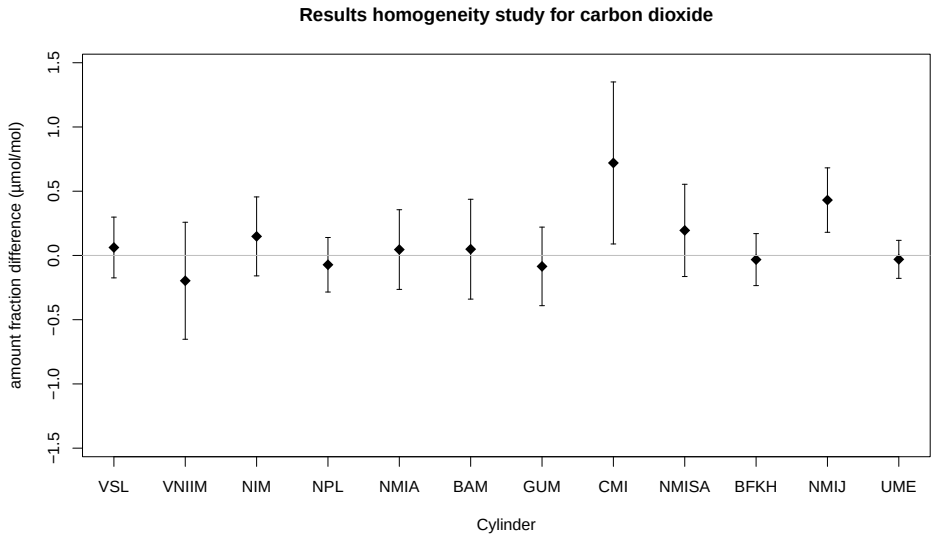


Figure 37: Corrections due to between-bottle homogeneity calculated for the amount fraction carbon dioxide (type LNG).

Figure 38 shows the results for ethane in high-calorific natural gas. Three corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 67 in annex B.

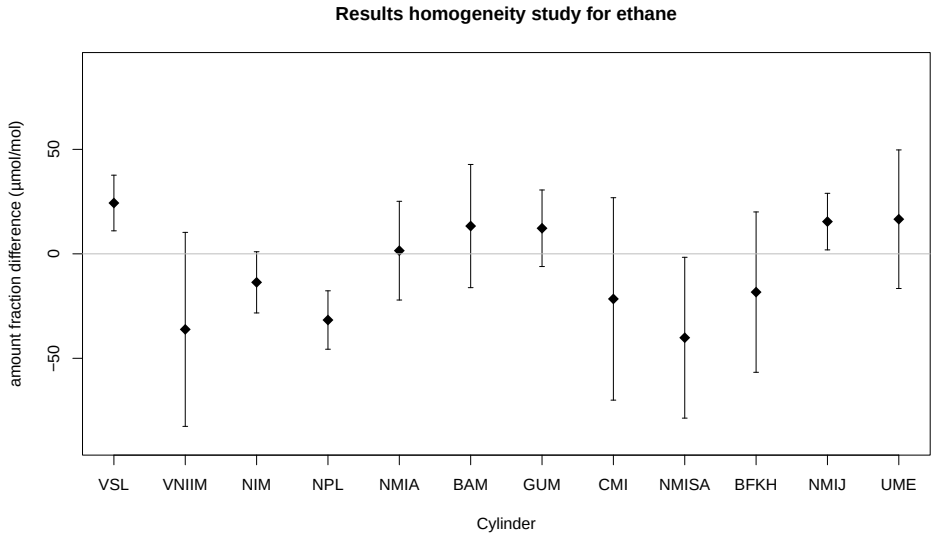


Figure 38: Corrections due to between-bottle homogeneity calculated for the amount fraction ethane (type LNG).

Figure 39 shows the results for propane in high-calorific natural gas. Two corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 68 in annex B.

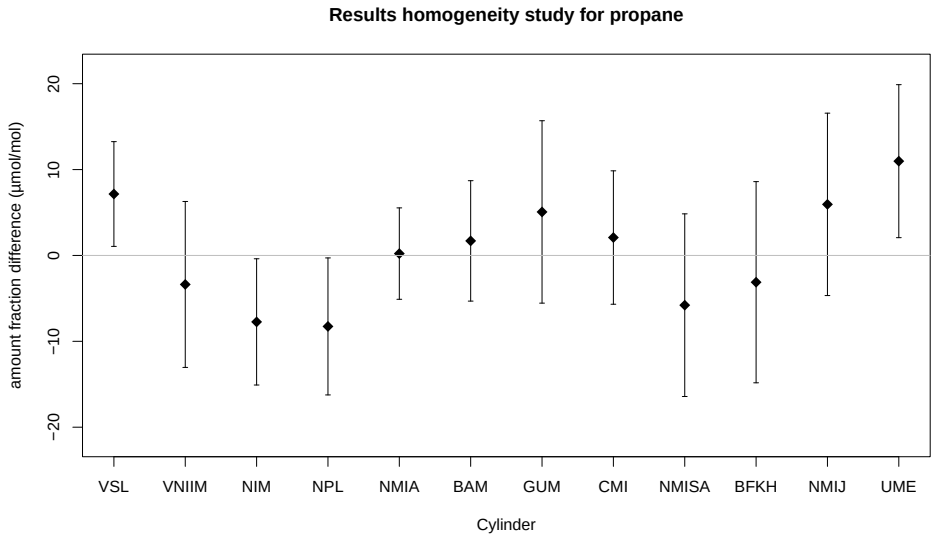


Figure 39: Corrections due to between-bottle homogeneity calculated for the amount fraction propane (type LNG).

Figure 40 shows the results for iso-butane in high-calorific natural gas. Five corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 69 in annex B.

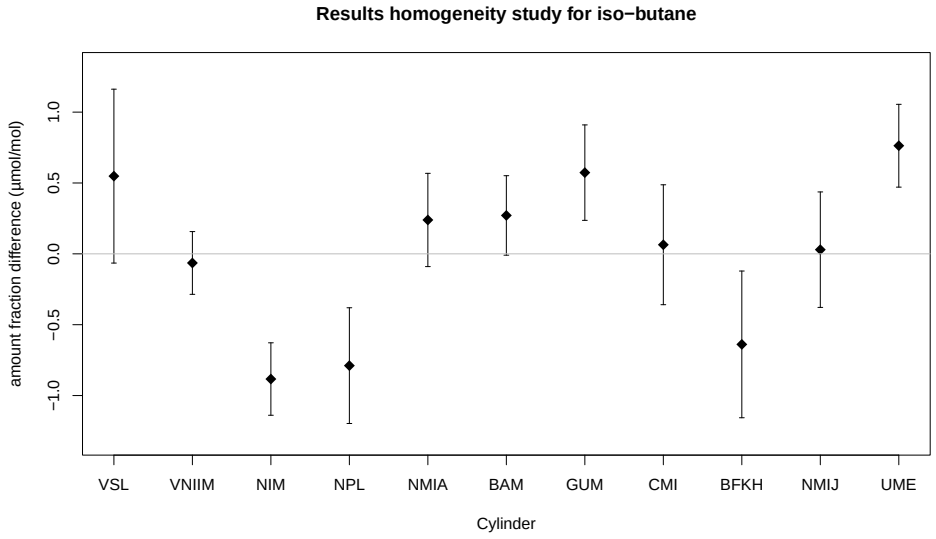


Figure 40: Corrections due to between-bottle homogeneity calculated for the amount fraction *iso*-butane (type LNG).

Figure 41 shows the results for n-butane in high-calorific natural gas. Several corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 70 in annex B.

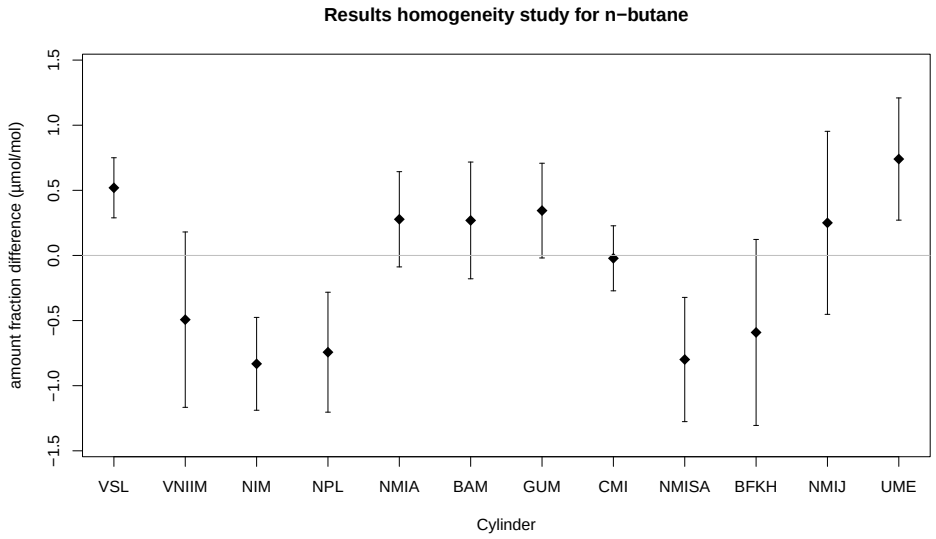


Figure 41: Corrections due to between-bottle homogeneity calculated for the amount fraction *n*-butane (type LNG).

Figure 42 shows the results for iso-pentane in high-calorific natural gas. Four corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 71 in annex B.

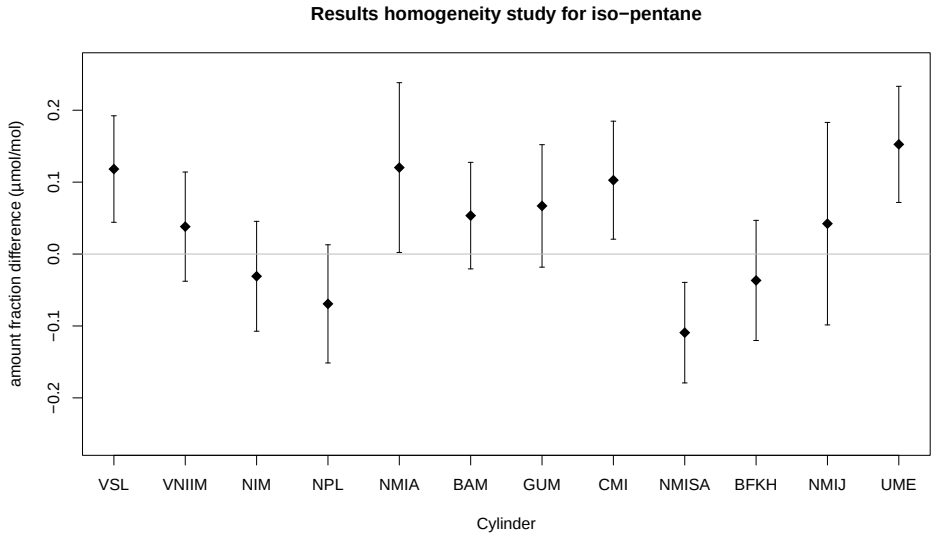


Figure 42: Corrections due to between-bottle homogeneity calculated for the amount fraction *iso*-pentane (type LNG).

Figure 43 shows the results for n-pentane in high-calorific natural gas. Two corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 72 in annex B.

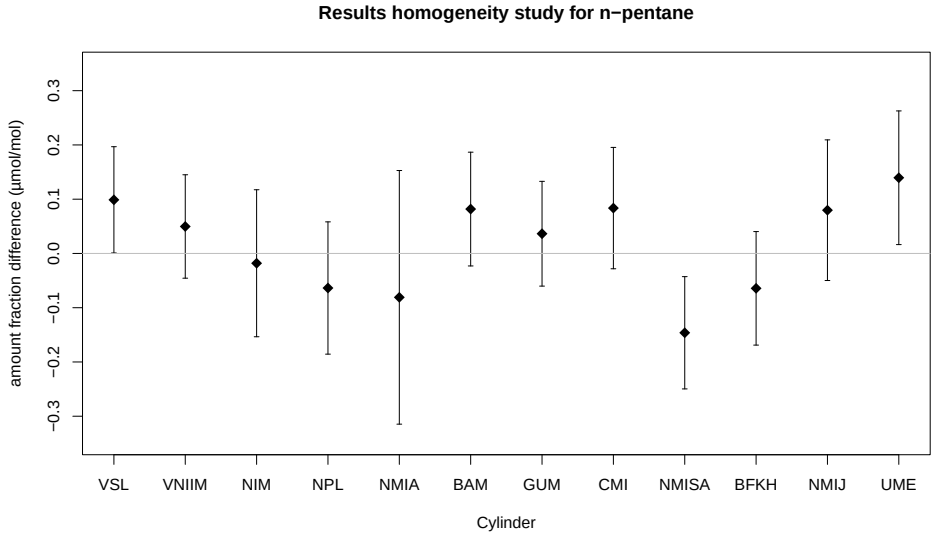


Figure 43: Corrections due to between-bottle homogeneity calculated for the amount fraction *n*-pentane (type LNG).

Figure 44 shows the results for methane in high-calorific natural gas. Two corrections are significant at the 95 % probability level. The numerical data of the corrections are given in table 73 in annex B.

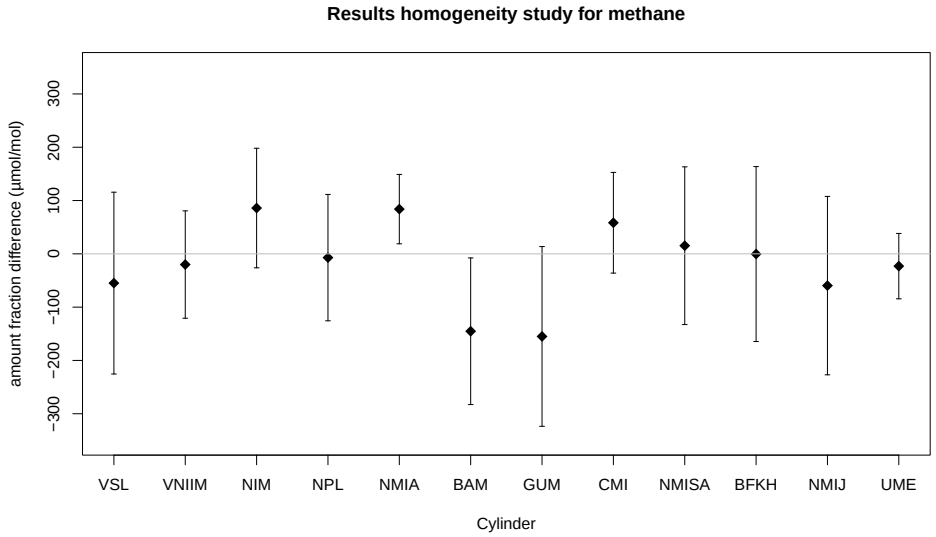


Figure 44: Corrections due to between-bottle homogeneity calculated for the amount fraction methane (type LNG).

The between-bottle homogeneity of the travelling standards for high-calorific natural gas is slightly less than that for low-calorific natural gas. Nevertheless, the effects are small. The computed corrections may be seemingly small, they are not necessarily so when considering the differences of the

degrees of equivalence. Hence the corrections and their associated uncertainties have been used in the subsequent evaluation of the data of this key comparison to ensure that if a result is considered discrepant, it is not so due to ignoring an effect from the between-bottle homogeneity.

5 Key comparison reference value and degrees of equivalence

5.1 Low-calorific natural gas

This section gives an overview over the reported results for the low-calorific natural gas, the KCRVs, and the degrees of equivalence. Unless stated otherwise, all uncertainty bars in the figures depict probabilistically-symmetric 95 % coverage intervals. These intervals have been computed using standard uncertainty from the MCMC output and a coverage factor $k = 2$.

The following results have been excluded from the calculation of the KCRV (see table 5). The participants that submitted these results provided results to replace them, so that the original results have been considered to be invalidated and hence not suitable for calculating the best estimate for the corresponding amount fraction. In the calculation of the degrees of equivalence, the original results have been used though. None of the new results was submitted before communicating the overview of results to the participating NMIs.

Table 5: Withdrawn results for low-calorific natural gas

Laboratory	Component
NIM	Nitrogen
NIM	Methane
NMISA	Ethane
KRISS	Nitrogen
KRISS	Carbon dioxide
KRISS	Hydrogen
KRISS	Helium
KRISS	Ethane
KRISS	Propane
KRISS	iso-Butane
KRISS	n-Butane
KRISS	n-Pentane
KRISS	neo-Pentane
KRISS	n-Hexane
KRISS	Methane

The stated values of τ were taken as the median of the posterior distribution. As this posterior is skewed (towards zero), there is choice between the mode (the maximum of the probability density function), the median, and the mean, as they are all three different. As in the subsequent calculation the uncertainty about τ does not play a role (the Guide to the expression of Uncertainty in Measurement (GUM) suite does not consider the uncertainty of an uncertainty component [29,30,35]), so a representative value is required. Generally, the median is considered to be the most representative value in case of a non-symmetric distribution.

Table 6: Results and key comparison reference values for nitrogen (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	11.9805	0.0120	2.0	11.9843	0.0113	0.0056	2.0
VNIIM	D322703	11.9400	0.0300	2.0	11.9844	0.0113	0.0056	2.0
SMU	D322740	11.9770	0.0340	2.0	11.9837	0.0115	0.0057	2.0
NIM	D322730	11.9670	0.0250	2.0	11.9860	0.0113	0.0056	2.0
NPL	D322694	11.9736	0.0180	2.0	11.9862	0.0113	0.0056	2.0
NMIA	D322744	11.9723	0.0050	2.0	11.9840	0.0113	0.0056	2.0
BAM	D322738	11.9791	0.0068	2.0	11.9834	0.0113	0.0056	2.0
GUM	D322721	12.0230	0.0480	2.0	11.9833	0.0117	0.0058	2.0
CMI	D322720	11.9932	0.0144	2.0	11.9851	0.0113	0.0056	2.0
NMISA	D322702	11.9632	0.0779	2.0	11.9849	0.0113	0.0056	2.0
NMIJ	D322719	11.9698	0.0574	2.0	11.9845	0.0113	0.0056	2.0
KRISS	D322706	11.9121	0.0238	2.0	11.9849	0.0113	0.0056	2.0
UME	D322708	12.0080	0.0240	2.0	11.9858	0.0113	0.0056	2.0

In table 6, the reported results and the KCRVs for nitrogen are shown. The LCS consists of the results of VSL, SMU, NPL, BAM, GUM, CMI, NMISA, NMIJ and UME. The consensus value is 11.985 cmol mol^{-1} with standard uncertainty 0.006 cmol mol^{-1}. The excess standard deviation τ is 0.008 cmol mol^{-1} (0.07 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 45. The results of VNIIM and KRISS are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 52 in annex B.

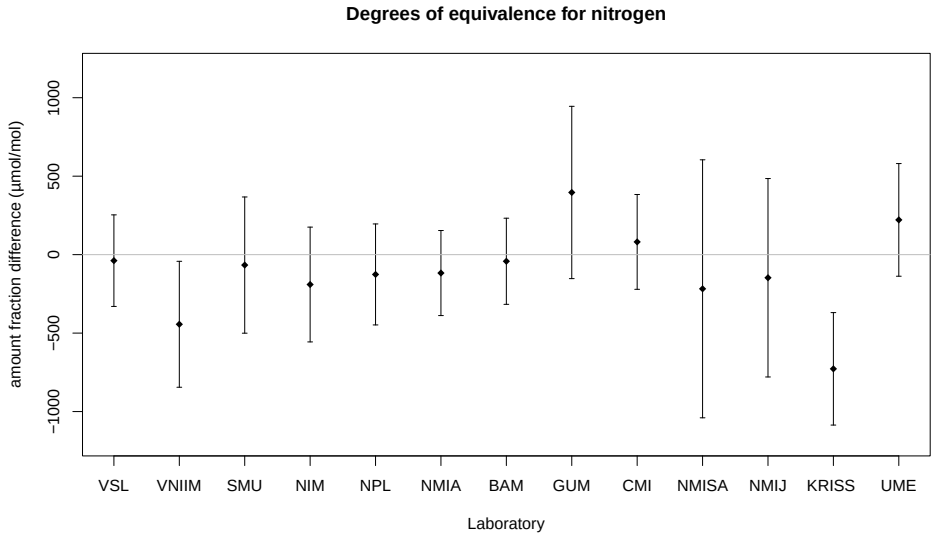
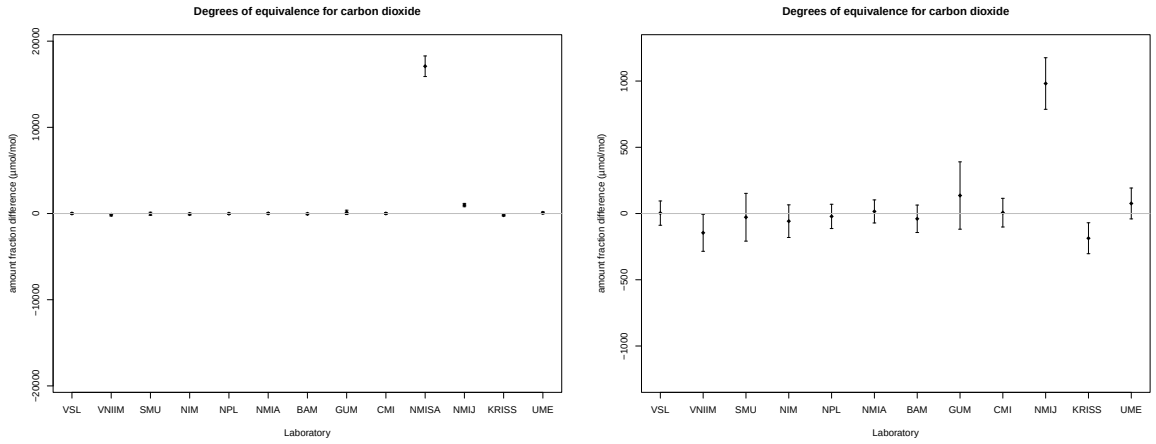


Figure 45: Degrees of equivalence for the amount fraction nitrogen (type IVa) (µmol mol^{-1}).

Table 7: Results and key comparison reference values for carbon dioxide (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	4.0052	0.0040	2.0	4.0049	0.0039	0.0020	2.0
VNIIM	D322703	3.9890	0.0110	2.0	4.0035	0.0046	0.0023	2.0
SMU	D322740	4.0010	0.0160	2.0	4.0038	0.0041	0.0021	2.0
NIM	D322730	3.9982	0.0091	2.0	4.0040	0.0042	0.0021	2.0
NPL	D322694	4.0008	0.0040	2.0	4.0029	0.0040	0.0020	2.0
NMIA	D322744	4.0070	0.0030	2.0	4.0054	0.0038	0.0019	2.0
BAM	D322738	3.9998	0.0062	2.0	4.0038	0.0042	0.0021	2.0
GUM	D322721	4.0189	0.0240	2.0	4.0053	0.0042	0.0021	2.0
CMI	D322720	4.0042	0.0069	2.0	4.0035	0.0041	0.0021	2.0
NMISA	D322702	5.7137	0.1191	2.0	4.0050	0.0042	0.0021	2.0
NMIJ	D322719	4.1034	0.0176	2.0	4.0053	0.0040	0.0020	2.0
KRISS	D322706	3.9853	0.0080	2.0	4.0040	0.0045	0.0023	2.0
UME	D322708	4.0130	0.0080	2.0	4.0054	0.0044	0.0022	2.0

In table 7, the reported results and the KCRVs for carbon dioxide are shown. The consensus value is 4.0044 cmol mol^{-1} with standard uncertainty 0.0017 cmol mol^{-1}. The excess standard deviation τ is 0.0024 cmol mol^{-1} (0.06 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 45. The results of VNIIM, NMISA, NMIJ and KRISS are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 53 in annex B.



(a) Complete dataset (b) Without NMISA

Figure 46: Degrees of equivalence for the amount fraction carbon dioxide (type IVa) (µmol mol^{-1}).

Table 8: Results and key comparison reference values for hydrogen (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	2.9983	0.0045	2.0	2.9994	0.0059	0.0029	2.0
VNIIM	D322703	2.9910	0.0130	2.0	2.9997	0.0059	0.0030	2.0
SMU	D322740	3.0100	0.0320	2.0	3.0018	0.0059	0.0030	2.0
NIM	D322730	3.0004	0.0075	2.0	2.9997	0.0059	0.0029	2.0
NPL	D322694	3.0008	0.0150	2.0	3.0025	0.0060	0.0030	2.0
NMIA	D322744	3.0088	0.0050	2.0	2.9995	0.0059	0.0030	2.0
BAM	D322738	3.0036	0.0037	2.0	3.0011	0.0059	0.0029	2.0
GUM	D322721	2.9970	0.0240	2.0	3.0001	0.0059	0.0030	2.0
CMI	D322720	2.9790	0.0198	2.0	3.0012	0.0059	0.0030	2.0
NMISA	D322702	3.0092	0.1266	2.0	2.9992	0.0060	0.0030	2.0
NMIJ	D322719	2.9133	0.0135	2.0	2.9987	0.0059	0.0030	2.0
KRISS	D322706	2.9829	0.0060	2.0	3.0020	0.0060	0.0030	2.0
UME	D322708	3.0080	0.0040	2.0	3.0018	0.0060	0.0030	2.0

In table 8, the reported results and the KCRVs for hydrogen are shown. The consensus value is 3.0007 cmol mol^{-1} with standard uncertainty 0.0029 cmol mol^{-1}. The excess standard deviation τ is 0.0046 cmol mol^{-1} (0.15 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 47. The result of NMIJ is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 54 in annex B.

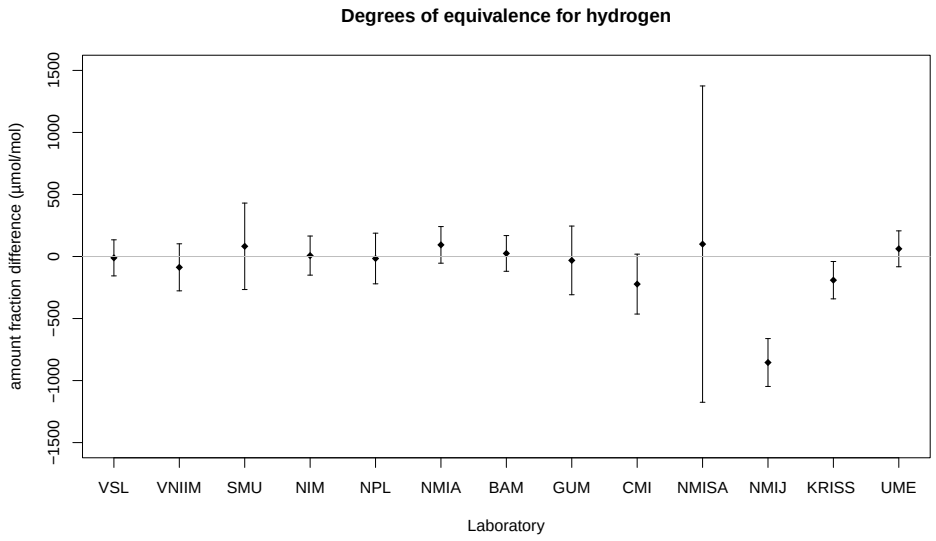


Figure 47: Degrees of equivalence for the amount fraction hydrogen (type IVa) (µmol mol^{-1}).

Table 9: Results and key comparison reference values for helium (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322727	0.50265	0.00101	2.0	0.50202	0.00083	0.00042	2.0
VNIIM	D322703	0.50040	0.00250	2.0	0.50214	0.00083	0.00041	2.0
SMU	D322740	0.50250	0.00540	2.0	0.50253	0.00084	0.00042	2.0
NIM	D322730	0.50140	0.00140	2.0	0.50212	0.00082	0.00041	2.0
NPL	D322694	0.50373	0.00252	2.0	0.50269	0.00084	0.00042	2.0
NMIA	D322744	0.50163	0.00110	2.0	0.50202	0.00082	0.00041	2.0
BAM	D322738	0.50269	0.00076	2.0	0.50237	0.00081	0.00041	2.0
GUM	D322721	0.50090	0.00300	2.0	0.50216	0.00083	0.00042	2.0
CMI	D322720	0.50440	0.00430	2.0	0.50241	0.00083	0.00041	2.0
NMISA	D322702	0.51201	0.02842	2.0	0.50197	0.00084	0.00042	2.0
NMIJ	D322719	0.49566	0.00161	2.0	0.50191	0.00086	0.00043	2.0
KRISS	D322706	0.49870	0.00150	2.0	0.50264	0.00084	0.00042	2.0
UME	D322708	0.50880	0.00140	2.0	0.50255	0.00085	0.00043	2.0

In table 9, the reported results and the KCRVs for helium are shown. The consensus value is 0.502 25 cmol mol^{-1} with standard uncertainty 0.000 39 cmol mol^{-1}. The excess standard deviation τ is 0.000 48 cmol mol^{-1} (0.09 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 48. The results of NMIJ, KRISS and UME are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 55 in annex B.

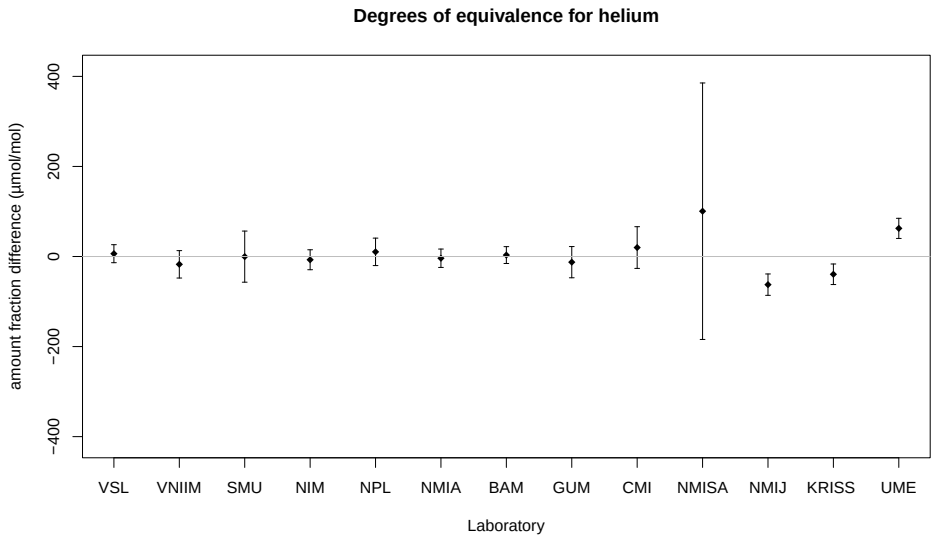


Figure 48: Degrees of equivalence for the amount fraction helium (type IVa) (µmol mol^{-1}).

Table 10: Results and key comparison reference values for ethane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.74439	0.00149	2.0	0.74499	0.00120	0.00060	2.0
VNIIM	D322703	0.74300	0.00400	2.0	0.74475	0.00162	0.00081	2.0
SMU	D322740	0.74600	0.00210	2.0	0.74509	0.00126	0.00063	2.0
NIM	D322730	0.74460	0.00190	2.0	0.74485	0.00128	0.00064	2.0
NPL	D322694	0.74597	0.00149	2.0	0.74527	0.00121	0.00060	2.0
NMIA	D322744	0.74559	0.00130	2.0	0.74512	0.00113	0.00056	2.0
BAM	D322738	0.74475	0.00313	2.0	0.74506	0.00145	0.00072	2.0
GUM	D322721	0.75100	0.00600	2.0	0.74519	0.00147	0.00074	2.0
CMI	D322720	0.74630	0.00320	2.0	0.74504	0.00140	0.00070	2.0
NMISA	D322702	0.74172	0.01874	2.0	0.74534	0.00136	0.00068	2.0
NMIJ	D322719	0.74413	0.00058	2.0	0.74473	0.00125	0.00062	2.0
KRISS	D322706	0.74057	0.00222	2.0	0.74473	0.00187	0.00094	2.0
UME	D322708	0.74450	0.00140	2.0	0.74482	0.00124	0.00062	2.0

In table 10, the reported results and the KCRVs for ethane are shown. The consensus value is 0.745 01 cmol mol^{-1} with standard uncertainty 0.000 40 cmol mol^{-1}. The excess standard deviation τ is 0.000 56 cmol mol^{-1} (0.08 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 49. The result of KRISS is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 56 in annex B.

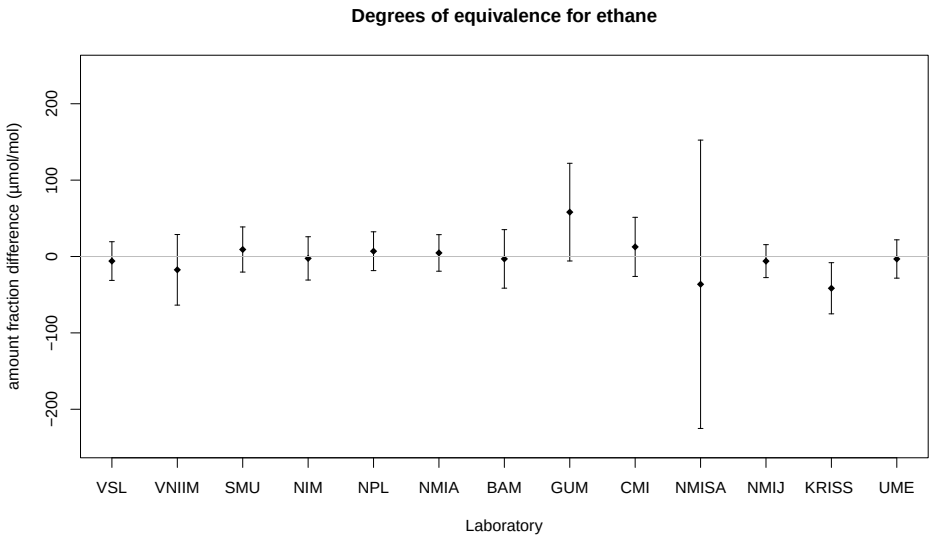


Figure 49: Degrees of equivalence for the amount fraction ethane (type IVa) (µmol mol^{-1}).

Table 11: Results and key comparison reference values for propane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.29866	0.00090	2.0	0.29858	0.00047	0.00024	2.0
VNIIM	D322703	0.29780	0.00160	2.0	0.29847	0.00048	0.00024	2.0
SMU	D322740	0.29890	0.00150	2.0	0.29845	0.00052	0.00026	2.0
NIM	D322730	0.29835	0.00081	2.0	0.29851	0.00049	0.00024	2.0
NPL	D322694	0.29842	0.00045	2.0	0.29842	0.00045	0.00022	2.0
NMIA	D322744	0.29856	0.00060	2.0	0.29856	0.00044	0.00022	2.0
BAM	D322738	0.29821	0.00101	2.0	0.29830	0.00046	0.00023	2.0
GUM	D322721	0.29790	0.00240	2.0	0.29850	0.00056	0.00028	2.0
CMI	D322720	0.30000	0.00130	2.0	0.29853	0.00050	0.00025	2.0
NMISA	D322702	0.29877	0.00717	2.0	0.29858	0.00055	0.00028	2.0
NMIJ	D322719	0.29809	0.00024	2.0	0.29845	0.00050	0.00025	2.0
KRISS	D322706	0.29653	0.00089	2.0	0.29834	0.00048	0.00024	2.0
UME	D322708	0.29900	0.00060	2.0	0.29861	0.00046	0.00023	2.0

In table 11, the reported results and the KCRVs for propane are shown. The consensus value is 0.298 49 cmol mol^{-1} with standard uncertainty 0.000 18 cmol mol^{-1}. The excess standard deviation τ is 0.000 30 cmol mol^{-1} (0.10 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 50. The result of KRISS is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 57 in annex B.

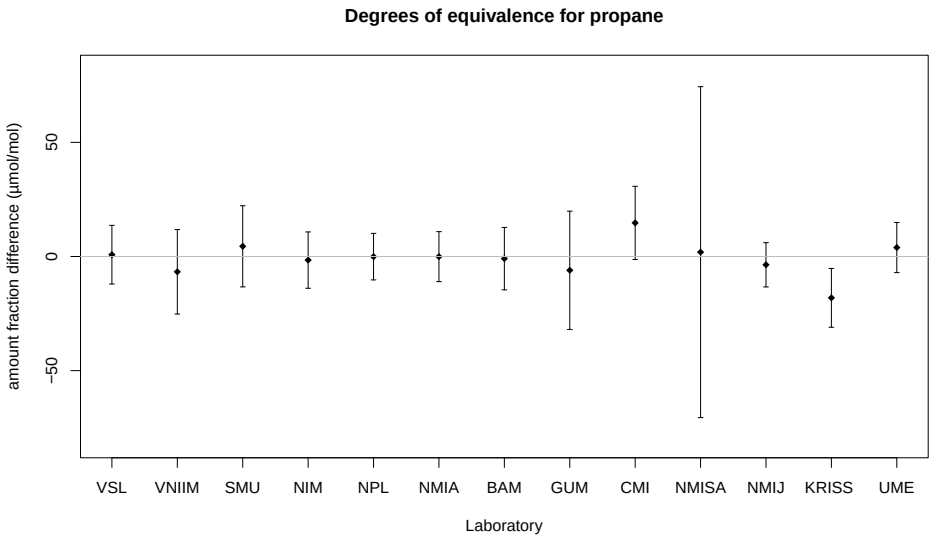


Figure 50: Degrees of equivalence for the amount fraction propane (type IVa) (µmol mol^{-1}).

Table 12: Results and key comparison reference values for iso-butane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.19979	0.00020	2.0	0.19983	0.00018	0.00009	2.0
VNIIM	D322703	0.19930	0.00150	2.0	0.19978	0.00018	0.00009	2.0
SMU	D322740	0.19980	0.00110	2.0	0.19970	0.00018	0.00009	2.0
NIM	D322730	0.19988	0.00050	2.0	0.19980	0.00018	0.00009	2.0
NPL	D322694	0.19964	0.00070	2.0	0.19970	0.00018	0.00009	2.0
NMIA	D322744	0.19988	0.00040	2.0	0.19980	0.00018	0.00009	2.0
BAM	D322738	0.19969	0.00018	2.0	0.19969	0.00017	0.00009	2.0
GUM	D322721	0.20700	0.00170	2.0	0.19982	0.00018	0.00009	2.0
CMI	D322720	0.19960	0.00140	2.0	0.19971	0.00018	0.00009	2.0
NMIJ	D322719	0.19955	0.00035	2.0	0.19983	0.00018	0.00009	2.0
KRISS	D322706	0.19880	0.00060	2.0	0.19969	0.00018	0.00009	2.0
UME	D322708	0.20010	0.00040	2.0	0.19974	0.00018	0.00009	2.0

In table 12, the reported results and the KCRVs for iso-butane are shown. The consensus value is 0.199 75 cmol mol^{-1} with standard uncertainty 0.000 08 cmol mol^{-1}. The excess standard deviation τ is 0.000 10 cmol mol^{-1} (0.05 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 51. The results of GUM and KRISS are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 58 in annex B.

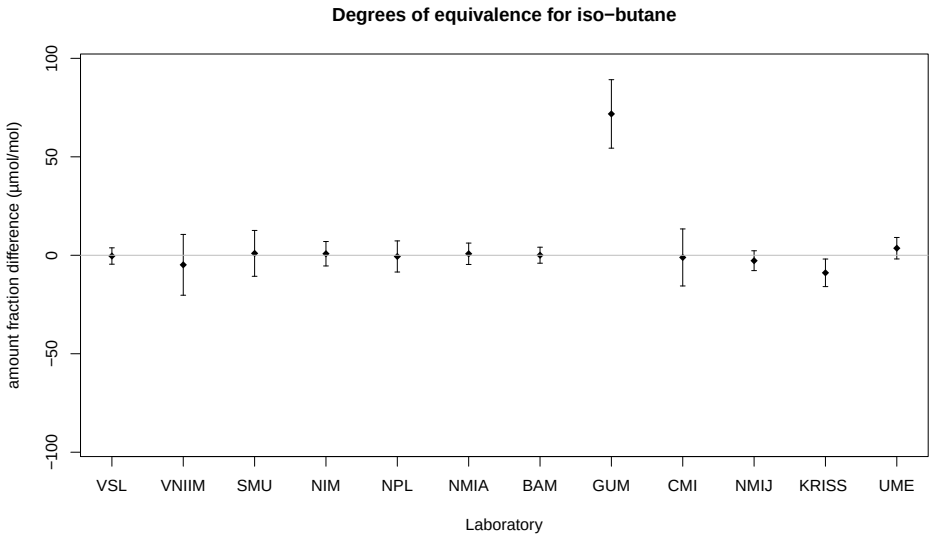


Figure 51: Degrees of equivalence for the amount fraction *iso*-butane (type IVa) (µmol mol^{-1}).

Table 13: Results and key comparison reference values for n-butane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.20021	0.00020	2.0	0.19996	0.00023	0.00012	2.0
VNIIM	D322703	0.19930	0.00160	2.0	0.19990	0.00024	0.00012	2.0
SMU	D322740	0.20010	0.00110	2.0	0.19980	0.00024	0.00012	2.0
NIM	D322730	0.19972	0.00050	2.0	0.19992	0.00024	0.00012	2.0
NPL	D322694	0.19978	0.00070	2.0	0.19983	0.00024	0.00012	2.0
NMIA	D322744	0.19998	0.00040	2.0	0.19993	0.00023	0.00012	2.0
BAM	D322738	0.19960	0.00020	2.0	0.19977	0.00023	0.00012	2.0
GUM	D322721	0.20040	0.00160	2.0	0.19995	0.00024	0.00012	2.0
CMI	D322720	0.19980	0.00150	2.0	0.19981	0.00024	0.00012	2.0
NMISA	D322702	0.20004	0.00467	2.0	0.19997	0.00024	0.00012	2.0
NMIJ	D322719	0.19920	0.00034	2.0	0.19998	0.00024	0.00012	2.0
KRISS	D322706	0.19837	0.00060	2.0	0.19982	0.00024	0.00012	2.0
UME	D322708	0.19980	0.00040	2.0	0.19988	0.00024	0.00012	2.0

In table 13, the reported results and the KCRVs for n-butane are shown. The consensus value is 0.199 88 cmol mol^{-1} with standard uncertainty 0.000 11 cmol mol^{-1}. The excess standard deviation τ is 0.000 18 cmol mol^{-1} (0.09 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 52. The results of NMIJ and KRISS are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 59 in annex B.

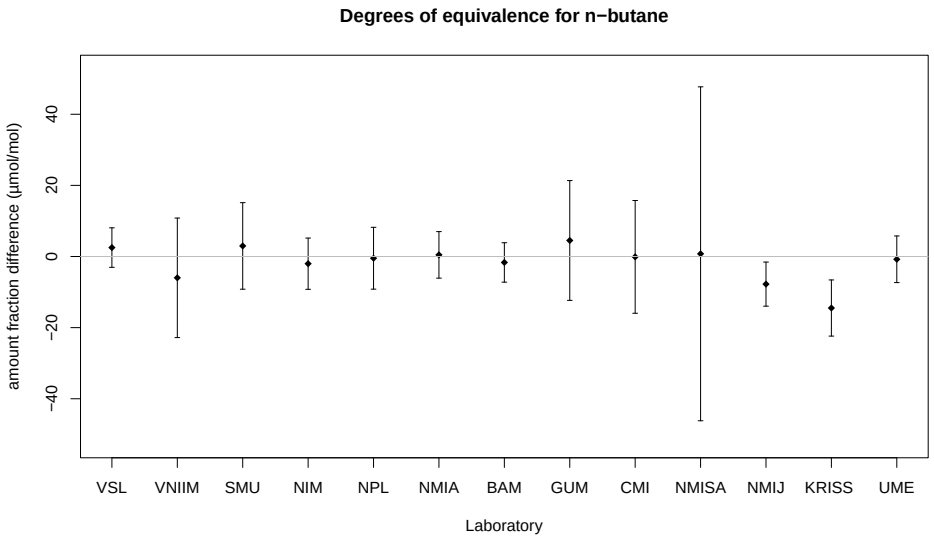


Figure 52: Degrees of equivalence for the amount fraction *n*-butane (type IVa) (µmol mol^{-1}).

Table 14: Results and key comparison reference values for iso-pentane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.04983	0.00012	2.0	0.04987	0.00012	0.00006	2.0
VNIIM	D322703	0.04990	0.00050	2.0	0.04987	0.00012	0.00006	2.0
SMU	D322740	0.04970	0.00043	2.0	0.04983	0.00012	0.00006	2.0
NIM	D322730	0.04985	0.00020	2.0	0.04986	0.00012	0.00006	2.0
NPL	D322694	0.04982	0.00020	2.0	0.04984	0.00012	0.00006	2.0
NMIA	D322744	0.05014	0.00014	2.0	0.04989	0.00012	0.00006	2.0
BAM	D322738	0.04984	0.00013	2.0	0.04984	0.00012	0.00006	2.0
GUM	D322721	0.04977	0.00050	2.0	0.04986	0.00012	0.00006	2.0
CMI	D322720	0.04990	0.00030	2.0	0.04983	0.00012	0.00006	2.0
NMIJ	D322719	0.04942	0.00005	2.0	0.04989	0.00012	0.00006	2.0
KRISS	D322706	0.04937	0.00147	2.0	0.04986	0.00012	0.00006	2.0
UME	D322708	0.04969	0.00014	2.0	0.04983	0.00012	0.00006	2.0

In table 14, the reported results and the KCRVs for iso-pentane are shown. The consensus value is 0.049 85 cmol mol^{-1} with standard uncertainty 0.000 06 cmol mol^{-1}. The excess standard deviation τ is 0.000 11 cmol mol^{-1} (0.23 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 53. The result of NMIJ is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 60 in annex B.

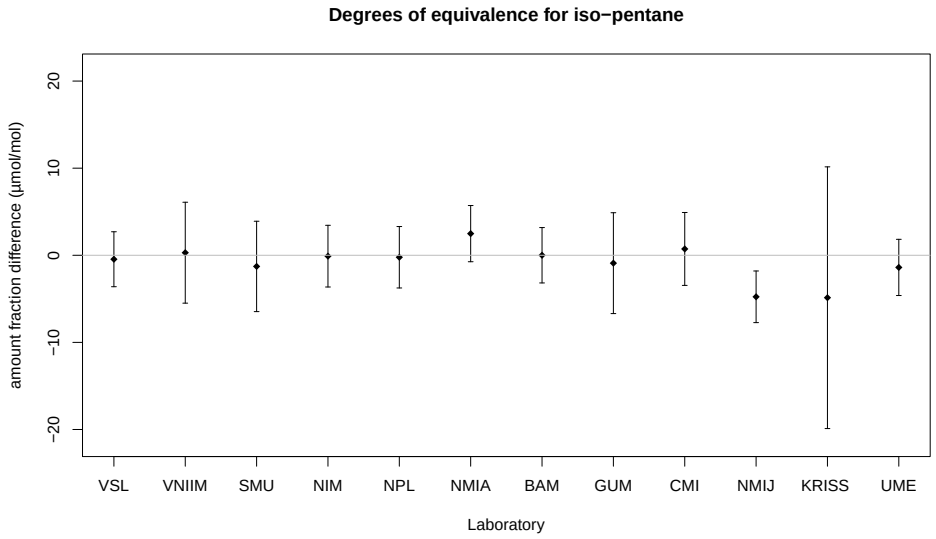


Figure 53: Degrees of equivalence for the amount fraction *iso*-pentane (type IVa) (µmol mol^{-1}).

Table 15: Results and key comparison reference values for n-pentane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.05027	0.00010	2.0	0.05019	0.00011	0.00006	2.0
VNIIM	D322703	0.05010	0.00040	2.0	0.05016	0.00012	0.00006	2.0
SMU	D322740	0.05021	0.00037	2.0	0.05014	0.00012	0.00006	2.0
NIM	D322730	0.05003	0.00015	2.0	0.05015	0.00013	0.00006	2.0
NPL	D322694	0.05018	0.00020	2.0	0.05015	0.00012	0.00006	2.0
NMIA	D322744	0.05023	0.00016	2.0	0.05022	0.00011	0.00005	2.0
BAM	D322738	0.05022	0.00022	2.0	0.05015	0.00011	0.00005	2.0
GUM	D322721	0.05058	0.00030	2.0	0.05021	0.00012	0.00006	2.0
CMI	D322720	0.05000	0.00030	2.0	0.05013	0.00013	0.00006	2.0
NMISA	D322702	0.05033	0.00117	2.0	0.05019	0.00013	0.00006	2.0
NMIJ	D322719	0.05008	0.00005	2.0	0.05017	0.00012	0.00006	2.0
KRISS	D322706	0.04953	0.00124	2.0	0.05015	0.00012	0.00006	2.0
UME	D322708	0.05012	0.00018	2.0	0.05014	0.00012	0.00006	2.0

In table 15, the reported results and the KCRVs for n-pentane are shown. The consensus value is 0.050 17 cmol mol^{-1} with standard uncertainty 0.000 05 cmol mol^{-1}. The excess standard deviation τ is 0.000 09 cmol mol^{-1} (0.18 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 54. The numerical values of the degrees of equivalence are given in table 61 in annex B.

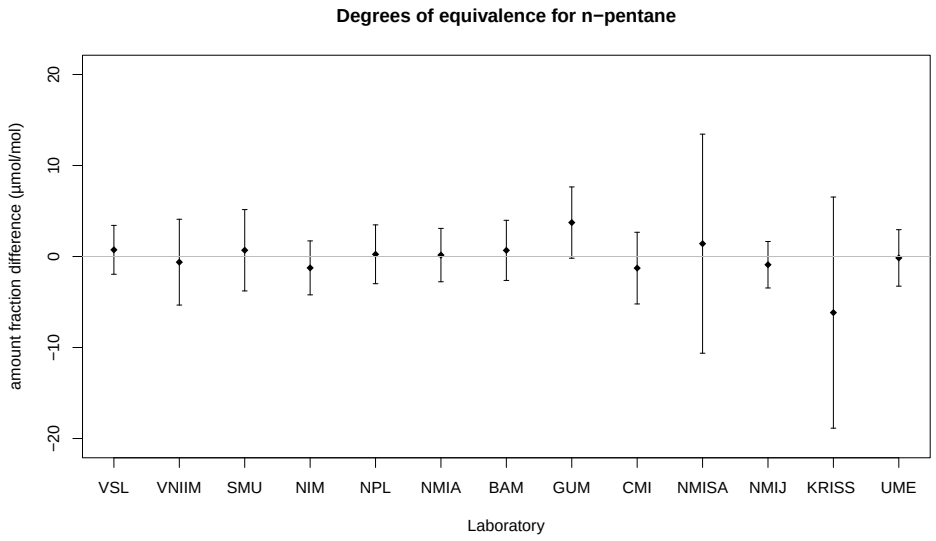


Figure 54: Degrees of equivalence for the amount fraction *n*-pentane (type IVa) (µmol mol^{-1}).

Table 16: Results and key comparison reference values for neo-pentane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.04940	0.00010	2.0	0.04936	0.00011	0.00005	2.0
VNIIM	D322703	0.04930	0.00030	2.0	0.04936	0.00011	0.00005	2.0
SMU	D322740	0.04966	0.00050	2.0	0.04933	0.00011	0.00005	2.0
NIM	D322730	0.04930	0.00016	2.0	0.04932	0.00011	0.00005	2.0
NPL	D322694	0.04927	0.00025	2.0	0.04932	0.00011	0.00006	2.0
NMIA	D322744	0.04929	0.00016	2.0	0.04934	0.00011	0.00005	2.0
BAM	D322738	0.04941	0.00012	2.0	0.04933	0.00010	0.00005	2.0
GUM	D322721	0.04948	0.00099	2.0	0.04937	0.00011	0.00006	2.0
CMI	D322720	0.04970	0.00050	2.0	0.04933	0.00011	0.00005	2.0
NMIJ	D322719	0.04919	0.00013	2.0	0.04935	0.00011	0.00005	2.0
KRISS	D322706	0.04910	0.00098	2.0	0.04931	0.00011	0.00005	2.0
UME	D322708	0.04901	0.00014	2.0	0.04931	0.00011	0.00005	2.0

In table 16, the reported results and the KCRVs for neo-pentane are shown. The consensus value is 0.049 34 cmol mol^{-1} with standard uncertainty 0.000 05 cmol mol^{-1}. The excess standard deviation τ is 0.000 08 cmol mol^{-1} (0.17 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 55. All results are consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 62 in annex B.

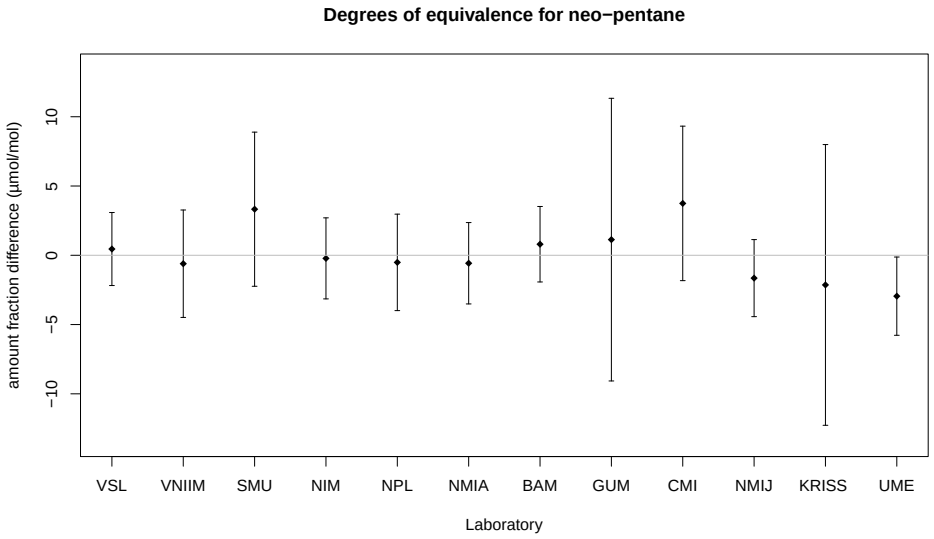


Figure 55: Degrees of equivalence for the amount fraction *neo*-pentane (type IVa) (µmol mol^{-1}).

Table 17: Results and key comparison reference values for n-hexane (type IVa) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{lab})$	k_{lab}	y_{KCRV}	$U(y_{KCRV})$	$u(y_{KCRV})$	k_{KCRV}
VSL	D322727	0.04957	0.00010	2.0	0.04971	0.00014	0.00007	2.0
VNIIM	D322703	0.04980	0.00060	2.0	0.04971	0.00013	0.00007	2.0
SMU	D322740	0.04966	0.00038	2.0	0.04965	0.00013	0.00007	2.0
NIM	D322730	0.04971	0.00013	2.0	0.04971	0.00013	0.00007	2.0
NPL	D322694	0.04981	0.00020	2.0	0.04968	0.00013	0.00007	2.0
NMIA	D322744	0.04962	0.00080	2.0	0.04974	0.00013	0.00007	2.0
BAM	D322738	0.04959	0.00016	2.0	0.04967	0.00013	0.00007	2.0
GUM	D322721	0.04998	0.00030	2.0	0.04974	0.00013	0.00007	2.0
CMI	D322720	0.04990	0.00030	2.0	0.04969	0.00013	0.00007	2.0
NMISA	D322702	0.05018	0.00117	2.0	0.04974	0.00013	0.00007	2.0
NMIJ	D322719	0.04945	0.00005	2.0	0.04978	0.00013	0.00007	2.0
KRISS	D322706	0.04920	0.00098	2.0	0.04970	0.00013	0.00007	2.0
UME	D322708	0.04953	0.00022	2.0	0.04966	0.00014	0.00007	2.0

In table 17, the reported results and the KCRVs for n-hexane are shown. The consensus value is 0.049 70 cmol mol^{-1} with standard uncertainty 0.000 06 cmol mol^{-1}. The excess standard deviation τ is 0.000 11 cmol mol^{-1} (0.22 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 56. The result of UME is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 63 in annex B.

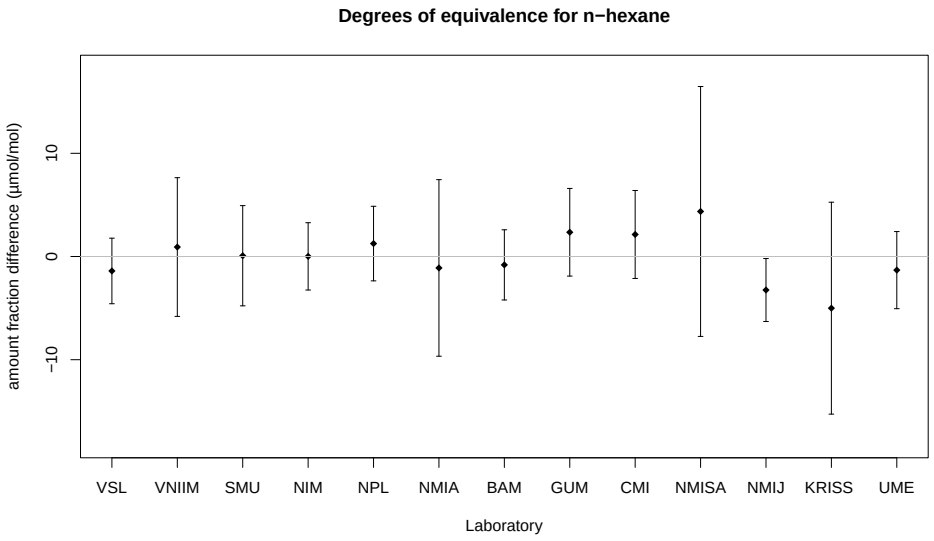


Figure 56: Degrees of equivalence for the amount fraction *n*-hexane (type IVa) (µmol mol^{-1}).

Table 18: Results and key comparison reference values for methane (type IVa) ($\mathrm{cmol\,mol^{-1}}$).

Lab	Mixture	y_{lab}	$U(y_{\mathrm{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\mathrm{KCRV}})$	$u(y_{\mathrm{KCRV}})$	k_{KCRV}
VSL	D322727	78.738	0.079	2.0	78.884	0.034	0.017	2.0
VNIIM	D322703	78.940	0.040	2.0	78.895	0.034	0.017	2.0
SMU	D322740	78.880	0.120	2.0	78.881	0.033	0.016	2.0
NIM	D322730	78.892	0.031	2.0	78.886	0.034	0.017	2.0
NPL	D322694	78.889	0.032	2.0	78.883	0.031	0.016	2.0
NMIA	D322744	78.867	0.050	2.0	78.879	0.032	0.016	2.0
BAM	D322738	78.873	0.012	2.0	78.876	0.029	0.015	2.0
GUM	D322721	78.815	0.079	2.0	78.877	0.032	0.016	2.0
CMI	D322720	78.874	0.026	2.0	78.879	0.030	0.015	2.0
NMISA	D322702	78.451	1.616	2.0	78.879	0.032	0.016	2.0
NMIJ	D322719	78.977	0.332	2.0	78.887	0.034	0.017	2.0
KRISS	D322706	78.989	0.079	2.0	78.876	0.034	0.017	2.0
UME	D322708	78.854	0.154	2.0	78.879	0.032	0.016	2.0

In table 18, the reported results and the KCRVs for methane are shown. The consensus value is $78.881\,\mathrm{cmol\,mol^{-1}}$ with standard uncertainty $0.013\,\mathrm{cmol\,mol^{-1}}$. The excess standard deviation τ is $0.018\,\mathrm{cmol\,mol^{-1}}$ (0.02 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 57. The results of VSL and KRISS are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 64 in annex B.

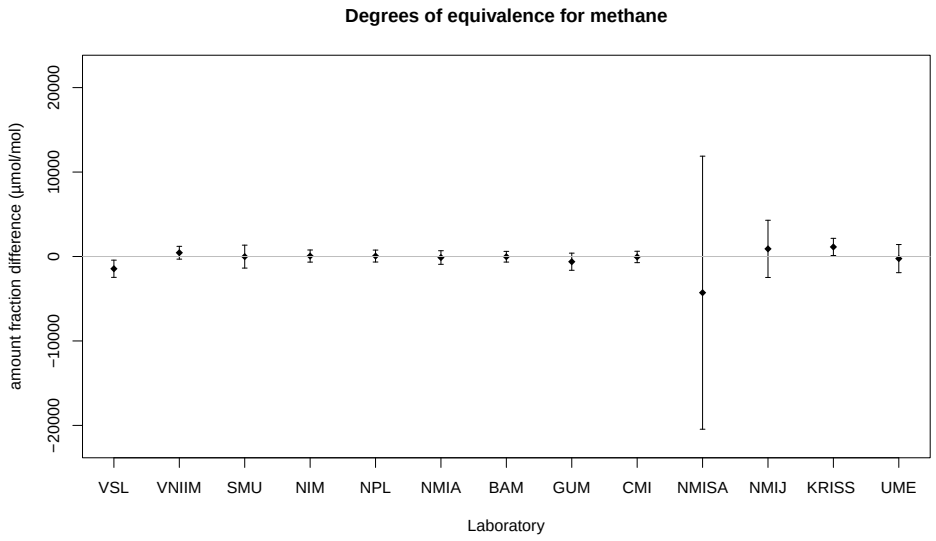


Figure 57: Degrees of equivalence for the amount fraction methane (type IVa) ($\mu\mathrm{mol\,mol^{-1}}$).

5.2 High-calorific natural gas

This section gives an overview over the reported results for the high-calorific natural gas, the KCRVs, and the degrees of equivalence. Unless stated otherwise, all uncertainty bars in the figures depict probabilistically-symmetric 95 % coverage intervals.

The following results have been excluded from the calculation of the KCRV (table 19). The participants that submitted these results provided results to replace them, so that the original results have been considered to be invalidated and hence not suitable for calculating the best estimate for the corresponding amount fraction. In the calculation of the degrees of equivalence, the original results have been used though. None of the new results was submitted before communicating the overview of results to the participating NMIs.

Table 19: Withdrawn results for high-calorific natural gas

Laboratory	Component
NIM	Nitrogen
NIM	Methane

Table 20: Results and key comparison reference values for nitrogen (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Lab	Mixture	y_{lab}	$U(y_{\mathrm{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\mathrm{KCRV}})$	$u(y_{\mathrm{KCRV}})$	k_{KCRV}
VSL	D322696	0.12210	0.00075	2.0	0.12186	0.00092	0.00046	2.0
VNIIM	D322705	0.12070	0.00080	2.0	0.12210	0.00082	0.00041	2.0
NIM	D322700	0.12460	0.00062	2.0	0.12152	0.00104	0.00052	2.0
NPL	D322741	0.12218	0.00061	2.0	0.12225	0.00077	0.00038	2.0
NMIA	D322718	0.12162	0.00060	2.0	0.12153	0.00086	0.00043	2.0
BAM	D322734	0.12204	0.00072	2.0	0.12160	0.00092	0.00046	2.0
GUM	D322699	0.11954	0.00048	2.0	0.12109	0.00080	0.00040	2.0
CMI	D322707	0.11960	0.00090	2.0	0.12184	0.00096	0.00048	2.0
NMISA	D322742	0.12056	0.00885	2.0	0.12137	0.00092	0.00046	2.0
BFKH	D322726	0.12070	0.00050	2.0	0.12123	0.00098	0.00049	2.0
NMIJ	D322736	0.12263	0.00051	2.0	0.12099	0.00102	0.00051	2.0
UME	D322701	0.12200	0.00020	2.0	0.12097	0.00085	0.00042	2.0

In table 20, the reported results and the KCRVs for nitrogen are shown. The consensus value is $0.121\,92\,\mathrm{cmol\,mol^{-1}}$ with standard uncertainty $0.000\,36\,\mathrm{cmol\,mol^{-1}}$. The excess standard deviation τ is $0.000\,42\,\mathrm{cmol\,mol^{-1}}$ (0.35 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 58. NIM and CMI report results that are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 65 in annex B.

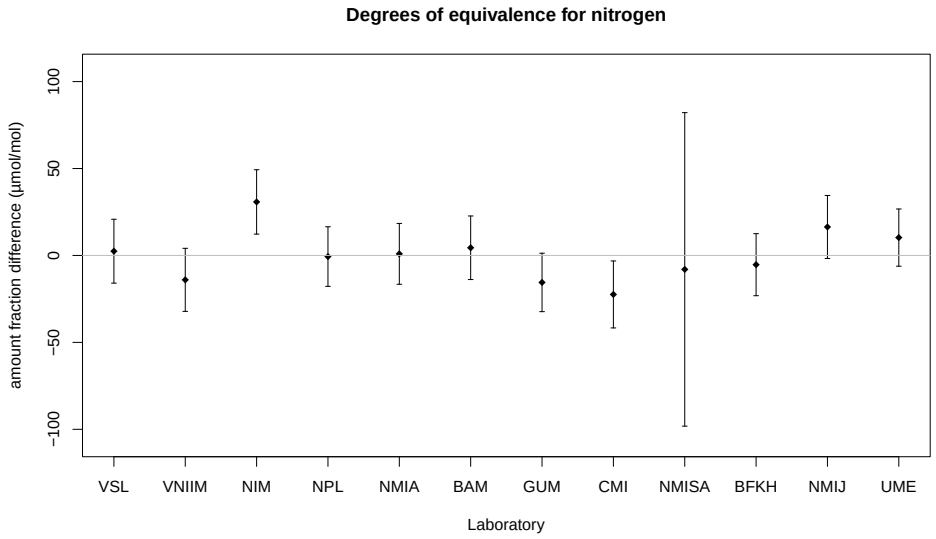


Figure 58: Degrees of equivalence for the amount fraction nitrogen (type LNG) (cmol mol^{-1}).

Table 21: Results and key comparison reference values for carbon dioxide (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	0.019956	0.000100	2.0	0.019899	0.000072	0.000036	2.0
VNIIM	D322705	0.019800	0.000150	2.0	0.019873	0.000080	0.000040	2.0
NIM	D322700	0.019780	0.000100	2.0	0.019908	0.000075	0.000037	2.0
NPL	D322741	0.019839	0.000397	2.0	0.019886	0.000072	0.000036	2.0
NMIA	D322718	0.019789	0.000300	2.0	0.019897	0.000075	0.000038	2.0
BAM	D322734	0.019952	0.000064	2.0	0.019898	0.000076	0.000038	2.0
GUM	D322699	0.019841	0.000040	2.0	0.019884	0.000072	0.000036	2.0
CMI	D322707	0.020000	0.000200	2.0	0.019965	0.000091	0.000045	2.0
NMISA	D322742	0.018645	0.001337	2.0	0.019912	0.000078	0.000039	2.0
BFKH	D322726	0.019800	0.000200	2.0	0.019890	0.000072	0.000036	2.0
NMIJ	D322736	0.020075	0.000045	2.0	0.019936	0.000072	0.000036	2.0
UME	D322701	0.019980	0.000120	2.0	0.019890	0.000070	0.000035	2.0

In table 21, the reported results and the KCRVs for carbon dioxide are shown. The consensus value is 0.019 893 cmol mol^{-1} with standard uncertainty 0.000 034 cmol mol^{-1}. The excess standard deviation τ is 0.000 056 cmol mol^{-1} (0.28 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 58. All results are consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 66 in annex B.

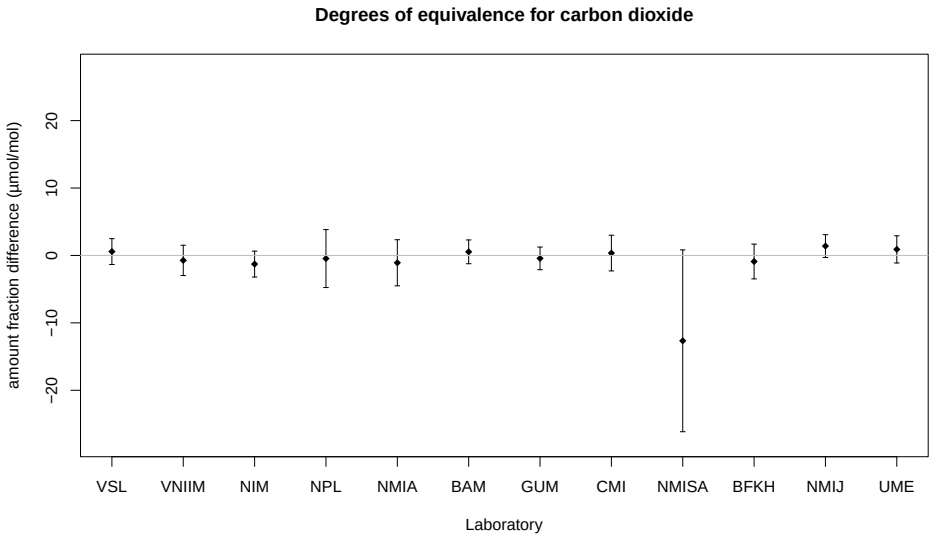


Figure 59: Degrees of equivalence for the amount fraction carbon dioxide (type LNG) (cmol mol^{-1}).

Table 22: Results and key comparison reference values for ethane (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	10.0039	0.0100	2.0	10.0029	0.0054	0.0027	2.0
VNIIM	D322705	9.9700	0.0500	2.0	9.9969	0.0070	0.0035	2.0
NIM	D322700	9.9880	0.0230	2.0	9.9991	0.0055	0.0028	2.0
NPL	D322741	9.9989	0.0200	2.0	9.9973	0.0055	0.0027	2.0
NMIA	D322718	10.0011	0.0060	2.0	10.0007	0.0055	0.0028	2.0
BAM	D322734	10.0027	0.0137	2.0	10.0018	0.0059	0.0030	2.0
GUM	D322699	9.9980	0.0800	2.0	10.0017	0.0056	0.0028	2.0
CMI	D322707	9.9598	0.0197	2.0	9.9984	0.0072	0.0036	2.0
NMISA	D322742	9.9619	0.2293	2.0	9.9965	0.0066	0.0033	2.0
BFKH	D322726	10.0060	0.0130	2.0	9.9987	0.0064	0.0032	2.0
NMIJ	D322736	9.9915	0.0136	2.0	10.0021	0.0054	0.0027	2.0
UME	D322701	10.0050	0.0080	2.0	10.0022	0.0059	0.0030	2.0

In table 22, the reported results and the KCRVs for ethane are shown. The consensus value is 10.0005 cmol mol^{-1} with standard uncertainty 0.0026 cmol mol^{-1}. The excess standard deviation τ is 0.0027 cmol mol^{-1} (0.03 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 60. CMI reports a result that is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 67 in annex B.

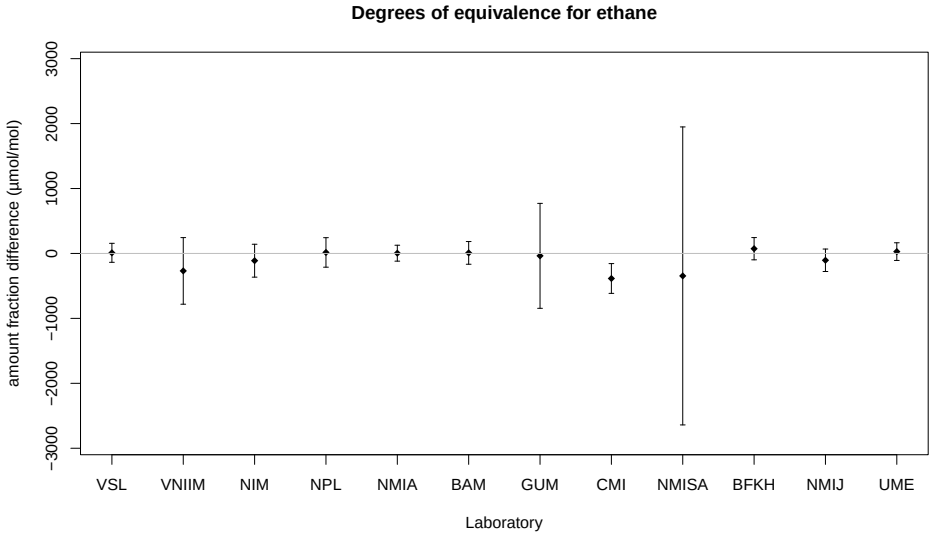


Figure 60: Degrees of equivalence for the amount fraction ethane (type LNG) (cmol mol^{-1}).

Table 23: Results and key comparison reference values for propane (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	1.99986	0.00221	2.0	2.00023	0.00157	0.00078	2.0
VNIIM	D322705	1.99100	0.01100	2.0	1.99918	0.00177	0.00089	2.0
NIM	D322700	1.99680	0.00500	2.0	1.99875	0.00165	0.00082	2.0
NPL	D322741	1.99762	0.00300	2.0	1.99869	0.00165	0.00082	2.0
NMIA	D322718	1.99860	0.00330	2.0	1.99954	0.00157	0.00078	2.0
BAM	D322734	1.99943	0.00241	2.0	1.99969	0.00160	0.00080	2.0
GUM	D322699	1.98700	0.00790	2.0	2.00003	0.00180	0.00090	2.0
CMI	D322707	2.00700	0.00560	2.0	1.99973	0.00167	0.00084	2.0
NMISA	D322742	1.99141	0.04478	2.0	1.99894	0.00184	0.00092	2.0
BFKH	D322726	2.00000	0.00200	2.0	1.99921	0.00176	0.00088	2.0
NMIJ	D322736	2.01611	0.00293	2.0	2.00011	0.00180	0.00090	2.0
UME	D322701	2.00100	0.00200	2.0	2.00062	0.00164	0.00082	2.0

In table 23, the reported results and the KCRVs for propane are shown. The consensus value is 2.000 cmol mol^{-1} with standard uncertainty 0.001 cmol mol^{-1}. The excess standard deviation τ is 0.001 cmol mol^{-1} (0.04 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 61. GUM, CMI and NMIJ report results that are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 68 in annex B.

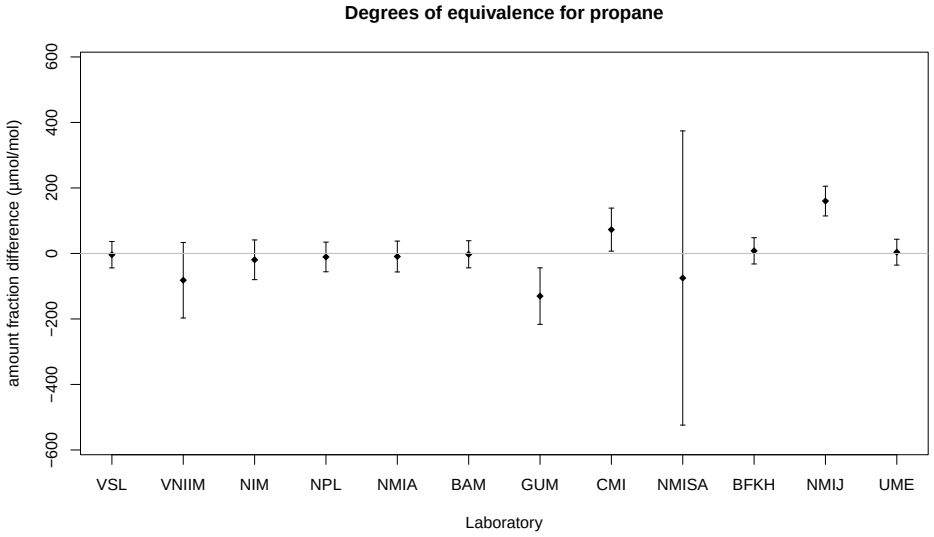


Figure 61: Degrees of equivalence for the amount fraction propane (type LNG) (cmol mol^{-1}).

Table 24: Results and key comparison reference values for iso-butane (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	0.14920	0.00015	2.0	0.14921	0.00013	0.00006	2.0
VNIIM	D322705	0.14910	0.00100	2.0	0.14915	0.00012	0.00006	2.0
NIM	D322700	0.14901	0.00037	2.0	0.14907	0.00012	0.00006	2.0
NPL	D322741	0.14914	0.00052	2.0	0.14908	0.00013	0.00006	2.0
NMIA	D322718	0.14932	0.00060	2.0	0.14918	0.00013	0.00006	2.0
BAM	D322734	0.14919	0.00017	2.0	0.14918	0.00012	0.00006	2.0
GUM	D322699	0.14940	0.00120	2.0	0.14921	0.00013	0.00006	2.0
CMI	D322707	0.14980	0.00100	2.0	0.14916	0.00013	0.00006	2.0
BFKH	D322726	0.14920	0.00050	2.0	0.14909	0.00013	0.00007	2.0
NMIJ	D322736	0.14892	0.00025	2.0	0.14916	0.00013	0.00006	2.0
UME	D322701	0.14930	0.00020	2.0	0.14923	0.00012	0.00006	2.0

In table 24, the reported results and the KCRVs for iso-butane are shown. The consensus value is 0.149 15 cmol mol^{-1} with standard uncertainty 0.000 06 cmol mol^{-1}. The excess standard deviation τ is 0.000 06 cmol mol^{-1} (0.04 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 62. All results are consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 69 in annex B.

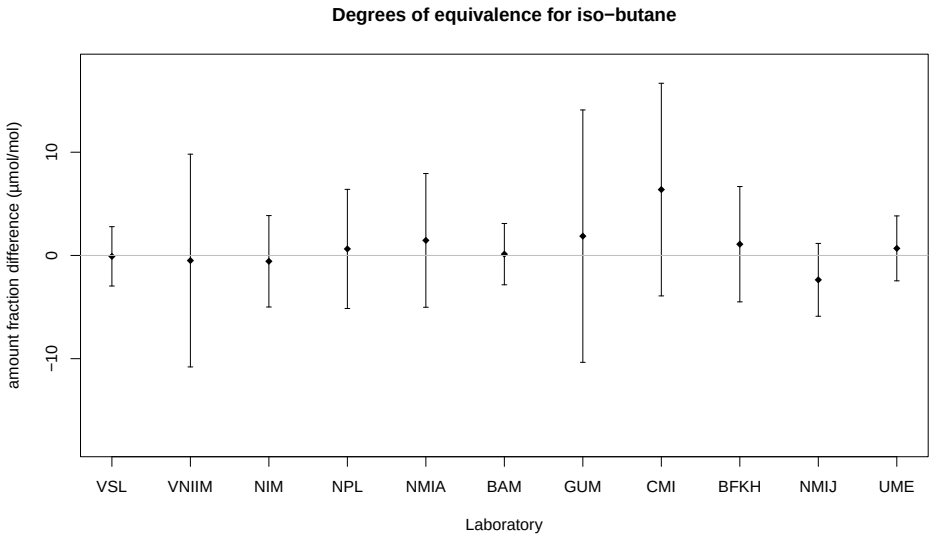


Figure 62: Degrees of equivalence for the amount fraction *iso*-butane (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Table 25: Results and key comparison reference values for n-butane (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Lab	Mixture	y_{lab}	$U(y_{\mathrm{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\mathrm{KCRV}})$	$u(y_{\mathrm{KCRV}})$	k_{KCRV}
VSL	D322696	0.14869	0.00015	2.0	0.14864	0.00019	0.00009	2.0
VNIIM	D322705	0.14810	0.00150	2.0	0.14854	0.00020	0.00010	2.0
NIM	D322700	0.14815	0.00039	2.0	0.14851	0.00019	0.00010	2.0
NPL	D322741	0.14847	0.00052	2.0	0.14852	0.00019	0.00010	2.0
NMIA	D322718	0.14865	0.00060	2.0	0.14862	0.00019	0.00010	2.0
BAM	D322734	0.14830	0.00018	2.0	0.14862	0.00019	0.00010	2.0
GUM	D322699	0.14780	0.00120	2.0	0.14863	0.00019	0.00010	2.0
CMI	D322707	0.14900	0.00100	2.0	0.14859	0.00019	0.00010	2.0
NMISA	D322742	0.15236	0.00356	2.0	0.14851	0.00019	0.00010	2.0
BFKH	D322726	0.14870	0.00040	2.0	0.14853	0.00020	0.00010	2.0
NMIJ	D322736	0.14817	0.00032	2.0	0.14862	0.00020	0.00010	2.0
UME	D322701	0.14870	0.00020	2.0	0.14866	0.00019	0.00010	2.0

In table 25, the reported results and the KCRVs for n-butane are shown. The consensus value is $0.148\,59\,\mathrm{cmol\,mol^{-1}}$ with standard uncertainty $0.000\,09\,\mathrm{cmol\,mol^{-1}}$. The excess standard deviation τ is $0.000\,10\,\mathrm{cmol\,mol^{-1}}$ (0.07 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 63. NMISA reports a result that is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 70 in annex B.

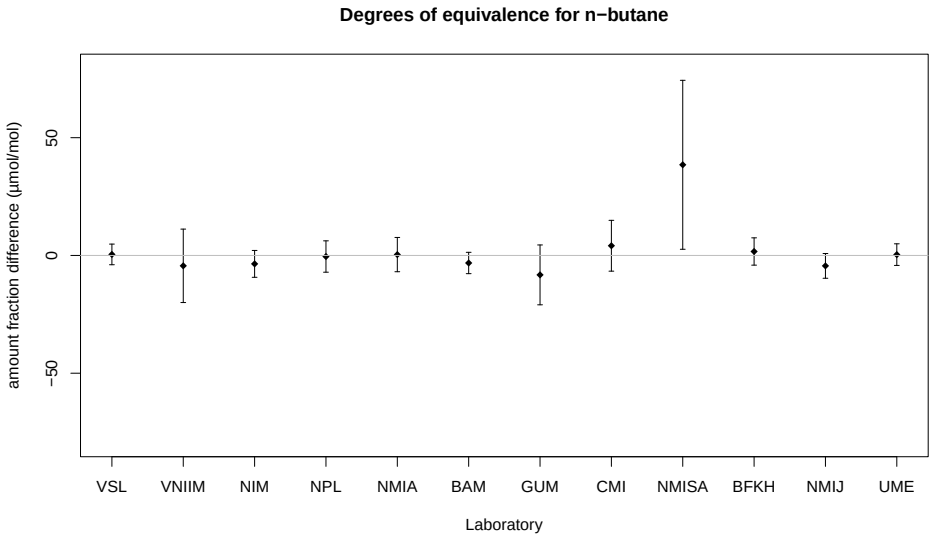


Figure 63: Degrees of equivalence for the amount fraction *n*-butane (type LNG) (cmol mol^{-1}).

Table 26: Results and key comparison reference values for iso-pentane (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	0.01992	0.00008	2.0	0.01991	0.00006	0.00003	2.0
VNIIM	D322705	0.01997	0.00019	2.0	0.01990	0.00006	0.00003	2.0
NIM	D322700	0.01988	0.00007	2.0	0.01990	0.00006	0.00003	2.0
NPL	D322741	0.01995	0.00008	2.0	0.01989	0.00006	0.00003	2.0
NMIA	D322718	0.02011	0.00008	2.0	0.01991	0.00006	0.00003	2.0
BAM	D322734	0.01989	0.00004	2.0	0.01991	0.00006	0.00003	2.0
GUM	D322699	0.01955	0.00020	2.0	0.01991	0.00006	0.00003	2.0
CMI	D322707	0.02020	0.00010	2.0	0.01991	0.00006	0.00003	2.0
NMISA	D322742	0.01969	0.00056	2.0	0.01989	0.00006	0.00003	2.0
BFKH	D322726	0.02010	0.00010	2.0	0.01990	0.00006	0.00003	2.0
NMIJ	D322736	0.01955	0.00005	2.0	0.01990	0.00006	0.00003	2.0
UME	D322701	0.02042	0.00006	2.0	0.01992	0.00006	0.00003	2.0

In table 26, the reported results and the KCRVs for iso-pentane are shown. The consensus value is 0.019 90 cmol mol^{-1} with standard uncertainty 0.000 03 cmol mol^{-1}. The excess standard deviation τ is 0.000 03 cmol mol^{-1} (0.14 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 64. NMIA, GUM, CMI, BFKH, NMIJ and UME report results that are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 71 in annex B.

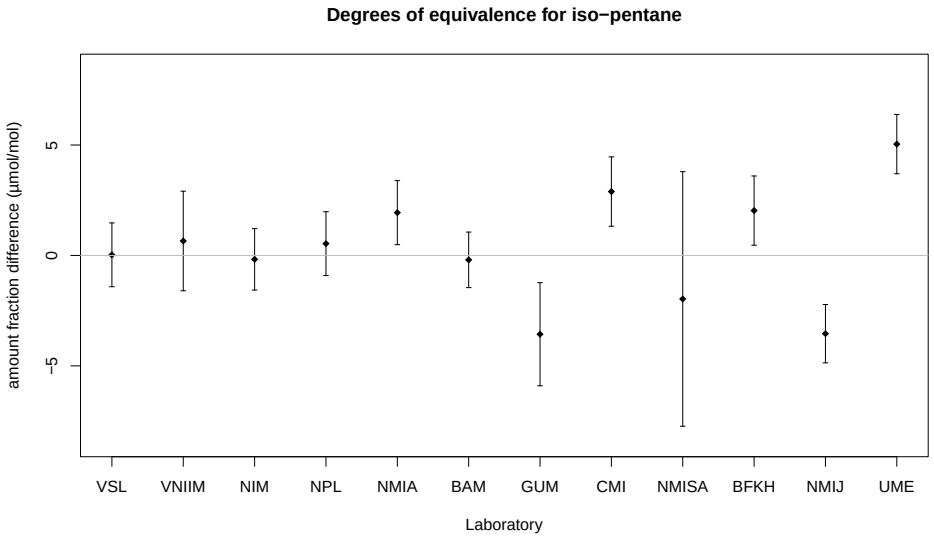


Figure 64: Degrees of equivalence for the amount fraction *iso*-pentane (type LNG) (cmol mol^{-1}).

Table 27: Results and key comparison reference values for n-pentane (type LNG) (cmol mol^{-1}).

Lab	Mixture	y_{lab}	$U(y_{\text{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\text{KCRV}})$	$u(y_{\text{KCRV}})$	k_{KCRV}
VSL	D322696	0.02012	0.00008	2.0	0.02010	0.00004	0.00002	2.0
VNIIM	D322705	0.02010	0.00014	2.0	0.02009	0.00004	0.00002	2.0
NIM	D322700	0.02000	0.00006	2.0	0.02009	0.00004	0.00002	2.0
NPL	D322741	0.02009	0.00008	2.0	0.02008	0.00004	0.00002	2.0
NMIA	D322718	0.02012	0.00010	2.0	0.02008	0.00005	0.00002	2.0
BAM	D322734	0.02010	0.00004	2.0	0.02010	0.00004	0.00002	2.0
GUM	D322699	0.02014	0.00012	2.0	0.02009	0.00004	0.00002	2.0
CMI	D322707	0.01990	0.00010	2.0	0.02010	0.00004	0.00002	2.0
NMISA	D322742	0.01997	0.00040	2.0	0.02007	0.00004	0.00002	2.0
BFKH	D322726	0.02010	0.00010	2.0	0.02008	0.00004	0.00002	2.0
NMIJ	D322736	0.01998	0.00007	2.0	0.02010	0.00004	0.00002	2.0
UME	D322701	0.02034	0.00006	2.0	0.02010	0.00004	0.00002	2.0

In table 27, the reported results and the KCRVs for n-pentane are shown. The consensus value is 0.020 09 cmol mol^{-1} with standard uncertainty 0.000 02 cmol mol^{-1}. The excess standard deviation τ is 0.000 03 cmol mol^{-1} (0.15 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 65. CMI and UME report results that are not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 72 in annex B.

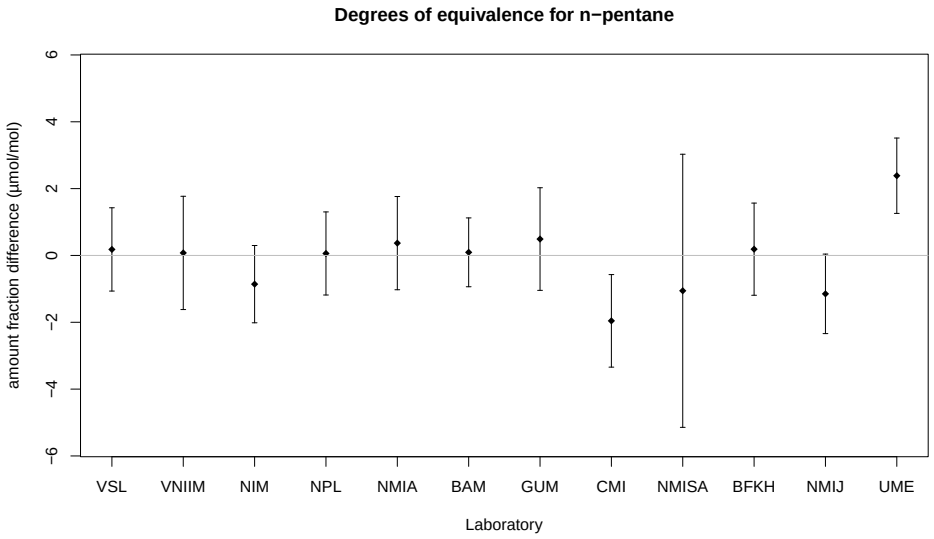


Figure 65: Degrees of equivalence for the amount fraction *n*-pentane (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Table 28: Results and key comparison reference values for methane (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Lab	Mixture	y_{lab}	$U(y_{\mathrm{lab}})$	k_{lab}	y_{KCRV}	$U(y_{\mathrm{KCRV}})$	$u(y_{\mathrm{KCRV}})$	k_{KCRV}
VSL	D322696	87.505	0.088	2.0	87.526	0.025	0.012	2.0
VNIIM	D322705	87.561	0.050	2.0	87.529	0.021	0.010	2.0
NIM	D322700	87.534	0.030	2.0	87.540	0.021	0.011	2.0
NPL	D322741	87.534	0.035	2.0	87.530	0.021	0.011	2.0
NMIA	D322718	87.521	0.050	2.0	87.539	0.019	0.010	2.0
BAM	D322734	87.518	0.015	2.0	87.517	0.020	0.010	2.0
GUM	D322699	87.519	0.088	2.0	87.516	0.025	0.012	2.0
CMI	D322707	87.555	0.027	2.0	87.537	0.020	0.010	2.0
NMISA	D322742	87.119	1.625	2.0	87.533	0.024	0.012	2.0
BFKH	D322726	87.515	0.028	2.0	87.531	0.022	0.011	2.0
NMIJ	D322736	87.162	0.273	2.0	87.525	0.025	0.012	2.0
UME	D322701	87.519	0.064	2.0	87.529	0.019	0.010	2.0

In table 28, the reported results and the KCRVs for methane are shown. The consensus value is $87.531\,\mathrm{cmol\,mol^{-1}}$ with standard uncertainty $0.009\,\mathrm{cmol\,mol^{-1}}$. The excess standard deviation τ is $0.010\,\mathrm{cmol\,mol^{-1}}$ (0.012 % as relative standard uncertainty). The degrees of equivalence computed from these data are shown in figure 66. NMIJ reports a result that is not consistent with the KCRV. The numerical values of the degrees of equivalence are given in table 73 in annex B.

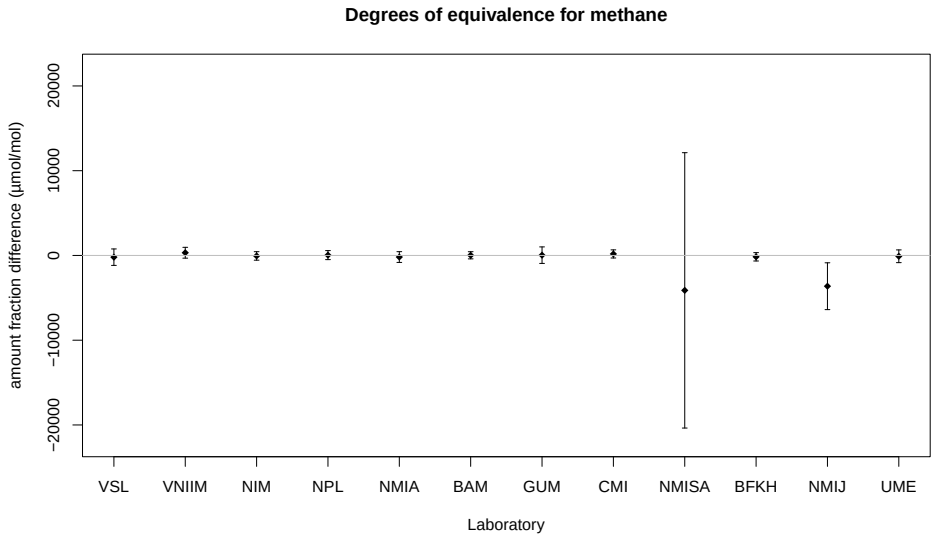


Figure 66: Degrees of equivalence for the amount fraction methane (type LNG) (cmol mol^{-1}).

6 Support to CMCs

The support of CMC claims is described in more detail in the ”GAWG strategy for comparisons and CMC claims” [36]. The results of this key comparison can be used to support CMC claims for the composition of natural gas in the following ranges (see table 29). CMCs outsite the listed ranges are not supported by the results of this key comparison without further evidence.

If an NMI participated only for one of the mixtures, then the respective columns in table 29 apply.

Table 29: Support to CMCs (cmol mol^{-1})

Component	Both mixtures		Low calorific mixture			High calorific mixture		
	CMC_{LB}	CMC_{UB}	x	CMC_{LB}	CMC_{UB}	x	CMC_{LB}	CMC_{UB}
Nitrogen	0.1	25	12	0.5	25	0.12	0.1	20
Carbon dioxide	0.02	20	4	0.5	20	0.02	0.02	10
Hydrogen	0.5	10	3	0.5	10			
Helium	0.05	2.5	0.5	0.05	2.5			
Ethane	0.2	25	0.75	0.2	20	10	0.5	25
Propane	0.05	12	0.3	0.05	10	2	0.1	12
iso-Butane	0.05	1.5	0.2	0.05	1.5	0.15	0.05	1.5
n-Butane	0.05	1.5	0.2	0.05	1.5	0.15	0.05	1.5
neo-Pentane	0.01	0.25	0.05	0.01	0.25			
iso-Pentane	0.01	0.25	0.05	0.01	0.25	0.02	0.01	0.25
n-Pentane	0.01	0.25	0.05	0.01	0.25	0.02	0.01	0.25
n-Hexane	0.01	0.25	0.05	0.01	0.25			
Methane	50	99.9	78.85	50	99.9	87.52	50	99.9

7 Conclusions

In previous key comparisons for natural gas, the submitted results were evaluated against KCRVs obtained from gravimetric gas mixture preparation. In this key comparison, a different design was chosen and the results have been benchmarked against a weighted mean computed from the LCS of the submitted results. The model also included a term to account for excess variability in the LCS, as the results for some of the measurands of the two mixtures were very different.

Most of the participants report one or a few (slightly) discrepant results. Partly this is due to the heterogeneity and heteroscedasticity of the datasets. There are also a few participants having several discrepant results, casting doubt at least on the followed measurement procedure. It is also remarkable that a discrepant result on a measurand in one mixture is not always followed by a discrepant result for the other mixture.

In all, the results in this key comparison demonstrate the good comparability of the national measurement standards maintained by the participating NMIs.

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Project reference

CCQM-K118

Completion date

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A Evaluation of the stability and homogeneity of the travelling standards

A.1 Low-calorific natural gas

In this annex, the underlying results of the combined stability and homogeneity study are provided for the low-calorific natural gas travelling standards.

In table 30, the results of the stability and homogeneity study for nitrogen are shown.

In table 31, the results of the stability and homogeneity study for carbon dioxide are shown.

In table 32, the results of the stability and homogeneity study for hydrogen are shown.

In table 33, the results of the stability and homogeneity study for helium are shown.

In table 34, the results of the stability and homogeneity study for ethane are shown.

In table 35, the results of the stability and homogeneity study for propane are shown.

In table 36, the results of the stability and homogeneity study for iso-butane are shown.

In table 37, the results of the stability and homogeneity study for n-butane are shown.

In table 38, the results of the stability and homogeneity study for iso-pentane are shown.

In table 39, the results of the stability and homogeneity study for n-pentane are shown.

In table 40, the results of the stability and homogeneity study for neo-pentane are shown.

In table 41, the results of the stability and homogeneity study for n-hexane are shown.

In table 42, the results of the stability and homogeneity study for methane are shown.

Table 30: Amount fractions and associated standard uncertainties of nitrogen (type IVa) ($\mathrm{cmol\,mol^{-1}}$).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	11.9815	0.0015	11.9790	0.0022	11.9811	0.0023	11.9823	0.0018	11.9791	0.0017	11.9804	0.0018
D322702	11.9784	0.0019	11.9785	0.0028	11.9800	0.0016	11.9802	0.0015	11.9796	0.0016	11.9787	0.0013
D322703	11.9790	0.0017	11.9798	0.0015	11.9802	0.0019	11.9791	0.0015	11.9791	0.0015	11.9754	0.0017
D322706	11.9792	0.0016	11.9798	0.0020	11.9816	0.0024	11.9776	0.0017	11.9800	0.0014	11.9780	0.0021
D322708	11.9805	0.0024	11.9810	0.0032	11.9806	0.0018	11.9801	0.0016	11.9792	0.0017	11.9804	0.0016
D322719	11.9806	0.0013	11.9782	0.0022	11.9781	0.0016	11.9792	0.0018	11.9781	0.0020	11.9773	0.0019
D322720	11.9789	0.0017	11.9790	0.0021	11.9788	0.0015	11.9798	0.0018	11.9797	0.0016	11.9808	0.0019
D322721	11.9775	0.0014	11.9793	0.0025	11.9699	0.0015	11.9802	0.0023	11.9794	0.0018	11.9798	0.0017
D322727	11.9803	0.0017	11.9759	0.0018	11.9779	0.0023	11.9783	0.0015	11.9797	0.0020	11.9798	0.0014
D322730	11.9800	0.0022	11.9789	0.0017	11.9830	0.0015	11.9805	0.0014	11.9792	0.0016	11.9802	0.0015
D322738	11.9769	0.0023	11.9814	0.0024	11.9790	0.0021	11.9771	0.0016	11.9788	0.0018	11.9763	0.0014
D322740	11.9793	0.0016	11.9804	0.0021	11.9708	0.0019	11.9801	0.0018	11.9790	0.0014	11.9788	0.0014
D322744	11.9791	0.0020	11.9786	0.0013	11.9791	0.0020	11.9790	0.0022	11.9772	0.0018	11.9776	0.0018

Table 31: Amount fractions and associated standard uncertainties of carbon dioxide (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	3.9995	0.0037	3.9999	0.0034	4.0022	0.0036	3.9993	0.0035	3.9991	0.0029	4.0012	0.0027
D322702	4.0013	0.0036	4.0011	0.0030	4.0012	0.0027	4.0015	0.0029	4.0031	0.0025	4.0027	0.0035
D322703	4.0009	0.0032	4.0002	0.0046	4.0007	0.0028	3.9995	0.0039	4.0005	0.0041	4.0001	0.0048
D322706	3.9995	0.0029	4.0021	0.0035	4.0008	0.0030	4.0010	0.0047	4.0020	0.0044	4.0010	0.0043
D322708	3.9997	0.0040	4.0024	0.0041	4.0026	0.0041	4.0013	0.0043	4.0005	0.0037	4.0021	0.0030
D322719	4.0018	0.0026	4.0024	0.0033	4.0022	0.0031	4.0018	0.0022	4.0023	0.0020	4.0027	0.0028
D322720	3.9996	0.0041	3.9999	0.0029	3.9997	0.0033	4.0018	0.0029	4.0003	0.0031	4.0003	0.0032
D322721	4.0015	0.0033	4.0020	0.0024	4.0025	0.0029	4.0013	0.0030	4.0029	0.0026	4.0015	0.0040
D322727	4.0009	0.0033	4.0009	0.0049	3.9997	0.0031	4.0031	0.0031	4.0026	0.0025	4.0019	0.0032
D322730	4.0007	0.0034	4.0024	0.0039	4.0007	0.0033	4.0018	0.0032	4.0010	0.0026	4.0009	0.0032
D322738	3.9997	0.0034	4.0011	0.0032	4.0010	0.0031	4.0017	0.0038	4.0019	0.0035	4.0020	0.0036
D322740	3.9990	0.0027	4.0016	0.0027	4.0008	0.0034	4.0003	0.0032	4.0015	0.0025	4.0008	0.0029
D322744	4.0018	0.0033	4.0023	0.0022	4.0027	0.0027	4.0017	0.0029	4.0014	0.0030	4.0016	0.0032

Table 32: Amount fractions and associated standard uncertainties of hydrogen (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	3.0045	0.0018	3.0043	0.0017	3.0035	0.0018	3.0050	0.0019	3.0039	0.0017	3.0035	0.0023
D322702	3.0001	0.0022	3.0010	0.0020	3.0012	0.0021	3.0015	0.0017	3.0001	0.0018	3.0012	0.0016
D322703	3.0021	0.0016	3.0019	0.0020	3.0019	0.0018	3.0012	0.0014	3.0013	0.0019	3.0001	0.0018
D322706	3.0043	0.0017	3.0047	0.0020	3.0041	0.0020	3.0031	0.0014	3.0035	0.0014	3.0027	0.0015
D322708	3.0036	0.0015	3.0037	0.0016	3.0025	0.0020	3.0039	0.0018	3.0030	0.0012	3.0031	0.0018
D322719	3.0015	0.0017	3.0000	0.0014	2.9995	0.0014	3.0005	0.0020	3.0009	0.0015	3.0002	0.0015
D322720	3.0027	0.0017	3.0018	0.0015	3.0032	0.0016	3.0032	0.0014	3.0033	0.0017	3.0033	0.0013
D322721	3.0007	0.0017	3.0010	0.0022	3.0028	0.0016	3.0021	0.0018	3.0012	0.0020	3.0020	0.0011
D322727	3.0015	0.0019	3.0003	0.0017	3.0005	0.0021	3.0010	0.0018	3.0012	0.0021	3.0016	0.0014
D322730	3.0020	0.0019	3.0007	0.0012	3.0039	0.0020	3.0030	0.0017	3.0006	0.0014	2.9999	0.0015
D322738	3.0022	0.0019	3.0039	0.0016	3.0028	0.0015	3.0029	0.0015	3.0024	0.0018	3.0021	0.0013
D322740	3.0038	0.0013	3.0028	0.0022	3.0051	0.0017	3.0034	0.0016	3.0026	0.0014	3.0031	0.0015
D322744	3.0016	0.0018	3.0007	0.0014	3.0011	0.0016	3.0018	0.0015	3.0008	0.0016	3.0006	0.0016

Table 33: Amount fractions and associated standard uncertainties of helium (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.5031	0.0005	0.5032	0.0004	0.5031	0.0004	0.5029	0.0004	0.5028	0.0004	0.5028	0.0004
D322702	0.5025	0.0005	0.5023	0.0006	0.5028	0.0004	0.5020	0.0004	0.5020	0.0003	0.5022	0.0004
D322703	0.5026	0.0004	0.5027	0.0004	0.5026	0.0004	0.5024	0.0003	0.5023	0.0003	0.5024	0.0004
D322706	0.5033	0.0004	0.5032	0.0005	0.5032	0.0003	0.5029	0.0004	0.5029	0.0003	0.5026	0.0003
D322708	0.5031	0.0006	0.5030	0.0005	0.5031	0.0003	0.5028	0.0004	0.5026	0.0004	0.5026	0.0004
D322719	0.5026	0.0005	0.5021	0.0004	0.5024	0.0004	0.5021	0.0005	0.5021	0.0004	0.5020	0.0005
D322720	0.5028	0.0005	0.5026	0.0003	0.5030	0.0003	0.5025	0.0003	0.5027	0.0004	0.5025	0.0004
D322721	0.5024	0.0003	0.5025	0.0005	0.5029	0.0004	0.5023	0.0004	0.5023	0.0003	0.5025	0.0004
D322727	0.5026	0.0004	0.5024	0.0005	0.5022	0.0004	0.5022	0.0005	0.5022	0.0004	0.5020	0.0004
D322730	0.5027	0.0004	0.5026	0.0003	0.5028	0.0005	0.5023	0.0004	0.5022	0.0003	0.5023	0.0004
D322738	0.5028	0.0006	0.5029	0.0004	0.5029	0.0005	0.5024	0.0003	0.5026	0.0004	0.5025	0.0003
D322740	0.5029	0.0004	0.5029	0.0005	0.5032	0.0004	0.5029	0.0004	0.5025	0.0004	0.5026	0.0004
D322744	0.5024	0.0006	0.5024	0.0004	0.5025	0.0004	0.5024	0.0003	0.5022	0.0004	0.5022	0.0004

Table 34: Amount fractions and associated standard uncertainties of ethane (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.7454	0.0018	0.7459	0.0014	0.7446	0.0013	0.7453	0.0013	0.7452	0.0012	0.7452	0.0017
D322702	0.7460	0.0013	0.7449	0.0017	0.7451	0.0009	0.7461	0.0014	0.7454	0.0016	0.7461	0.0012
D322703	0.7441	0.0016	0.7461	0.0017	0.7451	0.0016	0.7458	0.0023	0.7457	0.0019	0.7446	0.0023
D322706	0.7442	0.0024	0.7459	0.0018	0.7445	0.0017	0.7451	0.0020	0.7459	0.0023	0.7438	0.0022
D322708	0.7459	0.0017	0.7452	0.0016	0.7452	0.0013	0.7446	0.0017	0.7447	0.0019	0.7453	0.0012
D322719	0.7455	0.0023	0.7457	0.0012	0.7461	0.0016	0.7452	0.0019	0.7458	0.0017	0.7449	0.0016
D322720	0.7463	0.0022	0.7451	0.0013	0.7447	0.0015	0.7449	0.0015	0.7457	0.0016	0.7447	0.0013
D322721	0.7443	0.0014	0.7466	0.0024	0.7456	0.0016	0.7455	0.0014	0.7450	0.0015	0.7452	0.0013
D322727	0.7452	0.0011	0.7460	0.0018	0.7449	0.0012	0.7459	0.0017	0.7453	0.0015	0.7457	0.0012
D322730	0.7449	0.0013	0.7455	0.0015	0.7446	0.0015	0.7450	0.0014	0.7452	0.0014	0.7455	0.0015
D322738	0.7455	0.0012	0.7443	0.0019	0.7463	0.0016	0.7453	0.0024	0.7454	0.0023	0.7450	0.0013
D322740	0.7456	0.0013	0.7455	0.0019	0.7448	0.0013	0.7449	0.0016	0.7451	0.0017	0.7450	0.0010
D322744	0.7449	0.0013	0.7453	0.0009	0.7453	0.0017	0.7450	0.0012	0.7451	0.0013	0.7457	0.0015

Table 35: Amount fractions and associated standard uncertainties of propane (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.2983	0.0004	0.2983	0.0004	0.2983	0.0004	0.2985	0.0004	0.2983	0.0005	0.2983	0.0004
D322702	0.2985	0.0004	0.2987	0.0004	0.2985	0.0004	0.2986	0.0006	0.2984	0.0007	0.2983	0.0006
D322703	0.2985	0.0005	0.2984	0.0005	0.2983	0.0005	0.2985	0.0003	0.2985	0.0005	0.2983	0.0003
D322706	0.2983	0.0003	0.2984	0.0003	0.2984	0.0005	0.2980	0.0004	0.2983	0.0004	0.2980	0.0004
D322708	0.2983	0.0004	0.2985	0.0003	0.2985	0.0005	0.2985	0.0004	0.2985	0.0005	0.2983	0.0006
D322719	0.2985	0.0003	0.2983	0.0005	0.2985	0.0005	0.2985	0.0006	0.2986	0.0006	0.2987	0.0005
D322720	0.2982	0.0006	0.2981	0.0004	0.2984	0.0004	0.2984	0.0005	0.2986	0.0004	0.2985	0.0005
D322721	0.2984	0.0005	0.2985	0.0005	0.2982	0.0005	0.2986	0.0005	0.2986	0.0006	0.2984	0.0006
D322727	0.2987	0.0003	0.2981	0.0004	0.2982	0.0004	0.2987	0.0004	0.2985	0.0005	0.2985	0.0004
D322730	0.2985	0.0005	0.2986	0.0004	0.2984	0.0004	0.2984	0.0005	0.2985	0.0004	0.2982	0.0006
D322738	0.2982	0.0004	0.2983	0.0004	0.2981	0.0004	0.2982	0.0004	0.2983	0.0004	0.2983	0.0003
D322740	0.2985	0.0004	0.2983	0.0006	0.2983	0.0004	0.2985	0.0007	0.2983	0.0004	0.2982	0.0006
D322744	0.2983	0.0004	0.2985	0.0004	0.2984	0.0005	0.2985	0.0004	0.2984	0.0003	0.2986	0.0003

Table 36: Amount fractions and associated standard uncertainties of iso-butane (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.19965	0.00008	0.19971	0.00010	0.19969	0.00007	0.19966	0.00007	0.19967	0.00007	0.19965	0.00007
D322702	0.19977	0.00008	0.19981	0.00009	0.19981	0.00008	0.19981	0.00007	0.19979	0.00008	0.19983	0.00008
D322703	0.19974	0.00008	0.19975	0.00010	0.19980	0.00010	0.19973	0.00008	0.19978	0.00009	0.19975	0.00007
D322706	0.19962	0.00008	0.19963	0.00012	0.19966	0.00008	0.19965	0.00008	0.19970	0.00007	0.19968	0.00008
D322708	0.19964	0.00012	0.19970	0.00009	0.19969	0.00009	0.19975	0.00009	0.19967	0.00008	0.19977	0.00009
D322719	0.19977	0.00007	0.19982	0.00009	0.19978	0.00008	0.19989	0.00008	0.19980	0.00008	0.19978	0.00010
D322720	0.19961	0.00009	0.19961	0.00007	0.19972	0.00007	0.19962	0.00009	0.19970	0.00006	0.19974	0.00005
D322721	0.19975	0.00011	0.19983	0.00010	0.19977	0.00006	0.19983	0.00008	0.19980	0.00010	0.19978	0.00008
D322727	0.19981	0.00007	0.19981	0.00013	0.19976	0.00007	0.19984	0.00007	0.19981	0.00009	0.19979	0.00007
D322730	0.19975	0.00010	0.19978	0.00006	0.19977	0.00010	0.19982	0.00008	0.19974	0.00007	0.19976	0.00011
D322738	0.19964	0.00009	0.19967	0.00010	0.19972	0.00010	0.19961	0.00007	0.19969	0.00006	0.19963	0.00007
D322740	0.19960	0.00009	0.19972	0.00006	0.19964	0.00006	0.19965	0.00008	0.19969	0.00007	0.19968	0.00006
D322744	0.19980	0.00008	0.19972	0.00009	0.19978	0.00010	0.19979	0.00008	0.19976	0.00007	0.19978	0.00008

Table 37: Amount fractions and associated standard uncertainties of n-butane (type IVa) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.19998	0.00009	0.20006	0.00010	0.20001	0.00011	0.19994	0.00007	0.20000	0.00009	0.19993	0.00007
D322702	0.20007	0.00009	0.20013	0.00011	0.20016	0.00010	0.20008	0.00009	0.20011	0.00007	0.20013	0.00009
D322703	0.20004	0.00011	0.20006	0.00010	0.20016	0.00009	0.19998	0.00008	0.20003	0.00007	0.20004	0.00007
D322706	0.19995	0.00011	0.19994	0.00011	0.20002	0.00008	0.19994	0.00009	0.19995	0.00009	0.19994	0.00009
D322708	0.19997	0.00012	0.20006	0.00011	0.20002	0.00011	0.20004	0.00010	0.19998	0.00009	0.20007	0.00010
D322719	0.20012	0.00007	0.20017	0.00009	0.20010	0.00009	0.20016	0.00008	0.20010	0.00007	0.20010	0.00009
D322720	0.19989	0.00011	0.19993	0.00009	0.20001	0.00007	0.19987	0.00013	0.19998	0.00007	0.19995	0.00007
D322721	0.20008	0.00010	0.20013	0.00010	0.20012	0.00009	0.20010	0.00008	0.20007	0.00010	0.20006	0.00009
D322727	0.20015	0.00008	0.20015	0.00010	0.20006	0.00010	0.20012	0.00009	0.20008	0.00006	0.20006	0.00008
D322730	0.20009	0.00012	0.20010	0.00008	0.20010	0.00012	0.20008	0.00010	0.20002	0.00010	0.20002	0.00011
D322738	0.19999	0.00011	0.19996	0.00011	0.20000	0.00013	0.19988	0.00006	0.19994	0.00009	0.19987	0.00008
D322740	0.19995	0.00009	0.20001	0.00008	0.19995	0.00012	0.19991	0.00007	0.19996	0.00008	0.19992	0.00007
D322744	0.20017	0.00009	0.20003	0.00011	0.20007	0.00012	0.20005	0.00008	0.20007	0.00007	0.20005	0.00008

Table 38: Amount fractions and associated standard uncertainties of iso-pentane (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.04985	0.00006	0.04983	0.00004	0.04986	0.00006	0.04980	0.00006	0.04984	0.00007	0.04987	0.00009
D322702	0.04983	0.00006	0.04986	0.00005	0.04987	0.00008	0.04985	0.00005	0.04988	0.00008	0.04990	0.00007
D322703	0.04986	0.00007	0.04987	0.00005	0.04991	0.00009	0.04985	0.00005	0.04985	0.00007	0.04987	0.00005
D322706	0.04985	0.00007	0.04984	0.00005	0.04986	0.00006	0.04984	0.00006	0.04984	0.00005	0.04987	0.00005
D322708	0.04979	0.00007	0.04984	0.00004	0.04985	0.00007	0.04981	0.00008	0.04984	0.00008	0.04986	0.00008
D322719	0.04989	0.00007	0.04986	0.00007	0.04989	0.00008	0.04994	0.00006	0.04986	0.00007	0.04989	0.00006
D322720	0.04984	0.00008	0.04981	0.00007	0.04982	0.00006	0.04984	0.00007	0.04982	0.00007	0.04981	0.00006
D322721	0.04986	0.00003	0.04986	0.00004	0.04982	0.00007	0.04987	0.00008	0.04987	0.00008	0.04988	0.00008
D322727	0.04987	0.00006	0.04988	0.00006	0.04986	0.00005	0.04987	0.00007	0.04989	0.00006	0.04987	0.00008
D322730	0.04986	0.00006	0.04988	0.00009	0.04985	0.00006	0.04980	0.00008	0.04987	0.00007	0.04987	0.00007
D322738	0.04980	0.00008	0.04986	0.00006	0.04984	0.00005	0.04983	0.00006	0.04981	0.00006	0.04985	0.00005
D322740	0.04983	0.00005	0.04981	0.00004	0.04981	0.00007	0.04982	0.00005	0.04984	0.00006	0.04986	0.00007
D322744	0.04984	0.00007	0.04987	0.00006	0.04987	0.00005	0.04987	0.00006	0.04990	0.00006	0.04987	0.00005

Table 39: Amount fractions and associated standard uncertainties of n-pentane (type IVa) ($\mathrm{cmol\,mol^{-1}}$).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.05016	0.00011	0.05022	0.00011	0.05026	0.00011	0.05019	0.00010	0.05019	0.00011	0.05021	0.00015
D322702	0.05033	0.00014	0.05026	0.00009	0.05019	0.00011	0.05021	0.00012	0.05018	0.00014	0.05027	0.00008
D322703	0.05019	0.00008	0.05014	0.00014	0.05025	0.00011	0.05023	0.00008	0.05026	0.00011	0.05022	0.00008
D322706	0.05018	0.00006	0.05019	0.00011	0.05025	0.00011	0.05021	0.00007	0.05025	0.00010	0.05017	0.00009
D322708	0.05013	0.00013	0.05019	0.00013	0.05021	0.00009	0.05017	0.00012	0.05024	0.00011	0.05018	0.00012
D322719	0.05025	0.00008	0.05024	0.00009	0.05026	0.00015	0.05025	0.00008	0.05027	0.00009	0.05022	0.00010
D322720	0.05020	0.00010	0.05019	0.00013	0.05017	0.00010	0.05018	0.00012	0.05020	0.00010	0.05020	0.00012
D322721	0.05021	0.00011	0.05023	0.00012	0.05024	0.00008	0.05028	0.00010	0.05024	0.00011	0.05020	0.00011
D322727	0.05021	0.00010	0.05026	0.00009	0.05027	0.00011	0.05018	0.00010	0.05021	0.00015	0.05022	0.00012
D322730	0.05024	0.00011	0.05026	0.00012	0.05024	0.00011	0.05020	0.00013	0.05021	0.00013	0.05024	0.00016
D322738	0.05016	0.00011	0.05021	0.00011	0.05017	0.00009	0.05024	0.00007	0.05016	0.00010	0.05021	0.00005
D322740	0.05008	0.00014	0.05013	0.00013	0.05018	0.00008	0.05020	0.00009	0.05025	0.00008	0.05020	0.00009
D322744	0.05023	0.00008	0.05027	0.00008	0.05028	0.00011	0.05027	0.00007	0.05028	0.00006	0.05028	0.00009

Table 40: Amount fractions and associated standard uncertainties of neo-pentane (type IVa) ($\mathrm{cmol\,mol^{-1}}$).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.04928	0.00005	0.04928	0.00005	0.04932	0.00004	0.04941	0.00005	0.04941	0.00005	0.04939	0.00006
D322702	0.04934	0.00005	0.04933	0.00004	0.04935	0.00006	0.04945	0.00004	0.04942	0.00006	0.04943	0.00006
D322703	0.04936	0.00007	0.04932	0.00005	0.04936	0.00006	0.04943	0.00006	0.04941	0.00003	0.04941	0.00005
D322706	0.04931	0.00005	0.04931	0.00004	0.04929	0.00005	0.04938	0.00005	0.04937	0.00005	0.04939	0.00004
D322708	0.04928	0.00005	0.04931	0.00004	0.04933	0.00005	0.04937	0.00006	0.04941	0.00007	0.04935	0.00004
D322719	0.04935	0.00004	0.04934	0.00004	0.04935	0.00005	0.04945	0.00006	0.04941	0.00005	0.04942	0.00005
D322720	0.04932	0.00003	0.04932	0.00005	0.04934	0.00004	0.04942	0.00005	0.04941	0.00006	0.04938	0.00006
D322721	0.04934	0.00005	0.04934	0.00006	0.04931	0.00007	0.04945	0.00005	0.04943	0.00005	0.04944	0.00005
D322727	0.04933	0.00006	0.04935	0.00005	0.04936	0.00006	0.04941	0.00006	0.04943	0.00006	0.04942	0.00005
D322730	0.04932	0.00004	0.04935	0.00004	0.04931	0.00006	0.04936	0.00006	0.04941	0.00006	0.04940	0.00006
D322738	0.04931	0.00006	0.04931	0.00005	0.04929	0.00004	0.04938	0.00003	0.04937	0.00004	0.04938	0.00004
D322740	0.04933	0.00003	0.04928	0.00006	0.04928	0.00005	0.04937	0.00004	0.04941	0.00004	0.04941	0.00005
D322744	0.04932	0.00005	0.04931	0.00005	0.04932	0.00004	0.04940	0.00004	0.04942	0.00005	0.04943	0.00005

Table 41: Amount fractions and associated standard uncertainties of n-hexane (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	0.04954	0.00008	0.04955	0.00009	0.04961	0.00008	0.04951	0.00007	0.04958	0.00007	0.04959	0.00008
D322702	0.04960	0.00006	0.04963	0.00005	0.04962	0.00008	0.04961	0.00007	0.04962	0.00007	0.04968	0.00008
D322703	0.04960	0.00007	0.04958	0.00009	0.04961	0.00005	0.04958	0.00006	0.04955	0.00005	0.04966	0.00006
D322706	0.04958	0.00006	0.04958	0.00008	0.04955	0.00007	0.04960	0.00006	0.04958	0.00007	0.04962	0.00006
D322708	0.04944	0.00009	0.04954	0.00006	0.04961	0.00009	0.04956	0.00009	0.04961	0.00009	0.04959	0.00009
D322719	0.04962	0.00011	0.04964	0.00004	0.04963	0.00006	0.04973	0.00007	0.04968	0.00006	0.04967	0.00006
D322720	0.04946	0.00008	0.04954	0.00009	0.04960	0.00008	0.04961	0.00009	0.04958	0.00007	0.04962	0.00007
D322721	0.04957	0.00007	0.04963	0.00006	0.04964	0.00006	0.04964	0.00005	0.04963	0.00007	0.04967	0.00008
D322727	0.04962	0.00008	0.04960	0.00010	0.04963	0.00007	0.04954	0.00006	0.04967	0.00006	0.04965	0.00009
D322730	0.04958	0.00005	0.04964	0.00006	0.04960	0.00009	0.04954	0.00007	0.04962	0.00010	0.04963	0.00010
D322738	0.04955	0.00009	0.04959	0.00008	0.04953	0.00007	0.04955	0.00007	0.04949	0.00008	0.04962	0.00005
D322740	0.04945	0.00005	0.04951	0.00008	0.04961	0.00007	0.04952	0.00006	0.04961	0.00008	0.04961	0.00007
D322744	0.04959	0.00007	0.04957	0.00007	0.04965	0.00007	0.04964	0.00006	0.04964	0.00006	0.04966	0.00008

Table 42: Amount fractions and associated standard uncertainties of methane (type IVa) (µmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$	x_5	$u(x_5)$	x_6	$u(x_6)$
D322694	78.8746	0.0333	78.8817	0.0378	78.8705	0.0240	78.8732	0.0262	78.8745	0.0227	78.8799	0.0283
D322702	78.8771	0.0195	78.8640	0.0244	78.8627	0.0166	78.8788	0.0205	78.8789	0.0256	78.8755	0.0279
D322703	78.8725	0.0288	78.8764	0.0356	78.8989	0.0265	78.8752	0.0293	78.8716	0.0242	78.8815	0.0350
D322706	78.8648	0.0276	78.8631	0.0329	78.8742	0.0234	78.8722	0.0269	78.8648	0.0231	78.8689	0.0206
D322708	78.8731	0.0216	78.8772	0.0326	78.8694	0.0234	78.8745	0.0177	78.8629	0.0198	78.8811	0.0308
D322719	78.8641	0.0257	78.8680	0.0280	78.8726	0.0271	78.8823	0.0257	78.8913	0.0249	78.8873	0.0213
D322720	78.8664	0.0146	78.8709	0.0248	78.8772	0.0334	78.8845	0.0249	78.8754	0.0287	78.8850	0.0331
D322721	78.8582	0.0227	78.8613	0.0237	78.8793	0.0238	78.8709	0.0192	78.8826	0.0214	78.8782	0.0254
D322727	78.8672	0.0238	78.8714	0.0342	78.8818	0.0334	78.8789	0.0283	78.8783	0.0217	78.8791	0.0207
D322730	78.8907	0.0365	78.8611	0.0373	78.8778	0.0299	78.8841	0.0186	78.8823	0.0255	78.8717	0.0231
D322738	78.8534	0.0319	78.8850	0.0271	78.8675	0.0275	78.8735	0.0278	78.8765	0.0323	78.8601	0.0282
D322740	78.8753	0.0346	78.8641	0.0298	78.8727	0.0299	78.8706	0.0241	78.8757	0.0195	78.8792	0.0193
D322744	78.8684	0.0367	78.8521	0.0238	78.8711	0.0225	78.8873	0.0279	78.8752	0.0226	78.8813	0.0207

A.2 High-calorific natural gas

In table 43, the results of the stability and homogeneity study for nitrogen are shown.

Table 43: Amount fractions and associated standard uncertainties of nitrogen (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.12163	0.00027	0.12083	0.00022	0.12244	0.00042	0.12258	0.00034
D322699	0.12135	0.00019	0.12144	0.00025	0.12073	0.00035	0.12101	0.00023
D322700	0.12087	0.00015	0.12122	0.00022	0.12190	0.00028	0.12268	0.00034
D322701	0.12088	0.00017	0.12121	0.00026	0.12065	0.00025	0.12167	0.00028
D322705	0.12230	0.00038	0.12209	0.00029	0.12176	0.00042	0.12257	0.00034
D322707	0.12232	0.00034	0.12188	0.00019	0.12115	0.00028	0.12276	0.00050
D322718	0.12191	0.00018	0.12118	0.00030				
D322726	0.12117	0.00021	0.12096	0.00015	0.12212	0.00054	0.12304	0.00032
D322734	0.12184	0.00037	0.12096	0.00022	0.12066	0.00035	0.12285	0.00054
D322736	0.12111	0.00015	0.12108	0.00026	0.11988	0.00039	0.12225	0.00035
D322741	0.12226	0.00029	0.12264	0.00026	0.12197	0.00035	0.12235	0.00027
D322742	0.12125	0.00021	0.12144	0.00022	0.12082	0.00039	0.12236	0.00032

In table 44, the results of the stability and homogeneity study for carbon dioxide are shown.

Table 44: Amount fractions and associated standard uncertainties of carbon dioxide (type LNG) ($\mathrm{cmol\,mol^{-1}}$).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.01990	0.00004	0.01986	0.00002	0.01991	0.00002	0.01990	0.00002
D322699	0.01985	0.00001	0.01988	0.00002	0.01990	0.00002	0.01991	0.00002
D322700	0.01988	0.00002	0.01988	0.00002	0.01991	0.00002	0.01997	0.00004
D322701	0.01988	0.00002	0.01989	0.00002	0.01988	0.00001	0.01989	0.00004
D322705	0.01981	0.00002	0.01985	0.00002	0.01991	0.00002	0.01991	0.00002
D322707	0.02004	0.00006	0.01987	0.00002	0.01995	0.00002	0.01999	0.00002
D322718	0.01989	0.00002	0.01989	0.00002				
D322726	0.01987	0.00002	0.01990	0.00002	0.01990	0.00002	0.01986	0.00002
D322734	0.01989	0.00004	0.01987	0.00002	0.01993	0.00002	0.01984	0.00002
D322736	0.01995	0.00002	0.01994	0.00002	0.01992	0.00002	0.01990	0.00002
D322741	0.01985	0.00002	0.01988	0.00002	0.01988	0.00002	0.01989	0.00002
D322742	0.01988	0.00001	0.01988	0.00001	0.01999	0.00004	0.01996	0.00004

In table 45, the results of the stability and homogeneity study for ethane are shown.

Table 45: Amount fractions and associated standard uncertainties of ethane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	9.9997	0.0017	10.0000	0.0013	9.9999	0.0015	10.0020	0.0016
D322699	9.9983	0.0015	9.9986	0.0014	9.9976	0.0015	10.0020	0.0015
D322700	9.9944	0.0018	9.9973	0.0014	9.9975	0.0018	9.9966	0.0015
D322701	9.9959	0.0013	9.9970	0.0017	10.0010	0.0017	10.0030	0.0014
D322705	9.9928	0.0018	9.9888	0.0015	9.9992	0.0015	9.9971	0.0013
D322707	9.9890	0.0014	9.9974	0.0017	9.9995	0.0016	9.9972	0.0014
D322718	9.9968	0.0019	9.9990	0.0017				
D322726	9.9907	0.0014	9.9942	0.0014	9.9988	0.0013	9.9988	0.0020
D322734	9.9957	0.0022	10.0010	0.0025	9.9976	0.0015	10.0020	0.0012
D322736	9.9988	0.0015	9.9984	0.0021	10.0010	0.0013	9.9991	0.0013
D322741	9.9950	0.0017	9.9928	0.0015	9.9947	0.0017	9.9960	0.0013
D322742	9.9915	0.0013	9.9895	0.0016	9.9973	0.0014	9.9972	0.0015

In table 46, the results of the stability and homogeneity study for propane are shown.

Table 46: Amount fractions and associated standard uncertainties of propane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	1.99950	0.00019	1.99950	0.00014	2.00060	0.00021	2.00080	0.00023
D322699	1.99960	0.00033	1.99870	0.00019	2.00030	0.00020	2.00080	0.00016
D322700	1.99790	0.00018	1.99800	0.00014	1.99900	0.00021	1.99960	0.00021
D322701	1.99940	0.00018	1.99970	0.00018	2.00110	0.00018	2.00140	0.00023
D322705	1.99840	0.00033	1.99790	0.00030	1.99990	0.00021	2.00000	0.00020
D322707	1.99860	0.00025	1.99880	0.00014	2.00020	0.00023	2.00010	0.00021
D322718	1.99970	0.00020	1.99910	0.00018				
D322726	1.99760	0.00016	1.99810	0.00034	2.00010	0.00024	1.99960	0.00019
D322734	1.99920	0.00025	1.99840	0.00033	2.00020	0.00020	2.00020	0.00020
D322736	1.99940	0.00017	1.99880	0.00014	2.00120	0.00022	2.00040	0.00018
D322741	1.99820	0.00020	1.99770	0.00027	1.99870	0.00024	1.99970	0.00021
D322742	1.99810	0.00017	1.99760	0.00016	1.99970	0.00017	1.99970	0.00020

In table 47, the results of the stability and homogeneity study for iso-butane are shown.

Table 47: Amount fractions and associated standard uncertainties of iso-butane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.14935	0.00002	0.14925	0.00002	0.14925	0.00003	0.14921	0.00003
D322699	0.14929	0.00003	0.14930	0.00002	0.14924	0.00003	0.14923	0.00003
D322700	0.14912	0.00003	0.14911	0.00002	0.14912	0.00003	0.14915	0.00003
D322701	0.14932	0.00002	0.14925	0.00002	0.14929	0.00003	0.14928	0.00003
D322705	0.14922	0.00002	0.14922	0.00002	0.14919	0.00003	0.14917	0.00003
D322707	0.14927	0.00002	0.14920	0.00002	0.14917	0.00003	0.14922	0.00003
D322718	0.14925	0.00003	0.14922	0.00002				
D322726	0.14910	0.00002	0.14911	0.00002	0.14922	0.00003	0.14916	0.00003
D322734	0.14922	0.00004	0.14922	0.00003	0.14925	0.00003	0.14925	0.00003
D322736	0.14921	0.00003	0.14916	0.00003	0.14927	0.00003	0.14923	0.00003
D322741	0.14913	0.00002	0.14909	0.00003	0.14911	0.00003	0.14919	0.00003
D322742	0.14913	0.00002	0.14909	0.00003	0.14914	0.00003	0.14915	0.00003

In table 48, the results of the stability and homogeneity study for n-butane are shown.

Table 48: Amount fractions and associated standard uncertainties of n-butane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.14874	0.00002	0.14875	0.00002	0.14878	0.00003	0.14877	0.00003
D322699	0.14871	0.00004	0.14870	0.00003	0.14877	0.00003	0.14877	0.00003
D322700	0.14859	0.00002	0.14860	0.00003	0.14866	0.00003	0.14866	0.00003
D322701	0.14873	0.00002	0.14875	0.00003	0.14880	0.00003	0.14884	0.00003
D322705	0.14860	0.00004	0.14859	0.00003	0.14873	0.00003	0.14869	0.00003
D322707	0.14871	0.00003	0.14867	0.00003	0.14871	0.00003	0.14873	0.00003
D322718	0.14874	0.00003	0.14872	0.00003				
D322726	0.14857	0.00003	0.14859	0.00003	0.14872	0.00003	0.14869	0.00003
D322734	0.14871	0.00004	0.14868	0.00003	0.14877	0.00003	0.14876	0.00003
D322736	0.14870	0.00003	0.14864	0.00004	0.14881	0.00003	0.14876	0.00003
D322741	0.14860	0.00003	0.14858	0.00004	0.14864	0.00003	0.14869	0.00003
D322742	0.14860	0.00003	0.14857	0.00003	0.14868	0.00003	0.14865	0.00003

In table 49, the results of the stability and homogeneity study for iso-pentane are shown.

Table 49: Amount fractions and associated standard uncertainties of iso-pentane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.019946	0.000008	0.019936	0.000008	0.019933	0.000009	0.019935	0.000008
D322699	0.019938	0.000008	0.019931	0.000008	0.019933	0.000008	0.019928	0.000008
D322700	0.019920	0.000007	0.019915	0.000009	0.019925	0.000008	0.019938	0.000011
D322701	0.019940	0.000007	0.019945	0.000007	0.019938	0.000008	0.019941	0.000008
D322705	0.019938	0.000007	0.019933	0.000008	0.019927	0.000007	0.019918	0.000008
D322707	0.019944	0.000008	0.019929	0.000007	0.019931	0.000007	0.019941	0.000007
D322718	0.019939	0.000008	0.019937	0.000008				
D322726	0.019920	0.000008	0.019924	0.000008	0.019927	0.000007	0.019916	0.000008
D322734	0.019930	0.000009	0.019927	0.000008	0.019939	0.000007	0.019928	0.000009
D322736	0.019936	0.000008	0.019919	0.000008	0.019946	0.000008	0.019919	0.000008
D322741	0.019929	0.000008	0.019914	0.000010	0.019909	0.000008	0.019921	0.000007
D322742	0.019924	0.000008	0.019909	0.000007	0.019915	0.000007	0.019913	0.000009

In table 50, the results of the stability and homogeneity study for n-pentane are shown.

Table 50: Amount fractions and associated standard uncertainties of n-pentane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	0.020115	0.000017	0.020129	0.000017	0.020133	0.000008	0.020143	0.000008
D322699	0.020127	0.000017	0.020122	0.000017	0.020127	0.000008	0.020133	0.000009
D322700	0.020108	0.000016	0.020106	0.000017	0.020138	0.000009	0.020129	0.000008
D322701	0.020126	0.000016	0.020130	0.000016	0.020144	0.000010	0.020142	0.000009
D322705	0.020122	0.000017	0.020110	0.000017	0.020133	0.000008	0.020134	0.000009
D322707	0.020130	0.000018	0.020129	0.000017	0.020134	0.000008	0.020135	0.000009
D322718	0.020120	0.000017	0.020111	0.000017				
D322726	0.020098	0.000016	0.020105	0.000016	0.020125	0.000010	0.020123	0.000008
D322734	0.020117	0.000018	0.020113	0.000017	0.020138	0.000009	0.020138	0.000009
D322736	0.020121	0.000017	0.020109	0.000018	0.020142	0.000010	0.020136	0.000009
D322741	0.020104	0.000016	0.020104	0.000018	0.020116	0.000008	0.020132	0.000009
D322742	0.020101	0.000016	0.020096	0.000017	0.020113	0.000010	0.020115	0.000008

In table 51, the results of the stability and homogeneity study for methane are shown.

Table 51: Amount fractions and associated standard uncertainties of methane (type LNG) (cmol mol^{-1}).

Mixture	x_1	$u(x_1)$	x_2	$u(x_2)$	x_3	$u(x_3)$	x_4	$u(x_4)$
D322696	87.5220	0.0041	87.5240	0.0033	87.4980	0.0044	87.4900	0.0036
D322699	87.5090	0.0105	87.5110	0.0025	87.4800	0.0052	87.4920	0.0061
D322700	87.5150	0.0033	87.5330	0.0033	87.5270	0.0078	87.5140	0.0036
D322701	87.5050	0.0002	87.5140	0.0033	87.5120	0.0061	87.5170	0.0052
D322705	87.5120	0.0105	87.5110	0.0005	87.5250	0.0061	87.4960	0.0036
D322707	87.5120	0.0041	87.5310	0.0041	87.5070	0.0069	87.5180	0.0043
D322718	87.5220	0.0095	87.5220	0.0040				
D322726	87.5220	0.0058	87.5290	0.0067	87.5250	0.0097	87.4960	0.0044
D322734	87.5210	0.0086	87.5060	0.0123	87.4880	0.0052	87.4850	0.0052
D322736	87.5210	0.0050	87.5230	0.0033	87.5080	0.0061	87.4800	0.0069
D322741	87.5050	0.0025	87.5240	0.0059	87.4960	0.0061	87.5240	0.0043
D322742	87.5320	0.0058	87.5040	0.0040	87.5250	0.0029	87.4990	0.0044

B Degrees of equivalence

B.1 Low-calorific natural gas

In table 6, the reported results and the KCRVs for nitrogen are shown. The degrees of equivalence computed from these data are shown in table 52.

Table 52: Deviations due to batch inhomogeneity and degrees of equivalence for nitrogen (type IVa) (µmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	-4.6	6.4	-38	146	292	2.0
VNIIM	D322703	-4.1	7.2	-444	201	401	2.0
SMU	D322740	-11.2	12.8	-66	217	434	2.0
NIM	D322730	12.0	7.1	-190	183	366	2.0
NPL	D322694	14.2	7.0	-126	161	322	2.0
NMIA	D322744	-8.0	7.8	-117	136	271	2.0
BAM	D322738	-14.2	7.0	-42	137	274	2.0
GUM	D322721	-14.7	17.3	396	274	549	2.0
CMI	D322720	3.0	6.5	81	151	302	2.0
NMISA	D322702	1.1	6.3	-218	411	822	2.0
NMIJ	D322719	-2.6	6.4	-147	316	632	2.0
KRISS	D322706	0.7	7.8	-728	179	358	2.0
UME	D322708	10.1	7.1	221	179	359	2.0

In table 7 the reported results and the KCRVs for carbon dioxide are shown. The degrees of equivalence computed from these data are shown in table 53.

Table 53: Deviations due to batch inhomogeneity and degrees of equivalence for carbon dioxide (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	5.1	11.4	3.2	45.8	91.6	2.0
VNIIM	D322703	-8.3	15.6	-145.5	69.8	139.6	2.0
SMU	D322740	-5.8	10.8	-28.0	90.2	180.3	2.0
NIM	D322730	-3.9	12.0	-57.8	61.6	123.2	2.0
NPL	D322694	-14.3	11.7	-21.7	45.8	91.7	2.0
NMIA	D322744	10.9	10.0	15.8	43.5	87.1	2.0
BAM	D322738	-5.3	12.7	-39.8	51.8	103.7	2.0
GUM	D322721	9.4	11.0	136.0	127.0	254.1	2.0
CMI	D322720	-8.1	11.9	6.6	54.1	108.3	2.0
NMISA	D322702	6.5	12.7	17086.4	597.4	1194.7	2.0
NMIJ	D322719	9.3	11.3	981.4	97.3	194.6	2.0
KRISS	D322706	-3.7	15.4	-186.6	58.4	116.8	2.0
UME	D322708	10.3	14.4	76.0	58.3	116.6	2.0

In table 8 the reported results and the KCRVs for hydrogen are shown. The degrees of equivalence computed from these data are shown in table 54.

Table 54: Deviations due to batch inhomogeneity and degrees of equivalence for hydrogen (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	-13.3	6.9	-10.9	72.6	145.3	2.0
VNIIM	D322703	-9.9	6.7	-87.2	94.8	189.6	2.0
SMU	D322740	11.1	6.0	82.2	174.2	348.4	2.0
NIM	D322730	-10.3	5.9	7.4	78.8	157.6	2.0
NPL	D322694	17.7	7.2	-16.1	102.1	204.1	2.0
NMIA	D322744	-12.4	6.7	93.7	73.8	147.5	2.0
BAM	D322738	4.1	5.9	24.8	72.0	144.0	2.0
GUM	D322721	-5.7	6.2	-31.4	138.4	276.8	2.0
CMI	D322720	5.3	5.7	-222.4	120.7	241.5	2.0
NMISA	D322702	-14.6	7.4	99.9	637.4	1274.8	2.0
NMIJ	D322719	-19.7	6.8	-854.5	96.5	192.9	2.0
KRISS	D322706	12.6	6.9	-190.8	75.3	150.6	2.0
UME	D322708	11.1	6.3	62.0	72.3	144.7	2.0

In table 9 the reported results and the KCRVs for helium are shown. The degrees of equivalence computed from these data are shown in table 55.

Table 55: Deviations due to batch inhomogeneity and degrees of equivalence for helium (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	-2.2	1.7	6.2	10.0	20.0	2.0
VNIIM	D322703	-1.0	1.3	-17.4	15.2	30.4	2.0
SMU	D322740	2.9	1.5	-0.3	28.4	56.8	2.0
NIM	D322730	-1.3	1.4	-7.2	11.1	22.2	2.0
NPL	D322694	4.4	1.6	10.3	15.2	30.5	2.0
NMIA	D322744	-2.3	1.6	-3.8	10.2	20.4	2.0
BAM	D322738	1.3	1.4	3.2	9.4	18.7	2.0
GUM	D322721	-0.9	1.4	-12.6	17.3	34.7	2.0
CMI	D322720	1.6	1.3	19.9	23.2	46.3	2.0
NMISA	D322702	-2.7	1.5	100.6	142.4	284.8	2.0
NMIJ	D322719	-3.3	1.9	-62.5	11.9	23.7	2.0
KRISS	D322706	4.0	1.5	-39.5	11.4	22.8	2.0
UME	D322708	3.0	1.8	62.5	11.2	22.4	2.0

In table 10 the reported results and the KCRVs for ethane are shown. The degrees of equivalence computed from these data are shown in table 56.

Table 56: Deviations due to batch inhomogeneity and degrees of equivalence for ethane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	-0.2	4.5	-6.0	12.7	25.3	2.0
VNIIM	D322703	-2.7	6.9	-17.4	23.1	46.2	2.0
SMU	D322740	0.7	4.8	9.2	14.8	29.5	2.0
NIM	D322730	-1.6	5.0	-2.5	14.2	28.3	2.0
NPL	D322694	2.6	4.8	6.9	12.7	25.4	2.0
NMIA	D322744	1.1	4.2	4.7	12.0	23.9	2.0
BAM	D322738	0.5	5.9	-3.1	19.2	38.3	2.0
GUM	D322721	1.8	5.8	58.1	32.0	64.0	2.0
CMI	D322720	0.3	5.6	12.6	19.4	38.7	2.0
NMISA	D322702	3.3	5.5	-36.4	94.4	188.8	2.0
NMIJ	D322719	-2.8	5.3	-6.1	10.8	21.6	2.0
KRISS	D322706	-2.9	8.5	-41.6	16.7	33.5	2.0
UME	D322708	-1.9	5.0	-3.2	12.5	25.1	2.0

In table 11 the reported results and the KCRVs for propane are shown. The degrees of equivalence computed from these data are shown in table 57.

Table 57: Deviations due to batch inhomogeneity and degrees of equivalence for propane (type IVa) $\mu mol\,mol^{-1}$)

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.84	1.52	0.80	6.43	12.85	2.0
VNIIM	D322703	-0.22	1.49	-6.69	9.26	18.51	2.0
SMU	D322740	-0.40	1.87	4.47	8.89	17.77	2.0
NIM	D322730	0.16	1.67	-1.58	6.17	12.34	2.0
NPL	D322694	-0.69	1.50	-0.06	5.10	10.19	2.0
NMIA	D322744	0.72	1.34	-0.05	5.47	10.95	2.0
BAM	D322738	-1.89	1.39	-0.94	6.84	13.68	2.0
GUM	D322721	0.06	2.09	-6.04	12.96	25.92	2.0
CMI	D322720	0.35	1.71	14.73	8.02	16.04	2.0
NMISA	D322702	0.84	1.98	1.91	36.25	72.50	2.0
NMIJ	D322719	-0.42	1.79	-3.64	4.84	9.68	2.0
KRISS	D322706	-1.48	1.59	-18.12	6.44	12.87	2.0
UME	D322708	1.15	1.60	3.93	5.49	10.98	2.0

In table 12 the reported results and the KCRVs for iso-butane are shown. The degrees of equivalence computed from these data are shown in table 58.

Table 58: Deviations due to batch inhomogeneity and degrees of equivalence for iso-butane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.77	0.29	-0.37	2.08	4.15	2.0
VNIIM	D322703	0.30	0.32	-4.85	7.72	15.44	2.0
SMU	D322740	-0.51	0.26	0.97	5.82	11.64	2.0
NIM	D322730	0.49	0.31	0.79	3.10	6.20	2.0
NPL	D322694	-0.58	0.28	-0.60	3.95	7.90	2.0
NMIA	D322744	0.50	0.32	0.77	2.71	5.43	2.0
BAM	D322738	-0.67	0.28	0.04	2.03	4.06	2.0
GUM	D322721	0.69	0.36	71.78	8.69	17.38	2.0
CMI	D322720	-0.42	0.26	-1.10	7.24	14.48	2.0
NMIJ	D322719	0.77	0.31	-2.75	2.52	5.04	2.0
KRISS	D322706	-0.63	0.35	-8.90	3.50	7.00	2.0
UME	D322708	-0.12	0.36	3.59	2.73	5.46	2.0

In table 13 the reported results and the KCRVs for n-butane are shown. The degrees of equivalence computed from these data are shown in table 59.

Table 59: Deviations due to batch inhomogeneity and degrees of equivalence for n-butane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.79	0.31	2.51	2.78	5.55	2.0
VNIIM	D322703	0.19	0.33	-5.99	8.40	16.80	2.0
SMU	D322740	-0.78	0.32	2.97	6.08	12.17	2.0
NIM	D322730	0.40	0.39	-2.02	3.60	7.20	2.0
NPL	D322694	-0.54	0.33	-0.48	4.35	8.69	2.0
NMIA	D322744	0.50	0.34	0.46	3.27	6.54	2.0
BAM	D322738	-1.16	0.35	-1.67	2.77	5.54	2.0
GUM	D322721	0.66	0.36	4.51	8.42	16.84	2.0
CMI	D322720	-0.71	0.32	-0.11	7.93	15.85	2.0
NMISA	D322702	0.87	0.35	0.76	23.48	46.95	2.0
NMIJ	D322719	0.97	0.35	-7.77	3.10	6.20	2.0
KRISS	D322706	-0.67	0.39	-14.49	3.95	7.90	2.0
UME	D322708	-0.05	0.41	-0.78	3.28	6.56	2.0

In table 14 the reported results and the KCRVs for iso-pentane are shown. The degrees of equivalence computed from these data are shown in table 60.

Table 60: Deviations due to batch inhomogeneity and degrees of equivalence for iso-pentane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.22	0.24	-0.45	1.58	3.15	2.0
VNIIM	D322703	0.18	0.22	0.30	2.90	5.79	2.0
SMU	D322740	-0.25	0.21	-1.28	2.59	5.19	2.0
NIM	D322730	0.08	0.27	-0.10	1.77	3.54	2.0
NPL	D322694	-0.13	0.22	-0.23	1.76	3.53	2.0
NMIA	D322744	0.34	0.22	2.49	1.61	3.23	2.0
BAM	D322738	-0.13	0.21	0.00	1.59	3.18	2.0
GUM	D322721	0.09	0.21	-0.90	2.89	5.79	2.0
CMI	D322720	-0.26	0.27	0.73	2.09	4.19	2.0
NMIJ	D322719	0.42	0.28	-4.77	1.48	2.96	2.0
KRISS	D322706	0.03	0.23	-4.87	7.51	15.02	2.0
UME	D322708	-0.23	0.26	-1.39	1.61	3.23	2.0

In table 15, the reported results and the KCRVs for n-pentane are shown. The degrees of equivalence computed from these data are shown in table 61.

Table 61: Deviations due to batch inhomogeneity and degrees of equivalence for n-pentane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.23	0.41	0.73	1.34	2.68	2.0
VNIIM	D322703	-0.08	0.36	-0.62	2.36	4.71	2.0
SMU	D322740	-0.28	0.36	0.69	2.23	4.47	2.0
NIM	D322730	-0.15	0.46	-1.25	1.48	2.96	2.0
NPL	D322694	-0.17	0.43	0.24	1.62	3.23	2.0
NMIA	D322744	0.46	0.28	0.16	1.47	2.93	2.0
BAM	D322738	-0.18	0.28	0.67	1.65	3.30	2.0
GUM	D322721	0.37	0.40	3.73	1.96	3.92	2.0
CMI	D322720	-0.43	0.42	-1.27	1.97	3.94	2.0
NMISA	D322702	0.22	0.42	1.41	6.02	12.04	2.0
NMIJ	D322719	0.03	0.36	-0.90	1.28	2.55	2.0
KRISS	D322706	-0.21	0.36	-6.16	6.35	12.70	2.0
UME	D322708	-0.34	0.42	-0.16	1.55	3.10	2.0

In table 16, the reported results and the KCRVs for neo-pentane are shown. The degrees of equivalence computed from these data are shown in table 62.

Table 62: Deviations due to batch inhomogeneity and degrees of equivalence for neo-pentane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.18	0.21	0.45	1.32	2.64	2.0
VNIIM	D322703	0.22	0.19	-0.61	1.94	3.88	2.0
SMU	D322740	-0.11	0.20	3.33	2.78	5.56	2.0
NIM	D322730	-0.17	0.19	-0.22	1.46	2.93	2.0
NPL	D322694	-0.22	0.23	-0.51	1.74	3.48	2.0
NMIA	D322744	0.04	0.21	-0.58	1.47	2.94	2.0
BAM	D322738	-0.09	0.16	0.80	1.36	2.72	2.0
GUM	D322721	0.27	0.24	1.13	5.10	10.20	2.0
CMI	D322720	-0.14	0.17	3.75	2.79	5.58	2.0
NMIJ	D322719	0.12	0.18	-1.65	1.39	2.78	2.0
KRISS	D322706	-0.25	0.20	-2.14	5.07	10.13	2.0
UME	D322708	-0.34	0.21	-2.95	1.41	2.82	2.0

In table 17 the reported results and the KCRVs for n-hexane are shown. The degrees of equivalence computed from these data are shown in table 63.

Table 63: Deviations due to batch inhomogeneity and degrees of equivalence for n-hexane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.10	0.29	-1.40	1.59	3.18	2.0
VNIIM	D322703	0.04	0.23	0.92	3.36	6.72	2.0
SMU	D322740	-0.51	0.28	0.08	2.43	4.86	2.0
NIM	D322730	0.05	0.28	0.01	1.63	3.26	2.0
NPL	D322694	-0.23	0.31	1.25	1.81	3.61	2.0
NMIA	D322744	0.32	0.26	-1.11	4.28	8.55	2.0
BAM	D322738	-0.33	0.26	-0.81	1.70	3.40	2.0
GUM	D322721	0.41	0.24	2.35	2.12	4.25	2.0
CMI	D322720	-0.18	0.31	2.14	2.13	4.26	2.0
NMISA	D322702	0.36	0.25	4.36	6.05	12.11	2.0
NMIJ	D322719	0.72	0.26	-3.25	1.53	3.05	2.0
KRISS	D322706	-0.02	0.29	-5.01	5.13	10.27	2.0
UME	D322708	-0.42	0.30	-1.32	1.87	3.74	2.0

In table 18 the reported results and the KCRVs for methane are shown. The degrees of equivalence computed from these data are shown in table 64.

Table 64: Deviations due to batch inhomogeneity and degrees of equivalence for methane (type IVa) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322727	0.003	0.011	-0.145	0.051	0.102	2.0
VNIIM	D322703	0.014	0.011	0.045	0.038	0.076	2.0
SMU	D322740	0.000	0.009	-0.001	0.068	0.136	2.0
NIM	D322730	0.005	0.011	0.005	0.036	0.072	2.0
NPL	D322694	0.002	0.010	0.005	0.035	0.071	2.0
NMIA	D322744	-0.002	0.009	-0.012	0.040	0.080	2.0
BAM	D322738	-0.005	0.010	-0.003	0.032	0.063	2.0
GUM	D322721	-0.004	0.008	-0.062	0.051	0.101	2.0
CMI	D322720	-0.002	0.008	-0.005	0.034	0.068	2.0
NMISA	D322702	-0.002	0.008	-0.429	0.808	1.617	2.0
NMIJ	D322719	0.005	0.010	0.091	0.169	0.339	2.0
KRISS	D322706	-0.005	0.011	0.113	0.051	0.102	2.0
UME	D322708	-0.002	0.009	-0.025	0.083	0.167	2.0

B.2 High-calorific natural gas

In table 20, the reported results and the KCRVs for nitrogen are shown. The degrees of equivalence computed from these data are shown in table 65.

Table 65: Deviations due to batch inhomogeneity and degrees of equivalence for nitrogen (type LNG) (μmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	-0.6	3.5	2.4	9.2	18.4	2.0
VNIIM	D322705	1.8	2.0	-14.0	9.1	18.1	2.0
NIM	D322700	-4.0	3.8	30.8	9.3	18.5	2.0
NPL	D322741	3.3	0.9	-0.6	8.6	17.1	2.0
NMIA	D322718	-3.9	2.9	0.9	8.8	17.5	2.0
BAM	D322734	-3.2	3.4	4.4	9.1	18.3	2.0
GUM	D322699	-8.3	1.8	-15.5	8.4	16.8	2.0
CMI	D322707	-0.8	3.2	-22.4	9.6	19.3	2.0
NMISA	D322742	-5.5	2.5	-8.0	45.1	90.2	2.0
BFKH	D322726	-6.9	4.1	-5.3	8.9	17.8	2.0
NMIJ	D322736	-9.3	3.6	16.4	9.1	18.1	2.0
UME	D322701	-9.5	2.3	10.3	8.2	16.4	2.0

In table 21, the reported results and the KCRVs for carbon dioxide are shown. The degrees of equivalence computed from these data are shown in table 66.

Table 66: Deviations due to batch inhomogeneity and degrees of equivalence for carbon dioxide (type LNG) (μmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	0.06	0.12	0.57	0.96	1.92	2.0
VNIIM	D322705	-0.20	0.23	-0.73	1.12	2.25	2.0
NIM	D322700	0.15	0.15	-1.28	0.96	1.92	2.0
NPL	D322741	-0.07	0.11	-0.46	2.15	4.30	2.0
NMIA	D322718	0.05	0.16	-1.09	1.71	3.42	2.0
BAM	D322734	0.05	0.19	0.54	0.88	1.76	2.0
GUM	D322699	-0.09	0.15	-0.44	0.84	1.68	2.0
CMI	D322707	0.72	0.32	0.35	1.32	2.64	2.0
NMISA	D322742	0.19	0.18	-12.66	6.74	13.48	2.0
BFKH	D322726	-0.03	0.10	-0.90	1.29	2.58	2.0
NMIJ	D322736	0.43	0.13	1.39	0.85	1.69	2.0
UME	D322701	-0.03	0.07	0.90	1.01	2.02	2.0

In table 22, the reported results and the KCRVs for ethane are shown. The degrees of equivalence computed from these data are shown in table 67.

Table 67: Deviations due to batch inhomogeneity and degrees of equivalence for ethane (type LNG) (μmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	24.3	6.7	9.8	73.1	146.2	2.0
VNIIM	D322705	-36.2	23.2	-268.8	256.4	512.8	2.0
NIM	D322700	-13.6	7.3	-111.6	126.7	253.4	2.0
NPL	D322741	-31.7	7.0	15.6	113.6	227.1	2.0
NMIA	D322718	1.5	11.8	4.0	61.3	122.6	2.0
BAM	D322734	13.3	14.7	8.7	87.5	175.0	2.0
GUM	D322699	12.2	9.2	-36.9	404.0	808.0	2.0
CMI	D322707	-21.6	24.2	-385.6	114.6	229.2	2.0
NMISA	D322742	-40.1	19.2	-346.1	1147.3	2294.6	2.0
BFKH	D322726	-18.3	19.2	73.1	85.7	171.3	2.0
NMIJ	D322736	15.4	6.8	-105.0	86.4	172.9	2.0
UME	D322701	16.6	16.6	28.3	68.0	135.9	2.0

In table 23, the reported results and the KCRVs for propane are shown. The degrees of equivalence computed from these data are shown in table 68.

Table 68: Deviations due to batch inhomogeneity and degrees of equivalence for propane (type LNG) (μmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	7.2	3.0	-3.8	20.2	40.3	2.0
VNIIM	D322705	-3.4	4.8	-81.7	57.6	115.3	2.0
NIM	D322700	-7.7	3.7	-19.4	30.3	60.6	2.0
NPL	D322741	-8.3	4.0	-10.7	22.6	45.3	2.0
NMIA	D322718	0.2	2.7	-9.4	23.6	47.1	2.0
BAM	D322734	1.7	3.5	-2.6	20.7	41.4	2.0
GUM	D322699	5.1	5.3	-130.2	43.1	86.2	2.0
CMI	D322707	2.1	3.9	72.7	32.9	65.7	2.0
NMISA	D322742	-5.8	5.3	-75.0	224.6	449.2	2.0
BFKH	D322726	-3.1	5.9	7.9	20.0	40.0	2.0
NMIJ	D322736	5.9	5.3	159.9	22.7	45.4	2.0
UME	D322701	11.0	4.5	3.9	19.7	39.5	2.0

In table 24, the reported results and the KCRVs for iso-butane are shown. The degrees of equivalence computed from these data are shown in table 69.

Table 69: Deviations due to batch inhomogeneity and degrees of equivalence for iso-butane (type LNG) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	0.55	0.31	-0.09	1.44	2.87	2.0
VNIIM	D322705	-0.06	0.11	-0.49	5.15	10.30	2.0
NIM	D322700	-0.88	0.13	-0.57	2.21	4.43	2.0
NPL	D322741	-0.79	0.20	0.63	2.88	5.77	2.0
NMIA	D322718	0.24	0.16	1.46	3.24	6.48	2.0
BAM	D322734	0.27	0.14	0.13	1.48	2.97	2.0
GUM	D322699	0.57	0.17	1.87	6.11	12.22	2.0
CMI	D322707	0.06	0.21	6.38	5.15	10.30	2.0
BFKH	D322726	-0.64	0.26	1.09	2.79	5.59	2.0
NMIJ	D322736	0.03	0.20	-2.36	1.76	3.53	2.0
UME	D322701	0.76	0.15	0.69	1.57	3.14	2.0

In table 25, the reported results and the KCRVs for n-butane are shown. The degrees of equivalence computed from these data are shown in table 70.

Table 70: Deviations due to batch inhomogeneity and degrees of equivalence for n-butane (type LNG) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	0.52	0.12	0.44	2.19	4.38	2.0
VNIIM	D322705	-0.49	0.34	-4.41	7.80	15.59	2.0
NIM	D322700	-0.83	0.18	-3.58	2.85	5.70	2.0
NPL	D322741	-0.74	0.23	-0.45	3.33	6.66	2.0
NMIA	D322718	0.28	0.18	0.37	3.64	7.28	2.0
BAM	D322734	0.27	0.22	-3.20	2.26	4.53	2.0
GUM	D322699	0.34	0.18	-8.25	6.35	12.71	2.0
CMI	D322707	-0.02	0.12	4.12	5.40	10.79	2.0
NMISA	D322742	-0.80	0.24	38.49	17.93	35.87	2.0
BFKH	D322726	-0.59	0.36	1.68	2.90	5.79	2.0
NMIJ	D322736	0.25	0.35	-4.43	2.63	5.25	2.0
UME	D322701	0.74	0.23	0.35	2.29	4.59	2.0

In table 26, the reported results and the KCRVs for iso-pentane are shown. The degrees of equivalence computed from these data are shown in table 71.

Table 71: Deviations due to batch inhomogeneity and degrees of equivalence for iso-pentane (type LNG) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	0.12	0.04	0.03	0.72	1.44	2.0
VNIIM	D322705	0.04	0.04	0.66	1.13	2.25	2.0
NIM	D322700	-0.03	0.04	-0.18	0.70	1.39	2.0
NPL	D322741	-0.07	0.04	0.53	0.72	1.44	2.0
NMIA	D322718	0.12	0.06	1.94	0.72	1.45	2.0
BAM	D322734	0.05	0.04	-0.20	0.63	1.26	2.0
GUM	D322699	0.07	0.04	-3.57	1.17	2.33	2.0
CMI	D322707	0.10	0.04	2.89	0.78	1.57	2.0
NMISA	D322742	-0.11	0.03	-1.97	2.88	5.76	2.0
BFKH	D322726	-0.04	0.04	2.03	0.78	1.57	2.0
NMIJ	D322736	0.04	0.07	-3.54	0.66	1.32	2.0
UME	D322701	0.15	0.04	5.04	0.67	1.34	2.0

In table 27, the reported results and the KCRVs for n-pentane are shown. The degrees of equivalence computed from these data are shown in table 72.

Table 72: Deviations due to batch inhomogeneity and degrees of equivalence for n-pentane (type LNG) ($\mu mol\,mol^{-1}$).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	0.10	0.05	0.18	0.62	1.25	2.0
VNIIM	D322705	0.05	0.05	0.08	0.85	1.69	2.0
NIM	D322700	-0.02	0.07	-0.86	0.58	1.16	2.0
NPL	D322741	-0.06	0.06	0.06	0.62	1.24	2.0
NMIA	D322718	-0.08	0.12	0.37	0.70	1.40	2.0
BAM	D322734	0.08	0.05	0.09	0.51	1.03	2.0
GUM	D322699	0.04	0.05	0.49	0.77	1.54	2.0
CMI	D322707	0.08	0.06	-1.96	0.69	1.38	2.0
NMISA	D322742	-0.15	0.05	-1.06	2.04	4.09	2.0
BFKH	D322726	-0.06	0.05	0.19	0.69	1.38	2.0
NMIJ	D322736	0.08	0.06	-1.15	0.59	1.19	2.0
UME	D322701	0.14	0.06	2.39	0.56	1.13	2.0

In table 28, the reported results and the KCRVs for methane are shown. The degrees of equivalence computed from these data are shown in table 73.

Table 73: Deviations due to batch inhomogeneity and degrees of equivalence for methane (type LNG) (cmol mol^{-1}).

Lab	Mixture	β_j	$u(\beta_j)$	d_j	$u(d_j)$	$U(d_j)$	k_j
VSL	D322696	-0.0055	0.0085	-0.020	0.049	0.097	2.0
VNIIM	D322705	-0.0020	0.0050	0.032	0.032	0.064	2.0
NIM	D322700	0.0086	0.0056	-0.006	0.025	0.050	2.0
NPL	D322741	-0.0007	0.0059	0.004	0.027	0.053	2.0
NMIA	D322718	0.0084	0.0033	-0.019	0.032	0.064	2.0
BAM	D322734	-0.0145	0.0069	0.002	0.021	0.042	2.0
GUM	D322699	-0.0155	0.0084	0.003	0.049	0.097	2.0
CMI	D322707	0.0058	0.0047	0.018	0.024	0.048	2.0
NMISA	D322742	0.0015	0.0074	-0.412	0.812	1.625	2.0
BFKH	D322726	-0.0000	0.0082	-0.016	0.025	0.049	2.0
NMIJ	D322736	-0.0060	0.0084	-0.363	0.138	0.276	2.0
UME	D322701	-0.0023	0.0031	-0.010	0.038	0.075	2.0

C Measurement reports of the participating institutes

Measurement report BAM

Cylinder number: D322738 Hydrogen Enriched Natural Gas

normalised	Helium	Hydrogen	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	iso-Butane	n-Butane
x_{cert} / %	0,5027	3,0036	11,9792	78,8731	3,9999	0,7448	0,2982	0,19969	0,19996
$u(x_{cert})$ / %	0,0004	0,0018	0,0034	0,0062	0,0031	0,0016	0,0005	0,00009	0,00010
$u_{rel}(x_{cert})$	7,6E-04	6,1E-04	2,8E-04	7,9E-05	7,7E-04	2,1E-03	1,7E-03	4,4E-04	4,9E-04
$U_{rel}(x_{cert})$	1,5E-03	1,2E-03	5,6E-04	1,6E-04	1,5E-03	4,2E-03	3,4E-03	8,8E-04	9,8E-04

normalised	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane
x_{cert} / %	0,04941	0,04984	0,05022	0,04959
$u(x_{cert})$ / %	0,00006	0,00007	0,00011	0,00008
$u_{rel}(x_{cert})$	1,2E-03	1,3E-03	2,2E-03	1,6E-03
$U_{rel}(x_{cert})$	2,5E-03	2,7E-03	4,4E-03	3,3E-03

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

Background

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

Choice of method

For the determination of the 13 compounds the method of choice is GC with TCD or FID detection. Although FID could provide smaller uncertainties for the hydrocarbons, it was decided at BAM to use the Siemens Maxum II gas analyser during the entire campaign, which is equipped with TCD detection only.

Sample: labeling, packing, pre-information

The sample was provided by Westfalen AG in a 5-L cylinder with barcode 27600502931588-04 and cylinder number D322738 equipped with a valve which has DIN 477 thread No. 14 (test gas). The initial (and final) pressure was not measured.

Sample pretreatment

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

Devices used and flushing

A DIN 477 No. 14 (test gas)-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 a similar assembly was 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.

Measurement instruments & settings

A specially designed Siemens Maxum II process gas analyser was used applying "method 1" (a standard method to certify gas samples) which executes a sequence of 44 consecutive injections. The oven was set to 60 °C and 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.

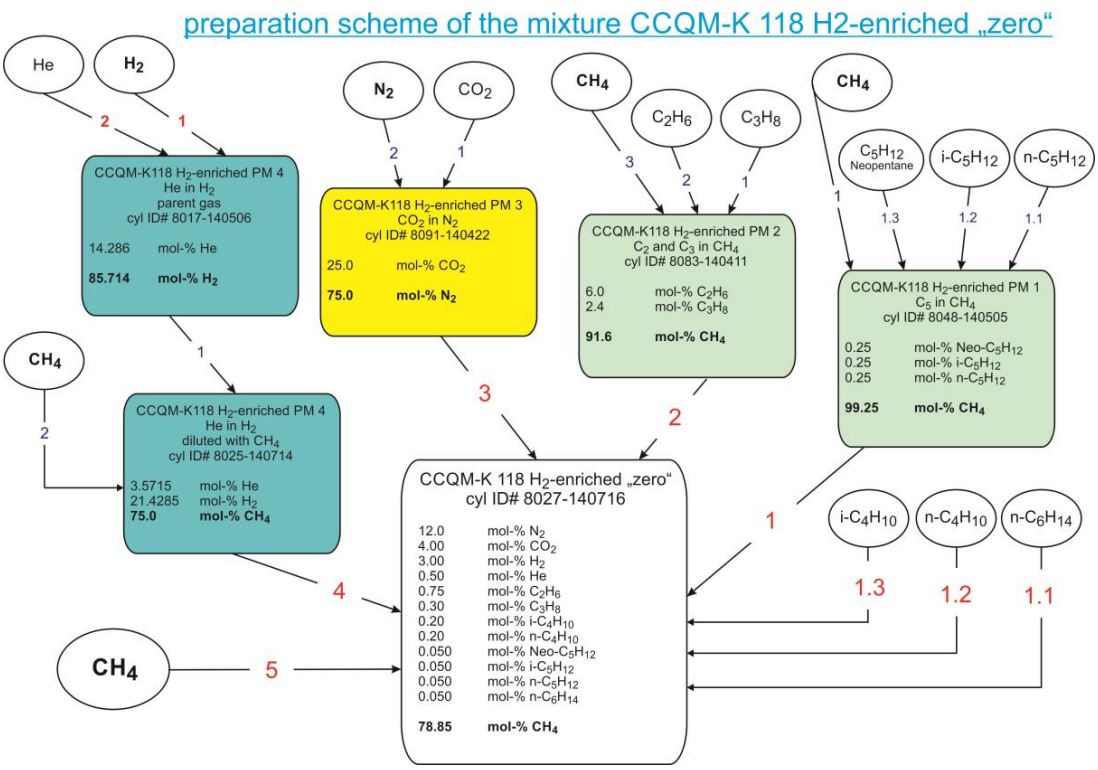
Channel 4 for propene and propane with Sorbitolchrom, TCEPCarbonblack and TCEPUnibeads columns.

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

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

Calibration

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

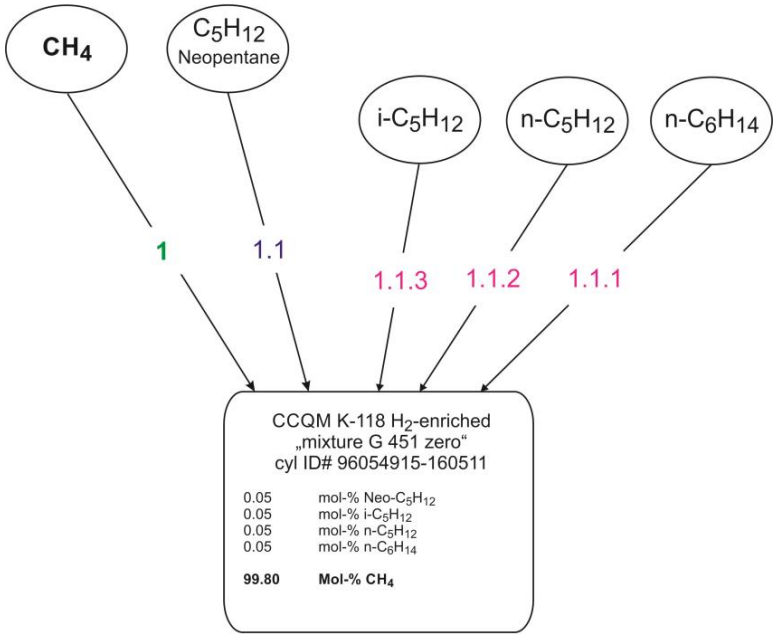
Final mixture
1.1 2.02 g n-C_6H_{14}
1.2 5.46 g n-C_4H_{10}

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

1.3 5.46 g i-C_4H_{10} 1 bar Total: 876.0 g
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

As the validation of the three gases showed a small deviation 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) 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.

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 C5 and C6 only) with three sequences were conducted. In each campaign, the sequences were portioned on two different days.

The calibration follows the two point calibration with bracketing (TPC) as basically described in ISO 12963. The practical implementation is briefly described and illustrated below with numbers for (an arbitrary measurement of propane. All other numbers are also available but stored in a big EXCEL spreadsheet.

From the three recorded measurements for each gas, the mean value (MW) and standard deviation (Stdev) (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_{zert} / %	0,27472
	$u(x_{zert})$ / %	0,00004
8056-140922	$u_{rel}(x_{zert})$	1,5E-04

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

bracketing calculation is performed to obtain the amount of substance fraction (Kuvernwert) 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 about equally (i.e. 38 % + 27 % + 32 %) form 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

As there were 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 sequence are compatible i.e. agree within their uncertainty. The three individual results are 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.)

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 used.

Raw data: 2019-07-18; for more details see \CCQM-K118_H2_enriched\Excel-Daten\3. Durchgang_7-2019

Results from the measurement campaign

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} / %	0,5027	3,0037	11,9797	78,8764	4,0000	0,7448	0,2982	0,19970	0,19997
$u(x_{cert})$ / %	0,0004	0,0017	0,0017	0,0249	0,0030	0,0016	0,0005	0,00007	0,00008
$u_{rel}(x_{cert})$	7,2E-04	5,7E-04	1,4E-04	3,2E-04	7,6E-04	2,1E-03	1,7E-03	3,6E-04	4,2E-04
$U_{rel}(x_{cert})$	1,4E-03	1,1E-03	2,9E-04	6,3E-04	1,5E-03	4,2E-03	3,4E-03	7,2E-04	8,4E-04

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane	Sum
x_{cert} / %	0,04941	0,04984	0,05022	0,04960	100,0042
$u(x_{cert})$ / %	0,00006	0,00007	0,00011	0,00008	0,0253
$u_{rel}(x_{cert})$	1,2E-03	1,3E-03	2,2E-03	1,6E-03	2,5E-04
$U_{rel}(x_{cert})$	2,4E-03	2,6E-03	4,3E-03	3,2E-03	5,1E-04

Consolidated results

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} / %	0,5027	3,0036	11,9792	78,8731	3,9999	0,7448	0,2982	0,19969	0,19996
$u(x_{cert})$ / %	0,0004	0,0018	0,0034	0,0062	0,0031	0,0016	0,0005	0,00009	0,00010
$u_{rel}(x_{cert})$	7,6E-04	6,1E-04	2,8E-04	7,9E-05	7,7E-04	2,1E-03	1,7E-03	4,4E-04	4,9E-04
$U_{rel}(x_{cert})$	1,5E-03	1,2E-03	5,6E-04	1,6E-04	1,5E-03	4,2E-03	3,4E-03	8,8E-04	9,8E-04

	neo-Pentane	iso-Pentane	n-Pentane	n-Hexane	Sum
x_{cert} / %	0,04941	0,04984	0,05022	0,04959	100,0000
$u(x_{cert})$ / %	0,00006	0,00007	0,00011	0,00008	0,0081
$u_{rel}(x_{cert})$	1,2E-03	1,3E-03	2,2E-03	1,6E-03	8,1E-05
$U_{rel}(x_{cert})$	2,5E-03	2,7E-03	4,4E-03	3,3E-03	1,6E-04

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

Remarks

The results obtained here are in very good agreement (i.e., abs(k) < 0,2) with measurements obtained in the similar 2018 campaign and also consistent to measurements (i.e., abs(k) < 0,5) obtained during the initial campaign in 2016.

First revision 2019-09-06: improved uncertainties for higher hydrocarbons (C4 to C6) due to new measurements with FID; new results are consistent with previous results

Second revision 2020-02-20: details for measurement and data treatment added; values unchanged.

Additional information

Customer:	VSL, CCQM-K118 H2-enriched
PAZ-No.	-
Sample arrival:	2015
Internal No.:	\CCQM-K118_H2_enriched\Excel-Daten\3. Durchgang_7-2019
Sample No.:	cylinder with barcode 27600502931588-04 and cylinder number D322738
Task:	Determination of amount-of-substance fractions
Period of measurement:	2019-07-15/17, 2019-09-05, 2019-09-06
Location:	Building AH 08.05 Room O1.285
Method:	GC with TCD and FID

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 report BAM LNG-type Natural Gas

Cylinder number: D322734

normalised	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	Isobutane	n-Butane	Isopentane	n-Pentane
x_{cert} / %	0,12204	87,51836	0,01995	10,00273	1,99943	0,14919	0,14830	0,01989	0,02010
$u(x_{cert})$ / %	0,00036	0,00740	0,00003	0,00683	0,00120	0,00009	0,00009	0,00002	0,00002
$u_{rel}(x_{cert})$	3,0E-03	8,5E-05	1,6E-03	6,8E-04	6,0E-04	5,7E-04	6,0E-04	9,1E-04	1,0E-03
$U_{rel}(x_{cert})$	5,9E-03	1,7E-04	3,2E-03	1,4E-03	1,2E-03	1,1E-03	1,2E-03	1,8E-03	2,0E-03

In the bottom line, the expanded relative measurement uncertainty $U = u_c \cdot k$ with $k = 2$ according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement (GUM).

Background

CCQM-K118 is an international interlaboratory comparison for energy gases organized by VSL and BAM, respectively. The study covers a H_2-enriched gas and another gas of LNG-type. This report provides the results of BAM as a participant for the LNG-type gas.

Choice of method

Gas chromatography was the method chosen for the determination of the entire compounds. Two different analyzers were used. The first GC was a Siemens Maxum II process GC equipped with multiple channels (12 in total for 6 trains) but exclusively TCD detection. The other was a two-channel Thermo Scientific Trace 1310 analytical model with TCD, FID, and methanizer option. Carbon dioxide as well as propane, isobutane, butane, isopentane, and pentane had to be analyzed also on that machine, since the concentrations were below the operation range of the TCD. Carbon dioxide had to be transformed by the methanizer.

Sample: labeling, packing, pre-information

The sample was provided by Westfalen AG in a 5-L cylinder with barcode 27600502931573-02 and cylinder number D322734 equipped with a valve which has DIN 477 thread No. 14 (test gas). The initial (and final) pressure was not measured.

Sample pretreatment

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

Devices used and flushing

A DIN 477 No. 14 (test gas)-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 a similar assembly was used. The assembly for the cylinders was not changed during the entire measuring campaign.

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

Measurement instruments & settings

The Siemens Maxum II process GC is specifically configured for the analysis of natural gas mixtures. Each channel is equipped with packed columns and an individual detector. The so called “method 1” (that is the standard method to certify natural gas samples which executes a preset sequence of 44 consecutive injections and operates in isothermal mode at 60 °C) was applied.

The measurement campaign on the Trace 1310 analyzer applying the same sequence consisted of two different cycles to achieve results with better uncertainties. In the first cycle, the carbon dioxide was determined by an FID after methanization. In the second cycle, the alkanes (C3 and larger) were analyzed on the hydrocarbon channel equipped with FID. Here, a temperature program was used that had been optimized before.

The operational procedures follow validated protocols that are monitored by BAM’s quality management system.

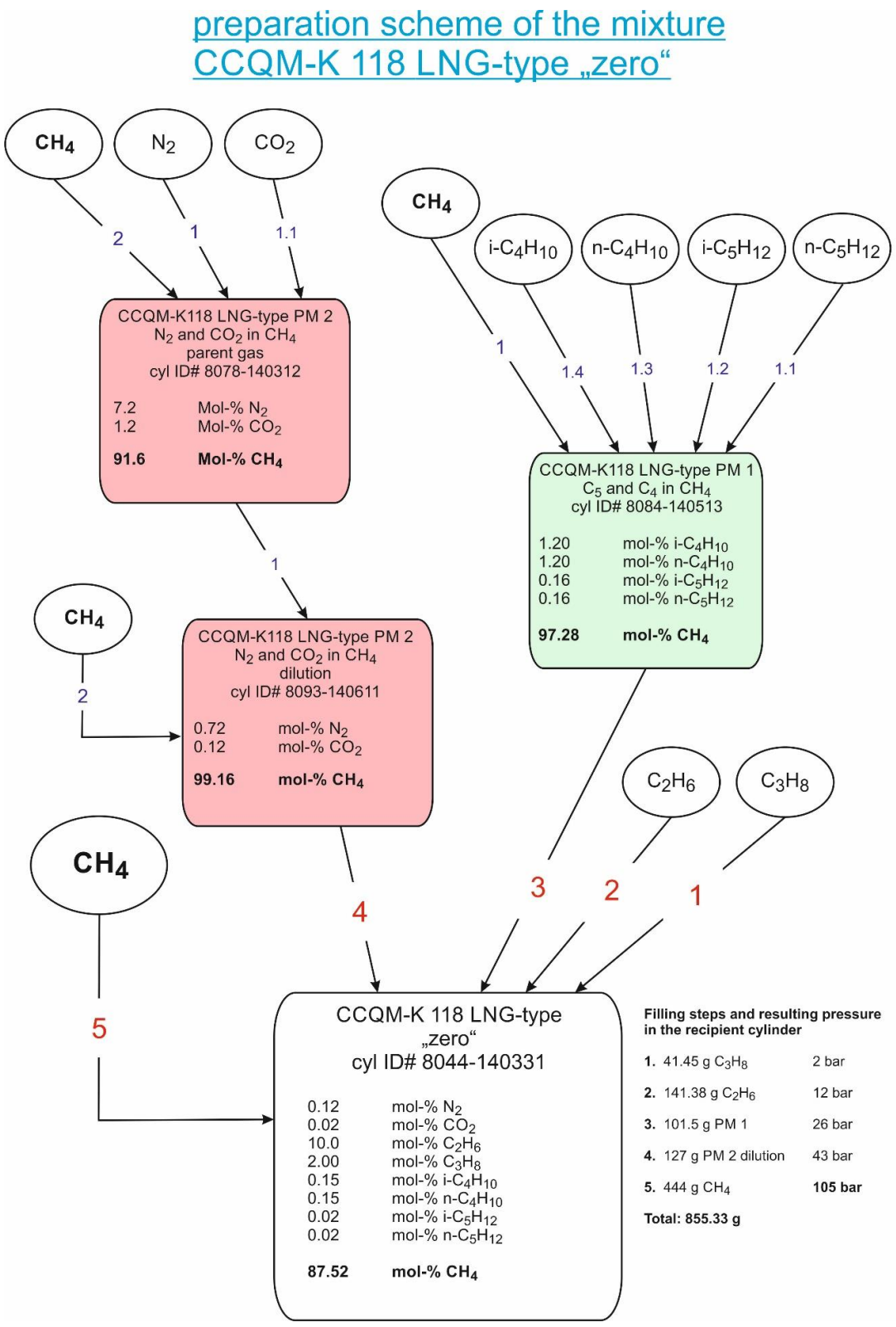
Calibration

Three calibration gases were prepared from gases of the highest commercially available purity by a gravimetric method according to DIN EN ISO 6142-1:2015 [1].

The composition of these gases represents a pair of “bracketing gases” with a composition + 5 % and – 5 % of the nominal composition as well as a sample of the nominal composition (“zero” sample) that has been agreed upon by CCQM. The following scheme exemplarily shows the preparation procedure of the zero sample (nominal composition).

Our gravimetric filling method operates exclusively with pressure differences to avoid any contamination (if movable parts, for example, in the use of compressors, get in contact with the gas). Here, three premixtures (PM) are required. The use of premixtures is to ensure safety during the operation and to implement the required uncertainty in the composition. Consecutive filling steps are numbered by “1, 2, …, etc.”, a subdivision “1.1, 1.2, 1.3, …” indicates that these compounds are introduced from smaller cylinders with “1” as the purging gas.

The filling sequence for the final mixture and the resulting pressure in the recipient cylinder are given in the scheme.



The composition of the calibration gases was:

		Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	Isobutane	n-Butane	Isopentane	n-Pentane
Cyl ID # 8022-140903	x_{cert} / %	0,11293	88,430354	0,018818	9,280201	1,845319	0,137957	0,139026	0,018543	0,018430
	$u(x_{cert})$ / %	0,000075	0,001503	0,000043	0,000464	0,000560	0,000015	0,000035	0,000011	0,000011
	$u_{rel}(x_{cert})$	6,8E-04	1,7E-05	2,3E-03	5,0E-05	3,0E-04	1,1E-04	2,6E-04	5,9E-04	5,9E-04
	$U_{rel}(x_{cert})$	1,4E-03	3,4E-05	4,5E-05	1,0E-04	6,1E-04	2,2E-04	5,1E-04	1,2E-03	1,2E-03

		Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	Isobutane	n-Butane	Isopentane	n-Pentane
Cyl ID# 8057-140903	x_{cert} / %	0,129302	86,616490	0,021620	10,715975	2,152895	0,159804	0,160886	0,021403	0,021558
	$u(x_{cert})$ / %	0,000070	0,001659	0,000039	0,000476	0,000628	0,000010	0,000041	0,000013	0,000013
	$u_{rel}(x_{cert})$	5,4E-04	1,9E-05	1,8E-03	4,4E-05	2,9E-04	6,4E-05	2,5E-04	6,0E-04	5,9E-04
	$U_{rel}(x_{cert})$	1,1E-03	3,8E-05	3,6E-03	8,9E-05	5,8E-04	1,3E-04	5,1E-04	1,2E-03	1,2E-03

Detailed weighing data for each mixture and each pre-mixture are deposited at BAM.

In a measurement campaign prior to the investigation of the sample, the sets of calibration gases (two “bracket gases” and a “zero” sample that displays the targeted composition) were found to be consistent.

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 analyzers at BAM.

Measurement outline

The analysis was executed according to the bracketing method [2].

In advance of a measurement sequence, the two calibration gases C1 (ID 8022) & C2 (ID 8057) and the sample S (ID 27600502931573-02) were connected to the GC. Governed by 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 (in total 44), from which only the last three were used for data evaluation. A complete sequence runs over a period of four hours on the Maxum process GC, six hours on the Trace 1310 for the CO_2 analysis, and six and a half hours on the Trace 1310 for the analysis of the alkanes.

Overall, three sequences were run on the Maxum and another six (three for CO_2 and three for the alkanes, respectively) on the Trace 1310. In each campaign, the sequences were portioned on two different days.

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. In the GC analysis, the main source of uncertainty is the precision of the applied detector.

The calculations were done according to the procedures recommended by GUM [3]. "*u*" stands for the uncertainty ($k = 1$), "*U*" for the expanded uncertainty ($k = 2$). See also the Tables.

Raw data: 2019-08-14, 2019-09-02, 2019-09-03;

for more details see: … \CCQM-K118_LNG\Excel-Daten\8022_D322734_8057_Gesamtauswertung

Results from the measurement campaign

From the direct measurement (i.e., not normalized) of all compounds the result is as follows. The results for CO_2 as well as propane, isobutane, n-butane, isopentane, and pentane were determined using the Trace 1310 GC (FID, methanizer for CO_2), the results for nitrogen, ethane and methane were determined using the Maxum II process GC (TCD).

	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	Isobutane	n-Butane	Isopentane	n-Pentane
X_{cert} / %	0,12205	87,52121	0,01995	10,00306	1,99949	0,14920	0,14830	0,01989	0,02011
$u(x_{cert})$ / %	0,00036	0,04019	0,00003	0,00614	0,00091	0,00006	0,00007	0,00002	0,00002
$u_{rel}(x_{cert})$	2,9E-03	4,6E-04	1,5E-03	6,1E-04	4,5E-04	4,1E-04	4,4E-04	8,1E-04	9,1E-04
$U_{rel}(x_{cert})$	5,9E-03	9,2E-04	3,1E-03	1,2E-03	9,1E-04	8,1E-04	8,9E-04	1,6E-03	1,8E-03

	Sum
X_{cert} / %	100,0033
$u(x_{cert})$ / %	0,0407
$u_{rel}(x_{cert})$	4,1E-04
$U_{rel}(x_{cert})$	8,1E-04

Consolidated results

The customers usually request normalized values (i.e., sum = 100.000) that almost do not change the values. However, the uncertainty of the main component (methane) becomes further reduced by this procedure.

	Nitrogen	Methane	Carbon-dioxide	Ethane	Propane	Isobutane	n-Butane	Isopentane	n-Pentane
x_{cert} / %	0,12204	87,51836	0,01995	10,00273	1,99943	0,14919	0,14830	0,01989	0,02010

$u(x_{cert})$ / %	0,00036	0,00740	0,00003	0,00683	0,00120	0,00009	0,00009	0,00002	0,00002
$u_{rel}(x_{cert})$	3,0E-03	8,5E-05	1,6E-03	6,8E-04	6,0E-04	5,7E-04	6,0E-04	9,1E-04	1,0E-03
$U_{rel}(x_{cert})$	5,9E-03	1,7E-04	3,2E-03	1,4E-03	1,2E-03	1,1E-03	1,2E-03	1,8E-03	2,0E-03

	Sum
x_{cert} / %	100,0000
$u(x_{cert})$ / %	0,0102
$u_{rel}(x_{cert})$	1,0E-04
$U_{rel}(x_{zert})$	2,0E-04

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

Remarks and references

The results obtained here are in very good agreement (i.e., abs(k) < 0,2) with measurements obtained in the similar 2018 campaign and also consistent to measurements (i.e., abs(k) < 0,5) obtained during the initial campaign in 2016.

[1] ISO 6142-1. Gas analysis – Preparation of calibration gas mixtures – Part I: gravimetric method for Class I mixtures, Geneva 2015.

[2] ISO 12963. Gas analysis – Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration, Geneva 2017.

[3] JCGM 100. Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM), BIPM 2008.

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 GC have been performed by Jeannette Pelchen, those using the Trace 1310 GC by Dr. Dirk Tuma. Reporting and calculations have been performed by Dr. Heinrich Kipphardt.

Appendix: Purity Tables with typical impurities

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	Air Liquide						
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
	i-Butane				99,97700	0,00690	6,9E-05

Material							
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	Air Liquide						
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	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

Measurement report BFKH

Cylinder number: D322726 LNG-type Natural Gas

NMI submitted values

Cylinder Identification number : **D322726** Component	Result x %(n/n)	Expanded Measurement Uncertainty U (k=2) %(n/n)
Nitrogen	0.1207	0.0005
Carbon dioxide	0.0198	0.0002
Ethane	10.006	0.013
Propane	2.000	0.002
iso-Butane	0.1492	0.0005
n-Butane	0.1487	0.0004
iso-Pentane	0.0201	0.0001
n-Pentane	0.0201	0.0001
Methane	87.515	0.028

Measurement No1

Date: 27.03.2019 Component	Result x %(n/n)	Expanded Measurement Uncertainty U (k=2) %(n/n)
Nitrogen	0.1195	0.0012
Carbon dioxide	0.0202	0.0002
Ethane	10.012	0.038
Propane	1.999	0.006
iso-Butane	0.1492	0.0007
n-Butane	0.1488	0.0005
iso-Pentane	0.0200	0.0001
n-Pentane	0.0201	0.0001
Methane	87.511	0.053

Measurement No2

Date: 28.03.2019 Component	Result x %(n/n)	Expanded Measurement Uncertainty U (k=2) %(n/n)
Nitrogen	0.1210	0.0006
Carbon dioxide	0.0196	0.0003
Ethane	10.000	0.004
Propane	2.000	0.001
iso-Butane	0.1489	0.0005
n-Butane	0.1484	0.0008
iso-Pentane	0.0201	0.0002
n-Pentane	0.0201	0.0002
Methane	87.523	0.020

MeasurementNo3

Date: 02.04.2019 Component	Result x %(n/n)	Expanded Measurement Uncertainty U (k=2) %(n/n)
Nitrogen	0.1215	0.0004
Carbon dioxide	0.0196	0.0003
Ethane	10.007	0.011
Propane	2.002	0.002
iso-Butane	0.1496	0.0011
n-Butane	0.1490	0.0008
iso-Pentane	0.0201	0.0001
n-Pentane	0.0202	0.0002
Methane	87.512	0.063

Calibration standard

Cylinder Identification Number: OMH134

Component	x %(n/n)	Expanded Measurement Uncertainty U (k=2) %(n/n)
Nitrogen	0.11983	0.0001
Carbon dioxide	0.020819	0.000025
Ethane	10.0528	0.0031
Propane	1.99678	0.00083
iso-Butane	0.14858	0.00013
n-Butane	0.14372	0.00014
iso-Pentane	-	-
n-Pentane	-	-
Methane	87.5174	0.0031

Method of preparation of the standard

Four mixtures were prepared before:

	Cylinder No	Composition	Component	g	Component	g
1.	OMH23	8.4 %(n/n) iso-Butane/ Methane	iso-Butane	63.3140	Methane	190.5387
2.	OMH31	8.8 %(n/n) n-Butane/ Methane	n-Butane	45.7418	Methane	131.1495
3.	OMH06	6 %(n/n) Nitrogen/ Methane	Nitrogen	30.0754	Methane	270.1350
4.	OMH55	1.3%(n/n) Carbon dioxide/Methane	Carbon dioxide	15.3340	Methane	414.2013

Weighing data of preparation of the standard

Step	Component	g
1.	Mixture 1	13.5900
2.	Mixture 2	12.6786

3.	Mixture 3	13.0754
4.	Mixture 4	10.0700
5.	Propane	34.5570
6.	Ethane	118.6366
7.	Methane	509.7834

Parent gases

Gas	Quality	Supplier
iso-Butane	99.95	Messer
n-Butane	99.95	Messer
Nitrogen	99.9999	Messer
Carbon dioxide	99.998	Siad
Propane	99.95	Messer
Ethane	99.95	Air Liquide
Methane	99.995	Messer

Verification measures confirmed the gravimetric method validity, their results were within the stated uncertainty of the standard in case of each components.

Instrumentation

HP 6890 GC-TCD/FID with two parallel coloumns:

to TCD: Restek Haysep A 8.8 m x 0.75 mm Sulfinert SST, Pressure in 10 bar He,

to FID: Restek Porapak PS 4.4 m x0.75 mm Sulfinert SST, Pressure in 4.5 bar He.

Isoterm method at 180 ^{0}C.

Calculation

The result came from the area data of the two parallel detectors. The bridge component was the Propane. *iso*-Pentane and *n*-Pentane results were calculated from the signs of *iso*-Butan and *n*-Butan of FID detector, which gives CH-proportional sign as were thoroughly examined previously.

10-10 sample injections were in case of the standard and the sample during the same run with 26 s differents. After the excluding the outliers, the 5-5 remained area data were used for the calculation.

The standard uncertainty of x_i component can be expressed as

$$u^2(x_i) = u^2_{xi,meas} + u^2_{sti} + u^2_{sti,meas} \quad (1)$$

$$U(x_i) = k \times u(x_i) \quad (2)$$

x_i amount-of-substance fraction of natural gas i component

$u_{xi,meas}$ uncertainty of measurements of natural gas i component

u_{sti} uncertainty of calibration standard value of i component

$u_{sti,meas}$ uncertainty of measurements of calibration standard i component

$U_{i,x}$ stated uncertainty of laboratory, at 95 % level of confidence (µmol/mol)

k assigned coverage factor for degree of equivalence

The table shows the detailed results in case of measurement made at 27.03.2019.

Component	x_i	$u_{xi,meas}$	u_{sti}	$u_{sti,meas}$	k	$U(x_i)$	$U(x_i)$
	%(n/n)	rel	rel	rel		rel	%(n/n)
Nitrogen	0.1195	0.00244	0.00083	0.0045	2	1.01 %	0.0012
Carbon dioxide	0.0202	0.0016	0.00120	0.0039	2	0.86 %	0.0002
Ethane	10.012	0.0019	0.00031	0.0001	2	0.38 %	0.038
Propane	1.999	0.0014	0.00042	0.0003	2	0.29 %	0.006
iso-Butane	0.1492	0.0017	0.00087	0.0014	2	0.45 %	0.0007
n-Butane	0.1488	0.0011	0.00097	0.0013	2	0.36 %	0.0005
iso-Pentane	0.0200	0.0026	0.00087	0.0014	2	0.54 %	0.0001
n-Pentane	0.0201	0.0026	0.00097	0.0013	2	0.54 %	0.0001
Methane	87.511	0.0001	0.00004	0.0003	2	0.06 %	0.053

The table shows the detailed results in case of measurement made at 28.03.2019.

Component	x_i	$u_{xi,meas}$	u_{sti}	$u_{sti,meas}$	k	$U(x_i)$	$U(x_i)$
	%(n/n)	rel	rel	rel		rel	%(n/n)
Nitrogen	0.1210	0.00178	0.00083	0.00139	2	0.46%	0.0006
Carbon dioxide	0.0196	0.00211	0.00120	0.00850	2	1.76%	0.0003

Ethane	10.000	0.00006	0.00031	0.00011	2	0.04%	0.0040
Propane	2.000	0.00017	0.00042	0.00007	2	0.06%	0.0011
iso-Butane	0.1489	0.00140	0.00087	0.00108	2	0.36%	0.005
n-Butane	0.1484	0.00247	0.00097	0.00132	2	0.56%	0.0008
iso-Pentane	0.0201	0.00140	0.00087	0.00623	2	1.25%	0.0002
n-Pentane	0.0201	0.00247	0.00097	0.00421	2	0.85%	0.0002
Methane	87.523	0.00008	0.00004	0.00008	2	0.02%	0.020

The table shows the detailed results in case of measurement made at 02.04.2019.

Component	x_i	$u_{xi,meas}$	u_{sti}	$u_{sti,meas}$	k	$U(x_i)$	$U(x_i)$
	%(n/n)	rel	rel	rel		rel	%(n/n)
Nitrogen	0.1215	0.00052	0.00083	0.00144	2	0.32%	0.0004
Carbon dioxide	0.0196	0.00544	0.00120	0.00546	2	1.55%	0.0003
Ethane	10.007	0.00030	0.00031	0.00045	2	0.11%	0.0112
Propane	2.002	0.00029	0.00042	0.00046	2	0.12%	0.0023
iso-Butane	0.1496	0.00081	0.00087	0.00367	2	0.75%	0.0011
n-Butane	0.1490	0.00111	0.00097	0.00250	2	0.55%	0.0008
iso-Pentane	0.0201	0.00337	0.00087	0.00367	2	0.68%	0.0001
n-Pentane	0.0202	0.00456	0.00097	0.00250	2	0.92%	0.0002
Methane	87.512	0.00027	0.00004	0.00024	2	0.07%	0.063

The submitted value of the component came from the average of the three measurements. The uncertainty of this value calculated from the root of sum of the independent uncertainty's square by divided 3.

Measurement report NMISA

Cylinder number: D32 2702 Hydrogen Enriched Natural Gas

Cylinder number: D32 2742 LNG-type Natural Gas

Calibration Standards

The calibration standards were prepared gravimetrically according to ISO 6142 at NMISA.The impurities in all pure gases were determined before use by GC-FID and PDHID except for n-butane, iso-pentane, n-pentane and n-hexane. The manufacture specification was used to estimate uncertainty in high pure n-butane, iso-pentane, n-pentane and n-hexane. Table **1** to **13** shows the purity tables of the starting materials including the premixtures.

Table 1. Purity table with uncertainties for the nominally pure CH_4 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
Ar	0.26	0.15
C_2H_6	0.065	0.037
CH_4	999993.173	1.413
CO_2	0.054	0.031
H_2	0.725	0.079
H_2O	2.5	1.4
N_2	3.114	0.025
O_2	0.109	0.063

Table 2. Purity table with uncertainties for the nominally pure N_2 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
Ar	128.3720	5.7941
C_2H_6	0.0648	0.0374
CH_4	0.0069	0.0040
CO	0.0436	0.0252
CO_2	0.0544	0.0314
H_2	0.5000	0.2887
H_2O	0.0100	0.0058
N_2	999870.9430	5.8015
O_2	0.0050	0.0029

Table 3. Purity table with uncertainties for the nominally pure CO_2 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
Ar	0.220	0.011
C_2H_6	0.006	0.003
CH_4	4.270	0.640
CO	0.022	0.013
CO_2	999172.257	41.000
H_2	0.040	0.002
H_2O	0.026	0.015
N_2	823.000	41.200

Table 4. Purity table with uncertainties for the nominally pure H_2 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CO	0.25	0.14
CO_2	0.25	0.14
CH_4	0.25	0.14
O_2	1.00	0.58
H_2O	1.00	0.58
N_2	2.50	1.44
H_2	999989.50	1.68

Table 5. Purity table with uncertainties for the nominally premix He in CH_4 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CH_4	950550.720	19.025
He	49442.784	18.982
N_2	2.963	0.024
H_2O	2.377	1.331
H_2	0.692	0.075
Ar	0.247	0.143
O_2	0.104	0.060

C_2H_6	0.062	0.035
CO_2	0.052	0.029
CO	0.001	0.000
CH_4	950550.720	19.025
He	49442.784	18.982

Table 6. Purity table with uncertainties for the nominally C_2H_6 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
C_2H_6	999992.50	2.18
CO	0.50	0.29
CO_2	0.50	0.29
N_2	1.50	0.87
O_2	0.50	0.29
C_xH_y	3.00	1.73
H_2O	1.50	0.87

Table 7. Purity table with uncertainties for the nominally C_3H_8 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
C_2H_6	120.00	6.00
propene	100.00	57.70
propane	998567.96	77.30
CO_2	2.50	1.44
CH_4	2.04	0.10
H_2	1000.00	100.00
H_2O	2.50	1.44
N_2	200.00	10.00
O_2	5.00	2.89

Table 8. Purity table with uncertainties for the nominally n-C_4H_{10} gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)

i-butane	360.00	18.00
C_2H_6	0.25	0.14
n-pentane	0.25	0.14
propane	122.00	6.10
H_2O	0.01	0.01
N_2	9500.00	475.00
n-butane	990175.00	499.00

Table 9. Purity table with uncertainties for the nominally iso-C_5H_{12} gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
H_2O	20.00	11.50
i-pentane	990000.00	11.50

Table 10. Purity table with uncertainties for the nominally n-C_5H_{12} gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
H_2O	5.00	2.89
n-pentane	990000.00	2.89

Table 11. Purity table with uncertainties for the nominally n-C_6H_{14} gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
H_2O	2000.00	1150.00
n-hexane	990000.00	1154.70

Table 12. Purity table with uncertainties for the nominally premix of He in CH_4 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CH_4	950550.720	19.025
He	49442.784	18.982
N_2	2.963	0.024

H_2O	2.377	1.331
H_2	0.692	0.075
Ar	0.247	0.143
O_2	0.104	0.060
C_2H_6	0.062	0.035
CO_2	0.052	0.029
CO	0.001	0.000

Table 13. Purity table with uncertainties for the nominally premix of N2/CO2 in CH_4 gas

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CH_4	985549.031	2.943
N_2	12486.455	2.208
CO_2	1960.213	1.335
H_2O	2.465	1.380
Ar	0.943	0.152
H_2	0.721	0.078
O_2	0.108	0.062
C_2H_6	0.064	0.036
CO	0.001	0.000

Two standard gas mixtures were prepared, hydrogen-enriched natural gas (D73 2238) and LNG-type natural gas (D67 9611) in10-liter cylinders. The mixtures were used to verify the samples (D32 2702 and D32 2742). A one-point calibration method was used to determine the mole fraction of samples. Table **14** and **15** shows the purity tables for hydrogen-enriched natural gas (D73 2238) and LNG-type natural gas (D67 9611)

Table 14. Purity table with uncertainties for hydrogen-enriched natural gas (D73 2238)

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CH_4	773660.8688	35.16987403
N_2	120554.552	8.88084944
CO_2	54839.54724	4.43758928
H_2	32903.65675	41.41221377

C_2H_6	7074.334811	2.91609358
He	5027.500147	1.9395425
Propane	2929.494749	1.97132371
n-butane	2082.948084	1.55846618
n-hexane	452.0014789	0.12749352
n-pentane	447.1960041	0.07245869
Ar	15.68229214	0.70558361
H_2O	2.90664308	1.09213573
i-butane	0.75906968	0.03791256
Propene	0.35347017	0.18292987
O_2	0.13959879	0.04852608
Ethane	0.02475934	0.02858952
CO	0.01477488	0.00567183
Ethyne	0.00176852	0.00204211

Table 15. Purity table with uncertainties for LNG-type natural gas (D67 9611)

Component	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol) (k=1)
CH_4	876335.7255	9.1238
C_2H_6	99659.6382	7.9624
Propane	20544.1381	2.3070
n-butane	1659.7897	0.9147
N_2	1206.6016	0.8490
n-pentane	190.8249	0.0370
i-pentane	186.8100	0.0368
CO_2	186.0012	0.1321
H_2	21.2093	2.0582
H_2O	2.3334	1.1067
Propene	2.0573	1.1870
i-butane	0.6035	0.0302
Ar	0.2929	0.1183
O_2	0.2272	0.0779
C_xH_y	0.1726	0.2990
CO	0.0288	0.0083

Instrumentation

Hydrogen-enriched natural gas sample D32 2702 and LNG-type natural gas sample D3 2702 were analysed using Gas Chromatography with thermal conductivity detector (TCD) and flame ionisation detector (FID) from Agilent (7890B). For N_2, CO_2, He, and H_2 dual thermal conductivity detector (TCD) was used and for all the hydrocarbons measurements, flame ionisation detector (FID) was used. Three columns were used in the analysis of the samples: Plot Fused Silica 50mx0.32mm Coating Al_2O_3/KCl, Molecular Sieve 5A 80/100 mesh 2mx2mm and Shincarbon ST 100/1200 mesh 2mx1mm. For all measurements the split mode was used, and helium and hydrogen were used as carrier gases.

Calibration method and value assignment

Configuration of analysis system: gas cylinder >> regulator >> MFC >> sample injection valve >>column >> detector >> integrator >> area comparison >> results. **A**-**B**-**A** method was used to assign the values of the component in both natural gas mixtures. Whereby **A** is reference and **B** is sample. Equation **1** below was used to assign the values of each component in the natural gas mixtures, C is the concentration.

$$C_B = C_A/C_B \qquad \textbf{(1)}$$

Uncertainty evaluation

All measured certification data and calculations for the component concentrations of have been reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated percentage relative uncertainties. These uncertainties are:

a) Gravimetric uncertainties of the Primary Standard Gaseous Mixtures (PSGMs).
b) Repeatability uncertainty (run-to-run).
c) Impurity of the parent gases

The results yielded an average concentration and a standard deviation. The predicted concentrations for each component in the samples were averaged, and a standard deviation calculated. The uncertainties of three measurements were combined as shown in Equation 2 below:

$$u_c = \sqrt{({u_{Meas1}}^2 + {u_{Meas2}}^2 + {u_{Meas3}}^2)/3} \qquad \textbf{(2)}$$

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor $k = 2$ as in Equation 3.

$U = k \times u_c$, where $k = 2$ **(3)**

Comparison results

The overall comparison results are shown in Table **16** and Table **17** for CCQM K118a and CCQM K118b, respectively

Table 16: CCQM K118a comparison results

Component	Fraction (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Nitrogen	0.119631813	0.000449552	2
Carbon dioxide	0.057136582	0.000687891	2
Hydrogen	0.030091661	0.000731108	2
Helium	0.005120103	0.000164105	2
Ethane	0.007417212	0.000108181	2
Propane	0.002987663	0.000041419	2
iso-Butane	Not analysed	Not analysed	Not analysed
n-Butane	0.002000447	0.00002698	2
iso-Pentane	Not analysed	Not analysed	Not analysed
n-Pentane	0.000503326	0.0000068	2
neo-Pentane	Not analysed	Not analysed	Not analysed
n-Hexane	0.000501761	0.0000068	2
Methane	0.78451051	0.009327155	2

Table 17: CCQM K118b comparison results

Component	Fraction (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Nitrogen	0.001205594	0.00005111	2
Carbon dioxide	0.000186452	0.00000772	2
Ethane	0.099619065	0.00132380	2

Propane	0.019914079	0.00025852	2
iso-Butane	Not analysed	Not analysed	Not analysed
n-Butane	0.001523601	0.00002056	2
iso-Pentane	0.00019693	0.00000326	2
n-Pentane	0.000199676	0.00000229	2
Methane	0.871194449	0.00938174	2

Conclusion

Iso-butane was not analysed for the hydrogen enriched natural gas and LNG-type natural gas samples. Neo-pentane was not analysed in the hydrogen enriched natural gas sample. Iso-pentane was not analysed in the hydrogen-enriched natural gas sample **Note:** This was due to unavailability of the high pure starting materials for this component in South Africa after several queries from suppliers.

References

1. https://www.bipm.org › common › pdf › final_reports › K16 › CCQM-K16
2. International Organization for Standardization, ISO 6142:2015(E). Gas analysis – Preparation of calibration gas mixtures - Gravimetric methods, 5th edition
3. https://www.bipm.org › common › documents › jcgm › JCGM_100_2008_E

Measurement report CMI

Cylinder number: D322707 LNG-type Natural Gas

Calibration standards

All standards were prepared individually according to ISO 6142 “Gas analysis - Preparation of calibration gases - Gravimetric Method”. Depending on the concentration of the components,standards were prepared individually from pure gases or from pre-mixtures which were individually prepared from pure gases.

RM-1_258977		
složka	Xi (mol)	Xi (mol)
Methane	87,7879	0,0279
Ethane	9,7991	0,0192
Propane	1,9585	0,0054
i-Butane	0,1463	0,0009
n-Butane	0,1449	0,0009
i-Pentane	0,0175	0,0001
n-Pentane	0,0175	0,0001
CO2	0,0190	0,0001
Nitrogen	0,1092	0,0008

RM-2_259004		
složka	Xi (mol)	Xi (mol)
Methane	87,5177	0,0297
Ethane	9,9957	0,0196
Propane	2,0033	0,0055
i-Butane	0,1514	0,0008
n-Butane	0,1500	0,0008
i-Pentane	0,0190	0,0001
n-Pentane	0,0203	0,0001
CO2	0,0211	0,0002
Nitrogen	0,1214	0,0009

RM-3_517195

složka	Xi (mol)	Xi (mol)
Methane	86,9873	0,0233
Ethane	10,3890	0,0201
Propane	2,1067	0,0057
i-Butane	0,1596	0,0006
n-Butane	0,1581	0,0006
i-Pentane	0,0224	0,0001
n-Pentane	0,0224	0,0001
CO2	0,0229	0,0001
Nitrogen	0,1316	0,0005

Instrumentation

Measured on the gas chromatograph DANI Master, with using columns (HayeSep Q 80/100 3m, Molsieve 5A 80/100 3m, MTX-1 60m), 2x TCD and FID detectors, oven temperature 40 - 175 °C, carrier gas helium, hydrogen and argon. All measurements were done in automatic way.

Calibration method and value assignment

Three independent measurements were carried out under repeatability conditions. Each measurement included ten sub-measurements.

Calibration and measurement methods	
Measurement method	Type of calibration curve
GC/2xTCD-FID	3 points, line

Uncertainty evaluation

The uncertainty evaluation was performed in accordance with ISO 6143.

Uncertainty estimation is given bellow:

$$U_{(xi)} = k.u_{(xi)}$$

u - combined uncertainty

k - coverage factor (k=2)

Standard deviation is combination of standard deviation (type A) and standard deviation (type B) .

$$u_{(xi)} = \sqrt{u_{a(xi)}^2 + u_{b(xi)}^2}$$

Measurement report CMI

Cylinder number: D322720 Hydrogen Enriched Natural Gas

Calibration standards

All standards were prepared individually according to ISO 6142 “Gas analysis - Preparation of calibration gases - Gravimetric Method”. Depending on the concentration of the components, standards were prepared individually from pure gases or from pre-mixtures which were individually prepared from pure gases.

CS1 - 185886		
složka	Xi (mol)	Xi (mol)
Methane	77,4296	0,0269
Ethane	0,8905	0,0018
Propane	0,4022	0,0011
i-Butane	0,3058	0,0014
n-Butane	0,3109	0,0014
Neopentane	0,0619	0,0006
i-Pentane	0,0613	0,0003
n-Pentane	0,0614	0,0003
hexane	0,0613	0,0004
CO2	4,2039	0,0075
Nitrogen	12,5058	0,0126
Hydrogen	3,0933	0,0229
Helium	0,6120	0,0046

CS2 - 685274		
složka	Xi (mol)	Xi (mol)
Methane	80,2356	0,0256
Ethane	0,5892	0,0012
Propane	0,1937	0,0005
i-Butane	0,1236	0,0008
n-Butane	0,1190	0,0008
Neopentane	0,0386	0,0003
i-Pentane	0,0399	0,0002

n-Pentane	0,0400	0,0002
hexane	0,0385	0,0002
CO2	3,9055	0,0073
Nitrogen	11,5137	0,0123
Hydrogen	2,7721	0,0211
Helium	0,3906	0,0030

CS3 - 517213		
složka	Xi (mol)	Xi (mol)
Methane	78,8701	0,0204
Ethane	0,7294	0,0015
Propane	0,2992	0,0008
i-Butane	0,2039	0,0013
n-Butane	0,2047	0,0013
Neopentane	0,0505	0,0004
i-Pentane	0,0498	0,0003
n-Pentane	0,0502	0,0003
hexane	0,0501	0,0003
CO2	3,9806	0,0049
Nitrogen	12,0038	0,0095
Hydrogen	3,0107	0,0129
Helium	0,4970	0,0043

Instrumentation

Measured on the gas chromatograph DANI Master, with using columns (HayeSep Q 80/100 3m, Molsieve 5A 80/100 3m, MTX-1 60m), 2x TCD and FID detectors, oven temperature 40 - 175 °C, carrier gas helium, hydrogen and argon. All measurements were done in automatic way.

Calibration method and value assignment

Three independent measurements were carried out under repeatability conditions. Each measurement included ten sub-measurements.

Calibration and measurement methods	
Measurement method	Type of calibration curve
GC/2xTCD-FID	3 points, line

Uncertainty evaluation

The uncertainty evaluation was performed in accordance with ISO 6143.

Uncertainty estimation is given bellow:

$$U_{(xi)} = k.u_{(xi)}$$

u - combined uncertainty

k - coverage factor (k=2)

Standard deviation is combination of standard deviation (type A) and standard deviation (type B) .

$u_{(xi)} = \sqrt{u_{a(xi)}^2 + u_{b(xi)}^2}$

Measurement report GUM

Cylinder number: D322721 Hydrogen Enriched Natural Gas

Calibration standards

Composition of calibration standards:

Cylinder number	Component	Assigned value mol/mol	Standard uncertainty mol/mol
D298405_1	n-C_4H_{10}	0,001880	0,0000060
	i-C_4H_{10}	0,001888	0,0000060
	C_3H_8	0,002969	0,0000076
	He	0,004994	0,000014
	C_2H_6	0,007422	0,000018
	H_2	0,031431	0,00010
	neo-C_5H_{12}	0,000482	0,0000046
	CO_2	0,040712	0,000028
	N_2	0,118776	0,000077
	n-C_5H_{12}	0,000449	0,00000054
	i-C_5H_{12}	0,000452	0,0000023
	n-C_6H_{14}	0,000458	0,00000053
	CH_4	0,788087	0,000079

Cylinder number	Component	Assigned value mol/mol	Standard uncertainty mol/mol
D751999_2	n-C_4H_{10}	0,001935	0,0000062
	i-C_4H_{10}	0,001917	0,0000062
	C_3H_8	0,002846	0,0000080
	He	0,004845	0,000015
	C_2H_6	0,007000	0,000019
	H_2	0,028268	0,00010
	neo-C_5H_{12}	0,000487	0,0000046
	CO_2	0,041827	0,000031
	N_2	0,119427	0,000078
	n-C_5H_{12}	0,000471	0,00000057
	i-C_5H_{12}	0,000481	0,0000024
	n-C_6H_{14}	0,000487	0,00000056

	CH_4	0,790010	0,000079

Cylinder number	Component	Assigned value mol/mol	Standard uncertainty mol/mol
D298406_1	n-C_4H_{10}	0,001521	0,0000050
	i-C_4H_{10}	0,001528	0,0000050
	C_3H_8	0,018337	0,000047
	C_2H_6	0,100218	0,000085
	CO_2	0,000191	0,00000048
	N_2	0,001189	0,0000029
	n-C_5H_{12}	0,000203	0,00000035
	i-C_5H_{12}	0,000205	0,0000011
	CH_4	0,876608	0,000044

Cylinder number	Component	Assigned value mol/mol	Standard uncertainty mol/mol
M60285_3	n-C_4H_{10}	0,001500	0,000003
	i-C_4H_{10}	0,001435	0,000003
	C_3H_8	0,01919	0,00003
	C_2H_6	0,09828	0,000145
	CO_2	0,0002021	0,0000010
	N_2	0,001366	0,0000105
	n-C_5H_{12}	0,0001915	0,00000095
	i-C_5H_{12}	0,0002054	0,00000105
	CH_4	0,8772	0,0009

Standards were prepared (by Central Office of Measures) by gravimetric method according to ISO 6142 from separate premixtures. The premixtures were prepared by using: n-butane 3.5, i-butane 3.5, propane 3.5, helium 6.0, ethane 3.5, hydrogen 5.0, neo-pentane 2.0, carbon dioxide 4.5, nitrogen 6.0, n-pentane 3.0, i-pentane 2.5, n-hexane 3.0 and methane 5.5. The minimal weighed sample of neo-pentane, i-pentane, n-pentan and n-hexane are 0,8 g and the minimal weighed for the other samples are 20 g. The minimal weighed sample of methane is 150g. The cylinders were evacuated on turbo molecular pump, filled up an weighted on the verification balance. All the standards were prepared in aluminum (with coated layers) cylinders. The standards were (and still are) under metrological control.

Instrumentation

The measurements were repeated 27 times for the sample and the standards by gas chromatograph Thermo Trace 1300 with TCD detector and FID detector with capillary column.

The cylinders (standards and sample) were in the same room for the whole time also during the measurements (temperature stabilization) and the mixtures were mixed up before the measurements. Samples were transferred to the instrument via the reducing valve and the automatic input pressure stabilization system.

Calibration method and value assignment

The measurements were made by using standards: D298405_1, D751999_2, D298406_1 and M60285_3 by one point calibration according to equation:

$$C_x = \frac{Y_x}{Y_w} \cdot C_w$$

where:

C_x – component concentration in sample gas mixture in mol/mol

C_w – component concentration in standard gas mixture in mol/mol

Y_x – chromatograph answer for sample gas mixture

Y_w – chromatograph answer for standard gas mixture

Uncertainty evaluation

The final uncertainty, consists of the following components:

- the uncertainty of standard preparation calculated according to ISO 6142
- the standard deviation of the measurement

Resolution of the chromatograph is negligible.

Measurement report KRISS

Cylinder Number: Luxfer D322706 Hydrogen-enriched natural gas

Results

Component	Fraction (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor*
Nitrogen	0.119121	0.000238	2
Carbon dioxide	0.039853	0.000080	2
Hydrogen	0.029829	0.000060	2
Helium	0.004987	0.000015	2
Ethane	0.007406	0.000022	2
Propane	0.002965	0.000009	2
iso-Butane	0.001988	0.000006	2
n-Butane	0.001984	0.000006	2
iso-Pentane	0.000494	0.000015	2
n-Pentane	0.000495	0.000012	2
neo-Pentane	0.000491	0.000010	2
n-Hexane	0.000492	0.000010	2
Methane	0.789892	0.000790	2

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

Measurement #1 (November 29th, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Nitrogen	0.119121	0.000128
Carbon dioxide	0.039865	0.000081
Hydrogen	0.029827	0.000022
Helium	0.004985	0.000004
Ethane	0.007407	0.000017
Propane	0.002967	0.000007

iso-Butane	0.001989	0.000004
n-Butane	0.001984	0.000005
iso-Pentane	0.000498	0.000011
n-Pentane	0.000490	0.000010
neo-Pentane	0.000491	0.000001
n-Hexane	0.000492	0.000003
Methane	0.789878	0.000661

Measurement #2 (November 30th, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Nitrogen	0.119118	0.000139
Carbon dioxide	0.039853	0.000026
Hydrogen	0.029830	0.000024
Helium	0.004987	0.000007
Ethane	0.007404	0.000007
Propane	0.002965	0.000004
iso-Butane	0.001988	0.000002
n-Butane	0.001984	0.000003
iso-Pentane	0.000492	0.000010
n-Pentane	0.000498	0.000010
neo-Pentane	0.000491	0.000001
n-Hexane	0.000492	0.000003
Methane	0.789898	0.000707

Measurement #3 (December 3rd, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)

Nitrogen	0.119124	0.000119
Carbon dioxide	0.039842	0.000054
Hydrogen	0.029830	0.000024
Helium	0.004989	0.000004
Ethane	0.007406	0.000013
Propane	0.002964	0.000006
iso-Butane	0.001987	0.000003
n-Butane	0.001983	0.000004
iso-Pentane	0.000491	0.000010
n-Pentane	0.000498	0.000010
neo-Pentane	0.000491	0.000001
n-Hexane	0.000492	0.000003
Methane	0.789901	0.000593

**Standard uncertainties estimated from replicate analysis of the test cylinder (D322706) only, not including uncertainties originated from gravimetric preparation and internal consistency test.

Calibration standards

- **Method of preparation**

For comparisons with the test cylinder (D322706) sent from the coordinating laboratory (BAM), a calibration gas cylinder (D693877) of KRISS primary standard mixtures (PSM) was newly prepared using a gravimetric method based on ISO 6142 as of October 22nd, 2018. The order of components injected into the PSM gas cylinder was *n*-hexane, *n*-pentane, *iso*-pentane, *neo*-pentane, a mixture of (propane + ethane + *iso*-butane + *n*-butane), a mixture of (hydrogen + helium), carbon dioxide, nitrogen, and finally methane.

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

Analyses of hydrocarbons and inorganic gas impurities in the pure gases of nitrogen, carbon dioxide, hydrogen, helium, ethane, propane, *iso*-butane, *n*-butane, and methane were conducted primarily using gas chromatographs (GC) with different detectors: pulse discharge detector (PDD), flame ionization detector (FID), thermal conductivity detector (TCD) and a dew-point meter (DPM) for analysis of moisture content. Analysis of hydrocarbons impurities in the pure liquids of *iso*-pentane, *n*-pentane, and *n*-hexane and the pure gas of *neo*-pentane were conducted using GC-FID. Analysis of moisture content in the pure liquid reagents were conducted using Karl-Fisher Analyser (KFA).

Component	Purity (cmol/mol)	Analysis method
Nitrogen	99.9997	DPM, GC-PDD, GC-FID, GC-TCD
Carbon dioxide	99.9989	DPM, GC-PDD, GC-FID, GC-TCD
Hydrogen	99.9990	DPM, GC-PDD, GC-FID, GC-TCD
Helium	99.9999	DPM, GC-PDD, GC-FID, GC-TCD
Ethane	99.9965	DPM, GC-PDD, GC-FID, GC-TCD
Propane	99.9982	DPM, GC-PDD, GC-FID, GC-TCD
iso-Butane	99.9534	DPM, GC-PDD, GC-FID, GC-TCD
n-Butane	99.8720	DPM, GC-PDD, GC-FID, GC-TCD
iso-Pentane	99.9670	GC-FID, KFA
n-Pentane	99.3600	GC-FID, KFA
neo-Pentane	99.9689	GC-FID, KFA
n-Hexane	99.4130	GC-FID, KFA
Methane	99.9992	DPM, GC-PDD, GC-FID, GC-TCD

- **Weighing data**
  Information on the mass of the pure liquid reagents and the source or the parent gas mixture cylinders to prepare the calibration cylinder (D693877) are summarized in the following table:

Component	source	Mass (g)
n-hexane	Pure liquid reagent	1.2569
n-pentane	Pure liquid reagent	1.0776
iso-pentane	Pure liquid reagent	1.0588
neo-pentane (3.02 %) in methane	Parent gas mixture	8.81
carbon dioxide	Pure gas	51.4
nitrogen	Pure gas	97.9
ethane (7.511 %)	Parent gas mixture	57.2

propane (2.036 %) *iso*-butane (1.9951 %) *n*-butane (2.014 %) in methane		
hydrogen (30.110 %) helium (5.076 %) in methane	Parent gas mixture	32.8
methane	Pure gas	291.0

Uncertainties due to impurities of all pure or parent gases used for gravimetric preparation of the calibration cylinder (D693877) were incorporated into the preparation uncertainty.

The mole fraction of each component in the calibration cylinder (D693877) and its standard uncertainty are summarized in the following table:

Component	Mole Fraction (cmol/mol)	Standard Uncertainty (cmol/mol)	Relative Standard Uncertainty (%)
Nitrogen	11.9776	0.0031	0.026
Carbon dioxide	4.0011	0.0014	0.035
Hydrogen	3.0210	0.0015	0.049
Helium	0.5086	0.00025	0.049
Ethane	0.7494	0.00026	0.035
Propane	0.3029	0.00011	0.035
iso-Butane	0.1992	0.00008	0.040
n-Butane	0.2009	0.00008	0.040
iso-Pentane	0.050342	0.0010	2.1
n-Pentane	0.05123	0.0010	2.0
neo-Pentane	0.05147	0.000015	0.028
n-Hexane	0.04980	0.00029	0.58
Methane	78.8354	0.020	0.025

Verification measures

- **Internal consistency between the KRISS PSMs**

The mole fraction of each component in the verification cylinder (D695886) used as the control of internal consistency with the calibration cylinder (D693877) and its standard uncertainty are summarized in the following table:

Component	Mole Fraction (cmol/mol)	Standard Uncertainty (cmol/mol)	Relative Standard Uncertainty (%)
Nitrogen	11.9878	0.0031	0.026
Carbon dioxide	3.9947	0.0014	0.036
Hydrogen	3.0104	0.0015	0.05
Helium	0.5068	0.00025	0.049
Ethane	0.7551	0.00027	0.035
Propane	0.3052	0.00011	0.035
iso-Butane	0.2008	0.00008	0.040
n-Butane	0.2024	0.00008	0.039
iso-Pentane	0.050545	0.0011	2.1
n-Pentane	0.05108	0.0011	2.1
neo-Pentane	0.05088	0.00001	0.028
n-Hexane	0.04993	0.00029	0.58
Methane	78.8322	0.020	0.025

Response factors of each component in the calibration cylinder (D693877) were compared with those in the verification cylinder (D695886) using a comparative analysis method based on ISO 6143, as of November 26th and 28th, 2018.

The relative standard uncertainty of internal consistency is in the following table:

Component	Maximum Distance of C from V |C-V|	Relative Distance of C from V[1] (%)	Relative Standard Uncertainty[2] (%)

Nitrogen	0.49	0.14	0.08
Carbon dioxide	1.71	0.08	0.04
Hydrogen	0.98	0.03	0.02
Helium	0.40	0.02	0.01
Ethane	3.14	0.13	0.08
Propane	5.61	0.19	0.11
iso-Butane	2.54	0.07	0.04
n-Butane	5.62	0.16	0.09
iso-Pentane	26.21	0.66	0.38
n-Pentane	9.04	0.22	0.13
neo-Pentane	7.71	0.20	0.12
n-Hexane	9.93	0.21	0.12
Methane	0.73	0.07	0.04

[1] Calculated using $[|C - V|/V \times 100]$ (%) assuming that the relative deviation (%) from the ratio of the response factor (C) of each component in the calibration cylinder (D693877) against that (D) in the verification cylinder (D695886)

[2] Calculated using $\left|[|C - V|/V \times 100]/\sqrt{3}\right|$ (%) assuming that the relative deviation (%) follows a rectangular probability distribution (B-type).

■ **Verification of instability of the calibration gas cylinder**

Past experiences of KRISS clearly indicate that hydrogen-enriched natural gas CRMs prepared by KRISS were stable within two years. Any significant change in the mole fraction of each component in the calibration cylinder (D693877) was not observed within 3 months after its gravimetric preparation. The uncertainty due to this instability was considered negligible relatively to other uncertainty sources (e.g., gravimetric preparation, internal consistency, and comparative analysis) and thus not included to the final uncertainty budget.

Instrumentation

Determination of mole fractions of carbon dioxide, ethane, propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane, and *n*-hexane components was conducted using GC-FID-methanizer (Agilent 6890A). Determination of mole fractions of nitrogen, hydrogen, helium, and methane was conducted using GC-TCD (Agilent 7890A). A MFC and a quick connector were assisted for the quick change of cylinders and maintaining the constant flow rate. GC signal was integrated as an area value for each peak.

Calibration method and value assignment

KRISS received the test cylinder (D322706) as of August 2nd, 2018. The test cylinder that BAM had sent to KRISS was made of Al with normal volumetric capacity of 5 L. The gas pressure values of the test cylinder (D322706) before and after the measurement at the KRISS laboratory were approximately 4.1 MPa and 2.0 MPa, respectively.

The overall procedures for calibration and value assignment are based on ISO 6143. We used a one-point calibration (in-situ, exact-match, bracketing) method for the determination of the mole fractions of the components in the test cylinder (D322706**)** of the coordinating laboratory (BAM) in comparison with the calibration cylinder (D693877) of KRISS. A bracketing method (D693877 - D322706 - D693877) was adopted as the comparison analysis for the value assignment and uncertainty evaluation of each component in the test cylinder (D322706**)**. After averaging multiple response values of the calibration cylinder (D693877) by taking drift compensation into account, the mole fraction of each component in the test cylinder (D322706) was calculated as a result by direct comparison between the average of the response values and the mole fraction of each component in the calibration cylinder (D693877).

Uncertainty evaluation

- **Model equation for a measurement data set (e.g., Measurement # *i*)**

A model equation of the measurand ($x_{test,i}$) was used for the one-point calibration method:

$$x_{test,i} = \left(\frac{A_{test,i}}{A_{cal,i}}\right) x_{cal}$$

where

i : the measurement #i (i=1,2,and 3)

$x_{test,i}$: the mole fraction of each component from the test cylinder (D322706**)** determined and reported by KRISS

($A_{test,i}$ /$A_{cal,i}$) : the ratio of GC response areas of each component between the test cylinder (D322706**)** and the calibration cylinder (D693877)

x_{cal} : the mole fraction of the calibration cylinder (D693877)

- **Combined uncertainty for a measurement data set (Measurement #*i*)**

The following equation to calculate the uncertainty of the measurand (x_{test}) considers the three different sources: the gravimetric preparation of the calibration cylinder (D693877), the internal consistency between the calibration cylinder (D693877) and the verification cylinder (D695886), and the ratio of the response areas of between the calibration cylinder (D693877) and the verification cylinder (D695886) for each component.

$$u(x_{test,i}) = x_{test,i}\sqrt{\left[\frac{u(A_{test,i}/A_{cal,i})}{A_{test,i}/A_{cal,i}}\right]^2 + \left[\frac{u(X_{cal})}{X_{cal}}\right]^2 + \left[\frac{u_i(f_{IC})}{f_{IC}}\right]^2}$$

where

$\frac{u_i(f_{IC})}{f_{IC}}$: relative standard uncertainty of internal consistency which is defined as the ratio of the response factor of a component between the calibration cylinder (D693877) and the verification cylinder (D695886) where the ratio is assumed 1.

- **Combined uncertainty for the overall data sets using Measurement #1 through #3**

As a result, the measurand [i.e., average mole faction (x_{test})] of each component and its combined uncertainty [$u(x_{test})$] of each component in the test cylinder were calculated using the four-day independent measurement data sets.

Average mole fraction (x_{test}):

$$x_{test} = \frac{1}{3}\sum_{i=1}^{3} x_{test,i}$$

Its combined uncertainty [$u(x_{test})$]:

$$u(x_{test}) = \frac{1}{3}\sqrt{\sum_{i=1}^{3} u^2(x_{test,i})}$$

Its expanded uncertainty [$U(x_{test})$]:

$$U(x_{test}) = k\, u(x_{test})$$

Therefore,

$$U(x_{test}) = \frac{k}{3}\sqrt{\sum_{i=1}^{3} u^2(x_{test,i})}$$

The expanded uncertainty was estimated at the approximately 95% level of confidence with the coverage factor (*k*) of 2, assuming that x_{test} of each component follows a normal distribution. This assumption was confirmed by the fact that the effective degree of freedoms of $u(x_{test})$ of each component, calculated by the Welch-Satterthwaite equation, was greater than 10.

Accordingly,

$$U(x_{test}) = \frac{2}{3}\sqrt{\sum_{i=1}^{3} u^2(x_{test,i})}$$

Measurement report NIM

Cylinder number: D322730 Hydrogen enriched natural gas

Measurement #1 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	15/08/19	0.119660916	0.03%	3
Carbon dioxide	15/08/19	0.039994664	0.01%	3
Hydrogen	15/08/19	0.029990321	0.03%	3
Helium	15/08/19	0.005013461	0.04%	3
Ethane	15/08/19	0.007446886	0.02%	3
Propane	15/08/19	0.002984407	0.06%	3
iso-Butane	15/08/19	0.001998434	0.04%	3
n-Butane	15/08/19	0.001998964	0.05%	3
iso-Pentane	15/08/19	0.000498735	0.14%	3
n-Pentane	15/08/19	0.000500831	0.05%	3
neo-Pentane	15/08/19	0.000493431	0.06%	3
n-Hexane	15/08/19	0.000497818	0.04%	3
Methane	15/08/19	0.788921132	0.04%	3

Measurement #2 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	27/08/19	0.11967779	0.03%	3
Carbon dioxide	27/08/19	0.039970013	0.03%	3
Hydrogen	27/08/19	0.030008847	0.03%	3
Helium	27/08/19	0.005013692	0.04%	3
Ethane	27/08/19	0.007443306	0.03%	3
Propane	27/08/19	0.002983507	0.01%	3
iso-Butane	27/08/19	0.001998245	0.03%	3
n-Butane	27/08/19	0.001995749	0.02%	3

iso-Pentane	27/08/19	0.000498064	0.01%	3
n-Pentane	27/08/19	0.000499839	0.04%	3
neo-Pentane	27/08/19	0.000492599	0.03%	3
n-Hexane	27/08/19	0.000496531	0.04%	3
Methane	27/08/19	0.788924815	0.03%	3

Measurement #3 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	02/09/19	0.119676436	0.004%	4
Carbon dioxide	02/09/19	0.039981654	0.01%	4
Hydrogen	02/09/19	0.030013319	0.01%	4
Helium	02/09/19	0.005014707	0.01%	4
Ethane	02/09/19	0.007446646	0.01%	4
Propane	02/09/19	0.002982507	0.02%	4
iso-Butane	02/09/19	0.001999778	0.01%	4
n-Butane	02/09/19	0.001996865	0.03%	4
iso-Pentane	02/09/19	0.00049862	0.06%	4
n-Pentane	02/09/19	0.00050017	0.02%	4
neo-Pentane	02/09/19	0.000492928	0.02%	4
n-Hexane	02/09/19	0.00049695	0.02%	4
Methane	02/09/19	0.78890242	0.004%	4

Final Results (hydrogen-enriched natural gas)

Component	**Result (mol/mol)**	**Expanded Uncertainty (mol/mol)**	**Coverage factor**[1]
Nitrogen	0.11967	0.00025	2

[1] The coverage factor shall be based on approximately 95% confidence.

Carbon dioxide	0.039982	0.000091	2
Hydrogen	0.030004	0.000075	2
Helium	0.005014	0.000014	2
Ethane	0.007446	0.000019	2
Propane	0.0029835	0.0000081	2
iso-Butane	0.0019988	0.0000050	2
n-Butane	0.0019972	0.0000050	2
iso-Pentane	0.0004985	0.0000020	2
n-Pentane	0.0005003	0.0000015	2
neo-Pentane	0.0004930	0.0000016	2
n-Hexane	0.0004971	0.0000013	2
Methane	0.78892	0.00031	2

Measurement report NIM

Cylinder number: D322700 LNG-type natural gas

Measurement #1 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	15/08/19	0.00124597	0.17%	3
Carbondioxide	15/08/19	0.00019759	0.14%	3
Ethane	15/08/19	0.09987021	0.01%	3
Propane	15/08/19	0.01996904	0.02%	3
iso-Butane	15/08/19	0.00149014	0.02%	3
n-Butane	15/08/19	0.00148159	0.01%	3
iso-Pentane	15/08/19	0.00019881	0.06%	3
n-Pentane	15/08/19	0.00020019	0.01%	3
Methane	15/08/19	0.87534645	0.03%	3

Measurement #2 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	23/08/19	0.00124219	0.12%	3
Carbondioxide	23/08/19	0.00019777	0.31%	3
Ethane	23/08/19	0.09991623	0.03%	3
Propane	23/08/19	0.01997218	0.05%	3
iso-Butane	23/08/19	0.00149007	0.02%	3
n-Butane	23/08/19	0.00148141	0.04%	3
iso-Pentane	23/08/19	0.00019880	0.03%	3
n-Pentane	23/08/19	0.00019994	0.02%	3
Methane	23/08/19	0.87530142	0.05%	3

Measurement #3 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	04/09/19	0.00124970	0.17%	3
Carbondioxide	04/09/19	0.00019804	0.18%	3
Ethane	04/09/19	0.09985345	0.01%	3
Propane	04/09/19	0.01996310	0.03%	3
iso-Butane	04/09/19	0.00149016	0.01%	3
n-Butane	04/09/19	0.00148151	0.00%	3
iso-Pentane	04/09/19	0.00019881	0.04%	3
n-Pentane	04/09/19	0.00019986	0.05%	3
Methane	04/09/19	0.87536535	0.01%	3

Final Results (LNG-type natural gas)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor[1]
Nitrogen	0.0012460	0.0000062	2
Carbondioxide	0.0001978	0.0000010	2
Ethane	0.099880	0.00023	2
Propane	0.019968	0.000050	2
iso-Butane	0.0014901	0.0000037	2
n-Butane	0.0014815	0.0000039	2
iso-Pentane	0.00019880	0.00000070	2
n-Pentane	0.00020000	0.00000065	2
Methane	0.87534	0.00030	2

[1] The coverage factor shall be based on approximately 95% confidence.

Calibration standards

The calibration gas mixtures of synthetic natural gas were prepared by using gravimetric method according to ISO6142.1-2015.

Source materials used for preparation were listed in Table 1~13.

Table 1. Purity data for pure CH4

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	25E-6	Normal	25E-6	5.0E-6
CO2	GC-PDHID	0.40E-6	Normal	0.40E-6	0.20E-6
CH4	/	/	/	0.9999702	5.3E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 2. Purity data for pure C2H6

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	1.1E-6	Normal	1.1E-6	0.55E-6
CO2	GC-FID(Ni)	0.20E-6	Normal	0.20E-6	0.10E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	/	/	/	0.9999943	1.8E-6
C3H8	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 3. Purity data for pure C3H8

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	9.3E-6	Normal	9.3E-6	1.9E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	/	/	/	0.999974	4.3E-6
C3H6	GC-FID	10.6E-6	Normal	10.6E-6	3.2E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 4. Purity data for pure i-C4H10

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	33.2E-6	Normal	33.2E-6	6.7E-6
CO2	GC-FID(Ni)	8.0E-6	Normal	8.0E-6	2.0E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	1.3E-6	Normal	1.3E-6	0.65E-6
C3H6	GC-FID	2.2E-6	Normal	2.2E-6	1.1E-6
i-C4H10	/	/	/	0.999878	10.6E-6
n-C4H10	GC-FID	67.2E-6	Normal	67.2E-6	6.7E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	8.5E-6	Normal	8.5E-6	4.2E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 5. Purity data for pure n-C4H10

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	48.8E-6	Normal	48.8E-6	4.9E-6
CO2	GC-FID(Ni)	16.6E-6	Normal	16.6E-6	3.3E-6

CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	14.4E-6	Normal	14.4E-6	7.2E-6
i-C4H10	GC-FID	59.5E-6	Normal	59.5E-6	6.0E-6
n-C4H10	/	/	/	0.999768	14.7E-6
neo-C5H12	GC-FID	63.6E-6	Normal	63.6E-6	6.4E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
1-C4H8	GC-FID	18.4E-6	Normal	18.4E-6	5.5E-6
2-C4H8	GC-FID	17.9E-6	Normal	17.9E-6	5.4E-6

Table 6. Purity data for pure neo-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	66.2E-6	Normal	66.2E-6	6.6E-6
CO2	GC-FID(Ni)	2.7E-6	Normal	2.7E-6	1.4E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
C3H8	GC-FID	88.5E-6	Normal	88.5E-6	8.9E-6
i-C4H10	GC-FID	5.45E-3	Normal	5.45E-3	5.4E-4
n-C4H10	GC-FID	21.1E-6	Normal	21.1E-6	2.1E-6
neo-C5H12	/	/	/	0.994334	5.4E-4
i-C5H12	GC-FID	10.5E-6	Normal	10.5E-6	1.1E-6
n-C5H12	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6

Table 7. Purity data for pure i-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	1.16E-3	Normal	1.16E-3	1.2E-4
CO2	GC-FID(Ni)	37.6E-6	Normal	37.6E-6	3.8E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	1.08E-4	Normal	1.08E-4	11E-6
C3H8	GC-FID	25.8E-6	Normal	25.8E-6	2.6E-6
i-C4H10	GC-FID	2.09E-3	Normal	2.09E-3	2.1E-4
n-C4H10	GC-FID	4.70E-3	Normal	4.70E-3	4.7E-4
neo-C5H12	GC-FID	4.00E-3	Normal	4.00E-3	4.0E-4
i-C5H12	/	/	/	0.9857899	7.0E-4

n-C5H12	GC-FID	2.05E-3	Normal	2.05E-3	2.1E-4
n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
cis-2-C5H10	GC-FID	22.8E-6	Normal	22.8E-6	2.3E-6

Table 8. Purity data for pure n-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	75.4E-6	Normal	75.4E-6	7.5E-6
CO2	GC-FID(Ni)	40.8E-6	Normal	40.8E-6	4.1E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
C3H8	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
i-C4H10	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
n-C4H10	GC-FID	18.1E-6	Normal	18.1E-6	1.8E-6
neo-C5H12	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
i-C5H12	GC-FID	3.66E-3	Normal	3.66E-3	3.7E-4
n-C5H12	/	/	/	0.995097	3.9E-4
n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
Other C5H10	GC-FID	1.07E-3	Normal	1.07E-3	1.1E-4

Table 9. Purity data for pure n-C6H14

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
2,2-dimethylbutane	GC-FID	768E-6	Normal	768E-6	76.8E-6
2,3-dimethylbutane	GC-FID	191E-6	Normal	191E-6	19.1E-6
2-methylpentane	GC-FID	1.01E-3	Normal	1.01E-3	1.01E-4
3-methylpentane	GC-FID	1.04E-3	Normal	1.04E-3	1.04E-4
n-C6H14	/	/	/	0.996463	1.73E-4
n-C7H16	GC-FID	506E-6	Normal	506E-6	50.6E-6
methylcyclopentane	GC-FID	11.0E-6	Normal	11.0E-6	1.1E-6
cyclohexane	GC-FID	11.0E-6	Normal	11.0E-6	1.1E-6

Table 10. Purity data for pure N2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-PDHID	ND	Rectangular	0.1E-6	0.06E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
O2	O2 Analyzer	0.05E-6	Rectangular	0.05E-6	0.03E-6
Ar	GC-PDHID	12.3E-6	Normal	12.3E-6	1.2E-6

N2	/	/	/	0.9999978	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.03E-6	0.02E-6
H2O	Dewpoint Meter	0.1E-6	Rectangular	0.1E-6	0.06E-6

Table 11. Purity data for pure CO2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
O2	GC-PDHID	0.52E-6	Normal	0.52E-6	0.1E-6
N2	GC-PDHID	19.8E-6	Normal	19.8E-6	2.0E-6
CO2	/	/	/	0.999975	3.3E-6
CH4	GC-FID	1.1E-6	Normal	1.1E-6	0.45E-6
C2H4	GC-FID	0.2E-6	Normal	0.2E-6	0.1E-6
C3H8	GC-FID	0.64E-6	Normal	0.64E-6	0.32E-6
H2O	Dewpoint Meter	2.5E-6	Normal	2.5E-6	1.0E-6

Table 12. Purity data for pure H2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	/	/	/	0.999998	1.2E-6
N2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.1E-6	0.06E-6

Table 13. Purity data for pure He

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-PDHID	ND	Rectangular	0.1E-6	0.06E-6
He	/	/	/	0.999998	1.2E-6
N2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.1E-6	0.06E-6
H2O	Dewpoint Meter	0.1E-6	Rectangular	0.1E-6	0.06E-6

In order to obtain the final synthetic natural gas PRMs, several pre-mixtures were prepared, and the weighing data for each pre-mixtures were listed in Table 14. Accordingly, final synthetic natural gas PRMs were gravimetrically prepared, and some of PRMs werelisted in Table 15-16.

Table 14. Preparation pre-mixtures

Cylinder No.	Source materials	Mass filled (g)	Std *u* for mass (g)	Mole fraction *c* (mol/mol)	Std $u_{c,r}$, relative
63909004#	n-C5	7.8692	0.005	5.3423E-3	0.070%
	iC5	6.8078	0.005	4.6005E-3	0.074%
	neoC5	7.1572	0.005	4.8715E-3	0.066%
	C1	321.6007	0.02	9.8508E-1	0.0008%
63909025#	nC4	24.469	0.005	2.3477E-2	0.022%
	iC4	24.633	0.005	2.3636E-2	0.022%
	C1	274.084	0.02	9.5286E-1	0.0009%
63909027#	H2	25.8605	0.005	7.6554E-1	0.088%
	He	9.8236	0.005	1.4646E-1	0.046%
	C3	65.0219	0.005	8.7995E-2	0.018%
L63204002#	CO2	15.1435	0.005	2.3188E-2	0.034%
	N2	57.4465	0.01	1.3821E-1	0.018%
	C1	199.651	0.02	8.3860E-1	0.003%

Table 15. Preparation of final PRMs

Cylinder No.	Source materials	Mass filled (g)	Std *u* for mass (g)
63909026# (LNG Type)	L63204002#	6.8380	0.005
	C3	39.2886	0.005
	63909004#	27.8822	0.005
	63909025#	48.6330	0.005
	C2	123.9981	0.01
	C1	504.4403	0.02
63909002# (H2-enriched Type)	nC6	1.41429	0.0002
	63909025#	62.3247	0.005
	63909027#	10.0205	0.005
	63909004#	72.5312	0.01
	C2	10.5795	0.005
	CO2	74.3927	0.01

	N2	131.3021	0.01
	C1	392.1318	0.02

Table 16. Gravimetrically prepared PRMs.

Components	c_{grav} (mol/mol)	$U_{grav,rel}(k=2)$	$u_{ver,rel}(k=1)$	$U_{i,rel}(k=2)$
63909002#				
CH4(Methane)	7.872E-01	0.006%	0.03%	0.06%
C2H6(Ethane)	8.664E-03	0.095%	0.10%	0.22%
C3H8(Propane)	3.613E-03	0.098%	0.10%	0.22%
C4H10(iso-Butane)	2.016E-03	0.053%	0.10%	0.21%
C4H10(n-Butane)	2.001E-03	0.050%	0.10%	0.21%
C5H12(neo-Pentane)	5.157E-04	0.180%	0.10%	0.27%
C5H12(iso-Pentane)	4.869E-04	0.207%	0.10%	0.29%
C5H12(n-Pentane)	5.654E-04	0.154%	0.10%	0.25%
C6H14(n-Hexane)	4.027E-04	0.077%	0.10%	0.21%
N2(Nitrogen)	1.154E-01	0.019%	0.10%	0.20%
CO2(Carbon_dioxide)	4.162E-02	0.029%	0.10%	0.20%
H2(Hydrogen)	3.143E-02	0.100%	0.10%	0.22%
He(Helium)	6.013E-03	0.130%	0.10%	0.24%
63909026#				
CH4(Methane)	8.731E-01	0.003%	0.03%	0.06%
C2H6(Ethane)	1.001E-01	0.020%	0.10%	0.20%
C3H8(Propane)	2.164E-02	0.030%	0.10%	0.20%
C4H10(iso-Butane)	1.550E-03	0.048%	0.10%	0.21%
C4H10(n-Butane)	1.539E-03	0.048%	0.10%	0.21%
C5H12(neo-Pentane)	1.956E-04	0.197%	0.10%	0.28%
C5H12(iso-Pentane)	1.846E-04	0.182%	0.10%	0.27%
C5H12(n-Pentane)	2.144E-04	0.135%	0.10%	0.24%
N2(Nitrogen)	1.273E-03	0.591%	0.10%	0.62%
CO2(Carbon_dioxide)	2.105E-04	0.208%	0.10%	0.29%

Verification of PRMs.

Synthetic natural gas PRMs were verified against old PRMs by GC-TCD(Micro GC490, Agilent, USA). Results showed that the relative bias was within 0.05% for the components above 1%mol/mol, 0.01% for balance gas of CH4, and 0.1% for the other components. Accordingly, the relative uncertainty due to verification were 0.01% for CH4, 0.05% for components above 1%mol/mol, and 0.1% for other components.

Instrumentation

Synthetic natural gas PRMs were analyzed by GC-TCD(Micro GC490, Agilent, USA). There are 4 channels within Micro GC490. Channel 1# includes pre-column of PPQ and separation column of Moleseive 5A(10m), and is used to analyze such components as He, H2, O2, N2, and CH4 while the other components are backflushed. Channel 2# includes pre-column of PPQ and separation column of PPQ(10m), and is used to analyze CO2 and C2H6, while C3H8 and other heavier components are backflushed. Channel 3# includes pre-column of PPQ and separation column of Al2O3(10m), and is used to analyze C3H8, i-C4H10 and n-C4H10. Channel 4# includes only 5CB(10m) column and analyzed neo-, iso-, n-C5H12 and n-C6H14.

Calibration method and value assignment

The K118 sample cylinders were kept in the room at room temperature for almost 1 month. Both our PRM and the sample cylinders were equipped with pressure regulators. The outlet of pressure regulators were connected with the inject port of GC(microGC490). The PRM and sample cylinder were measured alternatively in "PRM(10 replicates)-KC sample(10 replicates)-PRM(10 replicates)" mode. The mole fraction of sample was determined using single-point calibration method by the formula as below:

$$c_{KC,i} = c_{PRM,i} \cdot \frac{2\overline{A}_{KC,i}}{\left(\overline{A}_{PRM,i,pre} + \overline{A}_{PRM,i,post}\right)} \qquad (1)$$

$c_{KC,i}$ the mole fraction of i component in KC sample,

$c_{PRM,i}$ the mole fraction of i component in PRM,

$\overline{A}_{KC,i}$ the average Peak Area of i component in KC sample by GC-TCD,

$\overline{A}_{PRM,i,pre}$ the average Peak Area of i component in PRM before KC sample injection,

$\overline{A}_{PRM,i,post}$ the average Peak Area of i component in PRM after KC sample injection,

The KC sample was analyzed against PRM for n(n≥3) times, and n results were obtained. The average fraction of $c^*_{KC,i}$ was taken as the raw value for the i component in KC sample, while the measurement result, $c_{KC,i}$, for the i component in KC sample was determined based on normalization.

$$c^*_{KC,i} = \frac{\sum_{j=1}^{n} c_{KC,i,j}}{n} \qquad (2)$$

$$c_{KC,i} = \frac{c^*_{KC,i}}{\sum_{i=1}^{n} c^*_{KC,i}} \quad (3)$$

Uncertainty evaluation

The measurement uncertainty in raw fraction of *i* component was contributed by both PRM ($u_{i,rel}$) and measurement repeatability(RSD). While the uncertainty in a normalized fraction of *i* component was derived based on the formula (3).

References

ISO 6974-2, Natural gas - Determination of composition and associated uncertainty by gas chromatography - part 2: Uncertainty calculations, 2012.

Measurement report NMIA

Cylinder number: D322744 Hydrogen Enriched Natural Gas

Component	Composition	Standard uncertainty	Expanded uncertainty (k=2)
	cmol/mol	cmol/mol	cmol/mol
Nitrogen	11.9723	0.0025	0.0050
Carbon dioxide	4.0070	0.0015	0.0030
Hydrogen	3.0088	0.0025	0.0050
Helium	0.5016	0.00055	0.0011
Ethane	0.7456	0.00065	0.0013
Propane	0.2986	0.0003	0.0006
iso-Butane	0.1999	0.0002	0.0004
n-Butane	0.2000	0.0002	0.0004
iso-Pentane	0.05014	0.00007	0.00014
n-Pentane	0.05023	0.00008	0.00016
neo-Pentane	0.04929	0.00008	0.00016
n-Hexane	0.0496	0.0004	0.0008
Methane	78.867	0.025	0.050

Calibration standards

Method of preparation

NMI primary standards were prepared gravimetrically using a Sartorius CC10000S mass comparator according to ISO 6142.1. Environmental conditions were monitored during the use of the mass comparator to allow for the correction of buoyancy. The purity of the source gases was also included in the calculation of mixture composition and for the assignment of the concentration of each gas component.

Four calibration standards were manufactured in 2015 that span the target composition of the sample. The composition of the standards and their associated preparation uncertainties are shown below:

	FF51756		FF51757		FF51758		FF51759	
	(%mol)	u (%mol)	(%mol)	u (%mol)	(%mol)	u (%mol)	(%mol)	u (%mol)
Carbon Dioxide	4.0807	0.0007	4.0913	0.0007	3.9603	0.0007	4.0266	0.0007
Nitrogen	11.6963	0.0011	11.8702	0.0011	12.1284	0.0010	12.0428	0.0011
Helium	0.48861	0.00027	0.49968	0.00028	0.48726	0.00027	0.50556	0.00028
Hydrogen	3.0171	0.0014	3.0855	0.0014	3.0088	0.0013	3.1219	0.0014
Methane	79.0670	0.0022	78.7842	0.0022	78.7834	0.0021	78.6127	0.0022
Ethane	0.7454	0.0004	0.7623	0.0004	0.7433	0.0004	0.7713	0.0004
Propane	0.29523	0.00016	0.30192	0.00017	0.29442	0.00016	0.30548	0.00017
n-Butane	0.19908	0.00010	0.20208	0.00010	0.20323	0.00010	0.20772	0.00011
iso-Butane	0.19797	0.00009	0.20099	0.00009	0.19708	0.00009	0.19739	0.00009
n-Pentane	0.04864	0.00007	0.04937	0.00007	0.04965	0.00007	0.05074	0.00007
iso-Pentane (2-methyl butane)	0.04952	0.00006	0.05025	0.00006	0.04927	0.00006	0.04937	0.00006
neo-Pentane (2,2-dimethyl propane)	0.05017	0.00005	0.05131	0.00005	0.05003	0.00005	0.05191	0.00005
n-Hexane	0.06218	0.00035	0.04873	0.00035	0.04275	0.00034	0.05442	0.00035
Impurities:	(µmol/mol)	u (µmol/mol)	(µmol/mol)	u (µmol/mol)	(µmol/mol)	u (µmol/mol)	(µmol/mol)	u (µmol/mol)
Argon	13.53	0.05	13.73	0.05	14.03	0.05	13.93	0.05
Oxygen	0.53	0.13	0.53	0.13	0.53	0.13	0.53	0.12
Water	0.057	0.035	0.057	0.035	0.057	0.034	0.058	0.035
Carbon Monoxide	0.003	0.002	0.003	0.002	0.003	0.002	0.003	0.002
iso-Hexane (2-methyl pentane)	0.083	0.003	0.065	0.003	0.057	0.002	0.073	0.003
2,2-dimethyl butane	1.276	0.012	1.011	0.011	0.893	0.010	1.124	0.012
2,3-dimethyl butane	2.572	0.027	2.033	0.023	1.793	0.021	2.263	0.025
Propyne	2.200	0.006	2.250	0.006	2.194	0.006	2.276	0.006
Cyclobutane	1.22	0.13	1.25	0.13	1.21	0.13	1.26	0.13
Cyclopentane	0.143	0.011	0.146	0.011	0.143	0.011	0.148	0.011

– Purity table. Composition of parent gases (impurities in µmol/mol)

Cyclobutane	C4H8			2400				
Cyclopentane	C5H10			213		71		

Instrumentation

Analysis was performed using 2 gas chromatographs.

Instrument 1 (all components except helium): Bruker 456 GC (NGA configuration C). The system is configured with a 14 port valve and 6 port valve. The valves are installed in the multi-valve oven for flexible operation of the conventional column oven. The 14 port valve enables the system to introduce the sample stream simultaneously to three independent columns with automated detector switching. Two of the sample paths flow onto Molsieve and porous polymer columns to separate oxygen, nitrogen and carbon dioxide, ethane, methane, and the other via a non-polar capillary column (BR-1) to separate the hydrocarbon components up through C16. The 6 port valve is used to direct the separated components fraction to the TCD detector while components remaining on the Molsieve column are flushed to vent.

Instrument 2: Varian 3800 GC with TCD detector:

The hydrogen and helium analysis was performed on a GC-TCD with MS-5A column and a Porapack Q column used as the delay column before backflushing. Argon was used as the carrier for this analysis.

Calibration method and value assignment

A sequence S R_1 S R_2 S R_3 S R_4 S was created (S is sample; R_1 to R_4 are reference standards) with each step representing 7 repeat injections. The sequence was repeated 3 times for one complete analysis with the analysis performed unattended. The whole sequence was repeated twice (starting on the 30/11/18 and 3/12/18). Sample flow was controlled by employing low volume Messer regulators on each cylinder connected to a VICI 10-port stream selection valve then to a common Bronkhorst mass flow controller.

Analysis and value assignment was performed using equation 2 from ISO 12963 using single point calibrations.

The calculated concentration from each analysis against the individual standards was tabulated and the mean calculated for each component (24 values for each component, or 48 values for components measured on 2 detectors or instruments - hydrogen, methane, nitrogen, and ethane). The concentrations for all components were then normalized and the concentrations adjusted. On this occasion the changes due to normalization were only minor as the sum of the components was >99.99%.

Uncertainty evaluation

Measurement uncertainty was calculated using equation 3 from ISO 12963. Uncertainties were calculated from the uncertainties of the reference standards and the uncertainties due to the repeat analyses. As the standards were all nominally the same and the performance of the instrument was consistent, the uncertainties from each standard/sample pairing were common and a value was chosen approximately half way through the sequence as the value then represents what is routinely possible. When the component was measured on several detectors, the detector that gave the smaller uncertainty was generally chosen.

Measurement report NMIA

Cylinder number: D322718 LNG-type natural gas

Component	Composition	Standard uncertainty	Expanded uncertainty (k=2)
	cmol/mol	cmol/mol	cmol/mol
Nitrogen	0.12162	0.00032	0.00064
Carbon dioxide	0.01979	0.00015	0.00031
Ethane	10.001	0.003	0.006
Propane	1.9986	0.0016	0.0033
iso-Butane	0.14932	0.00030	0.00060
n-Butane	0.14865	0.00030	0.00060
iso-Pentane	0.020107	0.000042	0.000084
n-Pentane	0.020116	0.000050	0.000100
Methane	87.521	0.025	0.050

Calibration standards

Method of preparation

NMI primary standards were prepared gravimetrically using a Sartorius CC10000S mass comparator according to ISO 6142.1. Environmental conditions were monitored during the use of the mass comparator to allow for the correction of buoyancy. The purity of the source gases was also included in the calculation of mixture composition and for the assignment of the concentration of each gas component.

Four calibration standards were manufactured that span the target composition of the sample. The composition of the standards and their associated preparation uncertainties are shown below:

	MD5714		MD8888		MD8889		MD8891	
	(%mol)	u (%mol)	(%mol)	u (%mol)	(%mol)	u (%mol)	(%mol)	u (%mol)
Carbon Dioxide	0.01621	0.00003	0.0106	0.0000	0.0155	0.0000	0.0138	0.0000
Nitrogen	0.14526	0.00023	0.1042	0.0001	0.1523	0.0001	0.1358	0.0001
Methane	86.7631	0.0013	88.8480	0.0011	87.3493	0.0012	87.5315	0.0012
Ethane	9.8248	0.0010	9.2050	0.0010	10.0750	0.0010	9.9769	0.0010
Propane	2.65466	0.00065	1.51608	0.00064	1.95162	0.00068	2.01206	0.00068
n-Butane	0.26393	0.00050	0.14254	0.00010	0.19898	0.00013	0.20772	0.00011
iso-Butane	0.26645	0.00050	0.14458	0.00009	0.20497	0.00011	0.14014	0.00010
n-Pentane	0.01962	0.00004	0.00949	0.00002	0.01482	0.00002	0.15238	0.00009
iso-Pentane (2-methyl butane)	0.03886	0.00006	0.01430	0.00002	0.02752	0.00003	0.00946	0.00002
neo-Pentane (2,2-dimethyl propane)							0.01887	0.00003
n-Hexane							0.00002	0.00000

– Purity table. Composition of parent gases (impurities in µmol/mol)

Component	Carbon Dioxide	n-Butane	iso-Butane	n-Pentane	iso-Pentane
Cylinder/Gas ID	CO2_08A	nC4H10_01A	isoC4H10_01A	MD5707	MD5708
Argon					
Helium					
Nitrogen	0.8	3.1	0.5		
Oxygen	0.18	17	0.5		
Hydrogen		0.08			
Carbon Monoxide					
Carbon Dioxide	99.99986		1.3		
Methane	0.08	0.4	0.5		
Ethane	0.32	0.9	1.9		
Propane		55	34		
iso-Propanol					
n-Butane		99.98893		12	1060
iso-Butane		3.5	99.99555	80	
n-Pentane				99.4724	1500
iso-Pentane (2-methyl butane)		0.7	0.9	4869	99.6440
neo-Pentane (2,2-dimethyl propane)		30	4.9		1000
2,2-dimethyl butane				95	
2,3-dimethyl butane				149	
Cyclopentane				71	

Component	Methane	Methane	Ethane	Propane	Nitrogen
Cylinder/Gas ID	CH4_12A	CH4_13B	C2H6_01A	C3H8_01A	N2_06A
Argon		0.038			252
Helium		2.50			
Nitrogen		1.41	0.5	24	99.97465
Oxygen		0.60	0.5	1.5	0.92
Hydrogen		0.20			
Carbon Monoxide	0.011				
Carbon Dioxide	0.079	2.07	3.3		
Methane	99.99977	99.99932	26.4		0.6
Ethane	2.23		99.99683	17	
Propane			1	99.99575	
iso-Propanol					
n-Butane					
iso-Butane					
n-Pentane					
iso-Pentane (2-methyl butane)					
neo-Pentane (2,2-dimethyl propane)					
2,2-dimethyl butane					
2,3-dimethyl butane					
Cyclopentane					

Instrumentation

Analysis was performed using 2 gas chromatographs.

Instrument 1 (all components): Bruker 456 GC (NGA configuration C). The system is configured with a 14 port valve and 6 port valve. The valves are installed in the multi-valve oven for flexible operation of the conventional column oven. The 14 port valve enables the system to introduce the sample stream simultaneously to three independent columns with automated detector switching. Two of the sample paths flow onto Molsieve and porous polymer columns to separate oxygen, nitrogen and carbon dioxide, ethane, methane, and the other via a non-polar capillary column (BR-1) to separate the hydrocarbon components up through C16. The 6 port valve is used to direct the separated components fraction to the TCD detector while components remaining on the Molsieve column are flushed to vent.

Instrument 2: Varian 450 gas chromatograph with methanizer FID equipped with a 2m x 1/8" Hayesep R column was used for the measurement of carbon dioxide.

Calibration method and value assignment

A sequence S R_1 S R_2 S R_3 S R_4 S was created (S is sample; R_1 to R_4 are reference standards) with each step representing 7 repeat injections. The sequence was repeated 3 times for one complete analysis with the analysis performed unattended. The whole sequence was repeated three times (starting on the 24/01/2019, 26/01/2019 and the 25/02/2019; and on the second GC on the 1/02/2019, 4/02/2019 and the 22/02/2019). Sample flow was controlled by employing low volume Messer regulators on each cylinder connected to a VICI 10-port stream selection valve then to a common Bronkhorst mass flow controller.

Analysis and value assignment was performed using equation 2 from ISO 12963 using single point calibrations. Analysis values were confirmed using linear regression.

The calculated concentration from each analysis against the individual standards was tabulated and the mean calculated for each component (36 values for each component, or 72 values for components measured on 2 detectors or instruments – methane, carbon dioxide and ethane). The concentrations for all components were then normalized and the concentrations adjusted. On this occasion the changes due to normalization were only minor.

Uncertainty evaluation

Measurement uncertainty was calculated using equation 3 from ISO 12963. Uncertainties were calculated from the uncertainties of the reference standards and the uncertainties due to the repeat analyses. As the standards had uncertainties that were nominally the same and the performance of the instrument was consistent, the uncertainties from each standard/sample pairing were common and a value was chosen approximately half way through the sequence as the value then represents what is routinely achievable. When the component was measured on several detectors, the detector that gave the smaller uncertainty was generally chosen.

Measurement report NMIJ

Cylinder number: D322719 Hydrogen enriched natural gas

Measurement #1 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	31/7/2019	0.11947907	0.18%	5
Carbon dioxide	31/7/2019	0.040962158	0.29%	5
Hydrogen	17/9/2019 1st	0.029173404	0.18%	5
Helium	17/9/2019 1st	0.00496788	0.21%	5
Ethane	27/6/2019	0.007443453	0.07%	3
Propane	27/6/2019	0.002980095	0.07%	3
iso-Butane	19/6/2019	0.001997364	0.07%	3
n-Butane	19/6/2019	0.001993118	0.07%	3
iso-Pentane	12/6/2019	0.00049426	0.05%	3
n-Pentane	12/6/2019	0.000500798	0.09%	3
neo-Pentane	19/6/2019	0.00049187	0.17%	3
n-Hexane	23/5/2019	0.000494345	0.12%	3
Methane	31/7/2019	0.790609	0.20%	5

Measurement #2 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	1/8/2019	0.120525	0.24%	5
Carbon dioxide	1/8/2019	0.041080682	0.29%	5
Hydrogen	17/9/2019 2nd	0.029318174	0.14%	5
Helium	17/9/2019 2nd	0.004941753	0.11%	5
Ethane	28/6/2019	0.007441513	0.05%	3
Propane	28/6/2019	0.002980798	0.07%	3
iso-Butane	21/6/2019	0.00199151	0.07%	3
n-Butane	21/6/2019	0.001988678	0.07%	3

iso-Pentane	29/7/2019	0.000494088	0.06%	3
n-Pentane	29/7/2019	0.00050073	0.09%	3
neo-Pentane	21/6/2019	0.000490844	0.18%	3
n-Hexane	24/5/2019	0.000494455	0.07%	3
Methane	2/8/2019	0.793487	0.43%	5

Measurement #3 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	2/8/2019	0.119057285	0.27%	5
Carbon dioxide	2/8/2019	0.041151357	0.29%	5
Hydrogen	18/9/2019 1st	0.029032275	0.17%	5
Helium	18/9/2019 1st	0.004968267	0.19%	5
Ethane	10/7/2019	0.00743631	0.09%	3
Propane	10/7/2019	0.00297966	0.10%	3
iso-Butane	26/7/2019	0.001992611	0.08%	3
n-Butane	26/7/2019	0.001989168	0.10%	3
iso-Pentane	8/8/2019	0.000494936	0.05%	3
n-Pentane	8/8/2019	0.000501512	0.09%	3
neo-Pentane	26/7/2019	0.000490757	0.18%	3
n-Hexane	4/6/2019	0.000494499	0.11%	3
Methane	10/9/2019	0.785988	0.27%	5

Measurement #4 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	5/8/2019	0.119444659	0.20%	5
Carbon dioxide	5/8/2019	0.040796532	0.28%	5
Hydrogen	18/9/2019 2nd	0.029158317	0.20%	5

Helium	18/9/2019 2nd	0.004948349	0.17%	5
Ethane	11/7/2019	0.007444941	0.08%	3
Propane	11/7/2019	0.002982373	0.08%	3
iso-Butane	23/8/2019	0.00199949	0.16%	3
n-Butane	23/8/2019	0.001996234	0.19%	3
iso-Pentane	21/8/2019	0.000493688	0.05%	3
n-Pentane	21/8/2019	0.000500553	0.08%	3
neo-Pentane	23/8/2019	0.000493609	0.20%	3
n-Hexane	5/6/2019	0.000494833	0.12%	3
Methane	11/9/2019-1st	0.787526	0.24%	5

Measurement #5 (hydrogen-enriched natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	6/8/2019	0.119984645	0.33%	5
Carbon dioxide	6/8/2019	0.041180267	0.29%	5
Hydrogen	16/7/2019	0.028982155	0.44%	5
Helium	-	-	-	-
Ethane	12/7/2019	0.007440154	0.07%	3
Propane	12/7/2019	0.002981423	0.08%	3
iso-Butane	28/8/2019	0.001996757	0.07%	3
n-Butane	28/8/2019	0.001992951	0.07%	3
iso-Pentane	9/9/2019	0.000493918	0.04%	3
n-Pentane	9/9/2019	0.000500548	0.09%	3
neo-Pentane	28/8/2019	0.00049223	0.17%	3
n-Hexane	6/6/2019	0.000494437	0.09%	3
Methane	11/9/2019-2nd	0.791254	0.41%	5

Final Results (hydrogen-enriched natural gas)

Component	**Result (mol/mol)**	**Expanded Uncertainty (mol/mol)**	**Coverage factor[1]**
Nitrogen	0.11970	0.00057	2
Carbon dioxide	0.04103	0.00018	2
Hydrogen	0.02913	0.00014	2
Helium	0.004957	0.000016	2
Ethane	0.0074413	0.0000058	2
Propane	0.0029809	0.0000024	2
iso-Butane	0.0019955	0.0000035	2
n-Butane	0.0019920	0.0000034	2
iso-Pentane	0.00049418	0.00000048	2
n-Pentane	0.00050083	0.00000052	2
neo-Pentane	0.00049186	0.00000130	2
n-Hexane	0.00049451	0.00000050	2
Methane	0.7898	0.0033	2

[1] The coverage factor shall be based on approximately 95% confidence.

Measurement report NMIJ

Cylinder number: D322736 LNG-type natural gas

Measurement #1 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	19/8/2019	0.0012265	0.13%	5
Carbon dioxide	19/8/2019	0.000200926	0.11%	5
Ethane	24/7/2019	0.099722507	0.05%	3
Propane	24/7/2019	0.020121004	0.05%	3
iso-Butane	19/6/2019	0.001487677	0.08%	3
n-Butane	19/6/2019	0.001480148	0.09%	3
iso-Pentane	12/6/2019	0.000195728	0.07%	3
n-Pentane	12/6/2019	0.000200094	0.07%	3
Methane	12/9/2019 1st	0.86827	0.27%	5

Measurement #2 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	8/20/2019	0.0012277	0.15%	5
Carbon dioxide	8/10/2019	0.000200630	0.20%	5
Ethane	25/7/2019	0.099970234	0.07%	3
Propane	25/7/2019	0.020162734	0.08%	3
iso-Butane	21/6/2019	0.001486503	0.08%	3
n-Butane	21/6/2019	0.001478128	0.08%	3
iso-Pentane	29/7/2019	0.000195301	0.08%	3
n-Pentane	29/7/2019	0.000199628	0.12%	3
Methane	12/9/2019 2nd	0.87214	0.14%	5

Measurement #3 (LNG-type natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	28/8/2019	0.0012207	0.14%	5
Carbon dioxide	9/10/2019	0.000201144	0.26%	5
Ethane	26/8/2019	0.099867183	0.10%	3
Propane	26/8/2019	0.020145883	0.09%	3
iso-Butane	26/7/2019	0.00148978	0.10%	3
n-Butane	26/7/2019	0.001482496	0.13%	3
iso-Pentane	8/8/2019	0.000194637	0.09%	3
n-Pentane	8/8/2019	0.000198557	0.13%	3
Methane	13/9/2019 1st	0.87286	0.31%	5

Measurement #4 (LNG-type natural gas)

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Relative standard deviation (%)**	**number of replicates**
Nitrogen	3/9/2019	0.0012222	0.24%	5
Carbon dioxide	10/10/2019 1st	0.000200574	0.24%	5
Ethane	27/8/2019	0.100070625	0.11%	3
Propane	27/8/2019	0.020195671	0.09%	3
iso-Butane	23/8/2019	0.001492003	0.22%	3
n-Butane	23/8/2019	0.001485452	0.27%	3
iso-Pentane	21/8/2019	0.000196057	0.07%	3
n-Pentane	21/8/2019	0.000200448	0.10%	3
Methane	13/9/2019 2nd	0.87292	0.42%	5

Measurement #5 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	4/9/2019	0.0012344	0.15%	5
Carbon dioxide	10/10/2019 2nd	0.000200478	0.22%	5
Ethane	6/9/2019	0.099946426	0.04%	3
Propane	6/9/2019	0.020179977	0.05%	3
iso-Butane	28/8/2019	0.001490125	0.08%	3
n-Butane	28/8/2019	0.001482421	0.08%	3
iso-Pentane	9/9/2019	0.000195808	0.06%	3
n-Pentane	9/9/2019	0.000200303	0.08%	3
Methane	18/9/2019	0.87190	0.07%	3

Final Results (LNG-type natural gas)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor[1]
Nitrogen	0.0012263	0.0000051	2
Carbon dioxide	0.00020075	0.00000045	2
Ethane	0.099915	0.000136	2
Propane	0.020161	0.000029	2
iso-Butane	0.0014892	0.0000025	2
n-Butane	0.0014817	0.0000032	2
iso-Pentane	0.00019551	0.00000051	2
n-Pentane	0.00019981	0.00000071	2
Methane	0.8716	0.0031	2

[1] The coverage factor shall be based on approximately 95% confidence.

Calibration standards

Source gases and materials for calibration gas mixtures

NMIJ CRMs 4064-a, 4052-b, 4065-a, 4066-a, and 3407-c were used as source gases for calibration gas mixtures of ethane, propane, *i*-butane, *n*-butane, and carbon dioxide, respectively. Pure methane was purchased from Tokyo Gas Chemicals Co., Ltd. (Tokyo, Japan). Pure *i*-pentane, *n*-pentane, and *neo*-pentane were purchased from Takachiho Chemical Industrial Co., Ltd. (Tokyo, Japan). Pure *n*-Hexane was purchased from Sigma-Aldrich Co. LLC (St. Louis, MO USA). Pure Nitrogen and hydrogen were purchased from Japan Fine Products Co., Ltd. (Kawasaki, Kanagawa, Japan). Pure Helium was purchased from Air Liquide Kogyo Gas Ltd. (Tokyo, Japan). Purity tables of methane, ethane, propane, *i*-butane, *n*-butane, *n*-hexane, helium, hydrogen, nitrogen, and carbon dioxide were shown in tables 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10, respectively.

Table 1 Purity table with uncertainties for the pure methane

Component *i*	x_i	$u(x_i)$
Methane	999999	1
Nitrogen	0.25	0.14
Oxygen	0.05	0.03
Argon	0.05	0.03
Hydrogen	0.05	0.03
Carbon monoxide	0.05	0.03
Carbon dioxide	0.05	0.03
Ethane	0.05	0.03
Propane	0.05	0.03
i-Butane	negligible	
n-Butane	negligible	
i-Pentane	negligible	
n-Pentane	negligible	
neo-Pentane	negligible	
n-Hexane	negligible	

Unit: μmol mol^{-1}

Table 2 Purity table with uncertainties for the pure ethane

Component i	x_i	$u(x_i)$
Ethane	999923	40
Nitrogen	1	0.5
Oxygen	0.5	0.3
Water	67	40
Carbon dioxide	6	3
Methane	0.5	0.3
Propane	0.13	0.02
n-Butane	0.79	0.02

Unit: µmol mol^{-1}

Table 3 Purity table with uncertainties for the pure propane

Component i	x_i	$u(x_i)$
Propane	999915	15
Nitrogen	2	1
Oxygen	2	1
Water	53	15
Carbon dioxide	1	1
Ethane	4	2
Argon	2	1
i-Butane	2	1
n-Butane	2	1
Propene	17	2

Unit: µmol mol^{-1}

Table 4 Purity table with uncertainties for the pure *i*-butane

Component *i*	x_i	$u(x_i)$
i-Butane	99.942	0.015
Nitrogen	0.0001	0.0001
Oxygen	0.0001	0.0001
Water	0.051	0.015
Carbon dioxide	0.0006	0.0003
Propane	0.0007	0.0001
n-Butane	0.0004	0.0001
Butene	0.0054	0.0001
n-Pentane	0.0003	0.0002
neo-Pentane	negligible	

Unit: cmol mol^{-1}

Table 5 Purity table with uncertainties for the pure *n*-butane

Component *i*	x_i	$u(x_i)$
n-Butane	99.870	0.015
Nitrogen	0.0001	0.0001
Oxygen	0.0001	0.0001
Water	0.111	0.015
Carbon dioxide	0.0006	0.0003
Propane	0.0004	0.0001
i-Butane	0.0096	0.0003
Butene	0.0085	0.0002
neo-Pentane	negligible	

Unit: cmol mol^{-1}

Table 6 Purity table with uncertainties for the pure *n*-hexane

Component *i*	x_i	$u(x_i)$
n-Hexane	98.879	0.129
Nitrogen	0.110	0.063
Oxygen	0.040	0.023
Water	0.020	0.001
2-Methylpentane	0.284	0.043
3-Methylpentane	0.354	0.072
Methylcyclopentane	0.294	0.071
Cyclohexane	0.010	0.006
2,2,3-Trimethylbutane	0.009	0.005
Methane	negligible	

Unit: cmol mol^{-1}

Table 7 Purity table with uncertainties for the pure hydrogen

Component *i*	x_i	$u(x_i)$
Hydrogen	999999	0.37
Nitrogen	0.28	0.16
Oxygen	0.60	0.34
Carbon dioxide	0.01	0.01
Methane	0.01	0.01

Unit: µmol mol^{-1}

Table 8 Purity table with uncertainties for the pure helium

Component *i*	x_i	$u(x_i)$
Helium	999998	0.80
Nitrogen	1.28	0.74
Oxygen	0.52	0.30
Carbon dioxide	0.01	0.01
Methane	0.01	0.01

Unit: µmol mol^{-1}

Table 9 Purity table with uncertainties for the pure nitrogen

Component i	x_i	$u(x_i)$
Nitrogen	999996	2
Oxygen	2.17	1.25
Carbon dioxide	0.58	0.33
Water	1.47	0.85
Methane	0.025	0.014
Ethane	negligible	
Propane	negligible	
n-Butane	negligible	

Unit: μmol mol^{-1}

Table 10 Purity table with uncertainties for the pure carbon dioxide

Component i	x_i	$u(x_i)$
Carbon dioxide	999994	2
Nitrogen	0.87	0.50
Oxygen	0.43	0.25
Methane	0.005	0.003
Hydrogen	0.89	0.51
Water	3.6	2.1

Unit: μmol mol^{-1}

Preparation of calibration gas mixtures

The calibration gas mixtures were prepared by a gravimetric method using NMIJ's reported weighing systems. [1], [2] The syringe method [3], [4] was used in the preparation for calibration gas mixtures of *n*-hexane in methane. Preparation schemes of the gas mixtures were shown in Figures 1-7. Amount fractions of pentanes in the intermediate gas mixtures (Cylinder numbers: CPB21265, CPB21274, CPB28689, CPB28690, CPB29173, and CPB29176) were evaluated by a determination method using post-column GC-FID system. [5], [6]

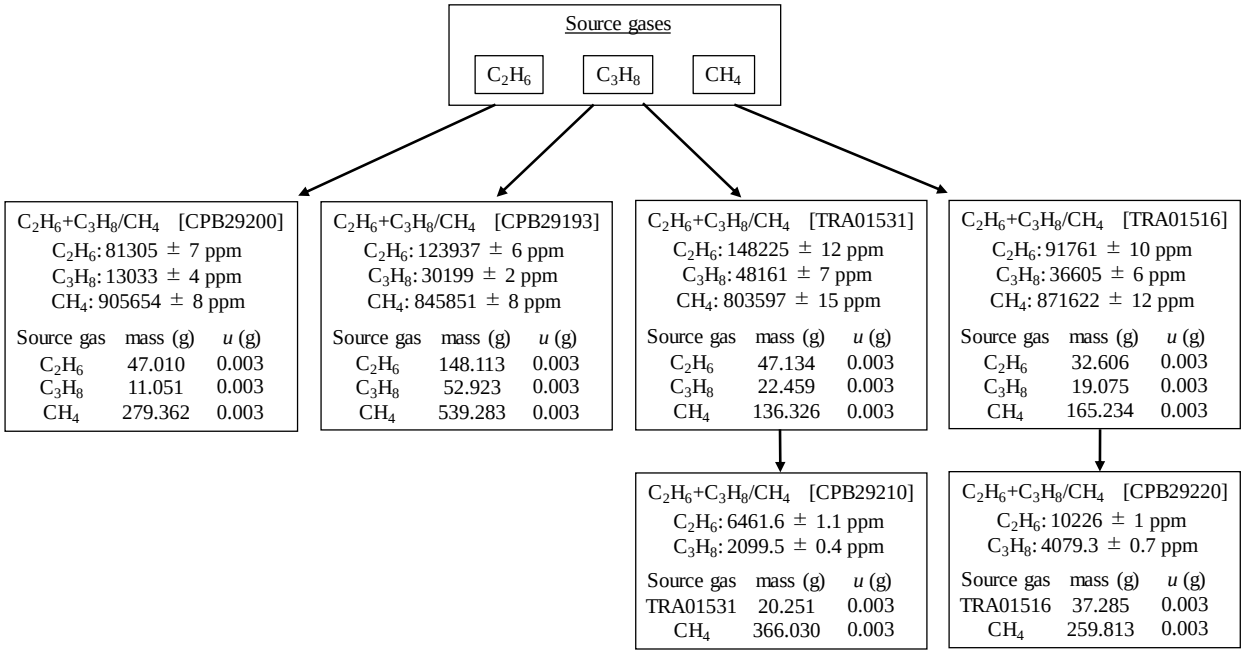


Figure 1 Preparation scheme for calibration gas mixtures of ethane and propane in methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Unit "ppm" means µmol mol^{-1}.

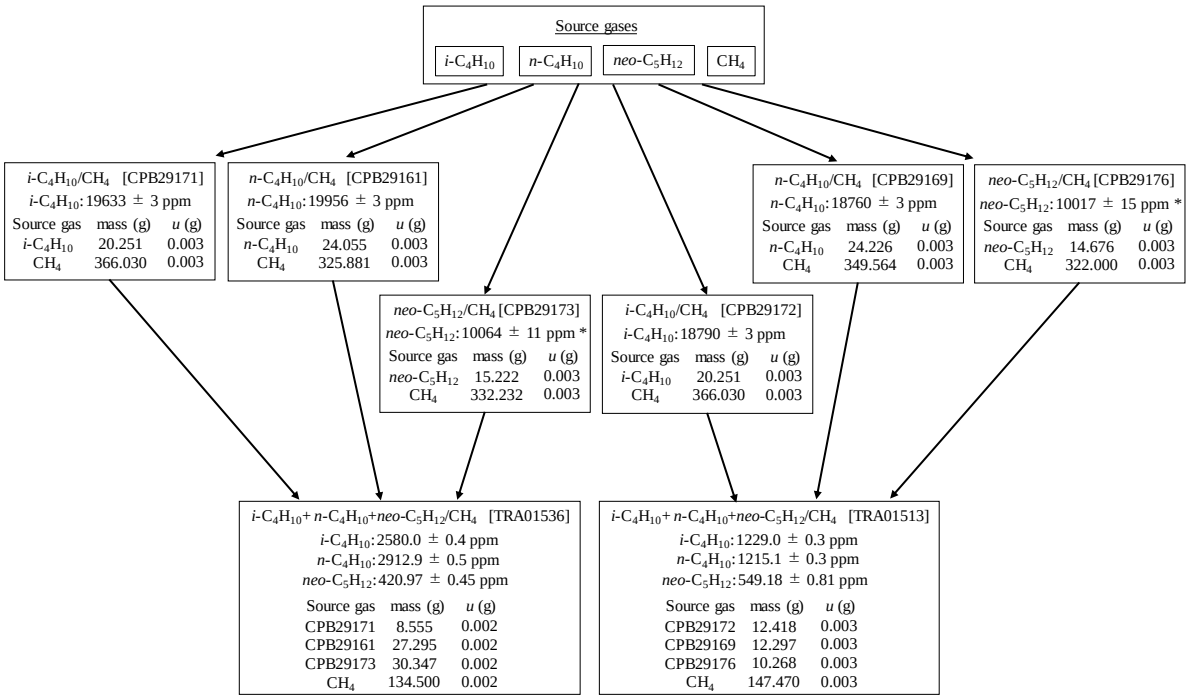


Figure 2 Preparation scheme for calibration gas mixtures of *i*-butane, *n*-butane and *neo*-pentane in methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Amount fractions of *neo*-pentane in the gas mixture of *neo*-pentane and methane were evaluated by the determination method using post-column GC-FID system. Unit "ppm" means μmol mol^{-1}.

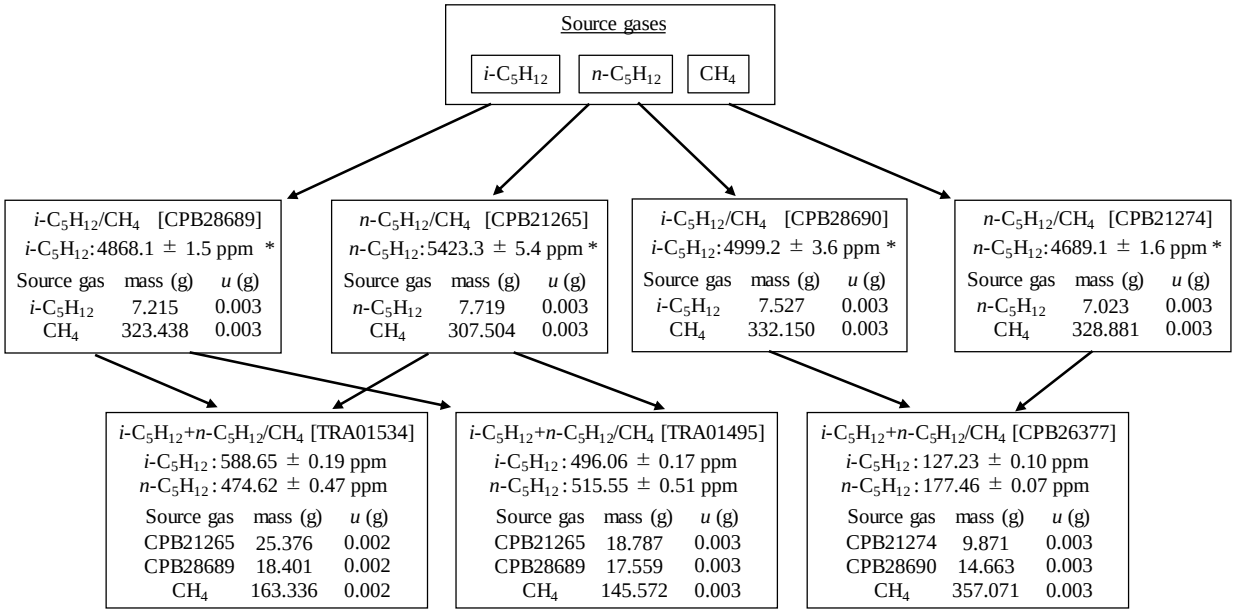


Figure 3 Preparation scheme for calibration gas mixtures of *i*-pentane and *n*-pentane in methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Amount fractions of *i*-pentane and *n*-pentane in the intermediate gas mixtures were evaluated by the determination method using post-column GC-FID system. Unit "ppm" means µmol mol^{-1}.

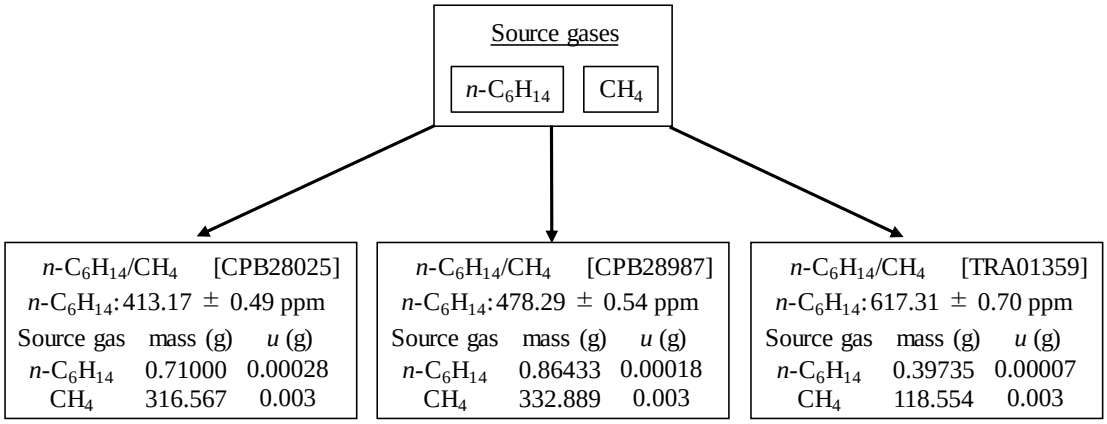


Figure 4 Preparation scheme for calibration gas mixtures of *n*-hexane and methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty.

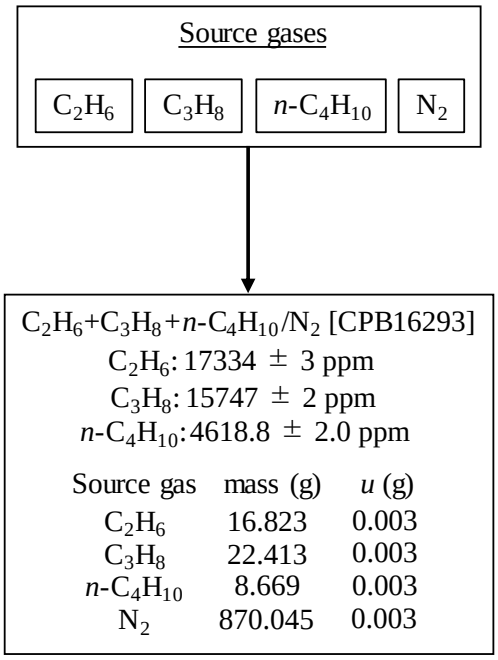


Figure 5 Preparation scheme for calibration gas mixtures of ethane, propane and *n*-butane in nitrogen. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Unit "ppm" means μmol mol^{-1}.

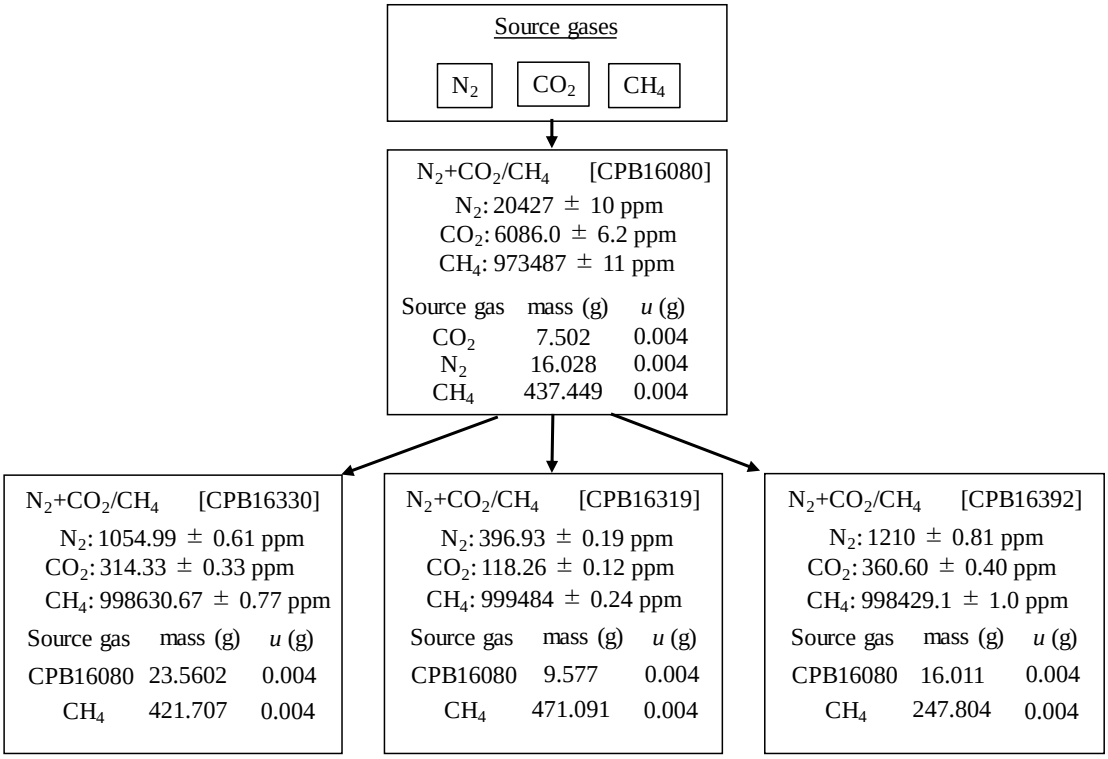


Figure 6 Preparation scheme for calibration gas mixtures of nitrogen and carbon dioxide in methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Unit “ppm” means μmol mol^{-1}.

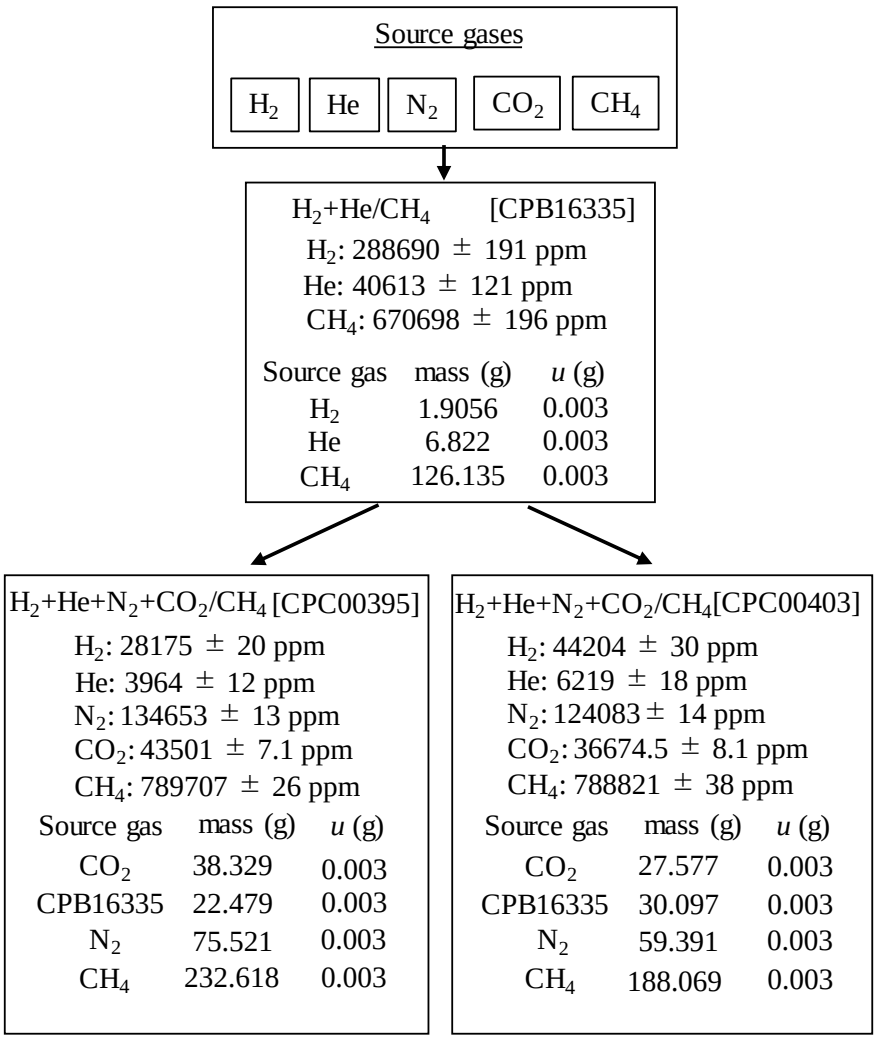


Figure 7 Preparation scheme for calibration gas mixtures of nitrogen and carbon dioxide in methane. The numeric value after the symbol ± of each mean value indicates a standard uncertainty. Unit "ppm" means μmol mol^{-1}.

Evaluation for concentrations of pentanes in the intermediate gas mixtures

Amount fractions of pentane in the intermediate gas mixtures were evaluated using the post-column reaction GC-FID system developed by NMIJ. Schematic diagram of the system was shown in Figure 8.

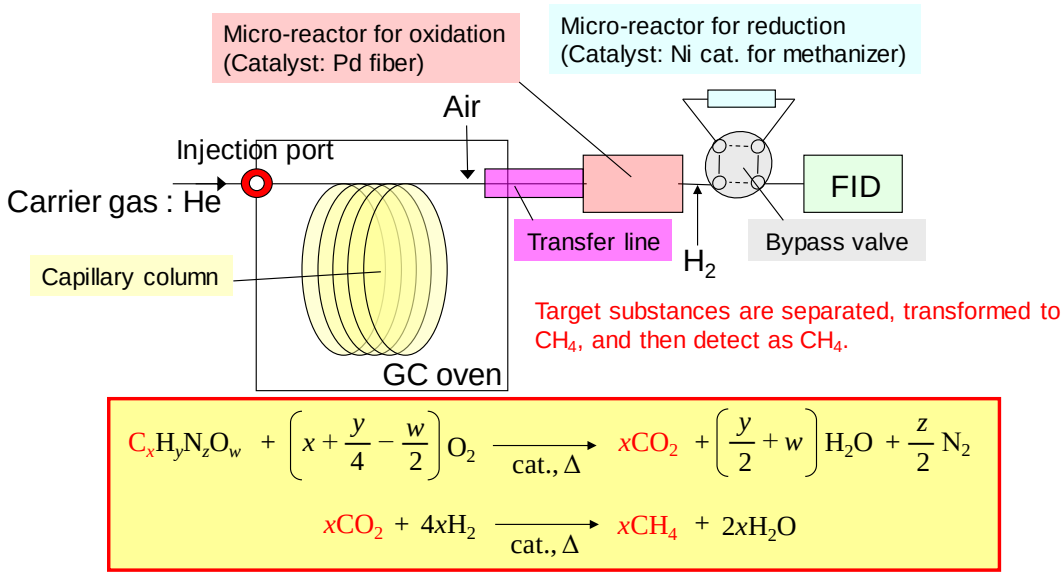


Figure 8 Schematic diagram of the post-column reaction GC-FID system.

In this system, injected analytes separated by column are completely converted to methane and then followed by detecting using FID. The sensitivity is proportional to the number of carbon atoms of an analyte, and irrespective of the compound. Therefore, it is not required to prepare all the standard materials related to the analytes to calibrate the system.

In this work, the system consists of a combination of a GC-FID unit (GC-2010, Shimadzu Corporation, Kyoto, Japan) and handmade oxidizing and reducing parts.[5] Operating condition for the post-column reaction GC-FID system was summarized in Table 11.

Table 11 Operating condition for the post-column reaction GC-FID system

Gas chromatograph	Shimadzu GC-2010
Injection method	Direct injection using 6-ports sampling valve
Sample volume	0.1 mL
Valve box temperature	130 ºC
Column	CP-Al_2O_3/KCl PLOT (Length 50 m, 0.53 mm i.d.)
Carrier gas, flow rate	He, 3.0 mL min^{-1}
Oven temperature	7 min hold at 40 ºC, 10 ºC min^{-1} up to 200 ºC, and hold for 5 min
FID Temperature	250 ºC

FID fuel gas	H_2, 42 mL min^{-1}
FID supporting gas	Purified air, 399 mL min^{-1}
FID makeup gas	He, 30 mL min^{-1}
Post-column reaction system	Handmade reaction system
Oxidizer	Purified air, 1 mL min^{-1}
Oxidizing catalyst	Palladium wool (Palladium textiles)
Oxidizing temperature	400 ºC
Reducer	H_2, 5 mL min^{-1}
Reducing catalyst	Nickel catalyst for methanizer
Reducing temperature	400 ºC
Transfer line temperature	240 ºC

The calibration gas mixture of ethane, propane, and *n*-butane in nitrogen (CPB16293) was used for calibration of the post-column reaction GC-FID system. Example of prepared calibration line was shown in Figure 9.

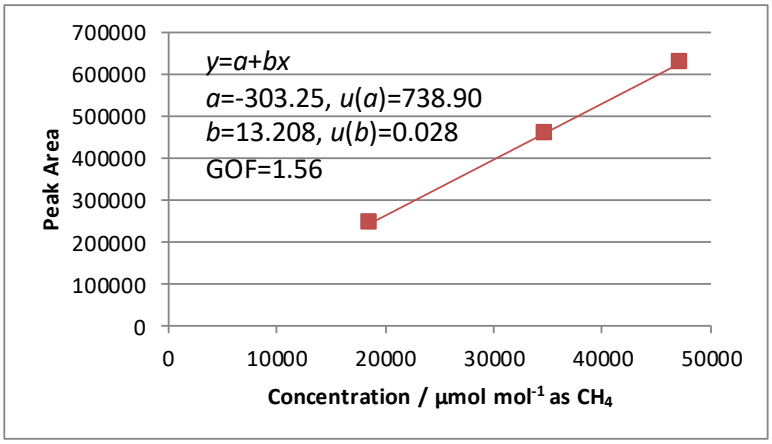


Figure 9 Example of prepared calibration line for the post-column reaction GC-FID system

Evaluation for amount fractions of pentanes in the intermediate gas mixtures was carried out, and obtained results were summarized in Table 12.

Table 12 Obtained results of amount fractions of pentanes in the intermediate gas mixtures

Cylinder No.	Target component *i*	Measurement result			
		x_i (μmol mol^{-1} as CH_4)	u_i (μmol mol^{-1} as CH_4)	x_i (μmol mol^{-1})	u_i (μmol mol^{-1})
CPB28689	*i*-Pentane	24341	8	4868.1	1.5
CPB28690	*i*-Pentane	24996	18	4999.2	3.6
CPB21265	*n*-Pentane	27116	27	5423.3	5.4
CPB21274	*n*-Pentane	23446	8	4689.1	1.6
CPB29173	*neo*-Pentane	50319	55	10064	11
CPB29176	*neo*-Pentane	50085	76	10017	15

Instrumentation

When determining amount fractions of target components in CCQM-K118's samples, we used two instruments, Micro GC 3000A (Agilent Technology, Santa Clara, CA USA) and GC-2010 (Shimadzu Corporation, Kyoto, Japan). Analytical conditions were summarized in Tables 13 and 14.

Table 13 Analytical conditions of Micro GC 3000A

	Analyte		
	N_2, CH_4	CO_2	H_2, He
Carrier gas	Helium	Helium	Argon
Injector type	Variable	Variable	Variable
Main column	Molsieve	PLOT U	Molsieve
Pre-column	PLOT U	PLOT Q	PLOT U
Oven temperature	85 ºC or 75 ºC	50 ºC	50 ºC

Table 14 Analytical conditions of GC-2010

Gas chromatograph	Shimadzu GC-2010
Detector	FID
Injection method	Direct injection using 6-ports sampling valve
Sample volume	0.1 mL
Valve box temperature	130 ºC
Column	CP-Al_2O_3/KCl PLOT (Length 50 m, 0.53 mm i.d.)
Carrier gas, flow rate	N_2, 5.0 mL min^{-1}
FID Temperature	200 ºC

FID fuel gas	H_2, 47 mL min^{-1}
FID supporting gas	Purified air, 400 mL min^{-1}
FID makeup gas	N_2, 30 mL min^{-1}
Oven temperature	[for ethane and propane]
	9 min hold at 40 ºC, 30 ºC min^{-1} up to 160 ºC, and hold for 6 min
	[for *i*-butane, *n*-butane, and *neo*-pentane]
	20 min hold at 50 ºC, 20 ºC min^{-1} up to 100 ºC, hold for 6 min, 20 ºC min^{-1} up to 150 ºC, hold for 6 min
	[for *i*-pentane and *n*-pentane]
	14 min hold at 100 ºC, 10 ºC min^{-1} up to 150 ºC, and hold for 6 min
	[for *n*-hexane]
	150 ºC, isothermal

Calibration method and value assignment

The calibration was carried out by "ISO6143 method" (3 point calibration line) in the case of analysing ethane and propane in K118.b sample, and nitrogen, carbon dioxide, *i*-pentane, *n*-pentane, and *n*-hexane analyses in K118.a and K118.b samples. For the ethane, propane, *neo*-pentane, hydrogen, and helium in K118.a sample, and *i*-butane and *n*-butane in K118.a and K118.b samples, the calibration was carried out by "bracketing method". Peak areas of the target components except hydrogen and helium in a chromatogram were recorded for the calibration. For hydrogen and helium, peak height was recorded, because the retention times of hydrogen and helium were close each other.

Calculation of Reported Values and Uncertainty

The final reported analytical amount fraction x was estimated by using the following equations;

$$x = \sum_{k=1}^{J} x_k \Big/ J \quad \ldots (1)$$

where J is the total number of "measurement #" and x_k is amount fraction of analyte. The standard uncertainty of the analytical amount fraction $u(x)$ is evaluated from the following equations;

$$u^2(x) = u^2(x)_{\text{ISO6143}} + u^2(x)_{\text{between-day}} \quad \ldots (2)$$

$$u^2(x)_{\text{ISO6143}} = \sum_{k=1}^{J} u^2(x_k)_{\text{ISO6143}}/J^2 \quad \ldots (3)$$

$$u^2(x)_{\text{between-day}} = \sum_{k=1}^{J} (x_k - x)^2/J(J-1) \quad \ldots (4)$$

where $u(x_k)_{ISO6143}$ is analytical amount fraction by a set of “calibration” and “sample measurement”.

References

[1] N. Matsumoto, T. Watanabe, M. Maruyama, Y. Horimoto, T. Maeda, K. Kato, "Development of mass measurement equipment using an electronic mass-comparator for the gravimetric preparation of reference gas mixtures", *Metrologia*, **41**, pp.178-188 (2004).

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[6] Takuro Watanabe, Tomohiro Sasaki, Tomotaka Yoshimura, Shoji Narukami, Takuya Shimosaka, "Application and Validation of a Determination Method Using Post-column Reaction Gas Chromatography of Nitrogen-containing Organic Compounds", *Anal. Sci.*, **34**, pp.853-857 (2018).

Measurement report NPL

Cylinder Number: D322694

Final Result GC-TCD/FID: (refer also to excel report files)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage Factor
Nitrogen	0.11973620	0.00017960	**2**
Carbon dioxide	0.04000765	0.00004001	**2**
Hydrogen	0.03000839	0.00015004	**2**
Helium	0.00503727	0.00002519	**2**
Ethane	0.00745967	0.00001492	**2**
Propane	0.00298417	0.00000448	**2**
iso-Butane	0.00199635	0.00000699	**2**
n-Butane	0.00199780	0.00000699	**2**
iso-Pentane	0.00049817	0.00000199	**2**
n-Pentane	0.00050177	0.00000201	**2**
neo-Pentane	0.00049266	0.00000246	**2**
n-Hexane	0.00049807	0.00000199	**2**
Methane	0.78888779	0.00031556	**2**

Cylinder Number: D322741

Final Result GC-TCD/FID: (refer also to excel report files)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage Factor
Nitrogen	0.00122184	0.00000611	**2**
Carbon dioxide	0.00019839	0.00000397	**2**
Ethane	0.09998919	0.00019998	**2**
Propane	0.01997620	0.00002996	**2**
iso-Butane	0.00149139	0.00000522	**2**
n-Butane	0.00148471	0.00000520	**2**
iso-Pentane	0.00019947	0.00000080	**2**
n-Pentane	0.00020087	0.00000080	**2**
Methane	0.87534324	0.00035014	**2**

Calibration standards

Two NPL Primary Reference Materials (PRMs) were prepared in accordance with ISO 6142[5]. The compositions were calculated to match the nominal amount fractions specified in the protocol. The purity of the source chemicals used to prepare the two PRMs were checked in accordance with ISO 19229[6]. The results are shown in the tables in this section.

Component	Supplier	Lot Number
Nitrogen	Air Products	-
Methane	CK Special Gases	97093072
Methane	CK Special Gases	97065353
Carbon dioxide	BOC	
Ethane	Air Liquide	1147793
Ethane	Air Liquide	5969917
Propane	Air Liquide	VCEB8381
iso-butane	Air Liquide	VCH17201
n-butane	Air Liquide	VC7750215
neo-pentane	Air Liquide	376267
iso-pentane	Sigma Aldrich	BCBV9550
n-pentane	Sigma Aldrich	BCB51143V
Helium	Air Products	-
Hydrogen	Air Products	-

Table 1: Summary of chemicals used and manufacturer.

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, $k = 1$ (cmol mol^{-1})
Argon	0.00005000	0.000005
Carbon monoxide	0.00000003	0.00000002
Oxygen	0.00000050	0.00000025
C_xH_y	0.00000050	0.0000005
Water	0.00000050	0.0000002
Nitrogen	99.99994817	0.00008735
Nitrogen monoxide	0.00000005	0.00000003
Sulphur dioxide	0.00000005	0.00000003
Methane	0.00000010	0.0000001
Hydrogen	0.00000010	0.0000001

Table 2: Purity analysis data for nitrogen.

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

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

Methane A

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Methane	99.999938	0.0000093
Nitrogen	0.00001	0.0000015
Oxygen	0.00001	0.0000015
C_xH_y	0.000002	0.0000003
Water	0.00004	0.000006

Table 3: Purity analysis data for methane used in NG843_CCQM.

Methane B

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Methane	99.999911	0.0000134
Nitrogen	0.000032	0.0000048
Oxygen	0.000017	0.0000026
C_xH_y	0.000002	0.0000003
Water	0.000038	0.0000057

Table 4: Purity analysis data for methane used in NG785_CCQM.

Carbon dioxide

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Argon	0.000005	0.0000029
Carbon monoxide	0.000005	0.0000029
Carbon dioxide	99.99998	0.000006
Nitrogen	0.000005	0.0000029
Oxygen	0.000005	0.0000029

Table 5: Purity analysis data for carbon dioxide.

Ethane A

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Ethane	99.99967	0.000088
Nitrogen	0.0001	0.00008
Oxygen	0.000025	0.00002
Methane	0.00003	0.00002
Propane	0.000025	0.00001
n-butane	0.00015	0.00002

Table 6: Purity analysis data for ethane used in NG785_CCQM.

Ethane B

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Nitrogen	0.00001	0.000005
Oxygen	0.000005	0.000005
Carbon monoxide	0.000005	0.000005
Carbon dioxide	0.000005	0.000005
Methane	0.00001	0.000005
Ethene	0.00003	0.000015
Propane	0.00001	0.000005
iso-butane	0.000005	0.000005
n-butane	0.00001	0.000005
Hydrogen	0.000005	0.000005
Water	0.00009	0.000045
Ethane	99.99999815	0.000050

Table 7: Purity analysis data for ethane used in NG843_CCQM.

Propane

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Ethene	0.002609	0.001329
Propane	99.996945	0.001404
iso-butane	0.000445	0.000075

Table 8: Purity analysis data for propane.

***i*-butane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Methane	0.000187	0.000059
Ethane	0.000085	0.000022
propane	0.000642	0.000082
iso-butane	99.997544	0.000423
n-butane	0.000669	0.000145
iso-butene	0.000682	0.000068
neo-pentane	0.000192	0.000047

Table 9: Purity analysis data for i-butane gas used in NG785_CCQM.

***i*-butane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Propane	0.000203	0.000067
iso-butane	99.998034	0.000322
n-butane	0.000673	0.000096
iso-butene	0.000703	0.000087
neo-pentane	0.000387	0.000071

Table 10: Purity analysis data for i-butane liquid used in NG843_CCQM.

***n*-butane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Methane	0.000594	0.000059
Propane	0.000536	0.000073
n-butane	99.995263	0.000513
iso-butane	0.000513	0.000072
trans-2-butene	0.00144	0.000144
cis-2-butene	0.001653	0.000165

Table 11: Purity analysis data for n-butane.

***neo*-pentane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Ethene	0.00587	0.001701
Ethane	0.015951	0.001595
Propene	0.013523	0.004792
Propane	0.106036	0.010604
Propyne	0.047947	0.004795
iso-butane	0.006915	0.000692
n-butane	0.177901	0.01779
neo-pentane	99.415721	0.026748
iso-butylene	0.067732	0.006773
Cyclobutane	0.133882	0.013388
iso-pentane	0.002931	0.000293
2,2-dimethylbutane	0.005591	0.003078

Table 12: Purity analysis data for neo-pentane.

***i*-pentane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
neo-pentane	0.041465	0.004146
iso-pentane	99.797363	0.020264
n-pentane	0.161172	0.016117

Table 13: Purity analysis data for i-pentane.

***n*-pentane**

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
iso-pentane	0.104687	0.010469
n-pentane	99.861616	0.014027
C5unknown	0.007198	0.000908
Cyclopentane	0.013919	0.001392
2met-pentane	0.01258	0.001258

Table 14: Purity analysis data for n-pentane.

Helium

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Carbon dioxide	0.000001	0.0000001
Methane	0.0000001	0.0000100
Helium	99.9999978	0.0005010
Carbon monoxide	0.0000001	0.0000010
Water	0.00001	0.0000010
Nitrogen	0.00001	0.0000150
Oxygen	0.000001	0.0000020

Table 15: Purity analysis data for helium.

Hydrogen

Component	Amount fraction (cmol mol^{-1})	Standard uncertainty, k = 1 (cmol mol^{-1})
Carbon monoxide	0.0000000058	0.0000000034
Carbon dioxide	0.000001	0.0000001100
Methane	0.0000000378	0.0000000218
Hydrogen	99.9999859936	0.0000050926
Water	0.0000010000	0.0000005774
Nitrogen	0.0000076639	0.0000044248
Oxygen	0.0000042075	0.0000024292
Argon	0.0000005715	0.0000003299

Table 16: Purity analysis data for hydrogen.

The mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. Mixtures were prepared in one stage from the pure liquid, liquified gas and gaseous components (via a transfer vessel, and direct addition to cylinder). Mixtures were produced in pairs and validated against each other and an existing suite of 9 validated PRMs. All four newly prepared mixtures were used in determining the amount fraction of the unknown mixtures. The composition of the four PRMs (NG843_CCQM, NG788_CCQM, NG875_CCQM and NG809_CCQM) are given in the following tables.

NG843_CCQM		
Component	**Amount fraction (cmol mol^{-1})**	**Standard uncertainty, k = 1 (cmol mol^{-1})**
Nitrogen	11.9454093	0.0014956
Methane	78.8766719	0.0025439
Carbon dioxide	4.0288615	0.0007896
Ethane	0.7735547	0.0000491
Propane	0.3008624	0.0000213
iso-butane	0.1998525	0.0000143
n-butane	0.2004957	0.0000168
neo-pentane	0.0492729	0.0000109
iso-pentane	0.0502271	0.0000105
n-pentane	0.0492834	0.0000103
n-hexane	0.0496021	0.0000068
Helium	0.4992158	0.0001870
Hydrogen	2.9764076	0.0014519

Table 17: Composition of NG843_CCQM.

NG788_CCQM		
Component	**Amount fraction (cmol mol^{-1})**	**Standard uncertainty, k = 1 (cmol mol^{-1})**
Nitrogen	11.6709923	0.0015017
Methane	79.0890123	0.0025565
Carbon dioxide	4.0621941	0.0007910
Ethane	0.7636175	0.0000488
Propane	0.3117851	0.0000219
iso-butane	0.2007173	0.0000144
n-butane	0.2057456	0.0000173
neo-pentane	0.0517200	0.0000114
iso-pentane	0.0480335	0.0000103
n-pentane	0.0508430	0.0000102
n-hexane	0.0504352	0.0000070
Helium	0.4883897	0.0001872
Hydrogen	3.0062226	0.0014589

Table 18: Composition of NG788_CCQM.

NG785_CCQM		
Component	**Amount fraction (cmol mol^{-1})**	**Standard uncertainty, k = 1 (cmol mol^{-1})**
Nitrogen	0.1260296	0.0000205
Methane	87.5043771	0.0014293
Carbon dioxide	0.0206796	0.0000038
Ethane	10.0040891	0.0012381
Propane	2.0004618	0.0007163
iso-butane	0.1520664	0.0000156
n-butane	0.1516238	0.0000157
iso-pentane	0.0200613	0.0000048
n-pentane	0.0204855	0.0000048

Table 19: Composition of NG785_CCQM.

NG809_CCQM		
Component	**Amount fraction (cmol mol^{-1})**	**Standard uncertainty, k = 1 (cmol mol^{-1})**
Nitrogen	0.1181291	0.0000196
Methane	87.4298177	0.0012200
Carbon dioxide	0.0198382	0.0000037
Ethane	10.0798954	0.0010436
Propane	2.0089337	0.0007073
iso-butane	0.1510627	0.0000110
n-butane	0.1520384	0.0000111
iso-pentane	0.0199966	0.0000046
n-pentane	0.0201619	0.0000046

Table 20: Composition of NG785_CCQM

Instrumentation

Two reference methods were used to determine the amount fractions of the mixture components.

Reference method 1:

- An Agilent Technologies 6890N Gas Chromatograph (GC) with 4.4 m Porasil-P and 4.4 m Porapak-PS custom-made packed columns. This GC is fitted with a Flame Ionisation Detector (FID) and a Thermal Conductivity Detector (TCD).

Reference method 2:

- An Agilent Technologies 7890B GC with DB-1 column (L = 30 m, D = 0.32 mm, FT = 5.00 µm), HP-PLOT Q PT column (L = 15m, D = 0.53 mm, FT = 4.00 µm), HP-PLOT MolSieve (L = 30 m,

D =0.53mm, FT = 50 µm), Hayesep Q 80/100 mesh (L = 2m, OD = 1/8 inch, ID = 2.0 mm), MolSieve 5A 80/100 mesh (L = 9ft, OD = 1/8 inch, ID =2 mm). This GC is fitted with an FID and two TCDs.

Calibration method and value assignment

The comparison mixture was assigned a value in accordance with ISO 6143[7] using a direct comparison method. The PRMs described above were prepared with amount fractions that differed by less than 6 % relative from the nominal composition of the comparison mixture. As the deviation range was within the linear response ranges of the detectors, the uncertainty contribution from analyser linearity was considered to be negligible.

The comparison mixture and an NPL PRM were connected to the GC (via an automated switching valve) using purpose-built minimised dead volume connectors and Silcosteel-passivated $^{1}/_{16}''$ internal diameter stainless steel tubing. NPL-designed flow restrictors or Swagelok needle valves were used to allow a stable sample flow of 25 ml min^{-1} to be maintained throughout the analysis.

The lines were thoroughly purged and flow rates were allowed to stabilise before commencing analysis. The reference method 1 was set up to alternate between the NPL and comparison mixtures every 8.2 minutes. Up to 10 injections of each mixture were performed in order to obtain a comprehensive dataset. The reference method 2 was set up to alternate between the NPL and comparison mixtures every 16 minutes. Up to 10 injections of each mixture were performed in order to obtain a comprehensive dataset.

Uncertainty evaluation

The ratio of the detector response (r) from the unknown cylinder and the NPL PRM was calculated using:

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

Where $A_{u,m}$ is the peak area from repeat m of the unknown cylinder, and $A_{s,m}$ is the peak area from repeat m of the NPL PRM.

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

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

Where n is the number of ratios. The amount fraction of each component in the unknown cylinder, x_u, is then calculated by:

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

Where x_s is the amount fraction of the component in the NPL PRM. The standard uncertainty of the measured amount fraction, $u(x_u)$, is calculated by:

7 International Organization for Standardization, "ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures"

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

Where $u(\bar{r})$ is calculated as the standard error of the mean.

Repeat measurements of x_u were averaged in order to obtain a final value for each component according to the below, where *N* is the total number of measurements:

$$x_f = \frac{\sum x_u}{N}$$

The standard uncertainty in x_f is calculated by:

$$u(x_f) = \frac{\sqrt{\sum_{i=1}^{N} u(x_{u_i})^2}}{N}$$

The final uncertainty is expressed as an expanded uncertainty $U(x_f)$, where the coverage factor, *k*, equals 2:

$$U(x_f) = 2u(x_f)$$

The following table details the uncertainty analysis for an example measurement of x_u.

quantity	unit	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution	Uncertainty type	distribution
x_s	mmol mol^{-1}	119.4541	0.0015	1.0026	0.00150	A	normal
$\bar{r}$	-	1.0026	0.0002	119.4541	0.02123	A	normal
x_u	**mmol mol^{-1}**	**119.766**					
$u(x_u)$	**mmol mol^{-1}**	**0.0213**					
$U(x_u)$	**mmol mol^{-1}**	**0.0426**					

To obtain the final amount fraction result for each component x_f, an average was taken of three independent measurements. The following table shows an example calculation for x_f and its uncertainty.

quantity	unit	Example value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution	Uncertainty type	distribution
x_{u1}	mmol mol^{-1}	119.736	0.0172	0.3333	0.0057	A	normal
x_{u2}	mmol mol^{-1}	119.706	0.0194	0.3333	0.0065	A	normal
x_{u3}	mmol mol^{-1}	119.766	0.0260	0.3333	0.0087	A	normal
$\boldsymbol{x_f}$	**mmol mol^{-1}**	**119.736**					
$\boldsymbol{u(x_f)}$	**mmol mol^{-1}**	**0.01223**					
$\boldsymbol{U(x_f)}$	**mmol mol^{-1}**	**0.02447**					

The final uncertainties are expressed as expanded uncertainties $U(x_f)$, where the coverage factor, k = 2, provides a level of confidence of approximately 95 %. The final uncertainties provided for the report are a combination of preparative, analytical and stability components.

Measurement report SMU

Cylinder number: D322740

Calibration standards

All calibration standards were made gravimetrically according ISO 6142-1 and verified against SMU Primary standard gas mixtures in accordance to ISO 6143. Impurities (hydrocarbons, oxygen, nitrogen, CO, CO_2) in parent gases were analysed on GC and FTIR. Each parent gas has its purity table with composition. The result values for parent gases are given in the table 1:

Table 1 Composition of pure gases

Parent gas/ liquid	mole fraction (mol/mol)	uncertainty k=1 (mol/mol)
Methane	0,9999328	0,0000033
Ethane	0,9999480	0,0000034
Propane	0,9999654	0,0000053
iso-Butane	0,9992421	0,0000080
n-Butane	0,998325	0,000032
neo-Pentane	0,991443	0,000022
n-Pentane	0,99853	0,00017
iso-Pentane	0,99847	0,00012
n-Hexane	0,99542	0,00012
CO_2	0,999818	0,000042
N_2	0,99999969	0,00000013
H_2	0,9999944	0,0000021
He	0,9999970	0,0000089

Preparation of Primary standard gas mixtures was carried out gravimetrically in 4 stages:

a) First premixture: H_2 and He.
b) Second premixture: C_1, C_2, C_3, i-C_4, n-C_4, neo-C_5.
c) Third premixture: 1. premixture, 2. premixture, CO_2, N_2, C_1.
d) Final mixture: 3. premixture and liquid componets i-C_5, n-C_5, n-C_6. Liquids were added to the cylinder through heated sample loop using syringe injection method.

All mixtures were prepared in aluminium cylinders, V= 5 dm^3. Inner surface of the cylinder was Aculife IV. Before preparation, the cylinder was evacuated at least 15 hours using dry evacuation system. The final value of vacuum was approximately $6x10^{-5}$ Pa.

The mass of added amount of parent mixture was determined by the difference of the cylinder masses before and after filling. Weighting of evacuated or filled cylinder were executed on automatic SMU balance system. During automatic weighting, the filled cylinder mass was not determined absolutely, but as a difference between filled cylinder mass and reference cylinder mass.

Three calibration mixtures were prepared for building of the linear calibration curve. For the verification GC method was used. All of target components corresponded to the validation criteria. Neither stability

changes were assumed for natural gas mixtures. To the validated PRM´s were assigned values of mole fraction of target component *k* (derived from the process of gravimetric preparation) and associated combined standard uncertainty calculated in accordance to the following formula (ISO 6142-1:2015):

$$u_{cert,x,k} = \frac{1}{2}\sqrt{u^2(x_{k,grav}) + u^2(x_{k,ver}) + (x_{k,grav} - x_{k,ver})^2}$$

Composition of calibration mixtures and associated standard uncertainties are shown in the table 2.

Table 2 SMU Primary calibration standards

Cylinder number	**Component**	**x (mol/mol)**	**u_{cert} (mol/mol)**	**$u_{cert,rel}$ (%)**
0050F_4	Nitrogen	0,11237	0,00018	0,16
	Carbon dioxide	0,045356	0,000026	0,06
	Hydrogen	0,04188	0,000066	0,16
	Helium	0,009647	0,000034	0,35
	Ethane	0,009883	0,000007	0,07
	Propane	0,0039028	0,0000029	0,07
	iso-Butane	0,0025950	0,0000023	0,09
	n-Butane	0,0024922	0,0000024	0,09
	iso-Pentane	0,0006108	0,0000020	0,32
	n-Pentane	0,0006062	0,0000018	0,29
	neo-Pentane	0,0006279	0,0000018	0,28
	n-Hexane	0,0005757	0,0000011	0,19
	Methane	0,76944	0,00030	0,04
0035F_3	Nitrogen	0,12785	0,00012	0,09
	Carbon dioxide	0,037911	0,000022	0,06
	Hydrogen	0,021114	0,000055	0,26
	Helium	0,0040634	0,0000050	0,12
	Ethane	0,0067122	0,0000047	0,07
	Propane	0,0027191	0,0000023	0,08
	iso-Butane	0,0017819	0,0000027	0,15

	n-Butane	0,0017280	0,0000032	0,19
	iso-Pentane	0,0004133	0,0000011	0,27
	n-Pentane	0,0004179	0,0000008	0,18
	neo-Pentane	0,0004248	0,0000014	0,32
	n-Hexane	0,0004204	0,0000006	0,13
	Methane	0,79443	0,00020	0,03
0062F_6	Nitrogen	0,122650	0,000070	0,06
	Carbon dioxide	0,024490	0,000015	0,06
	Hydrogen	0,02891	0,000035	0,12
	Helium	0,008177	0,000026	0,31
	Ethane	0,0074666	0,0000047	0,06
	Propane	0,0030871	0,0000031	0,10
	iso-Butane	0,0020003	0,0000025	0,12
	n-Butane	0,0019540	0,0000025	0,13
	iso-Pentane	0,0004987	0,0000019	0,38
	n-Pentane	0,0005256	0,0000018	0,34
	neo-Pentane	0,0004713	0,0000016	0,34
	n-Hexane	0,0005062	0,0000012	0,24
	Methane	0,79925	0,00024	0,03

Instrumentation

GC method

For this key comparison, following equipment of Slovak national standard of mole fraction in gaseous phase was used for the verification of calibration standards and for analytical measurement of unknown sample:

Table 3 Equipment for natural gas analysis

Equipment	**Specifications**
GC Varian 3600	
Columns set	molsieve 13 X packed 5 ft x1/8" S.S., short DC 200/500 packed 30%, 2 ft x 1/8" S.S., long DC 200/500 packed 30%, 30 ft x 1/8" S.S., buffer packed 1.5% OV 101 CGHP 100/120, 2 ft x 1/8" S.S.
Detectors	TCD, FID
electric or pneumatic valves	for dosing, backward flushing, shut-off for measured gas mixture
PC	control software for measurement on GC which records chromatograms to the PC
valve for gas mixture selection	1 output and min. 16 inputs, controlled from PC
mass flow regulator Brooks	(0-1) L N_2 / min; controlling unit with display
pressure sensor with display unit	(80-120) kPa; connection - thread 1/4‘ (1/8‘) Swagelok or NPT
distribution of gas (pipes, connections)	stainless steel, dimensions and threads 1/4‘,1/8‘ Swagelok
regulations of outlet pressure	outlet pressure (1.5-5)x10^2 kPa, stainless steel membrane input DIN-1, output 1/8‘ Swagelok
lines of pipes	stainless steel or FEP
measuring system of temperature, pressure and relative humidity of ambient air during measurement	resolution of: temperature: less than 0.05°C, pressure: less than 0.1 kPa, humidity: less than 0.2%

Analytical method GC settings:

GC method parameters for the11 component natural gas analysis are shown in the following tables:

Table 4 GC Settings

GC	L1; cm^3	L2; cm^3	Oven temperature; °C	Total time; min	F_EFC		M_EFC		Flow ACG; cm^3/min
					Pressure of FCG; kPa	Total flow; ml/min	Pressure of MCG; kPa	Total flow; ml/min	

Varian GC 3800	0.25	0.25	108	20.00	172.4	200	479.2	100	30

Table 5 Gas flows

Gas	Flow ml/min
Front carrier gas He	39.5
Middle carrier gas He	30.9
Auxiliary gas	30
Hydrogen	30
Air	300

Detectors:

FID C_2, C_3, i-C_4, C_4, i-C_5, C_5, neo-C_5, C_6

TCD C_1, N_2, CO_2

GC method parameters of the hydrogen and helium analysis are shown in the following tables:

Table 6 GC Settings

GC	L1; cm^3	L2; cm^3	Oven temperature; °C	Total time; min	F_EFC		M_EFC		Flow ACG; cm^3/min
					Pressure of FCG; kPa	Total flow; ml/min	Pressure of MCG; kPa	Total flow; ml/min	
Varian GC 3800	0.25	0.25	95	9.00	172.4	200	479.2	100	30

Table 7 Gas flows

Gas	Flow ml/min
Front carrier gas N_2	39.5
Middle carrier gas N_2	30.9

Detector TCD for H_2 and He.

Calibration method and value assignment

GC measurement method with several automated runs was used. All runs in first, third, fifth measurement sequence had rising molar fraction. Second, fourth. processed in reverse order. From each run was made one calibration curve. 3 point linear model of analytical curve was used. No corrections were used.

Data were subjected to the B_least program (weighted least square regression). Inputs to the B_least were: values of measured signals (peak areas) with their standard uncertainties and mole fractions certified values of calibration gas mixtures with their standard uncertainties.

Uncertainty of instrument response consisted from figure characterized roughly immediate repeatability and from signal drift estimated. B-least program for each run produced sample mole fraction with its standard uncertainty. From all runs results = average of mole fractions in one sequence were standard deviation found $u_1(\overline{x_i})$ and from runs results uncertainties the mean (through squares) was found $u_2(\overline{x_i})$. These 2 figures were combined to give standard uncertainty $u_{an}(\overline{x_i})$ for one sequence. Following formulas were used for the uncertainty calculations:

$$u_1(\overline{x}_i) = 1.3 * \sqrt{\frac{\sum_{j=1}^{n}(x_j - \overline{x}_i)^2}{n*(n-1)}}$$

$$u_2(\overline{x}_i) = \sqrt{\frac{\sum_{j=1}^{n} u(x_j)^2}{n^2}}$$

$$u_{an}(\overline{x}_i) = \sqrt{u_1(\overline{x}_i)^2 + u_2(\overline{x}_i)^2}$$

$$\overline{x}_i = \frac{\sum_{j=1}^{n} x_j}{n}$$

n- number of measuring runs

Final result of mole fraction was average value from 5 day results. Associated type A standard uncertainties were calculated as a standard deviation multiplied by 1.3 factor. The results are shown in the table 8.

Table 8 Measurement results with associated standard uncertainty type-A

Component	**1. meas. (mol/mol)**	**2. meas. (mol/mol)**	**3. meas. (mol/mol)**	**4. meas. (mol/mol)**	**5. meas. (mol/mol)**	$\overline{x}$ **(mol/mol)**	u_A **(mol/mol)**
Nitrogen	0,11984	0,11982	0,11969	0,11981	0,11971	0,119774	0,000040
Carbon dioxide	0,04005	0,04006	0,04001	0,04004	0,03992	0,040014	0,000032
Hydrogen	0,03033	0,02998	0,03002	0,03010	0,03005	0,030096	0,000080

Helium	-	0,005011	0,004999	0,005040	0,005048	0,005025	0,000015
Ethane	0,0074597	0,0074583	0,0074585	0,0074582	0,0074652	0,0074600	0,0000017
Propane	0,0029889	0,0029895	0,0029869	0,0029882	0,002989	0,0029885 0	0,0000059
iso-Butane	0,0020006	0,0020006	0,0019991	0,0019988	0,0019930	0,0019984	0,0000018
n-Butane	0,0020006	0,0020037	0,0020021	0,0020025	0,0019966	0,0020011	0,0000016
iso-Pentane	0,0004974	0,0004976	0,0004966	0,0004959	0,0004974	0,0004969 8	0,0000042
n-Pentane	0,0005026	0,0005026	0,0005018	0,000501	0,0005025	0,0005021 0	0,0000041
neo-Pentane	0,0004963	0,0004966	0,0004961	0,0004961	0,000498	0,0004966 2	0,0000046
n-Hexane	0,0004968	0,0004967	0,0004961	0,0004961	0,0004973	0,0004966 0	0,0000030
Methane	0,78911	0,78906	0,78843	0,78883	0,78877	0,78884	0,00016

Standard uncertainty type B was calculated as a combined value from maximum value from 5 day analysis uncertainties and uncertainty of gravimetrically prepared calibration gas (0035F_3). Results are shown in the table 9.

Table 9 Type-B uncertainty evaluation results

Comp.	**u_{an} 1. meas. (mol/mol)**	**u_{an} 2.meas. (mol/mol)**	**u_{an} 3. meas. (mol/mol)**	**u_{an} 4. meas. (mol/mol)**	**u_{an} 5. meas. (mol/mol)**	**$u_{an,max}$ (mol/mol)**	**u_{cert} (mol/mol)**	**u_B (mol/mol)**
Nitrogen	0,000073	0,000077	0,000098	0,000084	0,00011	0,00011	0,00012	0,00016
Carbon dioxide	0,000019	0,000021	0,000069	0,000053	0,000047	0,000069	0,000022	0,000072
Hydrogen	0,00010	0,000069	0,000041	0,00013	0,000035	0,00013	0,000055	0,00014
Helium	-	0,0000073	0,0000073	0,000022	0,0000070	0,000022	0,0000050	0,000023
Ethane	0,0000045	0,0000057	0,0000091	0,0000077	0,0000072	0,0000091	0,0000047	0,000010
Propane	0,0000023	0,0000021	0,0000046	0,0000038	0,0000073	0,0000073	0,0000023	0,0000077
iso-Butane	0,0000016	0,0000016	0,0000039	0,0000036	0,0000047	0,0000047	0,0000027	0,0000054
n-Butane	0,0000016	0,0000017	0,0000037	0,0000034	0,0000045	0,0000045	0,0000032	0,0000055

iso-Pentane	0,0000005	0,0000005	0,0000018	0,0000018	0,0000006	0,0000018	0,0000011	0,0000021
n-Pentane	0,0000005	0,0000005	0,0000016	0,0000015	0,0000004	0,0000016	0,0000008	0,0000018
neo-Pentane	0,0000007	0,0000008	0,0000020	0,0000012	0,0000017	0,0000020	0,0000014	0,0000024
n-Hexane	0,0000008	0,0000007	0,0000018	0,0000014	0,0000011	0,0000018	0,0000006	0,0000019
Methane	0,00040	0,00038	0,00033	0,00039	0,00055	0,00055	0,00020	0,000585

Total standard uncertainty was evaluated by following formula:

$$u(\bar{x}) = \sqrt{u_A^2 + u_B^2}$$

Expanded uncertainty (k=2) of final result:

$$U(\bar{x}) = 2 * u(\bar{x})$$

References

ISO 6142-1:2015 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 14912:2003 Gas analysis – Conversion of gas mixture composition data.

Measurement report UME

Cylinder number: D322708) for hydrogen-enriched

Cylinder number: D322701) for LNG-type

Calibration standards

Primary reference gas mixtures, hydrogen-enriched (low calorific) and LNG-type (high calorific) mixtures of natural gas, used in calibrations are given in Table 1 and Table 2, respectively. They were prepared individually in accordance with ISO 6142-1:2015 [1] and were verified at UME. Several pre-mixtures were individually prepared; these pre-mixtures were diluted to prepare six reference gas standards for hydrogen-enriched type and three reference gas standards for LNG-type mixture. The pure gases used for the preparation of gas mixtures are given in Table 3. The uncertainties of the primary reference gas mixtures were determined by combining the standard uncertainties of weighing, purity and molecular masses for all components. For H_2-enriched type mixtures only, standard uncertainties for i-pentane, n-pentane and n-hexane components from analyses were used.

Table 1. List of primary reference gas mixtures (H_2-enriched NG mixture)

Item	**Prepared By**	**Cylinder Number**	**Component**	**Mole Fraction** (mol/mol)	**Uncertainty (k=1)** (mol/mol)
1	UME	499803	Nitrogen	0.17967	0.00002
			Carbon dioxide	0.05980	0.00001
			Hydrogen	0.04051	0.00001
			Helium	0.007225	0.000003
			Ethane	0.012461	0.000003
			Propane	0.004993	0.000001
			iso-Butane	0.004007	0.000001
			n-Butane	0.003970	0.000001
			iso-Pentane	0.0001989	0.0000007
			n-Pentane	0.0002055	0.0000007
			neo-Pentane	0.0024976	0.0000055
			n-Hexane	0.0001959	0.0000004
			Methane	0.68422	0.00003

2	UME	266455	Nitrogen	0.12063	0.00001
			Carbon dioxide	0.04033	0.00001
			Hydrogen	0.03003	0.00001
			Helium	0.004970	0.000002
			Ethane	0.007506	0.000002
			Propane	0.003044	0.000001
			iso-Butane	0.001948	0.000001
			n-Butane	0.001996	0.000001
			iso-Pentane	0.0005347	0.0000009
			n-Pentane	0.0005201	0.0000013
			neo-Pentane	0.0004934	0.0000012
			n-Hexane	0.0004827	0.0000007
			Methane	0.78747	0.00002
3	UME	298291	Nitrogen	0.14925	0.00001
			Carbon dioxide	0.04990	0.00001
			Hydrogen	0.00503	0.00001
			Helium	0.000833	0.000001
			Ethane	0.002521	0.000001
			Propane	0.001023	0.000001
			iso-Butane	0.000997	0.000001
			n-Butane	0.001021	0.000001
			iso-Pentane	0.0003292	0.0000007
			n-Pentane	0.0003227	0.0000010
			neo-Pentane	0.0002861	0.0000007
			n-Hexane	0.0003060	0.0000004
			Methane	0.78814	0.00002
4	UME	499797	Nitrogen	0.09152	0.00001
			Carbon dioxide	0.03046	0.00001

			Hydrogen	0.04942	0.00001
			Helium	0.008180	0.000003
			Ethane	0.004957	0.000002
			Propane	0.002010	0.000001
			iso-Butane	0.003008	0.000001
			n-Butane	0.003005	0.000001
			iso-Pentane	0.0006980	0.0000015
			n-Pentane	0.0007177	0.0000019
			neo-Pentane	0.0006984	0.0000016
			n-Hexane	0.0006878	0.0000012
			Methane	0.80460	0.00003
5	UME	499761	Nitrogen	0.03210	0.00001
			Carbon dioxide	0.01068	0.00001
			Hydrogen	0.02056	0.00001
			Helium	0.003402	0.000002
			Ethane	0.009754	0.000002
			Propane	0.003956	0.000001
			iso-Butane	0.001868	0.000001
			n-Butane	0.001914	0.000001
			iso-Pentane	0.0009792	0.0000018
			n-Pentane	0.0009760	0.0000033
			neo-Pentane	0.0009734	0.0000023
			n-Hexane	0.0006769	0.0000013
			Methane	0.91179	0.00002
6	UME	499775	Nitrogen	0.00649	0.00001
			Carbon dioxide	0.00216	0.00001
			Hydrogen	0.00973	0.00001
			Helium	0.001611	0.000001

			Ethane	0.001485	0.000001
			Propane	0.000602	0.000001
			iso-Butane	0.000474	0.000001
			n-Butane	0.000486	0.000001
			iso-Pentane	0.0000964	0.0000003
			n-Pentane	0.0000993	0.0000004
			neo-Pentane	0.0001016	0.0000002
			n-Hexane	0.0000942	0.0000005
			Methane	0.97656	0.00001

Table 2. List of primary reference gas mixtures (LNG-type mixture)

Item	**Prepared By**	**Cylinder Number**	**Component**	**Mole Fraction** (mol/mol)	**Uncertainty (k=1)** (mol/mol)
1	UME	499821	Nitrogen	0.001222	0.000001
			Carbon dioxide	0.0002000	0.0000002
			Ethane	0.09889	0.00002
			Propane	0.01960	0.00001
			iso-Butane	0.001497	0.000001
			n-Butane	0.001486	0.000001
			iso-Pentane	0.0001998	0.0000005
			n-Pentane	0.0001993	0.0000005
			Methane	0.87668	0.00002
2	UME	499833	Nitrogen	0.001811	0.000001
			Carbon dioxide	0.0002965	0.0000002
			Ethane	0.10321	0.00002
			Propane	0.02046	0.00001
			iso-Butane	0.001064	0.000001
			n-Butane	0.001056	0.000001
			iso-Pentane	0.0000986	0.0000002
			n-Pentane	0.0000983	0.0000003

			Methane	0.87188	0.00003
3	UME	499855	Nitrogen	0.000610	0.000001
			Carbon dioxide	0.0000997	0.0000002
			Ethane	0.09471	0.00002
			Propane	0.01878	0.00001
			iso-Butane	0.003085	0.000001
			n-Butane	0.003062	0.000001
			iso-Pentane	0.0002975	0.0000007
			n-Pentane	0.0002967	0.0000007
			Methane	0.87903	0.00002

Table 3. List of pure gases

Component	Suppliers	Grade	Origin
Nitrogen	Linde	6.0	Turkey
Carbon dioxide	Linde	5.0	Turkey
Hydrogen	Linde	5.0	Germany
Helium	Hat Group	5.0	Turkey
Ethane	Air Liquide	3.5	Germany
Propane	Air Liquide	3.5	Germany
iso-Butane	Air Liquide	3.5	Germany
n-Butane	Air Liquide	3.5	Germany
iso-Pentane	Air Liquide	2.7	Germany
n-Pentane	Air Liquide	2.2	Germany
neo-Pentane	Air Liquide	2.0	Germany
n-Hexane	Air Liquide	2.2	Germany
Methane	Linde	5.5	Germany

Instrumentation

The hydrogen-enriched and LNG-type mixtures were analyzed on an Agilent 7890B gas chromatography instrument equipped with FID and two TCDs, split/splitless injector, gas injection valve, including GC ChemStation software (Rev. B. 04.03-SP2 [108]) to collect and process data. Carbon dioxide in LNG-type mixtures was analyzed on Agilent 6890N gas chromatography instrument equipped with FID-methaniser. The conditions for the analyses are given below:

a) Conditions for Agilent 7890B

Oven

Equilibration Time :1 min

Max Temperature :220 degrees C

Slow Fan :Disabled

Oven Program :On

60 °C for 1 min

#1 then 20 °C/min to 80 °C for 0 min

#2 then 30 °C/min to 190 °C for 0.33 min

Run Time :5.9967 min

Front SS Inlet He

Mode :Split

Heater :On 250 °C

Pressure :On 18 psi

Total Flow :On 86.452 mL/min

Septum Purge Flow :On 3 mL/min

Split Ratio :20 :1

Split Flow :79.479 mL/min

Column #1

Agilent G3591-81141 2 ft Unibeads IS 60-80 mesh

200 °C: Packed

In: PCM B-2 He

Out: Back Detector TCD

Pressure Program On

9.8 psi for 0 min

Run Time 5.9967 min

Column #2+#3

Agilent g3591-81142 4 ft Unibeads IS + Agilent g63591-81022 8 ft Molesieve 5A 60/80 mesh

200 °C: Packed

In: PCM B-1 He

Out: Other

Flow Program On

2.7527E+06 mL/min for 0 min

Run Time 5.9967 min

Column #4

Agilent G3591-81020 3 ft Hayesep Q 80-100 mesh

225 °C: Packed

In: PCM C-2 N2

Out: Aux Detector TCD

Pressure Program On

12.9 psi for 0 min

Run Time 5.9967 min

Column #5

Agilent G3591-81022 8 ft Molesieve 5A 60/80 mesh

350 °C: Packed

In: PCM C-1 N2

Out: Aux Detector TCD

Flow Program On

4.5247E+06 mL/min for 0 min

Run Time 5.9967 min

Column #6+#7+#8

Agilent 19091P-S12 25 m x 0.32mm x 8µm HP-AL/S

123-1015(cut) 2m x 0.32mm x 5µm DB-1

123-1015(cut) 0.45m x 0.32mm x 5µm DB-1

200 °C: 27 m x 320 µm x 8 µm

In: Front SS Inlet He

Out: Front Detector FID

(Initial) :60 °C

Pressure :18 psi

Flow :3.9739 mL/min

Average Velocity :60.334 cm/sec

Holdup Time :0.74584 min

Flow Program :On 3.9739 mL/min for 0 min

Run Time :5.9967 min

Front Detector FID

Heater :On 250 °C

H2 Flow :On 40 mL/min

Air Flow :On 350 mL/min

Makeup Flow :On 27 mL/min

Const Col + Makeup :Off

Back Detector TCD

Heater :On 250 °C

Reference Flow :On 45 mL/min

Makeup Flow	:On 2 mL/min
Const Col + Makeup	:Off
Negative Polarity	:Off

Aux Detector TCD

Heater	:On 250 °C
Reference Flow	:On 45 mL/min
Makeup Flow	:On 2 mL/min
Const Col + Makeup	:Off
Negative Polarity	:On

b) Conditions for Agilent 6890N

Oven

Equilibration Time	:0.30 min
Max Temperature	:300° C
Slow Fan	:Disabled
Oven Program	:On

30 °C for 5 min

Front Inlet He

Mode	:Split
Heater	:Off
Pressure	:On 21.35 psi
Total Flow	:On 50.4 mL/min
Split Ratio	:5 :1
Split Flow	:39.9 mL/min

Column #1+#2

Capillary Column

Agilent 19091P-Q04 30 m x 0.32 mm x 20.00 µm

Agilent 19095P-MS0 30 m x 0.53 mm x 25.00 µm

In: Back Inlet

Out: Front Detector FID

Mode: Constant flow

Flow: 8.0 mL/min

Nominal init pressure: 21.36 psi

Average velocity: 51 cm/sec

Front Detector FID

Heater	:On 250 °C
H2 Flow	:On 40 mL/min
Air Flow	:On 400 mL/min
Makeup Flow	:Off
Const Col + Makeup	:Off
Data rate	:20 Hz

Calibration method and value assignment

After the arrival of the cylinders from coordinator, they were stored in the laboratory at least 24 h. prior to analyses. Primary reference gas mixtures were also stored in the same laboratory during all measurements. Samples and the calibration standards were equipped with pressure reducers and connected to computer programmed multiposition valve gas sampling box. They were flushed at least 3 times before the first measurement. The pressures of sample and standard gases were controlled by a electronic pressure controller at 150 mbar.

The data was collected using ChemStation software. Each sample in the sequence was injected 8 to 12 times, and the first two injections in each case were discarded as they were considered as flushing of sample loop. The responses were averaged. The software “CurveFit” was utilized to determine the fitting data for the calibrations. The value for goodness of fit in each measurement was found to be less than 2 in each case whichever the function was used.

The assigned value was calculated by averaging the results of three independent sets of measurements.

Uncertainty evaluation

The measurement uncertainty of samples was determined according to ISO 6143:2001 [2], using the CurveFit software.

The largest uncertainty of the three sets of measurements for each component was taken as the standard uncertainty in the samples.

The expanded uncertainty was determined by multiplying the standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

References

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

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

Measurement report VNIIM

Cylinder number: D322703 Hydrogen-enriched natural gas

Cylinder number: D322705 LNG-type natural gas

Results for the Cylinder D322703 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Relative expanded uncertainty (%)	Coverage factor
He	23/04/19	0.5004	0.0025	0.50	2
H_2		2.991	0.013	0.45	2
N_2		11.942	0.031	0.26	2
CO_2		3.989	0.011	0.27	2
C_2H_6		0.7432	0.0041	0.55	2
C_3H_8		0.2978	0.0016	0.54	2
i-C_4H_{10}		0.1993	0.0015	0.73	2
n-C_4H_{10}		0.1993	0.0016	0.80	2
neo-C_5H_{12}		0.04932	0.00034	0.69	2
i-C_5H_{12}		0.04994	0.00048	0.97	2
n-C_5H_{12}		0.05009	0.00040	0.81	2
n-C_6H_{14}		0.04978	0.00056	1.1	2
CH_4		78.94	0.04	0.05	2

Results for the Cylinder D322705 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (cmol/mol)	Expanded uncertainty (cmol/mol)	Relative expanded uncertainty (%)	Coverage factor
N_2	25/06/19	0.1207	0.00084	0.70	2
CO_2		0.0198	0.00015	0.75	2
C_2H_6		9.9708	0.049	0.49	2
C_3H_8		1.9913	0.011	0.56	2

i-C_4H_{10}		0.1491	0.00096	0.64	2
n-C_4H_{10}		0.1481	0.00146	0.99	2
i-C_5H_{12}		0.01997	0.000190	0.95	2
n-C_5H_{12}		0.0201	0.000144	0.77	2
CH_4		87.56	0.05	0.06	2

Calibration standards

Calibration gas mixtures for each type of the 2 comparison mixtures were prepared in accordance with [1].

a) preparation of hydrogen-enriched natural gas calibration mixtures
- preparation of 2 types of premixtures:

2 premixtures (He 3,22 % + H_2 19,355 % + N_2) and

2 premixtures (neo-C_5H_{12} 1 % + CH_4)

- preparation of 3 target calibration gas mixtures with the composition close to the comparison hydrogen-enriched natural gas mixture

b) preparation of LNG-type natural gas calibration mixtures
- preparation of 2 types of premixtures:

2 mixtures (CO_2 0,5 % + N_2 3 % + CH_4) and

2 mixtures (n-C_4H_{10} 2 % + i-C_4H_{10} 2 % + CH_4)

- preparation of 3 target calibration gas mixtures with the composition close to comparison LNG-type natural gas mixture

All the mixtures were prepared in Luxfer cylinders (V=5 dm^3 and 10 dm^3).

Characteristics of pure substances used for preparation of the calibration standards are shown in the tables 1-13.

Table 1: Purity table for N_2

Monoblock Main component N_2 Mole fraction 99.9998572 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
Ar	0.916	0.011
O_2	0.0015	0.0009
CO_2	0.0025	0.0014
H_2	0.0025	0.0014
CH_4	0.0025	0.0014
CO	0.0025	0.0014
H_2O	0.50	0.05

Table 2: Purity table CO_2

Cylinder N 7225 Main component CO_2 Mole fraction 99.9999091%		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
N_2	0.364	0.011
CH_3OH	0.270	0.009
CO	0.010	0.006
CH_4	0.015	0.009
H_2	0.10	0.06
O_2	0.15	0.009

Table 3: Purity table H_2

Cylinder N 74318 Main component H_2 Mole fraction 99.9993504 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
N_2	6.3	0.4
O_2	0.15	0.09
CO_2	0.030	0.017
CH_4	0.015	0.009
CO	0.010	0.006

Table 4: Purity table He

Cylinder N 278584 Main component He Mole fraction 99.9999837 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
Ne	0.075	0.043
CO_2	0.0333	0.0013
H_2	0.0304	0.0009

N_2	0.0163	0.0006
O_2	0.0043	0.00025
Ar	0.0015	0.0009
CO	0.0010	0.0006
CH_4	0.0005	0.0003

Table 5: Purity table CH_4

Cylinder N 447875 Main component CH_4 Mole fraction 99.9996347 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
C_2H_6	0.8	0.4
CO_2	0.8	0.4
N_2	0.695	0.014
C_3H_8	0.25	0.14
n-C_4H_{10}	0.25	0.14
i-C_4H_{10}	0.25	0.14
O_2	0.208	0.008
Ar	0.15	0.09
He	0.15	0.09
H_2	0.10	0.06

Table 6: Purity table C_2H_6

Cylinder N 569 Main component C_2H_6 Mole fraction 99.9991814 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
N_2	3.1	0.1
H_2	2.2	0.1
CO_2	0.451	0.014
O_2	0.41	0.01
C_3H_8	0.25	0.08
n-C_4H_{10}	0.25	0.08
n-C_6H_{14}	0.25	0.08
He	0.25	0.08
i-C_4H_{10}	0.25	0.08
C_5H_{12}	0.25	0.08
neo-C_5H_{12}	0.25	0.08
i-C_5H_{12}	0.25	0.08
CH_4	0.015	0.005
CO	0.010	0.006

Table 7: Purity table C_3H_8

Cylinder N 312369 Main component C_3H_8 Mole fraction 99.99542 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
n-C_4H_{10}	20.2	0.5
C_3H_6	13.2	0.4
C_2H_6	9.7	0.5
i-C_4H_{10}	2.7	0.1

Table 8: Purity table i-C_4H_{10}

Cylinder N 4874 Main component i-C_4H_{10} Mole fraction 99.9772 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
n-C_4H_{10}	120	10
C_3H_8	102	4
i-C_4H_8	5.5	0.6

Table 9: Purity table n-C_4H_{10}

Cylinder N 3405 Main component n-C_4H_{10} Mole fraction 99.97095 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
neo-C_5H_{12}	244	7
i-C_4H_{10}	31	1.7
trans-2-C_4H_8	8.8	0.9
cis-2-C_4H_8	3.7	0.4
C_3H_8	3.0	0.3

Table 10: Purity table i-C_5H_{12}

Cylinder N 8027-1 Main component i-C_5H_{12} Mole fraction 99.6822 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
n-C_5H_{12}	2546	255
neo-C_5H_{12}	430	40
C_7H_8 (toluene)	72	7

n-C_7H_{16}	30	3
n-C_6H_{14}	27	3
C_6H_{12} (1-hexene)	16	1.6
C_5H_{10} (2-methyl-1-butene)	16	1.6
C_6H_{12} (cyclohexane)	11.5	1.3
C_5H_{10} (1-pentene	5.7	0.6
n-C_4H_{10})	5.1	0.5
n-C_9H_{20}	4.7	0.5
C_5H_{10} (cyclopentane)	2.9	0.3
C_5H_{10} (3-methyl-1-butene)	2.0	0.2
C_6H_{14} (2,2-dimethylbutane)	1.8	0.18
C_5H_{10} (2-methyl-2-butene)	1.4	0.13
C_6H_6	1.2	0.13
n-C_8H_{18}	1.0	0.10
C_5H_{10} (trans-2-pentene)	1.0	0.10
C_6H_{14} (2-methylpentane)	0.9	0.1
C_6H_{14} (3-methylpentane)	0.77	0.08

Table 11: Purity table n-C_5H_{12}

Bottle N LHC 30 Main component n-C_5H_{12} Mole fraction 99,132 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
n-C_4H_{10}	1,1	0.10
C_5H_{10} (cyclopentane)	890	90
n-C_6H_{14}	2.1	0.20
C_6H_{14} (3-methylpentane)	10	1.0
C_6H_{14} (2,3-dimethylbutane)	18	1.7
C_6H_{14} (2,2-dimethylbutane)	17	1.7
i-C_4H_{10}	9.7	1.0
i-C_5H_{12}	7700	267
i-C_6H_{14}	32	3
neo-C_5H_{12}	0.69	0.07

Table 12: Purity table neo-C_5H_{12}

Cylinder N M491431 Main component neo-C_5H_{12} Mole fraction 99,769 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
n-C_4H_{10}	1700	60
cis-2-C_4H_8	475	30
i-C_5H_{12}	59	1
C_3H_8	26	1.7
i-C_4H_{10}	25	1.6
n-C_5H_{12}	13	1.3

C_5H_{10} (cyclopentane)	12	1.3

Table 13: Purity table n-C_6H_{14}

Bottle N 3-012-06 Main component n-C_6H_{14} Mole fraction 99,8994 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
C_6H_{14} (3-methylpentane)	450	30
C_6H_{12} (methy-lcyclopentane)	280	19
n-C_5H_{12}	103	7
C_7H_8 (toluene)	91	6
n-C_7H_{16}	34	2.3
i-C_6H_{14}	23	1.5
C_6H_{12} (1-hexene)	14	0.09
C_6H_6	11	0.07

Verification measurements for all the mixtures were carried out by gas chromatography,

$u_{ver} \approx$ (0,2-0,6) % rel.

All verification measurements consisted of checking consistency between the batch of similar prepared mixtures.

The composition of calibration gas mixtures is given in the tables 14 and 15.

Table 14- The composition of hydrogen-enriched natural gas calibration mixtures

Cylinder number	Component	Mole fraction (cmol/mol)	Standard uncertainty due to weighing and purity (cmol/mol)
D720536	He	0.49962	0.00030
	H_2	3.0076	0.0012
	N_2	11.9545	0.0006

	CO_2	3.98286	0.00020
	C_2H_6	0.75068	0.00025
	C_3H_8	0.29893	0.00017
	i-C_4H_{10}	0.19886	0.00014
	n-C_4H_{10}	0.19929	0.00013
	neo-C_5H_{12}	0.049693	0.000014
	i-C_5H_{12}	0.051342	0.000030
	n-C_5H_{12}	0.049251	0.000030
	n-C_6H_{14}	0.050857	0.000007
	CH_4	balance	-
D720544	He	0.49604	0.00030
	H_2	2.9861	0.0011
	N_2	11.8691	0.0005
	CO_2	3.97602	0.00020
	C_2H_6	0.74939	0.00023
	C_3H_8	0.29714	0.00017
	i-C_4H_{10}	0.19902	0.00013
	n-C_4H_{10}	0.19927	0.00013
	neo-C_5H_{12}	0.049807	0.000014
	i-C_5H_{12}	0.051138	0.000030
	n-C_5H_{12}	0.050133	0.000030
	n-C_6H_{14}	0.050639	0.000007
	CH_4	balance	-
D720559	He	0.49565	0.00030
	H_2	2.9837	0.0011
	N_2	11.8597	0.0006
	CO_2	3.96703	0.00020
	C_2H_6	0.73725	0.00025
	C_3H_8	0.30058	0.00017

	i-C_4H_{10}	0.19876	0.00013
	n-C_4H_{10}	0.19848	0.00013
	neo-C_5H_{12}	0.048993	0.000013
	i-C_5H_{12}	0.051017	0.000030
	n-C_5H_{12}	0.049624	0.000030
	n-C_6H_{14}	0.049911	0.000007
	CH_4	balance	-

Table 15- The composition of LNG-type natural gas calibration mixtures

Cylinder number	Component	Mole fraction (cmol/mol)	Standard uncertainty due to weighing and purity (cmol/mol)
D720533	N_2	0.124239	0.000025
	CO_2	0.020607	0.000009
	C_2H_6	9.6937	0.0005
	C_3H_8	1.93642	0.00020
	i-C_4H_{10}	0.14628	0.00005
	n-C_4H_{10}	0.14374	0.00005
	i-C_5H_{12}	0.019855	0.000012
	n-C_5H_{12}	0.019301	0.000012
	CH_4	balance	-
D720563	N_2	0.119857	0.000023
	CO_2	0.019880	0.000009
	C_2H_6	10.0178	0.0005
	C_3H_8	2.02077	0.00022
	i-C_4H_{10}	0.15267	0.00005
	n-C_4H_{10}	0.15002	0.00005
	i-C_5H_{12}	0.020364	0.000012
	n-C_5H_{12}	0.020432	0.000013
	CH_4	balance	-

D720573	N_2	0.120058	0.000023
	CO_2	0.019910	0.000009
	C_2H_6	10.0904	0.0004
	C_3H_8	2.00733	0.00023
	i-C_4H_{10}	0.14924	0.00005
	n-C_4H_{10}	0.15070	0.00005
	i-C_5H_{12}	0.020552	0.000012
	n-C_5H_{12}	0.120058	0.000013
	CH_4	balance	-

Instrumentation

The instrument used for the measurements of the natural gas mixtures is Chromatograph «Chromatec-Crystal 5000.2» (“Chromatec”, Russia) with 3 detectors (3 measurement channels).

Operating mode

Channel/ Components measured	Column	Temperature mode of thermostat of columns	Detector	Carrier gas	Sample loop
(1) CO_2 and hydrocarbons	Hayesep R 80-100 mesh, l= 3 m, id= 2 mm	40°C–5 min-10°C/min - 230°C – (3-12) min	TCD t=180 °C	He flow rate - 15 ml/min	V=0.5 ml Heated valve, t=100 °C
(2) O_2 and N_2	NaX 60-800 mesh, l= 3 m метра, id= 3 mm		TCD t=180 °C	He flow rate - 15 ml/min	V=1.0 ml Heated valve, t=100 °C
(3) H_2 and He	NaX 60-800 mesh, l= 3 m метра, id= 3 mm		TCD t=180 °C	Ar flow rate - 15 ml/min	V=0.5 ml Heated valve, t=100 °C

Data collection: Software support “Chromatec Analytic”(Russia).

Calibration method and value assignment

Single point calibration method was used for value assignment.
Measurement sequence was in the order: $standard_i$ - sample -– $standard_i$.
For the both comparison mixtures 6 measurements in 6 days were carried out, that is 2 measurement cycles with each of the 3 prepared calibration mixtures (tables 14-15).

The amount of substance fraction for the each measurement result was calculated according to the formula $C_n = C_{n,st} \frac{A_n}{(A'_{n,st} + A''_{n,st})/2}$,

where C_n and $C_{n,st}$ – amount of substance fractions of the component n in the comparison and calibration mixtures;

A_n– analytical signal of the component n in the comparison gas mixture;

$A'_{n,st}$ and $A''_{n,st}$ analytical signals of the component n in the calibration standard before and after measurement of the comparison mixture.

Temperature corrections were not applied due to use of above-mentioned measurement sequence.

Uncertainty evaluation

Table 16. Uncertainty budget for the amount fraction of components in hydrogen-enriched natural gas (Cylinder D322703)

Component	Source of uncertainty	Estimate xi, cmol/mol	Type of evaluation	Standard uncertainty, $u(x_i)$, cmol/mol	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$, cmol/mol	Combined standard uncertainty, cmol/mol	Expanded uncertainty, cmol/mol (k=2)	Relative expanded uncertainty, %
He	Mole fraction in cal. gas mixture	0.4996	B	0.0003	1	0.0003	0.00124	0.00248	0.50
	Measurements	0.5004	A	0.0012	1	0.0012			
H_2	Mole fraction in cal. gas mixture	3.0076	B	0.0012	1	0.0012	0.0067	0.0134	0.45
	Measurements	2.9915	A	0.0066	1	0.0066			
N_2	Mole fraction in cal. gas mixture	11.9545	B	0.0006	1	0.0006	0.0156	0.0312	0.26

	Measurements	11.942	A	0.0156	1	0.0156			
CO_2	Mole fraction in cal. gas mixture	3.98286	B	0.00020	1	0.00020	0.00540	0.0108	0.27
	Measurements	3.989	A	0.00539	1	0.00539			
C_2H_6	Mole fraction in cal. gas mixture	0.75068	B	0.00025	1	0.00025	0.00205	0.00410	0.55
	Measurements	0.7431	A	0.00203	1	0.00203			
C_3H_8	Mole fraction in cal. gas mixture	0.29893	B	0.00017	1	0.00017	0.00080	0.00160	0.54
	Measurements	0.2978	A	0.00078	1	0.00078			
i-C_4H_{10}	Mole fraction in cal. gas mixture	0.19886	B	0.00014	1	0.00014	0.00073	0.00146	0.73
	Measurements	0.1993	A	0.00072	1	0.00072			
n-C_4H_{10}	Mole fraction in cal. gas mixture	0.19929	B	0.00013	1	0.00013	0.00080	0.00160	0.80
	Measurements	0.1993	A	0.00079	1	0.00076			
neo-C_5H_{12}	Mole fraction in cal. gas mixture	0.049693	B	0.000014	1	0.000014	0.000171	0.000342	0.69
	Measurements	0.04932	A	0.00017	1	0.00017			

i-C_5H_{12}	Mole fraction in cal. gas mixture	0.05134	B	0.000030	1	0.000030	0.000242	0.00048 4	0.97
	Measurements	0.04994	A	0.00024	1	0.00024			
n-C_5H_{12}	Mole fraction in cal. gas mixture	0.04925	B	0.00003	1	0.00003	0.000202	0.00040 4	0.81
	Measurements	0.05008	A	0.00020	1	0.00020			
n-C_6H_{14}	Mole fraction in cal. gas mixture	0.050857	B	0.000007	1	0.000007	0.000280	0.00056 0	1.1
	Measurements	0.0498	A	0.00028	1	0.00028			
CH_4		78.94			1			0.036	0.05

Table 16. Uncertainty budget for the amount fraction of components in LNG-type natural gas (Cylinder D322705)

Component	Source of uncertainty	Estimate xi, cmol/mol	Type of evaluation	Standard uncertainty, $u(x_i)$, cmol/mol	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$, cmol/mol	Combined standard uncertainty, cmol/mol	Expanded uncertainty, cmol/mol	Relative expanded uncertainty, %
N_2	Mole fraction in cal. gas mixture	0.124249	B	0.000025	1	0.000025	0.00042	0.00084	0.70
	Measurements	0.1207	A	0.00042	1	0.00042			
CO_2	Mole fraction in	0.02061	B	0.000009	1	0.000009	0.000075	0.00015	0.75

	cal. gas mixture								
	Measurements	0.01984	A	0.000075	1	0.000075			
C_2H_6	Mole fraction in cal. gas mixture	9.6937	B	0.0005	1	0.0005	0.0245	0.049	0.49
	Measurements	9.9708	A	0.0245	1	0.0245			
C_3H_8	Mole fraction in cal. gas mixture	1.9364	B	0.00020	1	0.00020	0.0056	0.011	0.56
	Measurements	1.9913	A	0.0056	1	0.0056			
i-C_4H_{10}	Mole fraction in cal. gas mixture	0.14628	B	0.00005	1	0.00005	0.00048	0.00096	0.64
	Measurements	0.1491	A	0.00048	1	0.00048			
n-C_4H_{10}	Mole fraction in cal. gas mixture	0.14374	B	0.00005	1	0.00005	0.00073	0.00146	0.99
	Measurements	0.1481	A	0.00073	1	0.00073			
i-C_5H_{12}	Mole fraction in cal. gas mixture	0.019855	B	0.000012	1	0.000012	0.000095	0.000190	0.95
	Measurements	0.01997	A	0.000094	1	0.000094			
n-C_5H_{12}	Mole fraction in cal. gas mixture	0.019301	B	0.000012	1	0.000012	0.000077	0.000144	0.77

	Measurements	0.0201	A	0.000076	1	0.000076			
CH_4		87.56						0.05	0.06

***Note:*

Methane mole fraction x_{CH4}*, cmol/mol, was calculated according to formula*

$$x_{CH4} = 100 - \sum x_i \ .$$

The combined standard uncertainty of methane amount fraction u_{CH4}*, cmol/mol, was calculated according to formula* $u_{CH4} = \sqrt{\sum u_{Xi}^2}$

x_i *– amount fraction of gas mixture components, cmol/mol.*

u_{xi} *- standard uncertainties of* x_i*, cmol/mol.*

Measurement report VSL

Cylinder number K118a: D322727

Cylinder number K118b: D322696

Table 21 Measurement 1 of hydrogen enriched mixture D322727

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	14-08-2019	0.11979000	0.01	6	0.00001825
Carbon dioxide	14-08-2019	0.04006800	0.01	5	0.00000705
Hydrogen	19-08-2019	0.02998700	0.05	6	0.00001719
Helium	19-08-2019	0.00502644	0.03	6	0.00000187
Ethane	14-08-2019	0.00744330	0.03	6	0.00000248
Propane	14-08-2019	0.00299100	0.05	6	0.00000165
iso-Butane	14-08-2019	0.00199770	0.01	6	0.00000044
n-Butane	14-08-2019	0.00200160	0.01	6	0.00000045
iso-Pentane	14-08-2019	0.00049768	0.02	6	0.00000019
n-Pentane	14-08-2019	0.00050243	0.02	6	0.00000022
neo-Pentane	21-08-2019	0.00049433	0.02	6	0.00000015
n-Hexane	14-08-2019	0.00049574	0.05	6	0.00000028
Methane	14-08-2019	0.78770800	0.04	6	0.00035800

Table 22 Measurement 2 of hydrogen enriched mixture D322727

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	20-09-2019	0.11982000	0.02	6	0.00002358

Carbon dioxide	20-09-2019	0.04004500	0.02	5	0.00000908
Hydrogen	02-09-2019	0.02998959	0.05	6	0.00001718
Helium	02-09-2019	0.00502580	0.04	6	0.00000248
Ethane	20-09-2019	0.00744500	0.02	6	0.00000150
Propane	20-09-2019	0.00298425	0.05	6	0.00000165
iso-Butane	20-09-2019	0.00199730	0.01	6	0.00000040
n-Butane	20-09-2019	0.00200320	0.01	6	0.00000046
iso-Pentane	20-09-2019	0.00049882	0.03	6	0.00000024
n-Pentane	04-11-2019	0.00050318	0.02	5	0.00000021
neo-Pentane	04-09-2019	0.00049376	0.03	6	0.00000026
n-Hexane	20-09-2019	0.00049614	0.05	6	0.00000029
Methane	20-09-2019	0.78728800	0.04	6	0.00035187

Table 23 Measurement 3 of hydrogen enriched mixture D322727

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	16-09-2019	0.11986000	0.05	6	0.00005844
Carbon dioxide	24-09-2019	0.04004200	0.01	4	0.00000605
Hydrogen	16-09-2019	0.02997210	0.05	6	0.00001717
Helium	16-09-2019	0.00502710	0.04	6	0.00000225
Ethane	24-09-2019	0.00744250	0.02	6	0.00000200
Propane	24-09-2019	0.00298438	0.05	6	0.00000176
iso-Butane	24-09-2019	0.00199890	0.01	6	0.00000050

n-Butane	24-09-2019	0.00200160	0.01	6	0.00000045
iso-Pentane	24-09-2019	0.00049843	0.03	6	0.00000025
n-Pentane	24-09-2019	0.00050237	0.01	6	0.00000020
neo-Pentane	05-09-2019	0.00049384	0.02	6	0.00000026
n-Hexane	24-09-2019	0.00049535	0.05	6	0.00000029
Methane	24-09-2019	0.78716270	0.04	6	0.00035667

Table 24 Results of hydrogen enriched mixture D322727

Component	Fraction (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Nitrogen	0.1198	0.00012	2
Carbon dioxide	0.04005	0.00004	2
Hydrogen	0.02998	0.00004	2
Helium	0.005026	0.000010	2
Ethane	0.007444	0.000015	2
Propane	0.002987	0.000009	2
iso-Butane	0.0019979	0.0000020	2
n-Butane	0.0020021	0.0000020	2
iso-Pentane	0.0004983	0.0000013	2
n-Pentane	0.0005027	0.0000010	2
neo-Pentane	0.0004940	0.0000010	2
n-Hexane	0.0004957	0.0000010	2
Methane	0.7874	0.0008	2

Table 25 Measurement 1 of LNG mixture D322696

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	04-09-2019	0.001220700	0.20	6	0.00000304
Carbon dioxide	14-08-2019	0.000199480	0.20	5	0.00000042
Ethane	14-08-2019	0.100081600	0.01	6	0.00001393
Propane	14-08-2019	0.020007600	0.05	6	0.00001084
iso-Butane	14-08-2019	0.001492300	0.01	6	0.00000030
n-Butane	14-08-2019	0.001487400	0.01	6	0.00000027
iso-Pentane	14-08-2019	0.000199240	0.02	6	0.00000008
n-Pentane	14-08-2019	0.000201210	0.03	6	0.00000010
Methane	14-08-2019	0.875118000	0.02	6	0.00019300

Table 26 Measurement 2 of LNG mixture D322696

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	20-09-2019	0.00122240	0.28	6	0.00000380
Carbon dioxide	20-09-2019	0.00019924	0.10	5	0.00000026
Ethane	20-09-2019	0.10002000	0.01	6	0.00001173
Propane	20-09-2019	0.01998775	0.05	6	0.00001084
iso-Butane	20-09-2019	0.00149210	0.01	6	0.00000029
n-Butane	20-09-2019	0.00148690	0.03	6	0.00000046
iso-Pentane	20-09-2019	0.00019909	0.02	6	0.00000010
n-Pentane	04-11-2019	0.00020111	0.02	6	0.00000008

Methane	20-09-2019	0.87490497	0.02	6	0.00019446

Table 27 Measurement 3 of LNG mixture D322696

Component	Date	Fraction (mol/mol)	Rel. std. deviation (%)	Number of replicates	Standard uncertainty (mol/mol)
Nitrogen	26-09-2019	0.00122020	0.28	7	0.00000376
Carbon dioxide	26-09-2019	0.00020000	0.17	6	0.00000030
Ethane	26-09-2019	0.10002000	0.01	7	0.00000874
Propane	26-09-2019	0.02000040	0.05	7	0.00001103
iso-Butane	26-09-2019	0.00149150	0.02	7	0.00000037
n-Butane	26-09-2019	0.00148620	0.02	7	0.00000038
iso-Pentane	26-09-2019	0.00019908	0.04	7	0.00000010
n-Pentane	26-09-2019	0.00020116	0.02	6	0.00000011
Methane	26-09-2019	0.87513920	0.02	7	0.00020194

Table 28 Results of LNG mixture D322696

Component	Fraction (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Nitrogen	0.001221	0.000008	2
Carbon dioxide	0.0001996	0.0000010	2
Ethane	0.10004	0.00010	2
Propane	0.019999	0.000022	2
iso-Butane	0.0014920	0.0000015	2
n-Butane	0.0014869	0.0000015	2
iso-Pentane	0.0001992	0.0000008	2
n-Pentane	0.0002012	0.0000008	2
Methane	0.8750	0.0009	2

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 was chosen as an example, this mixture was prepared using the parent gases illustrated in tables 1 to 12 below. 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. The purity data used for the calculation of the PSMs is summarised in Table 29-Table 40.

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

Table 29 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 30 Purity data nitrogen (mol mol^{-1})

Component	APN26B (nitrogen)	
	x	u(x)
Argon	0.000005000	0.000003000

Component	APN26B (nitrogen)	
	x	u(x)
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 31 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 32 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 33 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 34 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

Component	AL3643 (propane)	
	x	u(x)
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 35 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 36 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 37 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

Component	AL9865 (iso-pentane)	
	x	u(x)
n-pentane	0.004941000	0.000030000
Iso-pentane	0.994471000	0.000060000
Neo-pentane	0.000031000	0.000004500

Table 38 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 39 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 40 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

As an example, the weighing data of the preparation of VSL149269, one of the PSMs used for calibration, data are given in table 21. The “S” denotes the sample cylinder and the “R” the reference cylinder. VSL149269 is prepared by using mostly pre-mixtures and some pure gases, depending on the concentration. The pre-mixtures that are used have also been prepared in the same manner. The amount-of-substance fractions for VSL149269, calculated according to ISO-6142-1, are shown in table 22.

Table 41 Weighing data VSL149269

	Vacuum	VSL149226	VSL329437	VSL505186	VSL149249	AP9358	APCH4
S	7664.014	7699.128	7733.636	7752.466	7799.466	7979.374	8124.804

R	7644.440	7644.442	7644.445	7644.450	7644.455	7644.450	7644.453
S	7664.014	7699.129	7733.641	7752.469	7799.464	7979.379	8124.807
R	7644.441	7644.442	7644.448	7644.452	7644.454	7644.451	7644.455
S	7664.013	7699.129	7733.642	7752.470	7799.464	7979.378	8124.808
R	7644.440	7644.443	7644.448	7644.450	7644.454	7644.451	7644.455
S	7664.015	7699.130	7733.641	7752.470	7799.465	7979.381	8124.808
R	7644.443	7644.443	7644.448	7644.450	7644.453	7644.454	7644.454
S	7664.016	7699.132	7733.642	7752.469	7799.464	7979.381	8124.809

Table 42 Amount fractions for VSL149269 calculated according to ISO-6142-1

Component	VSL149269	
	x	u(x)
Argon	0.000000125	0.000000075
Methane	0.744000000	0.000017300
Carbon monoxide	0.000000100	0.000000060
Carbon dioxide	0.200000000	0.000014500
Ethene	0.000000000	0.000000000
Ethane	0.020000000	0.000002610
Propene	0.000000720	0.000000080
Propane	0.004000000	0.000000743
n-Butane	0.001000000	0.000000354
iso-Butane	0.000995000	0.000000353
1-pentene	0.000001820	0.000000041
n-pentane	0.001200000	0.000001110
iso-pentane	0.001160000	0.000001100
Hydrocarbons	0.000000504	0.000000020
Helium	0.002980000	0.000000885
Hydrogen	0.000000038	0.000000014
Water	0.000000393	0.000000025
Nitrogen	0.024900000	0.000003200
Oxygen	0.000001510	0.000000524
neo-pentane	0.000000113	0.000000006

Instrumentation

The analyses were performed on three different systems. The main system is an Agilent 7890A GC, configured for the analysis of the composition of natural gas and biogas. The back channel consists of a 100 µL sample loop, a HayeSep Q pre-column and HayeSep T column and a thermal conductivity detector (TCD). This channel is used for the separation of methane, carbon dioxide and ethane from the other components. Nitrogen, hydrogen, helium, oxygen and methane are separated and detected on the auxiliary channel equipped with a 500 µL sample loop, a Hayesep Q/ Molsieve 5A column and a TCD. The front channel is equipped with a 25 µL sample loop, a PDMS-column and a flame ionisation detector (FID). This channel is used for the separation of the hydrocarbons, except methane and ethane.
The carrier gas used for the front and back channel is helium and argon is used for the auxiliary channel. The temperature program for the front channel starts at 35 °C for 6 minutes, followed by a temperature

program of 10 °C min^{-1} to 100 °C, hold for 1.5 minutes. The other channels have no temperature program and are kept at 60 °C isothermal. The data collection is performed using ChemStation software.
The analyses on the hydrogen enriched mixture for neopentane were performed on a different system, which gives better results for neo-pentane using an aluminum oxide plot column. The system is an Agilent 7890A GC, configured for the analysis of the composition of 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. In a temperature programmed run, all hydrocarbons are then separated using a pre-column and an aluminum oxide plot column, with helium as carrier gas. 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 Chemstation software.
The analyses for the hydrogen enriched mixture were done on a different system for helium, hydrogen and nitrogen. These were performed on an Agilent 6890 N specially set up for natural gas analysis. Due to the higher amount of hydrogen, a better separation was required. Only the back channel is used, which consists of a 500 µL sample loop, a molsieve 13x column and a TCD with argon carrier. The temperature is set at 40 °C isothermal for 21 minutes, data collection is performed using Chemstation software.

Calibration method and value assignment

Most Primary Standard gas Mixtures (PSMs) used for the measurements of both Key Comparison mixtures 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. Two different methods are employed, one based on the recorded ambient pressure, and a second based on the peak area of the corresponding component that is obtained before and after the five injections of the mixture (either a PSM or a transfer standard).
The measurements were performed in two ways.
The first way; the measurement was carried out by using a correction cylinder 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.

The second way; the set of PSMs used for a measurement, and the Key Comparison mixtures to be measured, are connected to the gas chromatograph. A measurement of a cylinder consists of 6 injections, sometimes 7 injections were used for a measurement depending on the concentration and component. These injections are averaged and corrected for ambient pressure conditions.

The injection of the samples is done at ambient pressure. It is therefore reasonable to expect that the amount of gas injected depends on the ambient pressure. Hence it is customary to correct the observed peak areas *A* for influence of the ambient pressure *p* using

$$y = \frac{p_0}{p} A$$

where p_0 the reference pressure (101325 Pa). The choice of the reference pressure is arbitrary.

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

Results

An overview of the analytical results and the obtained calibration functions for all components is given in tables 23 – 56 and figures 1-18. Also the assigned value for the amount fraction(s) of the component of transfer standard(s) is given.

Table 43 PSMs used for the analyses of ethane for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL203633	0.249989	0.000064	112.831	0.060
VSL428524	0.251258	0.000064	113.463	0.020
VSL337388	0.500923	0.000091	227.064	0.060
VSL508460	0.503076	0.000092	227.908	0.070
VSL302676	0.791865	0.000121	359.681	0.090
VSL303661	0.999895	0.000142	454.886	0.070
VSL205246	1.500135	0.000229	683.319	0.060

Figure 1 2nd order curve fitting for ethane

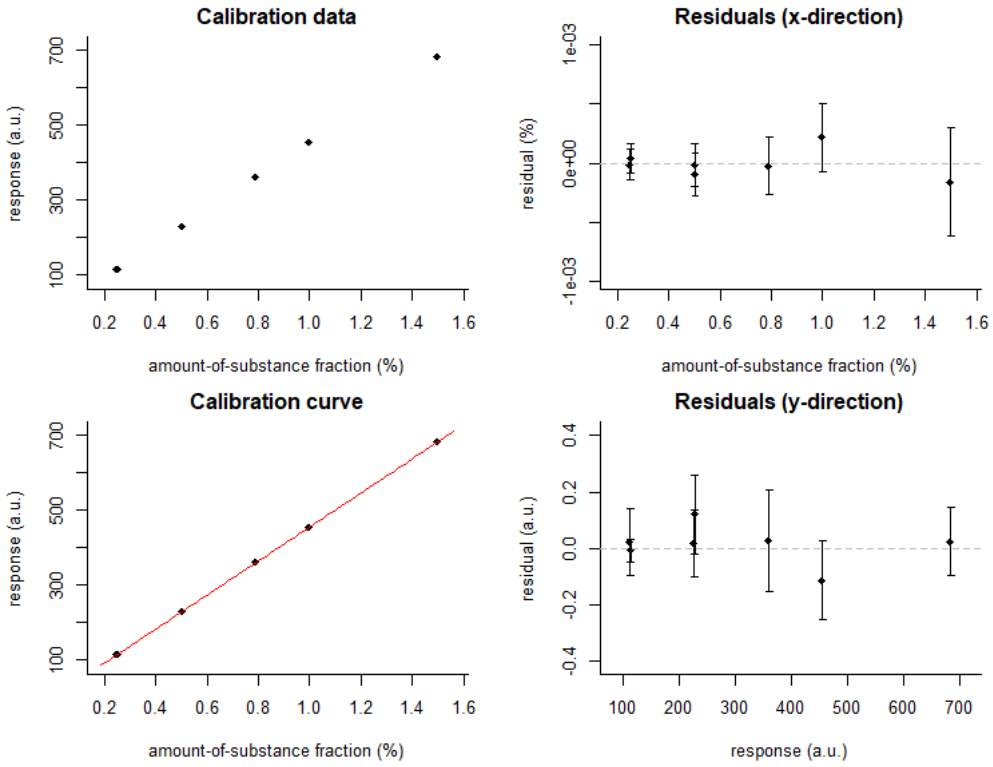

Table 44 Interpolation result of ethane for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	338.039	0.100	0.74433	0.00025

Table 45 PSMs used for the analyses of ethane for the LNG mixture

	x	u(x)	y	u(y)
VSL249460	2.99296	0.00059	1365.36	0.17
VSL147964	4.50828	0.00061	2055.50	0.28
VSL228640	4.75228	0.00063	2168.29	0.37
VSL300635	6.48492	0.00066	2955.63	0.62
VSL237408	7.96508	0.00073	3630.45	0.40
VSL400648	10.05028	0.00085	4575.71	0.19
VSL405161	10.98402	0.00087	4999.24	0.84

Figure 2 2nd order curve fitting for ethane

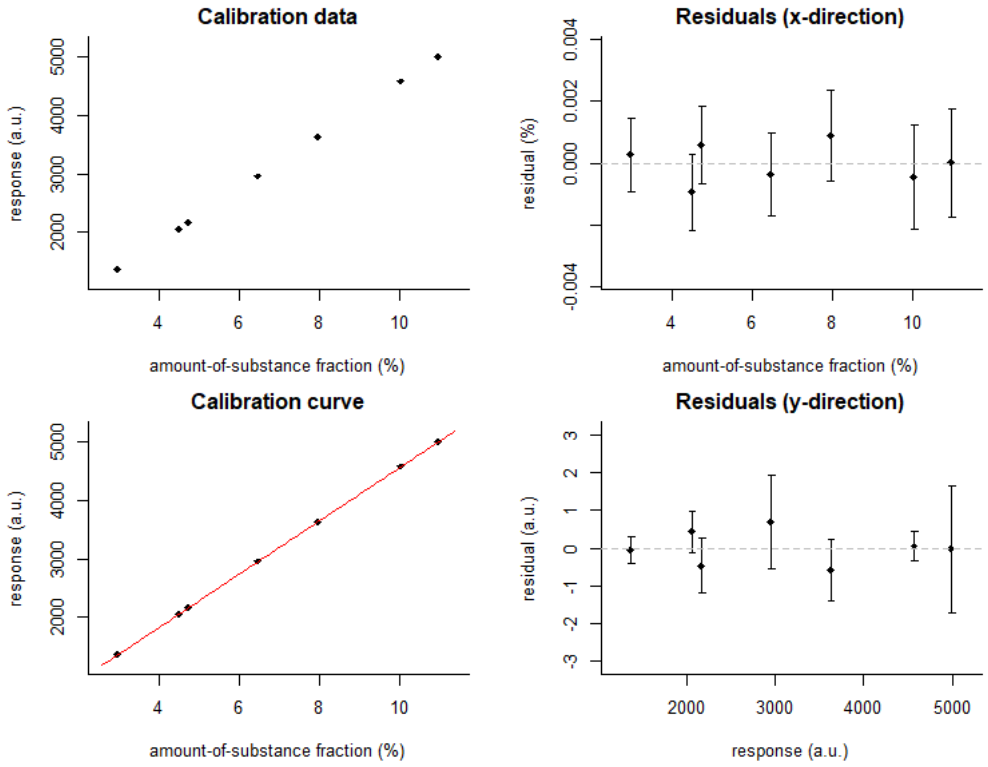

Table 46 Interpolation result of ethane for the LNG mixture

	y	u(y)	x	u(x)
WF2696	4556.86	0.53	10.0082	0.0014

For propane the relative uncertainty on the measured average respons (y) was set to 0.05 %.

Table 47 PSMs used for the analyses of propane for the LNG and hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL203633	0.200106	0.000056	132.921	0.066
VSL428524	0.200362	0.000043	133.021	0.067
VSL149269	0.399922	0.000074	266.482	0.133
VSL405161	0.601295	0.000134	400.309	0.200
VSL205246	0.803395	0.000125	534.762	0.267
VSL147964	1.005142	0.000134	669.739	0.335
VSL300635	1.992922	0.000399	1327.378	0.664

VSL228640	2.851979	0.000419	1896.087	0.948
VSL237408	3.009470	0.000425	1999.298	1.000
VSL337388	3.995741	0.000566	2647.149	1.324
VSL249460	4.997170	0.000497	3303.141	1.652
VSL207365	7.509359	0.000839	4947.012	2.474
VSL249470	9.959613	0.001349	6525.239	3.263

Figure 3 2nd order curve fitting for propane

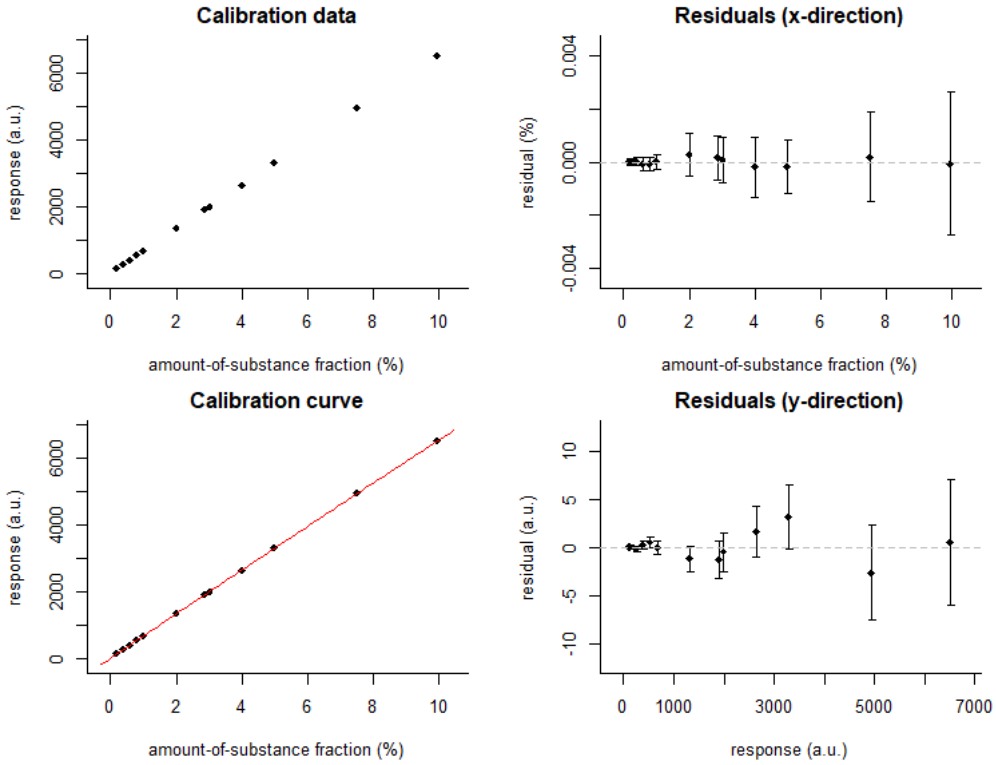

Table 48 Interpolation result of propane for the LNG and hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	198.988	0.099	0.29910	0.00016
WF2696	1331.17	0.67	2.0008	0.0011

For hydrogen the relative uncertainty on the measured average response (y) was set to 0.05 %.

Table 49 PSMs used for the analyses of hydrogen for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL338377	1.51153	0.00060	1882.68	0.94

VSL144201	2.00150	0.00072	2491.47	1.25
VSL144493	2.98423	0.00101	3721.81	1.86
VSL344162	2.98572	0.00101	3712.38	1.86
VSL328630	5.45955	0.00111	6797.87	3.40

Figure 4 Straight line curve fitting for hydrogen

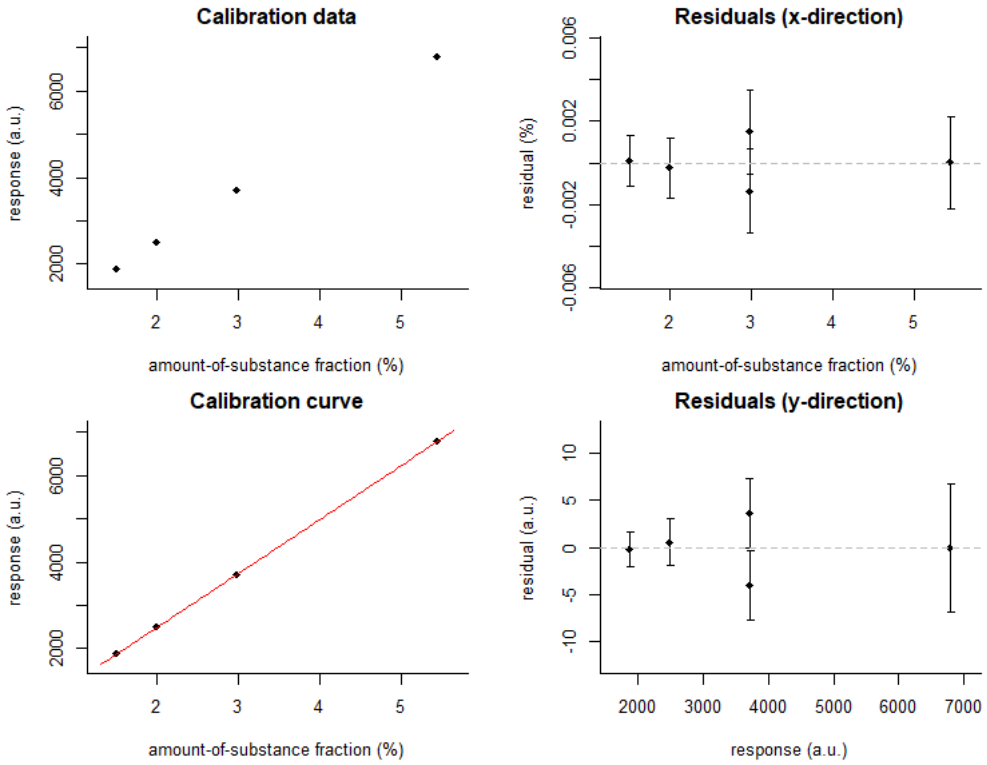

Table 50 Interpolation result of hydrogen for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	3733.9	1.9	2.9987	0.0017

For n-hexane the relative uncertainty on the measured average response (y) was set to 0.05 %.

Table 51 PSMs used for the analyses of n-hexane for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL505138	0.0099850	0.0000018	493.61	0.25
VSL376430	0.0200066	0.0000040	992.67	0.50
VSL226804	0.0219453	0.0000048	1089.13	0.54

VSL506294	0.0400392	0.0000072	1995.29	1.00
VSL318863	0.0598687	0.0000135	2975.08	1.49
VSL249242	0.0796002	0.0000488	3954.09	1.98
VSL328654	0.1002438	0.0000102	4985.76	2.49
VSL117470	0.2005717	0.0000205	9982.23	4.99
VSL728510	0.3951110	0.0000411	19615.11	9.81

Figure 5 2nd order curve fitting for n-hexane

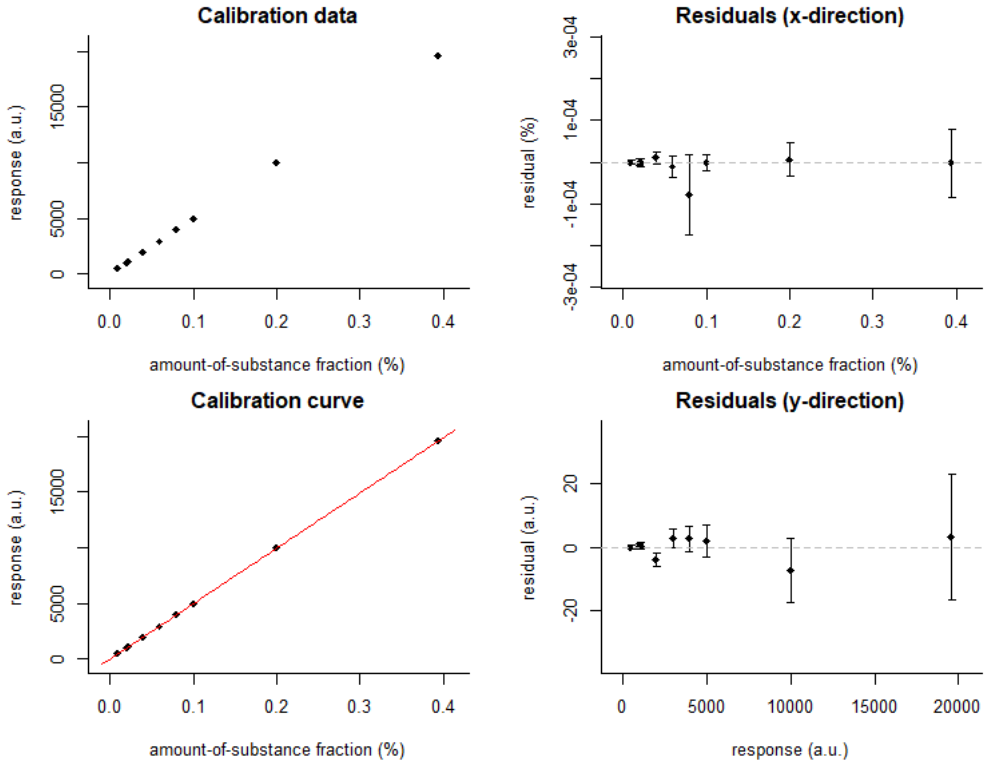

Table 52 Interpolation result of n-hexane for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	2465.7	1.2	0.049574	0.000028

Table 53 PSMs used for the analyses of nitrogen for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL149269	2.49129	0.00032	623.90	0.27
VSL237408	6.00169	0.00066	1504.08	0.41
VSL249470	9.05175	0.00170	2267.26	0.24
VSL147964	12.00070	0.00082	3002.36	0.35
VSL207365	16.03517	0.00139	4010.72	1.13
VSL300635	19.66533	0.00110	4914.92	0.70

Figure 6 2nd order curve fitting for nitrogen

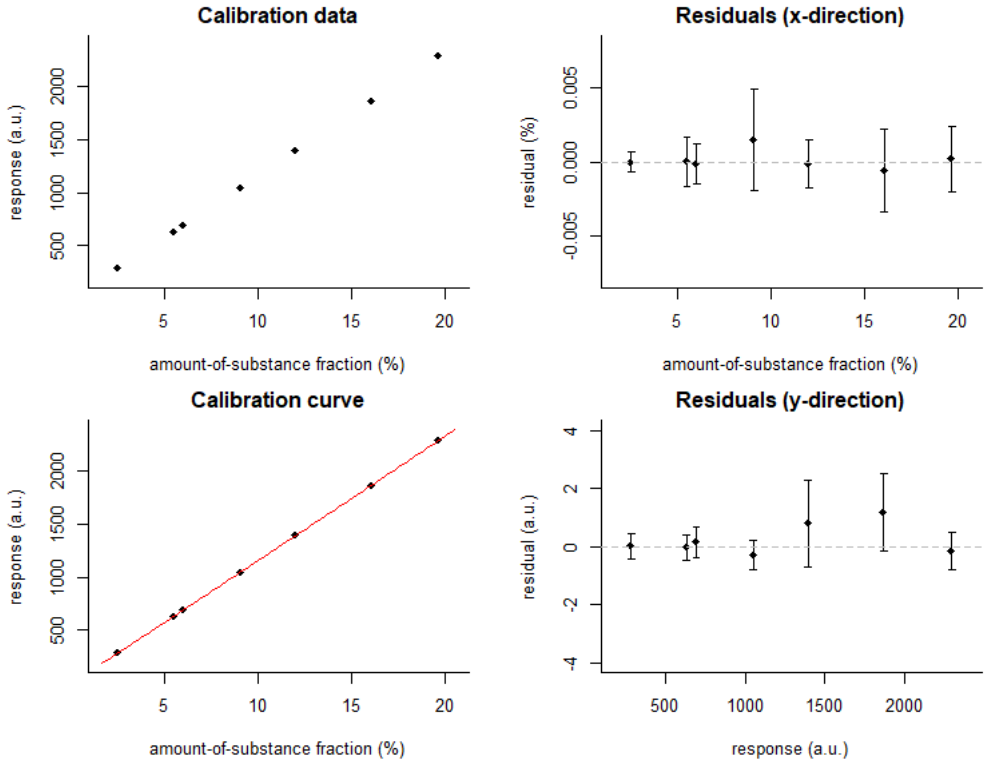

Table 54 Interpolation result of nitrogen for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	2997.97	0.35	11.9793	0.0018

Table 55 PSMs used for the analyses of nitrogen for the LNG mixture

	x	u(x)	y	u(y)
VSL203633	0.099895	0.000034	31.226	0.070
VSL251977	0.100130	0.000061	31.152	0.110
VSL337388	0.200335	0.000070	61.622	0.050
VSL303661	0.401677	0.000094	122.424	0.090
VSL205246	0.598395	0.000123	182.358	0.200
VSL249460	0.793918	0.000138	240.696	0.110

Figure 7 2nd order curve fitting for nitrogen

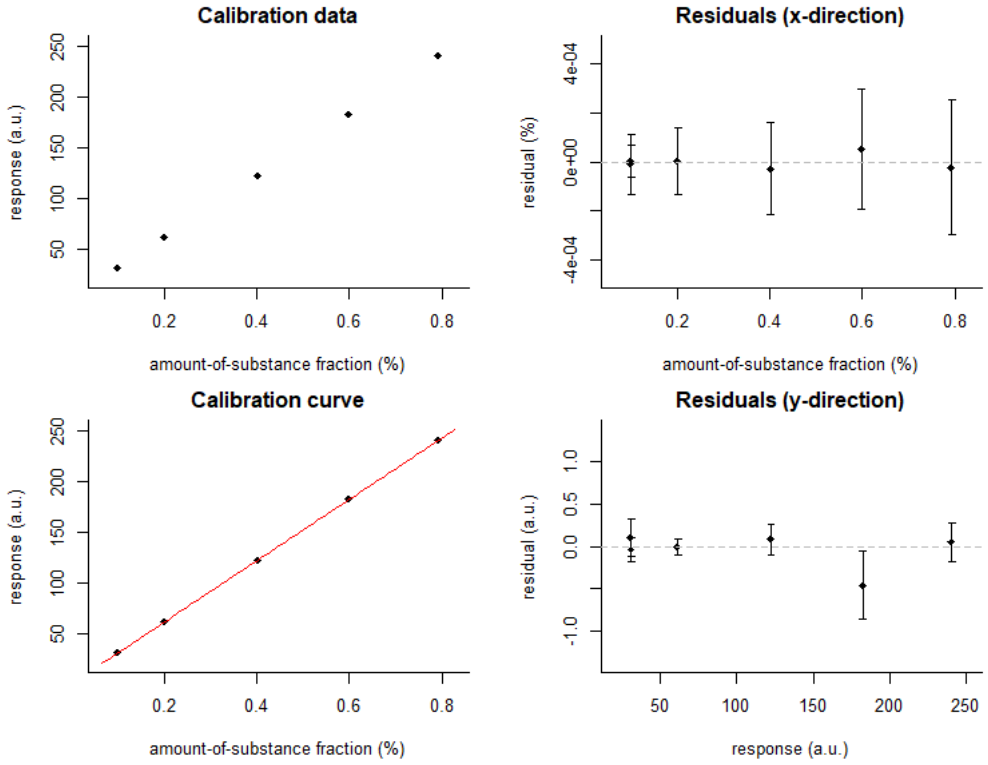

Table 56 Interpolation result of nitrogen for the LNG mixture

	y	u(y)	x	u(x)
WF2696	37.904	0.080	0.12207	0.00030

Table 57 PSMs used for the analyses of carbon dioxide for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL303661	0.400528	0.000069	199.748	0.020
VSL205246	0.598662	0.000118	299.037	0.040
VSL249460	0.803476	0.000123	401.205	0.020
VSL405161	1.194677	0.000175	596.589	0.240
VSL228640	2.404910	0.000404	1202.610	0.440
VSL300635	6.002381	0.000486	2994.852	1.590
VSL249470	9.009805	0.001276	4492.950	0.800
VSL147964	11.970361	0.000733	5954.582	1.330
VSL207365	16.014456	0.001237	7951.927	1.680
VSL149269	19.958888	0.001450	9883.010	2.230

Figure 8 2nd order curve fitting for carbon dioxide

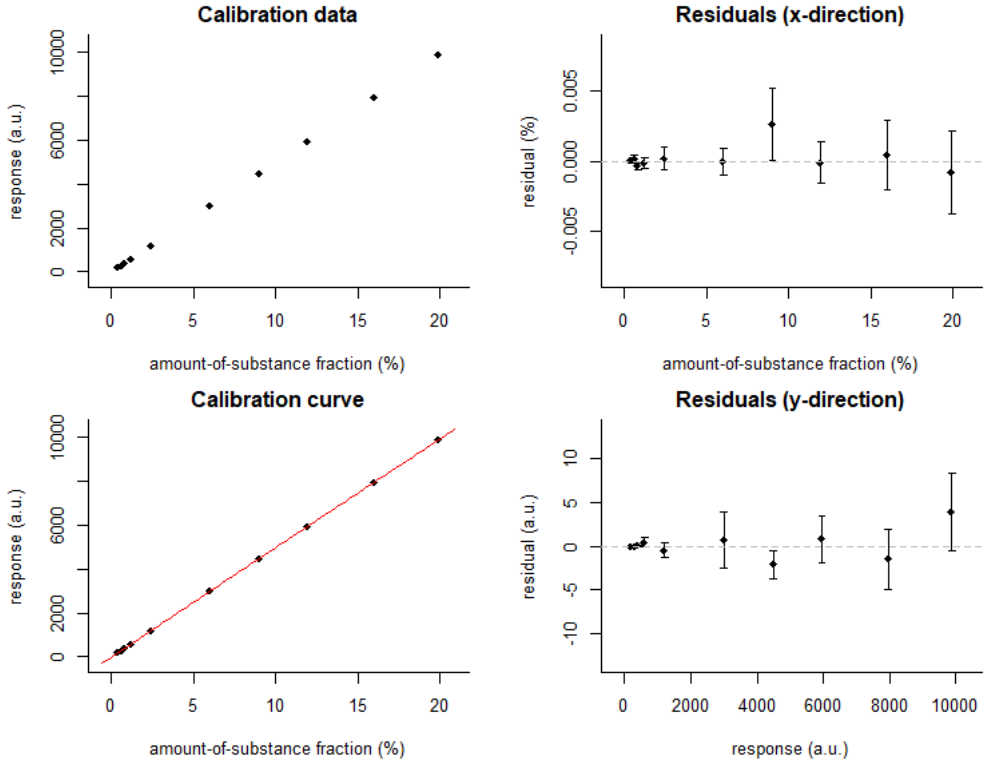

Table 58 Interpolation result of carbon dioxide for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	2001.55	0.16	4.0068	0.0007

Table 59 PSMs used for the analyses of carbon dioxide for the LNG mixture

	x	u(x)	y	u(y)
VSL447736	0.0192614	0.0000063	9.5030	0.0100
VSL400648	0.0199926	0.0000060	9.8890	0.0100
VSL424470	0.0409501	0.0000106	20.3210	0.0100
VSL302676	0.0496702	0.0000157	24.6730	0.0100
VSL428524	0.0993495	0.0000173	49.4570	0.0100
VSL203633	0.0998678	0.0000188	49.7080	0.0200
VSL337388	0.2007201	0.0000524	99.9760	0.0100
VSL508460	0.3033361	0.0000588	151.2680	0.0300
VSL303661	0.4005277	0.0000688	199.7480	0.0200
VSL205246	0.5986623	0.0001178	299.0370	0.0400

Figure 9 2nd order curve fitting for carbon dioxide

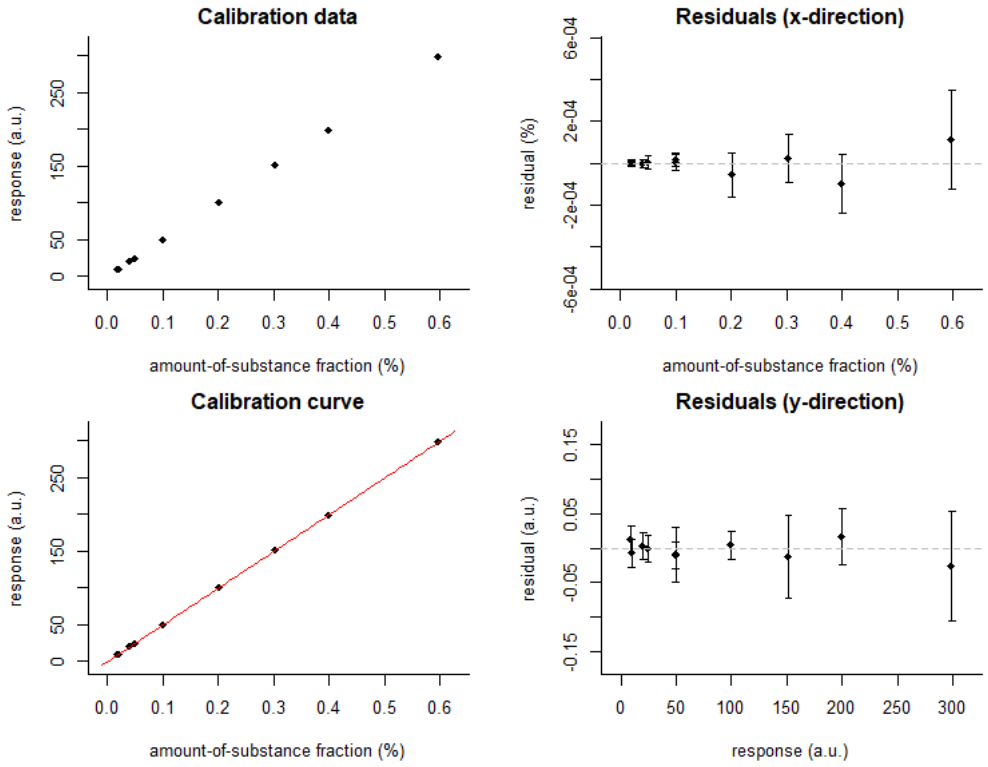

Table 60 Interpolation result of carbon dioxide for the LNG mixture

	y	u(y)	x	u(x)

WF2696	9.859	0.020	0.019948	0.000042

Table 61 PSMs used for the analyses of helium for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL147964	0.0251301	0.0000067	18.1880	0.0100
VSL300635	0.1005603	0.0000389	73.1310	0.0300
VSL149269	0.2975272	0.0000885	216.6740	0.0900
VSL303661	0.4992470	0.0000888	364.4640	0.1300
VSL344162	0.5006489	0.0001323	365.7930	0.1300
VSL405161	1.4065678	0.0001997	1034.1400	0.2700

Figure 10 2nd order curve fitting for helium

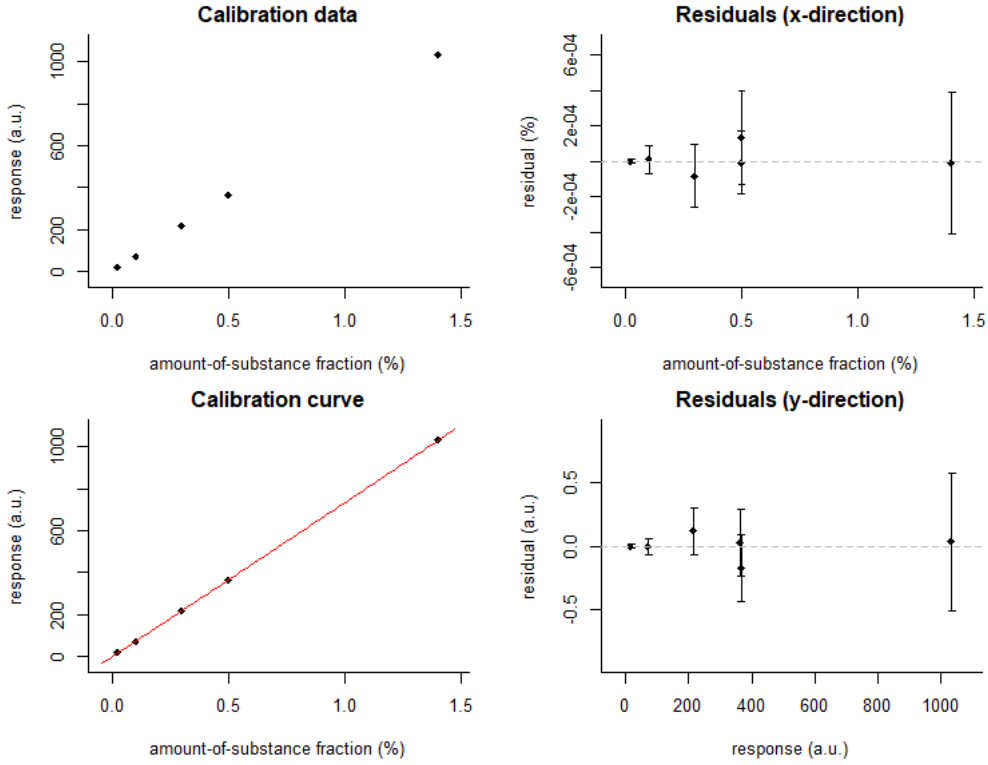

Table 62 Interpolation result of helium for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	366.99	0.11	0.50264	0.00019

Table 63 PSMs used for the analyses of iso-butane for the LNG and hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL249460	0.030334	0.000012	203.310	0.020
VSL303661	0.050234	0.000022	336.783	0.050
VSL428524	0.069570	0.000024	464.696	0.100
VSL149269	0.099544	0.000035	665.144	0.140
VSL205246	0.149813	0.000048	1002.497	0.090
VSL300635	0.200657	0.000059	1340.486	0.150
VSL405161	0.295654	0.000095	1973.866	0.280
VSL337388	0.495808	0.000377	3308.485	0.190
VSL147964	0.700259	0.000294	4674.235	0.200
VSL228640	0.802648	0.000295	5360.960	0.620
VSL207365	1.010662	0.000524	6743.491	0.440

Figure 11 2nd order curve fitting for iso-butane

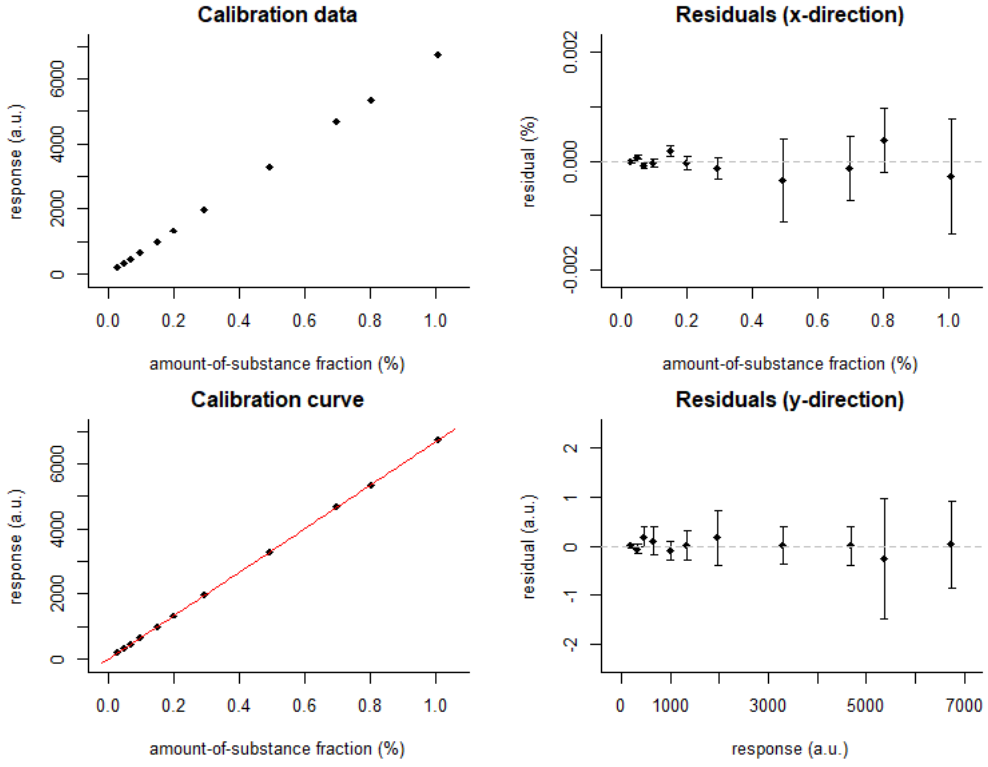

Table 64 Interpolation result of iso-butane for the LNG and hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2696	997.35	0.11	0.149234	0.000030
WF2727	1334.77	0.19	0.199769	0.000044

Table 65 PSMs used for the analyses of n-butane for the LNG and hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL249460	0.0300240	0.0000091	198.596	0.020
VSL428524	0.0699159	0.0000245	462.843	0.070
VSL149269	0.1000485	0.0000354	663.164	0.070
VSL205246	0.1498514	0.0000475	992.650	0.120
VSL300635	0.2007970	0.0000590	1331.479	0.130
VSL405161	0.2988479	0.0000951	1981.564	0.520
VSL337388	0.5039001	0.0003768	3342.639	0.160
VSL237408	0.7029395	0.0002958	4665.281	0.800
VSL228640	0.7948428	0.0002953	5275.914	0.850
VSL207365	0.9855487	0.0005242	6539.736	0.690

Figure 12 2nd order curve fitting for n-butane

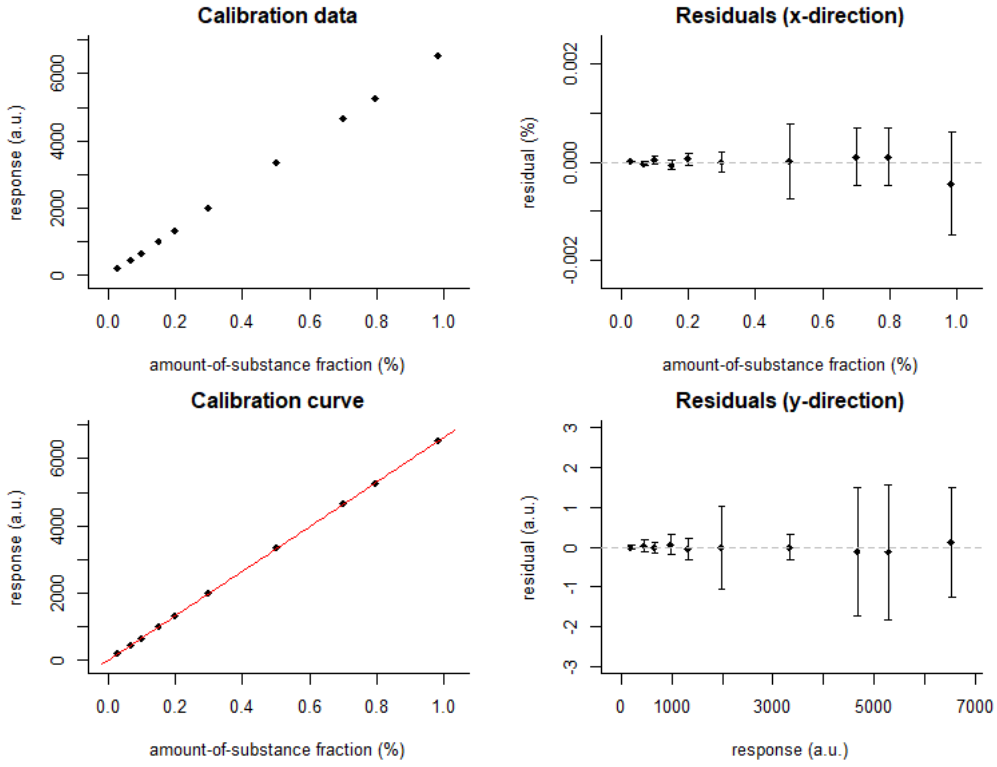

Table 66 Interpolation result of n-butane for the LNG hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2696	985.771	0.070	0.148739	0.000027
WF2727	1326.83	0.20	0.200160	0.000045

Table 67 PSMs used for the analyses of iso-pentane for the LNG and hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL302676	0.0078689	0.0000063	153.993	0.090
VSL508460	0.0100423	0.0000080	197.076	0.100
VSL147964	0.0194130	0.0000190	382.453	0.050
VSL237408	0.0297082	0.0000233	586.012	0.150
VSL249460	0.0399671	0.0000379	789.671	0.060
VSL300635	0.0585724	0.0000452	1156.803	0.370
VSL203633	0.0698355	0.0000522	1382.034	0.180
VSL337388	0.0890389	0.0000668	1758.762	0.090
VSL149269	0.1159475	0.0001105	2292.635	0.240
VSL405161	0.1997614	0.0002370	3953.182	0.770
VSL303661	0.2960751	0.0003021	5862.523	0.410

Figure 13 2nd order curve fitting for iso-pentane

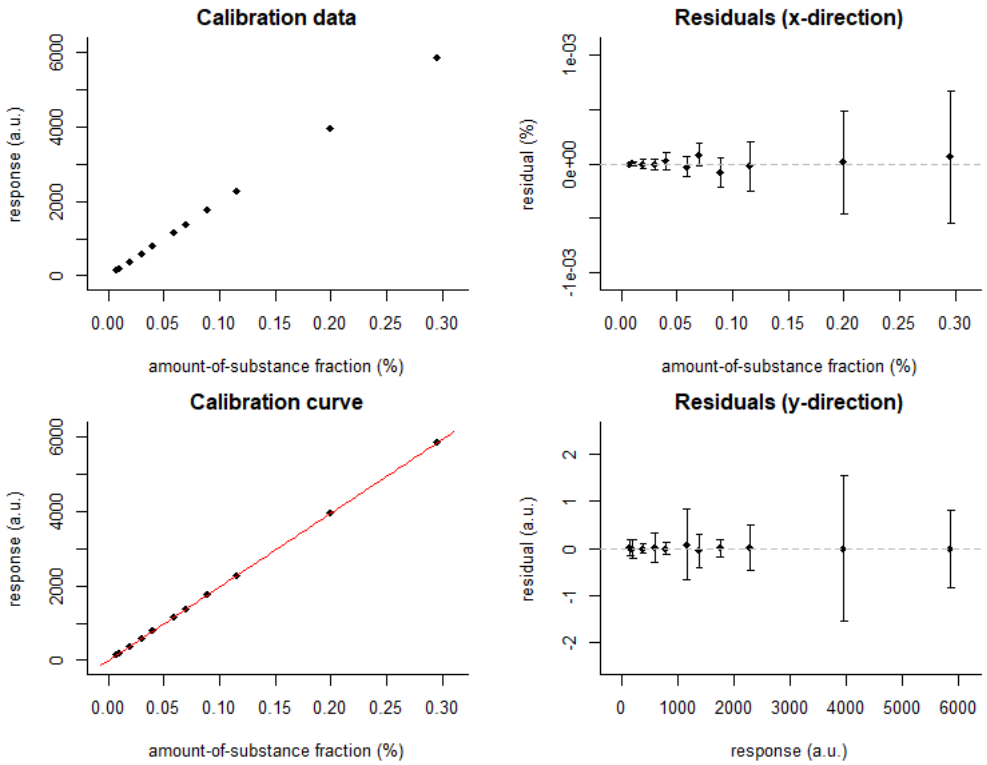

Table 68 Interpolation result of iso-pentane for the LNG and hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2696	392.566	0.070	0.0199242	0.0000077
WF2727	983.16	0.16	0.049768	0.000019

Table 69 PSMs used for the analyses of n-pentane for the LNG and hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL508460	0.0100301	0.0000080	197.249	0.060
VSL147964	0.0198669	0.0000190	391.458	0.100
VSL237408	0.0300028	0.0000234	593.769	0.150
VSL300635	0.0602626	0.0000454	1192.571	0.270
VSL203633	0.0702355	0.0000523	1387.970	0.170
VSL337388	0.0899219	0.0000670	1781.235	0.040
VSL149269	0.1200799	0.0001108	2378.456	0.210
VSL405161	0.1996338	0.0002377	3956.075	0.900

VSL303661	0.3013268	0.0003030	5959.864	0.520

Figure 14 2nd order curve fitting for n-pentane

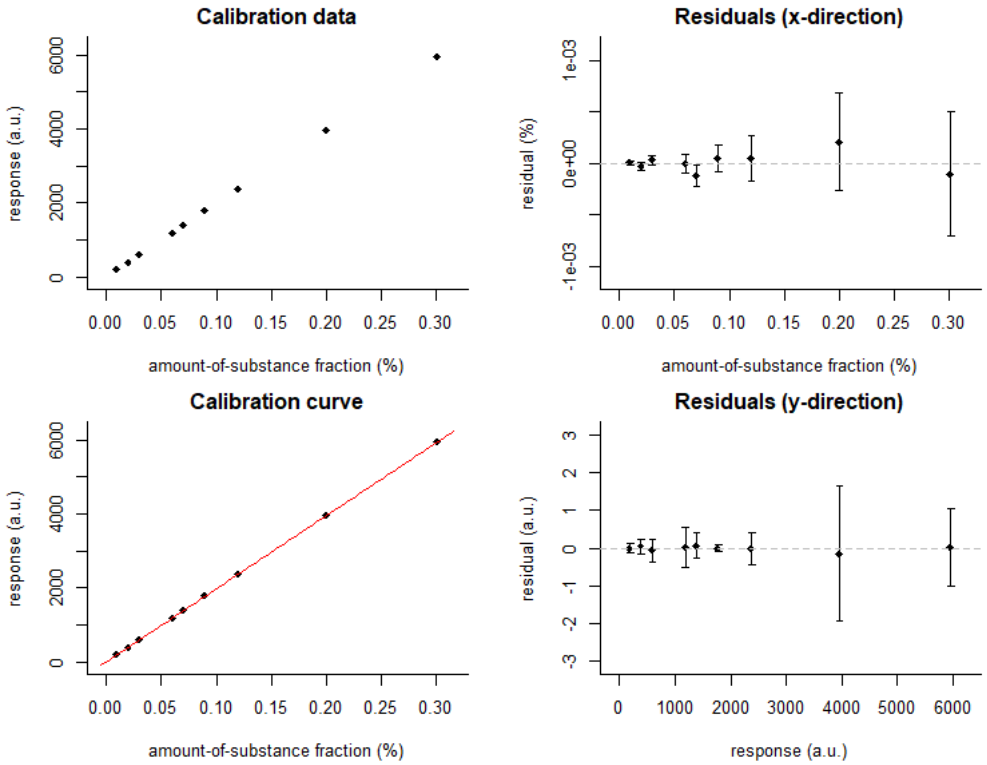

Table 70 Interpolation result of n-pentane for the LNG and hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2696	397.17	0.13	0.020121	0.000010
WF2727	994.02	0.24	0.050243	0.000022

Table 71 PSMs used for the analyses of neo-pentane for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL140074	0.0098977	0.0000042	195.889	0.090
VSL429296	0.0200155	0.0000076	396.642	0.090
VSL306324	0.0399187	0.0000147	793.159	0.290
VSL247817	0.0600261	0.0000270	1193.317	0.270
VSL402706	0.0800348	0.0000345	1591.485	0.250
VSL303658	0.0800555	0.0000353	1590.803	0.520

VSL248081	0.1999880	0.0000707	3987.193	0.980
VSL248562	0.3997315	0.0001368	7971.253	1.950
VSL203704	0.6006043	0.0003105	11988.505	5.140
VSL203653	0.7991969	0.0003432	15950.231	3.430
VSL249639	0.7999589	0.0003348	15990.722	2.800

Figure 15 2nd order curve fitting for neo-pentane

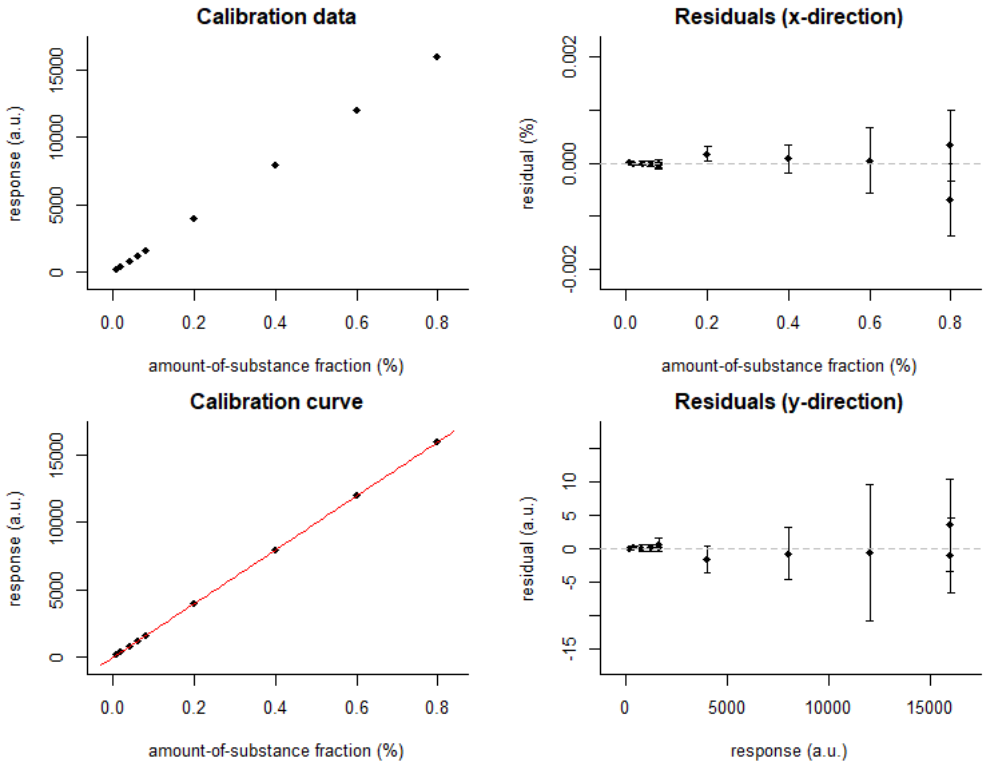

Table 72 Interpolation result of neo-pentane for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	982.54	0.23	0.049433	0.000015

For methane the relative uncertainty on the measured average response (y) was set to 0.02 %.

Table 73 PSMs used for the analyses of methane for the LNG mixture

	x	u(x)	y	u(y)
VSL207365	58.4445	0.0028	663.81	0.13
VSL300635	65.2328	0.0018	737.69	0.15

VSL147964	69.7502	0.0016	786.21	0.16
VSL249470	71.9770	0.0030	810.27	0.16
VSL149269	74.4160	0.0017	836.18	0.17
VSL237408	79.6987	0.0014	893.12	0.18
VSL405161	83.6127	0.0011	934.32	0.19
VSL400648	87.4611	0.0010	975.33	0.20
VSL228640	87.8436	0.0011	979.59	0.20
VSL249460	89.8723	0.0009	1001.25	0.20
VSL337388	93.8477	0.0008	1042.96	0.21
VSL205246	96.1994	0.0004	1068.03	0.21
VSL303661	96.8997	0.0005	1075.62	0.22
VSL428524	99.2101	0.0001	1099.80	0.22
VSL203633	99.2096	0.0002	1099.97	0.22

Figure 16 2nd order curve fitting for methane

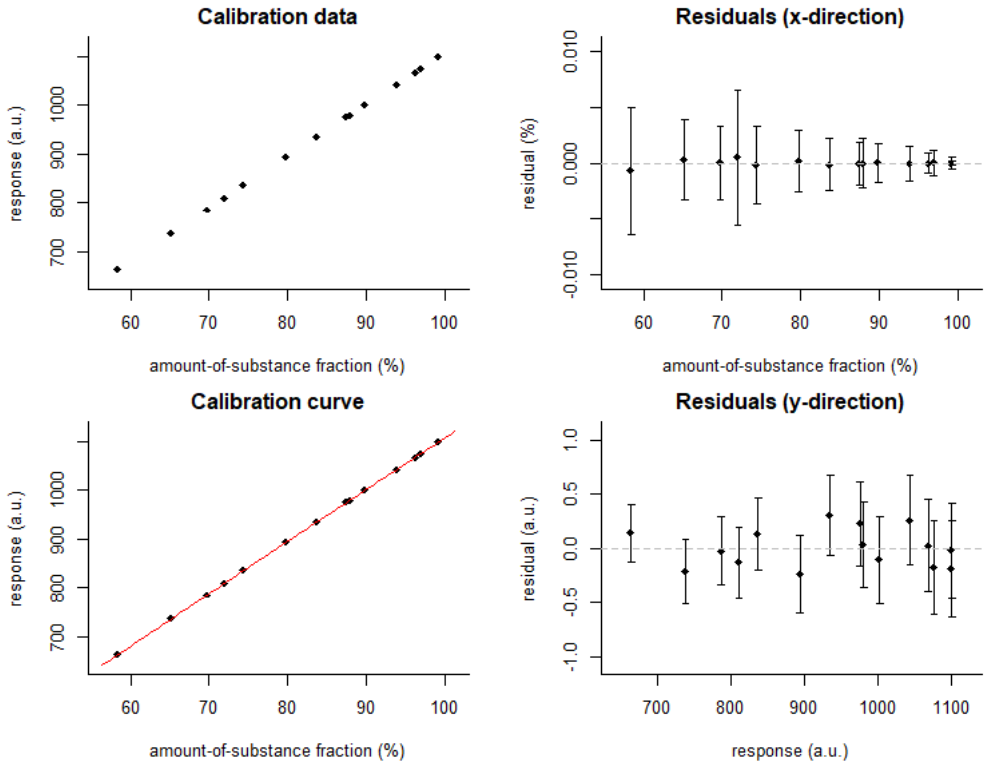

Table 74 Interpolation result of methane for the LNG mixture

	y	u(y)	x	u(x)
WF2696	976.10	0.20	87.512	0.019

For methane on the auxiliary channel the relative uncertainty on the measured average response (y) was set to 0.04 %.

Table 75 PSMs used for the analyses of methane on the auxiliary channel for the hydrogen enriched mixture

	x	u(x)	y	u(y)
VSL147964	69.7502	0.0016	779.94	0.31
VSL249470	71.9770	0.0030	804.82	0.32
VSL149269	74.4160	0.0017	832.33	0.33
VSL237408	79.6987	0.0014	889.82	0.36
VSL405161	83.6127	0.0011	932.82	0.37
VSL228640	87.8436	0.0011	979.58	0.39
VSL337388	93.8477	0.0008	1045.02	0.42
VSL205246	96.1994	0.0004	1071.07	0.43
VSL303661	96.8997	0.0005	1078.55	0.43
VSL428524	99.2101	0.0001	1103.93	0.44
VSL203633	99.2096	0.0002	1103.53	0.44

Figure 17 2nd order curve fitting for methane on the auxiliary channel

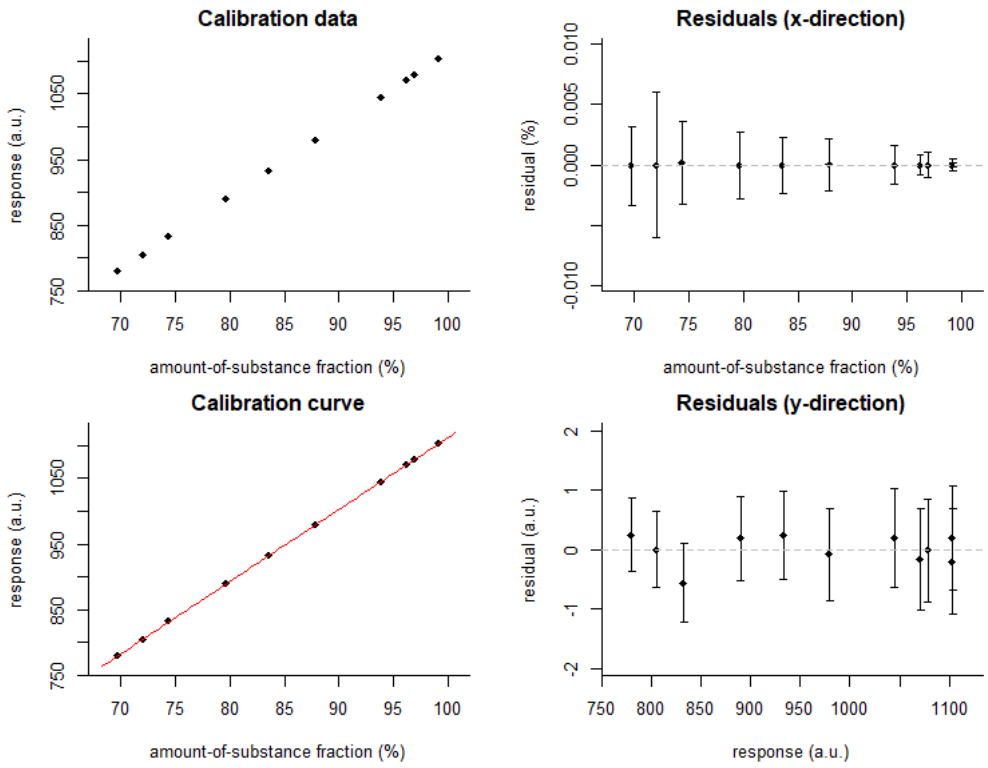

Table 76 Interpolation result of methane on the auxiliary channel for the hydrogen enriched mixture

	y	u(y)	x	u(x)
WF2727	879.79	0.35	78.771	0.036

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 57 and 58, 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 $k = 2$.

Table 77: Summary results of the three measurements of the LNG composition and the mean value and standard uncertainty (%)

Component	x_1	u(x_1)	x_2	u(x_2)	x_3	u(x_3)	τ	μ	u(μ)
Nitrogen	0.122070	0.000304	0.122240	0.000380	0.122020	0.000376	0.000000	0.122103	0.000376
Carbon dioxide	0.019948	0.000042	0.019924	0.000026	0.020000	0.000030	0.000029	0.019956	0.000042
Ethane	10.008160	0.001393	10.002000	0.001173	10.002000	0.000874	0.002945	10.003937	0.003072
Propane	2.000760	0.001084	1.998775	0.001084	2.000040	0.001103	0.000000	1.999856	0.001103
iso-Butane	0.149230	0.000030	0.149210	0.000029	0.149150	0.000037	0.000022	0.149201	0.000043
n-Butane	0.148740	0.000027	0.148690	0.000046	0.148620	0.000038	0.000055	0.148687	0.000067
iso-Pentane	0.019924	0.000008	0.019909	0.000010	0.019908	0.000010	0.000003	0.019915	0.000011
n-Pentane	0.020121	0.000010	0.020111	0.000008	0.020116	0.000011	0.000000	0.020115	0.000011
Methane	87.511800	0.019300	87.490497	0.019446	87.513920	0.020194	0.000000	87.505229	0.020194

Table 78 Summary results of the three measurements of the hydrogen-enriched natural gas and the mean value and standard uncertainty (%)

Component	x_1	u(x_1)	x_2	u(x_2)	x_3	u(x_3)	τ	μ	u(μ)
Nitrogen	11.979000	0.001825	11.982000	0.002358	11.986000	0.005844	0.000000	11.980462	0.002358

Carbon dioxide	4.006800	0.000705	4.004500	0.000908	4.004200	0.000605	0.001308	4.005175	0.001441
Hydrogen	2.998700	0.001719	2.998959	0.001718	2.997210	0.001717	0.000000	2.998289	0.001717
Helium	0.502644	0.000187	0.502580	0.000248	0.502710	0.000225	0.000000	0.502648	0.000225
Ethane	0.744330	0.000248	0.744500	0.000150	0.744250	0.000200	0.000000	0.744395	0.000200
Propane	0.299100	0.000165	0.298425	0.000165	0.298438	0.000176	0.000352	0.298656	0.000394
iso-Butane	0.199770	0.000044	0.199730	0.000040	0.199890	0.000050	0.000066	0.199793	0.000083
n-Butane	0.200160	0.000045	0.200320	0.000046	0.200160	0.000045	0.000080	0.200213	0.000092
iso-Pentane	0.049768	0.000019	0.049882	0.000024	0.049843	0.000025	0.000057	0.049830	0.000062
n-Pentane	0.050243	0.000022	0.050318	0.000021	0.050237	0.000020	0.000040	0.050266	0.000045
neo-Pentane	0.049433	0.000015	0.049376	0.000026	0.049384	0.000026	0.000027	0.049402	0.000038
n-Hexane	0.049574	0.000028	0.049614	0.000029	0.049535	0.000029	0.000026	0.049574	0.000039
Methane	78.770800	0.035800	78.728800	0.035187	78.716270	0.035667	0.000000	78.738455	0.035667

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[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

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[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.

D Amendments to the originally submitted measurement reports

CCQM-K118a-Natural gas KRISS

Cylinder Number: Luxfer D322706 Hydrogen-enriched natural gas
(Composition ID: Westfalen G328056)

Results

Component	Fraction (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor*
Nitrogen	0.119760	0.000238	2
Carbon dioxide	0.040070	0.000080	2
Hydrogen	0.029993	0.000060	2
Helium	0.005014	0.000015	2
Ethane	0.007446	0.000022	2
Propane	0.002982	0.000009	2
iso-Butane	0.001999	0.000006	2
n-Butane	0.001995	0.000006	2
iso-Pentane	0.000494	0.000015	2
n-Pentane	0.000501	0.000012	2
neo-Pentane	0.000494	0.000010	2
n-Hexane	0.000494	0.000010	2
Methane	0.788423	0.000790	2

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

Measurement #1 (November 29th, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Nitrogen	0.119741	0.000128
Carbon dioxide	0.040081	0.000081
Hydrogen	0.029996	0.000022
Helium	0.005014	0.000004
Ethane	0.007447	0.000017
Propane	0.002982	0.000007
iso-Butane	0.002000	0.000004
n-Butane	0.001995	0.000005
iso-Pentane	0.000494	0.000011
n-Pentane	0.000501	0.000010
neo-Pentane	0.000494	0.000001
n-Hexane	0.000494	0.000003

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Methane	0.788250	0.000661

Measurement #2 (November 30th, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Nitrogen	0.119770	0.000139
Carbon dioxide	0.040070	0.000026
Hydrogen	0.029987	0.000024
Helium	0.005016	0.000007
Ethane	0.007445	0.000007
Propane	0.002982	0.000004
iso-Butane	0.001999	0.000002
n-Butane	0.001995	0.000003
iso-Pentane	0.000494	0.000010
n-Pentane	0.000501	0.000010
neo-Pentane	0.000494	0.000001
n-Hexane	0.000494	0.000003
Methane	0.788470	0.000707

Measurement #3 (December 3rd, 2018)

Component	Fraction (mol/mol)	Standard Uncertainty** (mol/mol)
Nitrogen	0.119770	0.000119
Carbon dioxide	0.040059	0.000054
Hydrogen	0.029995	0.000024
Helium	0.005013	0.000004
Ethane	0.007446	0.000013
Propane	0.002981	0.000006
iso-Butane	0.001998	0.000003
n-Butane	0.001994	0.000004
iso-Pentane	0.000494	0.000010
n-Pentane	0.000501	0.000010
neo-Pentane	0.000494	0.000001
n-Hexane	0.000493	0.000003
Methane	0.788550	0.000593

**Standard uncertainties estimated from replicate analysis of the test cylinder (D322706) only, not including uncertainties originated from gravimetric preparation and internal consistency test.

Calibration standards

- **Method of preparation**

For comparisons with the test cylinder (D322706) sent from the coordinating laboratory (BAM), a calibration gas cylinder (D693877) of KRISS primary standard mixtures (PSM) was newly prepared using a gravimetric method based on ISO 6142 as of October 22nd, 2018. The order of components injected into the PSM gas cylinder was *n*-hexane, *n*-pentane, *iso*-pentane, *neo*-pentane, a mixture of (propane + ethane + *iso*-butane + *n*-butane), a mixture of (hydrogen + helium), carbon dioxide, nitrogen, and finally methane.

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

Analyses of hydrocarbons and inorganic gas impurities in the pure gases of nitrogen, carbon dioxide, hydrogen, helium, ethane, propane, *iso*-butane, *n*-butane, and methane were conducted primarily using gas chromatographs (GC) with different detectors: pulse discharge detector (PDD), flame ionization detector (FID), thermal conductivity detector (TCD) and a dew-point meter (DPM) for analysis of moisture content. Analysis of hydrocarbons impurities in the pure liquids of *iso*-pentane, *n*-pentane, and *n*-hexane and the pure gas of *neo*-pentane were conducted using GC-FID. Analysis of moisture content in the pure liquid reagents were conducted using Karl-Fisher Analyser (KFA).

Component	Purity (cmol/mol)	Analysis method
Nitrogen	99.9997	DPM, GC-PDD, GC-FID, GC-TCD
Carbon dioxide	99.9989	DPM, GC-PDD, GC-FID, GC-TCD
Hydrogen	99.9990	DPM, GC-PDD, GC-FID, GC-TCD
Helium	99.9999	DPM, GC-PDD, GC-FID, GC-TCD
Ethane	99.9965	DPM, GC-PDD, GC-FID, GC-TCD
Propane	99.9982	DPM, GC-PDD, GC-FID, GC-TCD
iso-Butane	99.9534	DPM, GC-PDD, GC-FID, GC-TCD
n-Butane	99.8720	DPM, GC-PDD, GC-FID, GC-TCD
iso-Pentane	99.9670	GC-FID, KFA
n-Pentane	99.3600	GC-FID, KFA
neo-Pentane	99.9689	GC-FID, KFA
n-Hexane	99.4130	GC-FID, KFA
Methane	99.9992	DPM, GC-PDD, GC-FID, GC-TCD

- **Weighing data**

Information on the mass of the pure liquid reagents and the source or the parent gas mixture cylinders to prepare the calibration cylinder (D693877) are summarized in the following table:

Component	source	Mass (g)
n-hexane	Pure liquid reagent	1.2569
n-pentane	Pure liquid reagent	1.0776
iso-pentane	Pure liquid reagent	1.0588
neo-pentane (3.02 %) in methane	Parent gas mixture	8.81
carbon dioxide	Pure gas	51.4
nitrogen	Pure gas	97.9
ethane (7.511 %) propane (2.036 %) *iso*-butane (1.9951 %) *n*-butane (2.014 %) in methane	Parent gas mixture	57.2
hydrogen (30.110 %) helium (5.076 %) in methane	Parent gas mixture	32.8
methane	Pure gas	288.416

Uncertainties due to impurities of all pure or parent gases used for gravimetric preparation of the calibration cylinder (D693877) were incorporated into the preparation uncertainty.

The mole fraction of each component in the calibration cylinder (D693877) and its standard uncertainty are summarized in the following table:

Component	Mole Fraction (cmol/mol)	Standard Uncertainty (cmol/mol)	Relative Standard Uncertainty (%)
Nitrogen	11.9776	0.0031	0.026
Carbon dioxide	4.0011	0.0014	0.035
Hydrogen	3.0210	0.0015	0.049
Helium	0.5086	0.00025	0.049
Ethane	0.7494	0.00026	0.035
Propane	0.3029	0.00011	0.035
iso-Butane	0.1992	0.00008	0.040
n-Butane	0.2009	0.00008	0.040
iso-Pentane	0.050342	0.0010	2.1

Component	Mole Fraction (cmol/mol)	Standard Uncertainty (cmol/mol)	Relative Standard Uncertainty (%)
n-Pentane	0.05123	0.0010	2.0
neo-Pentane	0.05147	0.000015	0.028
n-Hexane	0.04980	0.00029	0.58
Methane	78.8354	0.020	0.025

Verification measures

- **Internal consistency between the KRISS PSMs**

The mole fraction of each component in the verification cylinder (D695886) used as the control of internal consistency with the calibration cylinder (D693877) and its standard uncertainty are summarized in the following table:

Component	Mole Fraction (cmol/mol)	Standard Uncertainty (cmol/mol)	Relative Standard Uncertainty (%)
Nitrogen	12.0556	0.0031	0.026
Carbon dioxide	4.0173	0.0014	0.036
Hydrogen	3.0274	0.0015	0.05
Helium	0.5097	0.00025	0.049
Ethane	0.7594	0.00027	0.035
Propane	0.3070	0.00011	0.035
iso-Butane	0.2019	0.00008	0.040
n-Butane	0.2035	0.00008	0.039
iso-Pentane	0.05183	0.0011	2.1
n-Pentane	0.05137	0.0011	2.1
neo-Pentane	0.05117	0.00001	0.028
n-Hexane	0.05022	0.00029	0.58
Methane	78.7127	0.020	0.025

Response factors of each component in the calibration cylinder (D693877) were compared with those in the verification cylinder (D695886) using a comparative analysis method based on ISO 6143, as of November 26th and 28th, 2018.

The relative standard uncertainty of internal consistency is in the following table:

Component	Maximum Distance of C from V |C-V|	Relative Distance of C from V[1] (%)	Relative Standard Uncertainty[2] (%)
Nitrogen	0.48	0.14	0.08
Carbon dioxide	0.24	0.01	0.01
Hydrogen	0.91	0.03	0.01
Helium	0.29	0.01	0.01
Ethane	0.72	0.03	0.02
Propane	1.45	0.05	0.03
iso-Butane	1.03	0.03	0.02
n-Butane	0.99	0.03	0.02
iso-Pentane	33.21	0.84	0.49
n-Pentane	2.10	0.06	0.03
neo-Pentane	2.06	0.05	0.03
n-Hexane	1.01	0.02	0.01
Methane	0.7	0.07	0.04

[1] Calculated using $[|C - V|/V \times 100]$ (%) assuming that the relative deviation (%) from the ratio of the response factor (C) of each component in the calibration cylinder (D693877) against that (V) in the verification cylinder (D695886)

[2] Calculated using $\left|[|C - V|/V \times 100]/\sqrt{3}\right|$ (%) assuming that the relative deviation (%) follows a rectangular probability distribution (B-type).

■ **Verification of instability of the calibration gas cylinder**

Past experiences of KRISS clearly indicate that hydrogen-enriched natural gas CRMs prepared by KRISS were stable within two years. Any significant change in the mole fraction of each component in the calibration cylinder (D693877) was not observed within 3 months after its gravimetric preparation. The uncertainty due to this instability was considered negligible relatively to other uncertainty sources (e.g., gravimetric preparation, internal consistency, and comparative analysis) and thus not included to the final uncertainty budget.

Instrumentation

Determination of mole fractions of carbon dioxide, ethane, propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane, and *n*-hexane components was conducted using GC-FID-methanizer (Agilent 6890A). Determination of mole fractions of nitrogen, hydrogen, helium, and methane

was conducted using GC-TCD (Agilent 7890A). A MFC and a quick connector were assisted for the quick change of cylinders and maintaining the constant flow rate. GC signal was integrated as an area value for each peak.

Calibration method and value assignment

KRISS received the test cylinder (D322706) as of August 2nd, 2018. The test cylinder that BAM had sent to KRISS was made of Al with normal volumetric capacity of 5 L. The gas pressure values of the test cylinder (D322706) before and after the measurement at the KRISS laboratory were approximately 4.1 MPa and 2.0 MPa, respectively.

The overall procedures for calibration and value assignment are based on ISO 6143. We used a one-point calibration (in-situ, exact-match, bracketing) method for the determination of the mole fractions of the components in the test cylinder (D322706**)** of the coordinating laboratory (BAM) in comparison with the calibration cylinder (D693877) of KRISS. A bracketing method (D693877 - D322706 - D693877) was adopted as the comparison analysis for the value assignment and uncertainty evaluation of each component in the test cylinder (D322706**)**. After averaging multiple response values of the calibration cylinder (D693877) by taking drift compensation into account, the mole fraction of each component in the test cylinder (D322706) was calculated as a result by direct comparison between the average of the response values and the mole fraction of each component in the calibration cylinder (D693877).

Uncertainty evaluation

- **Model equation for a measurement data set (e.g., Measurement # *i*)**

A model equation of the measurand ($x_{\text{test,i}}$) was used for the one-point calibration method:

$$x_{test,i} = \left(\frac{A_{test,i}}{A_{cal,i}}\right) x_{cal}$$

where
i : the measurement #i (i=1,2,and 3)
$x_{test,i}$: the mole fraction of each component from the test cylinder (D322706**)** determined and reported by KRISS
($A_{test,i}$ /$A_{cal,i}$) : the ratio of GC response areas of each component between the test cylinder (D322706**)** and the calibration cylinder (D693877)
x_{cal} : the mole fraction of the calibration cylinder (D693877)

- **Combined uncertainty for a measurement data set (Measurement #*i*)**

The following equation to calculate the uncertainty of the measurand (x_{test}) considers the three different sources: the gravimetric preparation of the calibration cylinder (D693877), the internal consistency between the calibration cylinder (D693877) and the verification cylinder (D695886), and the ratio of the response areas of between the calibration cylinder (D693877) and the verification cylinder (D695886) for each component.

$$u(x_{test,i}) = x_{test,i}\sqrt{\left[\frac{u(A_{test,i}/A_{cal,i})}{A_{test,i}/A_{cal,i}}\right]^2 + \left[\frac{u(X_{cal})}{X_{cal}}\right]^2 + \left[\frac{u_i(f_{IC})}{f_{IC}}\right]^2}$$

where

$\frac{u_i(f_{IC})}{f_{IC}}$: relative standard uncertainty of internal consistency which is defined as the ratio of the response factor of a component between the calibration cylinder (D693877) and the verification cylinder (D695886) where the ratio is assumed 1.

- **Combined uncertainty for the overall data sets using Measurement #1 through #3**

As a result, the measurand [i.e., average mole faction (x_{test})] of each component and its combined uncertainty [$u(x_{test})$] of each component in the test cylinder were calculated using the four-day independent measurement data sets.

Average mole fraction (x_{test}):

$$x_{test} = \frac{1}{3}\sum_{i=1}^{3} x_{test,i}$$

Its combined uncertainty [$u(x_{test})$]:

$$u(x_{test}) = \frac{1}{3}\sqrt{\sum_{i=1}^{3} u^2(x_{test,i})}$$

Its expanded uncertainty [$U(x_{test})$]:

$$U(x_{test}) = k\, u(x_{test})$$

Therefore,

$$U(x_{test}) = \frac{k}{3}\sqrt{\sum_{i=1}^{3} u^2\left(x_{test,i}\right)}$$

The expanded uncertainty was estimated at the approximately 95% level of confidence with the coverage factor (k) of 2, assuming that x_{test} of each component follows a normal distribution. This assumption was confirmed by the fact that the effective degree of freedoms of $u(x_{test})$ of each component, calculated by the Welch-Satterthwaite equation, was greater than 10.

Accordingly,

$$U(x_{test}) = \frac{2}{3}\sqrt{\sum_{i=1}^{3} u^2\left(x_{test,i}\right)}$$

NIM

Cylinder number : D322730#

Measurement #1 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	15/08/19	0.119642	0.03%	3
Carbon dioxide	15/08/19	0.039994664	0.01%	3
Hydrogen	15/08/19	0.029990321	0.03%	3
Helium	15/08/19	0.005013461	0.04%	3
Ethane	15/08/19	0.007446886	0.02%	3
Propane	15/08/19	0.002984407	0.06%	3
iso-Butane	15/08/19	0.001998434	0.04%	3
n-Butane	15/08/19	0.001998964	0.05%	3
iso-Pentane	15/08/19	0.000498735	0.14%	3
n-Pentane	15/08/19	0.000500831	0.05%	3
neo-Pentane	15/08/19	0.000493431	0.06%	3
n-Hexane	15/08/19	0.000497818	0.04%	3
Methane	15/08/19	0.788940	0.04%	3

Measurement #2 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	27/08/19	0.119659	0.03%	3
Carbon dioxide	27/08/19	0.039970013	0.03%	3
Hydrogen	27/08/19	0.030008847	0.03%	3
Helium	27/08/19	0.005013692	0.04%	3
Ethane	27/08/19	0.007443306	0.03%	3
Propane	27/08/19	0.002983507	0.01%	3
iso-Butane	27/08/19	0.001998245	0.03%	3
n-Butane	27/08/19	0.001995749	0.02%	3
iso-Pentane	27/08/19	0.000498064	0.01%	3
n-Pentane	27/08/19	0.000499839	0.04%	3
neo-Pentane	27/08/19	0.000492599	0.03%	3
n-Hexane	27/08/19	0.000496531	0.04%	3
Methane	27/08/19	0.788944	0.03%	3

Measurement #3 (hydrogen-enriched natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	02/09/19	0.119658	0.004%	4
Carbon dioxide	02/09/19	0.039981654	0.01%	4
Hydrogen	02/09/19	0.030013319	0.01%	4
Helium	02/09/19	0.005014707	0.01%	4
Ethane	02/09/19	0.007446646	0.01%	4
Propane	02/09/19	0.002982507	0.02%	4
iso-Butane	02/09/19	0.001999778	0.01%	4
n-Butane	02/09/19	0.001996865	0.03%	4
iso-Pentane	02/09/19	0.00049862	0.06%	4
n-Pentane	02/09/19	0.00050017	0.02%	4
neo-Pentane	02/09/19	0.000492928	0.02%	4
n-Hexane	02/09/19	0.00049695	0.02%	4
Methane	02/09/19	0.788921	0.004%	4

Final Results (hydrogen-enriched natural gas)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor[1]
Nitrogen	0.119653	0.00025	2
Carbon dioxide	0.039982	0.000091	2
Hydrogen	0.030004	0.000075	2
Helium	0.005014	0.000014	2
Ethane	0.007446	0.000019	2
Propane	0.0029835	0.0000081	2
iso-Butane	0.0019988	0.0000050	2
n-Butane	0.0019972	0.0000050	2
iso-Pentane	0.0004985	0.0000020	2
n-Pentane	0.0005003	0.0000015	2
neo-Pentane	0.0004930	0.0000016	2
n-Hexane	0.0004971	0.0000013	2
Methane	0.788935	0.00031	2

[1] The coverage factor shall be based on approximately 95% confidence.

Report forms for CCQM-K118 NIM

Cylinder number : D322700#

Measurement #1 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	15/08/19	0.00122662	0.17%	3
Carbondioxide	15/08/19	0.00019759	0.14%	3
Ethane	15/08/19	0.09987021	0.01%	3
Propane	15/08/19	0.01996904	0.02%	3
iso-Butane	15/08/19	0.00149014	0.02%	3
n-Butane	15/08/19	0.00148159	0.01%	3
iso-Pentane	15/08/19	0.00019881	0.06%	3
n-Pentane	15/08/19	0.00020019	0.01%	3
Methane	15/08/19	0.875366	0.03%	3

Measurement #2 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	23/08/19	0.00122289	0.12%	3
Carbondioxide	23/08/19	0.00019777	0.31%	3
Ethane	23/08/19	0.09991623	0.03%	3
Propane	23/08/19	0.01997218	0.05%	3
iso-Butane	23/08/19	0.00149007	0.02%	3
n-Butane	23/08/19	0.00148141	0.04%	3
iso-Pentane	23/08/19	0.00019880	0.03%	3
n-Pentane	23/08/19	0.00019994	0.02%	3
Methane	23/08/19	0.875321	0.05%	3

Measurement #3 (LNG-type natural gas)

Component	Date (dd/mm/yy)	Result (mol/mol)	Relative standard deviation (%)	number of replicates
Nitrogen	04/09/19	0.00123029	0.17%	3
Carbondioxide	04/09/19	0.00019804	0.18%	3
Ethane	04/09/19	0.09985345	0.01%	3
Propane	04/09/19	0.01996310	0.03%	3
iso-Butane	04/09/19	0.00149016	0.01%	3
n-Butane	04/09/19	0.00148151	0.00%	3
iso-Pentane	04/09/19	0.00019881	0.04%	3
n-Pentane	04/09/19	0.00019986	0.05%	3
Methane	04/09/19	0.875385	0.01%	3

Final Results (LNG-type natural gas)

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor[2]
Nitrogen	0.00122660	0.0000062	2
Carbondioxide	0.0001978	0.0000010	2
Ethane	0.099880	0.00023	2
Propane	0.019968	0.000050	2
iso-Butane	0.0014901	0.0000037	2
n-Butane	0.0014815	0.0000039	2
iso-Pentane	0.00019880	0.00000070	2
n-Pentane	0.00020000	0.00000065	2
Methane	0.875357	0.00030	2

Calibration standards

The calibration gas mixtures of synthetic natural gas were prepared by using gravimetric method according to ISO6142.1-2015.

Source materials used for preparation were listed in Table 1~13.

Table 1. Purity data for pure CH4

Component	Method	Result (mol/mol)	Distributio n	Estimated *c* (mol/mol)	Std *u* (mol/mol)

[2] The coverage factor shall be based on approximately 95% confidence.

H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	2.5E-6	Normal	2.5E-6	0.5E-6
CO2	GC-PDHID	0.40E-6	Normal	0.40E-6	0.20E-6
CH4	/	/	/	0.9999927	1.8E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 2. Purity data for pure C2H6

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	1.1E-6	Normal	1.1E-6	0.55E-6
CO2	GC-FID(Ni)	0.20E-6	Normal	0.20E-6	0.10E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	/	/	/	0.9999943	1.8E-6
C3H8	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 3. Purity data for pure C3H8

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
N2	GC-PDHID	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	9.3E-6	Normal	9.3E-6	1.9E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	/	/	/	0.999974	4.3E-6
C3H6	GC-FID	10.6E-6	Normal	10.6E-6	3.2E-6
i-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C4H10	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 4. Purity data for pure i-C4H10

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	33.2E-6	Normal	33.2E-6	6.7E-6
CO2	GC-FID(Ni)	8.0E-6	Normal	8.0E-6	2.0E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	1.3E-6	Normal	1.3E-6	0.65E-6
C3H6	GC-FID	2.2E-6	Normal	2.2E-6	1.1E-6
i-C4H10	/	/	/	0.999878	10.6E-6
n-C4H10	GC-FID	67.2E-6	Normal	67.2E-6	6.7E-6
neo-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	8.5E-6	Normal	8.5E-6	4.2E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6

Table 5. Purity data for pure n-C4H10

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	48.8E-6	Normal	48.8E-6	4.9E-6
CO2	GC-FID(Ni)	16.6E-6	Normal	16.6E-6	3.3E-6
CH4	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C2H6	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
C3H8	GC-FID	14.4E-6	Normal	14.4E-6	7.2E-6
i-C4H10	GC-FID	59.5E-6	Normal	59.5E-6	6.0E-6
n-C4H10	/	/	/	0.999768	14.7E-6
neo-C5H12	GC-FID	63.6E-6	Normal	63.6E-6	6.4E-6
i-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C5H12	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
n-C6H14	GC-FID	ND	Rectangular	0.05E-6	0.03E-6
1-C4H8	GC-FID	18.4E-6	Normal	18.4E-6	5.5E-6
2-C4H8	GC-FID	17.9E-6	Normal	17.9E-6	5.4E-6

Table 6. Purity data for pure neo-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	66.2E-6	Normal	66.2E-6	6.6E-6
CO2	GC-FID(Ni)	2.7E-6	Normal	2.7E-6	1.4E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
C3H8	GC-FID	88.5E-6	Normal	88.5E-6	8.9E-6
i-C4H10	GC-FID	5.45E-3	Normal	5.45E-3	5.4E-4
n-C4H10	GC-FID	21.1E-6	Normal	21.1E-6	2.1E-6
neo-C5H12	/	/	/	0.994334	5.4E-4
i-C5H12	GC-FID	10.5E-6	Normal	10.5E-6	1.1E-6
n-C5H12	GC-FID	ND	Rectangular	5.3E-6	3.2E-6

n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6

Table 7. Purity data for pure i-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	1.16E-3	Normal	1.16E-3	1.2E-4
CO2	GC-FID(Ni)	37.6E-6	Normal	37.6E-6	3.8E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	1.08E-4	Normal	1.08E-4	11E-6
C3H8	GC-FID	25.8E-6	Normal	25.8E-6	2.6E-6
i-C4H10	GC-FID	2.09E-3	Normal	2.09E-3	2.1E-4
n-C4H10	GC-FID	4.70E-3	Normal	4.70E-3	4.7E-4
neo-C5H12	GC-FID	4.00E-3	Normal	4.00E-3	4.0E-4
i-C5H12	/	/	/	0.9857899	7.0E-4
n-C5H12	GC-FID	2.05E-3	Normal	2.05E-3	2.1E-4
n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
cis-2-C5H10	GC-FID	22.8E-6	Normal	22.8E-6	2.3E-6

Table 8. Purity data for pure n-C5H12

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
N2	GC-PDHID	75.4E-6	Normal	75.4E-6	7.5E-6
CO2	GC-FID(Ni)	40.8E-6	Normal	40.8E-6	4.1E-6
CH4	GC-FID	ND	Rectangular	10.6E-6	6.4E-6
C2H6	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
C3H8	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
i-C4H10	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
n-C4H10	GC-FID	18.1E-6	Normal	18.1E-6	1.8E-6
neo-C5H12	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
i-C5H12	GC-FID	3.66E-3	Normal	3.66E-3	3.7E-4
n-C5H12	/	/	/	0.995097	3.9E-4
n-C6H14	GC-FID	ND	Rectangular	5.3E-6	3.2E-6
Other C5H10	GC-FID	1.07E-3	Normal	1.07E-3	1.1E-4

Table 9. Purity data for pure n-C6H14

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
2,2-dimethylbutane	GC-FID	768E-6	Normal	768E-6	76.8E-6
2,3-dimethylbutane	GC-FID	191E-6	Normal	191E-6	19.1E-6
2-methylpentane	GC-FID	1.01E-3	Normal	1.01E-3	1.01E-4
3-methylpentane	GC-FID	1.04E-3	Normal	1.04E-3	1.04E-4
n-C6H14	/	/	/	0.996463	1.73E-4
n-C7H16	GC-FID	506E-6	Normal	506E-6	50.6E-6
methylcyclopentane	GC-FID	11.0E-6	Normal	11.0E-6	1.1E-6
cyclohexane	GC-FID	11.0E-6	Normal	11.0E-6	1.1E-6

Table 10. Purity data for pure N2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-PDHID	ND	Rectangular	0.1E-6	0.06E-6
He	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
O2	O2 Analyzer	0.05E-6	Rectangular	0.05E-6	0.03E-6
Ar	GC-PDHID	12.3E-6	Normal	12.3E-6	1.2E-6
N2	/	/	/	0.9999978	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.03E-6	0.02E-6
H2O	Dewpoint Meter	0.1E-6	Rectangular	0.1E-6	0.06E-6

Table 11. Purity data for pure CO2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
O2	GC-PDHID	0.52E-6	Normal	0.52E-6	0.1E-6
N2	GC-PDHID	19.8E-6	Normal	19.8E-6	2.0E-6
CO2	/	/	/	0.999975	3.3E-6
CH4	GC-FID	1.1E-6	Normal	1.1E-6	0.45E-6
C2H4	GC-FID	0.2E-6	Normal	0.2E-6	0.1E-6
C3H8	GC-FID	0.64E-6	Normal	0.64E-6	0.32E-6
H2O	Dewpoint Meter	2.5E-6	Normal	2.5E-6	1.0E-6

Table 12. Purity data for pure H2

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	/	/	/	0.999998	1.2E-6
N2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.1E-6	0.06E-6

Table 13. Purity data for pure He

Component	Method	Result (mol/mol)	Distribution	Estimated *c* (mol/mol)	Std *u* (mol/mol)
H2	GC-PDHID	ND	Rectangular	0.1E-6	0.06E-6
He	/	/	/	0.999998	1.2E-6
N2	GC-TCD	ND	Rectangular	2.0E-6	1.2E-6
CO2	GC-FID(Ni)	ND	Rectangular	0.03E-6	0.02E-6
CH4	GC-FID	ND	Rectangular	0.1E-6	0.06E-6
H2O	Dewpoint Meter	0.1E-6	Rectangular	0.1E-6	0.06E-6

In order to obtain the final synthetic natural gas PRMs, several pre-mixtures were prepared, and the weighing data for each pre-mixtures were listed in Table 14. Accordingly, final synthetic natural gas PRMs were gravimetrically prepared, and some of PRMs werelisted in Table 15-16.

Table 14. Preparation pre-mixtures

Cylinder No.	Source materials	Mass filled (g)	Std *u* for mass (g)	Mole fraction *c* (mol/mol)	Std $u_{c,r}$, relative
63909004#	n-C5	7.8692	0.005	5.3423E-3	0.070%
	iC5	6.8078	0.005	4.6005E-3	0.074%
	neoC5	7.1572	0.005	4.8715E-3	0.066%
	C1	321.6007	0.02	9.8508E-1	0.0008%
63909025#	nC4	24.469	0.005	2.3477E-2	0.022%
	iC4	24.633	0.005	2.3636E-2	0.022%
	C1	274.084	0.02	9.5286E-1	0.0009%
63909027#	H2	25.8605	0.005	7.6554E-1	0.088%
	He	9.8236	0.005	1.4646E-1	0.046%
	C3	65.0219	0.005	8.7995E-2	0.018%
L63204002#	CO2	15.1435	0.005	2.3188E-2	0.034%
	N2	57.4465	0.01	1.3821E-1	0.018%
	C1	199.651	0.02	8.3860E-1	0.003%

Table 15. Preparation of final PRMs

Cylinder No.	Source materials	Mass filled (g)	Std *u* for mass (g)
63909026# (LNG Type)	L63204002#	6.8380	0.005
	C3	39.2886	0.005
	63909004#	27.8822	0.005
	63909025#	48.6330	0.005
	C2	123.9981	0.01
	C1	504.4403	0.02
63909002# (H2-enriched Type)	nC6	1.41429	0.0002
	63909025#	62.3247	0.005
	63909027#	10.0205	0.005
	63909004#	72.5312	0.01
	C2	10.5795	0.005
	CO2	74.3927	0.01
	N2	131.3021	0.01
	C1	392.1318	0.02

Table 16. Gravimetrically prepared PRMs.

Components	c_{grav} (mol/mol)	$U_{grav,rel}(k=2)$	$u_{ver,rel}(k=1)$	$U_{i,rel}(k=2)$
63909002#				
CH4(Methane)	7.8725E-01	0.006%	0.03%	0.06%
C2H6(Ethane)	8.664E-03	0.095%	0.10%	0.22%
C3H8(Propane)	3.613E-03	0.098%	0.10%	0.22%
C4H10(iso-Butane)	2.016E-03	0.053%	0.10%	0.21%
C4H10(n-Butane)	2.001E-03	0.050%	0.10%	0.21%
C5H12(neo-Pentane)	5.157E-04	0.180%	0.10%	0.27%
C5H12(iso-Pentane)	4.869E-04	0.207%	0.10%	0.29%
C5H12(n-Pentane)	5.654E-04	0.154%	0.10%	0.25%
C6H14(n-Hexane)	4.027E-04	0.077%	0.10%	0.21%
N2(Nitrogen)	1.1543E-01	0.019%	0.10%	0.20%
CO2(Carbon_dioxide)	4.162E-02	0.029%	0.10%	0.20%
H2(Hydrogen)	3.143E-02	0.100%	0.10%	0.22%
He(Helium)	6.013E-03	0.130%	0.10%	0.24%
63909026#				
CH4(Methane)	8.7308E-01	0.003%	0.03%	0.06%
C2H6(Ethane)	1.001E-01	0.020%	0.10%	0.20%
C3H8(Propane)	2.164E-02	0.030%	0.10%	0.20%
C4H10(iso-Butane)	1.550E-03	0.048%	0.10%	0.21%
C4H10(n-Butane)	1.539E-03	0.048%	0.10%	0.21%

C5H12(neo-Pentane)	1.956E-04	0.197%	0.10%	0.28%
C5H12(iso-Pentane)	1.846E-04	0.182%	0.10%	0.27%
C5H12(n-Pentane)	2.144E-04	0.135%	0.10%	0.24%
N2(Nitrogen)	1.2535E-03	0.591%	0.10%	0.62%
CO2(Carbon_dioxide)	2.105E-04	0.208%	0.10%	0.29%

Verification of PRMs.

Synthetic natural gas PRMs were verified against old PRMs by GC-TCD(Micro GC490, Agilent, USA). Results showed that the relative bias was within 0.05% for the components above 1%mol/mol, 0.01% for balance gas of CH4, and 0.1% for the other components. Accordingly, the relative uncertainty due to verification were 0.01% for CH4, 0.05% for components above 1%mol/mol, and 0.1% for other components.

Instrumentation

Synthetic natural gas PRMs were analyzed by GC-TCD(Micro GC490, Agilent, USA). There are 4 channels within Micro GC490. Channel 1# includes pre-column of PPQ and separation column of Moleseive 5A(10m), and is used to analyze such components as He, H2, O2, N2, and CH4 while the other components are backflushed. Channel 2# includes pre-column of PPQ and separation column of PPQ(10m), and is used to analyze CO2 and C2H6, while C3H8 and other heavier components are backflushed. Channel 3# includes pre-column of PPQ and separation column of Al2O3(10m), and is used to analyze C3H8, i-C4H10 and n-C4H10. Channel 4# includes only 5CB(10m) column and analyzed neo-, iso-, n-C5H12 and n-C6H14.

Calibration method and value assignment

The K118 sample cylinders were kept in the room at room temperature for almost 1 month. Both our PRM and the sample cylinders were equipped with pressure regulators. The outlet of pressure regulators were connected with the inject port of GC(microGC490). The PRM and sample cylinder were measured alternatively in “PRM(10 replicates)-KC sample(10 replicates)-PRM(10 replicates)” mode. The mole fraction of sample was determined using single-point calibration method by the formula as below:

$$c_{KC,i} = c_{PRM,i} \cdot \frac{2\overline{A}_{KC,i}}{\left(\overline{A}_{PRM,i,pre} + \overline{A}_{PRM,i,post}\right)} \qquad (1)$$

$c_{KC,i}$ the mole fraction of i component in KC sample,

$c_{PRM,i}$ the mole fraction of i component in PRM,

$\overline{A}_{KC,i}$ the average Peak Area of i component in KC sample by GC-TCD,

$\overline{A}_{PRM,i,pre}$ the average Peak Area of i component in PRM before KC sample injection,

$\overline{A}_{PRM,i,post}$ the average Peak Area of i component in PRM after KC sample injection,

The KC sample was analyzed against PRM for n(n≥3) times, and n results were obtained. The average fraction of $c^*_{KC,i}$ was taken as the raw value for the i component in KC sample, while the measurement result, $c_{KC,i}$, for the i component in KC sample was determined based on normalization.

$$c^*_{KC,i} = \frac{\sum_{j=1}^{n} c_{KC,i,j}}{n} \quad (2)$$

$$c_{KC,i} = \frac{c^*_{KC,i}}{\sum_{i=1}^{n} c^*_{KC,i}} \quad (3)$$

Uncertainty evaluation

The measurement uncertainty in raw fraction of i component was contributed by both PRM ($u_{i,rel}$) and measurement repeatability(RSD). While the uncertainty in a normalized fraction of i component was derived based on the formula (3).

References

ISO 6974-2, Natural gas - Determination of composition and associated uncertainty by gas chromatography - part 2: Uncertainty calculations, 2012.